

CRANFIELD UNIVERSITY

RAGHVENDRA KUMAR MISHRA

**A Study of Control Mechanisms in Micro and Nano System-
Enhanced Polymer Nanocomposites under Mechanical and
Electrical Stimuli: An Experimental and Computational
Investigation**

School of Aerospace, Transport and Manufacturing

PhD in Manufacturing

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Supervisors:

Dr. Iva Chianella; Dr. Hamed Yazdani Nezhad; Professor Dr. Saurav
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ABSTRACT

Nanocomposite materials, particularly those reinforced with graphene nanoplatelets (GNPs) and Barium Titanate (BaTiO_3), have been the focus of extensive study within diverse industries aiming to enhance mechanical and electrical properties. This thesis investigates the intricate relationship between external mechanical and electrical stimuli and the effectiveness of these reinforcing agents within nanocomposites, presenting significant findings and novel contributions, while addressing an unexplored aspect within the field.

The research highlights a two-part exploration. The first part of the thesis details the creation of GNP/ BaTiO_3 polymer nanocomposite fibrils via mechanical stimulation, specifically cold drawing, emphasising the compatibility of recycled polypropylene (PP)/polyethylene terephthalate (PET) blends. The resulting fibrils, exhibiting a significant aspect ratio disparity of 400:1, have demonstrated substantially improved electrical, thermomechanical, and electromagnetic properties. This in-situ mechanical stimulation (cold drawing) not only alters the morphology but also enhances electrical conductivity, limits polymer chain mobility, and reinforces the PP matrix, significantly improving its electrical, thermomechanical, and electromagnetic interference shielding.

In the subsequent second part of the thesis, the study explored the integration of graphene-based materials and BaTiO_3 within epoxy composites. Computational modelling and statistical analysis have revealed the influence of these fillers on DC conductivity, dielectric properties, and thermal behaviour. In addition, a comprehensive examination of variations in filler thickness and volume percentage that seemed to significantly impact material's behaviour has been investigated for the first time under electric fields. Specifically, the investigation into BaTiO_3 nanoparticles and Si- BaTiO_3 in epoxy under electric fields has revealed the interplay between electrical stimuli, material properties, and mechanical behaviour, highlighting ferroelectric and piezoelectric effects observed in BaTiO_3 ceramics.

This comprehensive study not only contributes novel findings but also significantly fills a research gap within the field of nanocomposites by presenting an in-depth examination of mechanical and electrical responsiveness, a study that has not been previously undertaken in such a detailed and exhaustive manner. The research conducted, sheds light on the potential for advanced materials in diverse industrial applications and underscores the importance of material selection, offering a pioneering step towards potential industrial utilisation. Additionally, this research offers guidance for further computational exploration, particularly in selecting GNP and BaTiO₃ materials to enhance the electrical and thermal properties of the epoxy matrix.

Keywords:

Epoxy; Polypropylene, Polyethylene terephthalate, Barium titanate; Graphene nanoplatelets; electric field; Viscoelastic behaviour; thermal behaviour; intrinsic strain.

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TABLE OF CONTENTS

ACADEMIC INTEGRITY DECLARATION.....	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES	x
LIST OF TABLES	xv
LIST OF EQUATIONS	xvii
LIST OF ABBREVIATIONS	xix
1. Introduction	1
1.1 Fundamentals and introduction	2
1.2 Composites	3
1.3 Classification of composites based on matrix	4
1.4 Classification of composites based on reinforcement	9
1.5 Nanocomposites	13
1.6 Research gap and contribution to knowledge	21
1.7 Aims and objectives	22
1.8 Thesis structure	23
1.9 Materials and methods selection criteria	25
2. Literature Review and Background	26
2.1 Introduction	27
2.2 Structure–property-application relationships in graphene	28
2.3 Structure–property-application relationships in BaTiO ₃ dielectric	71

2.4 Conclusions	106
3. Graphene Nanoplatelets/Barium Titanate Polymer Nanocomposite Fibril by In-Situ Mechanical Stimulation: Electro-Thermo-Mechanical Material Properties - A Computational Predictions and Experimental Analysis	107
3.1 Introduction	108
3.2 Materials and methods	113
3.3 Characterisation	120
3.4 Results and discussion	127
3.5 Conclusions	168
4. Computational Analysis of Electrical and Thermal Properties In Ferroelectric BaTiO₃ Reinforced Epoxy Nanocomposites: An In-Situ Electric Field Study	169
4.1 Introduction	170
4.2 Literature review	173
4.3 Methodology	180
4.4 Boundary conditions used to model electrical properties	181
4.5 Optimising meshing for accurate simulations in Comsol Multiphysics 5.5 ...	186
4.6 Boundary conditions used to model thermal properties	187
4.7 Simulated DC conductivity of GNP embedded epoxy nanocomposite	190
4.8 Simulated DC conductivity of BaTiO₃/epoxy nanocomposite	197
4.9 Simulated thermal conductivity of GNPs embedded epoxy nanocomposite .	200
4.10 Simulated thermal conductivity of BaTiO₃/epoxy nanocomposites	204
4.11 Relationship of simulated results by Bayesian analysis	209
4.12 Conclusions	218

5. Experimental Exploration of Properties in BaTiO₃ Reinforced Epoxy Nanocomposites Under External Electric Field Effects: An In-Situ Electric Field Study	220
5.1 Introduction	221
5.2 Materials and methods	224
5.3 Characterisations	229
5.4 Results and Discussion	237
5.5 Conclusions	254
6. Concluding Insights and Future Directions	256
6.1 Summary of Findings	257
6.2 Implications and significance	263
6.3 Future research directions	265
6.4 Conclusion	267

LIST OF FIGURES

Figure 1-1. Classification of composites.....	4
Figure 1-2. Types of reinforcing elements in metal matrix composites.....	5
Figure 1-3. Stress - strain curves of a ceramic material and CMC.....	6
Figure 1-4. Classification of polymer matrix composites.....	7
Figure 1-5. Particulate composite.....	10
Figure 1-6. a) Laminate reinforcement arrangement: conversion to composite after consolidation using resin.....	11
Figure 1-7. Classification of nanomaterials based on their dimension.....	18
Figure 1-8. Preparation method of nanomaterials by top-down and bottom-up approach.....	18
Figure 1-9. Various forms of nanomaterials/ nanocomposites and application.....	20
Figure 2-1. The different types of nanocarbons, (A) Graphene nanoribbon, (B) Nano onion, (C) Pristine graphene, (D) Single-walled carbon nanotube (SWCNT), (E) Multi-walled carbon nanotube (MWCNT), (F) Graphene oxide (GO), (G) Functionalised graphene, (H) Fullerenes, (I) Nanodiamond	29
Figure 2-2. Application prospective of graphene and its derivatives	35
Figure 2-3. Thermal conductivity of Urethane Functionalised Graphene Oxide and polyurethane blends	44
Figure 2-4. Stress vs strain behaviour of Surface Modified Graphene Oxide Cross-linking with Hydroxyl Terminated Polybutadiene Polyurethane composite.....	44
Figure 2-5. Nyquist plots of Epoxy Composite Coatings Filled with Amino-Silane Functionalised Graphene Oxide	45
Figure 2-6. Enhanced Biosensor for Cholesterol and Bilirubin Detection: Graphene Oxide/Conducting Polymer Composite Nanocomposite.....	46
Figure 2-7. High-Performance Micro-Supercapacitors with Open-Shell Polymer-Graphene Composites.....	47
Figure 2-8. The interaction of polyaniline (PANI) and graphene nanoribbons (GNRs) with the SrTiO ₃ surface is driven by a strong thermodynamic force.....	48
Figure 2-9. Stimuli-Responsive Graphene Systems in Smart Technology.....	61
Figure 2-10. Statistical data from worldwide a) BaTiO ₃ as well as nano BaTiO ₃ interest by years, b) BaTiO ₃ as well as nano BaTiO ₃ interest by region (Top 15) (From google database- last 10 years)	73
Figure 2-11. Illustration of crystal structure of BaTiO ₃	76

Figure 2-12. Illustration of crystal phase of BaTiO ₃ , a) cubic phase(non-polar), b) tetragonal (polarised in direction <100>), c) orthorhombic phase in direction (polarized in direction <110>), d) rhombohedral in direction (polarised<111>), e) hexagonal phase..	79
Figure 2-13. a) 180°domain wall distinguishing domain by anti-parallel polarisations; (b) 90°domain wall distinguishing domain by perpendicular polarisations.....	86
Figure 2-14. Hysteresis loop of BaTiO ₃ / ferroelectric materials (P-E), spontaneous polarisation (P _s), remnant polarisation(±P _r), coercive field (E _c), polarisation (PP) and applied electric field (E).....	96
Figure 2-15. Preparation of BaTiO ₃ by solid-state chemistry reactions.....	102
Figure 3-1. Preparation Method of Nanofiller mixture (Proposed preparation methodology for remanufacturing high-performance multifunctional nanocomposite fibrils out of recycled polymer blends (herein PP/PET) and high-aspect-ratio functional nanosystems (herein GNPs/BaTiO ₃))	114
Figure 3-2. The exploratory setup for blends(B).....	115
Figure 3-3. Schematic representation of the experimental setup for GNPs and Barium titanate (IV) based nanocomposites (GBNC).....	116
Figure 3-4. Morphology of the in-situ fibrils microfibrillar composites.....	118
Figure 3-5. The variation of the electrical conductivity of GBFNC with draw ratio (external mechanical stimulation by cold drawing)	118
Figure 3-6. Schematic representation of the experimental setup for GNPs and Barium titanate (IV) based in-situ fibrils Nanocomposites (GBFNC).....	120
Figure 3-7. Variation of deformation parameters and fibrils morphology during drawing as a function of nanofillers.....	123
Figure 3-8. (a) Variation of electrical conductivity of PP/PET blend (B) and PP/PET in-situ fibrils composites (FC), (b) Variation of electrical conductivity of in-situ fibrils nanocomposites with varying the phr of GNPs+BaTiO ₃ , (c) Variation of electrical conductivity of GNPs+BaTiO ₃ nanocomposites and in-situ fibrils nanocomposites with varying the phr of GNPs+BaTiO ₃	129
Figure 3-9. Polarised optical microscopy (POM) microstructure of (a) PP/PET Blend (B) at 30°C as in form of spherulites (Spherical ring), (b) PP/PET-GNP- BaTiO ₃ nanocomposites (GBNC1) at 30°C as in form of spherulites (Spherical ring), (c) PP/PET-GNP- BaTiO ₃ fibrils nanocomposites (GBFNC1) at 130°C as in form of transcrystalline growth, (d) GBFNC1 at 30 °C as in form of trans-crystalline growth.....	131
Figure 3-10. (a)Crystallisation, (b) melting behaviour of polypropylene (PP) in B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3(Exo up tends to exothermic process)	134
Figure 3-11. Avrami exponent (<i>n</i>) for polypropylene, B, FC, GBNC1, GBFNC1, GBFNC2, and GBFNC3.....	136
Figure 3-12. Rate constant (<i>k'</i>) for polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3.....	136

Figure 3-13. Variation of (a) storage modulus, b) Loss modulus of GNPs+ BaTiO ₃ nanocomposites and in-situ GNPs+ BaTiO ₃ polyethylene terephthalate (PET) fibrils nanocomposites with varying the phr of GNPs+ BaTiO ₃	140
Figure 3-14. Analysis of storage modulus of GNPs+ BaTiO ₃ nanocomposites and in-situ GNPs+ BaTiO ₃ polyethylene terephthalate (PET) fibrils nanocomposites with varying the phr of GNPs+ BaTiO ₃ through two population approach.....	144
Figure 3-15. Analysis of Thermal conductivity of GNPs+ BaTiO ₃ nanocomposites (GBNC) and in-situ GNPs+ BaTiO ₃ polyethylene terephthalate (PET) fibrils nanocomposites (GBFNC) with varying phr of GNPs+ BaTiO ₃ through two population approach.....	146
Figure 3-16. a) Variation of storage modulus with frequency (hertz (Hz)), b) Variation of loss modulus with frequency (hertz (Hz)), c) Variation of complex viscosity with frequency (hertz (Hz))	149
Figure 3-17. Comparatives study of the (a) Tensile strength, (b) Tensile modulus of prepared samples.....	151
Figure 3-18. A Comparatives study of the experimental and theoretical for a) tensile modulus and b) strength.....	158
Figure 3-19. AFM images and surface roughness of samples, (a) Polypropylene (PP), (b) Polypropylene (PP)/ polyethylene terephthalate (PET) blend (B), (c) Polypropylene (PP)/ polyethylene terephthalate (PET) in-situ fibrils composites (FC), d) GBNC1, e) GBFNC1, f) GBNFC3, g) Surface roughness.....	162
Figure 3-20. SEM images, (a) Polypropylene (PP); (b) Polypropylene (PP)/ polyethylene terephthalate (PET) blend after surface extraction of polypropylene (PP) by hot xylene (B); (c) polypropylene (PP)/ polyethylene terephthalate (PET) in-situ fibrils composites after surface extraction of polypropylene by hot xylene (FC), d) GBNC1 cryo- fractured surfaces, e) GBNC3 cryo-fractured surfaces, f) GBFNC1 cryo- fractured surfaces, g) GBNFC3 cryo-fractured surfaces.....	165
Figure 3-21. Electromagnetic shielding effectiveness of polypropylene (PP), FC, GBNC1, GBNC3, GBFNC1, GBFNC1, GBFNC3.....	167
Figure 4-1. Model for GNP and BaTiO ₃ embedded nanocomposite; a) 1.0 vol% b) 3.0 vol%, c) 5.0 vol%, d) 7.0 vol%, e) 10.0 vol%.....	181
Figure 4-2. A free body diagram of the electrostatic simulation revealing the boundary conditions.....	185
Figure 4-3. The DC conductivity of GNPs with thickness of (100 nm) and Epoxy (Ep) composites with various types of mesh and meshing grain size.....	187
Figure 4-4. A free body diagram showing the boundary conditions used for heat transfer simulation.....	189
Figure 4-5. DC conductivity and dielectric constant of different GNP types and dimensions, (a) DC conductivity of epoxy, graphene oxide (GO), reduced graphene oxide, and various GNPs with thicknesses ranging from 1000 nm to 0.5 nm, (b) Dielectric constant of epoxy, graphene oxide (GO), reduced graphene oxide, and GNPs.....	191

Figure 4-6. The COMSOL solution for DC conductivity of various GNPs/Epoxy composites: a) DC conductivity of neat epoxy and epoxy/ graphene oxide (GO), b) DC conductivity of reduced graphene oxide and various GNPs with respect to thickness (1000nm(G1000nm), 100nm(G100nm), 10nm(G10nm), 5nm(G5nm), 1nm(G1nm)) composites.....	192
Figure 4-7. The COMSOL solution for the dielectric constant of a) epoxy/ various GNPs with respect to thickness (1000nm, 100nm, 10nm, 5nm, 1nm) nanocomposites, b) epoxy/ graphene oxide (GO), reduced graphene oxide composites.....	196
Figure 4-8. a) DC conductivity of BaTiO ₃ /Epoxy composites compared with pure epoxy, b) Dielectric constant of various BaTiO ₃ with respect to the various particle diameters of BaTiO ₃ (50nm, 105 nm, 130 nm, 300 nm, 1000 nm, 2000nm, 4200 nm), c) Dielectric constant of various BaTiO ₃ / Epoxy composites in various filler percentages.	199
Figure 4-9. Thermal properties of various GNPs/Epoxy composites: a) Thermal conductivity of graphene oxide (GO), reduced graphene oxide and various GNPs concerning thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm) composites, b) Thermal conductivity of epoxy/ graphene oxide (GO), reduced graphene oxide and various GNPs with respect to thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000nm)/ epoxy composites, c) Specific heat capacity of graphene oxide (GO), reduced graphene oxide and various GNPs with respect to thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm), d) Specific heat capacity of epoxy/graphene oxide (GO), reduced graphene oxide and various GNPs with respect to the thickness in nm (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm)/ epoxy composites, e) Thermal diffusivity of epoxy/ graphene oxide (GO), reduced graphene oxide and various GNPs with respect to the thickness in nm (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm)/ epoxy composites.....	204
Figure 4-10. Thermal conductivity of BaTiO ₃ /Epoxy composites: a) Thermal conductivity of composites having various BaTiO ₃ diameter (300 nm, 70 nm, 100 nm, 1100 nm) b) Thermal conductivity of BaTiO ₃ with respect to diameter 100 nm, c) Thermal conductivity of BaTiO ₃ with respect to diameter 70 nm.....	207
Figure 4-11. a) Thermal diffusivity of epoxy and epoxy/ BaTiO ₃ (100 nm diameter) composites, b) Thermal diffusivity of epoxy and epoxy/ BaTiO ₃ (300 nm diameter) composites, c) Thermal diffusivity of epoxy and epoxy/ BaTiO ₃ (1100nm diameter) composites.....	209
Figure 4-12. a) Posterior probability of DC conductivity of epoxy/ GNPs composites with respect to the DC conductivity of the simulated epoxy/GNPs composites, b) Posterior probability of Dielectric constant of epoxy/ BaTiO ₃ composites with respect to the Dielectric constant of the simulated epoxy/ BaTiO ₃ composites, c) Posterior probability of Thermal conductivity of epoxy/ GNPs composites with respect to the Thermal conductivity of the simulated epoxy/GNPs composites, d) Posterior probability of Thermal conductivity of the simulated epoxy/ BaTiO ₃ composites.....	218
Figure 5-1. Schematic diagram of the Hydroxylation Process of BaTiO ₃ nanoparticles (pre-treatment for adding of hydroxyl group (-OH) to the surface of BaTiO ₃)	225

Figure 5-2. Schematic diagram of the functionalisation process of BaTiO ₃ with 3-GPS. The epoxy nanocomposite fabrication process including Si-BaTiO ₃ functionalisation is schematically illustrated.....	227
Figure 5-3. Schematic diagram of the preparation of Epoxy/Si-BaTiO ₃ nanocomposites.....	229
Figure 5-4. Schematic illustration of the in-situ electric field induced tensile test measurements: a) Sample before testing, b) Testing setup, and c) Sample after testing, d) Strength of electric fields at point P to polarise the sample	232
Figure 5-5. In-situ electric field equipped Raman cha of BaTiO ₃ -epoxy nanocomposites.....	233
Figure 5-6. Depiction of the in-situ electric field induced DIC test measurement.....	235
Figure 5-7. A free body diagram showing the boundary conditions used for AC/DC simulation a) Fine meshing, b) Free body diagram.....	237
Figure 5-8. FTIR spectra of unmodified BaTiO ₃ and modified BaTiO ₃ , a) unmodified BaTiO ₃ , b) modified BaTiO ₃ (Si-BaTiO ₃)	240
Figure 5-9. SEM images of fractured cross-sections of epoxy nanocomposites with BaTiO ₃ at different weight loading, (a)-(c) images of 1 wt.%, 5 wt.% and 10wt% Si-BaTiO ₃ /epoxy nanocomposite, (d) unmodified 10wt% BaTiO ₃ /epoxy nanocomposite.	242
Figure 5-10. The tensile stress vs. elongation trends in Si- BaTiO ₃ -epoxy nanocomposites under increasing electrical voltage and varying content of Si-BaTiO ₃	244
Figure 5-11. The tensile stress vs. elongation data in 1wt.%, 5wt.% and 10wt.% Si-BaTiO ₃ -epoxy nanocomposites under 0V and 24V electrical voltage.....	245
Figure 5-12. The tensile modulus of Si-BaTiO ₃ -epoxy nanocomposites at different electrical voltage with varying content of 1 wt.%, 5 wt.% and 10wt%.....	246
Figure 5-13. Measurement of intensity and broadening of Raman peaks with respect to the wave number at different Si- BaTiO ₃ content and under electric fields of a-c) 0V (no field), d-f) 6V, g-i) 12V and j-l) 24V.....	249
Figure 5-14. Electric field Induced mechanical properties with digital image correlation (DIC), a) average displacement 5wt% Si- BaTiO ₃ /epoxy nanocomposite at 0V during test, b) average displacement 5wt% Si- BaTiO ₃ /epoxy nanocomposite at 24V, c) average displacement 10wt% Si- BaTiO ₃ /epoxy nanocomposite at 0V, d) average displacement 10wt% Si- BaTiO ₃ /epoxy nanocomposite at 24V test.....	251
Figure 5-15. Electric field Induced Electrical properties of Si- BaTiO ₃ /epoxy nanocomposite by COMSOL 5.5 Multi-physics at 24V, a) Electrical displacement field (c/m2), b) Dielectric Polarisation, c) Volumetric power dissipation density.....	254

LIST OF TABLES

Table 1.1 High temperature thermoplastics used in fibre reinforced plastic.....	9
Table 1-2. An overview of development in the field of nanotechnology with respect to the years.....	14
Table 2-1. An overview of properties of pristine graphene and their derivatives.....	29
Table 2-2. Preparation method of graphene by top-down approach.....	37
Table 2-3. Preparation method of graphene by bottom-up approach.....	39
Table 2-4. An outlook on applications of graphene in the field of polymer technology and analysis of effects of graphene on polymer matrixes properties.....	49
Table 2-5. Electromagnetic shielding effectiveness of various Graphene-based materials.....	69
Table 2-6. Different types of hierarchy crystal structure and its properties of BaTiO ₃	87
Table 2-7. Fundamental requirement of the ferroelectric materials/ BaTiO ₃ for ferroelectrics behaviour.....	92
Table 2-8. An overview of various methods for preparation of BaTiO ₃ and pros as well as cons.....	103
Table 3-1. Formulation of GNPs and Barium titanate(IV) based Nanocomposites (GBNC) and sample designation.....	116
Table 3-2. Formulation of GNPs and Barium titanate(IV) based in-situ fibrils Nanocomposites (GBFNC) and sample designation.....	120
Table 3-3. Melting, crystallisation temperature, percentage crystallinity ($\chi\%$), ΔH_f , degrees of crystallinity (X_c), rate constant (k'), and n (Note: $T_m(o_c)$, $T_c(o_c)$, $\Delta H_f(J/g)$, k' (min^{-1})).....	137
Table 3-4. A comparison table summarising the confinement of polymer chains on the filler surface for the different samples.....	141
Table 3-5. Comparison of Theoretical mechanical properties for PP/PET blends with different reinforcement types and concentrations.....	155
Table 4-1. Electrical conductivity values of epoxy's nanocomposites obtained from various processes (MWCNT means: Multi walled carbon nanotube, GNP means graphene nanoplatelets and GO refers to graphene oxide).....	174
Table 4-2. Thermal conductivity value of various epoxy nanocomposites (GNP means graphene nanoplatelets).....	175
Table 4-3. The dielectric constant of dielectric enhanced BaTiO ₃ /epoxy nanocomposites	177

Table 5-1. Characteristics of the BaTiO ₃	224
Table 5-2. Characteristics of the Si- BaTiO ₃ and epoxy.....	236

LIST OF EQUATIONS

(1-1).....	12
(1-2).....	12
(1-3).....	13
(1.4).....	13
(2-1).....	81
(2-2).....	94
(2-3).....	97
(2-4).....	98
(2-5).....	98
(2-7).....	98
(2-8).....	99
(2-9).....	99
(2-10).....	99
(2-11).....	99
(2-12).....	100
(2-13).....	100
(2-14).....	100
(2-15).....	101
(3-1).....	120
(3-2).....	121
(3-3).....	122
(3-4).....	123
(3-5).....	123
(3-6).....	124
(3.7).....	127
(3.8).....	135
(3.9).....	143
(3.10).....	143
(3.11).....	143
(3.12).....	143
(3.13).....	147

(3.14).....	153
(3.15).....	153
(3.16).....	154
(3.17).....	154
(3.18).....	154
(3.19).....	155
(3.20).....	155
(3.21).....	155
(4.1).....	182
(4.2).....	182
(4.3).....	184
(4.4)	185
(4.5)	188
(4.6).....	188
(4.7).....	210
(4.8).....	211
(4.9).....	212
(4.10).....	213
(5.1).....	231

LIST OF ABBREVIATIONS

Acronym	Definition
3-GPS	3-glycidoxypropyl trimethoxysilane
BaTiO ₃	Barium titanate
CNT	Carbon nanotube
CB	Carbon black
CSR	Core-shell rubber
CTBN	Carboxyl terminated butadiene-acrylonitrile
CTE	Coefficient of thermal expansion
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential scanning calorimeter
DMTA/DMA	Dynamic mechanical thermal analysis or Dynamic mechanical analysis
DW	Domain wall
Ep	Epoxy
E'	Storage modulus

E''	Loss modulus
FBG	Fibre Bragg gratings
FCC	Federal Communications Commission
FRP	Fibre reinforced polymer
FC	Microfibrillar composite
FTIR	Fourier-transform infrared spectroscopy
GO	Graphene oxide
GNPs	Graphene nanoplatelets
RGO	Reduced graphene oxide
GHz	Gigahertz
MHz	Megahertz
Mins	Minutes
LCP	Liquid crystalline polymer
PEEK	Polyether ether ketone

PMC	Polymer matrix composite materials
PP	Polypropylene
PET	Polyethylene terephthalate
PMMA	Polymethyl methacrylate
MWCNT	Multi wall Carbon nanotube
PTFE	Polytetrafluoroethylene
PZT	Lead zirconate titanate
Rpm	Revolutions per minute
S	Seconds
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
THz	Terahertz
T _c	Crystallisation temperature
T _g	Glass transition temperature

TGA	Thermogravimetric analysis
UV	Ultraviolet
VNA	Vector network analyser
vol. %	Volume percentage
wt. %	Weight percent

CHAPTER 1

Introduction

1.1 Fundamentals and introduction

Materials serve as the fundamental basis of our society, propelling advancements across various sectors such as engineering, construction, automotive, and consumer goods. The ongoing innovation in engineering and the development of novel materials are imperative for envisioning the future and guaranteeing progression for future generations[1,2]. Essential needs such as sustainable energy and cost-effective personal care are intricately linked to material characteristics. This interconnection emphasises the vital role of materials science and engineering in addressing these needs. Progress in materials is crucial for tackling these challenges and advancing society[3–6]. The requirement for durable and lightweight electrochemical products stems from the necessity of portable electronic devices[7]. These items require flexibility and resilience for prolonged durability, ensuring reliability and convenience for users. Advancements in materials and engineering are crucial for achieving these attributes[8–11]. This chapter presents recent advancements in polymer composites, encompassing their classification and applications. Its goal is to provide insights into the changing realm of polymer composites, their uses, and their importance in various fields. Grasping these advancements is crucial for the ongoing development and utilisation of these materials in diverse applications, including those related to electrochemical products and sustainable energy[12–20]. Polymers are made up of macromolecules with repeating units comprising thousands of atoms or fundamental units. During the industrial growth era of the 1940s to 1960s, numerous new polymeric units were discovered. Today, polymer technologists have devised various methods to modify established polymers, emphasising industrial production and widespread use. An important milestone, credited to Thomas Hancock, involved combining natural rubber with Gutta-percha, pioneering the creation of polymer blends—mixtures of two or more polymers producing new materials with distinct physical properties. These advancements have significantly impacted the field of materials science and engineering[21]. Polymer composites consist of two key elements: a matrix, commonly a polymer material, and a reinforcement phase, which can be fibres, particles, or other materials[22]. In other hand, Nanocomposites integrate

nanoscale particles into the matrix, notably enhancing their properties[23,24]. These materials find wide applications across industries, such as aerospace for lightweight yet sturdy components, automotive to boost fuel efficiency, biomedical fields for implants and drug delivery, and energy generation for wind turbine blades and solar panels[25–28]. Additionally, they are used in electronics for circuit boards and casings[29]. The future of polymer composites and nanocomposites seems promising, potentially playing a more significant role in diverse industries, fostering more sustainable and efficient technologies. Challenges involve maintaining consistent quality during production, addressing environmental concerns in composite disposal, and optimising component compatibility. Understanding these developments is crucial for realising the complete potential of polymer composites and nanocomposites in diverse industrial applications.

1.2 Composites

A composite is a combination of two or more materials intricately bonded together, comprising a continuous phase and a dispersed phase. This structural arrangement is crucial for the improved characteristics and varied applications of composites in industries like aerospace, automotive, and electronics[30]. The properties of composites heavily depend on the composition, quantity, size, and shape of their constituent materials. Introducing fillers and reinforcements significantly alters and improves both the physical and mechanical attributes of matrix. Conductive fillers enhance electrical and thermal conductivity, while extender fillers help economise material costs. These deliberate adjustments are essential for customising composites for specific applications, contributing to their adaptability across industries[31]. To bolster the strength and durability of polymers, metals, or ceramics, reinforcements such as particles, fibres, or textiles are utilised. These reinforcements markedly influence the properties of the base materials. Composites can be produced using diverse methods, such as in-situ polymerisation, solution processing, and melt blending. These fabrication techniques allow customisation for specific applications, expanding their versatile use across industries[32]. For example, melt blending is an efficient method for

creating polymer blends and uniformly dispersing fillers within a polymer matrix. The particular advantageous is large-scale industrial production due to its effectiveness in ensuring consistent composite materials. This method is crucial in optimising composite properties for diverse industrial applications [24].

1.3 Classification of composites based on matrix.

Polymer matrix composites (PMCs) comprise polymers and are categorised into thermoset, elastomeric, and thermoplastic types. Thermoset composites can be further classified into particulate, fibrous, and laminate subtypes. This classification system distinguishes PMCs based on their material composition and structure, aiding in their specific utilisation across various industries[31,33]. Fibrous composites are divided into artificial fibre and natural fibre composites. Synthetics fibre composites use materials like glass, boron, Kevlar, and carbon fibres, while natural fibre composites are sourced from jute, sisal, hemp, and bamboo. Another classification criterion is the size of the reinforcement species, leading to the categories of macro, micro, and nanocomposites. These classifications help specify the type and scale of composites used in various industrial applications[33]. The classification of composite and in particular polymers-based composite is presented in Figure 1-1.

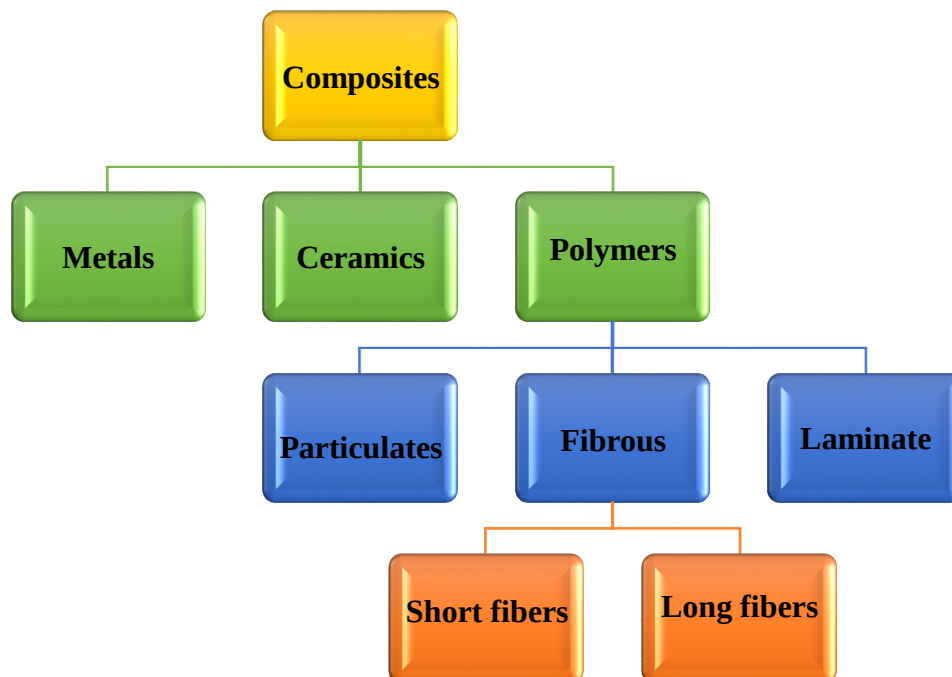


Figure 1-1. Classification of composites.

1.3.1 Metal matrix composites

Matrix metal composites (MMCs) are produced by integrating reinforcing materials into a continuous and uniform metal matrix. Normally, the matrix comprises lightweight metals like aluminium, magnesium, or titanium, providing a stable base for the added reinforcement. This blend yields MMCs with improved mechanical properties and varied applications in industries such as aerospace and automotive[34]. In severe environment applications, cobalt and cobalt-nickel chromium alloy matrices are often used in matrix metal composites (MMCs). Discontinuous metal matrix composites (DMMCs) can display either isotropic or anisotropic properties and are made from interlaced metal fibres. DMMCs can undergo extrusion, forging, or rolling processes, and the material's orientation influences its strength in an anisotropic structure. Initially, boron filaments were widely used as reinforcement in matrix metal composites, enhancing their mechanical properties and suitability for demanding industrial applications. Figure 1-2 illustrates the utilisation of discontinuous reinforcement in the form of monofilaments or "whiskers," short fibres, or particles. Alumina and silicon carbide are the primary reinforcing materials in this category. These reinforcements significantly improve the mechanical properties of composites, rendering them suitable for diverse industrial applications[34,35].

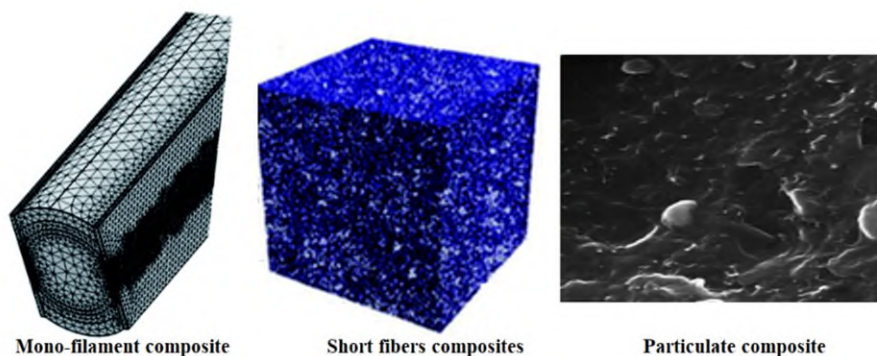


Figure 1-2. Types of reinforcing elements in metal matrix composites[36].

1.3.2 Ceramic matrix composites

Ceramic matrix composites (CMCs) are known for their impressive strength and modulus. These exceptional mechanical properties are attained by integrating ceramic reinforcement phases into a ceramic matrix, as shown in Figure 1-3. The increasing importance of continuous ceramic fibres, known for their pseudo-ductile behaviour, broadens the application of CMCs across various industries. This is especially significant in scenarios where traditional ceramics might be susceptible to brittleness[34,37].

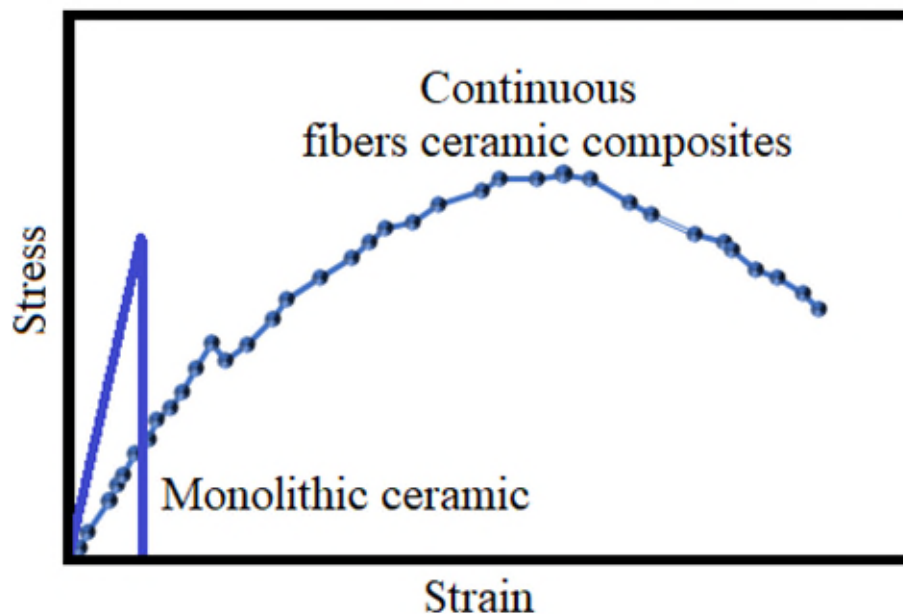


Figure 1-3. Stress - strain curves of a ceramic material and CMC[38].

Incorporating fillers into the ceramic matrix enhances properties such as electrical and thermal conductivity, thermal expansion, and hardness. Ceramic matrix composites (CMCs) are highly valued for their exceptional strength and high-temperature resistance. They excel in high-stress or high-temperature environments, offering stability, corrosion resistance, lightweight properties, and nonmagnetic, nonconductive characteristics, valuable across various industries. In summary, CMCs provide industrial appeal due to their toughness and durability, comparable to high-alloy steels and refractory metals. CMCs may contain residual metals post-processing and can utilise oxide or non-oxide matrices. Common materials like alumina and mullite, known for their thermal and chemical resistance, are prevalent, compatible with reinforcements such as

Portland cement and fly ash. Recent reinforcements like glass, mullite, alumina, carbon, and silicon carbide (SiC) fibres further enhance CMC properties, broadening their applications across diverse industries [35][29].

1.3.3 Polymer matrix composites

Polymers significantly enhance the mechanical properties and corrosion resistance of composite materials, proving vital in applications and industries where material durability and performance are critical. Strategically incorporating polymers improves the overall characteristics of composites, ensuring their suitability for diverse industrial requirements[33]. Polymers are preferred for their cost-effectiveness, ease of processing, and chemical resistance. However, they have limited mechanical strength and are mostly suitable for low-temperature applications. Figure 1-4 illustrates the wide spectrum of polymer matrix composites, showcasing their versatility across various industries and applications, despite their limitations in mechanical strength and high-temperature performance[39]. Polymer matrix composites perform exceptionally in applications needing strength, corrosion resistance, and heat tolerance. Their distinct attributes suit various industries and situations requiring these specific material properties for effective performance. These materials provide a balance between mechanical strength and resilience against environmental factors like corrosion and high temperatures.

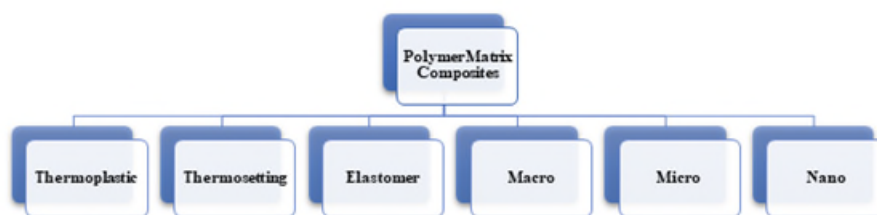


Figure 1-4. Classification of polymer matrix composites.

1.3.3.1 Thermoset matrix composites

Thermoset polymers, or resins, have long served as matrix materials in fibre-reinforced composites, particularly in automotive components. They offer advantages like thermal stability, chemical resistance, and low creep and stress relaxation compared to thermoplastic polymers, making them preferred in applications where these properties are crucial for performance[40]. Thermoset polymers have lower mechanical strain and stress relaxation compared to thermoplastic polymers. Yet, they have limitations such as a fixed shelf life, time-consuming manufacturing processes, and relatively lower impact strength and ductility. Common types of thermoset polymers include epoxy, unsaturated polyester, vinyl ester, and bismaleimide resins, each with distinctive properties and applications across various industries.

1.3.3.2 Thermoplastic matrix composites

Thermoplastic composites utilise matrices comprising thermoplastic polymers with amorphous or semi-crystalline structures. These matrices are reinforced with materials like glass, carbon, aramid, or metal fibres to enhance their mechanical properties, allowing a broad spectrum of applications across diverse industries. This approach leverages the flexibility and performance traits of thermoplastic composites[41]. Thermoplastic polymers in thermoplastic composites belong to two categories: high-temperature-based and engineering-based thermoplastics. High-temperature-based ones like polyphenylene sulphide (PPS), polyvinylidene fluoride (PVDF), and polyethylene terephthalate (PET) offer excellent impact and wear resistance. Engineering-based thermoplastics, such as polyamide and polyimide, provide diverse mechanical and thermal properties, making them versatile options for composite applications in various industries[42]. Table 1-1 shows the high-temperature thermoplastic polymers used in thermoplastic composites[43]. The table also reports the glass transition temperature (T_g) and the processing temperature (process temperature).

Table 1-1. High temperature thermoplastics used in fibre reinforced plastics [8].

Matrix	Morphology	Tg (°C)	Process Temp (°C)
PP	Semi crystalline	-10	190
PET	Semi crystalline	80	270
PEI	Amorphous	217	330
PPS	Semi crystalline	89	325
PEEK	Semi crystalline	156	340

1.3.3.3 Elastomer matrix composites

Rubber, present in composite products, imparts elasticity and flexibility akin to elastomers. For instance, rubber wheels in vehicles minimise noise and vibration, while rubber gloves and boots in construction safeguard hands and feet, reducing the risk of injury[44,45]. Some products, like reinforced rubbers, need stiffness in particular directions to perform their intended function. Short-fibre reinforced rubbers are more application-based because they are easy to make and have excellent flexibility. They are also less expensive than long fibre-reinforced rubbers, which makes them a more cost-effective option for certain applications. A lot of research has been done on such composites with synthetic fibres, like polyester, nylon, carbon, Kevlar, glass, and asbestos[46]. These composites are exceptionally durable and strong, and they are used in a variety of applications.

1.4 Classification of composites based on reinforcement

Particle reinforcements lack a specific orientation and are mainly used to improve the properties or optimise the production of isotropic materials. They contribute to enhancing material characteristics in all directions, proving valuable for enhancing performance and cost-effectiveness across various applications and

industries[47]. Isotropic materials possess uniform properties in all directions, as depicted in Figure 1-5. Nanomaterials often have an aspect ratio (length to diameter) close to unity, and the reinforcing particles can have diverse shapes like spherical, elliptical, cubic, platelet, or irregular geometries. The shape, size, and composition of these reinforcing particles significantly impact the strength and durability of composites, influencing the overall quality and performance of materials across varied applications and industries[39]. Certain particle fillers like clay and talc might not inherently reinforce materials, but carbon black is acknowledged as a reinforcing agent. When these fillers are combined, their synergistic effect can bolster the strength and durability of a product. This approach optimises material properties, especially in applications requiring increased robustness.

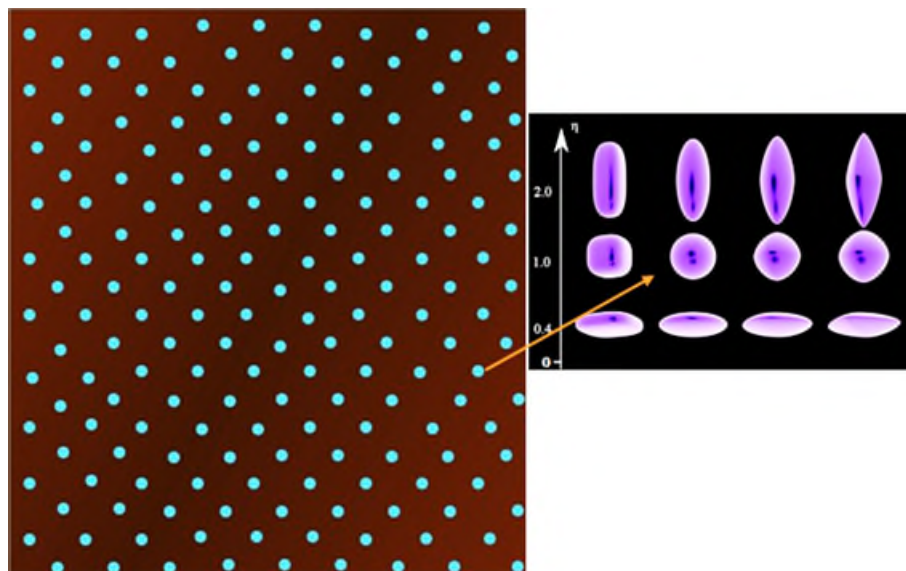


Figure 1-5. Example of particulate composite[48].

Laminated composites consist of two-dimensional sheets or panels, like wood, with considerable strength mainly in one direction. These sheets are assembled and bonded in layers, resembling a sandwich-like construction, as illustrated in Figure 1-6. This approach allows for the creation of materials with tailored strength characteristics, suitable for various applications and industries [49]. Laminate composites are widely used due to their blend of composite material strength and durability, coupled with the visual and tactile resemblance to

traditional wood products. This versatility makes them suitable for a variety of applications across industries where both performance and aesthetics are essential[50].

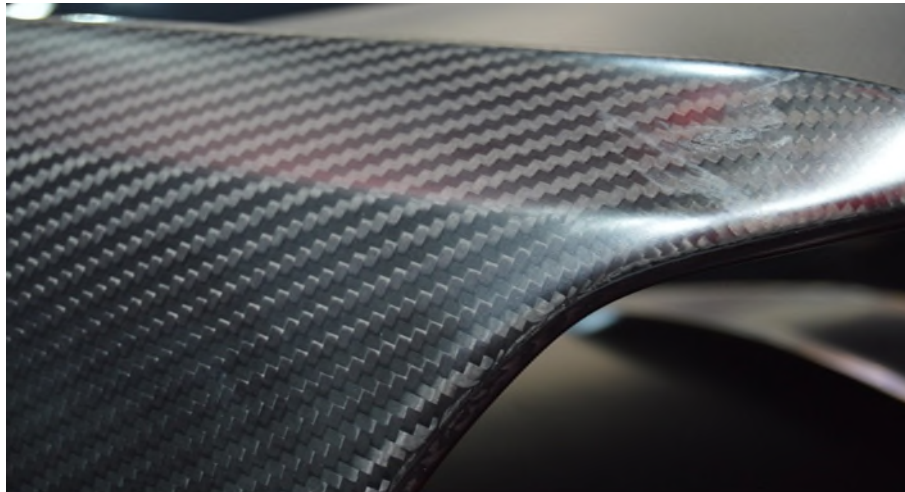


Figure 1-6. Laminate reinforcement arrangement: conversion to composite after consolidation using resin.

1.4.1 Matrix - fibre interface

Fiber-reinforced composites (FRCs) are favoured for their exceptional specific strength and modulus. These materials boast superior strength-to-weight and stiffness-to-weight ratios, proving valuable in applications where lightweight, high-performance materials are essential. FRCs are widely used across industries to meet specific performance demands[51]. Fiber-reinforced composites (FRCs) are widely used in industries such as aerospace, automotive, and sports due to their exceptional stiffness and lightweight properties. These materials bolster rigidity and strength when reinforcing fibres are incorporated into the polymer matrix. Their applications span various sectors, meeting the demand for high-performance, lightweight solutions[52]. The matrix in reinforced composites should enable easy fibre integration to improve impact strength, a crucial factor often lacking in matrices. Long (continuous) fibres perform well in load-bearing applications, while short (discontinuous) fibres are more suitable for bending applications, as they can handle a significant portion of the load. Analysis of long fibre-reinforced composites often overlooks the end-fibre effect,

concentrating on their load-bearing capacity[53]. Short-fibre reinforced composites experience amplified end effects as the aspect ratio of the fibre decreases, resulting in reduced compressive strength. Factors like low aspect ratio, inadequate dispersion, and improper fibre arrangement restrict stress in short-fibre composites. Oriented fibre composites, with fibres aligned along the applied load direction, improve load absorption, outperforming non-oriented counterparts in load-bearing capacity[54,55]. When a single fibre is incorporated into a matrix with a lower modulus, they endure different tensile stresses because of their differing moduli. This uneven stress distribution leads to strain discrepancies, resulting in damage to the system[56]. The lower elastic modulus of the matrix, relative to the fibre, results in longitudinal extension within the composite[57]. The disparity in longitudinal strains between short fibres and the area around the fiber's end creates shear stress along the fibre axis, stressing the fibres. This shear stress distribution transfers the load from the matrix to the fibres. When mechanical force is applied to the polymer matrix, it propagates uniformly until it reaches the matrix-fibre interface, facilitating efficient load transfer[58]. Effective stress dispersion and distribution throughout the fibre hinge on excellent bonding at the fibre-matrix interface, a critical determinant for composite strength. Strong interfaces are crucial for efficient load transmission to the fibre, as elaborated in the equations below. Thus, a robust interface is fundamental for achieving optimal composite performance[59]. A strong interface enhances the efficiency and effectiveness of composites. Theoretical calculations, as represented by the equations below, emphasise the significance of a robust interface in composite performance[60].

$$\epsilon_c = \epsilon_f = \epsilon_m \quad (1-1)$$

Where ϵ_c , ϵ_f , ϵ_m are the strain in the composite, the fibre, and the matrix, respectively. Under condition of elasticity, the following two equations can be applied.

$$\sigma_f = E_f \epsilon_f \quad (1-2)$$

$$\sigma_m = E_m \epsilon_m \quad (1-3)$$

Hence,

$$\frac{\sigma_c}{E_c} = \frac{\sigma_f}{E_f} = \frac{\sigma_m}{E_m} \quad (1-4)$$

Where σ_c , σ_f , σ_m are the stresses produced in the composites, fibre, and matrix, respectively. Similarly, E_c , E_f , E_m are the moduli of the composite, fibre, and matrix, respectively. Generally, E_f is higher than E_m and so the stress in the fibre is higher than that in the matrix. Equation (1.4) is called as rule of mixture.

1.5 Nanocomposites

In the current context, prioritising energy-efficient advanced technologies and sustainable development is vital. Individuals are pursuing these objectives through diverse approaches, with some focusing on advanced technologies and others on sustainable practices. However, both facets are crucial to address. Nanomaterials are increasingly prominent due to their favourable physicochemical properties, rendering them appealing for various applications[61]. The term "nano," stemming from Greek, signifies "one billionth" and pertains to the manipulation of compounds, atoms, or molecules to fashion structures with distinct properties, such as exceptional strength, lightweight, or improved electrical conductivity. The nanoscale is an invaluable realm in science, technology, engineering, and medicine, employed in diverse applications, from microchips in computers to advanced drug delivery systems[62]. The development of nanotechnology has been a gradual and sometimes challenging journey, dating back to the 19th century, riddled with setbacks and obstacles. However, recent years have shown a remarkable surge in nanotechnology, marked by substantial growth and groundbreaking innovations. This transformation highlights the sustained dedication to advancing nanoscience and its diverse applications. A comprehensive overview of the developing nanotechnology landscape is provided in Table 1-2, with respect to the specific year.

Table 1-2. An overview of development in the field of nanotechnology with respect to the years[63].

Year	Development in nanotechnology
1959	R. Feynman idea
1974	Taniguchi's 1974 definition was "the science and technology of materials at the nanometre scale"
1981	In 1981, IBM invented the Scanning Tunnelling Microscope
1985	Bucky Ball
1986	Engines of Creation is a K. Eric Drexler book on nanotechnology and atomic force microscopy
1989	The company logo for IBM was made up of unique atoms
1991	Carbon nanotubes, discovered by S. Iijima, are a one-dimensional crystalline form of carbon
1999	R. Freitas published the first book about Nanomedicine

2000	The National Nanotechnology Initiative was announced
2001	The Feynman Prize in Nanotechnology was given for the theoretical development of nanoscale electronic devices and carbon nanotubes
2002	Advancing model of molecular machine systems to improve the design of future generation systems
2003	The Feynman Prize in Nanotechnology went to the single-molecule biological motors study and the nano-scale silicon devices study
2004	The Feynman Prize in Nanotechnology and Nobel Prize in Chemistry go to the team that built stable protein structures and enzymes
2005-2010	Nanotechnology-based products, as well as robotics based on nanotechnology

<p style="text-align: center;">2011</p>	<p style="text-align: center;">The beginning of the molecular nano technology era is marked by the development of the nanotechnology device</p>
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Polymer nanocomposites (PNCs) are sophisticated materials combining polymer matrices with nanoscale reinforcing particles (1–100 nm). They utilise both thermoplastic and thermosetting polymers, leveraging nanomaterial properties to boost performance. These materials serve multiple industries, deriving exceptional properties from nanoscale components[64]. Nanofillers in polymer nanocomposites encompass diverse inorganic materials, like phyllosilicates, fullerenes, nanotubes, metals, and gases. When integrated at the nanoscale, these elements enhance the composite's properties, improving performance in various applications. The selection of nanofillers notably influences the final material's characteristics[65]. Polymer nanocomposites (PNCs) are used across aerospace, electronics, healthcare, and automotive industries. They employ two filler types: conductive fillers change properties like thermal conductivity, electrical resistivity, and flame resistance, while extender fillers primarily influence material costs. The selection of these fillers depends on specific performance and economic needs in diverse applications[66]. Polymer nanocomposites can be produced via methods such as melt blending, solution casting, emulsion casting, spinning, and sputtering. The choice of method depends on factors like desired material properties, application, and production scale. These techniques facilitate integrating nanoscale fillers into polymer matrices, augmenting their performance across various fields[67]. The production of layered silicate polymer nanocomposites involves two main methods: 1) Swelling of minerals with monomers, enabling penetration between mineral layers and polymerisation, and 2) Polymer penetration between mineral layers, creating nanocomposites in the molten or solution state. These processes generate two primary structures: intercalated and exfoliated, each with distinct properties and applications[68]. Method and structure selection rely on desired nanocomposite traits and intended applications[69,70]. In intercalated

nanocomposites, polymers penetrate the clay structure in a three-dimensional orderly manner, with some polymer layers within the gallery region. In exfoliated nanocomposites, individual 1nm thick clay layers disperse within a continuous polymer matrix, with spacing determined by clay loading. These structures distinctly impact the nanocomposite's properties and performance across applications[70,71].

1.5.1 Classification of nanofillers

Comprehensive understanding of material properties empowers researchers to choose appropriate materials for diverse everyday applications and develop innovative solutions for future requirements[72,73]. This understanding aids in optimising current materials and innovating improved materials for various applications[74]. Through material selection and transformative methods, it's feasible to surpass design constraints and create new materials with previously unattainable properties. This encompasses superior materials, varied compositions, and operation under diverse temperature conditions. These advances have propelled significant strides in materials science and technology[75]. As defined by the European Commission, nanomaterials consist of particles or components within the size range of 1 to 100 nanometres. This delineation aids in identifying materials with nanoscale properties for different applications and regulatory considerations[76]. Nanomaterials, 10,000 times smaller than the width of a human hair, are highly valuable in applications such as drug delivery, electronics, and energy due to their extremely compact size. Figure 1-7 outlines various types of nanomaterials, including gold, silver, graphene, and carbon nanotubes. These nanomaterials are synthesised through two distinct approaches: top-down and bottom-up, as depicted in Figure 1-8, allowing for diverse applications and innovation in nanotechnology. The top-down approach gradually reduces bulk materials to nanoscale structures via mechanical or chemical processes, which can be destructive. In contrast, the bottom-up approach begins with small molecules and incrementally adds atoms to form nanoscale structures, offering a more constructive method with fewer

defects and improved properties. This technique utilises atomic-sized sources for synthesising nanomaterials, expanding their potential applications[77].

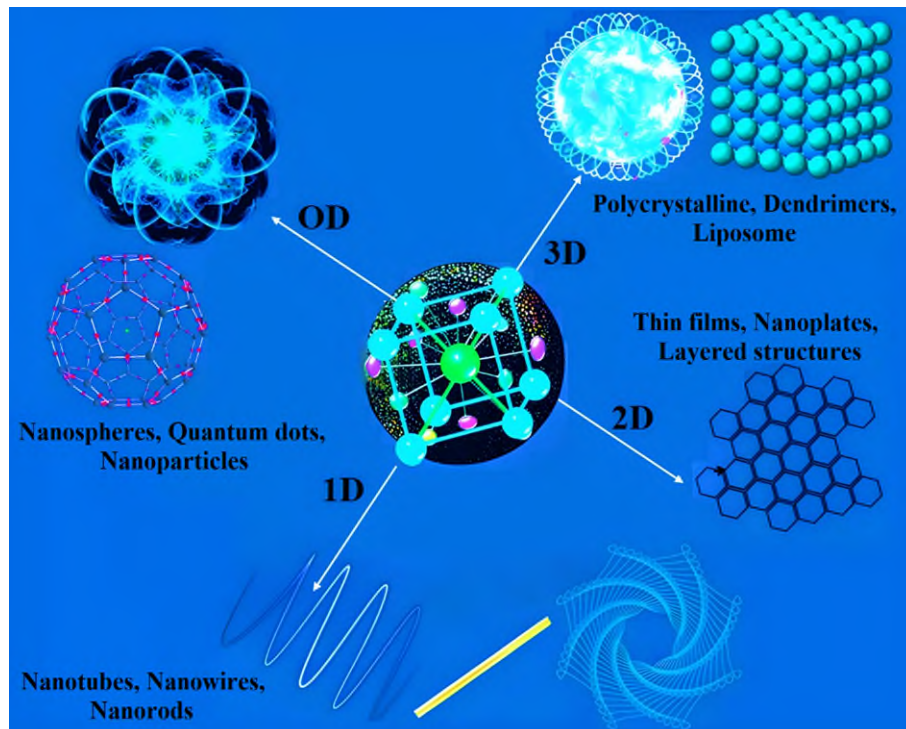


Figure 1-7. Classification of nanomaterials based on their dimension.

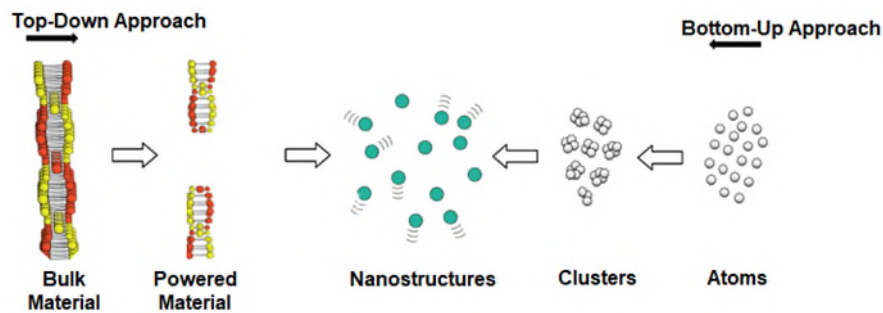


Figure 1-8. Preparation method of nanomaterials by top-down and bottom-up approach.

1.5.2 Applications of nanocomposites

Nanocomposites create high-performance smart materials capable of modifying their properties under stimuli. Advances in developing smart materials, derived from nanomaterials, span sectors like energy, health, electronics, and agriculture.

These materials possess the potential to revolutionise energy consumption, bolster health safety, elevate electronics standards, and refine agricultural practices, fostering innovation and efficiency in these fields[78]. Polymer technologists have innovated methods to modify established polymers, expanding their use in various applications. Thomas Hancock's blending of natural rubber with Gutta-percha marked a pivotal moment in rubber production. Polymer blends, achieved by combining two or more polymers, generate materials with unique physical properties, offering versatility and adaptability in material design and production[21]. These materials are utilised in actuators, chemical sensors, strain sensors, self-healing hydrogels, and controlled drug delivery systems. Their potential lies in their flexibility, durability, and responsiveness to environmental changes. With distinctive properties, they provide adaptable solutions and have documented uses in various fields[79]. Nanomaterial-based macro-assemblies, with significant surface areas and cross-linking capabilities, are employed across various industries. Their features, including extensive surface area and cross-linking sites, make them suitable for applications like gas sensors, elastic strain sensors, and self-healing materials. These materials offer versatile solutions due to their unique properties in diverse industrial contexts[239]. The thermo-mechanical properties of nanocomposites are highly sought after for applications in energy storage, water purification, environmental protection, and hybrid nanostructures. The ability to develop smart materials via advanced printing and their responsive behaviour to external stimuli using nanocomposites is particularly intriguing[81]. These advancements hold broad implications across various fields[82,83]. Smart materials are categorised as passive or active. Passive smart materials change properties without external stimuli, while active smart materials require external stimulation. These distinctions influence their applications and behaviour across various fields[84]. In recent years, carbon-based polymer composites and smart materials have gained significant popularity in aerospace, automotive, and biomedical applications[85,86], electronics, and more. Common materials in these technologies include graphene oxide, graphene, fullerene, and carbon nanotubes, offering unique properties for various applications[87,88]. For

electromagnetic interference (EMI) shielding, materials like copper, barium titanate, graphene, and iron oxide-based polymer nanocomposites are utilised. These materials offer EMI shielding by utilising their electrical conductivity, dielectric properties, and magnetism. High-performance nanomaterials and polymer nanocomposites with enhanced conductivity, surface area, and magnetic/dielectric characteristics are employed for effective EMI shielding, addressing electromagnetic interference (EMI)[89]. Nanocomposites incorporating nanomaterials are vital for EMI shielding due to their exceptional conductivity, magnetic, and dielectric properties, as well as their large surface area. This enhances their effectiveness in shielding electromagnetic interference[90]. Blending organic matrices with inorganic nanoparticles in composites is a promising method for creating advanced materials. This approach enhances material functionality and broadens application possibilities in various fields, as shown Figure 1-9.

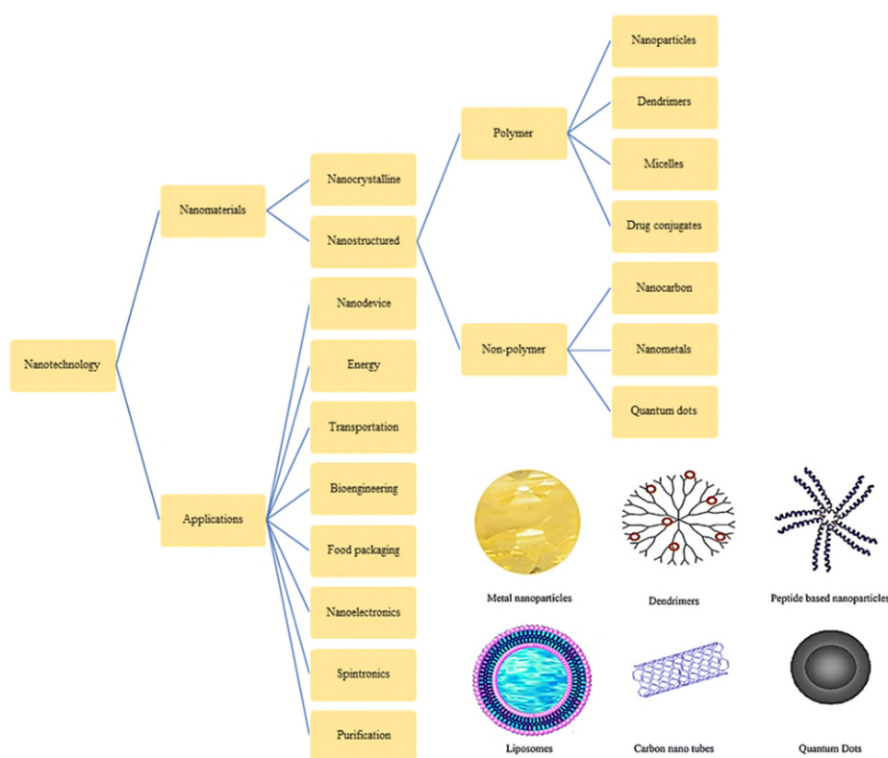


Figure 1-9. Various forms of nanomaterials/ nanocomposites and application[63].

Graphene, a two-dimensional material composed of a single layer of carbon atoms in a honeycomb lattice, has gained substantial attention due to its remarkable properties. With high electrical conductivity, thermal conductivity, mechanical strength, and flexibility, graphene shows promise for applications in electronics, photonics, energy storage, and various other fields. Section 2.1 in the next chapter covers graphene, emphasising its applications, manufacturing techniques, and transformative capabilities. Graphene's exceptional properties—mechanical, electronic, and thermal—drive its potential in electronics, textiles, and energy storage. The section explores nanoscale applications like nanofilms, nanoparticles, and their impact on electronics and energy fields. In Section 2.2, the focus shifts to BaTiO₃'s properties, crystal structure, and how incorporating it into polymer composites enhances their mechanical and electrical attributes. These improvements are valuable across multiple applications. Graphene-based materials, such as graphene oxide, reduced graphene oxide, graphene nanoplatelets, and BaTiO₃, serve as reinforcing agents in lightweight composites. When combined with various polymers, these materials produce composites with outstanding mechanical, electrical, thermal properties, and effective electromagnetic radiation shielding. The study highlights control mechanisms in micro and nano systems for enhancing polymer nanocomposites[87].

1.6 Research gap and contribution to knowledge

The analysis of literature on polymer nanocomposites and micro/nano systems has unveiled a substantial research gap. Specifically, it emphasises the necessity of understanding the simultaneous effects of mechanical and electrical stimuli on nanocomposites, alongside the complex regulatory mechanisms that govern their responses. This gap underscores the vital need for a comprehensive grasp of these external stimuli and their inherent link between the response of micro/nano reinforcement and the synergistic impact on smart polymer nanocomposites for real-world applications. This thesis aims to address these pivotal aspects, striving to provide a comprehensive understanding of how external stimuli interact with nanocomposite behaviour. By delving into these less-explored areas, the

research endeavours to offer transformative insights in materials science, potentially paving the way for groundbreaking advancements in this field.

1.7 Aims and objectives

The central aim of this thesis is to comprehensively explore the behaviour and characteristics of nanocomposites, specifically focusing on diverse nanomaterials like graphene (e.g., graphene nanoplates or GNP) and barium titanate (BaTiO_3) integrated with epoxy resins and thermoplastic polymers. The primary objective is to understand how these materials respond to both mechanical and electrical stimuli, particularly when observed at micro and nano scales. By uncovering the intricate mechanisms governing these nanocomposites under external influences, this research aims to bridge the existing gap in integrating micro and nano systems with polymer nanocomposites and their response to external stimuli. The comprehensive exploration aims to elucidate the nuanced interactions between these systems, contributing to an expanded understanding and potential applications in the field of materials science. Moreover, the study aims to evaluate the practical applications of these materials across diverse industries, especially focusing on thermoplastic polymers and nanocomposites made from plastic waste filled with GNPs/ BaTiO_3 . This research direction is committed to environmentally conscious materials innovation, addressing concerns about waste microbeads, and exploring varied applications across sectors. These aims align with and build upon pivotal research in the field, showcasing the diverse applications and progress within the realm of nanocomposites.

1.7.1 Objectives of the research:

The research objectives are structured to address critical gaps and aims:

1. Evaluate the influence of electrically conductive and nanodielectric fillers on the behaviour of polymer nanocomposite when these are subjected in to simultaneous mechanical and electrical forces. This evaluation encompasses

both thermoplastics and epoxy resins, employing a combination of experimental and computational tools to gauge their impact.

2. Generate fibril microstructures under mechanical stimuli and develop eco-friendly nanocomposites from recycled polypropylene and poly (ethylene terephthalate) combined with GNPs/ BaTiO₃ to mitigate the environmental impact of plastic waste. Evaluate the synergistic effects of various microstructures using a combination of experimental and computational tools such as MATLAB.

3. Utilise techniques such as Raman spectroscopy and COMSOL Multiphysics to scrutinise epoxy nanocomposite behaviour, aiming to provide in-depth insights. Investigate the expanded potential applications of epoxy/ BaTiO₃ nanocomposites under external stimuli, contributing to the field of materials science and engineering.

4. Reveal the fundamental principles guiding both thermoplastic and epoxy nanocomposites' responses through a combination of experimental and theoretical investigations. Additionally, clarify how polymer nanocomposites respond to mechanical and electrical stimuli via combined experimental and theoretical approaches.

5. Analyse the influence of external stimuli on the structure-property relationships of polymer nanocomposites by observing their responses. Investigate the combined impact of these stimuli on nanofillers, microstructure, and property correlations, facilitating interdisciplinary knowledge integration.

These outlined objectives highlight the extensive scope, purpose, and potential contributions intended to address the research gap within the domain of materials science and engineering.

1.8 Thesis structure

The research objectives are structured to align with each chapter of the research.

Chapter 1: Introduction

The Chapter 1 offers a comprehensive overview of the research's significance within the domain of materials science and engineering.

Chapter 2: Literature Review and Background

The Chapter 2 provides an extensive analysis of existing literature, emphasising the research gap, and setting the foundational framework for the study.

Chapter 3: Theoretical modelling and experimental validation

The Chapter 3 investigates the influence of mechanically regulated microstructures on thermoplastic/GNPs- BaTiO₃ nanocomposites under external mechanical stimuli, emphasising microstructure-properties correlations. It also uncovers the modifications in microstructure under external mechanical forces and their impact on properties using a diverse range of analytical tools for meticulous material characterisations.

Chapter 4: Computational modelling and Bayesian statistical analysis

The Chapter 4 investigates the impact of filler materials on specific properties of epoxy polymer matrix composites. It leverages computational models and Bayesian statistical analyses to delve into properties such as DC conductivity, dielectric constant, and thermal behaviour.

Chapter 5: Experimental validation of computational approach

The Chapter 5 validates computational model predictions presented in Chapter 4 through physical experiments. This chapter focuses on comprehending the influence of electric fields on material properties, specifically in an aerospace context. It incorporates in-situ real-time Raman spectroscopy measurements and includes Digital Image Correlation (DIC) and mechanical characterisations.

Chapter 6: Future prospects

The Chapter 6 envisions forthcoming developments and potential research trajectories, focusing particularly on understanding and utilising electric field effects on epoxy/GNPS- BaTiO₃ and thermoplastic nanocomposite materials.

The research methodology amalgamates theoretical insights, empirical validations, and data-driven analyses, aiming to advance the comprehension and application of nanocomposites across diverse domains.

1.9 Materials and methods selection criteria

The materials selected for the research were chosen based on their relevance to the objectives and accessibility. Epoxy resins were chosen for exploring aerospace applications, while thermoplastic polymers addressed environmental concerns and broader applications in electronics and automotive sectors. The use of conductive (GNPs) and dielectric (BaTiO₃) nanomaterials as fillers was selected due to their potential impact and availability, ensuring an ethical and feasible approach. The methodology aimed to comprehensively understand and enhance nanocomposite material properties, contributing significantly to the field of materials science and engineering.

CHAPTER 2

Literature Review and Background

2.1 Introduction

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, offers outstanding properties such as high surface area, remarkable mechanical strength, and excellent electrical and thermal conductivity. Its exceptional characteristics make it a promising material for diverse applications across various industries[91]. Graphene's exceptional properties, intricately linked to its structure, position it as an ideal choice for applications in electronics, energy storage, and sensing. The material's mechanical, electrical, and optical characteristics can be significantly influenced by minor alterations in its size, shape, and orientation, underscoring the importance of precise structural control for optimising its performance in various fields[92]. Defects such as vacancies and grain boundaries in graphene can alter its characteristics. Understanding the relationship between graphene's structure and properties is crucial for tailoring its attributes to specific applications. Techniques such as doping or functionalisation with different molecules or atoms provide control over its electrical properties, such as bandgap and carrier concentration[93]. Controlling grain size and orientation significantly enhances graphene's mechanical properties. This plays a vital role in applications such as graphene-based electrodes for energy storage, where its conductivity and surface area are essential. Moreover, graphene-based sensors demonstrate sensitivity and selectivity, making them well-suited for detecting various analytes[94]. Understanding the complex relationships between the structure, properties, and applications of graphene necessitates a multidisciplinary approach, including materials synthesis, characterisation, and device fabrication. This comprehensive understanding drives the creation of innovative graphene applications, maximising its unique properties[23]. Barium titanate (BaTiO_3) is a ferroelectric ceramic acclaimed for its high dielectric constant, piezoelectric features, and photorefractive effect. These attributes stem from its perovskite crystal structure comprising alternating BaO and TiO_2 layers, with dielectric properties intricately tied to the crystal structure and the impact of defects like vacancies and impurities[36]. Barium titanate (BaTiO_3) demonstrates its maximum dielectric constant during the ferroelectric phase transition, mainly due to its crystal structure and inherent defects. This material also showcases a

significant nonlinear dielectric response, making it suitable for high-capacitance capacitors and electronic devices. Its piezoelectric properties are attributed to the displacement of Ti^{4+} cations under an external electric field, enabling a wide range of applications[95]. The polarisation induced by this displacement serves in sensors, actuators, and electromechanical devices. BaTiO_3 's photorefractive effect, altering the refractive index upon light exposure, finds use in holography, optical data storage, and more. Its applications in electronics, optoelectronics, and various fields arise from its unique blend of dielectric, piezoelectric, and photorefractive properties.

The chapter examines the interplay between structure, properties, and applications of graphene and BaTiO_3 dielectric. Graphene's distinctive hexagonal lattice structure grants exceptional mechanical, electrical, and thermal properties, promising applications in electronics, energy storage, and composites. BaTiO_3 's discussion delves into its ferroelectric ceramic nature, high dielectric constant, piezoelectricity, and photo refractivity. The chapter explores how varying BaTiO_3 content affects its properties and suitability for applications in nonlinear optics, capacitors, and transducers. Understanding these relationships is crucial for material selection and optimisation in specific applications.

2.2 Structure–property-application relationships in graphene

A profound understanding of material characteristics empowers scientists to select optimal materials for diverse daily-use applications and develop innovative, tailor-made products to meet specific needs[74]. These advancements have driven innovative progress in materials science and technology, leading to the creation of more durable materials and the discovery of more efficient utilisation of existing ones[75]. As per the European Commission's definition, a nanomaterial consists of particles or constituents ranging between 1 to 100 nanometres in size[76]. Nanomaterials' diminutive size offers value across various applications. Different types of carbon nanomaterials include nano-onions, fullerene, carbon nanotubes (CNTs), graphene nanoribbons, and nano-diamonds, as depicted in Figure 2-1[76].

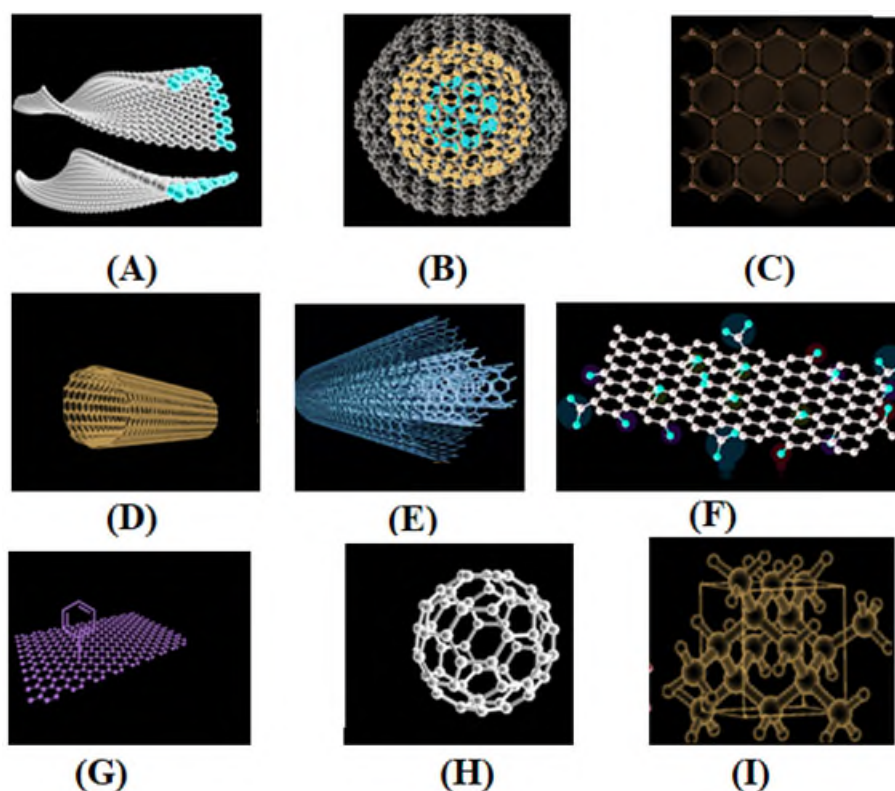


Figure 2-1. The different types of nanocarbons, (A) Graphene nanoribbon, (B) Nano onion, (C) Pristine graphene, (D) Single-walled carbon nanotube (SWCNT), (E) Multi-walled carbon nanotube (MWCNT), (F) Graphene oxide (GO), (G) Functionalised graphene, (H) Fullerenes, (I) Nanodiamond.

Graphene, a crucial carbon nanomaterial, was first isolated from graphite[96]. The resultant monolayer of graphite, known as graphene, is a single-atom-thick sheet and represents the thinnest stable material obtained[97,98]. The fundamental physical properties evidencing the exceptional nature of single layer, graphene nanosheets are presented in Table 2-1.

Table 2-1. An overview of properties of pristine graphene and their derivatives.

Properties of pristine (unmodified) graphene		
1	Surface Area	2630 m ² /g

2	Thermal Stability	1000 °C
3	Intrinsic mobility	200000 cm ² V ⁻¹ s ⁻¹
5	Young's Modulus	1TPa
6	Conductivity	Much more than SWCNTs
7	Thermal conductivity	5000 Wm ⁻¹ K ⁻¹
8	Optical transmittance	~98%
Properties of reduced graphene oxide (rGO)		
1	Surface Area	500-1000 (m ² /g)
2	Thermal Stability	~700 °C
3	Tensile Strength	Less than SWCNTs
4	Young's Modulus	0.25 TPa
5	Conductivity	Like CNTs
Properties of graphene oxide (GO)		
1	Surface Area	70-100 (m ² /g)

2	Thermal Stability	~150 °C
3	Young's Modulus	~207.6 GPa
4	Conductivity	Insulator

Graphene's introduction to commercial applications commenced in optoelectronics, utilising its exceptional light transmission (>90%) and remarkable electrical conductivity ($>1 \times 10^6$ S/m). This rare combination allows efficient light transmission and excellent electrical conductivity, making graphene well-suited for optoelectronic devices such as displays and photodetectors. This breakthrough stems from graphene's unique properties, making it an asset in the optoelectronics field[99]. Over the past five years, significant advancements in commercial products derived from graphene have emerged, particularly in tissue engineering. Graphene's outstanding attributes, like biocompatibility and mechanical strength, have propelled progress in creating scaffolds and substrates for tissue regeneration. This advancement showcases graphene's potential to transform tissue engineering and pave the way for medical breakthroughs, driven by its remarkable properties and their applications[100–103]. Graphene's thin, lightweight, and flexible nature has accelerated the production of commercial items such as display screens, photonics, and electric circuits[4,10,104]. These traits enable the development of robust and advanced technologies, particularly in sectors valuing flexibility and efficiency. Hence, graphene emerges as a leading force in advancing next-generation electronic devices and optical components, revolutionising industries with its exceptional attributes. Its adaptability proves valuable in bioimaging applications, utilising its thinness, flexibility, and biocompatibility for high-resolution imaging of biological structures[105–107]. Integrating graphene into imaging technologies enhances contrast and resolution while reducing invasiveness, promising breakthroughs in medical diagnostics and research. This advancement has the potential to transform medical imaging across settings, improving healthcare outcomes.

Graphene's versatility in drug delivery stems from its adaptable properties, serving as an effective carrier for therapeutic compounds[108,109]. Graphene's biocompatibility, ample surface area, and adaptable surface chemistry enable efficient drug loading and controlled release, advancing personalised medicine and enhancing treatment efficacy. This potential advancement shows promise in revolutionising drug delivery strategies and improving patient outcomes[110,111]. Graphene's exceptional electrical conductivity drives its integration into electronics, enabling high-speed data transmission and optimised device functionality. Its application extends to transistors, sensors, and interconnects, boosting performance and facilitating rapid, energy-efficient innovations in sectors like telecommunications, computing, and consumer electronics. This significant impact highlights graphene's pivotal role in shaping the future of electronic technologies[112–114]. Graphene's outstanding electrical conductivity and atomic thinness propel its integration as a channel material in field-effect transistors, enabling high-speed switching and reduced power consumption. This application extends to integrated circuits, wearable devices, and emerging technologies, enhancing electronic performance and energy efficiency across various industries[115]. Graphene's role as transparent conducting electrodes stems from its distinctive mix of transparency and electrical conductivity. These electrodes are used in touchscreens, solar cells, and flexible electronics, enabling unobstructed light transmission and efficient current flow. Graphene's versatility enhances the functionality of transparent electronic components across various applications[116,117]. Graphene's role in photodetectors relies on its outstanding electrical conductivity and broad light absorption range. This combination enables efficient light detection in various fields like imaging, communications, and environmental monitoring. Integrated into cameras and optical sensors, graphene-based photodetectors improve sensitivity and response speed, ultimately enhancing overall device performance[118–120]. Graphene's integration into Hall effect sensors is driven by its exceptional electrical characteristics and high sensitivity to magnetic fields. These sensors play a crucial role in measuring magnetic fields, finding diverse applications in automotive, industrial, and consumer electronics. Incorporating graphene in

sensor design enhances measurement accuracy and responsiveness, improving magnetic field detection across various industries[121,122]. Hall effect sensors utilise the Hall effect observed in conductive materials under the influence of a magnetic field and electric current. This phenomenon generates a voltage, called the Hall voltage, across the material perpendicular to the current and magnetic field. The Hall voltage is directly proportional to the magnetic field strength, enabling accurate magnetic field measurement. These sensors are extensively employed in diverse applications, notably in automotive systems for tasks like measuring wheel speed and detecting crankshaft position[123]. Graphene's incorporation into conductive ink capitalises on its remarkable electrical conductivity and compatibility with printing methods. These inks are vital for producing flexible circuits, electronic textiles, and printed electronics cost-effectively. Integrating graphene into conductive inks enables the creation of intricate conductive designs on various surfaces, fostering innovative applications in wearable and flexible electronics[124]. Graphene's role in spintronics leverages its outstanding electronic properties, including high electron mobility and extended spin diffusion length. The spin diffusion length is crucial for effective spin manipulation in devices, as spintronics utilises spin for information storage and processing. Graphene's spin-friendly attributes make it well-suited for spintronic applications such as magnetic tunnel junctions, enhancing data storage and computing capabilities across various sectors[125]. Graphene's contribution to fuel cells relies on its strong electrical conductivity and catalytic properties. Serving as a catalyst support, graphene enhances fuel cell electrode efficiency by converting chemical energy to electricity. Its significant surface area and electronic characteristics enable graphene to catalyse various reactions, from fuel cells to environmental cleanup, accelerating chemical processes and improving reaction rates through enhanced molecular interactions. This catalytic potential leads to enhanced reaction efficiency and selectivity across different applications[126–128]. "Catalyst support" in fuel cell electrodes pertains to materials that offer a stable structure for catalyst particles. Graphene, alongside other materials, enhances catalyst dispersion and accessibility, thereby improving the efficiency of electrochemical reactions. In hydrogen fuel cells,

graphene-based electrodes optimise clean energy generation through improved catalytic function[129–131]. Graphene's use in water filtration exploits its 2D structure and large surface area for effective contaminant adsorption. Employed in membrane systems, it purifies water from heavy metals and organics. Graphene-based membranes improve water treatment by enabling precise pore control, enhancing filtration efficiency and quality across various applications[132]. Graphene's outstanding adsorption and extensive surface area make it effective in removing contaminants such as heavy metals and organics from water and air. Used in filtration systems and as adsorbents, it provides sustainable solutions for mitigating environmental pollution. Its role extends across diverse applications, contributing to the improvement of water and air quality globally[133–135]. Graphene's atomic structure and conductivity enable interaction with electromagnetic fields, making it valuable for sensors, shielding, and communication systems. It enhances signal quality and reduces electromagnetic interference. Employed in materials and coatings, graphene contributes to improved electromagnetic shielding across diverse applications[136,137]. Graphene's impermeable structure and hydrophobic nature make it ideal for waterproof coatings, creating protective layers on surfaces to repel water and prevent moisture damage. In textiles, electronics, and construction materials, graphene-based coatings enhance product resilience in wet conditions by forming a durable barrier against water infiltration[138]. Graphene's inclusion as nanofillers in polymer blends capitalises on its mechanical strength and conductivity, reinforcing polymers and enhancing their properties. Dispersing graphene nanofillers within polymer matrices produces composite materials with enhanced strength and electrical performance. These composites are valuable in aerospace, automotive, and wearable technology for superior material properties[139–141]. Graphene's exploration in piezoelectric studies, biosensors, and infrared light detection leverages its electrical and mechanical properties[86]. It is studied for converting vibrations into signals, biomolecule detection, and sensing infrared light. These applications utilise graphene's sensitivity, surface area, and tunability, highlighting its potential in electronics, healthcare, and sensors[142–144]. Graphene's diverse utility stems

from its unique properties, applied in energy, coatings, and various fields, enhancing performance, and fostering innovation. This comprehensive review covers properties, applications, and advancements across fields, providing valuable insight and serving as a resource for researchers and engineers, and practitioners, as depicted in Figure 2-2.

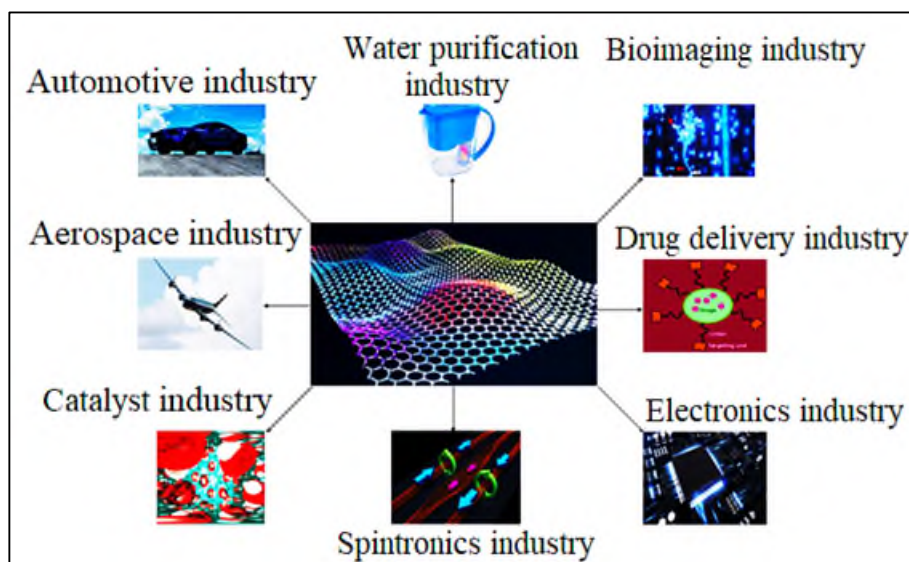


Figure 2-2. Application prospective of graphene and its derivatives.

2.2.1 Synthesis of graphene

Efficiently producing graphene presents challenges due to its complex atomic structure and the need for controlled synthesis conditions. Researchers aim to balance efficiency, cost, and quality in methods for applications in electronics, materials, and energy[145]. This exploration contributes to advancing graphene's potential across multiple sectors. The top-down method involves transforming graphite, CNTs, or carbon-based precursors into single-, bi-, and few-layer graphene through a delamination process. While considered destructive, it enables scalable production with applications in electronics, composites, and energy storage. Researchers refine top-down techniques to achieve controlled layering and customise graphene's properties, driving advancements in material engineering[77]. Conversely, the bottom-up method is a constructive approach that utilises atomic-sized carbon sources to synthesise graphene. This technique

yields graphene with fewer defects and superior properties compared to the top-down approach. By assembling carbon atoms into graphene structures, the bottom-up method offers precise control over the final material's quality and properties, making it valuable for applications requiring high purity and tailored characteristics. Researchers continue to explore and refine bottom-up methods to achieve advanced graphene structures for diverse applications in electronics, photonics, and beyond[146]. The variation in graphene production procedures leads to distinct morphological properties due to differences in the formation mechanisms and conditions. Factors such as precursor materials, reaction parameters, and synthesis techniques impact graphene's layers, defects, and structural features. These differences influence graphene's conductivity, mechanical strength, and other properties, making it essential to choose the appropriate synthesis method based on the desired application and performance requirements. Researchers tailor production procedures to achieve specific graphene morphologies for optimal performance in various industries, spanning from electronics to materials science[147]. To accurately ascertain its fundamental properties, graphene must be synthesised with the utmost purity. For instance, pristine single-layer graphene can be obtained through a method as simple as using scotch tape to exfoliate graphite. This approach isolates individual graphene layers by mechanically cleaving the material, resulting in high-purity graphene samples suitable for fundamental studies. This technique, known for its simplicity, has been used to explore the remarkable properties of graphene since its discovery in 2004[148]. While scotch tape exfoliation yields uncontaminated graphene samples, it is not a feasible route for large-scale production. The process is resource-intensive, expensive, and lacks scalability, making it unsuitable for generating significant quantities of graphene. As a manual and time-consuming method, it cannot address the demand for graphene in various industries and applications[149].

Researchers thus explore more efficient and scalable approaches to produce graphene in larger quantities for practical use. Numerous methods for producing pristine graphene exist, each with its advantages. Among these methods, physical approaches offer versatile routes. Chemical Vapor Deposition (CVD) and

Epitaxial growth on SiC enable controlled and scalable synthesis. Exfoliation methods like Mechanical Exfoliation and Thermal Exfoliation yield high-quality graphene. These techniques play a pivotal role in producing graphene for applications spanning electronics, energy, and materials science. These methods address the limitations of scotch tape exfoliation, offering diverse routes for producing pristine graphene with tailored properties for various industries and applications[150]. In the realm of chemical methods, the synthesis of Graphene Oxide (GO) sheets followed by their reduction stands out. This approach involves the oxidation of graphite to produce GO sheets, which are then reduced to rGO. These methods are widely used to tailor graphene properties for applications in electronics, nanocomposites, and energy storage, offering controlled and scalable fabrication[151]. Chemical methods provide a versatile way to modify graphene's structure and properties for diverse industrial and scientific applications. Tables 2-2 and 2-3 provide a comprehensive overview of the graphene fabrication methods. These tables offer insights into the challenges associated with each method, such as scalability limitations and energy inefficiencies. The brief descriptions highlight the key features of methods like CVD, liquid-phase exfoliation, and epitaxial growth, enabling researchers and engineers to compare and choose suitable approaches based on their specific requirements and objectives. This compilation of information aids in informed decision-making for efficient graphene production and utilisation, facilitating advancements across industries and applications[152].

Table 2-2. Preparation method of graphene by top-down approach.

Top-Down Approaches	Routes	Remarks	Ref.
Mechanical exfoliation	Utilising normal and shear forces	This method involves peeling graphite using ultra-sharp single crystal diamond or three-roll mill machines. It employs adhesive and shear force through ball milling and fluid	[153]

		dynamic methods. This technique is employed to isolate graphene layers and tailor its properties for applications in electronics, composites, and materials science.	
Arc discharge	Involving a carbon precursor (anode) and graphite rod (cathode) in a gas or liquid medium	This method uses arc discharge to produce graphene. Despite its expense due to vacuum equipment, gases like air, helium, and hydrogen (or even asphalt and water for cost reduction) are used. It yields 2 to 10 layers of graphene, finding application in electronics and materials research by precisely controlling graphene layer thickness and quality.	[154]
Oxidative exfoliation-reduction such as chemical, thermal, electrochemical reduction	Utilising methods like Hummer's and improved Hummer's method	This approach involves oxidation of graphite followed by reduction to achieve Reduced Graphene Oxides (rGO). Hummer's method, though less environmentally friendly, is well-established. The improved Hummers method offers a more cost-effective and environmentally conscious alternative, enhancing the synthesis of rGO for applications in diverse fields by controlling functional groups and properties.	[155]
Liquid Phase exfoliation	Involving the dispersion of graphite in solvents	This method leads to exfoliation and subsequent purification. It yields single-layer graphene dispersions, which are valuable for synthesis and functionalisation. This	[156]

		approach produces high-quality graphene materials suitable for various applications, providing a versatile and efficient route for graphene production and utilisation.	
Unzipping of carbon nanotube (CNT)	This method employs high strain rates (10 ⁸ –10/s) to break C–C bonds either axially or longitudinally	It results in the unrolling or unzipping of CNTs, leading to the formation of single, bi-, or few-layer graphene structures through the cutting of cylindrical configurations. This technique offers a way to synthesise graphene from CNTs, providing tailored graphene materials with potential applications in various fields.	[157]

Table 2-3. Preparation method of graphene by bottom-up approach.

Bottom-UP Approaches	Routes	Remarks	Ref.
Chemical Vapor Depositions	Hydrocarbon gases or biomass materials are utilised to synthesise graphene on copper (Cu) and nickel (Ni) films at elevated temperatures	Substrates like silicon, silicon oxide, sapphire, boron nitride, glass, and quartz are commonly employed. CVD yields high-quality graphene with low defects, a highly interconnected structure, and a large surface area. However, the process is expensive and requires careful control of growth conditions.	[153, 158]

Epitaxial Growth of Graphene on SiC	This method involves the decomposition of SiC in an inert environment to form a sp ² -hybridised graphene network	The quality of the graphene depends on whether it is grown on the Si face or C face of SiC, with the former generally yielding better quality. The number of graphene layers can be controlled by adjusting the processing temperature. This approach is utilised for creating high-quality graphene films on SiC substrates.	[159]
Substrate Free Gas Phase synthesis	This method involves gas-phase reactions without the use of substrates, a plasma generated by Ar gas is used to convert aerosol mixtures of liquid ethanol to graphene	The process involves the evaporation of ethanol in the plasma region, with different precursor liquids leading to variations in graphene nanosheet size. This approach has the potential to produce clean and high-quality graphene, showcasing promise for scalable synthesis in various applications.	[160]
Template route	In this method, templates made of metals, oxides, or polymers are used to guide the growth of graphene	This approach offers advantages such as high output, improved quality, and precise control over the resulting graphene structure. By utilising templates, researchers can achieve well-defined graphene architectures with tailored properties, making this technique valuable for applications across various industries and scientific domains.	[161, 162]

Organic synthesis	This method involves the use of polycyclic aromatic hydrocarbons to synthesise graphene	This approach is associated with challenges such as reduced graphene solubility and the occurrence of side reactions. Despite these drawbacks, researchers continue to explore organic synthesis techniques to produce graphene with controlled properties for diverse applications in areas such as electronics, materials science, and more.	[162]
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The increasing demand for lightweight and portable electronics, actuators, and meso-microscale devices has driven the quest for innovative microscale flexible mechanical energy storage solutions, replacing traditional electrochemical energy storage options. This shift addresses the rising need for effective and versatile energy storage across various applications, catalysing transformations in global industries and technological realms[8–11]. Polymers assume a critical role in this context, owing to their remarkable versatility and extensive applications. Their innate flexibility, lightweight attributes, and adjustable properties position them as essential components for designing cutting-edge microscale mechanical energy storage solutions. These polymers can be meticulously tailored to match the precise demands of emerging technologies, driving progress in fields such as portable electronics, robotics, and diverse miniaturised devices[12–20]. The mid-20th century's booming industrial expansion spurred the quest for innovative polymeric components, as diverse material properties became essential. With an extensive scope of potential applications, progress in polymerisation methods, and an increasing need for enhanced materials, the world witnessed relentless global exploration and synthesis of new polymeric architectures. This fervent pursuit engaged research institutions, academic hubs, and industries worldwide, shaping the course of scientific and technological evolution[163]. The ingenuity of polymer technologists is evident in their development of techniques to modify established

polymers, with a focus on industrial scalability and versatile usage. Notably, Thomas Hancock's pioneering work in amalgamating natural rubber and Gutta-percha laid the foundation for polymer blends[164]. This technique involves blending multiple polymers to engineer materials with customised physical attributes, augmenting their adaptability and relevance across various domains of science and technology. This innovation resonated globally, transforming the landscape of polymer science and applications[21]. In recent decades, carbon-based polymer composites have emerged as compelling subjects, driven by their multifaceted applications. This class encompasses carbon black, graphite, CNTs, graphene oxide, graphene, and their derivatives, seamlessly integrated into polymer matrices. By augmenting mechanical, electrical, and thermal attributes, these composite materials find utility across sectors such as aerospace, electronics, and automotive, propelling technological progress on a global scale[165,166]. In the recent 7-10 years, graphene-based polymer composites have witnessed a remarkable rise in prominence, fuelling a surge in research articles dedicated to their thermo-mechanical attributes. This trend stems from graphene's exceptional ability to significantly enhance mechanical strength, thermal conductivity, and electrical properties when integrated into polymer matrices. Researchers across academic and industrial domains are actively exploring these composites, striving to harness their full potential for cutting-edge applications and innovations[167]. For instance, the investigation of urethane functionalised graphene oxide (FGO) and polyurethane binder (PUB) blends demonstrated that incorporating graphene oxide and functionalised graphene oxide (0.5 wt.% loading) improved the thermal conductivity of the polyurethane binder (as depicted in Figure 2-3). Yet, increased FGO loading led to reduced thermal conductivity due to FGO sheet aggregation, impeding lattice vibration or phonon motion. This study highlights the impact of nanomaterial inclusion on thermal properties in polymeric blends, essential for optimising materials in applications like coatings, electronics, and insulation[168].

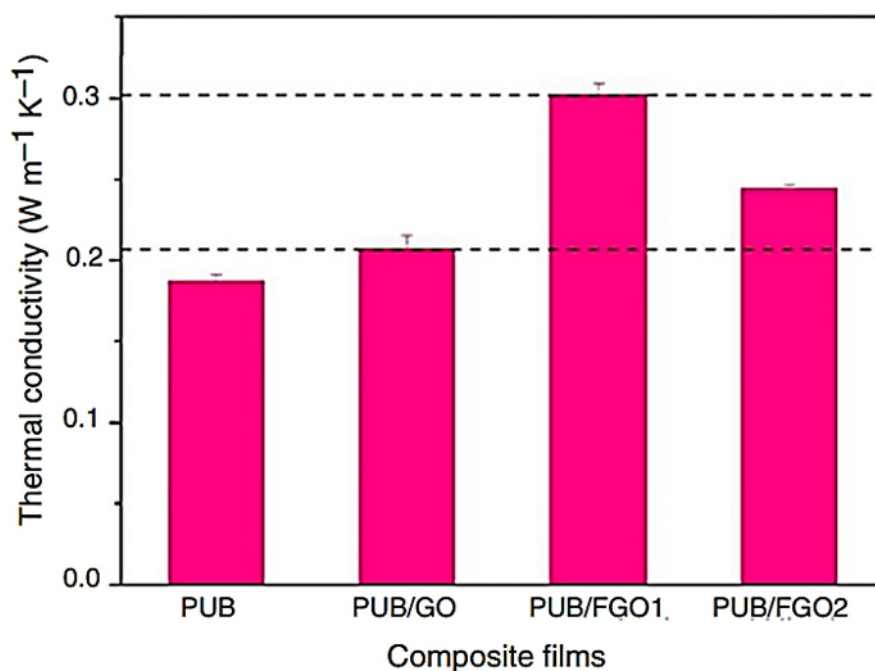


Figure 2-3. Thermal conductivity of Urethane Functionalised Graphene Oxide and polyurethane blends[168].

The mechanical properties of composites are influenced not solely by the fillers but also by the interfacial characteristics between the fillers and the polymer matrix. This interfacial interaction significantly affects factors such as strength, stiffness, and toughness of the composite material. Understanding and controlling these interfacial properties are crucial for optimising composite performance in various applications, including automotive components, structural materials, and aerospace components. Researchers investigate these interactions to tailor composite materials for specific mechanical requirements, ensuring enhanced overall performance[75]. The research reveals that integrating hydroxyl-terminated polybutadiene with modified graphene oxide (MGO) in polyurethane (PU)-based composites creates a robust interface between MGO and PU. This interface strengthening leads to notable improvements in static mechanical properties, as depicted in Figure 2-4. The findings underscore the significance of tailored interfacial interactions for optimising composite strength and durability, offering potential advancements in materials for industries like automotive, aerospace, and manufacturing. The

research's focus on enhancing interface bonding provides insights into designing high-performance composites with improved mechanical characteristics.

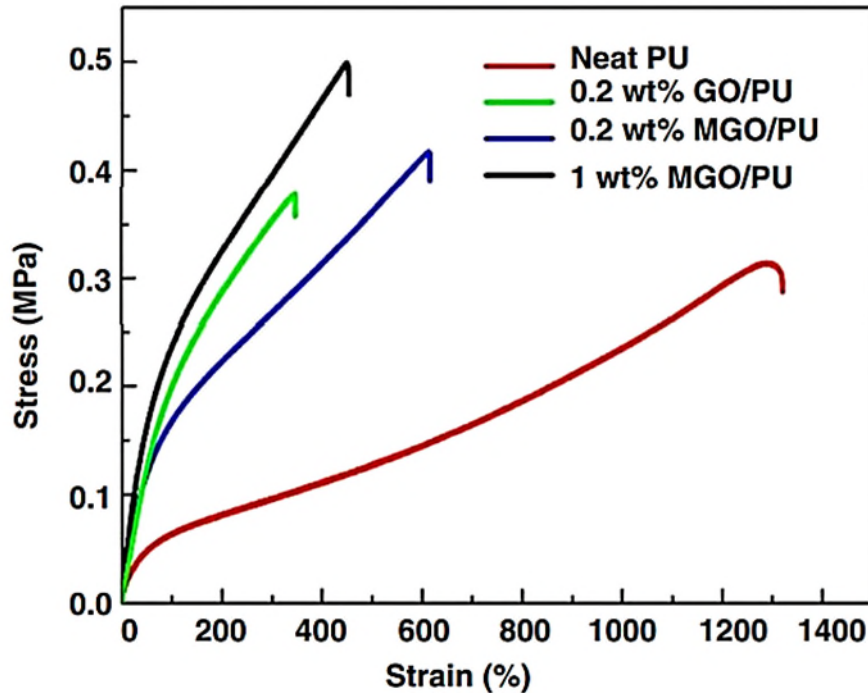


Figure 2-4. Stress vs strain behaviour of Surface Modified Graphene Oxide Cross-linking with Hydroxyl Terminated Polybutadiene Polyurethane composite[169].

Graphene's ability to enhance corrosion resistance in epoxy resin and other matrices stems from its impermeable and barrier-like characteristics. When incorporated, graphene forms a protective layer that hinders the penetration of corrosive agents, mitigating degradation and extending the material's lifespan. This property is valuable for applications in marine environments, infrastructure, and coatings, offering a viable solution for combating corrosion and enhancing material durability[170,171]. As demonstrated in Figure 2-5, the Nyquist plots of epoxy/Amino-Silane Functionalised Graphene Oxide (A-GO) composites immersed in NaCl solution for 7 days reveal that the composite with 0.1 wt.% AGO exhibits the highest corrosion resistance. This effect can be attributed to the optimised concentration of A-GO, which enhances the barrier properties against corrosive ions, slowing down corrosion processes. These findings have

implications for developing protective coatings and materials for applications in environments prone to corrosion, offering insights into tailoring composite formulations for enhanced durability and performance[172].

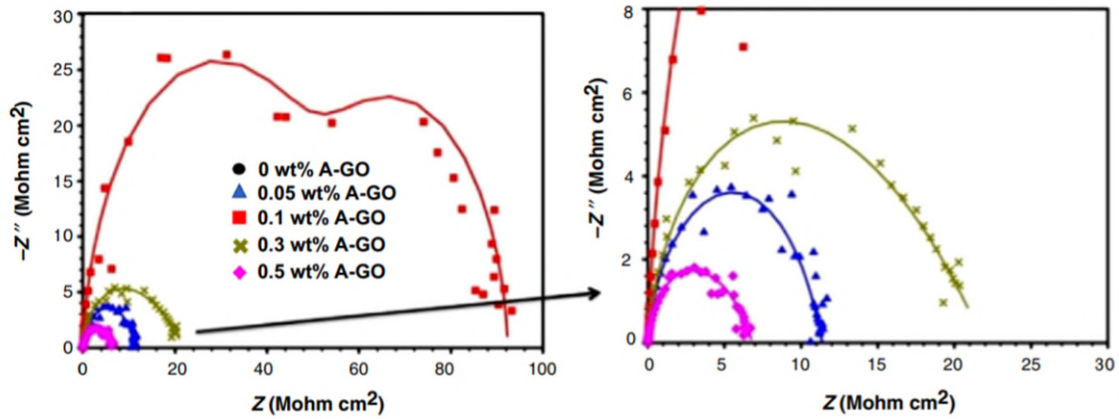


Figure 2-5. Nyquist plots of Epoxy Composite Coatings Filled with Amino-Silane Functionalised Graphene Oxide[172].

A study tackles challenges in triboelectric nanogenerators (TENGs) related to low power density and high internal impedance through innovative strategies. By introducing amino-functionalised reduced graphene oxide (AFGO) and graphite-fluorinated polymer (FG) pillars, the research modifies the tribo-positivity of polyurethane (PU) and the tribo-negativity of Eco flex (EC). This modification increases surface potentials, leading to enhanced surface charges and reduced triboelectric loss[173]. Triboelectric loss refers to the energy loss that occurs in a triboelectric system, which involves the generation of electric charges through friction between two different materials. In a triboelectric nanogenerator (TENG), when two materials come into contact and then separate, friction generates electric charges on their surfaces. However, not all the generated charges are effectively harvested as useful electrical energy. Some of these charges may recombine or dissipate before being collected, leading to a loss of potential energy that could have been converted into usable electricity[174]. Minimising triboelectric loss is important for improving the efficiency and performance of TENGs and other similar energy harvesting systems. The optimised TENG exhibits impressive electrical output, heightened mechanical conversion

efficiency, and potential applications in biomechanical energy harvesting. The research was conducted to address these issues and explore advanced solutions[175]. Biomechanical energy harvesting refers to the process of capturing and converting mechanical energy generated by human or animal movements into usable electrical energy. It involves utilising the mechanical forces or motions that occur naturally during activities like walking, running, or other bodily movements to generate electrical power. This energy can then be stored or used to power electronic devices or sensors. Biomechanical energy harvesting has applications in various fields, including wearable devices, medical implants, and portable electronics, where it offers a sustainable way to power these devices using the body's own movements as a power source[176]. The development of a nanocomposite comprising graphene oxide, zinc oxide, polypyrrole, and polyaniline addresses the need for cost-effective and precise disease detection, especially for cardiac conditions like arrest and arrhythmias. This nanocomposite significantly boosts the sensitivity of cholesterol and bilirubin detection, offering promising applications in high-sensitivity biosensors. Through a process involving sulfuric acid dispersion and glassy carbon electrodes, these biosensors demonstrate exceptional accuracy and specificity, making them valuable tools for reliable biomarker detection. Figure 2-6 visually depicts the advanced nanocomposite-based biosensor, showcasing heightened sensitivity, selectivity, and electrical conductivity to detect cholesterol and bilirubin accurately, catering to vital disease diagnosis needs[177].

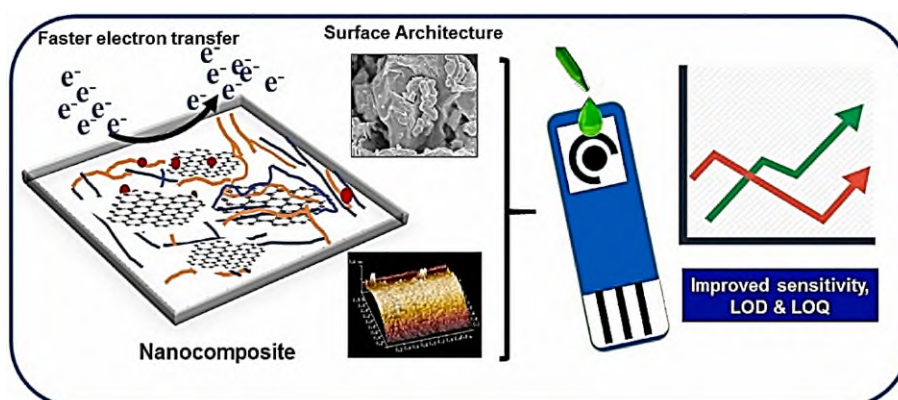


Figure 2-6. Enhanced Biosensor for Cholesterol and Bilirubin Detection: Graphene Oxide/Conducting Polymer Composite Nanocomposite[177].

Electro-deposition of a conjugated polymer with reduced graphene oxide can be used to create micro-supercapacitor electrodes. These electrodes exhibit remarkable capacitance, stability, and power density, making them suitable for on-chip power sources, rapid charging, and AC line filtering applications. The unique combination of extended polymer delocalisation and hierarchical electrode structure results in a wide potential window and ultrafast kinetics, as depicted in Figure 2-7. In summary, this research presents a transformative approach that enhances power, energy, and stability in redox supercapacitors. Through cost-effective electro-deposition, open-shell polymers and reduced graphene oxide create electrodes with exceptional attributes, including enhanced delocalisation, rapid kinetics, a wide potential window, and excellent capacitance retention. The successful application in a 120-Hz filter circuit highlights the potential of these materials as compact, high-performance power sources for wireless electronics, offering significant advantages in terms of maintenance and replacement costs[178].

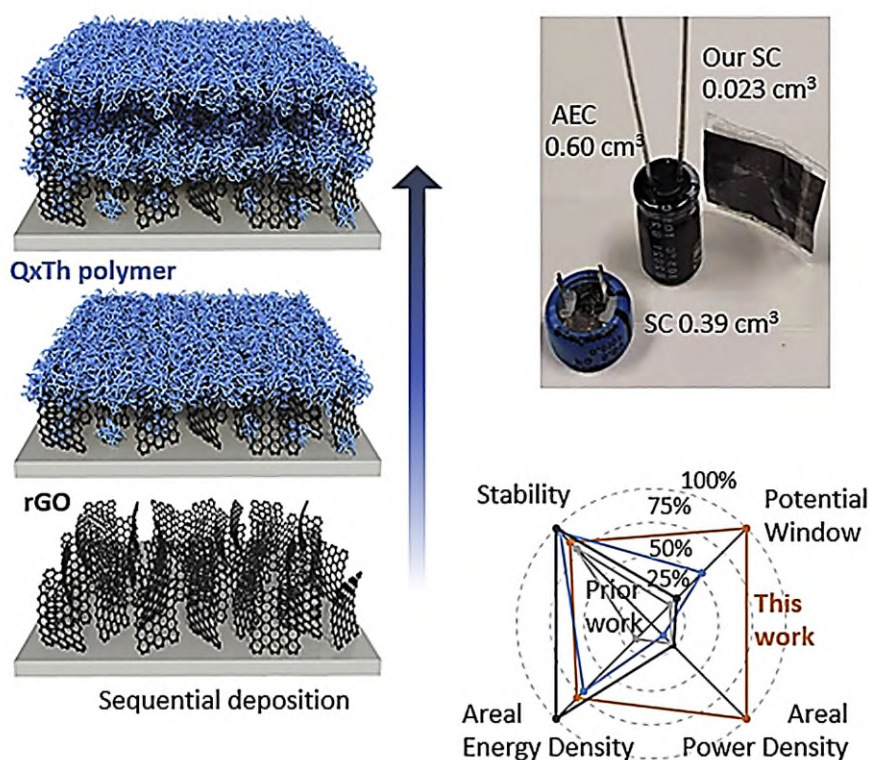


Figure 2-7. High-Performance Micro-Supercapacitors with Open-Shell Polymer-Graphene Composites[178].

A comprehensive computational investigation, employing density functional theory, thoroughly examines the interaction between polyaniline (PANI) and graphene nanoribbons (GNRs) with the {100} surface of SrTiO₃. The study delves into their impact on electronic structure, transport properties, lattice dynamics, and lattice thermal conductivity of SrTiO₃. Strong thermodynamic favourability is predicted for PANI and GNRs adsorption onto SrTiO₃, resulting in the incorporation of C/N 2p states into its bandgap. Co-adsorption leads to the bridging of SrTiO₃'s bandgap, inducing semi-metallic behaviour, while phonon spectra analysis reveals a significant reduction in phonon group velocities and lattice thermal conductivity within the composites. Figure 2-8 illustrates how PANI adsorption introduces N and C 2p states, while co-adsorption with GNRs induces semi-metallic behaviour. The electrical properties are profoundly influenced by GNR and/or PANI loading, with composite modelling projecting a substantial 68–88% decrease in lattice thermal conductivity. These findings lay the groundwork for enhancing thermoelectric performance in oxide-polymer composites, opening avenues for potential experimental validation[179].

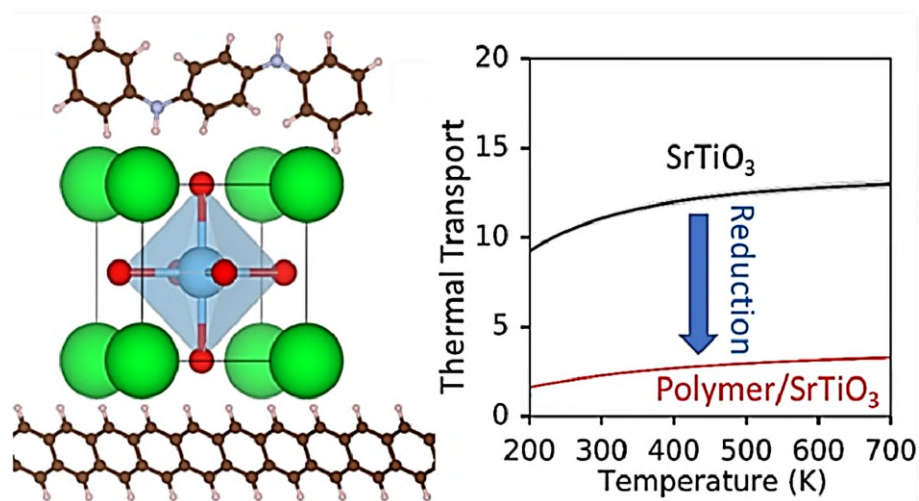


Figure 2-8. The interaction of polyaniline (PANI) and graphene nanoribbons (GNRs) with the SrTiO₃ surface is driven by a strong thermodynamic force[179].

Graphene-based polymer composites have dominated the polymer spectrum during the previous 7–10 years, and as a result, many studies on the thermo-mechanical characteristics of graphene-based polymer blends have been reported in the last 5 years [119]. The scientific literature on the use of graphene and its derivatives to improve the thermo-mechanical characteristics of polymer blends is extensive. Table 2-4 summarises the use and features of graphene-based polymer composites.

Table 2-4. An outlook on applications of graphene in the field of polymer technology and analysis of effects of graphene on polymer matrixes properties.

Blending partner	Nanofiller	Focused study	Ref.
Polypropylene (PP)	The integration of functionalised graphene into polypropylene (PP)	Enhancing thermo-mechanical properties is achieved by exploiting the unique characteristics of graphene-based additives to improve PP's mechanical strength, thermal conductivity, and other attributes.	[153]
The combination of PANI, PMMA, POM, and PPy	Reduced graphene oxide (rGO)	This composite formulation is designed to capitalise on the synergistic effects of these components to improve electrical conductivity and mechanical strength. The study focuses on investigating the conductivity and mechanical behaviour of the composite, aiming to uncover potential applications and	[180]

		benefits of this multifunctional combination.	
The incorporation of PP and PS	Graft-modified reduced graphene oxide (PP-g-rGO)	This study explores the interplay between the polymers and grafted rGO to improve thermal stability and mechanical strength. By analysing the composite's behaviour under varying conditions, the research aims to elucidate the potential applications and advantages of this tailored material combination.	[181]
PP combined with silica	Graphene oxide (GO)	This research aims to elucidate how the interactions between PP, silica, and GO influence the material's mechanical performance and overall compatibility. The study's findings contribute to a deeper understanding of how these components synergise to enhance the composite's mechanical attributes, offering insights into potential applications across various sectors.	[182]
Polyolefin (PO)	Incorporation of PP-g-rGO (graphene oxide-functionalised polypropylene)	This study aims to unravel the synergistic effects between PP-g-rGO and polyolefin, leading to improved flame retardancy and mechanical performance. By understanding the interplay of these components,	[183]

		researchers can develop safer and more robust materials suitable for applications demanding both flame retardancy and mechanical integrity.	
Nylon 6	Incorporation of graphene	This study seeks to understand how graphene's addition impacts both mechanical strength and electrical conductivity, offering insights into the potential for multifunctional materials.	[184]
PMMA	Expanded graphite	This study aims to elucidate how the introduction of expanded graphite influences the mechanical strength and electrical conductivity of the PMMA composite.	[185]
Poly (lactic acid) (PLA)	Graphene	This research delves into understanding how the incorporation of graphene influences the thermal stability and mechanical strength of PLA-based materials. The investigation spans various experimental techniques and analytical methods to gain insights into the mechanisms underlying the enhanced thermo-mechanical attributes, potentially paving the way for improved materials in diverse applications.	[186]

PA (Polyamide) and PPO (Polyphenylene Oxide)	Graphene oxide (GO)	The addition of graphene oxide (GO) to this PA/PPO blend aims to enhance its thermo-mechanical properties, potentially resulting in improved performance and applicability in different industries. This research investigates how the integration of GO influences the thermal stability and mechanical behaviour of the PA/PPO blend.	[187]
Poly (vinyl alcohol) (PVA)	Functionalised graphene	This research addresses the need for improved material strength and durability by exploring how the incorporation of functionalised graphene influences the mechanical behaviour of PVA. The study employs experimental techniques and characterisation to analyse the changes in tensile strength, modulus, and other mechanical attributes of the PVA-functionalised graphene composite.	[188]
Polypropylene (PP) blends	Graphene oxide (GO)	This study aims to elucidate how the presence of GO affects the thermal degradation temperature, crystallisation kinetics, and overall thermal stability of the PP matrix.	[189]

Polypropylene (PP)	Graphene	This investigation provides valuable insights into the potential of Graphene -modified PP nanocomposites for applications requiring heightened thermal resistance and mechanical performance.	[189]
Epoxy resin	Reduced graphene oxide (rGO)	This involves blending epoxy resin with rGO to investigate improvements in stiffness, strength, and toughness. The study explores how rGO reinforcement influences the mechanical behaviour of epoxy resin, facilitating potential applications in high-performance structural materials.	[190]
Polyurethane	GO	This entails combining GO with polyurethane to investigate improvements in tensile strength, flexibility, and other mechanical characteristics. The study delves into the effects of GO on polyurethane's mechanical behaviour, potentially leading to stronger and more resilient materials.	[191]

Poly (vinyl chloride) (PVC)	Graphene	By incorporating graphene into PVC, the study investigates potential improvements in tensile strength, thermal stability, and other relevant properties. This involves blending graphene with PVC, processing the composite, and evaluating changes in mechanical and thermal characteristics through tests and analysis.	[192]
Polyvinylidene fluoride (PVDF)	Organ silane-functionalised graphene oxide	This study focuses on assessing the impact of the modified graphene oxide on PVDF's tensile strength, modulus, and other mechanical attributes.	[193]
Polymethyl methacrylate (PMMA)	Graphite sheets	This investigation delves into the augmentation of PMMA's electrical properties by incorporating conductive graphite sheets.	[194]
Polyethylene (PE) and its derivative, Oriented Polyethylene (OPE)	Graphene	This investigation aims to improve the mechanical properties and conductivity of the polymers by incorporating graphene. The process involves the dispersion of graphene within PE/OPE matrices and subsequent presenting an avenue for advanced polymer applications.	[195]

<p>Polyvinyl Alcohol (PVA) and Conductive Polymer Poly(3,4-ethylenedioxythiophene) (PEDOT)</p>	<p>Hexagonal Boron Nitride (h-BN) nanoparticles and Graphene</p>	<p>This approach seeks to enhance the sensing capabilities of the composite by incorporating h-BN and graphene, thus improving its sensitivity to detect chemical substances. The blending PVA/W PPy with h-BN and graphene, followed by sensor characterisation to assess its chemoreceptive properties, offering a promising strategy for sensitive chemical sensing applications.</p>	<p>[196]</p>
<p>Polyethylene Terephthalate (PET)</p>	<p>Graphene</p>	<p>By incorporating graphene into PET, the composite material benefits from the exceptional mechanical properties of graphene, which include high tensile strength and stiffness. This improvement in mechanical strength occurs through the dispersion of graphene within the PET matrix</p>	<p>[197]</p>
<p>Chitosan (CS) and Polyvinylpyrrolidone (PVP)</p>	<p>GO</p>	<p>The incorporation of GO into the CS/PVP matrix improves the mechanical properties. Simultaneously, the flexibility of the composite is enhanced, enabling it to withstand deformation without sacrificing its strength. This enhancement results from the</p>	<p>[198]</p>

		interaction between the polymer matrix and GO in the composite.	
Waterborne Polyurethane/ Polyvinyl Alcohol (WPPy/PVA)	Graphene oxide (GO)	By incorporating GO into the WPPy/PVA matrix, the material gains improved dielectric properties, making it suitable for applications requiring efficient energy storage and transfer. This enhancement is achieved through the interaction between the polymer matrix and GO, leading to improved dielectric performance characterised by a higher dielectric constant and lower dielectric loss.	[199]
Epoxy	Graphene nanoplatelets (GNPs)	Shear mixing speed had an impact on the size of agglomerates and the mechanical properties of the composite, 3000 rpm and 2 h of mixing the average size of agglomerate were reduced than 1000 rpm and 1 h duration.	[200]
PVA	rGO	Tensile strength, as well as young's modulus, were enhanced.	[201]
Poly (isobutylene-co-isoprene)	rGO	Dielectric permittivity was enhanced.	[202]

PMMA	rGO	Electrical conductivity was increased.	[203]
Polyimide	Phenyl functionalised GO	Electrical conductivity was enhanced.	[204]
Polystyrene	Graphene	Electrical conductivity was improved.	[205]
Chitosan	Cryo-milled graphene	Tensile strength was increased.	[206]
PMMA	Graphene sheets	Thermal stability was improved.	[207]
Unsaturated polyester resin	Graphene nano sheets	Tensile strength, Thermal property, Flexural strength as well as Dielectric strength were improved.	[208]
Isotactic PP	Graphene nanosheets	Glass transition temperature, Thermal property, Electrical conductivity were increased.	[209]
PET	Graphene nanosheets	Electrical conductivity was enhanced.	[210]
Polystyrene	Graphene nanosheets	Graphene nanosheets, Thermal stability, glass transition temperature was increased.	[211]

Ethylene vinyl acetate copolymer	Poly (piperazine spirocyclic pentaerythritol bisphosphonate) grafted graphene oxide	Flame retardancy was improved.	[212]
PVA	Tryptophan functionalised graphene	Thermal stability, Tensile strength, young's modulus was enhanced	[212]
Polystyrene	Graphene-Polystyrene nanoparticles	Young's modulus, Tensile strength were improved.	[213]
PMMA	Imidazolium ionic liquids modified graphene nanosheets	The storage modulus, Glass transition temperature and Electrical conductivity were increased.	[214]
PMMA	Chemically modified graphene	Elastic modulus and Glass transition temperature were enhanced.	[215]
Thermoplastic polyurethane	Graphite nanoplatelets	Tensile modulus was increased.	[216]
Epoxy	Graphene oxide	Fracture toughness and uniaxial tensile fatigue life were increased.	[217]

Epoxy	Functionalised graphene	Flexural strength, as well as storage modulus, were enhanced.	[218]
Epoxy	GO	Storage modulus was increased.	[219]
Epoxy	GO	Elastic modulus was increased.	[220]
Unsaturated polyester	Functionalised graphene nanosheet	Thermal decomposition temperatures well as glass transition temperature were enhanced.	[221]
Epoxy	GO	Damping factor was increased.	[222]
Unsaturated polyester	rGO	Tensile strength, as well as young's modulus, were increased.	[223]
Bio-based polyester	Graphene	Thermal conductivity was increased.	[224]
Polyurethane	rGO	Elastic modulus was increased.	[225]
Polyether amine	Functionalised graphene oxide	Ultimate tensile strength, elastic modulus, fracture toughness, glass transition temperature was increased.	[226]
Polyurethane/ Epoxy	Graphene oxide	Fracture toughness was increased.	[227]

Epoxy	Graphene foam	Fracture toughness was increased.	[228]
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Smart materials are characterised by their ability to exhibit reversible responses to various environmental stimuli, including chemical, electrical, light, temperature, and mechanical factors[81]. These materials can change their properties or behaviours in a controlled manner, making them valuable for applications such as sensors, actuators, and adaptive systems. They are researched and developed across various fields, including materials science, engineering, and biotechnology, to harness their versatile properties for practical uses[229–232]. Smart materials have diverse applications in sensors, actuators, drug delivery, and beyond. However, traditional smart materials like piezoelectric ceramics and conducting polymers often face limitations such as slow response times and high energy consumption. This has spurred the development of innovative smart materials with improved performance, offering enhanced responsiveness, energy efficiency, and precision in various fields of technology and engineering[233]. Graphene-based materials stand out as promising solutions to overcome limitations in traditional smart materials. Their exceptional properties, including high conductivity, mechanical strength, and flexibility, make them ideal candidates for various applications. Researchers are exploring graphene's potential to revolutionise fields like electronics, energy storage, sensors, and biomedicine through innovative design and engineering approaches[234]. Graphene-based stimuli-responsive actuators offer unique transformations driven by external stimuli, utilising carbon-carbon bond stretching or rotation. Novel graphene hydrogel-based unimorph actuators demonstrate synchronous responses to photonic and humidity changes. With their versatile responsiveness to electrical, electrochemical, light, humidity, and heat stimuli, these actuators hold promise for applications in robotics and intelligent devices, owing to their diverse capabilities and potential for innovative design[235]. Chemically modified graphene (CMG) materials, encompassing graphene oxide (GO) and reduced graphene oxide (rGO), exhibit promise for scalable production and versatile applications. GO's oxygen-rich functional groups enable facile modification and dispersion, while rGO offers enhanced conductivity. These materials find use in areas like energy

storage, sensors, and advanced composites, owing to their tuneable properties and wide-ranging utility[236,237]. Graphene and its derivatives, along with composites containing magnetic nanoparticles, hold potential for advanced smart materials due to their exceptional properties. The addition of magnetic nanoparticles imparts magnetic responsiveness to graphene-based materials, facilitating applications such as targeted drug delivery and efficient water purification. These materials offer solutions for diverse fields like biomedicine and environmental remediation[238]. Techniques like chemical deposition and self-assembly are utilised to anchor nanoparticles onto graphene surfaces, ensuring even dispersion. These composite materials are applied in diverse sectors such as medical imaging and environmental remediation, benefiting from their magnetically responsive characteristics and improved mechanical properties. This approach enables controlled applications through the manipulation of nanoparticles on graphene substrates[78]. Recent progress in graphene-based smart systems has spurred the investigation of their responsiveness to a variety of external triggers, encompassing electricity, electrochemistry, humidity, light, and other stimuli (Figure 2-9). These adaptable smart materials hold promise for a wide array of applications across multiple domains, leveraging their distinct ability to transform diverse stimuli into corresponding actions.

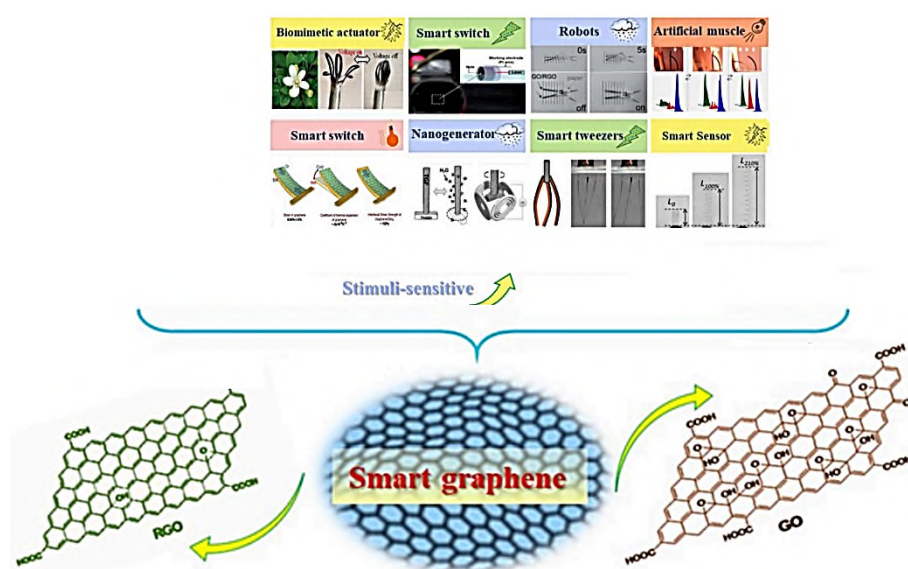


Figure 2-9. Stimuli-Responsive Graphene Systems in Smart Technology[235].

For example, the Fe₃O₄–graphene composite is employed in drug delivery and magnetic resonance imaging due to its magnetic responsiveness and biocompatibility. In drug delivery, the composite can be guided to target sites using external magnetic fields, enhancing precision. Additionally, its use in magnetic resonance imaging enables improved contrast and accurate diagnostics in medical imaging procedures[239]. These composites are efficient in water purification due to their ability to adsorb contaminants from water. The magnetic properties of the composite allow for easy collection of the adsorbed contaminants using an external magnetic field, simplifying the separation process. This approach is valuable for addressing water pollution issues and ensuring cleaner water resources[240]. Fe₃O₄ nanoparticles are immobilised on graphene surfaces using techniques like covalent bonding, chemical deposition, and self-assembly. These methods ensure the uniform distribution of nanoparticles on the graphene matrix, enhancing the composite's magnetic properties. These composite materials find applications in diverse fields, such as medicine and environmental remediation, leveraging their combined properties for targeted functionalities[241]. A 3D graphene framework embedded with uniformly distributed Fe₃O₄ nanoparticles achieves rapid actuation due to the synergistic effect of ferromagnetic properties and graphene's enhanced attributes. This composite material responds to external magnetic fields, enabling applications in responsive devices and systems, particularly in fields like robotics and smart materials[242]. Graphene-based materials find applications in actuators, chemical sensors, strain sensors, self-healing hydrogels, and controlled drug delivery due to their exceptional properties. Their versatility contributes to advancements in electronics, healthcare, and materials science, offering solutions for responsive and innovative technologies globally[79]. Graphene's efficient photothermal conversion in the near-infrared (NIR) region enables applications such as mechanical actuators, self-healing materials, drug delivery, and photothermal therapy. Its resonance vibration processes contribute to its efficacy in converting light into heat, expanding its potential across various fields[243]. Graphene-based materials are applied in wireless actuators using composites or bilayer films, while in self-healing hydrogels, NIR-induced heat

aids in fracture repair. Additionally, graphene's NIR absorption and drug-carrying capabilities facilitate controlled drug release and photothermal therapy, promising advancements in medical and materials applications[244,245]. Self-healing materials, relying on dynamic bonding in weak polymers, face mechanical limitations that restrict their practicality. These limitations stem from compromised strength and stiffness, hindering broader application despite their reparative capabilities. Research in material science aims to overcome these challenges and develop robust self-healing materials with enhanced mechanical properties for wider use[246]. Graphene oxide's 2D structure, functional groups, and biocompatibility make it ideal for pH-regulated drug delivery. For instance, doxorubicin can be loaded onto graphene oxide through interactions. In tumour acidic environments, drug-protonation disrupts interactions, enabling preferential drug release at the intended site, showcasing potential in targeted drug delivery[247]. Self-healing materials seek autonomous structural repair, often using dynamic bonding in hydrogels or films. However, mechanical constraints impede continuous healing. Enhanced materials with robust mechanics and efficient healing mechanisms are needed to broaden applications, addressing these limitations[248]. Chemically modified graphene's compatibility with various polymers is due to its conjugated structure and oxygenated functional groups. Its mechanical strength, thermal conductivity, and near-infrared absorption add value. Under near-infrared light, graphene generates heat in a composite, promoting polymer chain diffusion and entanglement for interface healing, enabling fracture repair[249]. Graphene-based materials (CMGs) offer mechanical strength and compatibility. When a graphene-polymer composite is exposed to NIR light, graphene converts energy to heat, facilitating fracture repair via polymer chain diffusion and entanglement. This process holds potential for self-healing materials in various applications[250]. The incorporation of graphene in materials achieves a balance between mechanical strength and healing efficiency. This contributes to self-healing hydrogels with potential medical applications. Graphene's role as a drug carrier and NIR absorber enables controlled drug delivery and therapies like photothermal therapy. For instance, rGO sheets loaded with doxorubicin exhibit potential for cancer therapy, while

rGO flakes act as photosensitisers for cancer cell photothermal therapy[251]. The accumulation of graphene oxide sheets in physiological buffers is linked to ion-induced surface charge blocking. Graphene oxide's 2D structure and modifiable functional groups make it attractive for pH-regulated drug delivery, driven by its biocompatibility. These features have spurred research in biomedical applications, materials engineering, and drug delivery strategies[252]. To enhance solubility in drug delivery environments, graphene-based materials are often modified with polymers or functional groups. This improves their compatibility and interaction in biological systems, achieved through chemical processes and techniques, resulting in tailored properties for applications like drug delivery systems[230]. Graphene-based macro-assemblies, characterised by their large surface area and flexible cross-linking points, show potential in gas and strain sensors, as well as self-healing materials. These assemblies offer unique properties due to their 3D structures, making them suitable for various applications in sensing and materials engineering[253]. Graphene's distinctive negative coefficient of thermal expansion (CTE) sets it apart, with greater effect in GO due to strong hydrophilic-water interactions causing length changes upon temperature variations. This thermoresponsive behaviour finds applications in actuators like bimorph films, where mismatched CTEs induce rolling and unrolling motions in response to temperature changes, offering potential in diverse fields such as electronics and robotics[254]. Thermoresponsive polymer-graphene composites, incorporating polymers like PNIPAM, find applications in various fields. A GO-PNIPAM composite serves as a thermoresponsive fluorescent sensor, utilising PNIPAM's covalent modification with fluorescent groups to achieve reversible photoluminescence changes upon temperature shifts. This innovation holds potential in fields like sensing and diagnostics, driven by its tuneable properties and responsiveness[255]. Poly(N-isopropylacrylamide) hydrogels undergo substantial volume changes at their LCST, yet their mechanical fragility poses challenges. The introduction of graphene enhances their mechanical strength and conductivity, establishing an interpenetrating network that can withstand volume fluctuations. This synergy creates durable temperature-induced volume changes, holding promise for applications in

responsive materials and sensors[256]. LCST stands for "Lower Critical Solution Temperature." It refers to the temperature at which a polymer or polymer solution undergoes a phase transition, usually from a soluble state to a less soluble or insoluble state. In the context of hydrogels, LCST represents the temperature at which the hydrogel undergoes a reversible change in its swelling behaviour, transitioning from a swollen state to a collapsed state as the temperature increases. This temperature-dependent phase transition is a crucial property in designing thermoresponsive materials and systems, as it can be exploited for various applications like drug delivery, sensors, and smart material. When graphene is subjected to tensile strain, its hexagonal lattice structure experiences distortion, which affects its electronic band structure. This deformation leads to changes in the graphene sheet's resistance. This phenomenon occurs due to the modification of the carbon-carbon bond lengths and angles under strain, influencing the electron behaviour and conductivity of the material. This behaviour is particularly relevant in strain sensors and flexible electronics applications[257]. Intrinsic graphene's piezoresistive behaviour makes it well-suited for strain sensors, as its electrical resistance changes with mechanical deformation. Graphene films produced via chemical vapor deposition (CVD) are preferred for strain sensors due to their exceptional crystalline quality, electrical conductivity, and ease of transfer onto different substrates. This enables the creation of highly sensitive and versatile strain sensing devices in various applications[258]. To ensure consistent strain sensing, CVD-grown graphene is often transferred onto an elastic substrate like polydimethylsiloxane or embedded within a polymeric matrix, forming a composite. This approach maintains the structural integrity of graphene while allowing it to deform along with the substrate, resulting in accurate and uniform strain responses. This strategy is applied in various fields such as wearable electronics and structural health monitoring[259]. The initial decrease in resistance in the graphene-based elastic material occurs as the strain relaxes existing wrinkles in the graphene film. Subsequently, resistance increases due to the distortion of the hexagonal honeycomb crystal structure as the material experiences further strain. This characteristic response is exploited in strain sensors to accurately measure mechanical deformation in various applications,

such as flexible electronics and structural monitoring[260,261]. Applying an electric field to a GO dispersion induces electrorheological behaviour, causing GO sheets to assemble. This behaviour is due to GO's oxygen groups and low conductivity, enabling dispersion without short circuits. Tuneable rheological properties of electrorheological fluids have applications in fields like materials science and fluid dynamics, impacting areas such as energy absorption and damping devices[262]. Applying an electric field to a graphene film induces charge-related expansion/contraction and enables electric power-to-thermal energy conversion. This leads to mechanical energy generation using graphene-based resonators or actuators. These phenomena find applications in mass sensing, micro actuators, and nanotechnology, impacting fields like materials science and sensing technologies[263,264]. Theoretical studies show that charge injection or immersion in ionic liquid electrolytes can induce strain in monolayer graphene sheets, causing bond expansion and electrical double layer formation. These strains enable direct electrical-to-mechanical energy conversion. Layered CMG films with intercalated ions also expand, making graphene suitable for electrochemical actuators with applications in materials engineering and actuator development[265]. Extensive research is directed towards harnessing graphene's unique properties for water treatment applications. Graphene's nanoscale structure and high surface area enable effective removal of bacteria, impurities, and pollutants from water, offering innovative solutions for enhanced water purification. These advancements in nanotechnology hold promise for addressing water quality issues and improving water treatment processes globally[266]. The introduction of small pores in graphene can transform its hydrophobic nature, allowing for rapid water permeation. This idea has driven research towards utilising porous graphene structures for water purification. Graphene's porous sheets enable the passage of water molecules while effectively blocking pollutants and toxins, offering a promising approach for enhancing water treatment processes and addressing water quality concerns globally[267]. Graphene oxide membranes possess exceptional gas impermeability and water permeability. By engineering precise mesh structures, these membranes can efficiently separate atomic species of similar sizes, making them promising

candidates for advanced filtration. This technology has the potential to revolutionise water treatment by converting seawater into potable water, addressing global water scarcity issues through innovative filtration techniques[268]. Research efforts are exploring the use of 3D graphene porous structures for efficient water purification. An ultrathin graphene oxide membrane demonstrated effective removal of various organic dyes. By analysing the membrane's pore size through methanol dissolution, its potential for precise filtration in water treatment is highlighted, offering a promising solution for addressing water contamination challenges[269]. The discovery of graphene oxide membranes with the ability to filter organic solvents is significant, presenting a unique solution for advanced filtration applications. These membranes hold promise for efficient separation and purification of organic solvents from different liquid mixtures, addressing challenges in industries such as chemical processing and environmental remediation[270]. The graphene-based sensing platform is a major leap in cost-effective real-time water pollutant diagnosis. With the ability to detect diverse contaminants like heavy metals, bacteria, nitrates, and phosphates, this versatile sensor offers comprehensive water quality assessment. Its potential impact spans various sectors, enhancing water monitoring and management in different environments[271]. The integration of graphene oxide and shrimp shell byproduct in a water treatment system presents an innovative impurity removal approach. Harnessing the properties of both materials, this eco-friendly solution demonstrates efficient water purification potential. With applicability across diverse regions, it underscores the promise of accessible and sustainable water treatment technologies[271]. The field of Electromagnetic Interference (EMI) shielding materials is undergoing transformation with the integration of polymeric systems and graphene-based components[272]. Unlike traditional materials, the utilisation of polymeric systems in EMI shielding harnesses the potential of single or multi-layered 2D graphene sheets. These sheets are derived through exfoliation of graphite along the c-axis, a process that can be achieved through mechanical, chemical, or thermal treatment methods[92]. This innovation presents a promising avenue for the development of lightweight, flexible, and efficient EMI

shielding materials with enhanced properties, contributing to advancements in electromagnetic protection technologies[273]. A graphene sheet offers a multitude of advantages when integrated into a polymeric system. Its large surface area, exceptional conductivity, and remarkable thermal properties make it a valuable component. This synergy of properties enhances the overall performance of polymeric materials, enabling the creation of efficient EMI shielding solutions with improved capabilities and applications in diverse fields[23]. A significant surface area is vital for EMI shielding due to the skin effect. Graphene's exceptional conductivity and high surface area make it indispensable for EMI shielding applications, particularly in creating effective barriers against electromagnetic interference. This unique combination of properties positions graphene as a key material for advancing EMI shielding technology across various industries[89]. The skin effect refers to the phenomenon in which alternating current tends to flow near the surface of a conductor rather than uniformly throughout its volume. This occurs due to the higher impedance encountered by the AC signal as it penetrates deeper into the conductor. In EMI shielding, the skin effect is relevant as it concentrates the current flow on the surface, making materials with a significant surface area, like graphene, highly effective in attenuating electromagnetic interference. Composites incorporating graphene offer improved properties to polymer matrices due to graphene's exceptional mechanical strength, thermal conductivity, gas barrier efficiency, electrical conductivity, and EMI shielding capabilities. These enhancements make graphene-based composites valuable in industries such as electronics, materials science, and aerospace, where enhanced material performance is essential for various applications[90]. The properties of graphene-based composites are influenced by factors like graphene dispersion, distribution, concentration, and interfacial interactions with the polymer matrix. Enhancing the interfacial properties can be achieved through functionalisation of graphene edges, which improves compatibility and adhesion between graphene and polymer. This approach enhances composite performance in applications spanning materials science, electronics, and more[40]. Functionalisation of graphene can indeed modify its properties, but the incorporation of metal nanoparticles and graphene

sheets into polymers can synergistically enhance electromagnetic wave absorption properties. This approach capitalises on the unique attributes of both components, resulting in improved EM wave absorption characteristics. Such composite materials find applications in EM shielding and related technologies, contributing to better performance in various fields[274]. Graphene-based composites have emerged as preferable alternatives to carbon nanotubes (CNTs) in radio frequency applications due to their enhanced properties. Specifically, oriented, and surface-functionalised graphene contribute to improved electromagnetic interference (EMI) shielding effectiveness in polymer matrices[23]. This advancement holds promise for more efficient EMI shielding solutions in various contexts[275]. A brief overview of the graphene-based polymer composites for EMI shielding application is illustrated in Table 2-5.

Table 2-5. Electromagnetic shielding effectiveness of various Graphene-based materials.

Materials	Frequency (Hz)	Shielding effectiveness by mechanism (dB)	Ref.
Functionalised graphene sheets 3.2vol%/polystyrene porous composites	8.2–12.4 GHz	29.3db primary absorption and secondary reflection mechanism (2mm thickness and porosity 60%)	[90]
Graphene 0.7 wt.% /PDMS foam composites	30 MHz–1.5 GHz	~30 dB Primary absorption and secondary reflection mechanism	[90]

Self-aligned in situ reduced graphene oxide (2 wt.% rGO)/ epoxy nanocomposites	1-4GHz	38 dB Primary absorption mechanism	[276]
(PMMA)/ 1.8 vol % graphene nanocomposite microcellular foams	8 to 12 GHz.	13–19 dB Primary absorption mechanism	[277]
Functionalised graphene sheets 3.2vol%/polystyrene porous composites	8.2–12.4 GHz	17.3dB Primary absorption and secondary reflection mechanism (2mm thickness and porosity 76%)	[90]
(PMMA)/ 0.8 vol %, graphene nanocomposite microcellular foams	8–12 GHz	7.5 dB Primary absorption mechanism	[276]
Reduced graphene oxide laminates	100 MHz	15.5 dB Primary absorption mechanism	[277]
Sulphur*(S)-doped reduced graphene	100 MHz	33.2 dB	[277]

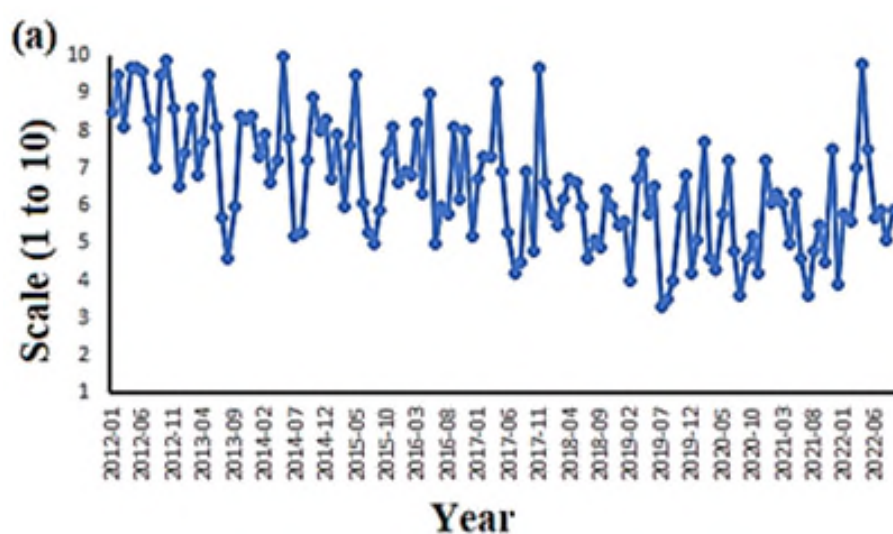
oxide laminates		Polarisation, Primary absorption mechanism	
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The literature review explores recent advancements in utilising graphene and its derivatives, highlighting their roles in fabricating polymer blend nanocomposites, hybrid nanostructures, and intelligent materials. It emphasises graphene's adaptable physical attributes, covering thermo-mechanical properties, electrical traits, and expansive surface area, showcasing its versatility. The section spans various disciplines, showcasing the widespread impact of graphene-based materials. From nanotechnology precision to biomedical engineering intricacies, from materials science to environmental applications, its far-reaching impact is evident[278].

2.3 Structure–property-application relationships in BaTiO₃ dielectric

BaTiO₃ is primarily sourced from titanium (IV) alkoxide, suspended in alcohol, and barium acetate dissolved in acetic acid. This synthesis method is utilised to produce BaTiO₃, highlighting the chemical components and suspension process involved [279]. BaTiO₃ is formed by calcining the solution at 1000 °C. Research on BaTiO₃ began in the early nineteenth century, initially identifying its crystal structure at high temperatures. Subsequent studies delved into crystal chemical principles, dielectric permittivity, dielectric constant, and space charge polarisation to understand its properties and behaviour[280]. The perovskite structure of BaTiO₃ provides lead-free ferroelectric and piezoelectric properties. This makes BaTiO₃ suitable for modern applications like multilayer ceramic capacitors, actuators, and piezoelectric sensors. Its unique structure contributes to its widespread use in these technologies[281]. These properties make BaTiO₃ a particularly suitable candidate for use in applications where environmental or safety concerns would be a concern. As shown in Figure 2-10a, the research interest on such material assessed on a scale from 1 to 10 indicates that academic/research institutes have been executing a wide range of activity on the

bulk BaTiO₃ as well as nano- BaTiO₃ in the last 10 years. The numbers in the y-axis represent the level of academic and research interest in relation to the time in years and months in the x-axis. The maximum popularity is represented by a value of 10, while a value of 5 indicates a medium level of popularity. In general, BaTiO₃ colloidal nanocrystals serve as the capacitive building blocks for polymer matrix and energy storage applications. The evaluation's findings that academic and research institutions all around the world have been working actively on barium titanate and nano barium titanate over the past ten years is illustrated in Figure 2-10b.



(b)

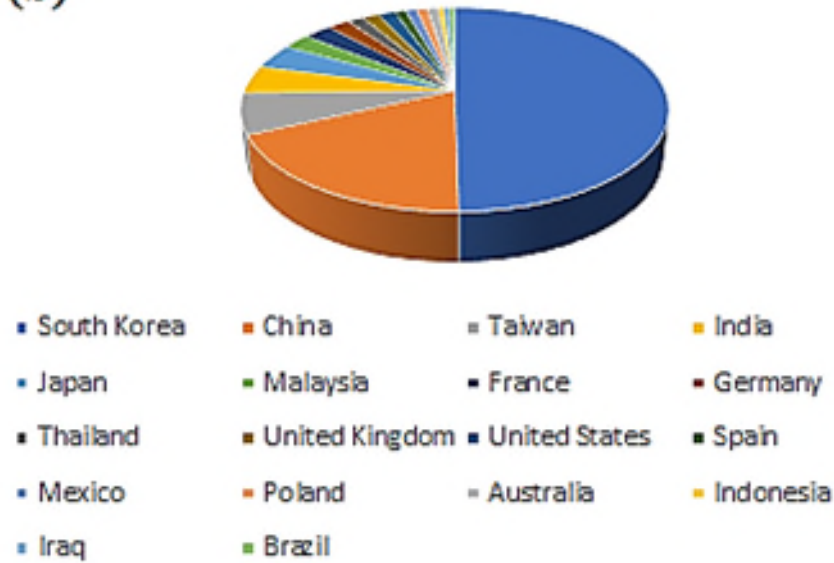


Figure 2-10. Statistical data from worldwide a) BaTiO₃ as well as nano BaTiO₃ interest by years, b) BaTiO₃ as well as nano BaTiO₃ interest by region (Top 15) (From google database- last 10 years).

Barium titanate (BaTiO₃), a white crystalline material, is synthesised by heating a mixture of TiO₂ and BaCO₃ at 1000- 1100°C. This process results in the formation of BaTiO₃, which is widely used in various technological applications due to its unique properties and perovskite crystal structure[282]. Barium titanate (BaTiO₃) can also be synthesised through the sol-gel route by processing titanium tetraisopropoxide and barium isopropoxide at 600°C. This method provides an alternative approach to producing BaTiO₃, which possesses valuable properties and a perovskite crystal structure, suitable for various technological applications[283]. BaTiO₃ is a versatile material renowned for its optical transparency, robust piezoelectric capabilities, and affordability. Its non-toxic nature, stability, longevity, and ease of handling further enhance its appeal. The material's ferroelectric properties find applications in displays, including smartphones and TVs, as well as in solar cells and memory devices, making it highly valuable across various industries[284]. Ferroelectric materials like BaTiO₃ exhibit inherent polarisation without an external electric field. They can switch polarity under an electric field, making BaTiO₃ ideal for actuators, transducers,

and sensors. Its chemical stability and high melting point further enhance its suitability for high-temperature applications[285]. BaTiO₃ has limited electrical conductivity, restricting its use in certain applications. Its ferroelectric nature involves long-range dipoles, ranging from microns to millimetres in length, contributing to its unique properties and applications [286]. BaTiO₃'s physical dimensions play a crucial role as they perturb the long-range polar order when confined in a compact volume. This perturbation results from the crystal's free energy and the increased content of interface-surface atoms, impacting its properties and behaviour[287]. The dielectric permittivity of BaTiO₃ is directly related to its physical dimensions, influencing the strength of the polar order and the quantity of interface-surface atoms. This polar order arrangement at the interface is crucial for understanding the material's behaviour and properties[288]. The polar ordering in BaTiO₃ relies on the quantity of interface-surface atoms, governed by the material's permittivity. The size effect, known as the BaTiO₃ anomaly, pertains to the physical phenomenon where BaTiO₃ dimensions reduce significantly in the nanoscale range. This reduction in size has notable implications for its properties and behaviour [289]. The reduction in size results in a lower Curie temperature and polarisation, referred to as an "intrinsic" size effect. This phenomenon signifies that as BaTiO₃ particles become smaller, their fundamental properties change, impacting their thermal and electrical behaviour[290]. The size effect is a significant aspect of nano-scale phenomena. The "intrinsic" size effect in BaTiO₃, occurring at the nanoscale (around 100 nm), leads to a reduction in its Curie temperature, illustrating how size impacts the material's behaviour. This phenomenon highlights the importance of considering size in understanding nanoscale properties[291]. The phenomenon arises from the altered behaviour of BaTiO₃ at smaller sizes. Long nanowires and spherical particles exhibit distinct ferroelectric characteristics because of variations in compressive surface tension and the depolarising field. Size-induced changes in behaviour is key in understanding these nanoscale materials[290]. Processing conditions such as temperature, humidity, and stress can influence BaTiO₃'s ferroelectricity and properties. Charged defects play a role in ferroelectric behaviour and affect BaTiO₃'s critical size. Increasing defect density enlarges the

critical size. Additionally, porosity is a potential factor to consider [292]. Porosity exceeding 5% leads to significant deterioration in the properties of ferroelectric BaTiO₃. Additionally, grain boundaries in perovskite BaTiO₃ exhibit lower permittivity or non-ferroelectric behaviour compared to grain cores. As BaTiO₃ size approaches the sub-micron and nanometric scales, the non-ferroelectric behaviour of grain boundaries intensifies[293]. The polarisation of BaTiO₃ is determined by the depolarisation field, resulting from an unbalanced charge. Additionally, stress and strain are factors that influence the ferroelectric properties of BaTiO₃. These factors play a crucial role in understanding and controlling BaTiO₃'s behaviour in various applications[294]. Changes in strain can impact polarisation, and vice versa, which is significant for understanding BaTiO₃'s ferroelectric characteristics. The domain walls in BaTiO₃ play a crucial role in its dielectric and piezoelectric properties, making their structure and composition essential considerations for material quality. Understanding these interactions is vital for controlling BaTiO₃ behaviour in various applications[295]. Domain walls represent boundaries between different regions within a material. In larger BaTiO₃, domain walls are three-dimensional, while in nano sized BaTiO₃, a single domain emerges with no distinct domain walls due to the merging of domains. This phenomenon impacts the material's properties and behaviour in different contexts[296]. The distinction in domain wall structure between sizes significantly influences material usage. Additionally, altering the Ba/Ti ratio doesn't notably impact domain walls. Enhancing permittivity in nanosized BaTiO₃ can be achieved by promoting domain wall motion and increasing the density of 90° domain walls, offering control over its properties[297]. BaTiO₃'s structure and content serve as both reinforcement and filler in various polymer matrices, including thermoplastics, thermosets, and elastomers. Bulk and nanostructured BaTiO₃ contribute to the polymer matrix's crystallinity, mechanical strength, dielectric performance, piezoelectricity, thermomechanical properties, and overall robustness. This synergy enhances the material's suitability for diverse applications[298]. BaTiO₃'s exceptional properties make it a sought-after choice for polymer matrix composites. Its high dielectric constant is attributed to its perovskite crystal structure, characterised by an ABO₃ oxide arrangement. This

unique structure enhances its suitability for various applications in composite materials[299]. In the ABO_3 structure of $BaTiO_3$, the Ti^{4+} ions occupy octahedral sites, forming corner-sharing octahedra with oxygen ions. Ba cations, larger in size, fill the interstices between these octahedral cages created by linked octahedra. This arrangement is essential to $BaTiO_3$'s unique properties, making it valuable for various applications in composite materials[298]. The structure is made up of close-packed layers of oxygen and bigger A-cations. The B cations are present in the octahedral interstices between the layers, as seen in Figure 2-11.

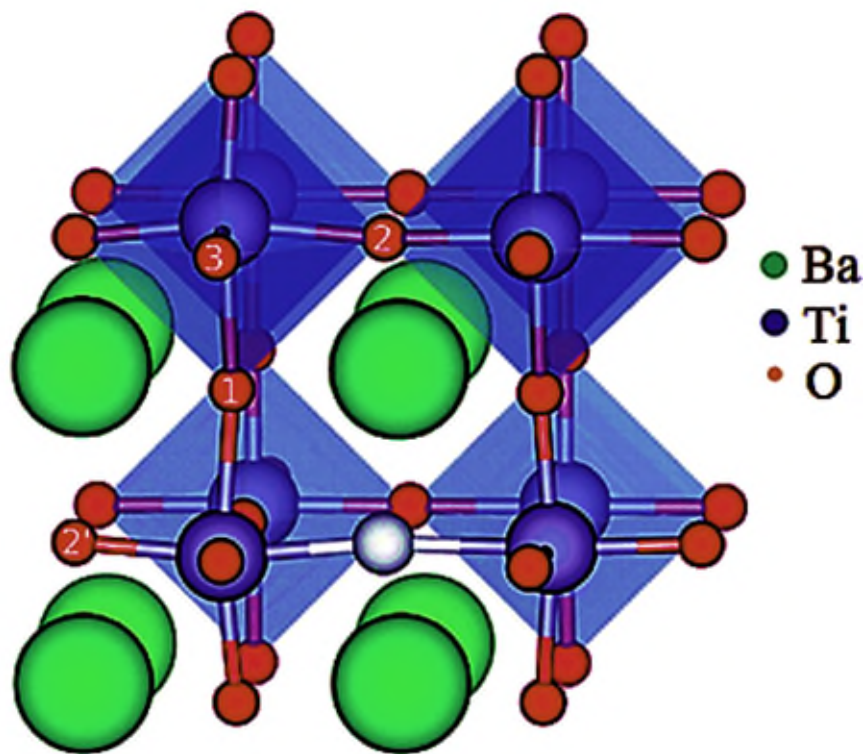


Figure 2-11. Illustration of crystal structure of $BaTiO_3$.

In recent years, both bulk $BaTiO_3$ and nano sized $BaTiO_3$ have garnered significant attention for their potential as innovative materials in the field of dielectric nanocomposites. These high-performance materials find applications in a broad spectrum of technologies, including consumer electronics, energy storage, piezoelectric devices, memory applications, sensors, and more, thanks

to their unique properties and versatility. Their use spans from microelectronics to optical computing, offering a wide range of opportunities for innovation and advancement[300]. Barium titanate undergoes distinct phase transitions as temperature decreases, transitioning from hexagonal to cubic, then tetragonal, orthorhombic, and finally to the rhombohedral phase. These phase changes are significant and contribute to the material's unique properties, making it valuable for various applications, especially as temperature-sensitive components in electronics and ceramics. The understanding and control of these phase transitions are essential for tailoring its behaviour in specific contexts[301], as shown in Figure 2-12. Barium titanate's chemical and mechanical properties make it highly desirable for ferroelectric applications. The size of particles and temperature play crucial roles in its dielectric properties. At the Curie point, larger-grain BaTiO₃ samples ($\geq 10\text{ }\mu\text{m}$) exhibit a higher dielectric constant compared to smaller-grain samples ($< 1\text{ }\mu\text{m}$) due to domain motion. Understanding these factors is essential for optimising its performance in ferroelectric applications[302]. At room temperature, fine-grained BaTiO₃ ($< 1\text{ }\mu\text{m}$) exhibits a higher dielectric constant than large-grained BaTiO₃ ($\geq 10\text{ }\mu\text{m}$) due to internal stresses. Understanding this size-dependent behaviour is essential for tailoring BaTiO₃ properties in various applications[303]. Doping and positive temperature coefficient resistors has been explored to enhance their performance and functionality. This involves introducing specific elements or compounds into BaTiO₃ to modify its electrical properties, expanding its potential in semiconductor devices and resistors [304]. The potential advantages and drawbacks of this emerging technology are still under evaluation. BaTiO₃ is typically considered an insulator with an energy gap of 3.05 eV at room temperature, meaning it does not conduct electricity under normal conditions[305]. N-type semiconductors in barium titanate can be achieved by using trivalent cations like La³⁺ and Y³⁺ or replace Ti⁴⁺ with pentavalent cations such as Nb⁵⁺ and Sb⁵⁺. Doping in barium titanate alters its electronic properties and conductivity, broadening its suitability for semiconductor applications[306]. Sintering barium titanate in air enhances its dielectric constant, but its resistivity rises when transitioning from ferroelectric to paraelectric, typically occurring above the Curie temperature of 120°C[307]. The

rise in resistivity with increasing temperature, known as the positive temperature coefficient of resistance, can be attributed to the balancing of extra positive charge by free electrons[308]. The phase transition provides an effective method to replace Ti^{4+} in pure barium titanate, leading to a higher positive temperature coefficient of resistance. This phenomenon is not observed in the insulating form of pure barium titanate[309]. The total conductivity is determined through the double-Schottky energy barrier model, which involves establishing an energy barrier near the grain boundary and analysing its height[310]. Conductivity is subsequently computed based on the height of the electrical potential barrier. These barrier systems arise due to the presence of isolated acceptor ions or adsorbed oxygen at grain boundaries[311]. The positive temperature coefficient of resistance disappears during sintering in a vacuum or reducing gas atmosphere. This is attributed to electron trapping near the grain boundaries due to acceptor states induced by impurities and barium vacancies, leading to the formation of double Schottky barriers [208]. Ionised barium vacancies arise from electron confinement within vacancies, leading to the creation of negatively and positively charged regions parallel to the boundaries. This phenomenon generates a potential barrier. As one approaches the Curie temperature, the scarcity of trapped electrons for conduction results in an increase in electrical resistance[312]. The increased porosity, higher BaTiO_3 barrier height, and enhanced oxygen transport in an oxidising environment promote to higher positive temperature coefficient of resistance (PTCR). Sintering in such conditions also affects grain boundary capacitance and the oxidation state of the grain boundary, further influencing electrical properties[313]. Materials like polymer composites, ceramic composites, V_2O_3 compounds, and BaTiO_3 -based compounds exhibit positive temperature coefficients of resistance (PTCR). In contrast, single crystals of barium titanate display negative temperature coefficients of resistivity (NTCR). These electrical behaviours are crucial in various applications and can be manipulated through material composition and processing[314].

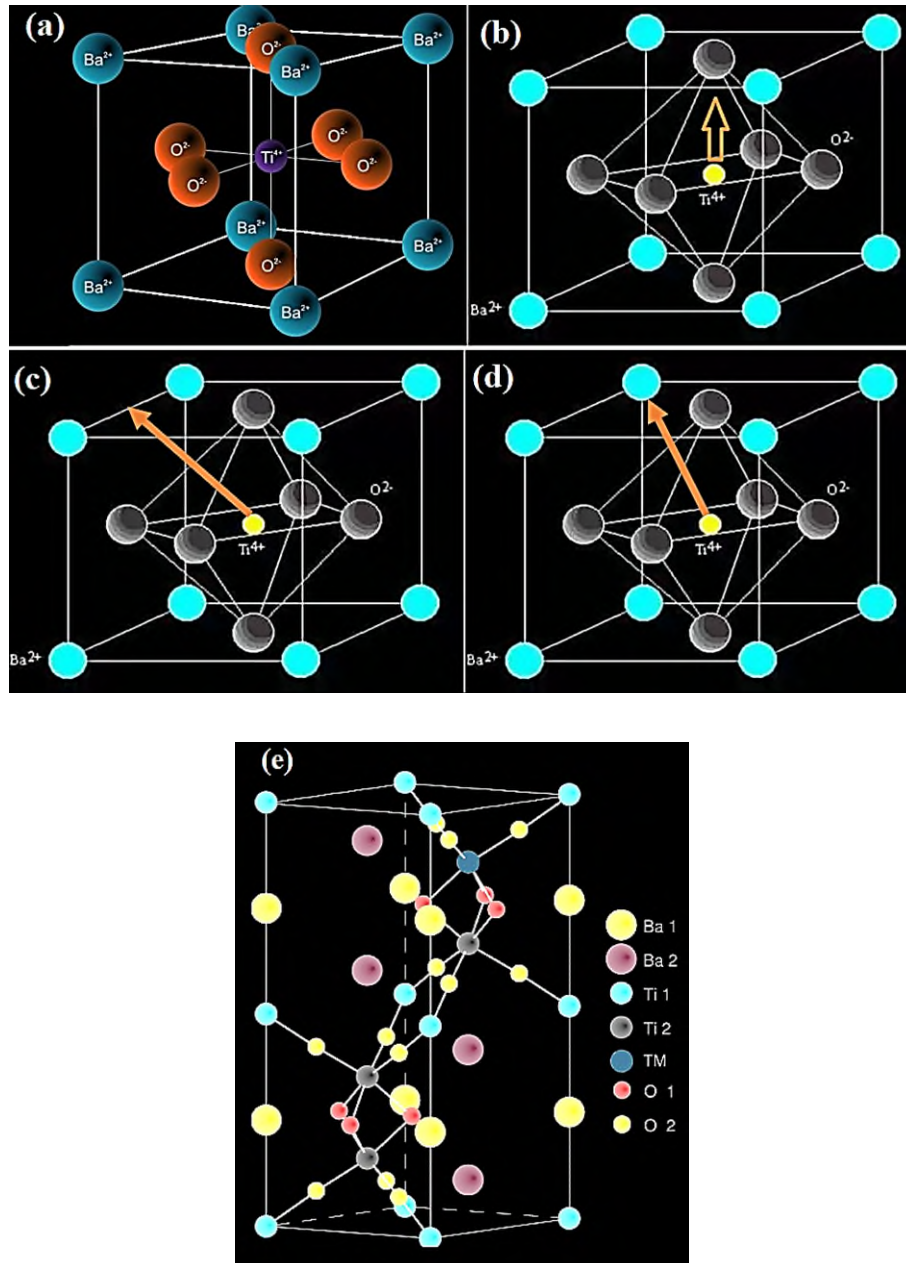


Figure 2-12. Illustration of crystal phase of BaTiO₃, a) cubic phase(non-polar), b) tetragonal (polarised in direction $\langle 100 \rangle$), c) orthorhombic phase in direction (polarised in direction $\langle 110 \rangle$), d) rhombohedral in direction (polarised $\langle 111 \rangle$), e) hexagonal phase.

BaTiO₃ can be synthesised using different methods, including solid-state reactions and chemistry-based procedures. The choice of synthesis method depends on the specific application and desired properties. These processes enable the creation of BaTiO₃ for various technological applications[315]. BaTiO₃

and nano- BaTiO₃ are sought-after as high-k dielectric materials, making them valuable reinforcements in polymer matrices. Their popularity in this role stems from their high permittivity and ability to enhance the dielectric properties of polymer composites, opening applications in various industries[316]. To achieve high dielectric properties in polymer composites, a substantial content of BaTiO₃ and nano- BaTiO₃ is necessary. This combination imparts mechanical flexibility and adjustable characteristics to the polymer matrix, enhancing its overall performance[317]. Increased BaTiO₃ content in polymer composites can lead to agglomeration due to limited interaction with the polymer matrix. This agglomeration negatively impacts mechanical and dielectric properties, emphasising the need for optimised formulations to maintain desired performance[307]. Understanding the relationship between compatibilisers, BaTiO₃, and polymer composites is essential for optimising composite performance. This research, in its early stages, explores smart materials in the context of energy storage applications like fuel cells, batteries, and capacitors, with the goal of developing efficient solutions for diverse needs[318]. BaTiO₃ and nano BaTiO₃-based materials, including composites and nanocomposites, offer improved dielectric properties, reduced energy loss, and enhanced polarisation due to their ionic, electronic, and atomic polarisability. This potential makes them promising candidates for energy storage applications, addressing challenges related to dielectric response and leakage current in high electric field environments[319]. BaTiO₃ and nano- BaTiO₃-rich polymer nanocomposites exhibit exceptional dielectric performance, including high energy density and adaptable polymer properties. When evaluating a dielectric material's energy storage capacity, these characteristics become particularly relevant[320], the energy density (U) in the dielectric medium may be defined as indicated in equation (2-1).

$$U = \frac{1}{2} \epsilon_0 \epsilon_r E^2 \quad (2-1)$$

Wherein, ϵ_0, ϵ_r are the free space permittivity and relative permittivity of the material, respectively, and E is the electric breakdown strength. The permittivity and electrical breakdown strength of a material determine its energy density. By

storing relative permittivity and electric breakdown strength, BaTiO₃ and nano-BaTiO₃-rich polymer nanocomposites are exceptional materials that may deliver high energy density nanocomposites [321]. BaTiO₃ and nano-BaTiO₃-rich polymer nanocomposites are suitable for high-energy-density applications like batteries, capacitors, and fuel cells. The dielectric properties and energy density of these materials are significantly influenced by the interfacial region and phase between the fillers and the polymer matrix, underscoring their importance in nanocomposite design and performance[322]. The properties of BaTiO₃ and polymer nanocomposites depend not just on the materials themselves but also on the processing methods used, such as melt blending, sol mixing, and electrospinning. Understanding these processes, tools, characterisations, applications, and challenges is essential for comprehending the roles and applications of BaTiO₃ and nano-BaTiO₃ in various industries[323].

2.3.1 BaTiO₃

Lead-based ferroelectric and piezoelectric materials find numerous applications in electronics, optics, photonics, and sensors due to their unique properties. These materials are used for their exceptional capabilities in these fields, contributing to technological advancements and innovations[324,325]. In the early twentieth century, due to health concerns related to lead and other hazardous elements, the European Union introduced regulatory legislation governing their commercial use. This regulation aimed to protect public health and the environment by limiting the exposure to such harmful substances[326]. This law established a framework for monitoring and controlling lead in products, imposing strict limits on lead content. It marked a significant milestone in the research of lead-free ferroelectric and piezoceramic materials as it compelled the development of alternatives to meet regulatory restrictions while maintaining desired material properties[327]. BaTiO₃'s unique ferroelectric and piezoelectric properties have gained recognition, enabling robust phase responses in electro-piezoelectric applications. Its applications extend to capacitive touchscreens, active speakers, and bioelectronics, highlighting its significance in various fields where precise phase control and sensing capabilities are crucial[328]. BaTiO₃'s

low-temperature phase transitions offer opportunities for structural enhancements to optimise ferroelectric and piezoelectric properties.

"Piezoelectricity" refers to electric charge generation under pressure, while "ferroelectricity" involves spontaneous electric polarisation in non-conductive crystals or dielectrics. These properties combine structural and electrical features, and piezoelectricity can occur in any ferroelectric material due to its asymmetry. Certain materials exhibit both ferroelectric and ferromagnetic behaviour, creating multifunctional capabilities[329]. Piezoelectric materials, like BaTiO_3 , generate electric charges on their surfaces when subjected to mechanical stress. The polarity of these surface charges changes with the direction of stress, defining them as piezoelectric materials. This property finds applications in various devices, converting mechanical energy into electrical signals and vice versa[330]. In piezoelectric materials, there are two forms of piezoelectricity: 1) quasi-static or spontaneous piezoelectricity, which occurs when the material is not exposed to external mechanical stress [331], and 2) dynamic or applied piezoelectricity[332]. Ferroelectric materials, including BaTiO_3 , can reorient their dipoles in response to an externally applied electric field, which is essential for their piezoelectric and pyroelectric properties. This property enables polarisation reversal, making them valuable in various applications involving the control of electric polarisation[333]. Ferroelectrics like BaTiO_3 are valuable in applications requiring precise polarities, including memory devices and sensors. The properties of BaTiO_3 , such as mechanical, thermal, dielectric, ferroelectric, and piezoelectric characteristics, can be tailored through crystal phase transitions during cooling. These changes in attributes with phase transitions enhance the versatility of BaTiO_3 for various applications[334,335]. Exploring BaTiO_3 or its phase transitions involves studying key variables like spontaneous polarisation, dielectric susceptibility, piezoelectric charge coefficients, and elastic compliances under zero electric field conditions, particularly during transitions like paraelectric to ferroelectric. These parameters are essential for understanding the material's behaviour and properties in various applications[336]. Nano BaTiO_3 is anticipated to find applications in nanoscale energy harvesting, capacitors, medical devices, and memory devices due to its

outstanding piezoelectricity, nonlinear optical properties, and biocompatibility. Its unique properties make it promising for various advanced technologies and devices[337]. BaTiO₃ and nano BaTiO₃ are intriguing materials valued for their composition. In practical applications, their crystalline structure, morphology, and dimensions play pivotal roles in determining their performance and suitability for specific purposes. These characteristics significantly influence their behaviour and utility in real-world scenarios[338]. Nano-sized BaTiO₃ remains relatively underexplored despite its remarkable biocompatibility, piezoelectric/ferroelectric potential, and nonlinear optical properties. Its untapped potential and applications warrant further research and development efforts to harness its unique characteristics for various uses[339].

2.3.2 Hierarchical structure of BaTiO₃

BaTiO₃'s complex hierarchical structure comprises ferroelectric domains with uniform polarisation orientation. These domains collectively contribute to the material's ferroelectric properties, making it a unique and valuable material for various applications. Further exploration of this structure can enhance our understanding of BaTiO₃'s functional characteristics[340]. The boundary between ferroelectric domains serves as a domain wall in BaTiO₃. These domain walls play a crucial role in the material's properties and functionality, making them significant for applications and research. Understanding their behaviour is essential for optimising BaTiO₃-based technologies[341]. BaTiO₃'s intricate structure makes it suitable for demanding applications where performance and stability are vital. The domain microstructure of BaTiO₃ crystals is primarily influenced by surface polishing and heat treatment, crucial factors for tailoring its properties to meet specific requirements[342]. The optical and electrical characteristics of BaTiO₃ crystals are affected by the crystal's surface properties, while heat treatment plays a key role in controlling the crystal composition. These factors are essential for tuning BaTiO₃'s properties to suit applications[343]. In ferroelectric materials like BaTiO₃, polarised domains form to minimise electrostatic and elastic energy. Domain walls act as boundaries between these domains, helping to separate them within a single BaTiO₃ phase or among

multiple BaTiO₃ phases. This organisation of local electric dipoles is fundamental to ferroelectricity[344]. Domain walls in different phases of BaTiO₃ are significant in ferroelectricity and its hierarchical structural organisation. The orientation of polarisation within these domain walls results in various types of domain walls in BaTiO₃ phases. These domain walls play a crucial role in the material's properties and behaviour[340]. Tetragonal ferroelectric materials like BaTiO₃ possess domain walls with 90° and 180° angles. These domain walls are responsible for the diverse polarisation orientations observed in different phases of BaTiO₃[288]. A barrier separates domains with opposite (180°) polarisations and matching strain conditions through a 180° domain wall, which is also known as a wall or domain wall. These domain walls help define the boundaries between different polarisation orientations within the material[288]. A barrier separates domains with perpendicular (90°) polarisations, known as a 90° domain wall. This type of domain wall is found in tetragonal ferroelectric materials like BaTiO₃. These domain walls define boundaries between polarisation orientations within the material, as shown in Figure 2-13 [288]. In orthorhombic ferroelectric materials, the domain structure serves to reduce electric field energy in 90° domains and minimise elastic energy in 180° domains. These domain structures are a key aspect of the material's behaviour and properties[288,340], including BaTiO₃, creates 60°, 90°, 120°, and 180° domain walls, whereas the domain structure of rhombohedral ferroelectric materials, including again BaTiO₃, forms 70.5°, 109.5°, and 180° domain walls. The domain structure in ferroelectric materials directly impacts characteristics like polarisation, electric field generation, and dielectric constant. It plays a crucial role in determining the material's electrical properties and behaviour[288]. In ferroelectric materials like BaTiO₃, a prevalent domain configuration is alternating domain stacking. This refers to the arrangement of domains with different polarisation directions in a stacked pattern. It influences the overall behaviour and properties of the material[345,346]. Stacking alternating domains in ferroelectric materials like BaTiO₃ helps minimise energy and aligns the overall polarisation more effectively with the external electric field. This alignment enhances the material's electrical properties and responsiveness to external stimuli[345,347]. An equilibrium domain wall spacing

results from the competition to reduce energy by merging different types of domains and utilising domain walls. This spacing represents a balanced arrangement that optimises the material's properties and energy efficiency [347,348]. The sandwich, stacking, and combined arrangements of alternating domains efficiently minimise the material's energy state. This organised mixture of ferroelectric domains, separated by twin borders, typically features very few single BaTiO₃ domains in the structure, particularly in thin needle-like forms. This configuration optimises the material's properties and energy efficiency[349]. In BaTiO₃, the domain wall thickness typically spans from one to a few lattice constants. This narrow range reflects the size of the transitional regions between different ferroelectric domains, where polarisation orientations shift. This property is vital in understanding BaTiO₃'s behaviour and functionality[350]. In ferroelectric materials like BaTiO₃, the domain size represents an equilibrium state, balancing the energies associated with domain walls, spontaneous polarisation, and strain-induced electric and elastic fields. This equilibrium contributes to the material's tightly packed atom arrangement, enhancing its properties. Understanding this balance is crucial for BaTiO₃'s behaviour and functionality[351]. The crystallographic orientations of BaTiO₃ or ferroelectric domains are primarily influenced by pressure, electric fields, and temperature. These conditions play a pivotal role in determining the arrangement and behaviour of the material's domains, impacting its overall properties and functionality. Understanding these influences is essential for manipulating BaTiO₃ for specific applications[351,352]. High pressure can lead to reduced volume, the formation of the cubic phase, or a decrease in the Curie temperature in BaTiO₃. This effect is significant in understanding the material's response to external pressure and its potential phase transitions, which have implications for its functional properties and applications[353]. A stronger electric field enhances the alignment of atoms (dipoles) in the crystal lattice, achieving 100% saturation in twinned domains. In this state, there is only one domain with the c-axis parallel to the applied field. Removing the electric field doesn't return the domain to its original configuration, resulting in some orientation relaxation. This phenomenon is significant for understanding domain behaviour under electric fields and their role in material

properties[354]. Keeping the domain in a closed electrical circuit allows for gradual relaxation and movement. Strong electric fields, like those in a microwave oven, can raise the material's Curie temperature. Near the Curie temperature, twin boundaries may become more twisted and bent, affecting the material's domain structure, and switching behaviour. Ferroelectric materials exhibit both pyroelectric and piezoelectric properties, contributing to their versatile applications in various technologies.

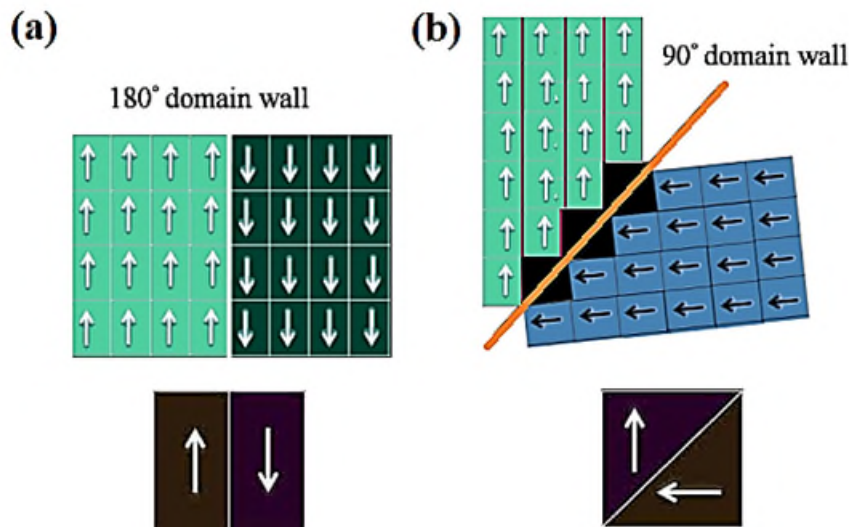


Figure 2-13. a) 180°domain wall distinguishing domain by anti-parallel polarisations; (b) 90°domain wall distinguishing domain by perpendicular polarisations.

Extensive efforts have been invested in methods to study domain substructure and visualise domains. Various microscopy techniques, such as scanning electron microscopy, transmission electron microscopy, and polarised light microscopy, are employed for this purpose[355,356]. Additionally, surface treatments like doping, functionalisation, and etching play a role in enhancing domain characterisation in materials like BaTiO₃[357]. Crystallography, including X-ray diffraction, is another valuable technique used to study domains in materials like BaTiO₃. It provides detailed insights into the hierarchical crystal forms and their characteristics, as summarised in Table 2-6 [358].

Table 2-6. Different types of hierarchical crystal structure and its properties of BaTiO₃.

Material ID (BaTiO ₃)	Crystal structure	Properties	Ref.
mp-5020 BaTiO ₃	(Cubic) Perovskite structured as well as crystallises in the trigonal R3m space group. Rhombohedral Lattice System, Symbol R3m	Non-magnetic, Band Gap 2.56 eV, number of atoms 15, Density 5.70 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) 96 GPa, Shear modulus (Voigt) 65 GPa, Poisson's Ratio 0.30, Total Dielectric Tensor ϵ_{ij} = ionic contributions + static (electronic and lattice) contributions= ϵ_{xx} = 38.45, ϵ_{yy} = 38.45, ϵ_{zz} = 20.72	[359]
mp-5777 BaTiO ₃	(Cubic) Perovskite structured and crystallises in the orthorhombic Amm2 space group, Orthorhombic Lattice System, Symbol Amm2	Non-magnetic, Band Gap 2.44 eV, number of atoms 10, Density 5.71 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) 107 GPa, Shear modulus (Voigt) 72 GPa, Poisson's Ratio 0.26, Total Dielectric Tensor ϵ_{ij} = ionic contributions + static (electronic and lattice) contributions= ϵ_{xx} = 13.29, ϵ_{yy} = 19.39, ϵ_{zz} = 6.262	[359]

mp-5986 BaTiO ₃	(Cubic) Perovskite structured and crystallises in the tetragonal P4mm space group, Tetragonal Lattice System, Symbol P4mm	Non-magnetic, Band Gap 1.96 eV, number of atoms 5, Density 5.75 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) 125 GPa, Shear modulus (Voigt) 79 GPa, Poisson's Ratio 0.23, Total Dielectric Tensor ϵ_{ij} = ionic contributions + static (electronic and lattice) contributions= ϵ_{xx} = 7.653, ϵ_{yy} = 7.653, ϵ_{zz} = 19.24	[359]
mp-558125 BaTiO ₃	BaTiO ₃ crystallises in the orthorhombic C222 ₁ space group, Orthorhombic Lattice System, Symbol C222	Non-magnetic, Band Gap 2.08 eV, number of atoms 60, Density 5.62 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) (Under research), Shear modulus (Voigt) (Under research), Poisson's Ratio (Under research), Total Dielectric Tensor ϵ_{ij} = (Under research)	[359]
mp-5933 BaTiO ₃	BaTiO ₃ with (Cubic) Perovskite-like structured and crystallises in the hexagonal P6 ₃ /mmc space group, Hexagonal	Non-magnetic, Band Gap 1.73 eV, number of atoms 30, Density 5.68 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) 140 GPa, Shear modulus (Voigt)	[359]

	Lattice System, Symbol $P6_3/mmc$.	78 GPa, Poisson's Ratio 0.27, Total Dielectric Tensor ϵ_{ij} = (Under research)	
mp-2998 $BaTiO_3$	$BaTiO_3$ with (Cubic) Perovskite structured and crystallises in the cubic $P\bar{m}3m$ space group, Cubic lattice System, symbol $Pm\bar{3}m$	Non-magnetic, Band Gap 1.67 eV, number of atoms 5, Density $5.89\text{ g}\cdot\text{cm}^{-3}$, Possible oxidation states Ba^{2+} , O^{2-} , Ti^{4+} , Bulk modulus (Voigt) 163 GPa, Shear modulus (Voigt) 108 GPa, Poisson's Ratio 0.23, Total Dielectric Tensor ϵ_{ij} = (Under research)	[359]
mp-644497 $BaTiO_3$	$BaTiO_3$ crystallises in the orthorhombic $Amm2$ space group, orthorhombic lattice System, symbol $Amm2$	Non-magnetic, Band Gap 0.32 eV, number of atoms 10, Density $3.47\text{ g}\cdot\text{cm}^{-3}$, Possible oxidation states Ba^{2+} , O^{2-} , Ti^{4+} , Bulk modulus (Voigt) 33 GPa, Shear modulus (Voigt) 20 GPa, Poisson's Ratio 0.28, Total Dielectric Tensor ϵ_{ij} = (Under research)	[359]
mp-1076932 $BaTiO_3$	$BaTiO_3$ crystallises in the orthorhombic $Amm2$ space group, Orthorhombic lattice System, symbol $Amm2$	Non-magnetic, Band Gap 0 eV, number of atoms 10, Density $3.08\text{ g}\cdot\text{cm}^{-3}$, Possible oxidation states Ba^{2+} , O^{2-} , Ti^{4+}	[359]
mp-995191 $BaTiO_3$	$BaTiO_3$ crystallises in the orthorhombic $Amm2$ space group, Orthorhombic lattice System, symbol $Amm2$	Non-magnetic, Band Gap 0 eV, number of atoms 10, Density $4.53\text{ g}\cdot\text{cm}^{-3}$, Possible oxidation states Ba^{2+} , O^{2-} , Ti^{4+} , Bulk modulus (Voigt)=33 GPa, Shear	[359]

		modulus (Voigt)= 19 GPa, Poisson's Ratio 0.44, Total Dielectric Tensor ϵ_{ij} = ionic contributions + static (electronic and lattice) contributions= (Under research	
mp-19990 BaTiO ₃	BaTiO ₃ crystallises in the tetragonal P4/mmm space group, Tetragonal lattice System, symbol P4/mmm	Non-magnetic, Band Gap 0 eV, number of atoms 5, Density 4.55 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ , Bulk modulus (Voigt) 97 GPa, Shear modulus (Voigt) 30 GPa, Poisson's Ratio 0.44, Total Dielectric Tensor ϵ_{ij} = (Under research)	[359]
mp-504715 BaTiO ₃	BaTiO ₃ is (Cubic) Perovskite structured and crystallises in the cubic P $\bar{m}$ 3m space group, cubic lattice System, symbol -P 423	Non-magnetic, Band Gap 0 eV, number of atoms 5, Density 3.85 g·cm ⁻³ , Possible oxidation states Ba ²⁺ , O ²⁻ , Ti ⁴⁺ ,	[359]

Domain walls, formed by electric fields or tension, are not limited to materials like BaTiO₃; they are also observed in biological systems, including plants and animals. These walls represent boundaries between distinct domains, and their formation and behaviour is of scientific interest across various fields[288]. Domain switching, which involves changing the polarisation direction of domains, is crucial in applications like communications and electrical devices. Stress typically induces 90° domain switching, while electric fields can lead to both 90° and 180° domain switching. This distinction in switching mechanisms is important for understanding and controlling the behaviour of ferroelectric materials[349]. Domain flipping is significant as it alters the overall polarisation direction,

impacting the material's electrical properties. This change in the macroscopic polarisation vector is important for various applications in which precise control of polarisation is required, such as in electronic devices and sensors. Understanding the mechanism of domain flipping is crucial for optimising the performance of ferroelectric materials[360]. For a ferroelectric material like BaTiO₃ to exhibit piezoelectric activity, it requires an average polarisation direction. The process of 90° domain flipping in BaTiO₃ can induce strains of up to 1.1%, which is essential for generating piezoelectric properties. This controlled change in polarisation direction is crucial for enabling the material to convert mechanical stress into electrical charge, a fundamental aspect of its piezoelectric behaviour [188]. Domain switching is the process of altering a material's electrical characteristics to enable electricity generation. This transformation can be achieved through a high electric field or, for piezoelectric materials, through mechanical stress. De-poling, on the other hand, involves reversing this process using an electric field or stress, restoring the material's original state. These mechanisms are fundamental for the electrical behaviour of ferroelectric and piezoelectric materials[361]. De-poling involves breaking the symmetry of a material to generate electricity. Domain switching between poled and depoled states enhances the piezoelectric and electrostrictive properties of materials. This process is crucial for improving the electrical behaviour and performance of such materials[360]. Electrostriction is a mechanical displacement induced by an electric field in all materials, occurring independently of the field's direction and occurring with twice the frequency due to the squared strain-field relationship. Grain boundary mismatch and residual tensions in polycrystal ferroelectrics pose challenges in achieving poled and depoled states, impacting material performance[362]. The significance of BaTiO₃ ferroelectric behaviour lies in its ability to maintain a stable polarisation state, exhibit hysteresis effects, and interplay with electrical, thermal, mechanical, temperature, electric field, pressure, and strain-dependent properties. Hysteresis refers to a system's state dependence on its history, such as multiple magnetic moments in a magnet based on prior magnetic field exposure or differences in measurements like

pressure when values increase versus decrease. Finally, Table 2-7 summarises the basic requirements of a ferroelectric material.

Table 2-7. Fundamental requirements of the ferroelectric materials/ BaTiO₃ for ferroelectrics behaviour.

Requirements of a ferroelectric's behaviour	Remarks	Ref.
Electrical properties	Spontaneous electric polarisation, reversal of electric polarisation in the presence of an external electric field.	[363]
Structural anisotropy as well as distortions	The presence of different ions in the crystal lattice provides ferroelectricity, and specific "d" orbital occupancy cations show ferroelectricity through distortion.	[364]
d0' electron configuration	The ABO ₃ -class perovskite form exhibits ferroelectricity due to the d0' electron pattern on the B-site cation.	[365]
Symmetry	Non-centre symmetric, allowing for electric polarisation and ferroelectricity.	[366]

2.3.3 Curie or transition temperature (T_c) of BaTiO₃

Dielectric materials are electrical insulators polarised by external electric fields. They are connected to piezoelectric, pyroelectric, and ferroelectric materials, which exhibit unique electrical properties in response to various stimuli such as pressure, temperature, and polarisation. These materials play crucial roles in electronic applications[298]. Dielectric permittivity is a critical property of dielectric materials as it quantifies their capacity to store electrical energy under an external electric field's influence. This property is fundamental in designing and utilising dielectric materials in various applications, especially in electronic devices[316]. A piezoelectric material responds to an external electric field by undergoing strain or stress changes, while it also changes its polarisation due to mechanical stimulation. Pyroelectric materials, which are a subset of piezoelectric materials,

exhibit polarisation changes in response to temperature variations. In essence, pyroelectric materials can be considered piezoelectric materials that undergo polarisation changes due to temperature fluctuations[367,368]. Ferroelectric materials display both pyroelectric and piezoelectric properties. This means they can change polarisation in response to temperature changes (pyroelectric) and undergo strain or stress changes in the presence of an external electric field (piezoelectric). These dual properties make them valuable in various applications, such as sensors and actuators[336]. Above the Curie temperature (T_{cw}), ferroelectric materials lose their spontaneous polarisation and transition to a paraelectric state. This transition occurs because the crystal's structure no longer supports spontaneous polarisation at higher temperatures[319]. The terms paraelectric and paramagnetic are often used interchangeably. When temperature increases, the dielectric constant (ϵ) decreases spontaneously in these materials due to the loss of spontaneous polarisation[362]. The Curie-Weiss law relates the dielectric constant to temperature above the Curie point. The Curie-Weiss temperature is different from the Curie point (T_c), as it is mainly influenced by electronic polarisation, not thermal effects[328]. Equation (2-2) is employed to describe the dielectric constant, and it distinguishes between first order and second-order phase transitions based on the relationship between the Curie or transition temperature (T_{cw}) and the Curie point (T_c). If T_{cw} is less than T_c , it indicates a first-order phase transition, while T_{cw} equal to T_c signifies a second-order phase transition.

$$\epsilon = \epsilon_0 + \frac{C}{(T - T_{cw})} \quad (2-2)$$

As the temperature approaches the Curie temperature, ϵ_0 , the dielectric constant of the material, becomes very small and can be neglected. This occurs because the material's polarisation behaviour changes significantly near the Curie temperature, leading to a diminishing dielectric constant[284]. Phase transitions involve a symmetry transformation and are classified as first-order or second order based on Gibbs free energy. First-order transitions exhibit a discontinuity in the first derivative of Gibbs free energy, while second-order transitions display continuity in the first derivative but a discontinuity in the second derivative. These distinctions characterise the nature of the phase change[306]. First-order phase

transitions exhibit a discontinuous change in the crystal's volume, entropy, and polarisation. In contrast, second-order phase transitions display continuous variations in volume, entropy, and polarisation, with discontinuous changes observed in specific heat. These characteristics differentiate the nature of the phase transition[329]. First-order phase transitions are characterized by latent heat, which is the absorption or release of energy during the transition. Second-order phase transitions are marked by the coefficient of expansion, which describes how a material's volume changes with temperature. These properties distinguish between the two types of phase transitions[366].

2.3.4 Spontaneous polarisation in BaTiO₃

Spontaneous polarisation (P_s) is an intrinsic dielectric property arising from internal processes, independent of external influences. It quantifies the electric dipole moment per unit volume of the dielectric material. Ferroelectric crystals feature uniform polarisation domains, where polarisation is aligned in the same direction. However, in the absence of an external electric field, neighbouring domains exhibit reversed polarization, contributing to the material's ferroelectric behaviour[302]. In the presence of an electric field, the polarisation of a non-linear material undergoes changes, forming hysteresis loops that depict closed curves of polarisation. As the intensity of the external electric field increases in the direction of spontaneous polarisation, it induces electronic, ionic, and dipolar contributions, resulting in an increase in polarisation (P). This behaviour characterises the response of ferroelectric materials to electric fields[354]. As the intensity of the electric field gradually increases, more domains align in its direction, leading to the polarisation reaching its maximum value, known as the saturation point. This phenomenon demonstrates the relationship between the electric field strength and the alignment of polarised domains in ferroelectric materials[351]. At this point, the entire specimen becomes a single domain, typically accompanied by crystal distortion and the alignment of polarisation directions. This state reflects the saturation of the material's polarisation under the influence of the electric field, resulting in a uniform polarisation orientation throughout the specimen[330]. The amplitude of spontaneous polarisation is

determined by extrapolating the saturation field value to zero. In the absence of an electric field, each domain exhibits a similar amplitude of spontaneous polarisation. However, reducing the electric field to zero results in a decrease in polarisation, which follows a specific path and does not reach zero at zero electric fields, leading to residual polarisation. This residual polarisation is a characteristic of ferroelectric materials and signifies their hysteresis behaviour[317]. Reversing the field's direction reduces the polarisation of nearly half of the crystal, effectively cancelling out the remaining polarisation. This process helps reset the crystal's polarisation to its initial state, removing any residual polarisation that may have occurred during previous electric field exposure. It's a key aspect of ferroelectric behaviour and materials[315]. A coercive field is employed to reset polarisation to zero. Gradually increasing the reverse field leads to polarisation saturation in the opposite direction, helping close the hysteresis loop. This process is crucial for achieving a neutral or zero polarisation state in ferroelectric materials, as shown in Figure 2-14[294].

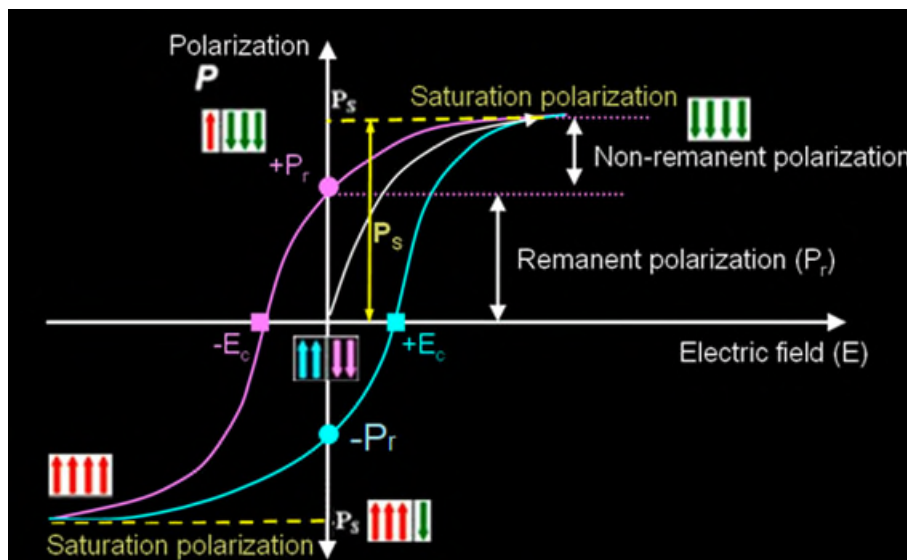


Figure 2-14. Hysteresis loop of BaTiO₃/ ferroelectric materials (P-E), spontaneous polarisation (P_s), remnant polarisation($\pm P_r$), coercive field (E_c), polarisation (PP) and applied electric field (E).

2.3.5 Dielectric property of BaTiO₃

Ferroelectric materials find extensive applications due to their unique characteristics, including high permittivity for capacitors (e.g., BaTiO_3), stable polarisation, pyroelectricity, piezoelectricity, and non-linear polarisability. These properties make them valuable in various fields and technologies, such as electronics, sensors, and energy harvesting, offering versatile solutions to numerous challenges[285]. BaTiO_3 /ferroelectrics are widely utilised in diverse applications such as capacitors, pyroelectric sensors, piezoelectric devices, ferroelectric memory, electrostrictive transducers, and thermistors. They are favoured for their exceptional properties like high permittivity, stable polarisation, pyroelectricity, piezoelectricity, and non-linear polarisability. These applications span various industries and benefit from the unique characteristics of BaTiO_3 /ferroelectric materials[346]. Capacitors are valued for their compact size, substantial capacitance, and high dielectric constant, making them essential components in various electronic devices. Ferroelectric materials with bi-stable polarisation are key for binary memory systems, including both volatile and non-volatile memory devices. Non-volatile memory doesn't require a holding voltage and is known for its high integration level, while volatile memory erases data when power is switched off, making them distinct in memory technology[303]. Data is captured by reversing or reorienting the polarity with a stronger electric field than the coercive force. To erase data, the polarisation is restored to its original state using an opposing polarity field. This process is fundamental in memory technology for writing and erasing data[304]. Data storage relies on both electrical and optical technologies. To study dielectric properties at the atomic or molecular level, the local field (E_{loc}) at these scales, distinct from the macroscopic field (E), is considered. Understanding E_{loc} is essential for exploring fundamental phenomena in dielectric materials[307]. The local field plays a crucial role in aligning a material's atoms or molecules, leading to polarisation. It's responsible for the microscopic polarisation behaviour within dielectric materials, contributing to their overall electrical properties. Understanding the local field is essential for comprehending the polarisation phenomena in these materials[293]. Equation (2-3) demonstrates the relationship between the polarisation amplitude (P) and the macroscopic electric field (E) at a particular point within a dielectric material. This

equation elucidates how the local field influences polarisation, offering insights into the material's electrical behaviour and response to external forces. Understanding this relationship is fundamental in studying dielectric properties.

$$\mathbf{P} = \epsilon_0 \chi_e \mathbf{E} \quad (2-3)$$

where, ϵ_0 , and χ_e , are the permittivity of free space and dielectric susceptibility, respectively. The polarisation produced in the material per unit electric field is called dielectric susceptibility [318]. The degree of resistance to the flow of charge is called the dielectric constant (relative permittivity) of Material (ϵ_r), which is expressed by the ratio of the dielectric displacement (D) to the macroscopic field intensity (E) in an isotropic medium, as shown equation (2-4) [308].

$$\epsilon_r = \frac{D}{\epsilon_0 E} \quad (2-4)$$

The relation between the dielectric constant and dielectric susceptibility(χ_e) for the isotropic medium is expressed in equation (2-5) [286]. However, the dielectric property is dependent on the direction of the field and illustrated through the components of the susceptibility tensor or the dielectric tensor of the second rank [369].

$$\chi_e = \frac{P}{\epsilon_0 E} = \epsilon_r - 1 \quad (2-5)$$

The local electric field (Lorentz field) is the main term to describe the polarisability α of an atom. Polarisability α is a proportionality constant between induced dipole moments (μ) and the local field (E_{loc}), as mentioned in equation (2-6) [312].

$$\mu = \alpha(E_{loc}) \quad (2-6)$$

Polarisability (α) is a tensor quantity in the case of a non-spherical atom or isotropic medium, and dielectric constant is dependent upon the arrangement of atoms within the crystal (as it is macroscopic property), and polarisability is an atomic property [370]. If the total number of atoms per unit volume is N, and each atom exhibits the same polarisability (α), the total polarisation of the crystal is a

product of the local field and polarisabilities of the atom's times, as mentioned in equation (2-7). [370]

$$\mathbf{P} = \sum_j \mathbf{N}_j \alpha_j (\mathbf{E}_{loc})_j \quad (2-7)$$

where N_j , α_j , $E_{loc}(j)$ are the concentration, polarisability of atom j and the local field at atom sites j ; the local field is described by equation (2-8) (the Lorentz relation).

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_P + \frac{\mathbf{P}}{3\epsilon_0} = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} \quad (2-8)$$

where the polarisation field (opposite to the externally applied field) and the externally applied field are represented by E_P and E_0 , respectively. As previously stated, the electric field on the site of an atom or molecule is known as the local field (E_{loc}), which is separate from the macroscopic field (E). The local field also includes the Lorentz field [371]. The macroscopic field is an average value that remains constant across the medium. The Lorentz field (E_{loc}), on the other hand, is tiny and periodic [372]. This is quite big at molecular locations; it aids in successfully polarising molecules, and polarisation is found to be larger than polarisation under ordinary field conditions [373]. As a result, the total polarisation of the crystal (P) may be expressed as equation (2-9).

$$\mathbf{P} = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} \sum_j \mathbf{N}_j \alpha_j \quad (2-9)$$

For an isotropic media, the relationship between total polarisation and dielectric susceptibility (χ_e) may be represented as the equation (2-10) [374],

$$\chi_e = \frac{P}{\epsilon_0 E} = \frac{\sum_j N_j \alpha_j}{(\epsilon_0 - \frac{1}{3} \sum_j N_j \alpha_j)}, \quad \epsilon_r = 1 + \frac{\frac{\sum_j N_j \alpha_j}{\epsilon_0}}{1 - \frac{1}{3\epsilon_0} \sum_j N_j \alpha_j} = \frac{1 + \frac{2}{3\epsilon_0} \sum_j N_j \alpha_j}{1 - \frac{1}{3\epsilon_0} \sum_j N_j \alpha_j} \quad (2-10)$$

Finally, it can be written as by solving the value of $\sum_j N_j \alpha_j$, as mentioned in equation (2-11),

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \sum_j N_j \alpha_j \quad (2-11)$$

Equation (2-11) is known as the Clausius-Mossotti relation; it expresses the link between dielectric constant and atomic polarisability and applies to the Lorentz field and the Lorentz field equation [375] $E_{loc} = E_0 + E_p + \frac{P}{3\epsilon_0} = E + \frac{P}{3\epsilon_0}$. Finally, total polarisation (α) may be written as the sum of electronic (e), ionic i and dipolar (d) polarisabilities, the latter being the most important factor or contributing to polarisation, as shown in equation 2-12 [376]. The dielectric constant develops because of electronic polarisability in the high-frequency region since ionic and dipolar contributions are minimal at high frequencies due to the inertial influence on ions and molecules [375].

$$\alpha = \alpha_e + \alpha_i + \alpha_d \quad (2-12)$$

Electronic polarisability is caused by electron dislocation in an atom relative to the atomic nucleus in the presence of an external electric field [377]. In terms of optical frequencies, electronic polarisability provides the polarisation and dielectric constant of a material; in the case of electronic polarisability, there is a link between the refractive index (n) and dielectric constant, as seen in equation (2-13) [378].

$$n^2 = \epsilon_r, \quad \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\epsilon_0} \sum_j N_j \alpha_{ej} \quad (2-13)$$

The relative dislocation of positive and negative ions from equilibrium locations causes ionic polarisability, and the distance must be smaller than the distance between neighbouring ions. In the case of ionic polarisability, there is a relationship between the displacement of positive and negative ions (d), a charge on each ion, dipole moment per molecule, and dielectric constant, dipole moment per molecule (μ)= qd, total ionic polarisation (Pi)= Nqd, and thus total ionic polarisability can be expressed as in equation (2-14) [379].

$$P_i = E_0 \sum_j N_j \alpha_{ij} \quad (2-14)$$

The persistent dipole moment induces dipolar polarisability (orientational polarisability). The permanent dipole moment exhibits arbitrary orientations with zero external electric fields and provides zero net polarisation. Permanent dipoles

provide dipolar polarisation by orienting themselves in the direction of the external electric field. As noted in the equation, Debye's quantum theory calculates the dipolar polarisability (α_d) per dipole (2-15) [380].

$$\alpha_d = \frac{\bar{\mu}}{E} = \frac{\mu^2}{3kT} \quad (2-15)$$

Where k , T , and μ are Boltzmann's constant, absolute temperature, and atom dipole moment, respectively. The crystal distortion provides electrical and ionic polarisability and is temperature independent. According to the equation, dipolar polarisability is temperature dependant (2-15) [381,382].

2.3.6 Methods of preparation of BaTiO₃

The shape and size of BaTiO₃-based materials are pivotal in shaping their magnetic, electrical, and optical characteristics. This influence stems from the spatial geometry effect, wherein the arrangement and dimensions of these materials intricately impact their properties. Understanding this phenomenon is essential for tailoring the desired attributes of BaTiO₃-based materials in various applications[383,384]. Significant progress in material technology focuses on precise manufacturing and self-organisation of inorganic materials with consistent geometrical shapes. Innovations in tape-casting techniques have enabled the production of dielectric layers under 20 micrometres thick. Utilising high dielectric constant ceramics like BaTiO₃ enhances capacitance in compact capacitor devices, offering substantial benefits in miniaturised electronic components[385]. The ferroelectric tetragonal structure of BaTiO₃ forms at higher temperatures, promoting grain growth and aggregation. In contrast, the non-ferroelectric cubic structure is synthesised at lower temperatures, such as 500°C using sol-gel methods. These temperature variations play a crucial role in controlling the material's structural properties[386]. BaTiO₃ can be compatible with polymeric materials when synthesised at very low temperatures, expanding its applications in microelectronics. Various titanium precursors and synthesis routes are employed to control BaTiO₃'s structure and morphology. Bulk-scale production, as depicted in Figure 2-14, often involves solid-state chemical

reactions between BaCO_3 and TiO_2 powders at high temperatures, offering cost-effectiveness but requiring solutions for associated drawbacks[385]. Solid-state reactions for BaTiO_3 synthesis can result in large particle sizes, wide size variations, and particle agglomeration due to high-temperature calcination. This limits the reliability of electrical components using solid-state BaTiO_3 . To address this, low-temperature methods must be employed to produce fine and uniform BaTiO_3 structures suitable for metal electrodes and cost-effective multilayer capacitors[387].

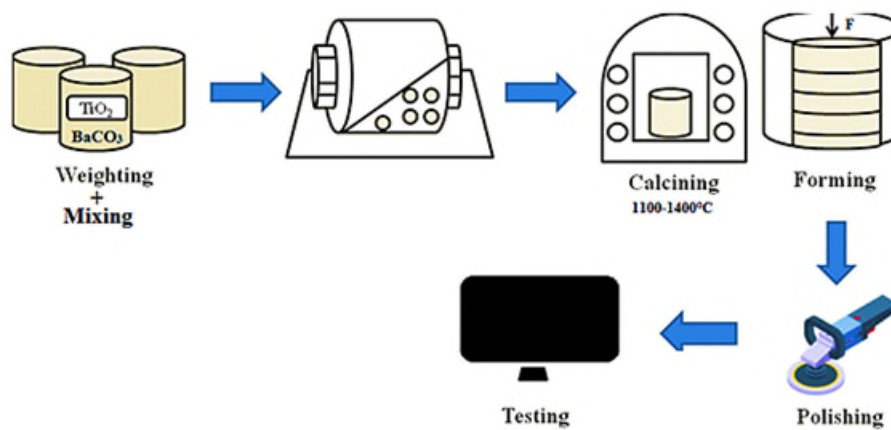


Figure 2-15. Preparation of BaTiO_3 by solid-state chemistry reactions.

Mechanochemical processes, like high-intensity ball milling, are employed to modify the microstructure and sintering properties of BaTiO_3 . This method enhances the material's characteristics and can be used to optimise its properties for various applications[388]. Mechanochemical techniques are superior to traditional solid-state reactions and wet-chemistry procedures for BaTiO_3 production due to their efficiency in creating finely tuned microstructures and improved material properties. This method offers a more controlled and effective means of manufacturing BaTiO_3 for a wide range of applications[389]. Mechanochemical synthesis offers several advantages, including cost-effectiveness, the use of locally available oxides, elimination of intermediate temperature calcination, and simplified operation. Additionally, mechanically activated powders have enhanced sintering properties compared to traditional methods. BaTiO_3 can be produced by mixing BaCO_3 and TiO_2 and subjecting

them to high-energy ball milling at medium temperatures, such as 800°C, providing a more efficient manufacturing process[390]. Mechanical activation and sintering treatment significantly impact dielectric characteristics. Activated samples exhibit higher relative permittivity. Porosity, with low porosity and high densification in non-activated BaTiO₃ samples, enhances dielectric permittivity. Grain size of the raw material influences crystal structure, leading to a change from tetragonal to pseudo-cubic when particle size decreases. This affects BaTiO₃'s crystal structure and dielectric properties[391]. Reduced grain size lowers the ferroelectric phase transition temperature. Various chemistry-based methods have emerged to produce high-purity, fine BaTiO₃ particles at low temperatures, affecting sample microstructure. These methods enable the production of fine barium titanate particles through diverse chemical approaches[392]. Various methods like hydrothermal, sol-gel, and microwave heating are used for BaTiO₃ preparation, affecting its properties. These chemistry-based approaches offer versatility in generating fine BaTiO₃ particles for diverse applications. Different techniques influence the microstructure and characteristics of the produced BaTiO₃ materials[393]. Two widely recognised methods for BaTiO₃ preparation are the sol-gel technique and the hydrothermal process. These chemistry-based approaches offer controlled synthesis and tailored properties for various applications, influencing microstructure and characteristics[394]. While the sol-gel technique can lead to the formation of barium carbonate due to carbon-based raw materials, the hydrothermal method may introduce H₂O and OH⁻ lattice defects in microscopic barium titanate particles. These limitations in each method need to be addressed for precise control over the properties and structure of BaTiO₃ materials[395]. Evaluating the size effect of hydrothermal-produced samples can be exceptionally difficult due to the various factors and complexities involved in this technique. Table 2-8 provides a summary of multiple methods for synthesising BaTiO₃, each with its own advantages and challenges, offering researchers a range of options for their specific needs in material preparation.

Table 2-8. An overview of various methods for preparation of BaTiO₃ and pros as well as cons (Remarks).

Methods	Process	Remarks	Ref.
Mechanochemical process	In high-energy ball milling, the powder is mechanically activated.	Low cost, avoids intermediate temperature calcination, easy method, lower activation energies seen in non-activated BaTiO ₃ .	[396]
Hydrothermal method	BaTiO ₃ production at low temperatures, different particle sizes with different synthesis conditions.	Fabrication as powders or thin films yields exceptionally reactive powder in the sintering direction, yields crystalline powders with exact particle size and self-controlled form, and contaminants alter the microstructure of the BaTiO ₃ film.	[397]
Sol-gel method	After drying, a stable colloidal (sol) solution that gels into a film, based on dissolved organometallic molecular precursors (generally alkoxides)	Used to achieve high purity, small size, and homogeneous BaTiO ₃ at low temperatures, as well as control of composition and surface shape.	[398]
Spray pyrolysis	Titanium stearate can be utilised as a precursor by	A high-purity barium titanate with excellent	[399]

	employing the combustion of metal nitrates (oxidisers) and carbohydrazide as the fuel source.	stoichiometry, used for complicated development, multi-layered thin films via layer-by-layer growth.	
Exothermal combustion process	Using titanium and barium sources such as barium nitrate, titanium dioxide (TiO_2), and titanyl nitrate ($\text{TiO}(\text{NO}_3)_2$), as well as reducing agents such as glycine ($\text{C}_2\text{H}_5\text{NO}_2$), carbamide ($\text{H}_4\text{N}_2\text{O}$), and glycerol ($\text{C}_3\text{H}_5(\text{OH})_3$).	Single-step synthesis of barium titanate, pseudo-cubic lattice, good property stability across a wide temperature range, and electromagnetic field absorption.	[400]
RF-sputtering method	60-160W RF power on a block of platinum and fused quartz substrate	Electrically conductive electrodes with a low sputtering rate; greater voltages are required to improve the sputtering rate.	[401, 402]

BaTiO_3 has established itself as a premier dielectric material in materials science and technology due to its exceptional properties, including high dielectric permittivity, stability, and versatility. Its applications span various fields, from capacitors to memory devices, making it a highly regarded material in the realm of advanced materials and electronics. BaTiO_3 is valued in electrical applications due to its high dielectric constant and heat resistance. Researchers are exploring its potential in polymer blend nanocomposites, offering tuneable properties for diverse electrical and electronic applications, including thermo-mechanical

attributes and dielectric characteristics. This material shows promise in advancing electrical and electronic devices. BaTiO₃ and BaTiO₃-based polymer nanocomposites are contributing to the development of advanced materials for energy storage, hybrid nanostructures, and smart materials. Their adaptability as nanofillers is driving innovation in these fields, paving the way for next-generation high-performance materials.

2.4 Conclusions

In conclusion, graphene and its derivatives stand as transformative materials, profoundly influencing diverse scientific and technological fields. This comprehensive review outlines their multifaceted role, showcasing their adaptability in various applications within nanoscience, nanotechnology, and practical domains. The narrative skilfully navigates through graphene's versatile properties, highlighting its impact in materials science, green chemistry, and numerous innovation-rich applications. From energy storage to environmental protection, graphene's widespread applications and unique attributes contribute significantly to scientific progress and technological innovation. Similarly, BaTiO₃ has cemented its position as a premier dielectric material, prized for its high dielectric permittivity, stability, and versatility. Its applications span across electrical devices and advanced materials, making it an esteemed component in various electronic applications. Exploring its potential in polymer blend nanocomposites reveals promising prospects for tuneable electrical and mechanical properties, advancing the realms of electrical devices and energy storage. BaTiO₃ and its polymer nanocomposites stand as catalysts for next-generation materials, driving innovation in energy storage, hybrid nanostructures, and smart material development.

CHAPTER 3

Graphene Nanoplatelets/Barium Titanate Polymer Nanocomposite Fibril by In-Situ Mechanical Stimulation: Electro-Thermo-Mechanical Material Properties - A Computational Predictions and Experimental Analysis

3.1 Introduction

Plastic waste poses a critical environmental challenge, with approximately eight million tons entering our oceans annually, leading to significant and irreversible harm to marine ecosystems[403]. This issue underscores the urgent need for sustainable solutions and responsible waste management practices[404]. Plastic waste is now a highly visible and widespread form of pollution, inflicting severe harm on both living organisms and the environment. It contaminates water and soil, poses threats to wildlife, and causes substantial environmental degradation. Addressing this crisis requires concerted efforts to reduce, recycle, and properly manage plastic waste globally[405]. The detrimental impacts of plastic waste on the environment underscore the urgent need to develop innovative strategies for its elimination or substantial reduction. This priority requires exploring new technologies, regulations, and consumer behaviours aimed at minimising plastic pollution and its consequences. Addressing this challenge is crucial for preserving ecosystems and combating environmental degradation[406]. Conductive polymer nanocomposites hold great promise as a solution to various contemporary technological challenges. Their unique properties make them suitable for a wide range of applications, particularly in electronics, energy storage, and materials science. These materials offer innovative solutions to enhance performance and functionality in diverse fields[405,407]. Conductive polymer nanocomposites offer distinct advantages over traditional materials, making them a promising solution[408]. Recycling current plastic waste into new products, like electrically conductive polymers, presents an immediate opportunity to address the plastic waste issue. However, large-scale adoption of nature-based polymers still faces challenges in mass production[409]. The nanocomposites combine the functional and structural properties of nanomaterials and polymers for benefiting traceability, properties tailoring and recyclability [405,407], with emerging applications in electronics, energy storage,

biomedical devices, and automotive parts [410–415]. On the other hand, immiscible polymer blend-based nanocomposites are particularly appealing because they offer characteristics that traditional composites do not. Blends of immiscible polymers contain two or more polymers that do not mix but instead generate distinct phases in a composite material, which enables the development of various immiscible polymer blend-based nanocomposites. Fundamentally, the performance of polymer blend-based composites and nanocomposites is underpinned by the blended microstructure, its morphological features and filler dispersion [416], providing a control over parts remanufacture out of blend combinations, which again benefit sustainable developments. Such blends are being used in an increasing number of applications due to their superior mechanical, thermal, and electrical properties when compared to non-composite polymers. Their microstructure can be tailored via dispersion of functional fillers such as nanoparticles, carbon nanotubes (CNT), or graphene, which may greatly influence the performance of resulting final blends [23], despite the challenge of achieving strong filler-polymer adhesion, and compatibility within blending components [417]. Several experiments have been carried out to produce compatible, electrically conductive polymer nanocomposites via combining novel process techniques and nano-scale functional fillers into immiscible polymer blends [418,419]. The main challenge has been to find a way to incorporate these nano-scale fillers into immiscible polymer blends to create compatible and stable electrically conductive composites [420]. This owes to the fact that conductive nanocomposites often exhibit excellent conductivity [421], high stiffness [422], heat resistance [423], decreased gas permeability [424] and superior electromagnetic interference (EMI) shielding properties compared to those in neat polymer or immiscible polymer blends [425]. Conductive fillers used in conjunction with composites (such as fibre-reinforced thermoplastic composites) or polymer blends can improve the electrical, thermal [164], and mechanical performance, broadening the potential for generating micro-fibre composites (FC) [426,427].

For this purpose, a variety of carbon-based materials can be used as reinforcement and/or conducting fillers including carbon black [428], single-walled

CNT [429], multi-walled CNT [430], carbon nanofibres (CNFs), graphene nanoplatelets (GNPs) [431] in a variety of polymer matrices. Due to their optimal polymer-compatibility, recyclability, and low-cost processability, these composites have been employed in many industrial applications[91]. There is also a high demand for electrically conductive polymer composites that fulfil the performance standards required in electronics [432], EMI shielding [433] and other applications [434–436]. Such performance is influenced by a variety of parameters, including particulate and fibril morphologies[437] suggesting numerous combinations of blends/composites/nanocomposites, and/or nanofiller dispersion and distribution [435,438–442]. Additionally, there is indeed a high demand for low electrical percolation threshold in polymer composite materials [443]. The electrical percolation threshold is an essential parameter in polymer composites, which indicates the minimum concentration of conductive fillers required to generate a continuously conductive network. Nanofillers such as graphene, due to their small size and high surface energy, often form in agglomerates, making the creation of a continuous conducting network at lower concentrations challenging[23]. However, a low electrical percolation threshold is beneficial since it requires a smaller concentration of nanofillers, allowing for the composite material to maintain its mechanical properties, while achieving the desired electrical conductivity, thus resulting in low energy requirements for material processing and low costs[444]. Thus, having a low electrical percolation threshold is particularly advantageous for composite materials that require both high electrical conductivity and thermomechanical properties [445,446]. Another crucial issue to consider in waste management is sustainability and recyclability. Microbeads, for instance, are a type of plastic waste that can harm marine life and the environment. To reduce the negative impact of plastic waste on marine ecosystems, natural alternatives such as salt, sugar, or crushed fruit kernels can replace plastic microbeads. Additionally, sustainable waste management measures, such as recycling, can help reduce plastic waste build-up in landfills and seas. Some materials, such as polypropylene, polyethylene terephthalate, and nanofillers like GNPs and barium titanate (BaTiO_3) can be recycled at minimal production temperature, energy, emission, and costs. If this is realised

and quantified for large scale, it would add to prioritising sustainability and recyclability in plastic waste management and reduce the harm caused by microbeads on marine ecosystems [25,29].

Graphene Nanoplatelets (GNPs) and Barium Titanate (BaTiO_3) are combined to produce high-performance composites with various applications[447]. These composites offer improved mechanical properties such as improved strength and stiffness, electrical conductivity for applications[448–450] such as sensors and electronics, enhanced dielectric properties for capacitors and energy storage devices, and good compatibility with polymer matrices, enabling their use in diverse fields including aerospace, automotive, electronics, energy, and more[451]. Additionally, polymer blend composites have been investigated as a solution to mitigate microwave radiation pollution and enhance EMI shielding performance[435,452]. The papers highlight the importance of selective confinement or dispersion of nanofillers in specific phases of the blend to improve composite properties[453]. One of the literature studies focused on polystyrene (PS)/ethylene-co-methyl acrylate (EMA) blends, demonstrating that confining carbon nanotubes and carbon nanofibres in the EMA phase significantly reduced the electrical percolation threshold, resulting in improved microwave absorbing properties[454]. Another study explored EMA/thermoplastic polyolefin (TPO) blends, showing that preferential distribution of carbon particles in the EMA phase led to excellent EMI shielding performance at low filler loading[455]. Carbon black reinforcement in a polystyrene/EMA blend enhanced EMI shielding performance [456]. Lastly, a solution mixing technique was employed to create lightweight blend composite films with improved electrical properties, thermal conductivity, and microwave shielding performance[457]. These studies collectively emphasise the potential of polymer blend composites in addressing microwave radiation pollution and enhancing EMI shielding in various applications[458]. The incorporation of fibrils morphology and the combination of GNPs and BaTiO_3 in composites based on recycled plastic offers a synergistic effect. This approach addresses the microbead problem by utilising recycled plastic instead of virgin materials. The enhanced mechanical properties and functionality of these composites contribute to sustainability efforts by promoting the reuse of plastic

waste and reducing the environmental impact associated with microbead pollution[459,460].

In this chapter, we investigate the electro-thermo-mechanical material properties of a graphene nanoplatelets/barium titanate polymer nanocomposite. We specifically focus on the effects of fibre drawing as a form of mechanical stimulation, unravelling the unique characteristics induced by this process through computational predictions and comprehensive experimental analysis. "Fiber drawing is a fundamental mechanical process in our research, characterised by the application of mechanical force to profoundly alter the material's structure. As the fibres undergo the drawing process, they undergo substantial mechanical deformation, resulting in profound modifications to their orientation, alignment, and overall morphology. These mechanical transformations exert a remarkable influence on the material's properties, spanning its electrical conductivity, thermal behaviour, and mechanical strength. Considering these substantial effects, we firmly establish fibre drawing as a legitimate form of mechanical stimulation within the scope of our study, contributing to a deeper understanding of the material's electro-thermo-mechanical properties. This study explores the scalability of recycled polypropylene (PP)/Polyethylene terephthalate (PET) blends with GNPs/ BaTiO₃ to create conductive composite blends. It also investigates in-situ fibrils-based composites through mechanical stimulation (e.g., cold drawing or stretching) and quantifies their electrical, thermomechanical, and EMI properties. The goal is to develop viable materials from recycled plastics with enhanced properties. The primary goal of this study was to introduce a multifunctional composite formed through in-situ composites reinforced with fibrils. This composite utilised blended and recycled plastics, transformed via external mechanical stimulation (e.g., cold drawing or stretching), to enhance its properties. The aim was to develop a sustainable material with improved functionality. The resulting material aims to substitute current polymer blends and polymer nanocomposites based on the p-products, meeting their specific property requirements while achieving low percolation thresholds and favourable mechanical, electrical, and thermal features. It has been observed that the proposed composites in the fibril form

exhibit superior electrical, thermomechanical, and electromagnetic shielding properties, and a greater reinforcing impact than the particles-based blended nanocomposites. This would suggest a remanufactured and property-enhanced material system with a low percolation threshold, excellent electrical conductivity, thermal, mechanical, and electromagnetic shielding properties capable of benefiting a variety of multi-functional and recyclable materials and applications.

3.2 Materials and methods

The polymers were extruded using a single-screw Noztek filament extruder. Recycled polypropylene (acquired from PP bottles with average molecular weight of 500,000 g/mol and average density of 907.5 kg/m³) employed in this study had a melt flow index (MFI) of - 11.0 g/10 min, as well as melting and glass transition temperatures of 167°C and -10°C, respectively (measured by differential scanning calorimetry, DSC)[403]. As an attempt to acquire a relatively large-scale laboratory container, the melt-flow index (MFI) of recycled polypropylene was tested in a 2.1 kg batch at a fixed temperature of 200°C at 10 rpm in a single screw nozzle filament extruder. The MFI of recycled polyethylene terephthalate bottles was determined using a Noztek filament extruder within a 500 g recycled polyethylene terephthalate batch with a fixed temperature profile at 240°C (acquired from PET bottles with average molecular weight of 35,000 g/mol, average density of 1370 kg/m³). DSC was used to calculate the melting and crystallisation temperatures of recycled polypropylene and polyethylene terephthalate. To introduce high-performance functional properties, the GNPs and BaTiO₃ powders with specifications of 2.0-2.25 g/cm³ for Graphene platelets (GNPs) and average particle size < 2µm for BaTiO₃ were supplied by Sigma-Aldrich. They were mixed in the blend without any modification, and both had a thickness in a few nanometres. Additionally, the density of GNPs and BaTiO₃ was 6.08 g/ml and 250°C, respectively. The GNPs had an aspect ratio of nearly 400, while BaTiO₃ had an aspect ratio of 1. Both Graphene platelets (GNPs) and BaTiO₃ had a thickness in a few nanometres, with average particle sizes of < 2µm and < 3µm, and densities of 2-2.25 and 6.08g/ml at 250°C, respectively.

3.2.1 Processing of GNPs and Barium titanate(IV) mixture

In a beaker, the solvents chloroform and acetone were mixed in a 2:1 ratio. The beaker was placed on the magnetic stirrer, and equal amounts of GNPs and BaTiO₃ were measured and added. To avoid solvent evaporation, the beaker was securely covered. The beaker was then heated at 50°C for 60 minutes while magnetically stirred to produce a mixture of GNPs and BaTiO₃, after which sonication was performed to obtain a uniform dispersion of the nanomaterial's mixture in the solvent. The combination was then heated until dried out in a vacuum oven for 8 hours at 80°C, as illustrated in Figure 3-1, which highlights the methodology used for remanufacturing of the multifunctional nanocomposites.

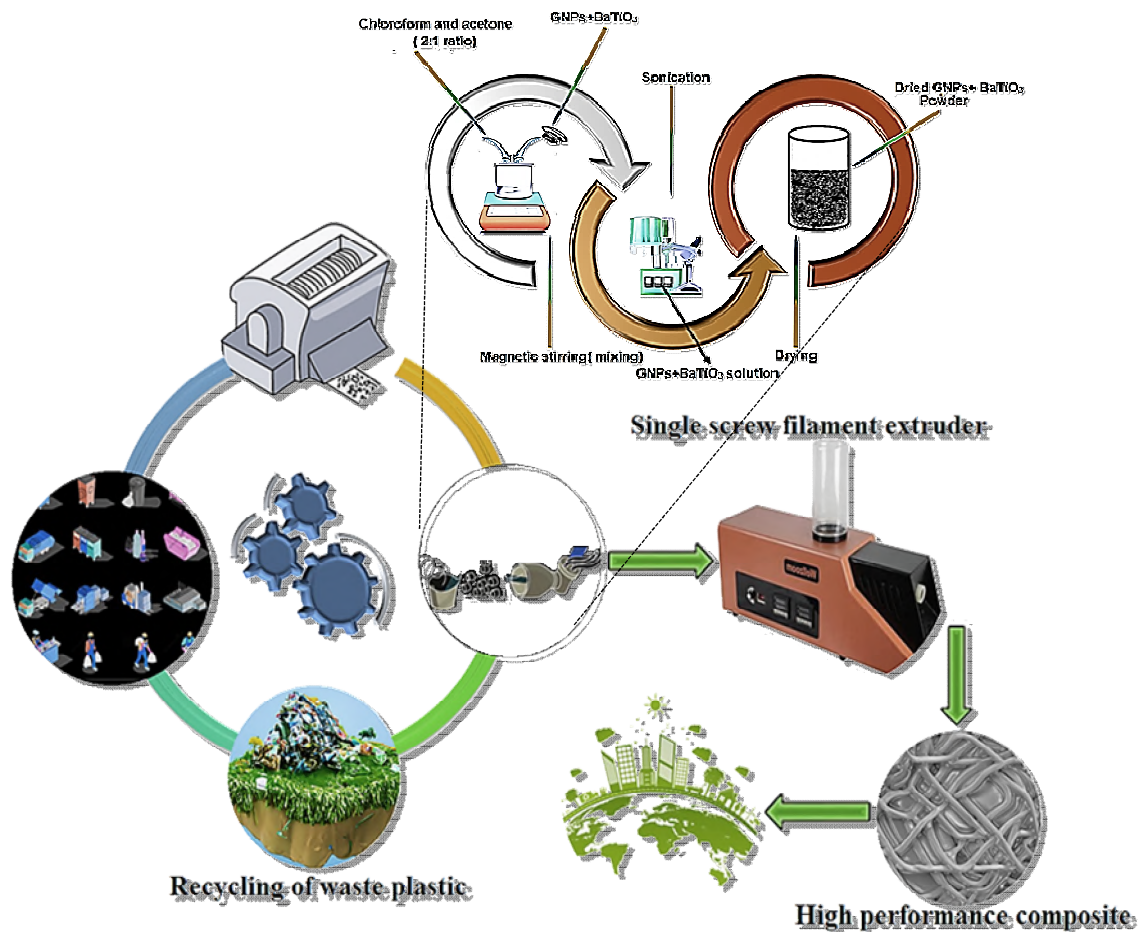


Figure 3-1. Preparation Method of Nanofiller mixture (Proposed preparation methodology for remanufacturing high-performance multifunctional

nanocomposite fibrils out of recycled polymer blends (herein PP/PET) and high-aspect-ratio functional nanosystems (herein GNPs/BaTiO₃)).

3.2.2 Processing of (polypropylene / polyethylene terephthalate) Blends (B)

Before melt mixing, recyclable polypropylene and polyethylene terephthalate were preheated in a vacuum oven for 8 hours at 80°C. Melt mixing was then performed using a single screw Noztek filament extruder at 230°C and 10 rpm to achieve a fixed weight ratio of 85/15. The extruded strands were crystallised using the air chilling process before being hot-pressed at a pressure of 10 MPa at 180°C for 5 minutes, as illustrated in Figure 3-2.

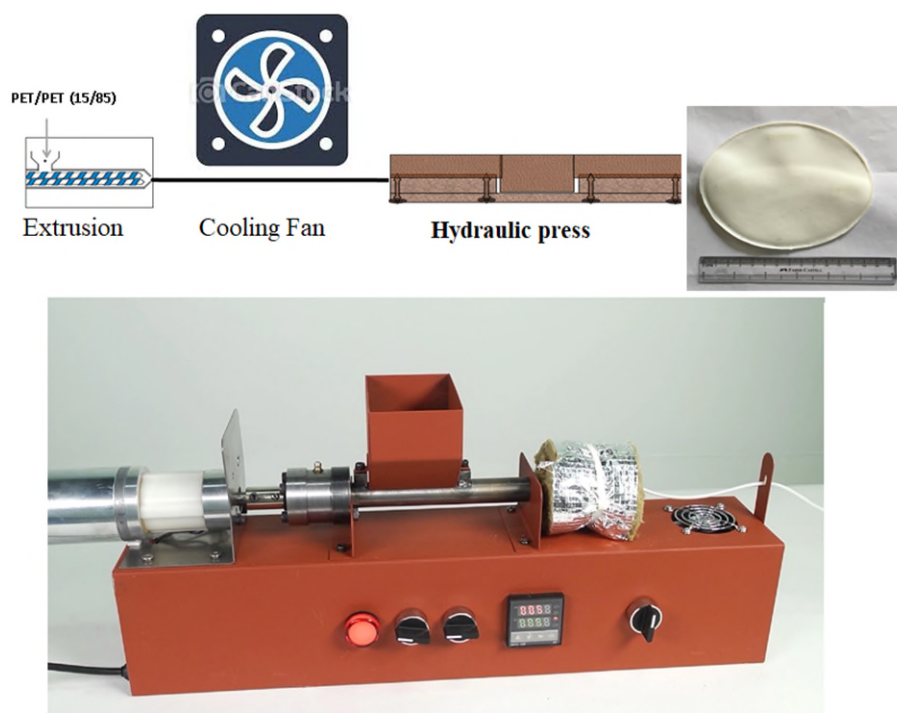


Figure 3-2. The exploratory setup for blends(B).

3.2.3 Preparation of GNPs and Barium titanate(IV) based Nanocomposites (GBNC)

Initially, recycled polypropylene, recycled polyethylene terephthalate, GNPs, and barium titanate(IV) mixes were vacuum-dried for 8 hours at 100°C. Various

recycled polypropylene, recycled polyethylene terephthalate, GNPs, and Barium titanate(IV) mixes were created utilising a single screw Noztek filament extruder. The needed quantities of GNPs and barium titanate(IV) mixes were calculated as phr (parts per hundred matrix) of total fixed polypropylene and polyethylene terephthalate (85/15 ratio). The mixing was done at 230°C and 10 rpm. The air-chilling process was used to crystallise the extruded strands. The crystalline strands were then hot-pressed for 5 minutes at 180°C at a pressure of 10 MPa, as shown in Figure 3-3 and Table 3-1.

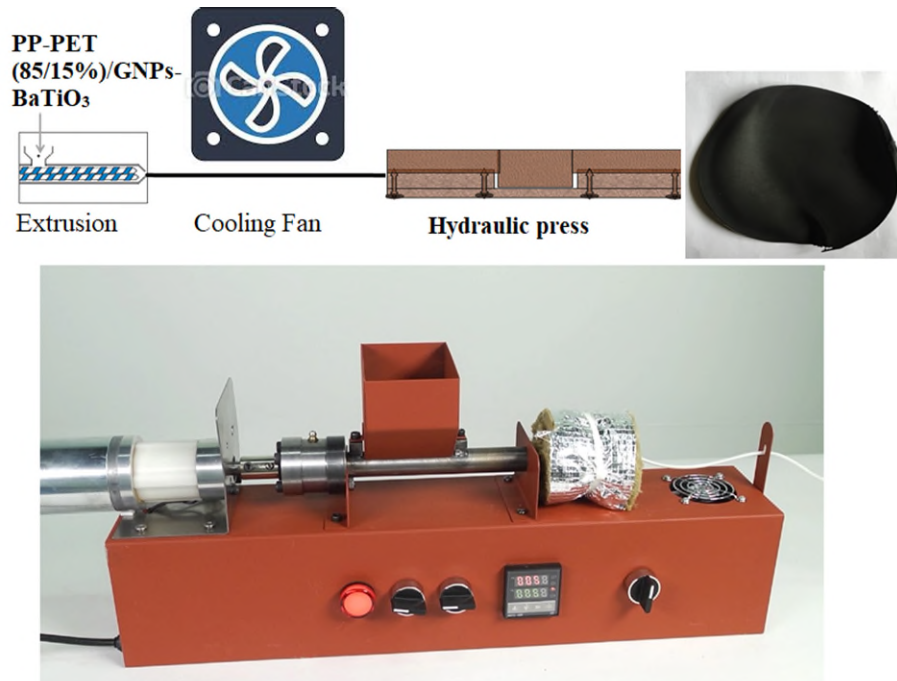


Figure 3-3. Schematic representation of the experimental setup for GNPs and Barium titanate(IV) based nanocomposites (GBNC).

Table 3-1. Formulation of GNPs and Barium titanate(IV) based Nanocomposites (GBNC) and sample designation.

Samples	GNPs(Phr)	BaTiO ₃ (Phr)	Designation
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PP- polyethylene terephthalate (85/15%)	-	-	B
PP- polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	1(phr)		(GBNC1)
PP- polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	2(phr)		(GBNC2)
PP- polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	3(phr)		(GBNC3)

5.2.4 Preparation of in-situ fibrils based composites (FC)

Recycled polypropylene and polyethylene terephthalate in-situ fibrils composites were created using a single-screw Noztek filament extruder and drawing process at an 85/15 fixed weight ratio. Before using the single screw Noztek filament extruder and drawing process, recyclable polypropylene and polyethylene terephthalate were warmed in a vacuum oven for 8 hours at 80°C. Following drying, the recycled polymers were extruded in the form of strands at 230°C at 10 rpm, followed by air cooling and drawing. The drawing was done at several draw ratios, but draw ratio 8 was chosen, as detailed in the next section. The pulled strands were hot-pressed for 5 minutes at 180°C (below the melting point

of polyethylene terephthalate to retain the in-situ polyethylene terephthalate fibrils), as illustrated in Figure 3–4.



Figure 3-4. Morphology of the in-situ fibrils microfibrillar composites.

3.2.5 Preparation of GNPs and Barium titanate(IV) based in-situ fibrils Nanocomposites (GBFNC)

Initially, recycled polypropylene, recycled polyethylene terephthalate, GNPs, and Barium titanate(IV) mixes were vacuum-dried for 8 hours at 100°C. Using the single screw Noztek filament extruder, various compositions of recycled polypropylene, recycled polyethylene terephthalate, GNPs, and Barium titanate(IV) mixes were created. The required GNPs and Barium titanate(IV) mixes were measured as phr of total fixed polypropylene and polyethylene terephthalate (85/15 ratio). The mixing was done at 230°C and 10 rpm. Air cooling crystallised the extruded strands before being drawn at various draw ratios. As demonstrated in Figure 3-5, a draw ratio of 8 was chosen for each sample because it had improved electrical conductivity with an adequate fibrillar zone.

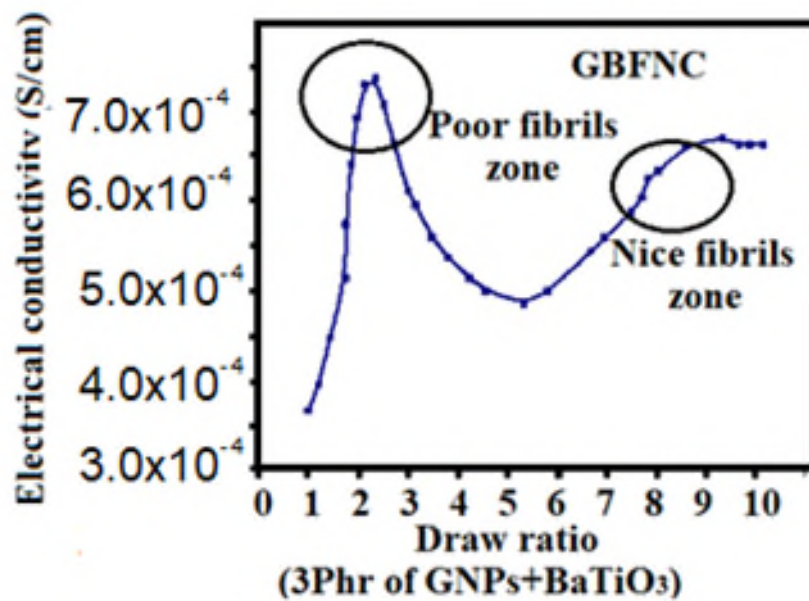


Figure 3-5. The variation of the electrical conductivity of GBFNC with draw ratio (external mechanical stimulation by cold drawing).

The drawn strands were hot-pressed for 5 minutes at 180 °C (below the melting point of polyethylene terephthalate to retain the in-situ polyethylene terephthalate fibrils), as illustrated in Figure 3-6 and Table 3-2.



Figure 3-6. Schematic representation of the experimental setup for GNP and Barium titanate(IV) based in-situ fibril Nanocomposites (GBFNC).

Table 3-2. Formulation of GNP and Barium titanate(IV) based in-situ fibril Nanocomposites (GBFNC) and sample designation.

Samples	GNPs(Phr)	BaTiO ₃ (Phr)	Designation
PP- polyethylene terephthalate (85/15%)	-	-	FC
PP- polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	1(phr)		(GBFNC1)
Polypropylene - polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	2(phr)		(GBFNC2)
Polypropylene - polyethylene terephthalate (85/15%)/GNPs- BaTiO ₃	3(phr)		(GBFNC3)

3.3 Characterisation

3.3.1 Theoretical study of orientation parameter during drawing for in-situ fibrils composites and nanocomposites

The amorphous and crystalline orientation parameters were utilised to estimate the degree of orientation of the amorphous and crystalline components, as well as the formation of fibrils [461,462]. The deformation configuration relevant for

measuring the degree of stiffness and aspect ratio of fibrils during the drawing process is assumed to be the degree of orientation of the polymer's amorphous-crystallite phase. The orientation parameters were measured using the amorphous and crystalline orientation models at a drawing ratio of 8, where A_i = Area of undrawn strands, A_f = Area of drawn strands during drawing, as illustrated in equations (3-1) and (3-2).

Crystalline Orientation parameter,

$$\langle P2 \rangle = \frac{1}{2} \left[\frac{2 \times \left(\frac{A_i}{A_f} \right)^3 + 1}{\left(\frac{A_i}{A_f} \right)^3 - 1} - \left(\left(\frac{3 \times \left(\frac{A_i}{A_f} \right)^3}{\left(\left(\frac{A_i}{A_f} \right)^3 - 1 \right)^{\frac{3}{2}}} \right) \times \arctan \left(\left(\left(\frac{A_i}{A_f} \right)^3 - 1 \right)^{\frac{1}{2}} \right) \right) \right] \quad (3-1)$$

Amorphous Orientation parameter,

$$\langle P2 \rangle = \frac{1}{5N} \times \left(\left(\frac{A_i}{A_f} \right)^2 - \frac{1}{\left(\frac{A_i}{A_f} \right)} \right) \quad (3-2)$$

For all drawn samples, the orientation parameters were computed using a fixed draw ratio of 8. Figure 3-7a-b shows that when the nanofiller concentration increases, the crystallites and amorphous orientation parameters decrease due to the stiffness agglomeration and viscosity induced effects from the nanofillers in the polymer system. The changes in crystallite and amorphous chain orientation parameters are the results of the fillers' impact on the orientation of the polyethylene terephthalate crystallites lamella and amorphous chain when drawing. During drawing, an axial elongational force causes mechanical strain that affects the orientation of the amorphous chain and crystalline lamella, exhibiting a difference in fibril shape in in-situ fibrils composites and in-situ fibrils nanocomposites (GBFNC). The polymer system's variation with nanofiller concentration results in increased stiffness and viscosity. The draw ratio used is insufficient in the presence of nanofillers to distort and orient the amorphous chain and crystalline lamella inside the extruded strands. This is demonstrated by a considerable reduction in the orientation characteristics of amorphous and

crystallite lamella in in-situ fibrils with nanofiller concentration. The semicrystalline polymer is made up of two regions: amorphous and lamellar (crystalline). An axial force is generated in the amorphous zone during the drawing. The shape of tiny fibril coalescence is closely connected to the stress generated in the amorphous area as well as lamella alignment. As the nanofiller concentration increases, the stress decreases in this location, as seen in Figure 3-7c. The nanofillers withstand the axial load at higher capacity due to possessing higher mechanical properties than the polymer, and mitigate the level transmitted to the polymer. The angle of the orientation graph for all samples indicates a rather similar trend. Figure 4-7d shows the angle of orientation of the polymer chain in the drawn state with respect to the undrawn state, and this relationship is approximated using the following equation (3-3) [463,464];

$$\tan\theta = \left(\left(\frac{A_i}{A_f} \right)^{\frac{-3}{2}} \right) \times \tan\theta' \quad (3-3)$$

where θ' is the polymer chain's orientation angle before drawing, θ is the orientation angle after drawing, A_i is the area of undrawn extruded strands, which is simplified to be $(\pi d_i^2)/4$. We assume that all the samples were in the same state before drawing; therefore, we use the same $\tan\theta'$ value for all the samples[465]. The ratios of orientation angles of drawn state to undrawn state ($\tan\theta/\tan\theta'$), were noticeably diversified across the samples. As predicted, the values and curves for the ratio of orientation angles of the drawn state decreased as the nanofillers concentration decreased. The fibril composite (FC) ratio near 0.01 shows the system's maximum orientation. The ratios in the case of GBFNC are between those for the FC and BaTiO₃ (labelled as B). The link between nanofiller concentration and orientation and polymer fibrils may explain this behaviour. As a result, the $\tan\theta/\tan\theta'$ ratio for the undrawn composites BaTiO₃ and GBNC is one. Consequently, our findings confirm the rise in orientation with decreasing nanofiller content. The scanning electron microscopy (SEM) on the extruded blends confirms the decrease in their drawing and chain orientation capabilities when the nanofiller content is reduced (to be elaborated later).

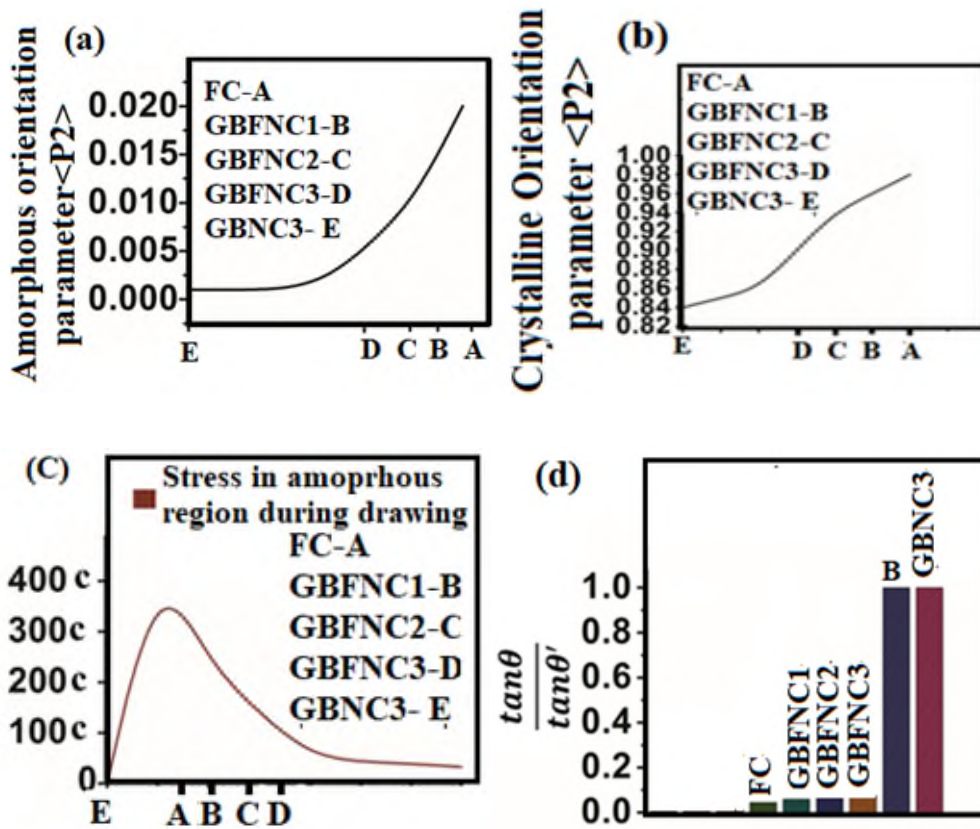


Figure 3-7. Variation of deformation parameters and fibrils morphology during drawing as a function of nanofillers.

3.3.2 Electrical conductivity

A four-point probe method was used to assess the electrical properties [466]. The average electrical resistance (R) of compression-moulded thin sheets (10mm×10mm×0.4mm) was measured using a continuous current source and a voltmeter (Keithley, Ohio, USA). To increase electrical contact in the four-point probe technique, a silver paste was added on the external surface of the composites. All measurements were taken at room temperature, and each composition received an average of five readings [467,468]. The following equations were invoked for the estimation of electrical resistivity and conversion into electrical conductivity, as mentioned in equations (3-4) and (3-5). When t/s is very small ($t \ll s$), with t being the thickness and s the minimum span between the probes.

$$\text{volume resistivity}(\rho) = \frac{(\pi \times t \times R_{\text{average}})}{\ln 2} \quad (3-4)$$

$$t=0.4 \times 10^{-1} \text{cm}, s=2 \times 10^{-1} \text{cm}.$$

ρ = volume resistivity ($\Omega - \text{cm}$), t = the sample thickness(cm),

$$\frac{V}{I} = R = \text{Average Resistance of specimens (ohm)}.$$

s = Spacing between probe (cm)

Finally,

$$\text{Electrical conductivity } (\sigma) = \frac{1}{\text{volume resistivity } (\rho)} \quad (3-5)$$

5.3.3 Trans crystallisation structure by polarised light microscope

A Zeiss polarised light microscope paired with a hot stage arrangement was used to explore the trans-crystallisation [466] of polypropylene around in-situ fibrils. To avoid the melting of polyethylene terephthalate fibrils during the measurements, the GBFNC-containing fibrils were melted on the sample holder at 180°C for 5 minutes to guarantee the homogeneity of the melt. The sample was then cooled at a rate of 10°C/min to various crystallisation temperatures ranging from 180 to 30°C. A stepwise chilling regime was used to determine the best conditions for the trans-crystallisation of polypropylene around polyethylene terephthalate fibrils. While the sample was cooling, the crystallisation was examined with a light microscope [469].

3.3.4 Differential scanning calorimetry

The materials' thermal properties [470] were investigated using DSC (DSC, Q-20, TA Instruments, USA) in nitrogen. The samples were heated from room temperature to 210°C at a rate of 10°C/min and then allowed to cool to room temperature at a rate of 10°C/min. The melting and crystallisation characteristics of the polypropylene in the nanocomposites were observed. T_c corresponds to

the peak crystallisation temperature of the polypropylene, T_m is the melting temperature, and H_f is the heat of the fusion of the polypropylene phase in the sample. To make use of the connection, percentage of the crystallinity of the polypropylene ($\chi\%$) was estimated by equation (3-6),

$$\chi_c = \frac{(\Delta H_f \times 100)}{\Delta H_{fo} \times w} \quad (3-6)$$

ΔH_f is the heat of fusion of the polypropylene phase in the sample. The value of ΔH_{fo} , the heat of fusion of 100% crystalline polypropylene is used as 207 J/g and 'w' is the mass fraction of polypropylene in the blend/composite.

3.3.5 Dynamic mechanical thermal analyser (DMTA)

The examination of viscoelastic properties was conducted with a dynamic mechanical thermal analyser (DMA 800, Perkin Elmer, USA). Rectangular sample specimens of 12.75 mmx7.6mmx0.5 mm were investigated[471]. The investigation was performed in a single cantilever mode at a recurrence of 1Hz, from 0°C to 150°C with a heating rate of 2°C/min [472].

3.3.6 Rheological analysis

Dynamic rheology of polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3 was studied using a Modular Rheometer (MCR102, Anton Paar, USA), utilising a 50 mm parallel plate[473]. Dynamic complex viscosity, storage and loss moduli were examined as an angular frequency extending from 0.1 to 100 rad/s at 215°C and a strain rate of 1% as recommended by [474].

3.3.7 Static mechanical properties

The sample's tensile strength was estimated using a Universal Testing Machine (UTM) (Instron 5900, Instron, USA) at a crosshead speed of 1 mm/min (as per ASTM standard D882). The load cell had a force of 1000 N and a gauge length of 20 mm [475].

3.3.8 Topology by atomic force microscopy

Atomic force microscopy (AFM) was used extensively for characterising the surface morphology of samples. An AFM system (Nano Surf Easy Scan2, Switzerland) was used to measure the surface roughness and surface morphology of samples. For the measurement of surface roughness and topology, fracture surfaces were prepared by sample-tearing after their immersion in liquid nitrogen for 2 hours [476].

3.3.9 Morphological analysis

The morphological investigation was carried out with the aid of a JEOL JSM 6390 scanning electron microscopy. The samples were photographed at a 20 kV acceleration voltage. In the instance of cross-sectional microstructure analysis, fracture surfaces were prepared by cryo-fracturing for 2 hours in liquid nitrogen. Prior to SEM, all sample surfaces were coated with a thin layer of gold to make them conductive [477].

3.3.10 Electromagnetic interference shielding by vector network analyser

EMI shielding is defined as the ability of a material to attenuate an EM signal [478]. It is measured in dB and is the ratio of incident electromagnetic field strength and the transmitted electromagnetic field strength. Here, the effect of morphology and nanofillers on the EMI shielding efficacy has been studied. EMI Shielding effectiveness was measured by using a Vector Network Analyzer (operating at 2.8GHz) for a sample size of 10mmx7mmx1mm [272].

3.3.11 Thermal conductivity by transient plane source (TPS) method

To determine the thermal conductivity of polymers and polymer nanocomposites, researchers frequently rely on the transient plane source (TPS) technique [479]. This approach involves the use of a compact, thin, and flat sensor that applies a continuous heat flow to the surface of the sample. On the opposite side of the sample, a thermocouple is employed to monitor the temperature increase, allowing for the determination of the sample's thermal conductivity based on the time it takes to reach a steady state. To perform the TPS measurement, a small portion of the sample material is typically crushed into a thin disc or pellet shape

with a diameter of approximately 10 mm and a thickness of around 0.5 mm. The sample is then placed between the two parts of the TPS sensor, sandwiched in place. Once the sample is secured in the TPS sensor, the system is attached to a computer-controlled data acquisition system. This system provides a steady heat flux to the sample surface and records the temperature rise over time on the opposite side of the sample. Using equation (3-7), the thermal conductivity of the sample can be estimated [479].

$$k = \frac{Q \times t}{[4\pi A(T_2 - T_1)]} \quad (3-7)$$

where k is the thermal conductivity of the sample, Q is the heat flux applied to the sensor, t is the time it takes for the temperature to reach a steady state, A is the area of the sensor, and T_1 and T_2 are the initial and steady-state temperatures recorded by the thermocouple.

3.4 Results and discussion

3.4.1. Electrical conductivity

Figure 3-8(a) depicts the DC electrical conductivity values of PP/PET blend (B) and PP/PET in-situ fibril composites (FC). Both PP and PET blend(B) and PP/PET in-situ fibril composites (FC) are insulating in nature. In this case, the conductivity enhancement due to the inclusion of PET fibres may not be significant, as shown in the figure. However, without additional PET fibrils (e.g., spherical morphology of PET), the electrical conductivity is lower. It is observed that the conductivity increases when fibril morphology is introduced into the system. Figure 3-8(b) depicts the DC electrical conductivity values of GBFNC measured by the 4-probe technique and plotted as a function of GNPs+ BaTiO₃ content (e.g., 1, 2, 3 phr). The conductivity of samples was augmented by increasing the GNPs+ BaTiO₃ content. A noteworthy improvement in electrical conductivity has been observed with 3 phr of GNPs+ BaTiO₃ confirming that such composition promotes the development of a significantly increasing electrically

conducting network in in-situ nanocomposites (GBFNC). Figure 3-8(c) shows the DC electrical conductivity for the GBFNC and GBNC. It has been found that the DC conductivity of GBFNC and GBNC is dissimilar for the same content of GNPs+ BaTiO₃ with GBFNC exhibiting a higher DC conductivity than that of the GBNC, by a minimum order of two. This evidences that nanocomposites of GNPs+ BaTiO₃ in tandem with in-situ fibrils provide a substantially higher electrically conducting network than the GNPs+ BaTiO₃ based nanocomposites alone. This effect owes to the introduced alignment of the GNPs+ BaTiO₃ inter-particle separation in the in-situ fibrils-based nanocomposites. Therefore, it can be established that the morphology of the polyethylene terephthalate phase also affects the conductivity of nanocomposites. In this research, we found that the morphology of the fibrils plays a significant role in enhancing conductivity. The fibrils exhibit a unique structure that facilitates a tunneling mechanism and creates a current flow path, effectively reducing the spacing distance between fillers. This arrangement leads to a notable enhancement in conductivity. Furthermore, it is important to consider the type of filler used, as it can also impact the conductivity of the fibrils. For instance, carbon black, being a more conductive filler, tends to contribute to higher conductivity compared to graphene platelets. Additionally, the concentration of the filler is another factor influencing the conductivity of the fibrils. Typically, as the concentration of the filler increases, the conductivity of the fibrils shows a corresponding increase. Lastly, the morphology of the system itself can impact the conductivity of the fibrils. For instance, spherical fillers generally exhibit lower conductivity when compared to flake-shaped fillers. These considerations highlight the multifaceted nature of conductivity in fibril-based composites.

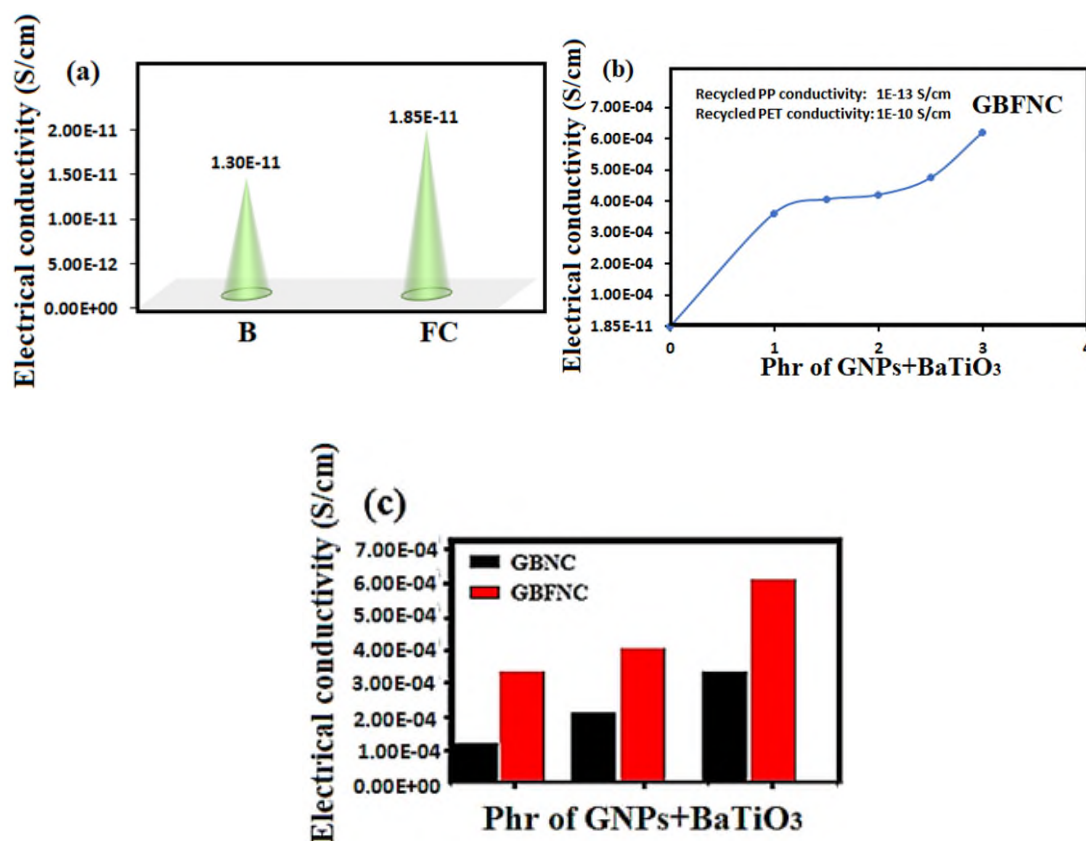


Figure 3-8. (a) Variation of electrical conductivity of PP/PET blend (B) and PP/PET in-situ fibrils composites (FC), (b) Variation of electrical conductivity of in-situ fibrils nanocomposites with varying the phr of GNPs+BaTiO₃, (c) Variation of electrical conductivity of GNPs+BaTiO₃ nanocomposites and in-situ fibrils nanocomposites with varying the phr of GNPs+BaTiO₃.

3.4.2 Trans crystallisation structure by polarised light microscope

The formation of a transcrystalline layer around the in-situ polyethylene terephthalate (PET) fibrils is visualised in Figure 8. Figures 3-9(a-d) show the crystal morphology of B, GBNC1, and GBFNC1, where a series of microstructures of the polypropylene (PP) matrix have been formed for different samples at different temperatures. Figure 3-9(a), depicting the crystal morphology of B, shows circular-shaped crystallisation patterns, known as spherulites, in a neat PP/PET blend. These spherulites are formed by the crystallisation of PP in concentric rings that grow radially. Spherulites are formed

by heterogeneous nucleation and favor the increased crystallinity of the PP matrix. Figure 3-9(b) shows the crystallisation microphotographs of GBNC1 at 30°C. Compared to the neat PP/PET blend, the spherulites in GBNC1 are smaller in size. In contrast, Figures 3-9(c-d) show the trans-crystallisation of the PP matrix in GBFNC1 at different temperatures. This is due to the presence of PET-graphene nanoplatelets-barium titanate (GNPs- BaTiO₃) fibrils, which promote the trans-crystalline evolution of PP. In a transcrystalline structure, PP crystals are arranged transversely with respect to the PET-GNPs- BaTiO₃ fibril axis (i.e., backbone). The closer proximity of the fibres in GBFNC1 hinders the growth of spherulites at the surface of the PET-GNPs- BaTiO₃ fibrils. Overall, the results of this study suggest that the presence of GNPs- BaTiO₃ fibrils can promote the trans-crystalline evolution of the PP matrix and lead to smaller spherulites. This has important implications for the design of high-performance polymer composites made by such blends, with improved crystallisation behaviour, thus improved mechanical properties.

The observed phenomena can be attributed to several factors. Firstly, the incorporation of GNPs- BaTiO₃ fibrils into the PP/PET blend provides heterogeneous nucleation sites for PP crystallisation. Compared to the neat PP/PET blend, the presence of these fibrils promotes the formation of PP crystals in a trans-crystalline manner rather than the typical spherulitic manner. This trans-crystalline structure offers distinct advantages in terms of mechanical properties and overall performance. Secondly, the closer proximity of the fibres in the GBFNC1 sample hampers the growth of spherulites on the surface of the PET-GNPs- BaTiO₃ fibrils. The fibres act as a physical barrier that impedes the diffusion of PP molecules, which is necessary for the growth of spherulites. As a result, the formation of spherulites is limited, and the crystalline structure becomes more oriented along the fibrils. Lastly, the trans-crystalline structure of the PP matrix in GBFNC1 exhibits enhanced resistance to deformation compared to the spherulitic structure observed in the B and GBNC1 samples. The interconnected nature of the trans-crystalline structure makes it more difficult to break, leading to improved mechanical properties and a higher degree of deformation resistance. Hence, the presence of GNPs- BaTiO₃ fibrils in the

PP/PET blend promotes trans-crystalline formation, restricts spherulite growth, and enhances the resistance to deformation. These factors contribute to the improved properties observed in the GBFNC1 sample compared to the other samples (B and GBNC1).

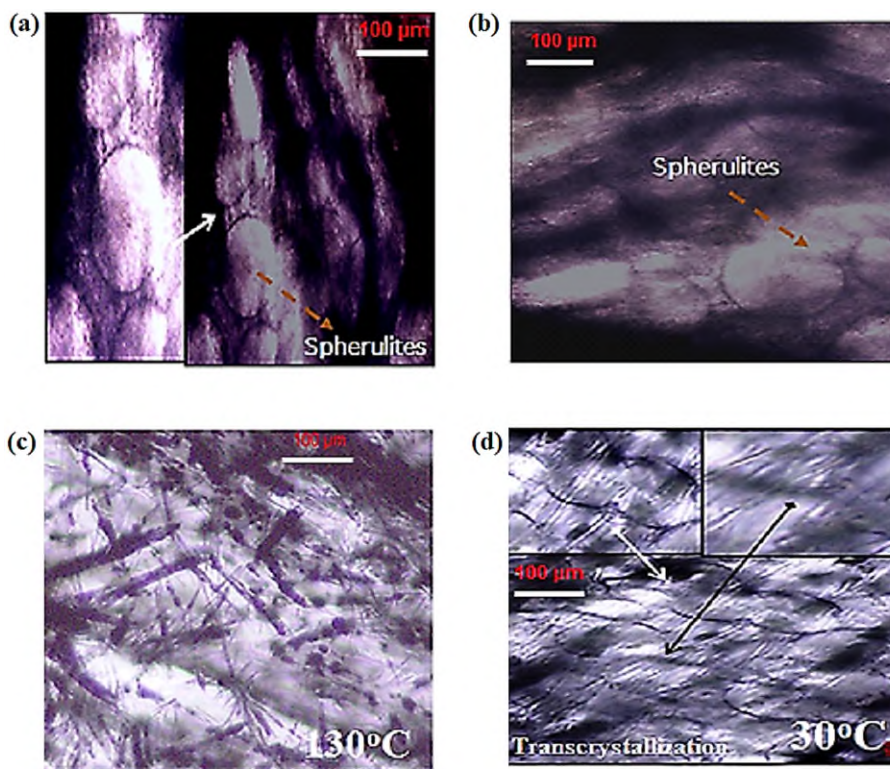


Figure 3-9. Polarised optical microscopy (POM) microstructure of (a) PP/PET Blend (B) at 30°C as in form of spherulites (Spherical ring), (b) PP/PET-GNP- BaTiO₃ nanocomposites (GBNC1) at 30°C as in form of spherulites (Spherical ring), (c) PP/PET-GNP- BaTiO₃ fibrils nanocomposites (GBFNC1) at 130°C as in form of transcrystalline growth, (d) GBFNC1 at 30 °C as in form of trans-crystalline growth.

3.4.3 Differential scanning calorimetry

Our study included polypropylene (P), an extruded blend of PP/PET (85/15) referred to as B, a composite comprising of a polypropylene matrix and PET fiber (85/15) referred to as FC, and several extruded blend nanocomposites and extruded nanocomposites consisting of a polypropylene matrix, PET fiber, and GNPs- BaTiO₃ at different concentrations. We determined the peak crystallisation

temperature (T_c), melting temperature (T_m), and the heat of fusion (ΔH_f), of the polypropylene phase in the samples using DSC. We also calculated the crystallinity (X_c) of the materials using equation 3-6. Figures 3-10a and 3-10b depict the melting and crystallisation behaviour of polypropylene in the polypropylene-polyethylene-terephthalate blend (B), FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3 groups observed by DSC. The inclusion of polyethylene terephthalate increased the crystallisation temperature of polypropylene significantly. The crystallisation temperature (T_c) of plain polypropylene was 116°C, whereas the polypropylene component crystallised at 120°C in sample B. Because of the existence of long polyethylene terephthalate fibrils functioning as nuclei for polypropylene crystallisation, the crystallisation temperature of polypropylene was determined to be 124°C for FC[480]. Along with polyethylene terephthalate fibrils, GNPs- BaTiO₃ present in the sample also contributed as nucleating agents in the GBFNC1, GBFNC2 and GBFNC3. Therefore, crystallisation of polypropylene shifted towards the higher temperature than those of GBNC1 and GBNC2. The percentage crystallinity ($\chi\%$) of the FC is significantly higher than the polypropylene and B, and the percentage crystallinity ($\chi\%$) of the GBFNC1, GBFNC2 and GBFNC3 are higher than GBNC1 and GBNC2. The long and slender polyethylene terephthalate (PET) fibrils in FC and PET-GNPs- BaTiO₃ fibrils in GBFNC1, GBFNC2, and GBFNC3 act as a region for the trans crystallisation of polypropylene. The trans-crystalline layer generated around the fibrils can produce a strong fiber/matrix contact, leading to improved mechanical properties of the resulting nanocomposites. This is because the trans-crystalline structure provides a mechanism for load transfer between the matrix and the reinforcing fibres, which results in an enhanced stiffness and strength. The fascinating observation is that the T_c end set is the highest for GBFNC3. This ascertains that the crystallisation process of polypropylene surrounding the polyethylene terephthalate -GNPs- BaTiO₃ fibrils in GBFNC1, GBFNC2 and GBFNC3 is prolonged in comparison with B, FC, GBNC1, GBNC2. As a result, it may be deduced that the morphology and orientation of the dispersed component polyethylene terephthalate-GNPs- BaTiO₃ fibrils can tremendously alter the crystallinity of the polypropylene. The values of melting

temperature (T_m), crystallisation temperature (T_c) and % of crystallinity ($\chi\%$) have been tabulated in Table 3-3. Our research has revealed that the T_m and T_c values of materials can vary depending on the composition and concentration of GNPs- BaTiO₃. The extruded nanocomposites containing GNPs- BaTiO₃ at maximum concentration (GBFNC3) displayed the highest T_m and T_c values, with T_m and T_c values of 178°C and 127°C, respectively. Our findings suggest that adding fibrils and GNPs- BaTiO₃ to polypropylene/PET blends and composites can significantly improve crystallinity, with greater effects at higher GNPs- BaTiO₃ concentrations. When GNPs- BaTiO₃ is introduced to polypropylene-based materials, the percentage crystallinity and heat of fusion increase, as do the melting and crystallisation temperatures. This implies that GNPs- BaTiO₃ can act as nucleating agents in the materials, promoting crystallisation and enhancing the degree of crystallinity. The degree of crystallinity (χ_c) values for various samples are presented in Table 3-3, which includes Polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3. DSC measurements were used to calculate the degree of crystallinity, following the procedure outlined in the previous section. The crystallinity value for polypropylene was found to be 38.0%, while GBFNC3 had a crystallinity value of 56.5%. GBFNC3 showed the highest degree of crystallinity among the samples, while polypropylene exhibited the least. The variations in crystallinity values among the samples can be attributed to differences in molecular structure and processing conditions. These values are valuable for understanding the crystallisation behaviour of the materials and can be utilised for studying crystallisation kinetics. Additionally, this method can provide additional insights into the crystallisation process by estimating rate constant k' , time of nucleation (t_0), and Avrami exponent or index (n) values for each sample. Overall, our findings suggest that the addition of GNPs- BaTiO₃ to polypropylene-based materials can significantly enhance the degree of crystallinity, with the highest crystallinity values observed at higher GNPs- BaTiO₃ concentrations. The concentration of GNPs- BaTiO₃ and fibrils morphology has two effects on the percentage crystallinity of blend components. Firstly, BaTiO₃ acts as a nucleating agent, promoting crystal formation and increasing the crystallinity percentage. Secondly, BaTiO₃ acts as a filler, occupying space in the

polymer matrix and hindering crystal growth, also leading to a higher percentage of crystallinity in the blend components. These results offer valuable insights into the properties of nanocomposites and may have implications for the development of new materials with enhanced properties.

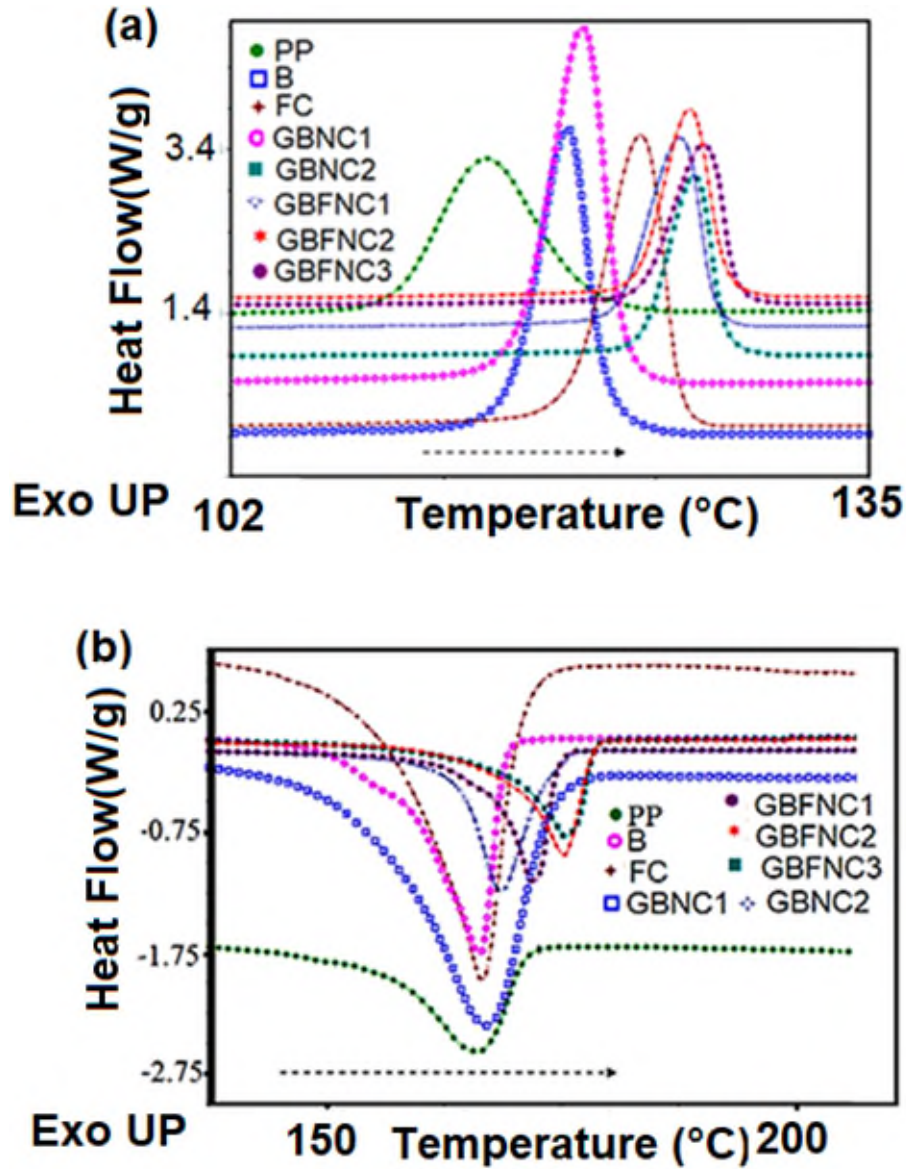


Figure 3-10. (a)Crystallisation, (b) melting behaviour of polypropylene (PP) in B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3(Exo up tends to exothermic process).

The degree of crystallinity, represented by χ_c , is an important parameter for understanding the crystallisation behaviour of materials. It provides information

on the amount of crystallised material at a given time. To determine χ_c , DSC information is collected by heating or cooling the sample at a controlled rate while measuring temperature changes or heat flow. The onset temperature of crystallisation is then determined from the DSC curve, which shows a distinct exothermic peak indicating the onset of crystallisation. Nonlinear regression analysis is used to fit the curve and obtain values for k' , t_0 , and n . These values can then be used to calculate the crystallisation activation energy. The Avrami equation can be used to approximate the kinetics of the crystallisation process based on the DSC data, given by equation 3-8 [481][62]:

$$(X_c) = 1 - \exp[-k'(t - t_0)^n] \quad (3-8)$$

Using the Avrami equation in MATLAB, one can perform nonlinear regression analysis on experimental data and determine the crystal growth dimension and rate of crystal growth. Figure 3-11 displays the n values for various samples, including polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3. The corresponding values of n for each sample are shown in Table 3-3. The results indicate that n varies across, with polypropylene exhibiting the highest value of 3.3, followed by B with 3.1 and FC with 2.9. The other samples have lower Avrami indices, with GBFNC3 having the lowest value of 2.4. The n is a measure of the type and shape of crystal growth. The value of n smaller than 3 denotes spherulite growth, while a value of 3 indicates lamellar or fibrillar growth. The results reveal that polypropylene, B, and GBNC1 primarily exhibit nodular growth, whereas the other samples display lamellar or fibrous growths. This outcome suggests that the material composition and processing conditions can influence the type and shape of crystal growth. Thus, the crystalline growth of polypropylene, B, and GBNC1 is mainly 3D, whereas GBFNC3 corresponds to more aligned form. This demonstrates the evolution of the transcrystalline structure, as evidenced by the previous section. The rate constant (k') is a crucial parameter that relates the rate of a chemical reaction to the concentrations of reactants. In the context of crystallisation, k' signifies the rate at which a supersaturated solution transforms into a crystalline solid. The higher the

temperature, the higher the rate of molecular motion, faster nucleation and crystal growth, and thus higher k' values. k' values for various polypropylene samples range from 0.015 to 0.040 min⁻¹, as shown in Figure 3-12 and Table 3-3.

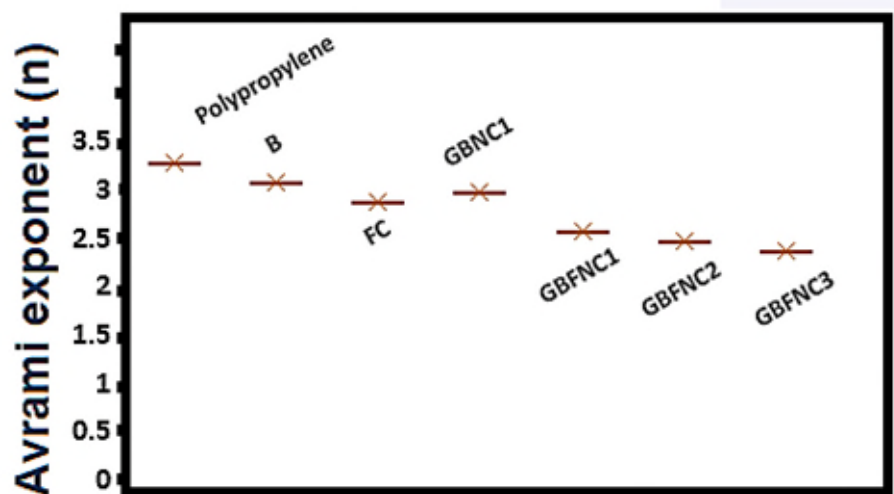


Figure 3-11. Avrami exponent (n) for polypropylene, B, FC, GBNC1, GBFNC1, GBFNC2, and GBFNC3.

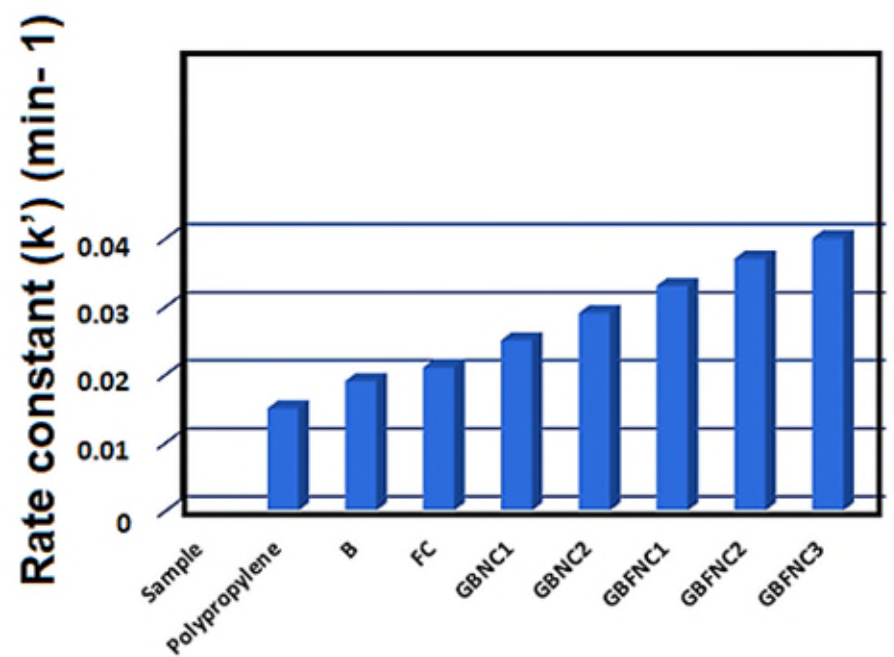


Figure 3-12. Rate constant (k') for polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3.

The higher the k' value, the faster the material crystallises. The fastest crystallising sample, GBFNC3, has a k' value of 0.040 min⁻¹, indicating that a high degree of crystallinity can be reached in a short time. This can be a good candidate for applications that require fast turnaround times. The slowest crystallising sample, polypropylene, had a k' value of 0.015 min⁻¹, indicating that longer processing times may be required to achieve the desired level of crystallinity. However, polypropylene is still widely used due to its excellent combination of mechanical, thermal, and chemical properties. The k' values of other samples range between 0.019 to 0.040 min⁻¹ (Table 3-3). The addition of GNPs, BaTiO₃, and fibrous morphology have a significant effect on increasing the crystallisation rate constant (k'), as well as increasing the surface area of the material and providing more sites for nucleation, producing more seed crystals that can grow rapidly into larger crystals. BaTiO₃ and fibrils act as effective nucleating agents, promoting crystal nucleation and enhancing the crystal growth rate. Furthermore, GNPs improve the thermal conductivity of the composites, allowing faster heat transfer during crystallisation and more efficient cooling, which may also contribute to the overall increase in crystallisation.

Table 3-3. Melting, crystallisation temperature, percentage crystallinity ($\chi\%$), ΔH_f , degrees of crystallinity (X_c), rate constant (k'), and n (Note: $T_m(o_c)$, $T_c(o_c)$, ΔH_f (J/g), k' (min⁻¹)).

Sample	T_m	T_c	$\chi\%$	ΔH_f	X_c	k'	n
Polypropylene	165	116	38	78.66	38.0	0.015	3.3
B	166	120	41	100.1	40.4	0.019	3.1

FC	167	124	44.5	108.3	43.4	0.021	2.9
GBNC1	167.5	121	50.6	122.6	48.2	0.025	3.0
GBNC2	169	125	53.5	129.9	51.3	0.029	-
GBFNC1	172	125.53	55.2	133.9	52.2	0.033	2.6
GBFNC2	175	126	57.4	139.4	54.6	0.037	2.5
GBFNC3	178	127	59.2	78.66	56.5	0.040	3.3

3.4.4 Dynamic mechanical thermal analyser (DMTA)

The storage moduli (E') of polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3 are shown in Figure 3-13a. The storage modulus shows the stiffness behaviour of the prepared materials. It was observed that the addition of GNPs- BaTiO₃ and polyethylene terephthalate fibrils improved the storage modulus of FC, GBNC1, GBNC2, GBNC3, GBFNC1, GBFNC2 and GBFNC3 compared to neat polypropylene and B. The results also describe the effect of the addition of GNPs- BaTiO₃ and polyethylene terephthalate (PET) fibrils on the mechanical properties of various composites (FC, GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3) at elevated temperatures. It suggests that the addition of these materials increases the stiffness and elasticity of the composites, and that the fibril morphology of PET has a stronger reinforcing effect than the spherical morphology of PET. The effect of the fibrils is observed at both lower and higher temperatures. However, as the temperature increases above 80°C, the influence of the fibrils on the storage modulus decreases, causing a decrease in the storage modulus. The decrease in storage modulus observed above 80°C in the study is likely due to the glass transition temperature (T_g) of PET, which is typically in the range of 70-80 °C. Above this temperature, the PET

chains become more mobile, leading to a decrease in the stiffness and reinforcement provided by the fibrils. The storage modulus of GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3 is still greater than polypropylene, B, FC above the 80 °C threshold. The loss modulus (E'') is a measure of the energy dissipated during sinusoidal strain, and it helps to quantify the viscous properties of the sample, as shown in Figure 3-13b. As the temperature increases, the loss modulus of all the systems studied in the research increases before reaching a maximum and then dropping again. The higher content of GNPs- BaTiO₃ and the specific fibril morphology present in the samples lead to a higher loss modulus, indicating a higher energy dissipation and more viscous behaviour. This can be attributed to the hindering of the chain mobility of polymer molecules above the glass transition temperature of polypropylene by the GNPs- BaTiO₃ and fibrils morphology, which increases energy dissipation due to frictional behaviour and increases viscous behaviour. The highest loss modulus was observed for GBFNC3, which had the highest content of GNPs- BaTiO₃ and the specific fibril morphology. The specific combination of high GNPs- BaTiO₃ content and fibril morphology in GBFNC3 resulted in the highest loss modulus, indicating higher energy dissipation at elevated temperatures. This is due to the GNPs- BaTiO₃ and fibrils hindering the chain mobility of polypropylene above its glass transition temperature, which increases frictional behaviour and energy dissipation at the interface.

To understand the influence of confinement on the mechanical properties of these nanocomposites, the experimental data of Dynamic Mechanical Analysis (DMA) was employed to measure the storage modulus (E') and loss modulus (E'') at different temperatures. The confinement factor was then calculated using the equation: $\text{Confinement} = (E' - E'') / E'$. The confinement of polymer chains on the filler surface is affected by a number of factors, including the type of polymer, the type of filler and reinforcement, the filler and reinforcement content, and the temperature[482]. In general, the confinement of polymer chains increases with increasing the filler and reinforcement content and decreasing temperature[483]. The confinement of polymer chains on the filler surface has a significant impact on the mechanical properties of nanocomposite materials[484]. For example,

nanocomposite materials with high confinement of polymer chains typically have higher storage moduli and higher loss moduli[485]. This is because the confined polymer chains are less mobile and more likely to undergo viscous flow[486]. The confinement of polymer chains on the filler surface is also an important factor in the thermal, mechanical, electrical properties of nanocomposite materials. For example, nanocomposite materials with high confinement of polymer chains typically have higher thermal conductivities, higher mechanical and higher dielectric constants. A higher confinement of polymer chains leads to a higher storage modulus and a higher loss modulus [486]. Table 3-4 shows the confinement factors of polymer chains on the filler surface in different samples and temperatures. The confinement factors of the polymer chains were determined using dynamic mechanical analysis (DMA). The DMA results showed that the confinement factors of the polymer chains decreased with increasing temperature. This is because the polymer chains become more mobile at higher temperatures, and they are less likely to be confined to the space between the filler particles. The confinement factors of the polymer chains also varied depending on the type of filler. The confinement factors were highest for the nanocomposites that contained GNPs- BaTiO₃. This is because GNPs and BaTiO₃ have a high surface area, which provides more opportunities for the polymer chains to interact with the filler surface. The results of this study highlight the significant influence of polymer chain confinement on the filler surface in nanocomposites. Understanding and optimising the confinement of polymer chains can help tailoring the mechanical properties and performance of nanocomposite materials for various applications.

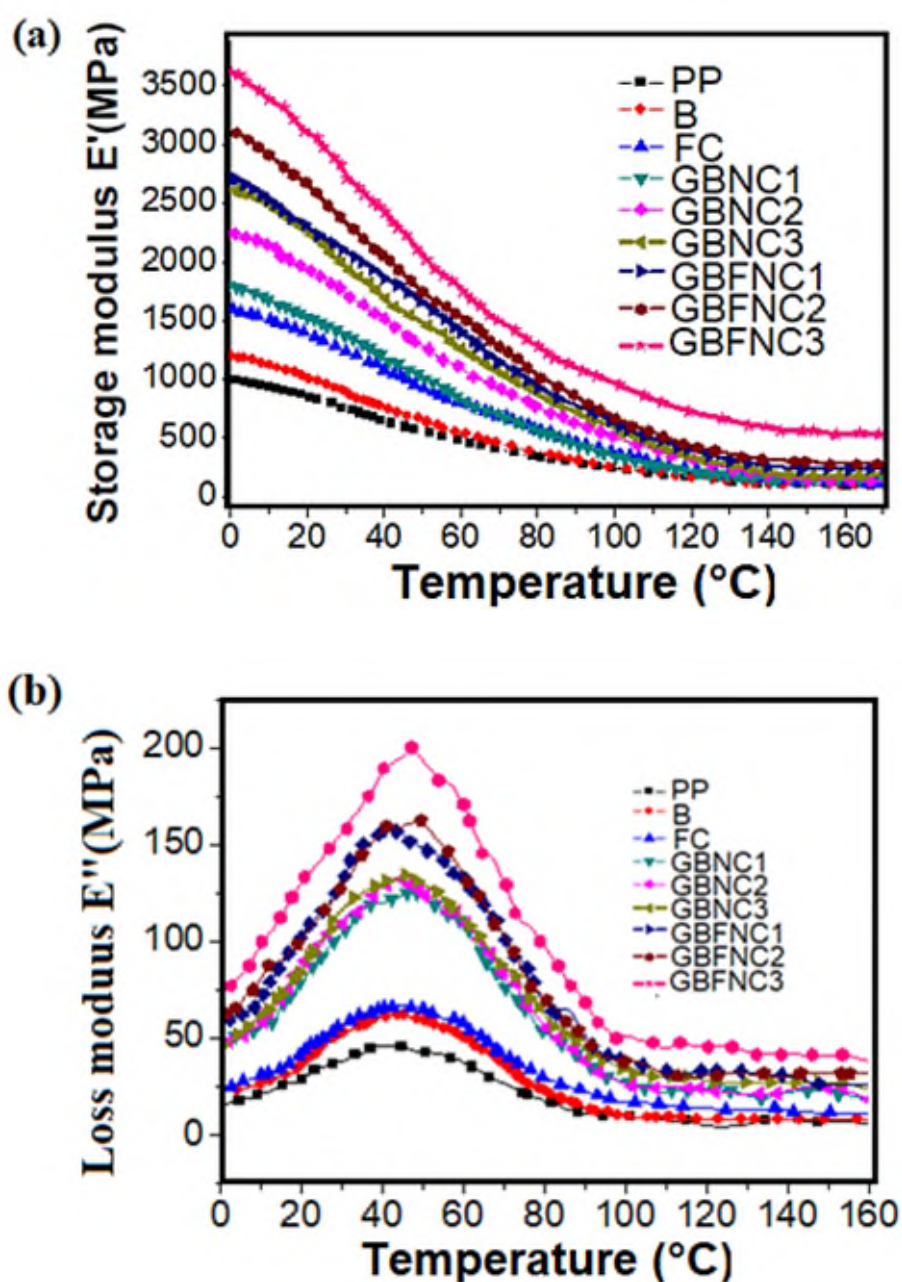


Figure 3-13. Variation of (a) storage modulus, b) Loss modulus of GNP/BaTiO₃ nanocomposites and in-situ GNP/BaTiO₃ polyethylene terephthalate (PET) fibrils nanocomposites with varying the phr of GNP/BaTiO₃.

Table 3-4. A comparison table summarising the confinement of polymer chains on the filler surface for the different samples.

Sample	Confinement Factor at 0°C	Confinement Factor at 50°C	Confinement Factor at 90°C	Significance of Fibrils Morphology and GNPs- BaTiO₃
B	0.9792	0.9087	0.9294	-
FC	0.9798	0.9111	0.9333	
GBNC3	0.9815	0.9167	0.9400	The presence of GNPs- BaTiO ₃ within the polypropylene matrix contributes to the confinement of polymer chains.
GBFNC3	0.9818	0.9280	0.9536	The combination of GNPs- BaTiO ₃ and polyethylene terephthalate fibrils enhances the confinement of polymer chains on the filler surface.

To investigate the reinforcing effect of fillers and fibril shape within the polypropylene matrix, the two-population method was used. This method analyses the mechanical properties of composites with two distinct populations of particles or fibres, each with its own properties, and calculates the overall properties of the composite based on the properties of each population and their concentration[487]. According to this model, the individual reinforcing effects of GNPs- BaTiO₃ as well as polyethylene terephthalate fibrils on the elastic performance of the composite can be studied. This additive approach helps determine the reinforcing effect and the morphological effect of GNPs- BaTiO₃ within the polypropylene matrix. The effect of GNPs- BaTiO₃ was estimated by using the GBNC experiment for conductive ternary blends nanocomposites (CNBC), as mentioned in from equations 3-9 to 3-12, as follows:

$$\frac{E_{GBNC}^{add}}{E_{PP}} = \frac{E_{GNPs-BaTiO3}}{E_{PP}} + \frac{E_{PP/PET(B)}}{E_{PP}} - 1 \quad (3-9)$$

$$\frac{E_{GBNC}^{add}}{E_{PP}} + 1 = \frac{E_{GNPs-BaTiO3}}{E_{PP}} + \frac{E_{PP/PET(B)}}{E_{PP}} \quad (3-10)$$

$$E_{GBNC}^{add} + E_{PP} = E_{GNPs-BaTiO3} + E_{PP/PET(B)} \quad (3-11)$$

$$E_{GBNC}^{add} + E_{PP} - E_{PP/PET(NB)} = E_{PP/GNPs-BaTiO3(GBNC)}$$

For in-situ fibrils nanocomposites (GBFNC):

$$\frac{E_{GBFNC}^{add}}{E_{PP}} = \frac{E_{GNPs-BaTiO3}}{E_{PP}} + \frac{E_{FC}}{E_{PP}} - 1 \quad (3-12)$$

$$E_{GBFNC}^{add} + E_{PP} - E_{FC} = E_{PP/GNPs-BaTiO3(GBFNC)}$$

The reinforcing effect of GNPs- BaTiO₃ and polyethylene terephthalate fibrils within the polypropylene matrix was predicted by an additive approach from

experimental DMTA data. The additive approach model considered the response of composites constituting an assortment of reinforcing materials within the matrix. In this way, based on the additive approach, this research measured the effect of morphology and concentration of the GNPs- BaTiO₃ on the effective storage modulus of the polypropylene matrix. As shown in Figure 3-14, the $E_{PP/GNPs-BaTiO_3(GBNC1)}$, $E_{PP/GNPs-BaTiO_3(GBNC2)}$, $E_{PP/GNPs-BaTiO_3(GBNC3)}$, $E_{PP/GNPs-BaTiO_3(GBFNC1)}$, $E_{PP/GNPs-BaTiO_3(GBFNC2)}$, $E_{PP/GNPs-BaTiO_3(GBFNC3)}$ are the theoretical values obtained by using the model. The theoretical storage modulus value of $E_{PP/GNPs-BaTiO_3(GBNC)}$ showed the reinforcement effect of GNPs- BaTiO₃ within the polypropylene matrix in the entire temperature range.

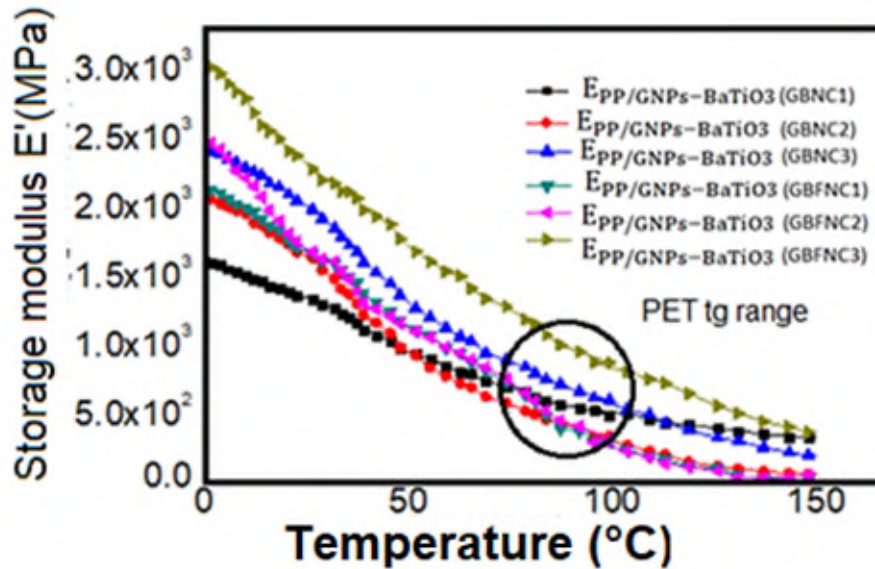


Figure 3-14. Analysis of storage modulus of GNPs+BaTiO₃ nanocomposites and in-situ GNPs+BaTiO₃ polyethylene terephthalate (PET) fibrils nanocomposites with varying the phr of GNPs+BaTiO₃ through two population approach.

A coupled influence of GNPs- BaTiO₃ and polyethylene terephthalate -GNPs- BaTiO₃ fibrils was observed on the storage modulus of polypropylene. It was also found that the GNPs- BaTiO₃ had substantial reinforcement effect in the polypropylene matrix at lower as well higher temperatures. The stiffness effect of polyethylene terephthalate-GNPs- BaTiO₃ fibrils and GNPs- BaTiO₃ was found to

be dominant in the case of the polyethylene terephthalate-GNPs- BaTiO₃ fibrils, which improved the storage modules. The GNPs- BaTiO₃, on account of its high aspect ratio, stiffness, and thermal stability, is a more favourable reinforcing agent at lower and higher temperatures. Furthermore, polyethylene terephthalate fibrils have a positive reinforcing effect along with GNPs- BaTiO₃. Henceforth, it could be concluded that polyethylene terephthalate fibrils combined with GNPs- BaTiO₃ in-situ nanocomposites (GBFNC) can induce a stronger reinforcing effect than merely GNPs- BaTiO₃ nanocomposites (GBNC).

3.4.5 Thermal conductivity

Figure 3-15 illustrates thermal conductivity values for various materials. Polypropylene exhibits the lowest thermal conductivity at 0.218 W/m.K, while GBFNC3 has the highest value at 1.34 W/m.K, indicating superior heat transfer efficiency, six times that of polypropylene, making it a more efficient conductor of heat. This data highlights GBFNC3's enhanced thermal properties. Thermal conductivity values vary due to factors like material composition and microstructure. Fillers like GNPs and BaTiO₃ notably boost polypropylene's thermal conductivity by creating additional heat transfer sites within the polymer matrix. This enhancement results in more efficient heat transfer through the material, highlighting the role of fillers in improving thermal properties. Reinforcement morphology, as seen in materials like PET fibrils in GBFNC samples, impacts thermal conductivity. High thermal conductivity in these materials is attributed to factors like the large surface area and high aspect ratio of graphene nanoplatelets, BaTiO₃, and PET fibrils. This morphology enhances heat transfer within the composite. In GBNC samples, GNPs and BaTiO₃ serve as thermal conduits, boosting thermal conductivity. Utilising drawing methods like in-situ fibrils and a drawing-screw extruder unit enhances thermal conductivity by improving filler dispersion and forming a uniform fibrils morphology, as observed in GBFNC samples. This promotes efficient heat transfer within the composite. The presence of GNPs and BaTiO₃ enhances polymer thermal conductivity by serving as electrical conduits and improving heat transfer. Fibrils further enhance this conductivity. This understanding is essential for designing

materials with specific thermal conductivity requirements for various applications. In conclusion, this research focused on the development of multifunctional composite materials by recycling blended plastics, such as polypropylene and polyethylene terephthalate, with the incorporation of graphene nanoplatelets (GNPs) and barium titanate (BaTiO_3). The study explored how external mechanical stimulation, such as cold drawing or stretching, could create in-situ fibrils and enhance thermal properties of these composites. The results showed that the addition of GNPs and BaTiO_3 significantly improved the thermal conductivity of the polymers, acting as electrical conduits and enhancing heat transfer. Furthermore, the presence of fibrils, particularly those from PET, contributed to high thermal conductivity due to their large surface area and aspect ratio. This research highlights the importance of filler dispersion and morphology in achieving the desired thermal properties for specific applications.

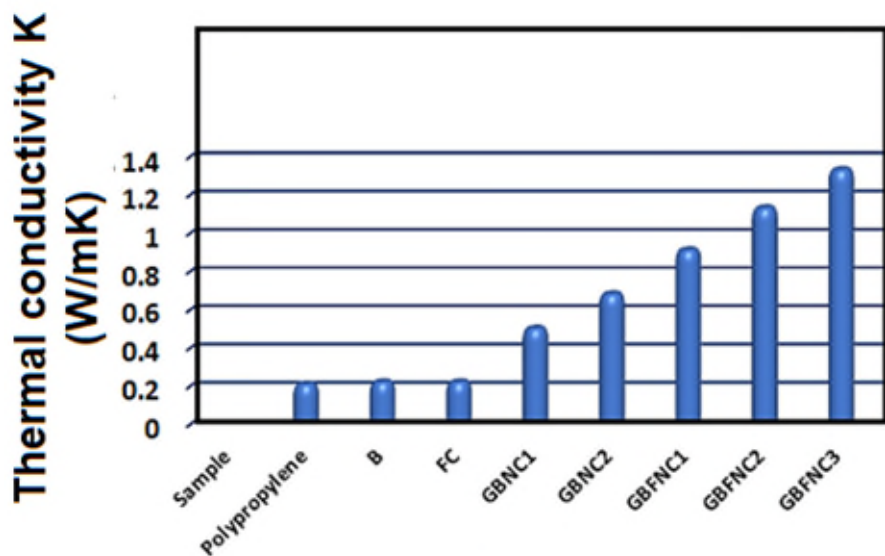


Figure 3-15. Analysis of Thermal conductivity of GNPs+ BaTiO_3 nanocomposites (GBNC) and in-situ GNPs+ BaTiO_3 polyethylene terephthalate (PET) fibrils nanocomposites (GBFNC) with varying phr of GNPs+ BaTiO_3 through two population approach.

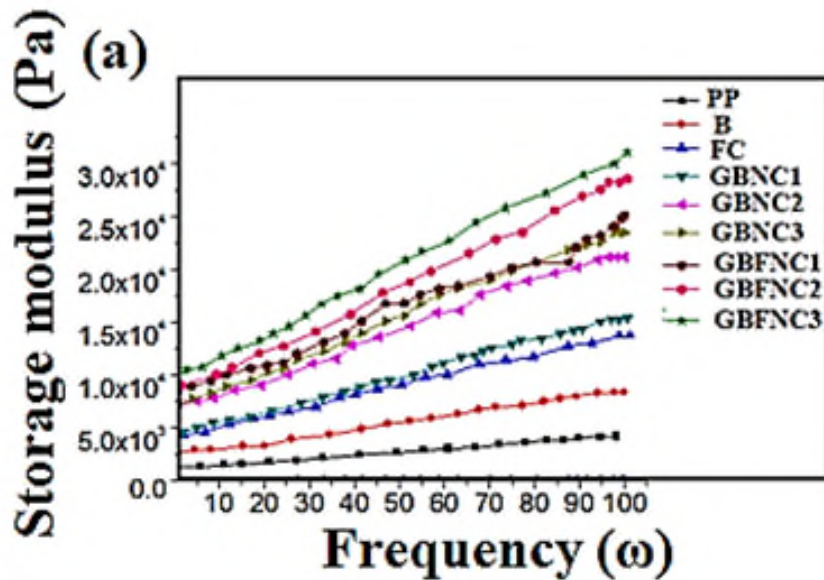
3.4.6 Rheological analysis

As shown in Figure 3-16a, the storage modulus (G') values of all samples increased with angular frequency. GBFNC3 has the greatest storage modulus values over the full test frequency range. The inclusion of polyethylene terephthalate fibrils in addition to GNPs- BaTiO₃ is the clear cause of GBFNC3's high G' values. The storage modulus values of GBNC1, GBNC2, GBFNC1, GBFNC2, and GBFNC3 samples are greater than those of polypropylene, B, and FC. This effect can be attributed to the elastic characteristics of the polypropylene matrix being enhanced by polyethylene terephthalate fibrils and GNPs- BaTiO₃. Furthermore, the polypropylene/polyethylene terephthalate blend (B) contains exclusively spherical polyethylene terephthalate domains that are incapable of contributing to the storage modulus like the fibrils in FC, therefore, FC has a higher storage modulus than polypropylene and B. The loss modulus (G'') values were also found to increase with frequency (ω) as shown in Figure 3-16b. This heralds the viscous behaviour of polypropylene, B, FC, GBNC1, GBNC2, GBFNC1, GBFNC2 and GBFNC3. The loss moduli for GBFNC1, GBFNC2 and GBFNC3 were higher than polypropylene, B, FC across the overall frequency range. This indicates that the polyethylene terephthalate fibrils and GNPs- BaTiO₃ affect viscous behaviour of the composites, however, polyethylene terephthalate fibrils and GNPs- BaTiO₃ contribute more to improving the elastic behaviour of nanocomposites than the viscous behaviour. In comparison to the viscoelastic nature of polypropylene, polyethylene terephthalate inclusions are stiff. Furthermore, the fibrillar shape of the polyethylene terephthalate phase is retained in the isotropic polypropylene matrix, mimicking the environment of fiber-reinforced thermoplastic composites. Figure 3-16c depicts the complex viscosity (n^*) against angular frequency (ω) curves, where n^* is calculated using Equation 3-13.

$$n^* = \left[\left(\frac{G'}{\omega} \right)^2 + \left(\frac{G''}{\omega} \right)^2 \right]^{1/2} \quad (3-13)$$

With increasing frequency, the complex viscosity of all samples diminishes (Figure 3-16c). GBFNC3 has the highest complex viscosity throughout the whole

frequency range. The GBNC has a higher n^* than FC, B, and polypropylene. The viscosity of the polypropylene-polyethylene-terephthalate blend is lower than that of FC. This is consistent with the stiffness impact of GNPs- BaTiO₃ and polyethylene terephthalate fibrils in the polypropylene matrix at lower and higher frequencies. All the samples, however, show a linear decrease in viscosity with frequency. In contrast to polypropylene, B, and FC, the inclusion of GNPs- BaTiO₃ and GNPs- BaTiO₃ mixed with polyethylene terephthalate fibrils resulted in a greater reduction of complex viscosity with frequency increase. Moreover, the fibril morphology of the polymer along the GNPs- BaTiO₃ leads to shear-thinning behaviour at high shear and frequency. This behaviour is critical for comprehending how these materials can be used in a variety of applications.



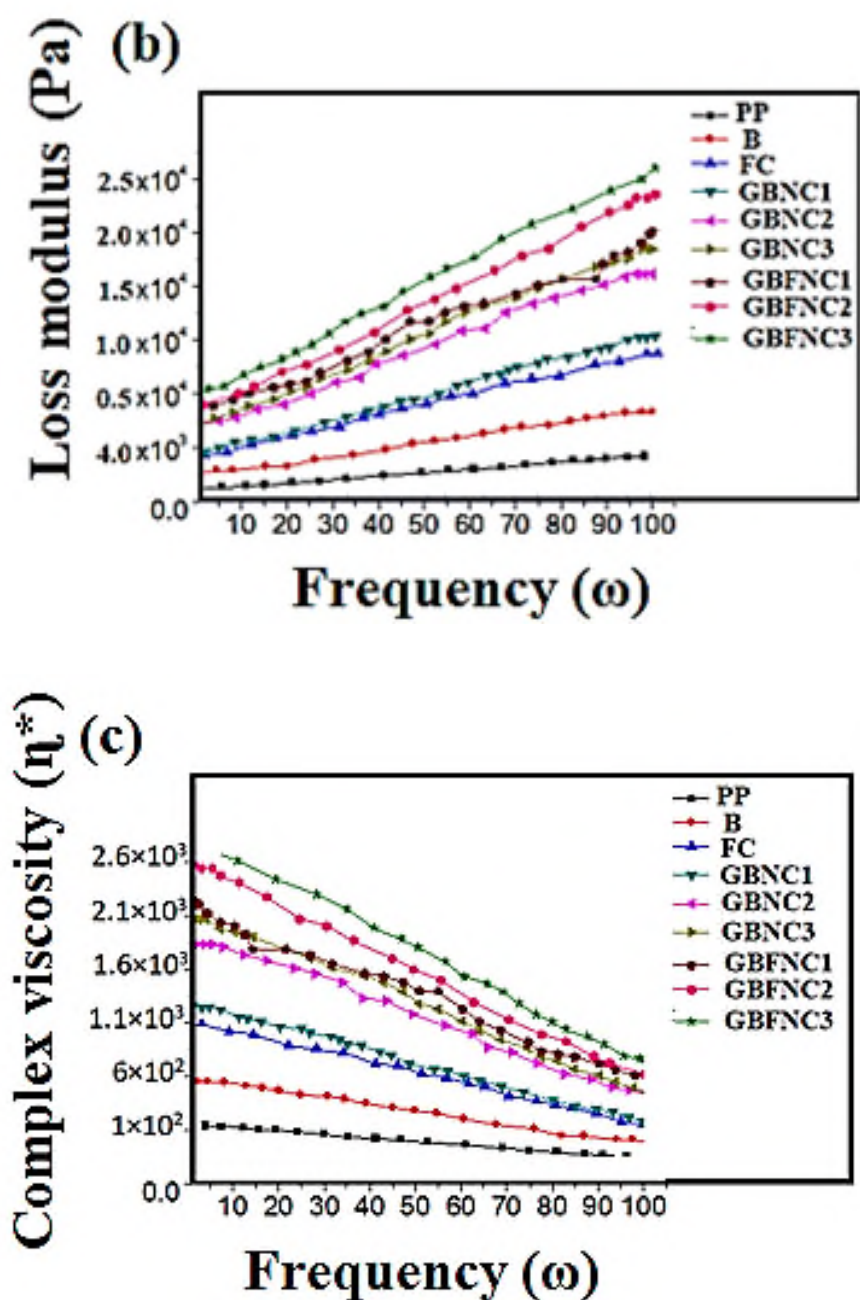


Figure 3-16. a) Variation of storage modulus with frequency(hertz (Hz)), b) Variation of loss modulus with frequency(hertz (Hz)), c) Variation of complex viscosity with frequency(hertz (Hz)).

3.4.7 Static mechanical properties

Tensile testing was used to determine the tensile strength and modulus of the prepared samples, as illustrated in Figure 3-17-a and 3-17-b. The tensile test was

performed to assess the amount of reinforcement provided by polyethylene terephthalate fibrils and GNPs- BaTiO₃ in the polypropylene matrix. Tensile strength and modulus were measured for polypropylene, B, FC, GBNC1, GBNC2, GBNC3, GBFNC1, GBFNC2, and GBFNC3, and mean tensile strength and modulus values were calculated. Figure 3-17-a shows that the polyethylene terephthalate fibrils morphology in the polypropylene matrix (FC) significantly increases the polypropylene matrix's tension-bearing capacity, which then in turn enhances the tensile strength of FC in comparison to B (spherical microstructures of polyethylene terephthalate). GBFNC3 (fibrils morphology of polyethylene terephthalate-GNPs- BaTiO₃) and GBNC3 (spherical structure of polyethylene terephthalate-GNPs- BaTiO₃) show a comparable outcome, with GBFNC3 having a greater tensile strength than GBNC3. Figure 3-17-a shows that increasing the concentration of GNPs- BaTiO₃ in the polypropylene matrix enhanced the system's tensile strength, almost uninterruptedly and coherently. Nevertheless, the combination of polyethylene terephthalate fibrils and GNPs- BaTiO₃ improved tensile strength more than simply GNPs- BaTiO₃. Two fundamental elements can underlie this: a) polyethylene terephthalate - GNPs- BaTiO₃ fibrils work as a superior reinforcing agent and load-bearing component; b) polyethylene terephthalate fibrils with GNPs- BaTiO₃ function as a nano-compatibiliser between polyethylene terephthalate fibrils and polypropylene matrix. It demonstrates that GBFNC outperforms polypropylene, B, and GBNC in all situations. Similar patterns were seen for tensile modulus, as illustrated in Figure 3-17-b. Figure 3-17-b shows that the polyethylene terephthalate fibrils in the polypropylene matrix (FC) in conjunction with GNPs- BaTiO₃ (GBFNC1, GBFNC2 and GBFNC3) significantly increase the tensile modulus of the polypropylene matrix and demonstrate the superiority of GBFNC over other samples in terms of elastic characteristics.

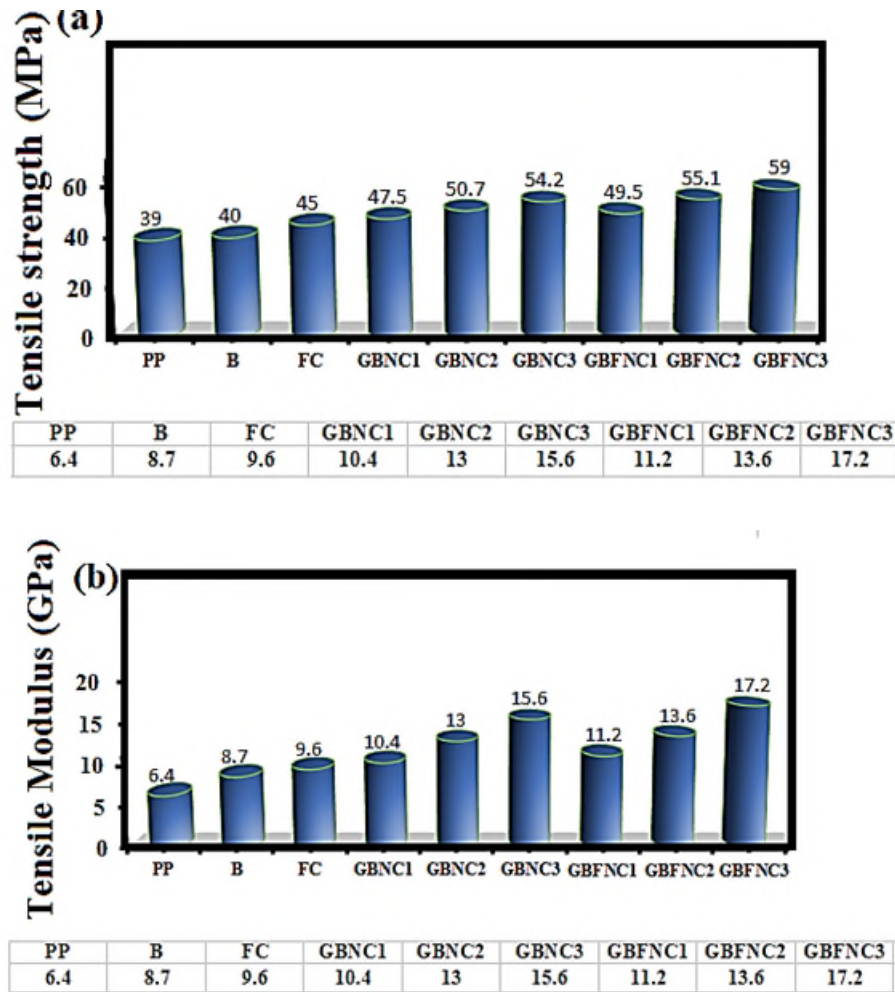


Figure 3-17. Comparatives study of the (a) Tensile strength, (b) Tensile modulus of prepared samples.

This section explores the impact of GNPs- BaTiO₃ nanoparticles and fibrils morphology on the mechanical properties of PP composites through theoretical calculations. The Halpin-Tsai parameter is a critical factor in the analysis, determining the ratio of the modulus or strength of the constituent material to that of the composite based on the volume fraction of the constituent material. The analysis focuses on the performance of the composites, determined by the GNPs- BaTiO₃ nanoparticles and fiber volume fraction and aspect ratio. The reinforcement efficiency factor is used to measure the effectiveness of the reinforcing fiber in enhancing the properties of the composites. The tensile strength of the matrix material (PP) measures its resistance to deformation under tensile loads, while the tensile strength of the fiber-reinforced material (PET) and

GNPs- BaTiO₃ nanoparticles measures the strength of the fibres and nanoparticles against deformation under tensile load. Fibrils form a network that directionally reinforces a polymer matrix, thereby enhancing the composite's mechanical properties. The aspect ratio and surface area of the fibres also impact the composite's mechanical properties. The increased aspect ratio and surface area of GNPs- BaTiO₃ nanoparticles enhance the interfacial adhesion between the fiber and matrix, thereby improving the mechanical properties.

To investigate the mechanical properties of GNPs and BaTiO₃ reinforced polypropylene/polyethylene terephthalate, a theoretical calculation was performed using the Halpin-Tsai parameter to determine the reinforcement efficiency factor. It was assumed that the fibres are aligned or likely to be aligned in the direction of mechanical test, therefore would have a strengthening effect in that direction. It was also assumed that GNPs- BaTiO₃ is evenly distributed in the blend. The tensile modulus was predicted using the law of mixtures, and the reinforcement efficiency factor was calculated as the ratio between the effective elastic modulus of the composite and the elastic modulus predicted by the mixed law. The aspect ratio of the GNPs- BaTiO₃ used in the mixture was approximately 296 as calculated below. The material studied in this research included a PP homopolymer, an extruded blend of PP/PET (B) with 85% by weight PP and 15% by weight PET containing PET particles with a diameter of approx. 5 microns, and an extruded composite (FC) containing PP/PET fibres with a weight ratio of 85:15 and a PET fiber of 5 microns in diameter and 2 cm in length as per our SEM investigations (the 2 cm used as the gauge length during the mechanical testing). The simulations were conducted based on the following assumptions, which are listed below for clarity and precision:

The weight ratio of GNPs to BaTiO₃ is considered 1:1, so each constituent have a weight of 0.5 grams. The density range provided for GNPs is 2.0-2.25 g/cm³, the average density of 2.125 g/cm³ was utilised. The density of BaTiO₃ remained constant at 6.08 g/cm³. The volume of GNPs was calculated as follows: $(V_{fGNP}) = 0.5 \text{ g} / 2.125 \text{ g/cm}^3 = 0.235 \text{ cm}^3$. The volume of BaTiO₃ remained the same: $(V_{fBaTiO3}) = 0.5 \text{ g} / 6.08 \text{ g/cm}^3 = 0.082 \text{ cm}^3$. The volume fraction of GNPs in the

mixture was calculated as: $(V_{f,GNP}) = 0.235 \text{ cm}^3 / (0.235 \text{ cm}^3 + 0.082 \text{ cm}^3) = 0.741$. Similarly, the volume fraction of BaTiO₃ was calculated as: $(V_{f,BaTiO_3}) = 0.082 \text{ cm}^3 / (0.235 \text{ cm}^3 + 0.082 \text{ cm}^3) = 0.259$. Using the volume fractions and assuming that the GNPs and BaTiO₃ were aligned in the direction of the mechanical testing, and that the aspect ratio of GNPs is 400 and that of BaTiO₃ is 1, the aspect ratio of the combined GNPs- BaTiO₃ was estimated as follows:

Aspect Ratio = $V_{f,GNP} \times 400 + V_{f,BaTiO_3} \times 1) / (V_{f,GNP} + V_{f,BaTiO_3}) = (0.741 \times 400 + 0.259 \times 1) / (0.741 + 0.259) = 296.26 / 1 = 296.26$. The tensile strength of PET fiber is approx. 150 MPa. Specimens were tested under unilateral tension. Samples were assumed to be homogeneous and isotropic. The PP/PET (B) granule blend and PP/PET (FC) fiber blend cannot be mixed due to the incompatibility of PP and PET.

The Halpin-Tsai model is commonly used to estimate the composite's basic properties and assumes that fibres are long and thin, with a diameter of approximately [488] 10 micrometers as per the SEM analysis. The volume fraction of fiber is calculated based on the weight fraction of the composite material. Assuming that the Young's modulus of bulk BaTiO₃ is approximately 75 GPa, while GNP's Young's modulus is approximately 1 TPa with an ultimate strength of up to 130 GPa [479,489,490]. Tensile strength and modulus were estimated using the rule of mixtures, which assumes that the composite material behaves as a linear elastic solid. Halpin-Tsai parameter (β) is defined by equation (3-14) as a theoretical model to estimate the effective elastic modulus of a composite material. It relates the elastic modulus of a composite to the elastic modulus of the individual constituents and the geometry of the composite structure[491]. The equation was used to calculate the Halpin-Tsai parameter (β) [492]for B, FC, GBFNC, GBFNC nanocomposites consisting of a PPT/PET and GNPS- BaTiO₃.

$$\beta = \left(\frac{\left(\frac{E_f}{E_m} - 1 \right)}{\left(\frac{E_f}{E_m} + \beta \right)} \right) \quad (3-14)$$

Here, E_f and E_m are the moduli of elasticity of the reinforcing reinforcement and matrix material, respectively, while f is the reinforcement efficiency factor, which is defined by:

$$f = \left(\frac{(1+\beta V_f)}{(1-V_f\beta)} \right) \quad (3-15)$$

The volume fraction of reinforcement (V_f) is calculated via:

$$V_f = \left(\frac{(m_f)}{(m_f + m_m)} \right) \times \left(\frac{(\rho_m)}{(\rho_f)} \right) \quad (3-16)$$

where m_f and m_m are the mass fractions of the reinforcement and matrix materials, respectively, and ρ_m and ρ_f are their respective densities. This is applicable for sample B and FC, while the equation (3-17) is valid for the other samples such as GBNC and GBFNC.

$$V_f = \left(\frac{(m_f)}{(m_{PET} + m_{BaTiO_3} + m_{GNPs} + m_m)} \right) \times \left(\frac{(\rho_m)}{\left(\frac{m_{PET} \times \rho_{PET} + m_{BaTiO_3} \times \rho_{BaTiO_3} + m_{GNPs} \times \rho_{GNPs}}{m_{PET} + m_{BaTiO_3} + m_{GNPs}} \right)} \right) \quad (3-17)$$

where the density of the PET fibrils or density of PET is ρ_{PET} and the densities of the BaTiO₃ nanoparticles, GNPs, and PP matrix are ρ_{BaTiO_3} , ρ_{GNPs} , and ρ_m , respectively. m_{PET} , m_{BaTiO_3} , and m_{GNPs} are the mass fractions of the PET fiber, BaTiO₃ nanoparticles, and GNPs, respectively.

Once above parameters are determined, the theoretical, rule of mixture based tensile strength σ_{RM} and modulus E_{RM} can be calculated using the following equations [493–495]. The Halpin-Tsai equation (3-18) for theoretical tensile modulus of a composite is:

$$E_{Tc} = E_m \left[\frac{1+V_f\beta}{1-V_f\beta} \right] \quad (3-18)$$

where E_{Tc} = theoretical tensile modulus of the composite E_m = elastic modulus of the matrix material V_f = volume fraction of the reinforcement material β = Halpin-Tsai parameter, which is a measure of the shape and orientation of the reinforcement material in the matrix. The Halpin-Tsai equation (3-19) for theoretical tensile strength of a composite is:

$$\sigma_{Tc} = \sigma_m \left[1 + V_f\beta \left(\frac{\sigma_f}{\sigma_m} - 1 \right) \right] \quad (3-19)$$

where σ_{Tc} = theoretical tensile strength of the composite and σ_m = tensile strength of the matrix material. Finally, the tensile strength σ_{RM} and tensile modulus E_{RM} of blend, composites, nanocomposites are given by:

$$\sigma_{Tc} = (1 - V_f)\sigma_m + V_f\sigma_f \quad (3-20)$$

$$E_{RM} = (1 - V_f)E_m + V_fE_f \quad (3-21)$$

where σ_m and E_m are the tensile strength and modulus of the matrix material, while σ_f and E_f are those of the reinforcing fibres. Table 3- 5 presents the analysis of various composite materials based on PET fibres and PET fibres reinforced with GNP- BaTiO₃ particles. The composites were analysed for their mechanical properties, including modulus and strength. The table also includes the percentage of PET and GNP- BaTiO₃ by weight and volume, respectively, for each sample. Theoretical tensile modulus and strength are calculated based on the properties of the individual constituents by Halpin-Tsai parameter model, whereas the rule of mixture predicts the modulus and strength for the composites. Reinforcement efficiency factor is defined as the ratio of experimental modulus or strength to the theoretical values predicted by the Rule of Mixtures. This

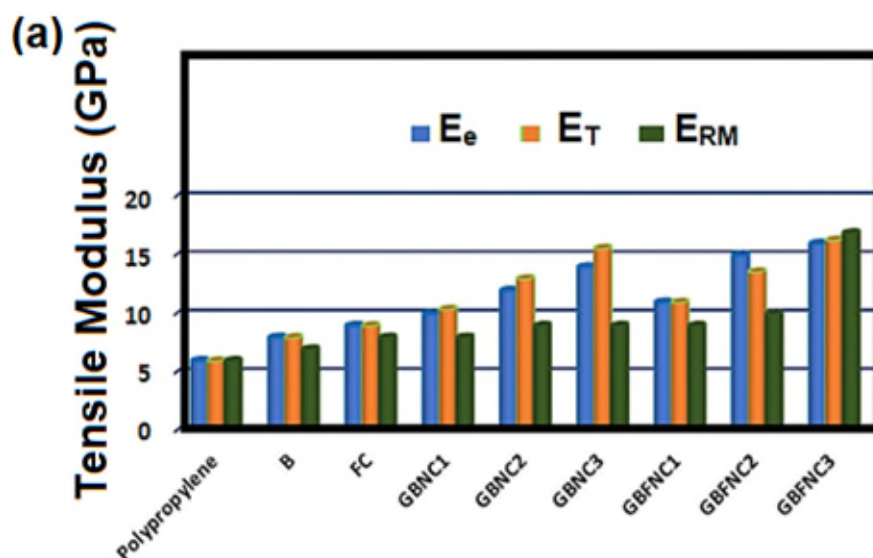
suggests that the PET fibrils are effectively reinforcing the PP matrix, resulting in an improvement in mechanical properties. The reinforcement efficiency factor also provides insight into the effectiveness of the reinforcement. As seen in the table, the efficiency factor increases with increasing GNP- BaTiO₃ volume fraction, indicating that the particles are effectively reinforcing the PP matrix.

Table 3-5. Comparison of Theoretical mechanical properties for PP/PET blends with different reinforcement types and concentrations.

Sample	PET wt. %	GNPs- BaTiO ₃ vol%	Halpin-Tsai Parameter	Rule of Mixtures Predicted Modulus (GPa)	Theoretical Tensile Modulus (GPa) Halpin-Tsai	Theoretical Tensile Strength (MPa) Halpin-Tsai	Rule of Mixtures Tensile Strength (MPa)	Reinforcement Efficiency
PP	0	0	-	6	6	39	39	-
B	15	0	0.0215 (w.r.t PET)	8	7	41	41	0.17 (w.r.t PET)
FC	15	0	0.027 (w.r.t PET)	9	8	45	45	0.224 (w.r.t PET)
GBNC1	15	0.22 (1phr)	0.181	10.4	8	47.4	49.1	0.324
GBNC2	15	0.44 (2phr)	0.251	13.0	9	50.7	52.5	0.468

GBNC3	15	0.66 (3phr)	0.317	15.6	9	54.2	56.2	0.534
GBFNC1	15	0.22 (1phr)	0.181	11.0	9	49.5	50.8	0.324
GBFNC2	15	0.44 (2phr)	0.251	13.6	10	55.1	56.9	0.468

Figure 3-18 presents the results of an experiment that was conducted to measure the tensile strength and modulus of various composite materials, including PP, B, FC, GBNC1, GBNC2, GBNC3, GBFNC1, GBFNC2, and GBFNC3. Figure 3-17 shows the experimental tensile moduli and strength for the different materials (blue bars), along with their corresponding theoretical moduli predicted above from the Halpin-Tsai equation (green bar) and the rule of mixture (orange bar), demonstrating an accurate prediction for the tensile strength (and not the moduli) by the theory. The modulus for the GBFNC3 was accurately predicted by the theory.



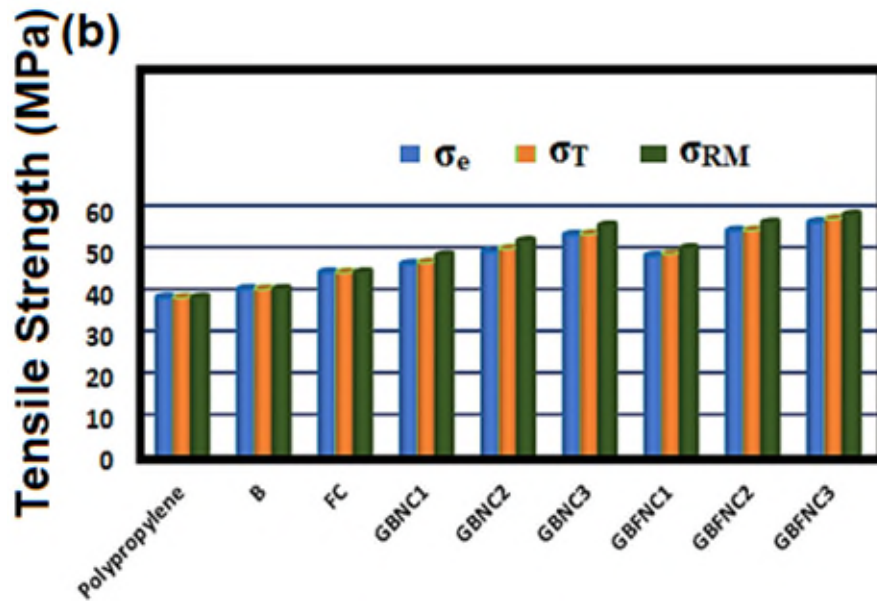


Figure 3-18. A Comparatives study of the experimental and theoretical for a) tensile modulus and b) strength.

5.4.8 Tropology by atomic force microscopy

Surface morphology plays a critical role in determining the physical and chemical properties of materials, was investigated using Atomic Force Microscopy (AFM) and results are shown in Figure 3-19(a-f). The AFM images provided valuable insights into the distinct morphologies exhibited by each sample. The AFM images provided clear visual representations of the surface morphology for each sample. Figure 3-19(a) displayed the surface morphology of PP. In Figure 3-19(b), the blend B showed spherical distributions of polyethylene terephthalate within the polypropylene matrix. Figure 3-19(c) exhibited the fibrillar morphology of the polypropylene/polyethylene terephthalate in-situ fibrils composites FC, indicating the presence of elongated structures within the composite. The distribution of GNPs- BaTiO₃ within the polypropylene matrix for the GBNC1 sample is displayed in Figure 3-19d, while Figures 3-19e and 3-18f demonstrated the distribution of GNPs- BaTiO₃ and the fibrillar morphology for the nanocomposites GBFNC with 1 and 3 phr of GNPs- BaTiO₃, respectively. The AFM images presented distinct surface morphologies for each material. The spherical distribution of polyethylene terephthalate within the polypropylene

matrix in the polypropylene-polyethylene-terephthalate blend in sample B suggests phase separation and could have implications for the material's mechanical and thermal properties. The presence of fibrillar structures in the polypropylene/polyethylene terephthalate in-situ fibrils composites in sample FC indicates enhanced interfacial adhesion and the potential for improved mechanical performance. The distribution of GNPs- BaTiO₃ within the polypropylene matrix for the GBNC1 sample suggests effective dispersion, which could lead to enhanced electrical and thermal properties. The presence of GNPs- BaTiO₃ in the polypropylene/polyethylene terephthalate-GNPs- BaTiO₃ in-situ fibrils in samples GBFNC further modifies the morphology, potentially resulting in improved multifunctional properties. To verify the surface morphology observations seen in the AFM study, relevant findings from previous research papers were consulted. Specifically, examination of a study presenting AFM images of untreated PET samples, depicting the surface morphology of graphene nanoplates obtained through exfoliation using potassium, aided in supporting the understanding of the spherical distribution of polyethylene terephthalate within the polypropylene matrix observed in sample B[496,497]. Additionally, reference was made to another study that offered AFM images of BaTiO₃ thin films, both untreated and irradiated at a dosage of 1×10^{11} ions cm⁻². These images aided in comprehending the distribution of GNPs- BaTiO₃ within the polypropylene matrix in the GBNC1 sample, highlighting effective dispersion of the nanoparticles[498]. Additionally, the findings of a separate study that unveiled elementary fibrils on the surfaces of parenchyma-type secondary walls (pSW) were taken into account[499]. This information supported our interpretation of the fibrillar morphology observed in sample FC and in the nanocomposites samples, GBFNC, with 1 and 3 phr of GNPs- BaTiO₃. By incorporating these references, we have enhanced the scientific validity and credibility of our analysis of the surface morphology observed in the investigated materials. In conclusion, AFM was successfully utilised to investigate the surface morphology of our samples, revealing distinctive morphologies for each material, offering valuable insights into their surface characteristics. Further investigation and analysis are necessary to elucidate the relationship between these morphological features

and the material's properties, enabling the development of advanced functional materials with tailored performance. Surface roughness is an essential parameter influencing the functional properties of materials. This study investigates the influence of morphology and GNPs- BaTiO₃ content on the surface roughness of polypropylene-based nanocomposites. The surface roughness was characterised using Atomic Force Microscopy (AFM), and the relationship between morphology, GNPs- BaTiO₃ content, and surface roughness was analysed. AFM was employed to assess the surface roughness of the investigated materials. Images were captured for polypropylene (PP), polypropylene-polyethylene-terephthalate blend (B), polypropylene/polyethylene terephthalate in-situ fibrils composites (FC), GNPs- BaTiO₃ within the polypropylene matrix (GBNC1), and polypropylene/polyethylene terephthalate-GNPs- BaTiO₃ in-situ fibrils nanocomposites (GBFNC) with varying GNPs- BaTiO₃ content. The obtained AFM images were analysed to quantify and compare the surface roughness of each sample. Figure 3-19g presents the AFM image demonstrating the surface roughness of polypropylene, B, FC, GBNC1, GBFNC1, GBFNC2, and GBFNC3. It is observed that the surface roughness is influenced by both the morphology of the samples and the GNPs- BaTiO₃ content. The presence of fibrils morphology in FC and GBFNC samples significantly increased the surface roughness, indicating the development of textured structures on the material's surface. Moreover, an increase in the GNPs- BaTiO₃ content also contributed to higher surface roughness. Furthermore, the combination of GNPs- BaTiO₃ and polyethylene terephthalate fibrils exhibited a pronounced effect on the surface roughness of the samples. Notably, GBFNC3, with the highest GNPs- BaTiO₃ content, demonstrated the highest surface roughness among all the investigated samples. The observed increase in surface roughness can be attributed to several factors. The presence of fibrils morphology introduces additional roughness features on the material's surface, resulting in enhanced roughness values. Additionally, the higher content of GNPs- BaTiO₃ promotes agglomeration or dispersion of nanoparticles, thereby further modifying the surface morphology and increasing the surface roughness. The combination of GNPs- BaTiO₃ with polyethylene terephthalate fibrils creates a pronounced

impact on the surface roughness. The interaction between these components influences the formation of surface features, resulting in higher roughness values.

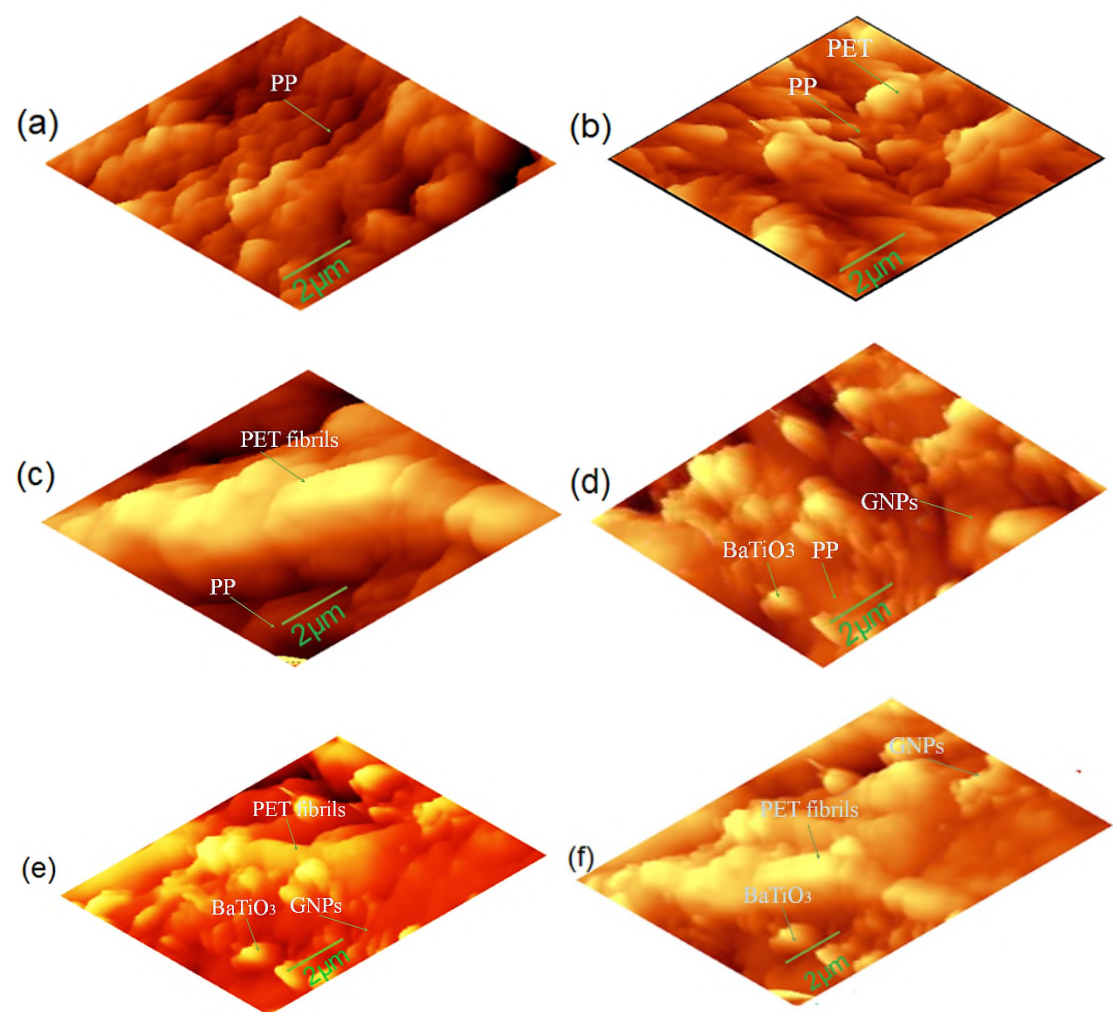
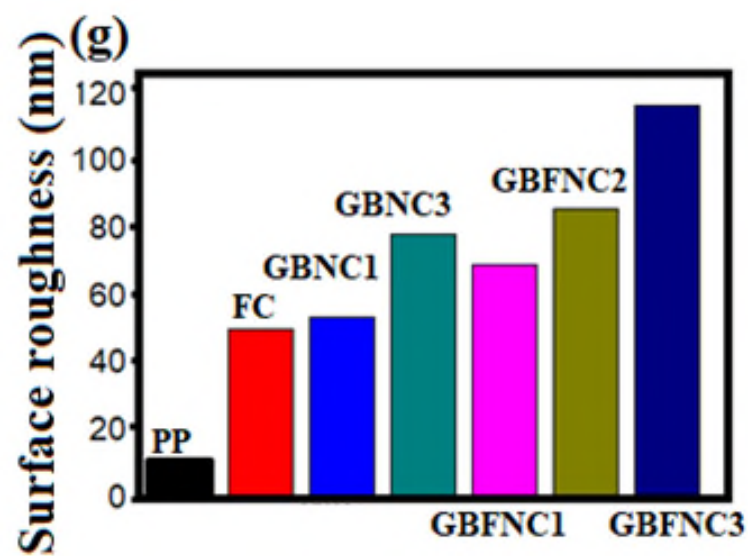


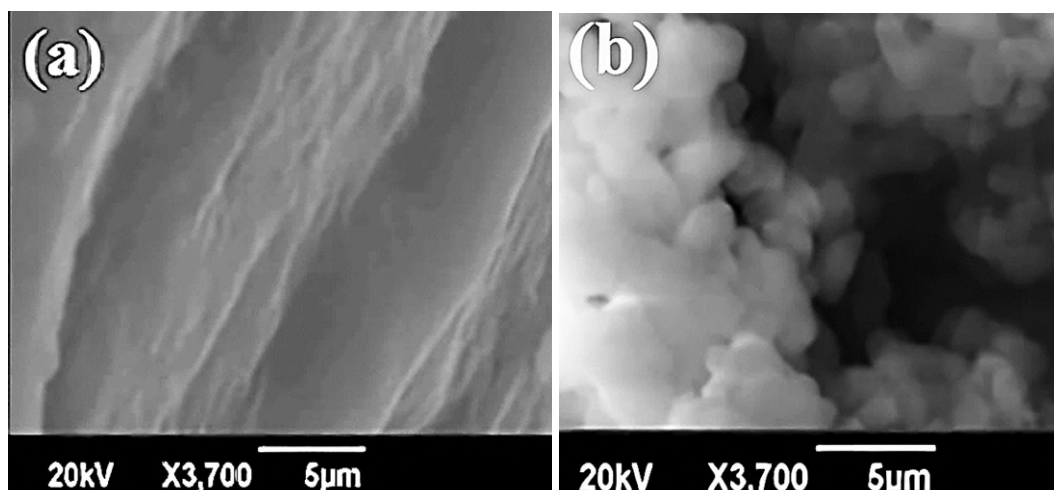
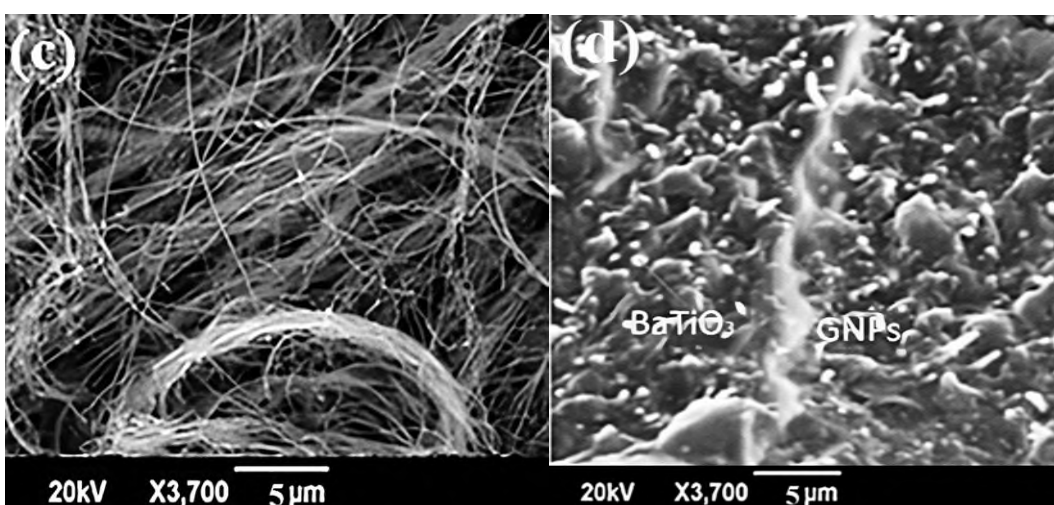
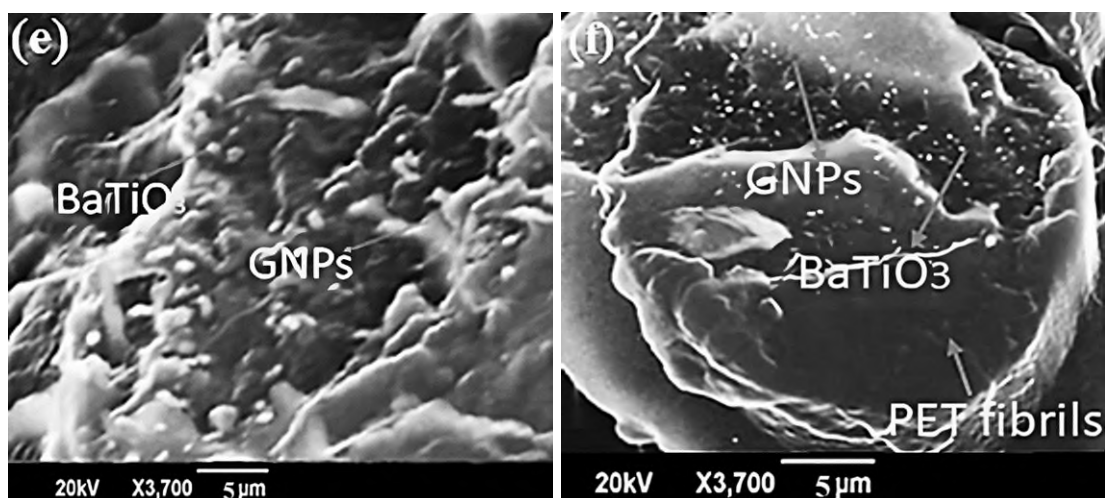
Figure 3-19. AFM images and surface roughness of samples, (a) Polypropylene (PP), (b) Polypropylene (PP)/ polyethylene terephthalate (PET) blend (B), (c) Polypropylene (PP)/ polyethylene terephthalate (PET) in-situ fibrils composites (FC), d) GBNC1, e) GBFNC1, f) GBNFC3, g) Surface roughness.

5.4.8 Morphological analysis

In Figure 3-20(a-g), SEM microstructures of various materials are presented, including polypropylene (PP), polypropylene-polyethylene-terephthalate blend (B), in-situ fibrils microfibrillar composites (FC), GNPs- BaTiO₃-based nanocomposites with different concentrations (GBNC1 and GBNC3), and GNPs- BaTiO₃-based in-situ fibrils nanocomposites with different concentrations (GBFNC1 and GBFNC3). Figure 3-20a displays the morphology of neat PP, while Figure 3-20b illustrates the unique morphology of the polypropylene-polyethylene-terephthalate blend (B). B's morphology results from coalescence and breakup of polyethylene terephthalate particles during extrusion, leading to their distribution as spherical and curved shapes within the polypropylene matrix. Elongation forces during extrusion are evident from the curved morphology of the polyethylene terephthalate component, causing its distribution as beads in polypropylene. Figure 3-20(c) confirms the generation of in-situ polyethylene terephthalate fibrils throughout the drawing process, with their diameters falling within the micrometre range. This indicates the formation of fibrillar structures in the composites, significantly influencing their mechanical properties. Figures 3-20d and 3-20e depict the morphology of GNPs- BaTiO₃-based nanocomposites (GBNC1 and GBNC3). Here, the absence of fibrils morphology and the uniform distribution of GNPs- BaTiO₃ particles can be noticed. GNPs- BaTiO₃ nanoparticles influence the polymer matrix's crystallisation behaviour and lead to a uniform dispersion within it.

To gain a deeper understanding of the morphological differences, images of GBNC (GBNC1 with 1 phr of GNPs- BaTiO₃ and GBNC3 with 3 phr of GNPs- BaTiO₃) were compared with those of GBFNC (GBFNC1 with in-situ polyethylene terephthalate fibrils along with 1 phr of GNPs- BaTiO₃ and GBFNC3 with in-situ

polyethylene terephthalate fibrils with 3 phr of GNPs- BaTiO₃). Figures 3-20(f) and 3-20(g) represent the morphology of GBFNC1 and GBFNC3, respectively, where GNPs- BaTiO₃ nanoparticles are combined with in-situ fibrils, and the fibrils' diameters remain in the micrometre range. Interestingly, the diameters of the fibrils in GBFNC1 and GBFNC3 are larger than those observed in neat in-situ polyethylene terephthalate fibrils, in line with previous theoretical calculations. The SEM images of GNPs- BaTiO₃ nanoparticles typically reveal their distinctive two-dimensional structure. GNPs, or graphene nanoplatelets, are characterised by thin and flat nanoplatelets with a highly ordered arrangement of carbon atoms. This unique structure gives them excellent mechanical, electrical, and thermal properties, making them desirable reinforcements in nanocomposites. On the other hand, SEM images of in-situ fibrils showcase the morphology of the polyethylene terephthalate (PET) fibrils that have been generated throughout the drawing process. These fibrils have diameters within the micrometre range. The formation of fibrillar structures in composites significantly influences their mechanical properties, contributing to enhanced strength and stiffness[451,500]. When combined in nanocomposites, such as GNPs- BaTiO₃-based in-situ fibrils nanocomposites (GBFNC), SEM images depict the coexistence of both GNPs- BaTiO₃ nanoparticles and in-situ fibrils[501]. The presence of GNPs- BaTiO₃ nanoparticles restricts the orientation of the polymer chains and bears the elongational force, reinforcing the composites and leading to increased stiffness. In summary, SEM microstructures offer valuable insights into the morphology of different composites, and the presence of GNPs- BaTiO₃ nanoparticles and in-situ fibrils significantly influence their properties and mechanical performance. The combination of different materials and their morphologies plays a crucial role in tailoring the mechanical characteristics of the composites for specific applications in diverse fields.



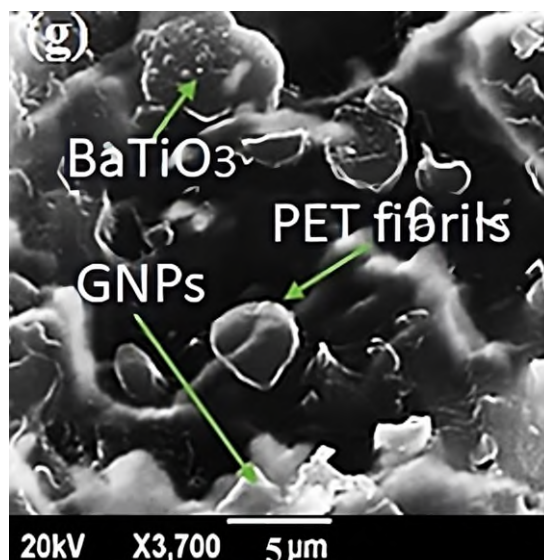


Figure 3-20. SEM images, (a) Polypropylene (PP); (b) Polypropylene (PP)/ polyethylene terephthalate (PET) blend after surface extraction of polypropylene (PP) by hot xylene (B); (c) polypropylene (PP)/ polyethylene terephthalate (PET) in-situ fibrils composites after surface extraction of polypropylene by hot xylene (FC), d) GBNC1 cryo- fractured surfaces, e) GBNC3 cryo-fractured surfaces, f) GBFNC1 cryo- fractured surfaces, g) GBNFC3 cryo-fractured surfaces.

5.4.9 Electromagnetic interference shielding by vector network analyser

Figure 3-21 illustrates the influence of morphology and GNPs- BaTiO₃ concentration on the shielding effectiveness (SE) of polypropylene-based blends and nanocomposites against electromagnetic interference (EMI). EMI poses significant challenges in various industries as it leads to signal interference, data corruption, and equipment failure. Materials with high electrical conductivity and dielectric constant are utilised as EMI shielding materials to address this issue. The aim of this research was to investigate the impact of morphology and GNPs- BaTiO₃ concentration on the SE of polypropylene-based blends and nanocomposites. The materials were prepared through melt blending, and the SE was evaluated using a standard EMI shielding test. The results demonstrated a clear relationship between the GNPs- BaTiO₃ content and the SE. Increasing the concentration of GNPs- BaTiO₃ improved the SE of the materials. This

enhancement can be attributed to the conductive and dielectric nature of GNPs- BaTiO_3 particles, which create pathways for the reflection, absorption, and dissipation of electromagnetic waves. Additionally, the morphology of the materials significantly influenced their SE. Among the investigated samples, the material with in-situ polyethylene terephthalate (PET) fibrils exhibited the highest SE. This outcome can be attributed to the larger surface area provided by the fibrils, facilitating enhanced interaction with the GNPs- BaTiO_3 particles and further improving the SE of the material. BaTiO_3 acts as a dielectric filler within the polymer matrix, providing pathways for electromagnetic wave absorption and dissipation. GNPs, serving as conductive fillers, improve the electrical conductivity of the material, facilitating the attenuation of electromagnetic waves and enhancing the EMI shielding properties. PET fibrils, with their high aspect ratio and increased surface area, play a crucial role in enhancing EMI shielding capabilities. These fibrils enhance the interaction between conductive fillers and the polymer matrix, resulting in improved electrical conductivity and EMI shielding performance. The combination of BaTiO_3 and GNPs within the polymer matrix exhibits a synergistic effect on EMI shielding properties, surpassing the individual shielding effectiveness of BaTiO_3 or GNPs alone. Material morphology significantly influences EMI shielding properties. The presence of PET fibrils increases the material's surface area, facilitating enhanced interaction between the conductive fillers and the polymer matrix, and contributing to improved electrical conductivity and overall EMI shielding performance. Materials incorporating BaTiO_3 , GNPs, and PET fibrils exhibit enhanced EMI shielding properties, making them suitable for various applications, including electronic devices, automotive systems, aerospace equipment, and other industries where reliable EMI protection is essential.

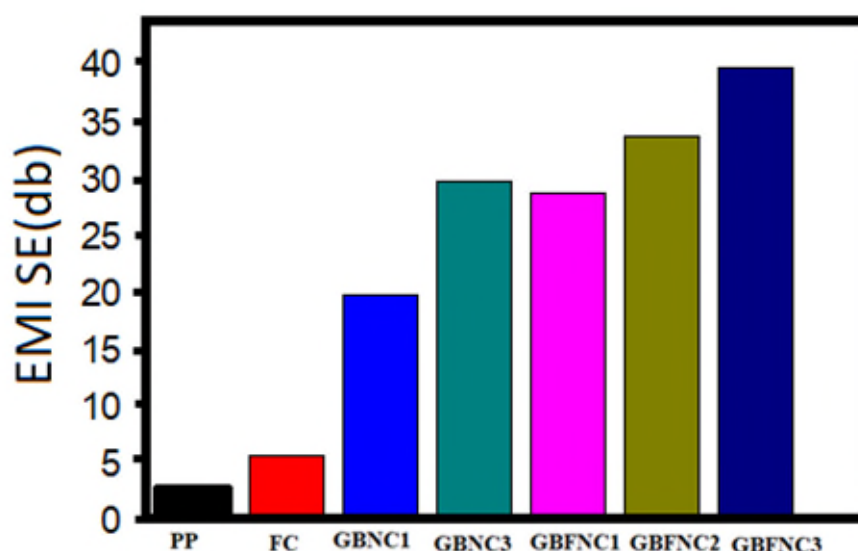


Figure 3-21. Electromagnetic shielding effectiveness of polypropylene (PP), FC, GBNC1, GBNC3, GBFNC1, GBFNC1, GBFNC3.

This study highlights the potential for enhancing the SE of polypropylene-based blends and nanocomposites by increasing the GNPs- BaTiO₃ concentration and manipulating the material's morphology. These findings have important implications for the development of novel EMI shielding materials suitable for a wide range of applications. By understanding the relationship between morphology, GNPs- BaTiO₃ concentration, and SE, researchers and engineers can design and optimise EMI shielding materials to meet specific requirements. The ability to tailor the SE of materials opens up opportunities for applications in industries such as electronics, telecommunications, aerospace, and automotive, where effective EMI protection is crucial. The impact of BaTiO₃, GNPs, and PET fibrils on EMI shielding is substantial. BaTiO₃ acts as a dielectric filler, while GNPs provide conductivity, and PET fibrils enhance material surface area, resulting in improved electrical conductivity and enhanced EMI shielding capabilities. Understanding the synergistic effects and morphology-related enhancements enables the development of advanced EMI shielding materials tailored to specific application requirements. These findings contribute to the advancement of EMI shielding technologies, promoting improved performance and reliability in the face of increasing EMI challenges.

3.5 Conclusions

Chapter 3 investigated the impact of different filler arrangements within polymer nanocomposites. Specifically, the inclusion of in-situ fibrils of polyethylene terephthalate and GNPs/ BaTiO₃ led to significantly enhanced electrical conductivity. This aligns with the objective of exploring how filler structures influence the electrical properties of nanocomposites. The chapter highlighted the evolution of trans-crystalline structures in the polypropylene matrix due to the presence of polyethylene terephthalate fibrils. This unique structure influenced the arrangement of polypropylene crystals relative to the fibril backbone. Understanding these changes directly addresses the objective of comprehending how nanocomposite behaviour relates to alterations in the polymer matrix. The research indicated that the combined effects of GNPs/ BaTiO₃ and polyethylene terephthalate fibrils were found to be additive in reinforcing the polypropylene matrix. GNPs/ BaTiO₃ displayed dominance at varying temperatures, showcasing potential applications in different industries. This correlates with the objective of assessing how different fillers collectively impact nanocomposite properties. Notably, the study unveiled the improvement in tensile strength in the polypropylene matrix due to the presence of polyethylene terephthalate fibrils. Additionally, the electromagnetic interference shielding effectiveness of the nanocomposites was observed to increase with specific changes in filler content and morphology. These findings directly correspond to the objective of enhancing mechanical and electromagnetic properties in nanocomposites. Chapter 3 provided critical insights into tailoring the properties of polymer-based nanocomposites. Understanding how filler microstructures impact electrical, mechanical, and electromagnetic properties opens avenues for tailored industrial applications, aligning with the objective of customising nanocomposites for diverse industry-specific needs. Therefore, Chapter 3 comprehensively investigates and aligns with the stipulated objectives, providing insights into the dynamic interplay of fillers within nanocomposites and their direct influence on electrical, mechanical, and electromagnetic properties.

CHAPTER 4

Computational Analysis of Electrical and Thermal Properties in Ferroelectric BaTiO₃ Reinforced Epoxy Nanocomposites: An In-Situ Electric Field Study

4.1 Introduction

Polymer composites and nanocomposites utilise multiple phases or reinforcements, like nanomaterials or fibres, to enhance their properties. They are engineered for targeted performance enhancements in sectors like automotive, aerospace, and electronics. This amalgamation allows customisation of material attributes to meet diverse industrial demands[502–505]. Polymer composites and nanocomposites excel through intentional design and processing, surpassing pristine materials. This improvement results from precise material engineering, offering tailored performance advantages in specialised applications due to their customised properties[502–505]. Polymers in their pure state are typically insulators because they lack conductive pathways in their molecular structure, resulting in low electrical conductivity. This property restricts their ability to readily conduct electric charge[3]. Epoxy polymers, due to their insulating nature, face limitations in high-value manufacturing sectors like aerospace, where electrical conductivity or specific properties may be essential. These limitations arise from their inability to conduct electricity, potentially requiring alternative materials with the desired electrical or thermal characteristics in aerospace applications[503,506,507]. In the automotive sector, epoxy polymers, primarily insulating, may encounter constraints when specific electrical or thermal conductivity is required. This can lead to a preference for alternative materials with the necessary conductive properties in specific automotive components or applications[502–505]. In the energy industry, insulating materials like epoxy polymers may prove unsuitable for applications requiring efficient heat dissipation or electrical conductivity. This can lead to a search for alternative materials with improved thermal and electrical characteristics to enhance energy-related technologies[503,506,507]. In biomedical applications, the suitability of insulating polymers like epoxy may be restricted, as specific medical devices or treatments demand materials with particular electrical or thermal characteristics. This prompts the investigation of alternative materials or composite solutions to meet the distinctive requirements of biomedical applications[503,506,507]. Incorporating additives or fillers into the polymer matrix boosts composite performance, enhancing electrical conductivity

and lightning strike protection. This is vital in industries like aerospace and automotive, where electrical conduction and lightning protection are crucial. It involves enhancing material properties through filler integration to meet specific application demands[508–511]. Incorporating additives or fillers into the polymer matrix enhances composite performance, particularly in electromagnetic shielding. This is crucial in industries like aerospace, automotive, and electronics, where EMI shielding is essential. It involves optimising material properties to mitigate electromagnetic interference[508–511]. The addition of fillers in the polymer matrix can provide anti-static properties, a necessity in industries like electronics manufacturing and cleanroom environments to prevent static electricity buildup. This ensures safe and controlled environments, reducing the risk of damage to sensitive electronic components[508–511]. The incorporation of fillers in the polymer matrix can improve the composites' capability to store and release strain energy. This is beneficial in applications where materials are required to absorb and dissipate mechanical energy, like impact-resistant materials or damping components in mechanical systems[508–511]. These properties, including conduction, lightning strike protection, electromagnetic shielding, anti-static behaviour, and strain energy storage, are essential in the aerospace sector for creating advanced composite materials capable of meeting the rigorous demands of aerospace applications[508–511].

Carbon-based fillers, notably carbon nanotubes (CNTs) and carbon black (CB), are favored for their outstanding electrical and thermal conductivity, along with reasonably good mechanical properties. This makes them ideal for producing high-performance conductive composites in various applications[512]. Graphene has gained significant scientific attention for its potential as a conductive filler material, thanks to its exceptional electrical and thermal conductivity, along with favourable mechanical properties. Graphene, a 2D carbon sheet with hexagonal bonding, exhibits remarkable electrical conductivity, reaching $1 \text{ to } 6 \times 10^5 \text{ S m}^{-1}$ in ideal isolated conditions[513]. Graphene-based materials (GRMs) encompass a range of substances, including pristine graphene, graphene nanoplatelets (GNPs), and chemically modified structures like graphene oxide (GO). These materials offer diverse properties and applications due to their distinct chemical

compositions and structures. Researchers explore these GRMs for various purposes, capitalising on their unique characteristics[514]. The functional properties of polymer-based nanocomposites are significantly influenced by the morphological differences among graphene-based materials (GRMs) and pristine graphene. These variations impact how these materials interact within the composite, leading to tailored properties for specific applications. Researchers carefully consider these morphological distinctions when designing nanocomposites for diverse uses[515]. Graphene-t polymer-based nanocomposites, including graphene-epoxy and graphene-thermoplastic nanocomposites, exhibit remarkable strength and electrical conductivity. These materials have potential applications across various industries, such as aerospace and electronics, due to their enhanced properties. Ongoing research aims to further harness their capabilities for improved performance[16]. Graphene possesses high intrinsic thermal and electrical conductivity at room temperature, making it a promising material for various applications. Its exceptional properties open opportunities in industries like aerospace and electronics, where enhanced thermal and electrical performance is critical. Researchers continue to explore its potential in these areas[515]. The incorporation of thermally conducting fillers has enhanced the thermal conductivity of composites. Nevertheless, addressing thermal percolation remains a challenging issue in composite materials. This pertains to the challenge of achieving a continuous and efficient heat-conducting network within the composite, impacting its thermal performance[513]. It's important to note that in some research, it has been suggested that thermal percolation thresholds may not occur at all in certain composite materials. This implies that in these specific cases, the traditional concept of a percolation threshold for thermal conductivity may not apply. This phenomenon challenges conventional understanding and warrants further investigation[516]. Based on the previous scientific study, incorporating a small fraction of graphene fillers into epoxy composites can significantly enhance their electrical and thermal conductivity. This improvement is substantial, increasing the thermal conductivity from 0.2 W/mK to 2.2 W/mK, representing a remarkable 1000% (10^3 order) enhancement. This demonstrates

the remarkable potential of graphene fillers in improving the properties of epoxy composites[503,504]. Ongoing research is actively investigating composites with higher concentrations of graphene fillers to further explore their electrical and thermal properties. This research aims to push the boundaries of graphene-enhanced composites and uncover new possibilities for improving these materials[16,514,515]. The mixing conditions, often referred to as loading conditions, have a significant impact on enhancing thermal conductivity. These conditions influence the dispersion and interaction of fillers within the composite, ultimately affecting its thermal properties. This observation highlights the importance of optimising mixing processes for improved thermal conductivity in composites[517]. The aim of this research is to use theoretical and Bayesian statistical analysis to numerically assess the DC conductivity, dielectric properties, and thermal characteristics of Epoxy/GNP and Epoxy/ BaTiO₃ nanocomposites at varying filler content. This involves creating a geometric model with uniformly distributed nanofillers and applying static-electric current and heat transfer simulations using COMSOL Multiphysics® v5.5. The goal is to understand how these properties change with different filler concentrations[518,519]. The obtained data underwent Bayesian analysis to determine the sensitivity of the estimated values, which were also compared to existing literature when applicable. This approach helps assess the reliability of the results and ensures alignment with prior research efforts.

4.2 Literature review

Ongoing research endeavors are actively investigating the electrical and thermal properties of epoxy composites filled with graphene[520]. It has become evident that the conditions during the mixing process, often referred to as loading conditions, play a crucial role in enhancing thermal conductivity. Extensive prior research has focused on constructing a diverse range of epoxy composites and assessing their electrical conductivity. A compilation of such studies is presented in Tables 4-1 and 4-2 for reference.

Table 4-1. Electrical conductivity values of epoxy's nanocomposites obtained from various processes (MWCNT means: Multi walled carbon nanotube, GNP means graphene nanoplatelets and GO refers to graphene oxide).

“Resin material”	“Filler material”	Electrical conductivity (S/m)	Fabrication Process	Ref
Epoxy	1.0 wt% MWCNT	0.121	Three rolls mill	[512]
Epoxy	30 wt.% GNPs	0.161	Three rolls mill	[512]
Vinyl –ester	3.0 wt.% GNPs	2.93	Mechanical stirring and sonication	[508]
Epoxy	12 wt.% GNPs	23	Vacuum Assisted	[508]
Epoxy	24 wt.% GNPs	56	Vacuum Assisted	[508]
Natural Rubber	10 vol% GNPs	15	Magnetic stirrer	[510]
Epoxy	0.52 vol.%GNPs	0.05	Solution blending	[521]

Epoxy	0.16 vol.%GNP	10	Solution blending	[522]
Epoxy	0.12 vol.%rGO	1	Solution blending	[523]
Epoxy	0.78 vol.%f- GO	1	Solution blending	[524]

Table 4-2. Thermal conductivity value of various epoxy nanocomposites (GNP means graphene nanoplatelets).

“Resin material”	“Filler material”	Thermal conductivity (W/mk)	Processing	Ref.
Epoxy	10.0 vol% GNPs	0.7	-	[525]
Epoxy	21.8/21.8 vol% (GNPs/h- BaTiO ₃)	6.5	-	[513]
Epoxy	21.8/1 vol%	4.7	-	[513]

	(GNPs/h-BaTiO ₃)			
Epoxy	6.0 wt.% GNPs	10	-	[526]
Epoxy	4.0 wt.% GNPs	0.45	-	[527]
Epoxy	10.0 wt.% GNPs	0.7	Mapping	[528]
Epoxy	10.0 vol% GNPs	5.1	-	[18]
Epoxy	3.8 wt.% GNPs	1.6	-	[529]

Dielectric materials, capable of maintaining high dielectric field strength with minimal dielectric loss, are fundamental components in microelectronic device structures. They are crucial for enabling the proper functioning of electronic devices due to their ability to store electrical energy efficiently. These materials find extensive use in microelectronics and provide essential electrical insulation and energy storage properties[530]. However, their limited dielectric permittivity (ϵ) restricts their potential applications. This limitation arises from their relatively low capacity to store electrical energy efficiently. This factor impacts their usability in various electronic applications[281]. Enhancing dielectric permittivity in two-phase composite materials is desirable. However, increasing filler content for this purpose can compromise flexibility and other mechanical properties. This trade-off is a consideration in material design for specific applications[531]. Barium titanate (BaTiO₃) is a perovskite electro-ceramic nanomaterial known for its high

dielectric constant and electrical properties. Researchers have explored BaTiO₃-enhanced polymer nanocomposites, uncovering improved dielectric, piezoelectric, and ferroelectric characteristics[282]. Especially in compositions with exceptionally high BaTiO₃ content, these enhancements are particularly pronounced. Researchers have focused on such high-loading BaTiO₃ polymer nanocomposites[532]. Even with a lower BaTiO₃ content in the polymer composite, it can enable in-situ sensing to monitor the material's mechanical behaviour. This provides valuable insights into the composite's performance[533]. The dielectric permittivity of polymer composites containing ceramic fillers is typically influenced by increasing the ceramic nanomaterial content. This adjustment allows control over the composite's dielectric properties[532]. A summary drawn from the literature on the various values of dielectric constant of BaTiO₃/epoxy nanocomposites is summarised in Table 4-3.

Table 4-3. The dielectric constant of dielectric enhanced BaTiO₃/epoxy nanocomposites.

Resin	Fillers	Dielectric constant	The investigative method used	Ref.
Epoxy	0.3 vol% BaTiO ₃	210	Modeling	[534]
Epoxy	0.6 vol% BaTiO ₃ (particles size: 442nm)	65	Experimental	[535]

Epoxy	0.6vol% BaTiO ₃ (78nm)	25	Experimental	[242]
Epoxy	0.7 vol% BaTiO ₃ (Particle size: 160nm)	60	Modeling	[243]
Epoxy	0.6 vol% BaTiO ₃ (Particle size:1000 nm)	70	Modeling	[244]
Epoxy	5.0 wt.% BaTiO ₃ (not nano)	4.01	Experimental	[539]
Epoxy	10.0 wt.% BaTiO ₃ (not nano)	7.5	Experimental	[283]
Polydimethylsiloxane	0.43 vol% GNPs	11	Modelling	[540]

Epoxy	10.0 vol% BaTiO ₃ (not nano)	26	Experimental	[541]
Polyvinylidene fluoride	0.4 vol% BaTiO ₃ - Fe ₃ O ₄	140	Modelling and Experimental	[542]

In the realm of scientific research, numerical modeling using COMSOL Multiphysics is a favored method for predictive investigations involving a diverse range of scenarios. COMSOL employs a conventional physics-based interface to solve partial differential equations, making it a versatile tool. It has been effectively utilised in the past to explore capacitance and dielectric properties, showcasing its broad utility in scientific inquiry[543,544]. In scientific research, the distribution of the electric field within dielectric nanocomposites featuring a core-shell structure has been analysed using the phase-field modeling method. This approach helps answer why and how electric fields are distributed within these materials and where this phenomenon occurs. It complements the versatile capabilities of COMSOL Multiphysics in understanding complex physical processes for predictive investigations[545]. Continuing with scientific investigations, further studies have delved into the dielectric behaviour of spherical core and shell structures within core-shell configurations. These studies aim to understand why electric behaviour varies, how it occurs, and where it is observed within these intricate materials. This research complements the use of COMSOL Multiphysics and phase-field modeling to unravel complex physical phenomena in predictive scientific inquiries[546]. Currently, there is a noticeable gap in the existing literature regarding the investigation of the impact of filler materials like graphene and BaTiO₃ on epoxy nanocomposites. This represents a critical avenue for exploration, and it aligns with the COMSOL modeling

methodology described in the subsequent section, offering an opportunity to advance our understanding of these materials in scientific research.

4.3 Methodology

Epoxy-based nanocomposites have garnered significant attention in materials science due to their versatile properties. In this study, the focus is on the precise modeling and simulation of nanocomposites, specifically incorporating nanofillers such as graphene (GNP) and Barium Titanate (BaTiO_3). The objective is to gain insights into the influence of these fillers on the material's behaviour. A systematic methodology is employed, commencing with the development of accurate geometric models using SolidWorks®. To ensure the reliability of the simulations, several key assumptions were established:

Assuming defect-free and coherent bonding between the filler and epoxy material enables uniform dispersion and strong inter-particle attachment. The nanocomposite was assumed to possess homogenous and uniform filler dispersion, with all particles sharing identical sizes.

1. For ease of modeling and analysis, the filler particle size was considered to be spherical.
2. The nanocomposite geometry was treated as non-porous (continuum) and modeled to adhere to linear solid elastic materials compliance.

Crafted precise geometric models of the epoxy-based nanocomposites using SolidWorks®. The models depicted core-shell structures with varying filler content, as shown in Figure 4-1. Realism in simulations was attained by accurately assigning material properties to both the filler and epoxy matrix, meticulously selected based on experimental data and literature review. An optimal balance between computational resources and simulation accuracy was achieved through careful selection of mesh size and refinement level.

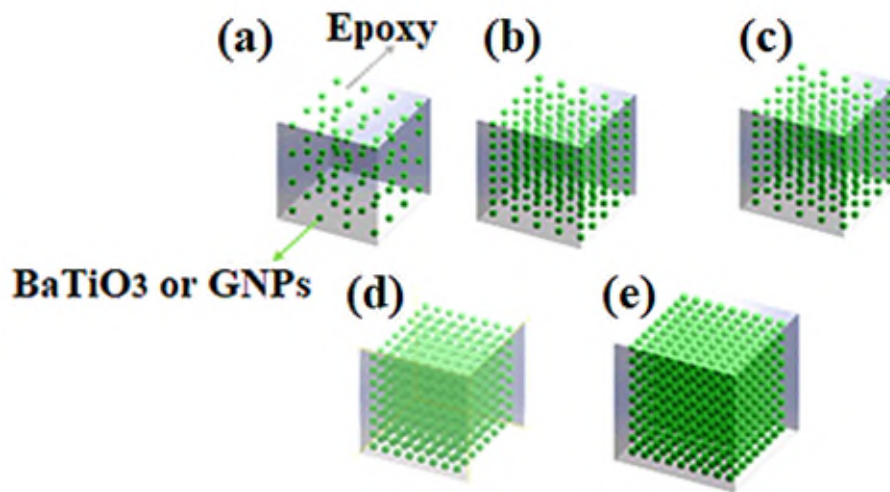


Figure 4-1. Model for GNP and BaTiO₃ embedded nanocomposite; a) 1.0 vol% b) 3.0 vol% , c) 5.0 vol%, d) 7.0 vol%, e) 10.0 vol%.

Geometric models were imported into COMSOL Multiphysics to configure simulations via its physics-based interface, solving partial differential equations. Real-world nanocomposite interactions were emulated through applied boundary conditions. Precision and convergence were ensured with rigorous solver settings, alongside sensitivity analyses. Simulations provided data on electric field distribution, dielectric properties, and other characteristics, informing filler influence on material behaviour. Findings were analysed within the context of our assumptions and modeling approach, offering insights into accuracy and implications. Deviations and limitations were acknowledged. This methodology provides a systematic framework for modeling and simulating epoxy-based nanocomposites with GNPs and BaTiO₃ fillers, laying the groundwork for deeper exploration of filler impacts on material properties.

4.4 Boundary conditions used to model electrical properties

This study focuses on assessing the DC conductivity of epoxy-based nanocomposites. To achieve this, electro-static analytical formulae rooted in Ohm's Law were utilised. The aim was to precisely measure the electrical behaviour of these nanocomposites. Electro-static analytical formulae based on Ohm's Law were utilised for measurements, ensuring accuracy in assessing the

electrical properties of the nanocomposites[547]. The electro-static physics was used in COMSOL Multiphysics 5.5's AC/DC module. This module facilitated precise modeling and simulations for understanding electrical behaviour, continuing the comprehensive approach to study filler material effects in epoxy-based nanocomposites. The DC conductivity was determined through a direct link between electrical conductivity and electric field, while the dielectric constant was measured by relating relative permittivity, dielectric constant, and electric field. This approach ensured accurate assessment of electrical properties in the study of epoxy-based nanocomposites, given by the following equations(4-1) to (4-4) [547].

$$\mathbf{J} = \sigma \mathbf{E} \quad (4-1)$$

$$\mathbf{E} = -\nabla V \quad (4-2)$$

where σ is the material's conductivity (fillers or matrix), $\mathbf{E}$, V , and $\mathbf{J}$ are the applied electric field vector, potential difference, and electric current density vector, respectively. The first equation (4-1) states that the electric current density is proportional to the electric field, with the proportionality constant being the electrical conductivity. The second equation (4-2) states that the electric field is equal to the negative gradient of the electric potential. The gradient operator ∇ is a vector operator that takes a scalar field and returns a vector field that points in the direction of the steepest ascent of the scalar field. In other words, the gradient of a scalar field tells how fast the scalar field is changing at a particular point. In the case of the electric potential, the gradient of the electric potential is the electric field. This means that the electric field points in the direction of the greatest increase in the electric potential. The magnitude of the electric field tells how fast the electric potential is changing. The equations $\mathbf{J}=\sigma\mathbf{E}$ and $\mathbf{E}=-\nabla V$ are used to describe the relationship between the electric current density, the electric field, and the electric potential in a conducting medium. These equations are used in many applications, such as the design of electrical circuits and the study of electromagnetic waves.

In the realm of materials science and electrical engineering, understanding the electrostatic properties of composite materials is crucial. This comprehensive guide outlines the step-by-step process of simulating the electrostatic behaviour of epoxy-based nanocomposites, particularly focusing on the incorporation of BaTiO₃ and GNPs (Graphene Nanoplatelets) as fillers. Utilising COMSOL Multiphysics, a powerful computational platform, Delving into electrostatic simulations, Figure 4-2 illustrates a schematic representation of the boundary conditions used in the electrostatic simulations of epoxy/ BaTiO₃ and epoxy/GNPs nanocomposites. Extensive optimisation efforts in previous work have identified the following as the most suitable boundary conditions:

- Fixed Reference Impedance of 50 Ohms: This boundary condition sets a constant reference impedance of 50 ohms on various faces within the simulation domain. It ensures consistency and stability in the electrostatic simulations, aiding in accurate results. These optimised boundary conditions play a pivotal role in ensuring the reliability and accuracy of the electrostatic simulations, allowing to gain valuable insights into the behaviour of these nanocomposite materials under various electrical scenarios.

The detailed description of the boundary conditions used in the electrostatic simulations of epoxy/ BaTiO₃ and epoxy/GNPs nanocomposites provides crucial insights into the simulation setup. Here's a breakdown of these boundary conditions:

- Insulation of Faces (Except Ground and Terminal): All faces of the composite material, except for the designated ground and terminal regions, were insulated using what is metaphorically referred to as "electrical tape. This insulation effectively isolates these faces from the electrostatic simulations, preventing the flow of electric current or voltage across them. Equation (4-3) represents this insulating condition, where 'n' represents a scalar variable that signifies the insulating state.

- Ground Boundary Condition (Terminal 2 - 0V): On one side of the composite element, a ground boundary condition was applied. This condition specifies that the electric potential at this side is set to 0 volts, creating a reference point for voltage measurements. This can also be referred to as "Terminal 2."
- Terminal Boundary Condition (Terminal 1 - 230V): On the opposite side of the composite element, a terminal boundary condition was employed. This condition applies an electric potential of 230 volts, establishing a potential difference across the composite. This can also be referred to as "Terminal 1."
- Steady-State Simulation (No Time Derivatives): The electrostatic simulations were conducted using the stationary equation. In a stationary simulation, the electric potential and field do not vary with time, making it a steady-state analysis. Consequently, no time derivative terms were employed in the simulation, as there were no time-dependent voltage fluctuations.

These boundary conditions and simulation choices are essential for accurately modeling the electrostatic behaviour of the nanocomposites, enabling researchers to study their electrical properties in a controlled and well-defined environment.

$$nJ = 0 \quad (4-3)$$

The simulation of the composite system's distributed capacitance using the COMSOL 5.5 Multiphysics dielectric constant model, as expressed by equation (4-4), is a critical aspect of understanding the electrical behaviour of epoxy-based nanocomposites. The term "distributed capacitance" refers to the capacitance distributed throughout the composite material, indicating how the material stores electrical charge when subjected to an electric field. To simulate this distributed capacitance, researchers utilise the dielectric constant model available in COMSOL 5.5 Multiphysics. Equation (3-4) represents the relationship between

electric displacement (D), relative permittivity (ϵ_r), electric field (E), and vacuum permittivity (ϵ_0).

$$D = \epsilon_0 \epsilon_r E \quad (4-4)$$

wherein E is the applied electric field, ϵ_r and ϵ_0 denote the relative permittivity of reinforcement or matrix, and vacuum permittivity. Electric displacement (D) signifies the ability of the material to store electrical charge in response to an applied electric field. Relative permittivity (ϵ_r) characterises how a material's ability to store charge compares to that of a vacuum. It provides insights into the material's dielectric properties. The electric field (E) represents the strength and direction of the applied electric field. Vacuum permittivity (ϵ_0) is a fundamental physical constant representing the permittivity of free space. By utilising this equation and the dielectric constant model within COMSOL 5.5, simulating and analysing how the composite material responds to changes in electric field strength and direction aids in gaining a comprehensive understanding of the material's behaviour, valuable in various applications, including electronics and materials science.

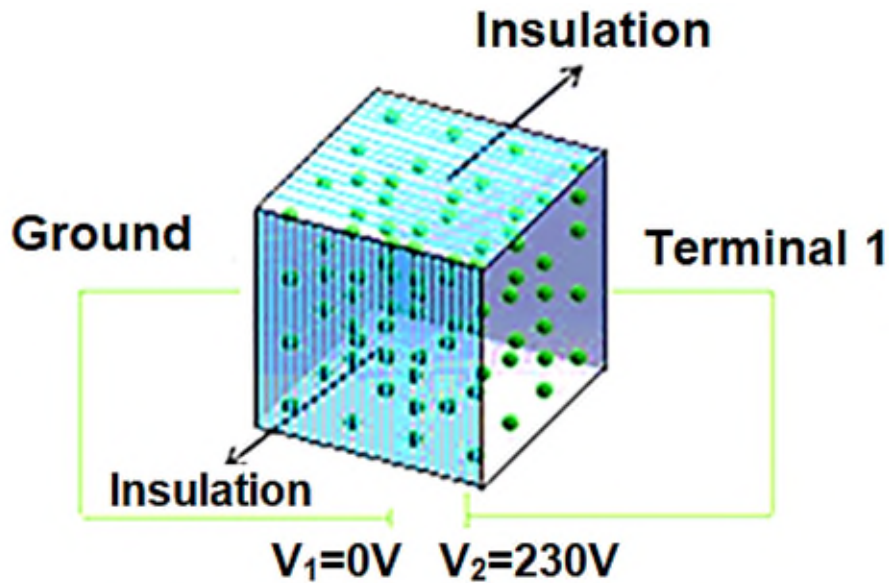


Figure 4-2. A free body diagram of the electrostatic simulation revealing the boundary conditions.

4.5 Optimising meshing for accurate simulations in Comsol

Multiphysics 5.5

Defining boundary conditions and selecting an appropriate mesh are pivotal steps in ensuring the precision and reliability of simulations conducted in COMSOL Multiphysics 5.5. Meshing, the process of discretising the simulation domain, plays a central role in numerically solving partial differential equations, thus mirroring real-world phenomena with precision. In the context of this study investigating epoxy-based nanocomposites, the meshing strategy employed was notable for its meticulous approach. Instead of treating the entire composite material as a single entity, a component-wise meshing strategy was employed, providing a higher degree of control and optimisation for each constituent of the composite. For the overarching simulation, a 3D-rectangular (tetrahedral) mesh with an extra fine grain was selected, characterised by its ability to effectively capture intricate geometries. The designation of "extra fine grain" referred to the mesh's level of detail or resolution, a crucial factor in obtaining accurate results. A finer mesh, while providing enhanced geometric fidelity, does entail increased computational demands. The choice of a 3D-rectangular tetrahedral mesh with an extra fine grain is a common practice in 3D simulations, as it strikes a balance between computational efficiency and precision. The "extra fine grain" ensures that the mesh accurately represents the geometric intricacies, facilitating precise modeling of electrical behaviour within the nanocomposite. It's worth noting that COMSOL Multiphysics 5.5 offers a range of meshing tools and options to cater to the diverse needs of researchers and engineers. This flexibility empowers users to tailor the meshing process to suit the specific demands of their simulations. Intriguingly, mesh sensitivity analyses revealed that variations in mesh size and type had a limited influence on the simulation outcomes. Properties under study exhibited minimal fluctuations when subjected to diverse mesh sizes and types, as illustrated in Figure 4-3. A pragmatic approach was adopted, utilising the average values of the studied features across different mesh types. Ultimately, the 3D-rectangular (tetrahedral) mesh with an extra fine grain was employed to finalise the simulation, consistent in delivering average

property values. This meticulous approach to meshing, guided by sensitivity analyses, underscores the commitment to achieving accurate and reliable simulation results in the exploration of epoxy-based nanocomposites. Leveraging advanced meshing techniques within COMSOL Multiphysics 5.5 ensures that simulations closely mirror the real-world behaviour of these materials, facilitating deeper insights and informed research directions.

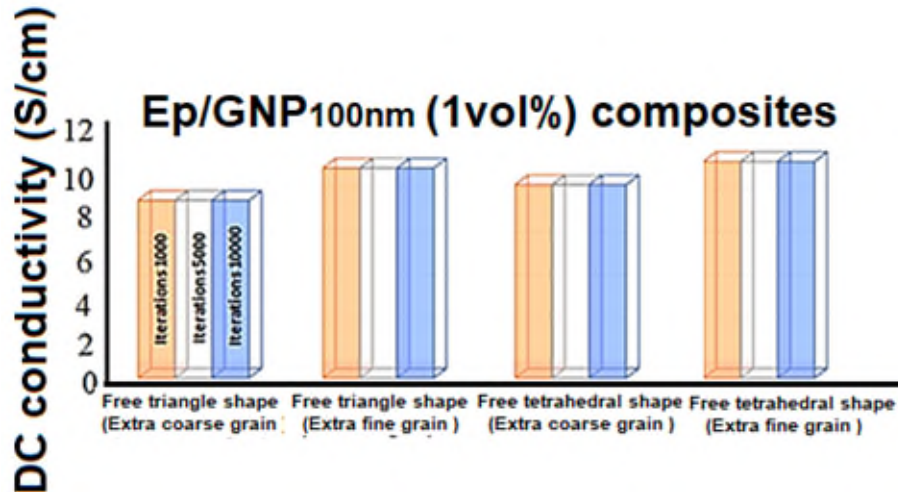


Figure 4-3. The DC conductivity of GNPs with thickness of (100 nm) and Epoxy (Ep) composites with various types of mesh and meshing grain size.

4.6 Boundary conditions used to model thermal properties

Temperature and electrical potential share a fundamental analogy in their ability to drive the flow of heat and electrical current, respectively. Just as a gradient in electrical potential induces the movement of electric charge (current), a gradient in temperature leads to the flow of heat. In the realm of heat transfer, this phenomenon is referred to as heat conduction, and it is governed by principles similar to those seen in electrical conductivity. In the context of simulation and modeling, COMSOL Multiphysics 5.5 offers the Heat Transfer Module, which serves as a valuable tool for studying essential heat transfer mechanisms. These mechanisms encompass not only conduction and convection but also radiative heat transfer. One of the fundamental equations used to describe temperature distribution within solid domains adheres to Fourier's law of heat conduction.

Mathematically, Fourier's law of heat conduction, as expressed in equation(4-5), describes how heat flux (q) is directly proportional to the temperature gradient (∇T) and the material's thermal conductivity (k). This relationship is a cornerstone of heat conduction analysis and provides insights into how heat flows within a continuous solid medium:

$$\mathbf{q} = -k\nabla T \quad (4-5)$$

In this equation, q represents the heat flux, denoting the rate of heat transfer per unit area. k stands for the thermal conductivity of the material, expressed in watts per meter per Kelvin ($W/(m \cdot K)$). ∇T symbolises the temperature gradient, indicating how temperature changes with position within the material. This equation essentially states that heat flows from regions of higher temperature to lower temperature, with the magnitude of heat transfer dependent on both the temperature gradient and the material's ability to conduct heat (thermal conductivity). Employing equations like Fourier's law of heat conduction within the Heat Transfer Module of COMSOL Multiphysics 5.5 aids in gaining valuable insights into heat conduction phenomena, benefiting the analysis and design of various thermal systems and processes.

The estimation of thermal properties within solids interfaces is a critical aspect of heat transfer analysis. This may be calculated using Equation (4-6) [259].

$$\rho c_p \mathbf{u}_{trans} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q \quad (4-6)$$

This equation (3-6) is derived from the principles of heat transfer and provides insights into how thermal properties are related. ρ represents the density of the material. C_p denotes the specific heat capacity of the material. U_{trans} refers to the transient term, indicating changes over time. ∇T represents the temperature gradient, indicating how temperature varies with position within the material. ∇q represents the divergence of the heat flux vector, which signifies how heat is spreading or converging within the material. Q represents any internal heat generation within the material. In essence, this equation captures the balance of thermal energy within a solid material. It considers how the material's density,

specific heat capacity, temperature gradients, and heat fluxes interact to determine the distribution of thermal energy. The first term on the left-hand side ($\rho_{cp} u_{trans} \cdot \nabla T$) accounts for the change in thermal energy due to the material's density, specific heat capacity, and transient effects. The second term on the left-hand side ($\nabla \cdot q$) captures how heat is transported within the material, whether it's spreading out (positive divergence) or converging (negative divergence). The right-hand side (Q) represents any internal heat generation within the material, which could result from various sources such as chemical reactions or external heating. By solving this equation within the context of COMSOL Multiphysics 5.5's

Figure 4-4 illustrates the boundary conditions applied in the heat transfer simulation, providing a visual representation of the simulation setup.

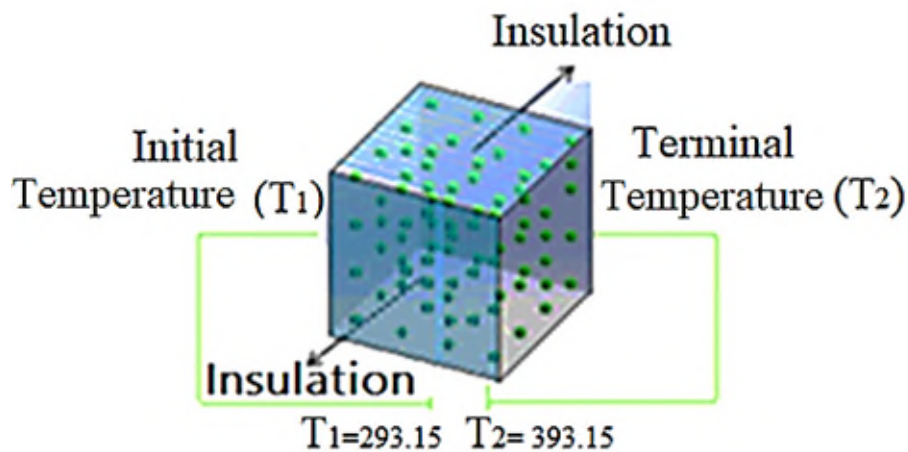


Figure 4-4. A free body diagram showing the boundary conditions used for heat transfer simulation.

Heat Transfer Module can be used to analyse how thermal properties impact heat transfer and temperature distribution within solid materials. This analysis is crucial for understanding and optimising the behaviour of thermal systems and materials in various applications, including electronics, materials science, and engineering. The heat transfer simulation involved several key parameters: specific heat capacity (C_p) in J/kgK, change in heat flow due to conduction (∇q) in W/m², and the translational motion velocity vector (u_{trans}) in m/s. Boundary conditions were set as follows: (a) a fixed reference temperature of 293.15 K; (b) thermal

insulation on all faces except the initial and terminal temperatures, with one side at 293.15 K (T_1) and the other at 393.15 K (T_2); (c) Heat transfer was governed by the stationary equation with the insulation condition represented as $nq=0$, where n is a scalar variable and q represents heat transfer.

4.7 Simulated DC conductivity of GNP embedded epoxy nanocomposite

In the realm of flexible electronics, carbon-based conductive nanofillers like graphene nanoplatelets (GNP) are gaining increasing attention due to their dual advantages of flexibility and low electrical resistance. In the simulation studies conducted, a diverse set of graphene compositions, including graphene oxide (GO), reduced graphene oxide (RGO), and various GNP variants with thicknesses ranging from 1000 nm down to 0.5 nm (GNP1000, GNP100, GNP10, GNP5, GNP1, GNP0.5), were strategically employed as nanofillers, integrated within the epoxy matrix (Ep). This comprehensive approach facilitated a meticulous examination of how diverse nanofiller types and dimensions influence the electrical characteristics of flexible electronic materials. The disparity among various types becomes evident when observing the finite element (FE) solutions. Figure 4-5 provides insights into the DC conductivity and dielectric constant of different GNP types and dimensions. These solutions encompass electrical conductivity and dielectric constant simulations for all graphene-based compositions, vividly illustrated in Figure 4-5a and b. Figure 4-5a illustrates the DC conductivity of epoxy, graphene oxide (GO), reduced graphene oxide, and various GNPs with thicknesses ranging from 1000 nm to 0.5 nm. Figure 4-5b illustrates the dielectric constant of epoxy, graphene oxide (GO), reduced graphene oxide, and GNPs. These visual representations help elucidate the electrical properties of these materials.

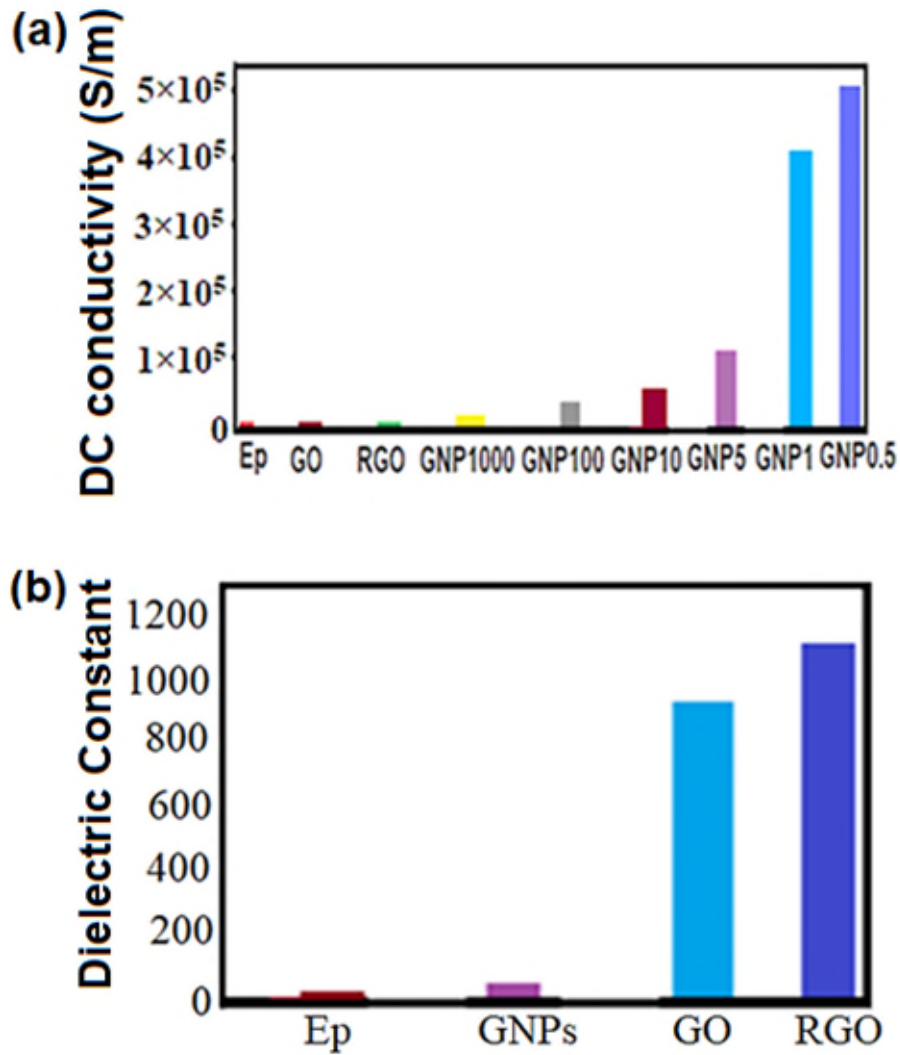


Figure 4-5. DC conductivity and dielectric constant of different GNP types and dimensions, (a) DC conductivity of epoxy, graphene oxide (GO), reduced graphene oxide, and various GNPs with thicknesses ranging from 1000 nm to 0.5 nm, (b) Dielectric constant of epoxy, graphene oxide (GO), reduced graphene oxide, and GNPs.

Figure 4-6a provides insight into the DC conductivity of epoxy/GO composites. These composites exhibit an increase in DC conductivity compared to neat epoxy. However, it's crucial to note that the DC conductivity of epoxy/GO composites remains relatively low. This is primarily due to the inherent poor electrical conductivity of graphene oxide (GO). Figure 4-6b delves into the DC

conductivity of composites that incorporate reduced graphene oxide (RGO) and graphene nanoplatelets (GNPs). These composites showcase substantially higher DC conductivity in comparison to both neat epoxy and epoxy/GO composites. This remarkable improvement can be attributed to the superior electrical conductivity properties of GNPs and RGO, which outperform GO in this aspect.

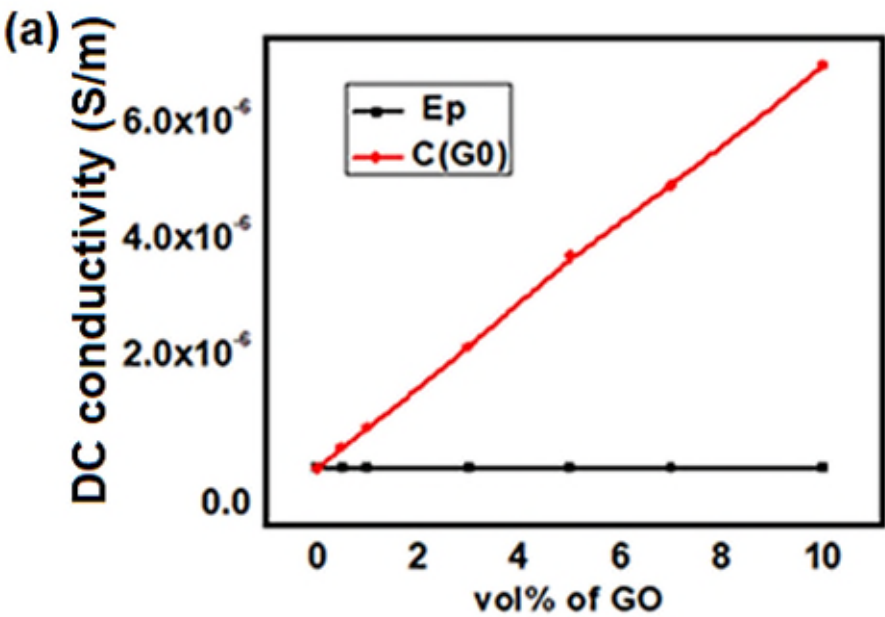
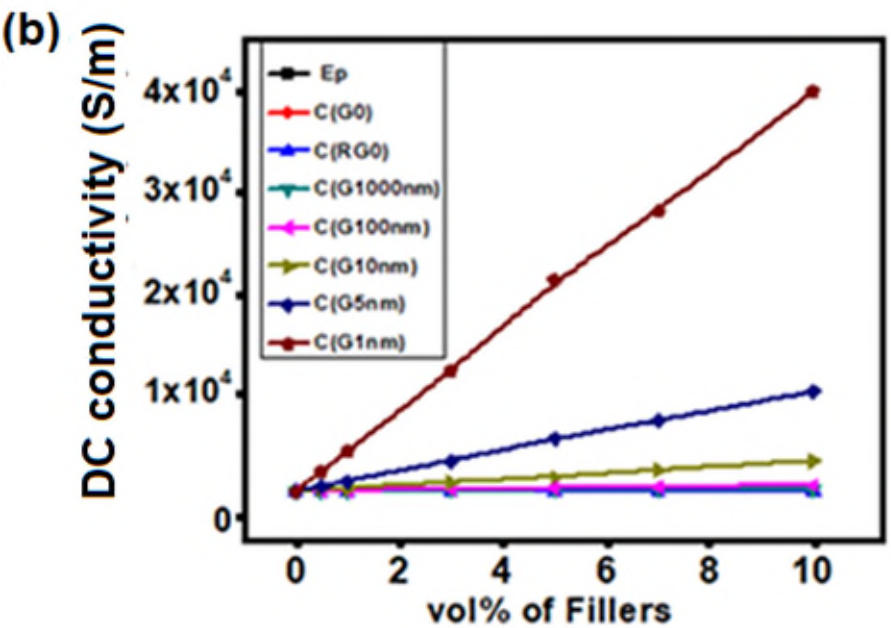


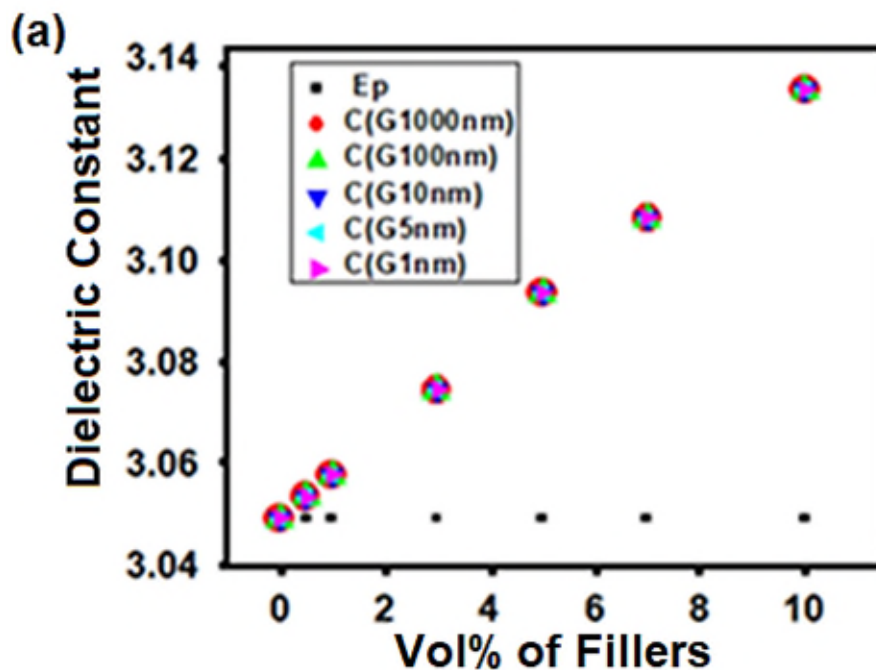
Figure 4-6. The COMSOL solution for DC conductivity of various GNPs/Epoxy composites: a) DC conductivity of neat epoxy and epoxy/graphene oxide (GO), b) DC conductivity of reduced graphene oxide and various GNPs with respect to thickness (1000nm(G1000nm), 100nm(G100nm), 10nm(G10nm), 5nm(G5nm), 1nm(G1nm)) composites.

Increasing the thickness of graphene nanoplatelets within epoxy composites leads to higher DC conductivity values. Among the different thicknesses tested, the most significant increase in DC conductivity is observed with 1 nm thick GNPs. The observation of higher conductivity in composites with thinner graphene layers, such as the 1 nm thick GNPs, indicates ballistic conductivity. Ballistic conductivity refers to a phenomenon where electrons experience minimal scattering during their movement, allowing for efficient electrical conduction. The overall conductivity in polymer composites, including these graphene-embedded epoxy nanocomposites, can be attributed to the tunneling mechanism of electrons. In this mechanism, the interconnected network of conductive fillers, such as GNPs and RGO, acts as a conduit for electron transport through the insulating epoxy matrix. This facilitates the efficient conduction of electricity within these composite materials. These findings highlight the critical role of nanofiller type, thickness, and the tunneling mechanism in determining the electrical properties of flexible electronic materials. By carefully selecting nanofillers and optimising their characteristics, researchers can tailor these materials for various applications in flexible electronics.

Figure 4-7 presents COMSOL simulation data for the dielectric constant of graphene-enhanced nanocomposites. This data is essential for comprehending the material's electrical characteristics and its suitability for electronic devices and flexible electronics applications. It offers insights into how the dielectric constant varies with different graphene types and proportions, aiding in material selection and optimisation for specific purposes. The dielectric constant (ϵ) quantifies a material's capacity to store electrical energy under an applied electric field. This property is essential for the function of capacitors, insulators, and various electronic components. It determines how efficiently a material can store

electrical charge, impacting the performance of electronic devices. The figure likely illustrates changes in the dielectric constant based on different graphene nanofiller types and concentrations. These insights are valuable for understanding material behaviour and its relevance in electrical engineering and electronics applications, aiding in the design and optimisation of electronic components. Figures 4-7a and b showcase the dielectric constant trend in composites as the proportion of different graphene types ranges from 0.2 to 10.0 vol%. This data reveals how the material's dielectric constant varies with different graphene content, providing valuable insights into its electrical characteristics and its applicability in various contexts within electrical engineering and electronics. Understanding how the dielectric constant responds to different graphene concentrations is crucial for optimising electronic components in diverse applications. Figure 4-7a depicts the dielectric constant of epoxy composites with varying thicknesses of graphene nanoplatelets (GNPs) from 1000nm to 1nm. This graph offers insights into how the dielectric constant changes with different GNP thicknesses, providing essential information about their electrical properties and potential applications in electronics. Figure 6(b) clearly demonstrates that all the reduced graphene oxide (RGO) samples exhibited a notable enhancement in the dielectric constant compared to other graphene-based nanocomposites with similar filler content, indicating RGO's superior dielectric properties in these composites. This figure underscores the significant influence of both graphene content and composition on the dielectric constant of the composites, primarily due to charge accumulation effects. This data provides crucial insights into tailoring electrical properties for specific applications. The data in Figure 4-7 emphasises that both graphene content and composition significantly influence the dielectric constant of composites due to charge accumulation effects. Interestingly, composites containing GNP-epoxy maintain consistent dielectric constants regardless of GNP thickness. Therefore, when selecting graphene for a polymer matrix, it's crucial to consider both the graphene type's dielectric characteristics and the thickness of graphene nanoplatelets (GNPs) to achieve the desired electrical properties for specific applications. This insight aids in tailoring materials for optimal electrical

performance. The enhanced dielectric constant in reduced graphene oxide (RGO) samples, compared to other graphene-based nanocomposites with similar filler content, can be attributed to several factors. RGO has fewer oxygen-containing functional groups and defects compared to graphene oxide (GO). These defects in GO can lead to a higher dielectric constant due to charge trapping and scattering. This insight aids in understanding the improved dielectric properties of RGO and its suitability for specific applications. In RGO, the reduction process eliminates some defects, contributing to improved dielectric properties. RGO typically boasts higher charge carrier mobility than other graphene-based materials, enabling more unrestricted charge movement within the material and resulting in a more favourable dielectric response. This information clarifies the advantageous dielectric characteristics of RGO in electronic applications.



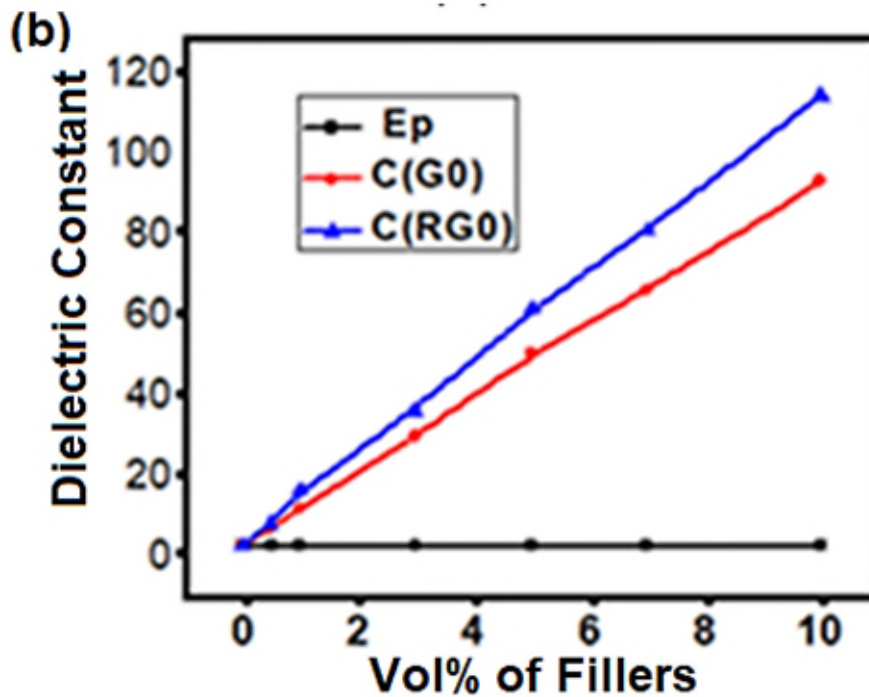
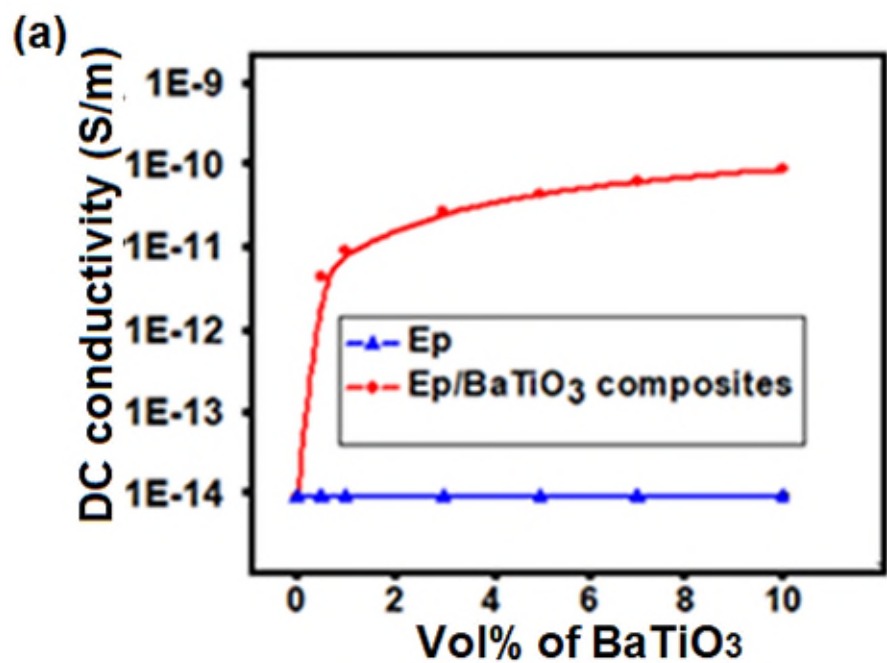
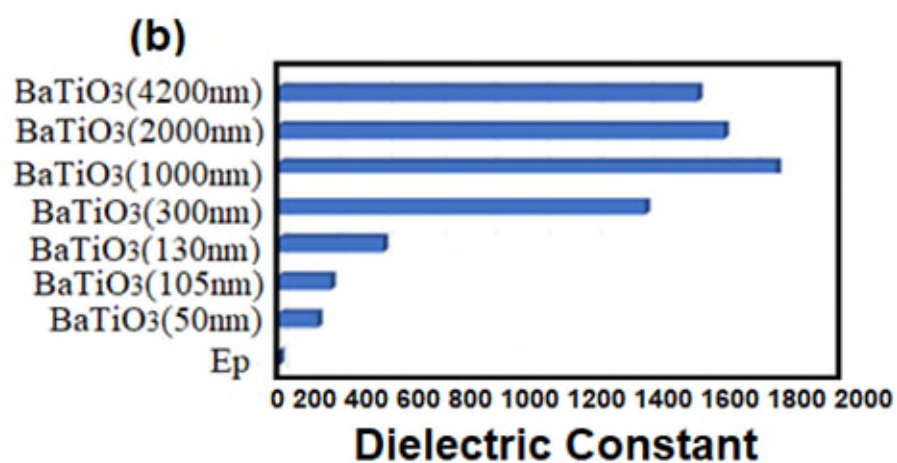


Figure 4-7. The COMSOL solution for the dielectric constant of a) epoxy/ various GNPs with respect to thickness (1000nm, 100nm, 10nm, 5nm, 1nm) nanocomposites, b) epoxy/ graphene oxide (GO), reduced graphene oxide composites.

Enhanced structural integrity and fewer defects in RGO foster better interactions with the polymer matrix, promoting a uniform dispersion of graphene fillers and minimising charge traps, ultimately improving dielectric properties. The selection of graphene type and thickness can impact the dielectric constant, with thinner layers sometimes displaying distinct behaviours linked to quantum confinement effects or charge accumulation at interfaces. This insight underscores the importance of careful graphene selection for tailored dielectric characteristics in electronic applications. The specific composition and thickness of RGO chosen for the study were likely optimal for enhancing the dielectric constant. The improvement in RGO-based nanocomposites' dielectric constant results from reduced defects, enhanced charge mobility, improved filler-matrix interactions, and RGO's intrinsic properties. Together, these factors collectively contribute to the enhanced dielectric performance observed in the study, highlighting the multifaceted nature of this improvement.

4.8 Simulated DC conductivity of BaTiO₃/epoxy nanocomposite

This section provides an in-depth analysis of simulated results for the DC conductivity and dielectric constant of epoxy/ BaTiO₃ nanocomposites. The central objective is to investigate the influence of incorporating BaTiO₃ filler material on the electrical characteristics of these composites. This exploration aids in comprehending the materials' behaviour in electronic applications. Figure 4-8(a) visually illustrates the electrical conductivity of two significant materials: neat epoxy and epoxy composites with varying BaTiO₃ concentrations. Notably, an increase in the BaTiO₃ filler content leads to a corresponding increase in the electrical conductivity of the BaTiO₃-epoxy composites. This trend is crucial for understanding the impact of BaTiO₃ on electrical behaviour in these composites, particularly in electronic applications. The observed phenomenon is critical, indicating the formation of conductive pathways within the composite material attributed to BaTiO₃. As a result, the electrical conductivity of epoxy/ BaTiO₃ composites surpasses that of pure epoxy. However, it's essential to consider the absolute values of electrical conductivity for a comprehensive understanding of their significance in practical applications. Both neat epoxy and BaTiO₃ exhibit notably low electrical conductivity when compared to other conducting nanofillers. Neat epoxy demonstrates an electrical conductivity on the order of 1.0×10^{-14} s/m, whereas BaTiO₃ exhibits even lower electrical conductivity, approximately 1.0×10^{-9} s/m. These values highlight the relatively insulating nature of both materials in their pure forms. The notable improvement in electrical conductivity in epoxy/ BaTiO₃ composites is primarily attributed to the presence of BaTiO₃ filler material, despite its initially low conductivity. This observation highlights the intricate interplay between filler content and electrical properties within these nanocomposites, providing valuable insights for their design and optimisation in diverse electronic applications. These findings emphasise the transformative role of fillers in enhancing the electrical behaviour of composite materials.



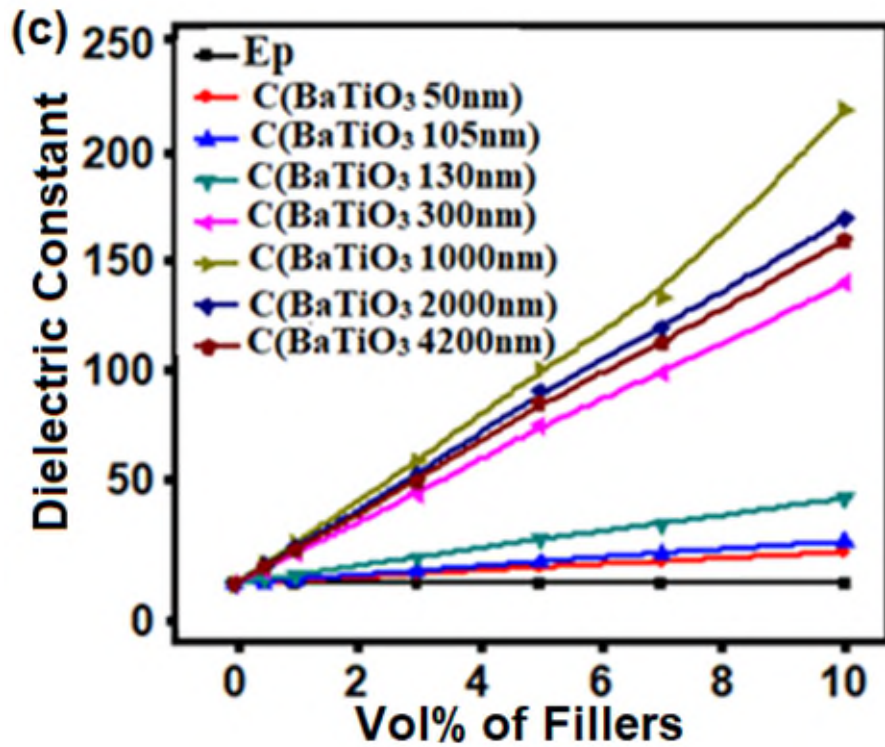


Figure 4-8. a) DC conductivity of BaTiO₃/Epoxy composites compared with pure epoxy, b) Dielectric constant of various BaTiO₃ with respect to the various particle diameters of BaTiO₃ (50nm, 105 nm, 130 nm, 300 nm, 1000 nm, 2000nm, 4200 nm), c) Dielectric constant of various BaTiO₃/ Epoxy composites in various filler percentages.

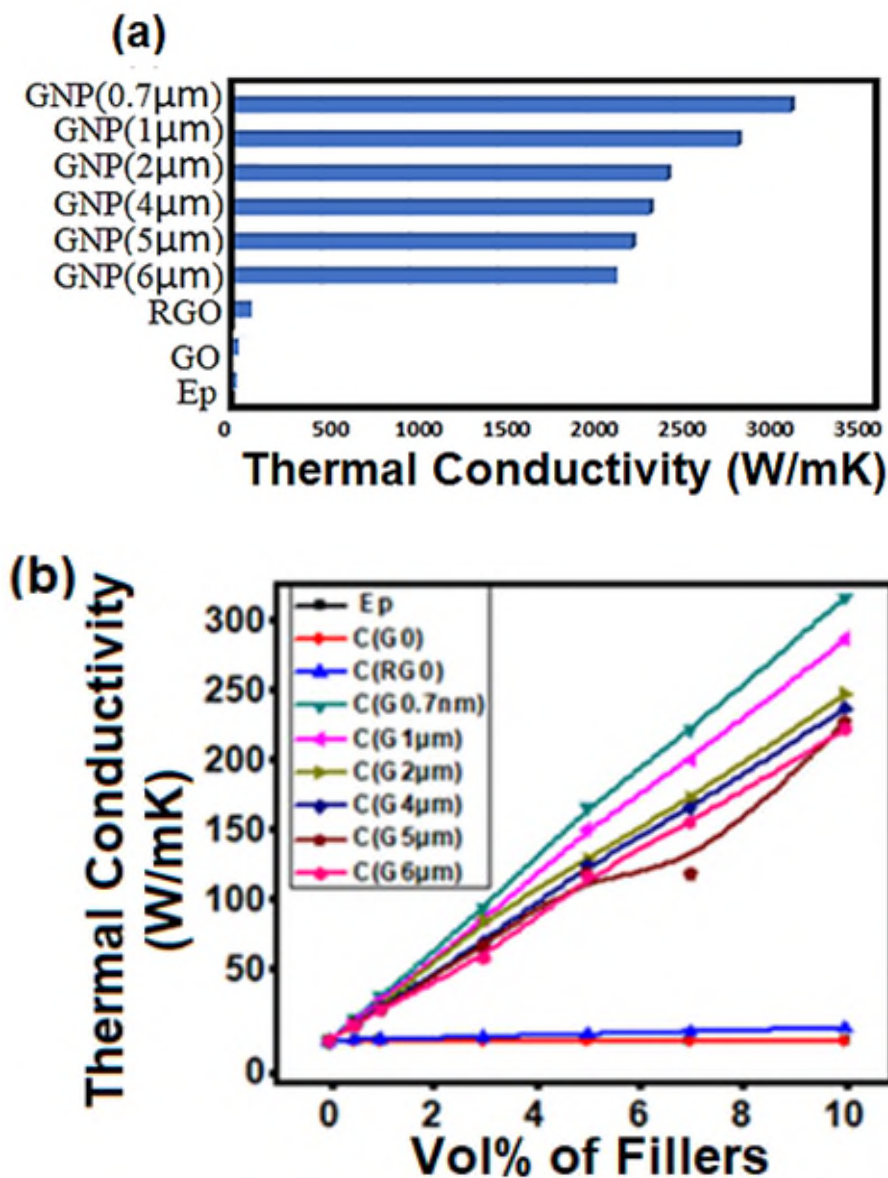
The data in Figure 4-8(b) highlights the connection between the dielectric constant and the crystal structure of BaTiO₃, particularly in particles with varying diameters. This relationship is attributed to lattice expansion as particle size decreases, impacting the dielectric behaviour. These insights offer valuable information about how particle size and crystal structure influence the dielectric properties of BaTiO₃, essential for understanding charge storage mechanisms in BaTiO₃-epoxy composites within electronic applications. These insights are crucial for comprehending how particle size and crystal structure influence the dielectric behaviour of BaTiO₃ in electronic applications. BaTiO₃, serving as a dielectric material, possesses dielectric properties and the capacity to store electric charge within the polymer matrix. This information aids in understanding the charge storage capabilities of BaTiO₃-epoxy composites in the presence of

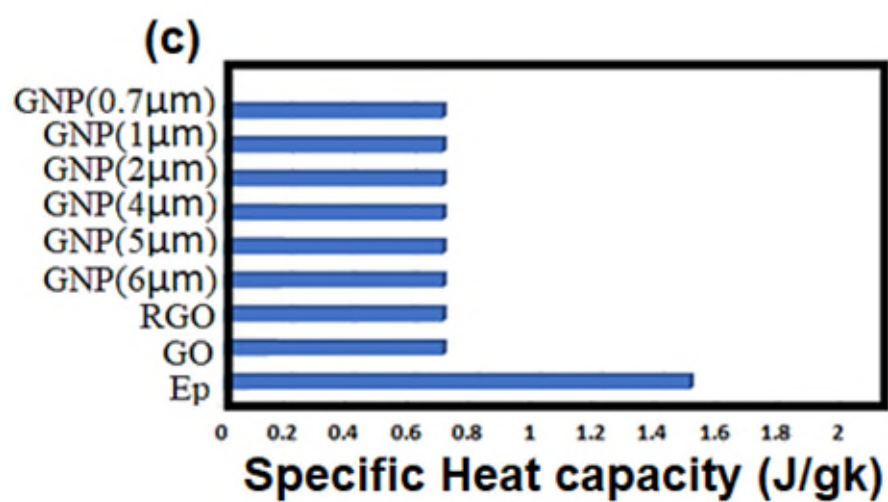
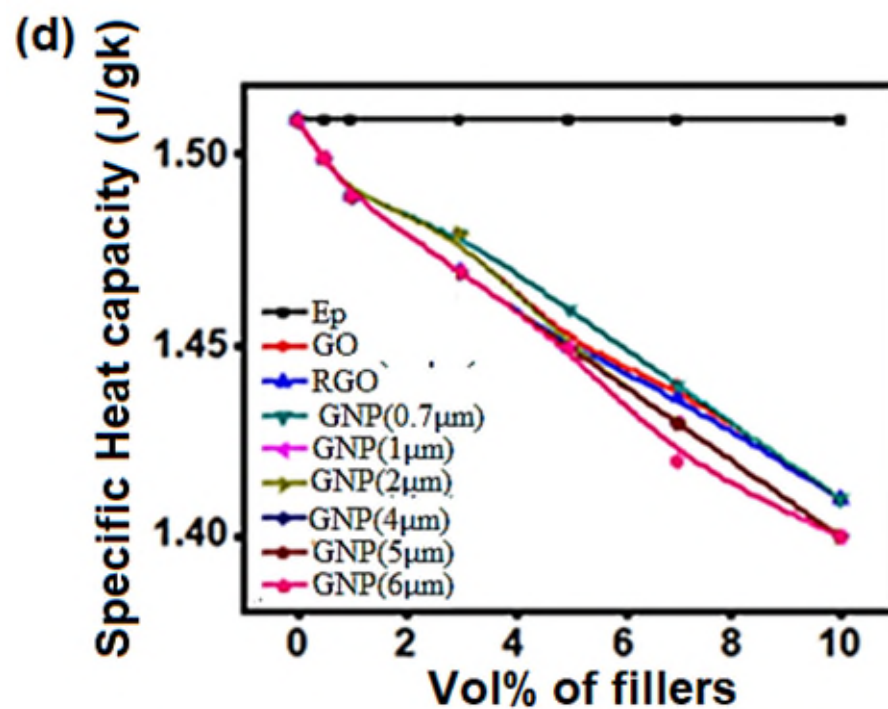
an external electric field in electronic applications. The dielectric constant is crucial for assessing the charge storage capacity of BaTiO₃-epoxy composites in the presence of an external electric field, especially in electronic devices relying on dielectric materials for energy storage and charge management. The relationship between dielectric constant and crystal structure in Figure 4-8(b) provides valuable insights into how BaTiO₃'s charge storage capability varies with particle size, guiding material design for specific electronic applications and capacitors. These findings provide essential insights into how particle size and crystal structure affect BaTiO₃'s dielectric behaviour. Such understanding is vital for comprehending the mechanisms of charge storage in BaTiO₃-epoxy composites, especially in electronic applications. The consistent increase in the dielectric constant across different BaTiO₃ particle diameters in Figure 4-8(c) suggests that BaTiO₃-epoxy composites consistently exhibit higher dielectric constants than neat epoxy. This improvement is primarily due to the inclusion of BaTiO₃, enhancing the charge storage capacity of these composites, making them valuable for applications requiring efficient dielectric materials. Understanding this behaviour is crucial for designing electronic components and capacitors with enhanced charge storage capabilities. Therefore, BaTiO₃-epoxy composites are ideal for applications requiring elevated dielectric constants, including capacitors and energy storage devices. These results emphasise the vital role of BaTiO₃ as a dielectric material in enhancing the electrical characteristics of composites, making them valuable for a wide range of electronic applications. Understanding this significance is crucial for optimising materials in the design of advanced electronic components. The improvement in the dielectric constant of BaTiO₃-epoxy nanocomposites is attributed to dipole alignment, primarily at the epoxy-BaTiO₃ interface. This alignment leads to a higher dielectric constant due to the accumulation of free charges at the interface, enhancing the electrical properties of these composites.

4.9 Simulated thermal conductivity of GNPs embedded epoxy nanocomposite

The thermal conductivity of nanocomposites is influenced by filler structure, quantity, and thermal properties. Figure 4-9a displays the thermal conductivity of various GNPs and neat epoxy, while Figure 4-9b presents the resulting thermal conductivity of graphene/epoxy nanocomposites. Notably, GNP0.5/epoxy nanocomposites exhibit the highest thermal conductivity, with GO, RGO, and epoxy showing lower values compared to graphene nanoplatelets. This variation is attributed to differences in filler properties and loading quantities, affecting thermal conductivity in these materials. The increase in thermal conductivity with a higher volume fraction of graphene is attributed to the various states of graphene and the thickness of graphene nanoplatelets. These findings reveal a consistent trend in thermal conductivity within epoxy composites as a response to different structural variations in graphene. Additionally, an overall increase in thermal conductivity with rising filler content in graphene/epoxy nanocomposites is observed across all cases. This behaviour highlights the impact of graphene content on thermal conductivity in these materials. These results confirm the significant influence of structural changes and nanoscale properties on thermal conductivity. Nanoscale effects, such as ballistic conductivity, contribute to the enhanced thermal conductivity at this level. Ballistic conductivity reduces heat loss during conduction by minimising phonon vibration scattering at the nanoscale, resulting in higher thermal conductivity. This sensitivity to structural transformations and nanoscale characteristics is essential for understanding and optimising thermal properties in nanocomposite materials. The simulation framework also allowed for the extraction of specific heat capacity data for various materials, as shown in Figure 4-9c. Specific heat capacity represents the heat required to change the material's temperature by one degree. Figure 4-9d displays the specific heat capacity of nanocomposites containing different graphene types compared to pure epoxy, with respect to the thickness of graphene nanoplatelets. The data reveals that as the graphene filler content varies from 0.2% to 10.0 vol%, the specific heat capacity decreases. Graphene-based composites exhibit lower specific heat capacity compared to neat epoxy, indicating that graphene influences the composite's specific heat capacity and results in faster temperature rise due to its lower specific heat and excellent

thermal conductivity. Figure 4-9e presents changes in thermal diffusivity across various composite types simulated. Generally, thermal diffusivity decreases with increasing filler content. However, composite samples containing graphene with different thicknesses and epoxy show an increasing trend in thermal diffusivity with higher filler content. This indicates that greater thermal diffusivity results from the larger mean free path of phonon-phonon interactions, influenced by the mean free path, thermal conductivity, and specific heat of the nanofillers.





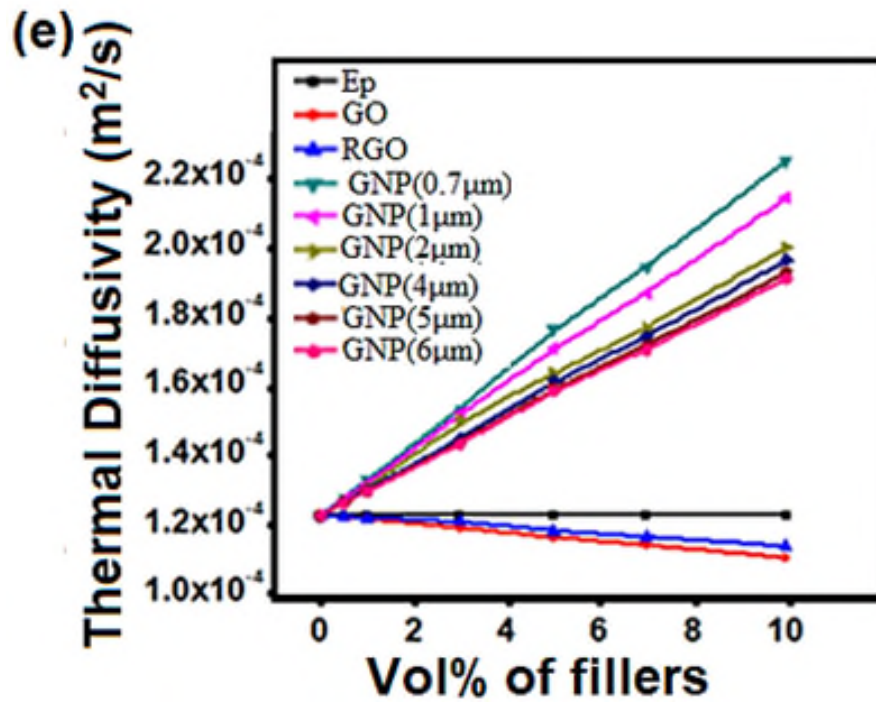
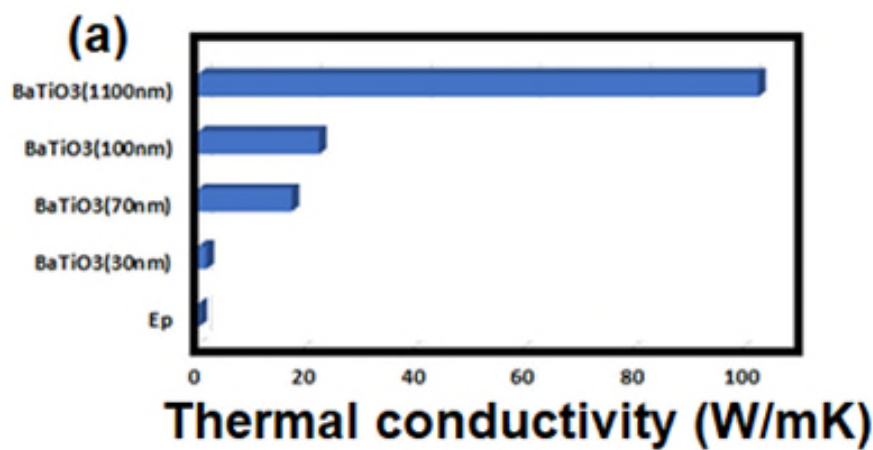
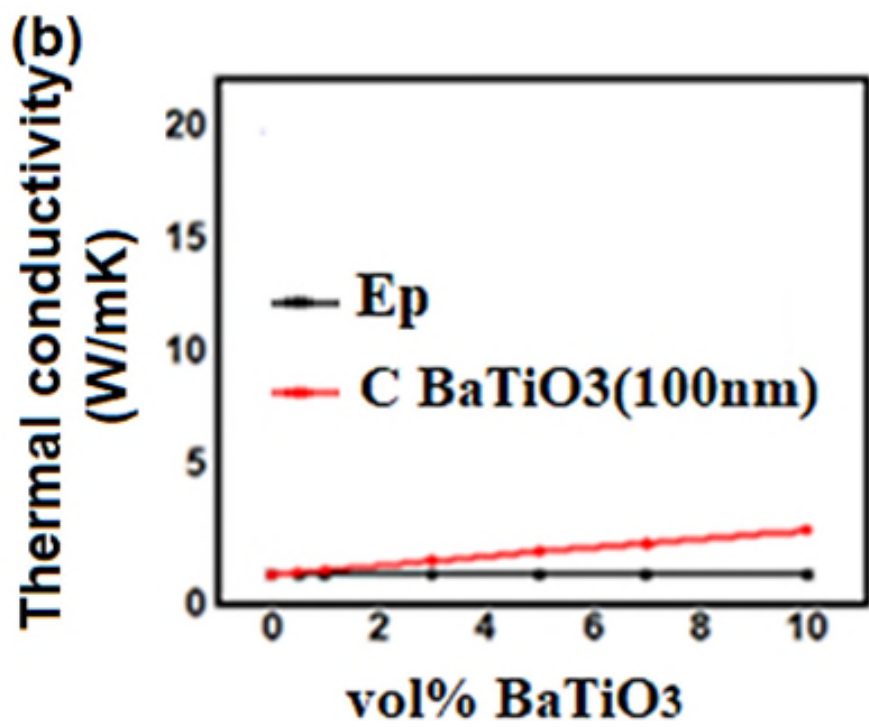


Figure 4-9. Thermal properties of various GNPs/Epoxy composites: a) Thermal conductivity of graphene oxide (GO), reduced graphene oxide and various GNPs concerning thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm) composites, b) Thermal conductivity of epoxy/ graphene oxide (GO), reduced graphene oxide and various GNPs with respect to thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000nm)/ epoxy composites, c) Specific heat capacity of graphene oxide (GO), reduced graphene oxide and various GNPs with respect to thickness (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm), d) Specific heat capacity of epoxy/graphene oxide (GO), reduced graphene oxide and various GNPs with respect to the thickness in nm (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm)/ epoxy composites, e) Thermal diffusivity of epoxy/ graphene oxide (GO), reduced graphene oxide and various GNPs with respect to the thickness in nm (0.7 nm, 1000 nm, 2000 nm, 4000 nm, 5000 nm, 6000 nm)/ epoxy composites.

4.10 Simulated thermal conductivity of BaTiO₃/epoxy nanocomposites

The relationship between thermal conductivity, thermal diffusivity, and specific heat capacity is such that reducing thermal diffusivity leads to an increase in thermal conductivity. This phenomenon is important for understanding how materials conduct and transfer heat, impacting their suitability for various applications that require specific thermal properties. Thermal diffusivity is a material property that describes how quickly heat can travel through a substance. It is a measure of how well a material conducts heat in relation to how quickly it can respond to changes in temperature. In mathematical terms, thermal diffusivity is calculated as the ratio of a material's thermal conductivity (its ability to conduct heat) to its heat capacity (its ability to store heat). A higher thermal diffusivity indicates that heat can propagate through the material more rapidly. It's a key parameter in understanding heat transfer and thermal behaviour in various materials and systems. Figure 4-10 illustrates how the thermal conductivity of BaTiO₃ and BaTiO₃/epoxy composites varies with changes in the diameter of BaTiO₃ particles. This data provides insights into how particle size influences thermal conductivity, which is crucial for understanding heat transfer properties in these materials. The relationship between particle size and thermal conductivity in BaTiO₃ composites is significant for applications where heat management and conductivity are important factors. Figure 4-10 confirms that the diameter of BaTiO₃ particles plays a role in altering thermal conductivity, with larger particles contributing to improved thermal conductivity. This observation highlights the impact of particle size on heat transfer properties in BaTiO₃ composites. It suggests that by manipulating particle size, thermal conductivity can be tailored for specific applications where efficient heat transfer is essential. Increasing the volume fraction of BaTiO₃ enhances the thermal conductivity of BaTiO₃/epoxy composites. Figure 4-10a presents the thermal conductivity of BaTiO₃ with different particle diameters. This information illustrates the potential for improving heat transfer properties in composite materials by adjusting the volume of BaTiO₃ fillers. Figure 4-10b-c highlights the influence of BaTiO₃ particle diameter on the thermal conductivity of BaTiO₃/epoxy composites. An increase in the diameter of BaTiO₃ particles correlates with improved thermal conductivity in these simulated composites. This information underscores the importance of

particle size control in optimising the thermal properties of BaTiO₃/epoxy composites for heat management applications. Increasing both the proportion and size of BaTiO₃ particle in epoxy composites has been found to enhance thermal conductivity. The improvement in thermal conductivity is linked to the uniform network of BaTiO₃ particles within the composites, facilitating efficient heat transfer. BaTiO₃ nanoplatelets come in various sizes, influencing their properties and potential uses. Smaller nanoplatelets may display distinct dielectric and piezoelectric behaviours compared to larger ones, which can affect their suitability for specific applications requiring tailored thermal properties.



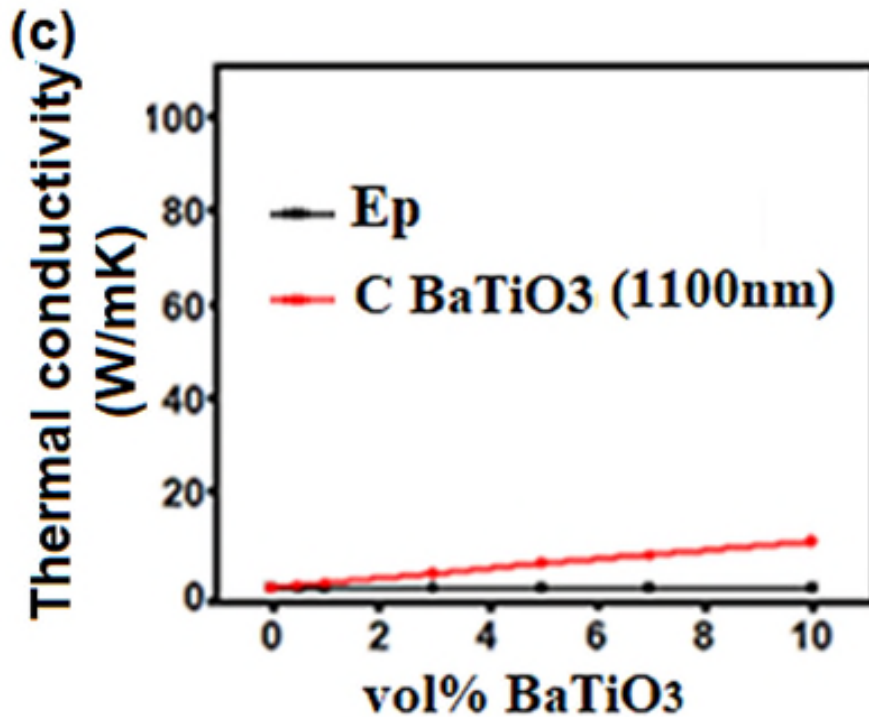
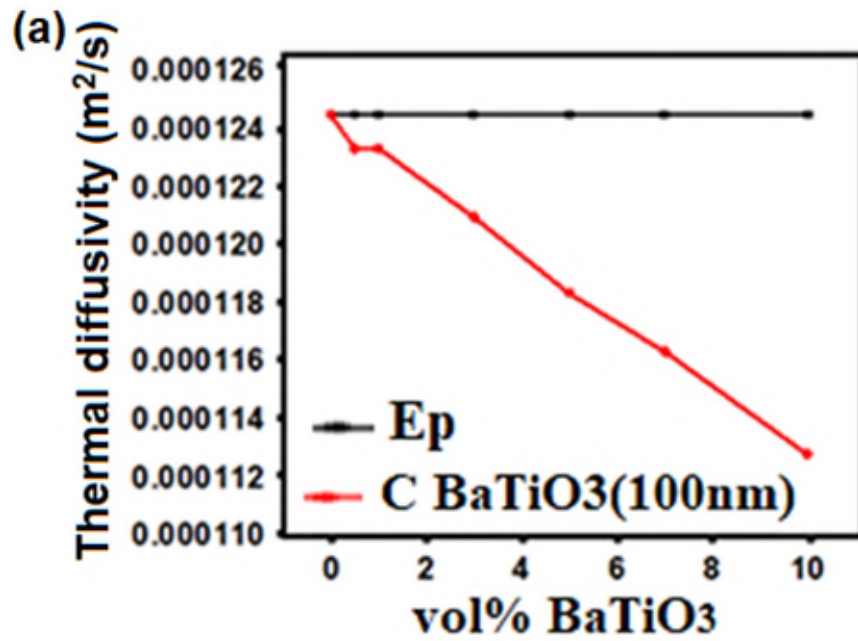
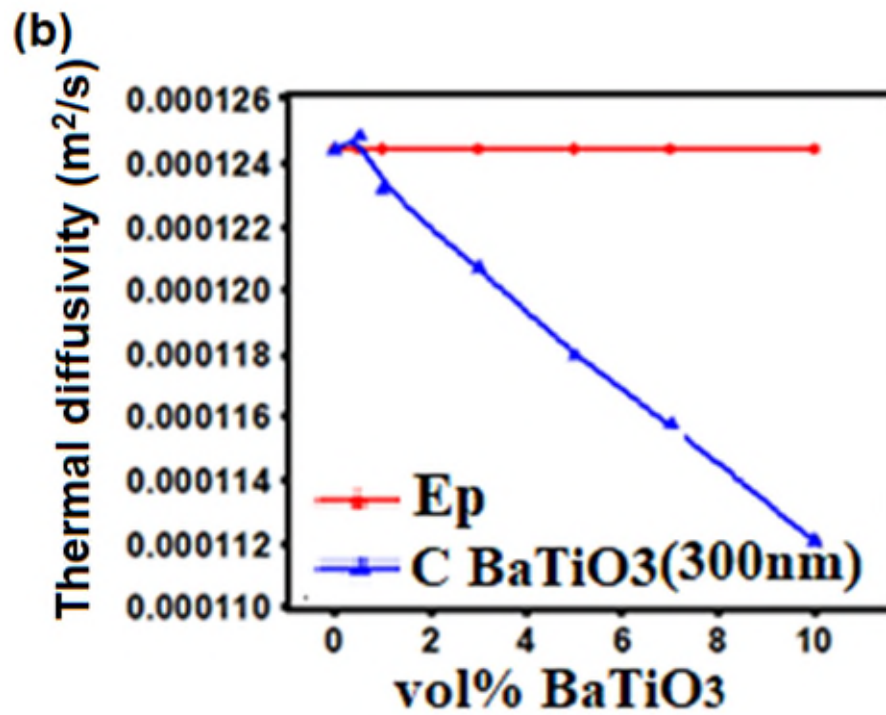


Figure 4-10. Thermal conductivity of BaTiO₃/Epoxy composites: a) Thermal conductivity of composites having various BaTiO₃ diameter (300 nm, 70 nm, 100 nm, 1100 nm) b) Thermal conductivity of BaTiO₃ with respect to diameter 100 nm, c) Thermal conductivity of BaTiO₃ with respect to diameter 70 nm.

Figures 4-11a-c illustrate changes in thermal diffusivity for BaTiO₃/epoxy composites with varying filler materials. The decreasing thermal diffusivity trend from lower to higher diameter BaTiO₃ and within epoxy/ BaTiO₃ composites can be attributed to the larger mean free path of phonon-phonon interactions in higher diameter BaTiO₃ particles and the resulting attenuation of heat transfer within the composite. This reflects the impact of particle size on thermal properties, influencing heat transfer efficiency in these materials. The decrease in thermal diffusivity with rising filler volume is attributed to the increased mean free path of phonons within the material. This phenomenon highlights the refractory or heat-resistant characteristics of BaTiO₃, indicating that as more BaTiO₃ is added, the

material becomes less efficient at conducting heat due to reduced phonon scattering.



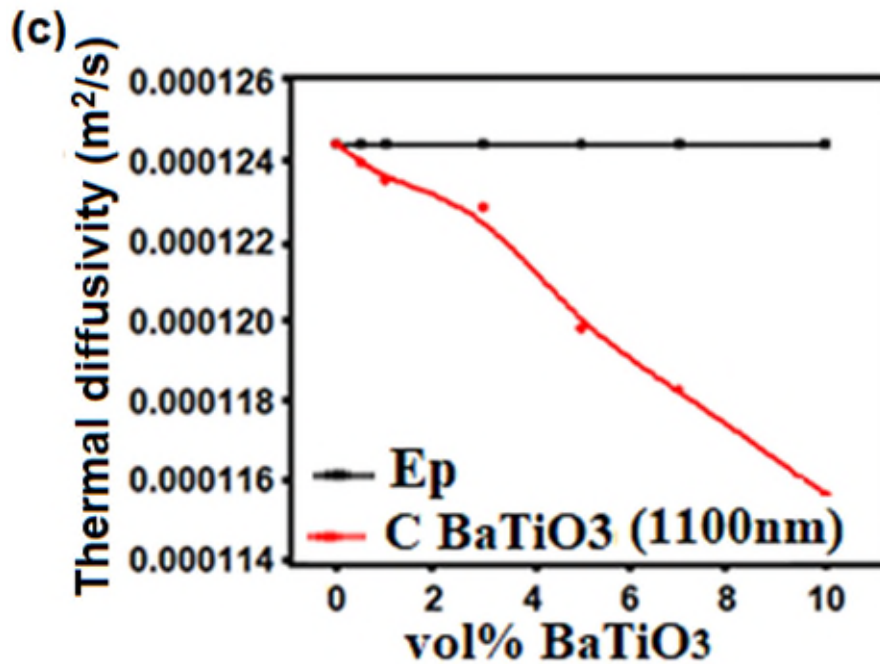


Figure 4-11. a) Thermal diffusivity of epoxy and epoxy/ BaTiO₃ (100 nm diameter) composites, b) Thermal diffusivity of epoxy and epoxy/ BaTiO₃ (300 nm diameter) composites, c) Thermal diffusivity of epoxy and epoxy/ BaTiO₃ (1100nm diameter) composites.

4.11 Relationship of simulated results by Bayesian analysis

Bayesian analysis, employed in academic research, seeks to comprehend dataset connections by modeling uncertainty and updating beliefs with new data. This approach unveils patterns and relationships within the data, contributing to informed decision-making across various scientific domains. Bayesian methods enhance research and industry applications through probabilistic modeling and inference. This approach, crucial for diverse scientific studies, aims to uncover insights by comprehending interrelationships in results. Its objective is to aid informed decision-making by revealing meaningful connections within datasets. Bayesian analysis is applied in academic research to enhance understanding and contribute to scientific investigations across various domains, using probabilistic modeling and inference. In this context, Bayesian analysis is a powerful tool for

uncovering crucial relationships within complex datasets, offering valuable insights for research, industry, and decision support. Its application adapts to scientific objectives, often utilising probabilistic modeling and inference to derive meaningful conclusions from data. This approach significantly enhances a wide range of scientific investigations.

Bayes' theorem is fundamental, linking conditional probability density functions and essential in Bayesian statistical inference. It calculates updated distributions with prior knowledge. In Finite Element (FE) analysis, Bayesian methods advance the field, particularly in reliability applications, enhancing theory and implementation for informed decision-making in research and industry. They're also valuable in studying deterioration behaviour in laser life tests, offering a more accurate reliability assessment by combining prior information with observed data[549]. Bayesian techniques have been applied to address probabilistic risk problems and evaluate the reliability of complex systems. This approach accounts for uncertainties and provides a more comprehensive understanding of system performance [550]. Bayesian analysis is valuable in accelerated testing scenarios where data may be limited. It aids in making predictions about the reliability of systems under various conditions [551]. Bayes' theorem, as expressed in equation (4-7):

$$P\left(\frac{A}{B}\right) = \frac{P(A)P(B/A)}{P(B)} \quad (4-7)$$

is a powerful tool for updating probabilities when certain information is known. It facilitates informed decision-making and enhances the accuracy of predictions in various fields, including reliability analysis and risk assessment. In Bayes' theorem, the terms $P\left(\frac{A}{B}\right)$, $P(A)$, $P(B/A)$, and $P(B)$ represent different probabilities and conditional probabilities. $P\left(\frac{A}{B}\right)$ represents the posterior probability. It is the probability of event (A) occurring given that event (B) has occurred. In other words, it tells us the updated probability of (A) based on new information provided by (B). $P(A)$ is the prior probability of event (A). It represents our initial belief or probability assessment for event (A) before considering any new information from

event (B). $P\left(\frac{B}{A}\right)$ is the likelihood. It represents the probability of event (B) occurring given that event (A) has occurred. It quantifies how well event (A) explains or predicts event (B). $P(B)$ is the marginal probability or the probability of event (B) occurring without any conditions. It is the overall probability of event (B) and serves as a normalising factor to ensure that the posterior probability ($P(A|B)$) is a valid probability distribution. In Bayesian inference, the goal is often to update our beliefs (the prior probability $P(A)$ based on new evidence or data (the likelihood $P\left(\frac{B}{A}\right)$ to obtain a more informed or updated belief (the posterior probability $P\left(\frac{A}{B}\right)$). Bayes' theorem provides a formal framework for making this update while considering the overall probability of the new evidence $P(B)$. Equations (4-7) and (4-8) are part of Bayes' theorem, which is a fundamental concept in probability theory and statistical inference. These equations describe conditional probability, where the probability of one event occurring is calculated given that another event has already occurred. Similarly,

$$P\left(\frac{B}{A}\right) = \frac{P(B)P(A/B)}{P(A)} \quad (4-8)$$

$P(B/A)$ is the probability of event B happening given that event A has occurred. $P(B)$ is the probability of event B happening independently of event A. Equation (4-8), $P(B/A)$ is the probability of event B happening given that event A has occurred. $P(B)$ is the probability of event B happening independently of event A. $P(A/B)$ is the probability of event A happening given that event B has occurred. $P(A)$ is the probability of event A happening independently of event B. These equations are used to update probabilities based on new information. They are widely used in various fields, including statistics, machine learning, and Bayesian analysis, to make inferences and predictions when dealing with uncertain or conditional events. Bayes' theorem is a powerful tool for updating beliefs or probabilities as more data becomes available. Equation (4-9) is an extension of Bayes' theorem when there are two possible cases for event A, one where it occurs (A) and one where it doesn't occur (A_i). This equation allows you to calculate the probability of event B given the presence or absence of event A.

$P(B)$ is the probability of event B occurring. $P(A)$ is the probability of event A happening. $P(B/A)$ is the probability of event B happening given that event A has occurred. $P(A_f)$ is the probability of event A not occurring (the complement of $P(A)$), and it's equal to $1 - P(A)$. The probability of event B can be calculated by considering both scenarios: when event A occurs ($P(A)P(B/A)$) and when event A does not occur ($P(A_f)P(B/A_f)$), weighted by the probability of event A itself ($P(A)$). It takes into account both cases of event A happening or not happening. This formulation is useful in situations where event A and its complement (not A or A_f) are both relevant to the analysis, and assess the impact of both scenarios on the probability of event B.

$$P(B) = \frac{P(A)P\left(\frac{B}{A}\right) + P(A_f)P(B/A_f)}{P(A)} \quad (4-9)$$

Equation (4-10) is an extension of Bayes' theorem used to calculate the probability of event A occurring given that event B has occurred. This formula is often used in various applications, including testing scenarios where the main aim is to assess the chances of a test being correct or incorrect. $P(A/B)$ is the probability of event A occurring given that event B has occurred (the updated or posterior probability). $P(A)$ is the prior probability of event A happening before considering event B. $P(B/A)$ is the likelihood of event B occurring given that event A has occurred. $P(A_f)$ is the probability of event A not occurring (the complement of $P(A)$). $P(B/A_f)$ is the likelihood of event B occurring given that event A has not occurred. The equation essentially says that the probability of event A occurring after observing event B can be calculated by considering both scenarios: when event A occurs ($P(A)P(B/A)$) and when event A does not occur ($P(A_f)P(B/A_f)$), and then normalising these probabilities by dividing by the sum of both scenarios (the denominator). This normalisation ensures that the probabilities sum up to 1. In testing scenarios, this formula can help assess the likelihood of a test result being correct (event A) or incorrect (event A_f) given the observed outcome (event B). It's a fundamental tool in Bayesian statistics for updating beliefs or probabilities based on new evidence or observations.

$$P\left(\frac{A}{B}\right) = \frac{P(A)P\left(\frac{B}{A}\right)}{P(A)P\left(\frac{B}{A}\right) + P(Af)P(B/Af)} \quad (4-10)$$

In practical applications, these terms model and analyse a wide range of problems to refine understanding of uncertain events. Bayes' theorem is fundamental in Bayesian statistics and inference for making probabilistic inferences and decisions. In the context of nanocomposites, several correlated terms are linked to filler content and the probability of specific outcomes or behaviours. The filler content significantly impacts nanocomposite properties, potentially enhancing mechanical strength, thermal conductivity, and electrical conductivity. The probability of achieving desired property improvements is influenced by filler dispersion, size, and matrix compatibility. Uniform filler dispersion affects final properties, while poor dispersion leads to property variations. Agglomeration negatively impacts properties, influenced by factors like filler type and processing conditions. Property probability distributions may vary with filler content, potentially increasing the likelihood of improved properties while introducing variability. Higher filler content might lower the probability of material failure by enhancing mechanical properties. Optimising filler content aims to maximise desired properties by assessing the probability of achieving the best combination. Bayesian analysis and probabilistic modeling help quantify probability distributions for nanocomposite properties based on filler content, aiding in understanding and optimising relationships for specific applications. This section analyses a dataset of electrical and thermal characteristics of epoxy composites containing graphene (GNPs) and epoxy composites containing BaTiO₃ using a Bayesian model for probabilistic estimation. The goal is to estimate various material properties while considering uncertainties.

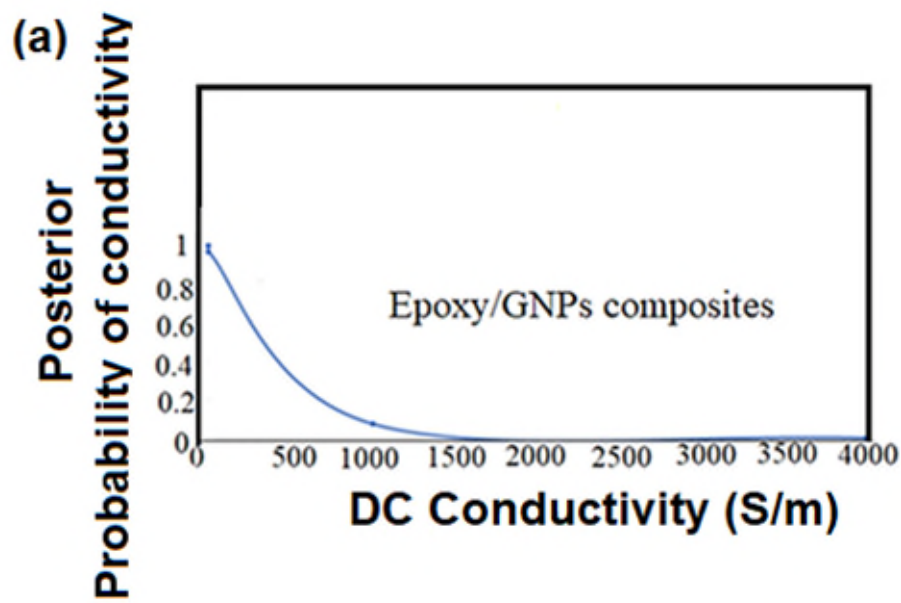
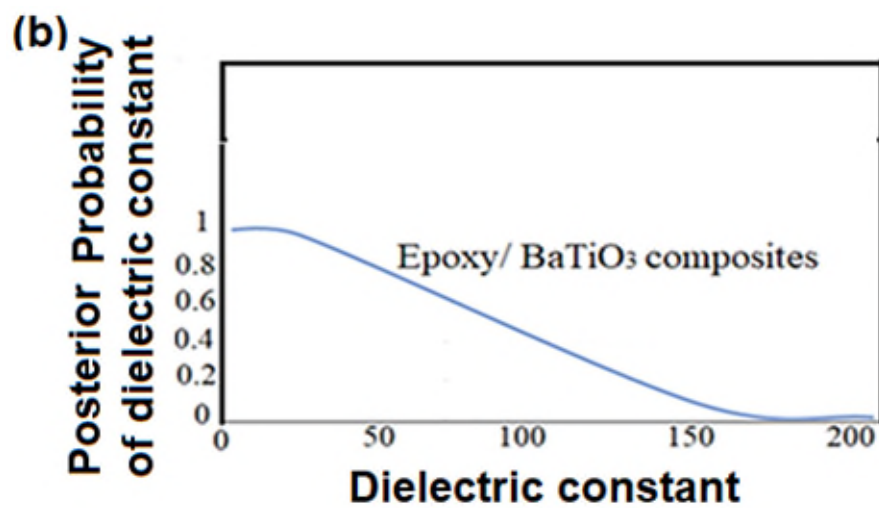
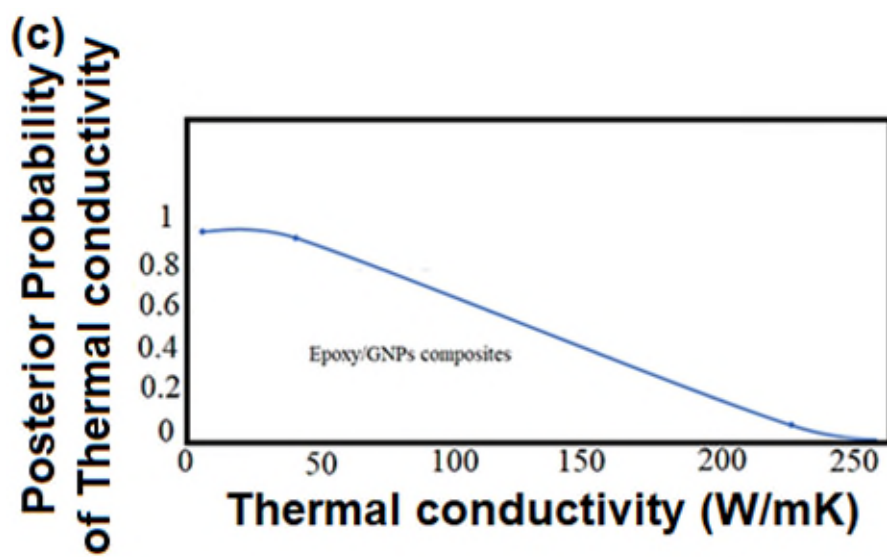
The posterior probability of DC conductivity of Epoxy/GNPs composites is the probability distribution obtained for the DC conductivity of epoxy/GNPs composites, incorporating both prior information and the dataset. Starting with a prior probability distribution (initial belief about the conductivity) in Bayesian analysis, it is then updated based on the observed data to reflect our updated belief about the conductivity of these composites. Similarly, the posterior

probability of the dielectric constant of Epoxy/ BaTiO₃ composites represents the probability distribution for the dielectric constant of epoxy/ BaTiO₃ composites after incorporating prior knowledge and the dataset. Bayesian analysis refines our understanding of the dielectric constant based on available information. The posterior probability of thermal conductivity of Epoxy/GNPs composites pertains to the probability distribution for the thermal conductivity of epoxy/GNPs composites. Utilising Bayesian methods, this probability is updated to account for uncertainty and variability in the data. The posterior probability of thermal conductivity of the simulated Epoxy/ BaTiO₃ composites is a probability distribution related to the thermal conductivity of simulated epoxy/ BaTiO₃ composites. Bayesian analysis estimates this property with a level of uncertainty based on available information. These posterior probabilities in Bayesian analysis are calculated by combining prior probabilities (initial beliefs or knowledge) with the likelihood of the data given those beliefs. This framework accounts for uncertainty and updates our understanding of material properties based on observed measurements. These posterior probabilities can be used for predictions, assessing estimate reliability, and making informed decisions in scientific research and engineering applications, providing the best estimates of material properties while considering inherent uncertainty in the measurements and prior knowledge.

The Bayesian technique, illustrated in Figure 4-12, is employed to establish probability distributions for key material properties, specifically electrical conductivity, dielectric constant, and thermal conductivity. Its primary goal in this context is to derive probability distributions for these specific material properties, which are crucial for characterising the behaviour of epoxy composites containing graphene (GNPs) and epoxy composites containing BaTiO₃. This analysis facilitates a more comprehensive understanding of the variability and uncertainty linked to these properties. Bayesian analysis commences by defining prior probability distributions for the material properties of interest. These priors encapsulate our initial beliefs or knowledge about the properties before considering any experimental or observed data. Typically, these are based on existing literature, theoretical models, or expert opinions. The technique

integrates observed data or experimental measurements of electrical conductivity, dielectric constant, and thermal conductivity for the epoxy/GNPs and epoxy/ BaTiO₃ composites. These data points serve to refine our understanding by updating our prior beliefs. The likelihood function quantifies the alignment of the observed data with different values of the material properties. It measures the likelihood of observing the data given specific property values, crucial in updating our prior beliefs to generate posterior probability distributions. Bayesian analysis combines the prior probability distributions with the likelihood function using Bayes' theorem. This mathematical framework updates our prior beliefs based on observed data, resulting in posterior probability distributions that represent our refined understanding of the material properties. The outputs of the Bayesian technique yield posterior probability distributions for electrical conductivity, dielectric constant, and thermal conductivity for both epoxy/GNPs and epoxy/ BaTiO₃ composites. These distributions offer a probabilistic representation of these properties, indicating the most likely values and the level of associated uncertainty. They are valuable for various purposes, including predictions, assessing the reliability of property estimates, and quantifying uncertainties. Consequently, these distributions serve as a powerful tool for informed decision-making in scientific research and engineering applications. In this study's Bayesian analysis, a crucial observation emerged: an inverse relationship between the simulated DC conductivity, dielectric constant, and thermal conductivity of the composites and their corresponding posterior probabilities was noted. This finding implies that higher simulated values correlate with decreased chances of these electrical and thermal properties in the posterior probabilities. It underscores the importance of considering composite characteristics in understanding their electrical and thermal behaviours. As simulated values increase, they introduce more uncertainty or variability into the posterior probabilities due to complex influencing factors. This understanding is essential for informed decision-making in applications where electrical and thermal properties are critical, such as in electronic device material design or thermal management systems. It emphasises the need to control and optimise composite parameters for desired electrical and thermal performance. Further

research is warranted to delve deeper into the mechanisms behind this inverse relationship and explore strategies for enhancing predictability and control in composite materials. Understanding that the posterior distribution in Bayesian analysis represents the updated belief about a parameter or property after incorporating observed data, the choice between two posterior distributions, such as one with a value of 1 and another with a value of 0.1, depends on the context and the underlying statistical model. Assessment of the quality of the statistical model used to generate these posterior distributions is crucial. Model assumptions, data quality, and model fit to the data influence the credibility of the posterior estimates. Consultation with domain experts or statisticians familiar with the specific problem aids in assessing the appropriateness of a posterior distribution. Regarding the observed trend in this study on nanocomposite materials, it suggests that the properties of nanofillers don't directly translate to the manufactured composites' properties. Several additional factors appear to reduce the composites' performance compared to the pristine properties of the individual fillers. This finding underscores the complexity of nanocomposite materials and the necessity to consider various factors beyond filler addition. Improving composite performance necessitates a comprehensive approach considering factors like filler interaction, dispersion within the matrix, and other manufacturing variables. The implication is that achieving optimal nanocomposite performance requires a holistic understanding of the composite system and controlling multiple variables rather than solely relying on filler properties. This insight holds value for the development of nanocomposite materials across multiple applications, emphasising the need for a comprehensive approach beyond just the properties of individual fillers in electronics, materials science, and other fields.



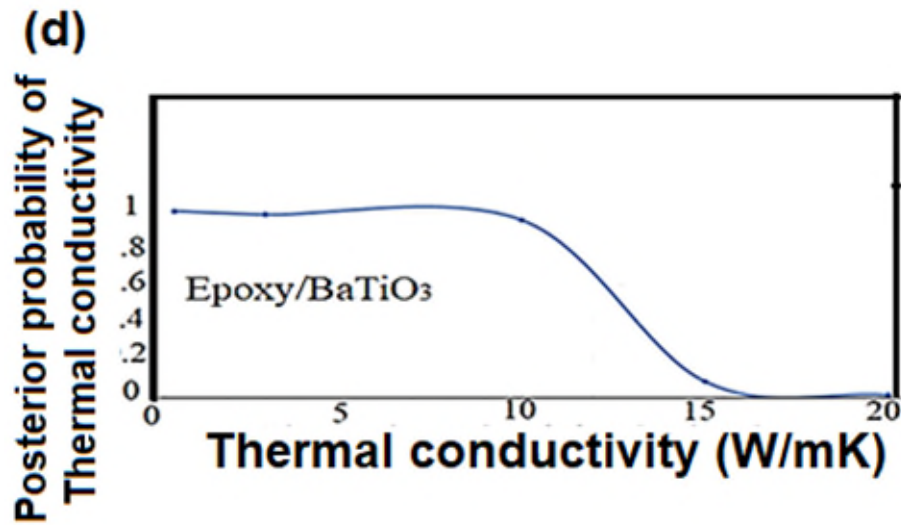


Figure 4-12. a) Posterior probability of DC conductivity of epoxy/ GNPs composites with respect to the DC conductivity of the simulated epoxy/GNPs composites, b) Posterior probability of Dielectric constant of epoxy/ BaTiO₃ composites with respect to the Dielectric constant of the simulated epoxy/ BaTiO₃ composites, c) Posterior probability of Thermal conductivity of epoxy/ GNPs composites with respect to the Thermal conductivity of the simulated epoxy/GNPs composites, d) Posterior probability of Thermal conductivity of the simulated epoxy/ BaTiO₃ composites.

4.12 Conclusions

In this context, the exploration outlined in the research precisely aligns with the overarching objectives of the thesis, systematically investigating the electrical and thermal properties of graphene and BaTiO₃-reinforced epoxy nanocomposites. The research rigorously estimated essential properties, including DC conductivity, dielectric constant, thermal diffusivity, specific heat capacity, and thermal conductivity. These properties formed the foundation of the investigation, directly addressing the objective of evaluating the influence of various nanofillers on the properties of epoxy nanocomposites. The primary focus was to comprehend how different fillers, such as graphene derivatives (e.g., graphene oxide, nanoplatelets) and BaTiO₃, impact the properties of epoxy

nanocomposites. The observed enhancements in electrical and thermal properties as filler material volume increased effectively fulfilled this objective. Bayesian analysis served as a crucial tool, quantitatively assessing the impact of fillers on electrical and thermal properties. This analytical approach was particularly valuable in understanding DC conductivity and dielectric constant, aligning perfectly with the objective of evaluating nanofiller impact through quantitative means. The chapter's work holds significance in the broader context of optimising the properties of these nanocomposites for potential applications across diverse industrial domains. By improving their electrical and thermal characteristics, new possibilities for utilisation have been unveiled, directly resonating with the objective of exploring applications in varied industries. In summary, this chapter dedicates itself to directly addressing the thesis objectives by providing an extensive and profound exploration of the behaviours and properties of graphene and BaTiO₃-reinforced epoxy nanocomposites. Through meticulous analysis and simulation, the research illuminates the substantial impact of nanofillers on these composites, offering invaluable quantitative insights that can guide future research and practical applications within this field.

CHAPTER 5

Experimental Exploration of Properties in BaTiO₃ Reinforced Epoxy Nanocomposites Under External Electric Field Effects: An In-Situ Electric Field Study

5.1 Introduction

Fiber-reinforced polymer (FRP) composites find widespread use in high-performance industries owing to their remarkable specific strength and modulus. This exceptional strength-to-weight ratio makes them ideal for applications demanding lightweight yet sturdy materials. FRP composites are employed in diverse sectors, including aerospace, automotive, and construction, leveraging their unique properties for enhanced performance and durability[355]. FRP composites, primarily composed of thermoset epoxy resins featuring a robust cross-linked structure, exhibit exceptional properties. Nevertheless, their brittleness in the transversal direction represents a limitation, particularly in scenarios involving impact loading or high strain rates. This constraint necessitates further research and engineering solutions to enhance their resilience in these specific conditions, ensuring their continued applicability in high-performance sectors[552]. To improve the properties of the polymer matrix in composite manufacturing, researchers have emphasised incorporating micro- and nano-fillers, such as rubber tougheners, as a secondary phase. This strategy has gained extensive attention as modifying fiber properties during the manufacturing process is challenging. Consequently, significant research has been devoted to optimising these filler materials to enhance the overall performance of composites in various applications[553]. Researchers have sought to enhance the properties of polymer matrices in fiber-reinforced composites through various means. These include the addition of rubber tougheners, nanoparticles, silica particles, carbon nanoparticles, clay, and fiber coatings. Additionally, altering the curing process has been investigated as an alternative to modifying fiber properties during composite manufacturing, addressing the challenges associated with such modifications. These approaches aim to optimise composite performance for diverse applications[554][555]. Researchers can customise the mechanical properties of fiber-reinforced composites by integrating rubber tougheners, nanoparticles, silica particles, carbon nanoparticles, clay, and fiber coatings into the polymer matrix while adjusting the curing process. This allows for the enhancement of stiffness and toughness, vital for various applications. These strategies provide

alternatives to altering fiber properties during composite manufacturing, offering versatility in tailoring composite characteristics to meet specific needs[556]. To enhance fracture toughness in composite materials, rubber tougheners such as core-shell rubber or liquid rubbers are incorporated into the polymer matrix. These tougheners absorb energy during deformation and reduce stress concentration. Studies have shown that adding rubber tougheners to epoxy resin can substantially boost composite fracture toughness by up to 200%, offering an efficient means to enhance mechanical properties without altering fiber characteristics during fabrication[557]. Incorporating rubber tougheners into polymer matrices can enhance fracture toughness in composites, but exceeding a critical concentration threshold may cause particle clustering, diminishing mechanical strength. Careful selection and optimisation of toughener type and quantity are crucial to attain desired composite mechanical properties. Despite this challenge, integrating rubber tougheners remains a promising avenue for improving the mechanical performance of epoxy composites[558]. To prevent rubber toughener agglomeration in polymer matrices, surface modifications and the use of multiple toughening agents are viable strategies. However, coupling agents, while improving bonding, can potentially reduce elastic modulus, tensile strength, and glass transition temperature in epoxy composites. An innovative method proposed by Sung et al. involves toughening epoxy matrices in composites through pre-stressing using expandable hollow microspheres under heating. This approach offers a novel way to enhance composite mechanical properties without the potential drawbacks associated with other toughening techniques[559]. Phase-transition toughening utilises expandable microspheres to induce volume dilation, enhancing composite performance. However, it may lead to increased weight and potential compromises in mechanical properties. Transformation toughening, on the other hand, triggers a second phase formation under stress, creating a compressive force around crack tips to resist propagation. This mechanism effectively improves fracture toughness in materials like ceramics and polymer matrix composites, offering versatile toughness enhancement options[559].

This study delves into the active toughening impact of thin and high aspect ratio Si- BaTiO₃-epoxy nanocomposites under a low electric field. It utilises in-situ tensile testing and real-time in-situ Raman spectroscopy to assess the mechanical response and intrinsic behaviour of these composites. The investigation aims to understand how electric field application influences their toughness, providing valuable insights into their potential applications and performance enhancement. In this study, in-situ tensile testing and real-time in-situ Raman spectroscopy were used to assess how Si- BaTiO₃-epoxy nanocomposites respond mechanically and exhibit intrinsic strain when exposed to electric field stimulation. This approach allows for the examination of how the application of an electric field impacts the composite's mechanical behaviour and strain characteristics, offering valuable insights into their behaviour under such conditions and potential applications. The study's findings provide crucial insights into the active toughening mechanism observed in Si- BaTiO₃-epoxy nanocomposites. These insights have significant implications for the design and enhancement of high-performance epoxy matrix composites, offering potential for improved mechanical properties and broader applications in advanced materials. Furthermore, this article investigates the active toughening effect of BaTiO₃-epoxy nanocomposites when subjected to an electric field. The findings indicate that the application of an electric field enhances the failure stress and strain characteristics of these nanocomposites. This knowledge is valuable for understanding and optimising the mechanical performance of such composites, with potential applications in advanced materials. In the 1 wt.% nanocomposites, the tensile modulus increased as the electric field strength increased, while it decreased in the case of 5 and 10 wt.%. Additionally, the Raman data consistently showed an increase in intensity and broadening of peaks with higher electric field strength and BaTiO₃ content. These observations indicate the intricate relationship between electric field, filler content, and mechanical and spectroscopic properties, providing valuable insights for tailoring the behaviour of nanocomposites. The high-content nanocomposites exhibited a softening effect due to BaTiO₃'s dipolar displacement, which outweighed the stiffening trend caused by electric fields seen in the 1 wt.% specimen. This observation suggests

that the interplay between filler content and dipolar effects can result in varying mechanical responses, and the findings may not be universally applicable to other nanocomposites. Understanding these complex interactions is crucial for tailoring the properties of different nanocomposite systems effectively. These findings offer significant insights into the active toughening mechanisms of these nanocomposites, particularly regarding the interplay between dipolar displacement and electric field effects. These insights hold important implications for designing and enhancing high-performance polymer matrix composites, guiding future research and applications in advanced materials. Understanding these complex interactions can lead to improved composite properties and broader industrial applications.

5.2 Materials and methods

The epoxy utilised in this investigation was Araldite LY1564, which was supplied by Huntsman in the United Kingdom. The coupling agent for surface functionalisation utilised in this investigation, 3-glycidoxypropyl trimethoxy silane (3-GPS), as well as the hydrogen peroxide (H_2O_2 , 30%) and acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 99.9%), were all supplied by Sigma-Aldrich, UK. Fisher Scientific International, Inc., UK provided the ethanol ($\text{C}_2\text{H}_6\text{O}$, 99.9%) utilised in the BaTiO_3 dispersion. Nanostructure & Amorphous Materials Inc. in the United States provided the BaTiO_3 . Table 5-1 summarises the properties of BaTiO_3 .

Table 5-1. Characteristics of the BaTiO_3 .

Characteristics	Value
Phase	Tetragonal
Size	200 nm
Density	5.85 g/cm ³

Specific surface area (SSA)	6-7m ² /g Spherical
-----------------------------	--------------------------------

5.2.1 Pre-treatment (Hydroxylation process)

In the synthesis process, 10 g of BaTiO₃ nanoparticles were combined with a 230 mL H₂O₂ solution in a round bottom flask. The mixture underwent 30 minutes of sonication in an ultrasonic bath and was then refluxed for six hours at 108°C, maintained at 100 rpm using a mechanical stirrer. This procedure aimed to facilitate the reaction by providing controlled heating without losing H₂O₂, potentially contributing to the synthesis of specific materials or compounds. The recovery of the BaTiO₃ nanoparticles involved centrifuging the solution for 15 minutes at 4500 rpm, followed by three washes with deionised water. Subsequently, the refluxed BaTiO₃ nanoparticle suspensions were dried in an 80°C oven for 24 hours. This process aimed to separate and collect the synthesised nanoparticles while removing excess reactants and solvents, resulting in purified and dry nanoparticles for further use or analysis, as illustrated in Figure 5-1.

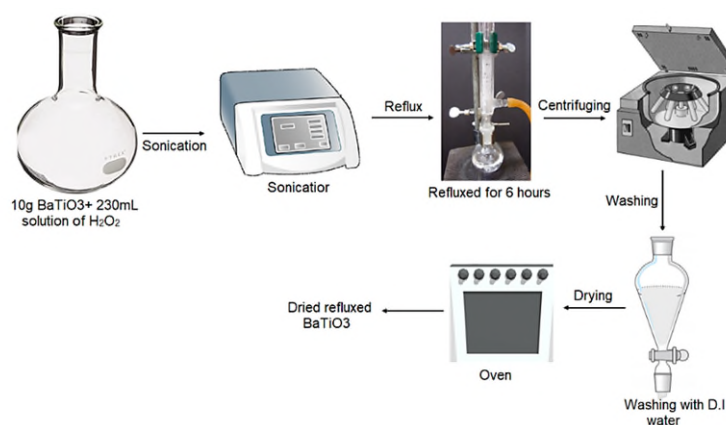


Figure 5-1. Schematic diagram of the Hydroxylation Process of BaTiO₃ nanoparticles (pre-treatment for adding of hydroxyl group (-OH) to the surface of BaTiO₃).

5.2.2 Preparation of silane modified barium titanate (Si-BaTiO₃)

To enhance processability and filler dispersion in nanocomposites, 3-glycidoxypropyl trimethoxy silane (3-GPS) was introduced to the refluxed BaTiO₃ nanoparticles. A solution containing 1 wt.% 3-GPS relative to the BaTiO₃ reflux was prepared for this purpose. The addition of 3-GPS is aimed at modifying the surface properties of the nanoparticles, improving their compatibility with the polymer matrix, and promoting better dispersion within the nanocomposite for enhanced performance. In the protocol, a 150 mL solution of ethanol and deionised water (9:1) was initially prepared in a beaker. Acetic acid drops were then incrementally added using a pipette, with vigorous mixing after each drop until a pH level of 3.5-4 was reached, as measured by a METTLER TOLEDO pH meter. This step was likely performed to create an acidic environment, which can be necessary for certain chemical reactions or material preparations. Following pH adjustment, the mixture was vigorously agitated for 3 minutes to achieve a clear solution. The low pH values in the solution play a crucial role in facilitating the silane functionalisation process. This acidic environment likely promotes effective bonding and chemical interactions between the silane agent and the nanoparticles, enhancing their surface properties for subsequent use in nanocomposites. A portion of the 3-GPS solution equivalent to 0.1 g was introduced into the acidified solution. Subsequently, the mixture was placed in an ultrasonic bath for 30 minutes to ensure the formation of a uniform and homogeneous solution. This step is essential to facilitate the proper dispersion and interaction of the 3-GPS silane agent with the solution, contributing to the desired surface modification of the nanoparticles for subsequent applications. To improve the wetting of the filler, 10 g of hydroxylated BaTiO₃ powder particles were introduced into the silane solution. The mixture was then subjected to agitation in an ultrasonic bath for 10 minutes. This process aims to enhance the interaction between the silane solution and the filler particles, promoting effective wetting and ensuring better adhesion in subsequent composite formation or material applications. The mixture underwent refluxing for six hours in a silicone oil bath on a hotplate at the boiling point of ethanol, 78°C, while stirred at 100 rpm using a mechanical stirrer. Following refluxing, the BaTiO₃ material was subjected to three washes with deionised water and subsequent centrifugation at 4500 rpm.

This process was likely employed to remove residual solvents and impurities, ensuring the purification and isolation of the synthesised BaTiO₃ nanoparticles for further use or analysis. The silane-treated BaTiO₃ (Si- BaTiO₃) powder was dried for 24 hours at 110°C. This step aimed to prevent the condensation of silanol groups on the surface of the nanoparticles. By drying at this temperature, the material's properties and reactivity could be preserved for subsequent applications without the risk of unwanted chemical reactions or alterations, as shown in Figure 5-2. Finally, the particles were crushed in a mortar and pestle to create the nanocomposite.

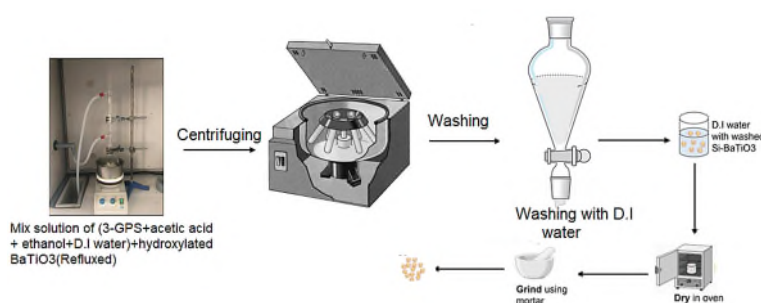


Figure 5-2. Schematic diagram of the functionalisation process of BaTiO₃ with 3-GPS. The epoxy nanocomposite fabrication process including Si-BaTiO₃ functionalisation is schematically illustrated.

5.2.3 Preparation of silane modified Barium titanate (Si-BaTiO₃)/ epoxy nanocomposites

Begin by dispersing Si- BaTiO₃ nanoparticles in ethanol. The specific weight of nanoparticles to ethanol should align with the desired concentration, which can vary (e.g., 1%, 5%, or 10% by weight of the epoxy resin). Ultrasonication is employed to ensure proper dispersion and prevent agglomeration of nanoparticles. This step helps create a stable suspension. Simultaneously, prepare the epoxy resin in accordance with the manufacturer's guidelines. It's crucial to ensure thorough mixing and degassing to eliminate any trapped air bubbles within the resin. Achieving a bubble-free epoxy resin is essential to maintain uniformity in the resulting nanocomposite. Gradually introduce the prepared nanosuspension (Si- BaTiO₃ in ethanol) into the epoxy resin while

maintaining continuous stirring. This step is pivotal for achieving a consistent distribution of nanoparticles within the epoxy matrix. Uniform dispersion enhances the mechanical, electrical, and thermal properties of the nanocomposite by maximising nanoparticle integration. After the nanosuspension is thoroughly mixed with the epoxy resin, the mixture is stirred overnight under controlled conditions (e.g., 300 rpm and 80°C) within a fume hood. This controlled process allows for gradual ethanol evaporation without inducing nanoparticle precipitation. It ensures the formation of a well-blended nanocomposite structure. Post-solvent evaporation, the epoxy mixtures are carefully reweighed to confirm the complete removal of ethanol. This step ensures the nanocomposite's integrity and composition accuracy. Add the appropriate curing agent as per the epoxy resin manufacturer's recommendations. Mixing the curing agent thoroughly with the epoxy-nanosuspension mixture is essential. Proper blending initiates the curing process, facilitating chemical cross-linking that contributes to the nanocomposite's mechanical and thermal properties. The mixture is then placed in a vacuum oven set at a specific temperature (e.g., 30°C) for a specified duration (e.g., 1 hour). This step is crucial for the removal of any remaining air bubbles and for complete ethanol extraction. Transfer the prepared epoxy-nanosuspension mixture into suitable molds or onto substrates. The moulding process follows the epoxy resin manufacturer's prescribed curing conditions, often involving controlled heating to precise temperature and duration specifications. Curing is vital for the formation of strong molecular bonds, resulting in the hardening of the composite and the achievement of desired mechanical, electrical, and thermal properties. The completed nanocomposite samples, initially measuring 100 x 20 x 0.3 mm³, can be further tailored to specific dimensions using precision equipment like a cut-off machine. Figure 5-3 illustrates the step-by-step process involved in creating epoxy nanocomposites with improved mechanical, electrical, and thermal properties through the integration of Si- BaTiO₃ nanoparticles. The process includes nanosuspension preparation, epoxy resin mixing, gradual introduction of nanosuspension into the resin, controlled solvent evaporation, curing agent addition, air bubble removal,

moulding, and sample sizing. Each step is crucial to achieving a homogenous and high-performance nanocomposite material. This comprehensive and meticulous process ensures the fabrication of high-quality epoxy nanocomposites with enhanced properties, making them suitable for diverse applications in various industries. The specific properties of the nanocomposites can be fine-tuned by adjusting factors such as nanoparticle concentration and processing conditions to meet specific performance requirements.

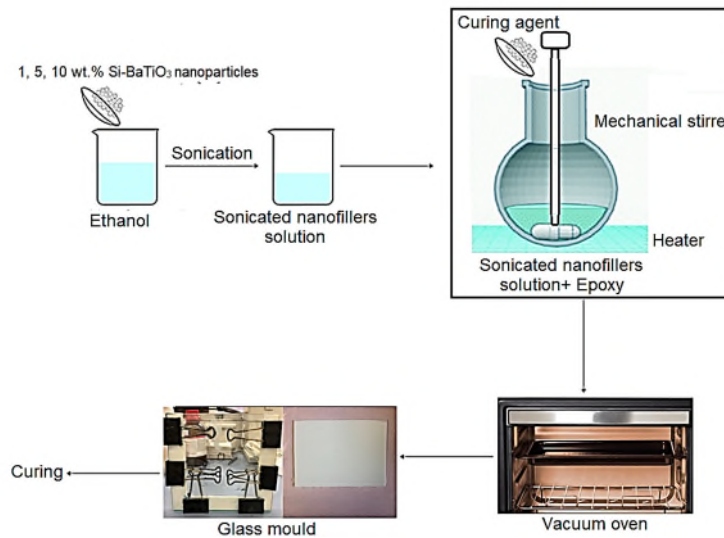


Figure 5-3. Schematic diagram of the preparation of Epoxy/Si-BaTiO₃ nanocomposites.

5.3 Characterisations

5.3.1 Microstructure analysis

The investigation focused on the microstructure of cryo-fractured surfaces in cured nanocomposites with different BaTiO₃ weight percentages. Cryo-fracturing was achieved using liquid nitrogen, a method chosen for its ability to create well-defined fracture surfaces at extremely low temperatures. This approach provides valuable insights into the composite's internal structure and properties. The morphology of the fracture surface was analysed using a TESCAN Vega 3 field emission scanning electron microscope. Gold sputtering was employed to apply a thin gold coating to each sample prior to analysis, ensuring high electrical

conductivity during microscopy. This preparation method enhances the quality of imaging and allows for detailed examination of the fracture surface.

5.3.2 Electric field induced tensile test

In our study, an Instron tensile tester was employed to conduct tests on specimens measuring $65 \times 10 \times 0.3 \text{ mm}^3$ in dimensions. Insulating tape was applied to both ends of the specimens to ensure secure clamping and prevent electrical interference during testing. This approach maintained the integrity of the testing environment and facilitated accurate measurements. To establish electrical contact with the in-situ electric field, the specimens were coated with a layer of silver paste. Figure 5-4 illustrates the configuration of the in-situ electric probes within the tensile testing setup, along with a typical specimen before and after testing (post-failure). This ensured that electrical continuity was maintained throughout the experiment, allowing for the assessment of the specimens' behaviour under electric fields. The purpose of varying the applied voltage (0 V, 6 V, 9 V, and 24 V) on the specimens was to investigate the influence of electric fields on their tensile properties. The tests maintained a constant strain rate of 1 mm/min and a consistent effective length of approximately 30mm between the upper and lower clamps. This controlled setup allowed for the examination of how different electric field strengths affected the nanocomposite's behaviour during tensile testing. The tests were conducted to identify significant variations in tensile strength, elongation, and modulus when an electric field was present or absent. To quantify the strength of the electric field at specific points, voltage per cm was measured, calculated by dividing the voltage by the distance between the measurement points. This measurement method aimed to assess the impact of different electric field strengths on the nanocomposite's mechanical properties during tensile testing. The provided information explains that at different voltages (6V, 9V, and 24V), the mean voltage density through the 0.3 mm thick specimen varies. This measurement characterises the electric field strength through the thickness of the sample. The maximum area density of 1.6 kV/cm^2 is calculated when considering both the current flow through the 5 mm distance between the probes and the specimen's thickness. This data helps assess the distribution and

intensity of the electric field within the nanocomposite during testing. The provided values indicate that the electric field strength applied to the BaTiO₃ nanoparticles within the nanocomposite is relatively low. This assessment is made considering the specified voltage levels and geometric factors during testing. It helps understand the intensity of the electric field within the nanocomposite under these conditions. The characterisation performed in reference on BaTiO₃-epoxy nanocomposites with varying volume percentages and different dimensions used DC voltages at magnitudes of 3 kV and above to polarise the nanocomposites. This corresponds to an electric field intensity of approximately 30 kV/cm through the thickness, which is about 20 times higher than the field intensity in our study. These differences in voltage and field intensity can significantly affect the material's behaviour and properties [560–562]. The research in reference applied significantly higher electric fields to polarise similar specimens. When comparing this material to others with varying preparation parameters and uncertainties, it's important to consider that different electric field strengths can lead to varying material responses and properties. The choice of electric field strength plays a critical role in the behaviour of these materials [560–562]. However, a simplified comparison can be made by examining how the material's response varies with the BaTiO₃ volume percentage. This provides a basis for understanding differences in material behaviour under different conditions. Estimating the Vol.% of the examined BaTiO₃ particles was accomplished using the approach introduced in Khaleque et al., with its expression given by equation (5-1)[560–562]:

$$\text{Vol.}_{\text{BaTiO}_3} \cong \left(\frac{\left(\frac{\rho_{\text{BaTiO}_3}}{\rho_{\text{pol}}} \right)}{\frac{\text{wt}_{\text{BaTiO}_3}}{\rho_{\text{pol}}}} - \frac{\rho_{\text{BaTiO}_3}}{\rho_{\text{pol}}} + 1 \right)^{-1} \quad (5-1)$$

The assumption of a six-fold higher density for BaTiO₃ compared to the polymer (e.g., 6 g/cm³ and 1 g/cm³ for BaTiO₃ and epoxy, respectively) leads to estimated volume percentages of approximately 0.17%, 0.87%, and 1.82% for 1, 5, and 10 wt.%. While these volume percentage calculations are rough approximations, they suggest a significantly lower concentration of BaTiO₃ in the current study compared to the range of 10-60% used in previous research that employed higher

kV levels for BaTiO₃ particle polarisation[562]. The research findings indicate that the permittivity of the nanocomposite becomes significantly higher, reaching three times that of the polymer alone, at 30 Vol.% of BaTiO₃. In cases where the Vol.% of BaTiO₃ is much lower, as in our study, the permittivity of the nanocomposite is only slightly higher than that of the polymer and can be assumed to be nearly identical. To precisely describe and quantify the actual polarisation level in dielectric nanocomposites with relatively low dielectric content, such as in our research, further analytical and in-situ field-equipped experimental characterisations are necessary and currently under investigation.

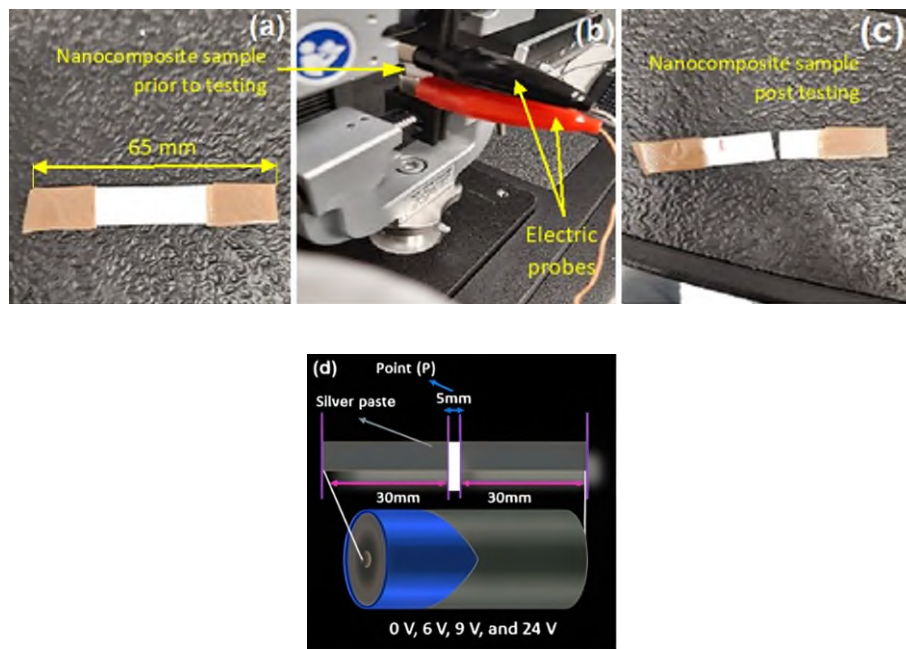


Figure 5-4. Schematic illustration of the in-situ electric field induced tensile test measurements: a) Sample before testing, b) Testing setup, and c) Sample after testing, d) Strength of electric fields at point P to polarise the sample .

5.3.3 Electric field induced raman spectroscopy

Raman spectroscopy, a non-destructive technique, allows for the analysis of material vibrational modes. It is extensively employed in material characterisation to reveal molecular and crystalline structure details and detect any remaining strain within the material. This method provides valuable insights into material

properties and structural characteristics. In Raman spectroscopy, the selection of the excitation wavelength is critical. The commonly used wavelength of 514 nm strikes a balance between achieving high resolution and maintaining strong signal intensity, making it a popular choice for Raman measurements. The study utilised in-situ Raman spectroscopy with an electric connection to examine how the nanocomposite material responds to an external electric field, specifically focusing on its polarisation behaviour. The study varied the voltage applied to the specimen between 0 V, 6 V, 9 V, and 24 V. In-situ Raman spectroscopy was employed to continuously monitor changes in the material's vibrational modes as it responded to the applied electric field in real-time. In the setup for in-situ Raman spectroscopy, electrodes are used to apply an electric voltage to the specimen while simultaneously acquiring Raman spectra. This configuration allows for the examination of how the material's vibrational modes respond to the applied electric field. In-situ Raman spectroscopy is a valuable technique for studying how materials respond to external electrical stimuli, providing crucial insights for developing materials with customised electrical properties. The set-up for in-situ Raman spectroscopy equipped with an electric connection is shown in Figure 5-5.

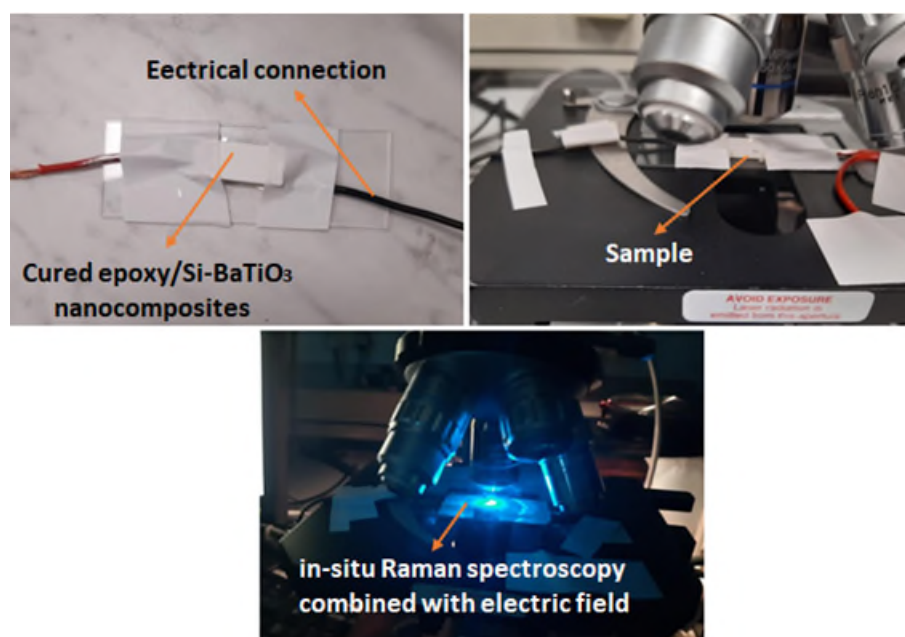


Figure 5-5. In-situ electric field equipped Raman spectroscopy of BaTiO₃-epoxy nanocomposites.

5.3.4 Electric field induced tensile testing with digital image correlation (DIC)

Tensile testing combined with digital image correlation was employed to compute average displacement, average strain, and average principal stress in Si-BaTiO₃ nanoparticles/epoxy nanocomposites. These measurements were conducted under the influence of in-situ electric fields with voltage levels ranging from 0 V to 6 V, 9 V, and 24 V. In each case, three specimens were prepared, and the evaluation was carried out at room temperature. An electro-mechanical load frame with a load cell capacity of 1 kN was used to subject the samples to uniaxial stress. The samples were subjected to stretching at a constant strain rate of 1 mm/min. These samples had dimensions of 65×10×5 mm³, with a gauge length of approximately 30 mm. To facilitate 3D Digital Image Correlation (DIC) measurements, a random speckle pattern was applied. This was achieved through a two-step process: initially, a uniform white base coat was spray-painted, followed by the addition of a random black speckle pattern. Photographs of the specimens were captured using CCD cameras equipped with 2.8/50 lenses. The correlation and analysis of these images, including the determination of average displacement, average strain, and average principal stress, were carried out using GOM's ARAMIS software. The configuration for conducting in-situ Electric Field Induced Tensile testing with digital image correlation (DIC) is illustrated in Figure 5-6.

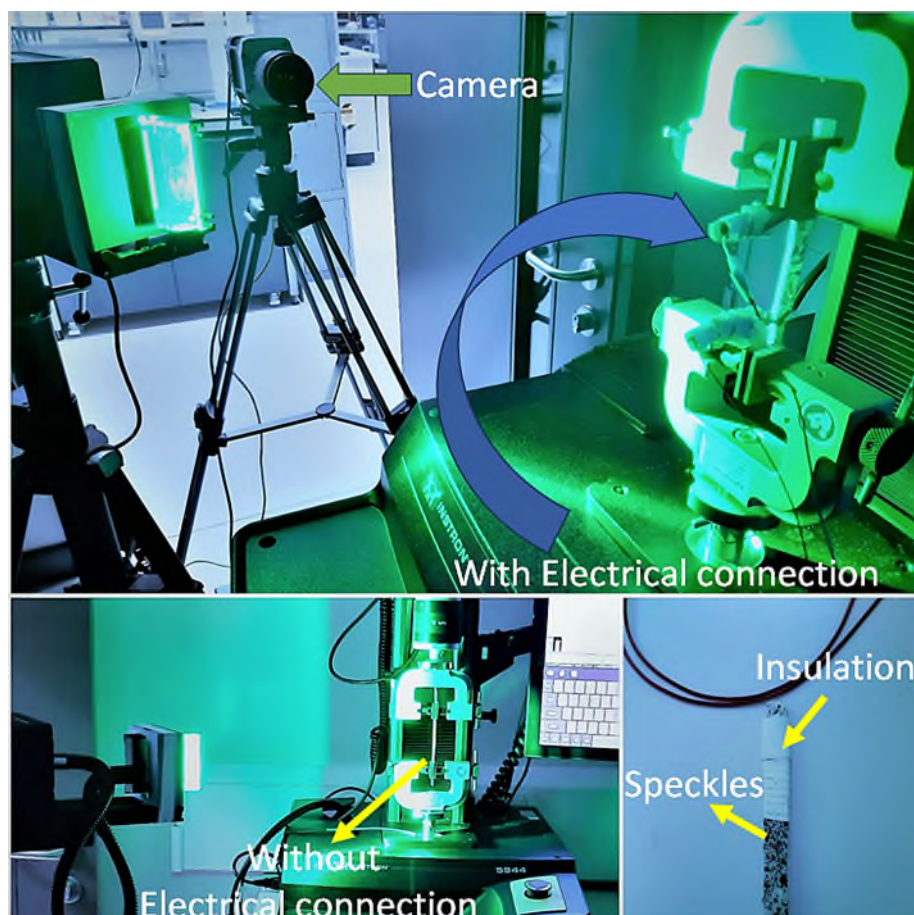


Figure 5-6. Depiction of the in-situ electric field induced DIC test measurement.

5.3.5 Theoretical electric field induced electrical properties by COMSOL Multiphysics

Araldite LY1564 epoxy resin was employed for the experimental work in this study. Surface functionalisation of BaTiO₃ nanoparticles was employed to replicate the nanocomposite conditions, facilitating the investigation of specific behaviours and properties. This approach allowed for a controlled study of the epoxy nanocomposites' characteristics under various conditions and configurations. Table 5-2 provides a summary of the properties of Si- BaTiO₃ and epoxy materials. DC conductivity was determined using Ohm's Law and electrostatic analytical formulas. This analytical approach allowed for the calculation of electrical conductivity properties based on the provided material characteristics and formulas. The electrostatic model was created with COMSOL

Multiphysics v5.5's AC/DC module. The direct link between electrical conductivity and the electrical field was used to determine electrical displacement field (C/m²). The dielectric polarization and volumetric power dissipation density were measured in terms of the content of BaTiO₃. The finite volume method was employed, considering the content of BaTiO₃ in vol% during this simulation. The fine meshing of BaTiO₃-GNPs/ Epoxy nanocomposite model and the free body diagram that were used are shown in Figure 5-7.

Table 5-2. Characteristics of the Si- BaTiO₃ and epoxy.

Characteristics	Value
Phase(Si- BaTiO ₃)	Tetragonal
Size(Si- BaTiO ₃)	200 nm
Density (Si- BaTiO ₃)	5.85 g/cm ³
Dielectric constant (Si- BaTiO ₃) (Si- BaTiO ₃)	2000(average)
Dc conductivity of Si- BaTiO ₃ (S/m)	1.×10 ⁻⁹ s/m
Dc conductivity of Araldite LY1564 Molded Epoxy	1.×10 ⁻¹⁴ s/m

Density of Araldite LY1564 Molded Epoxy	1.16 (g/cm ³)
Dielectric constant of Araldite LY1564 Molded Epoxy	3.49

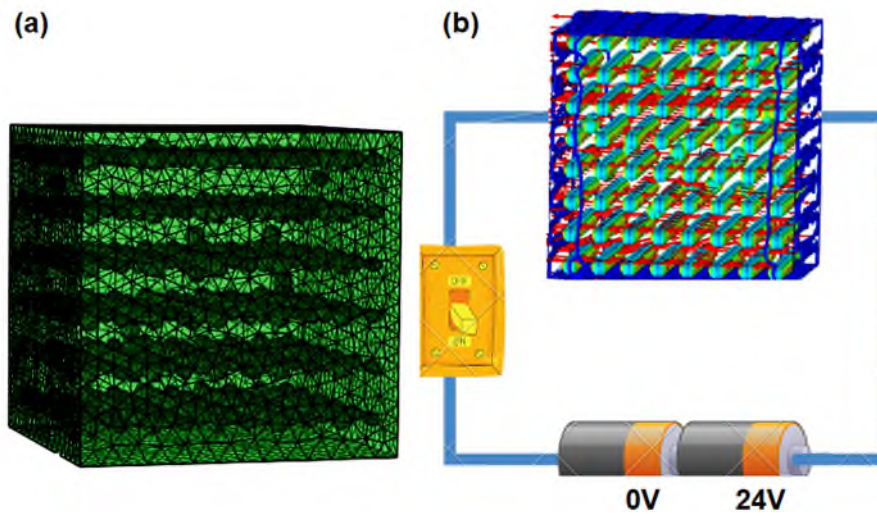


Figure 5-7. A free body diagram showing the boundary conditions used for AC/DC simulation a) Fine meshing, b) Free body diagram.

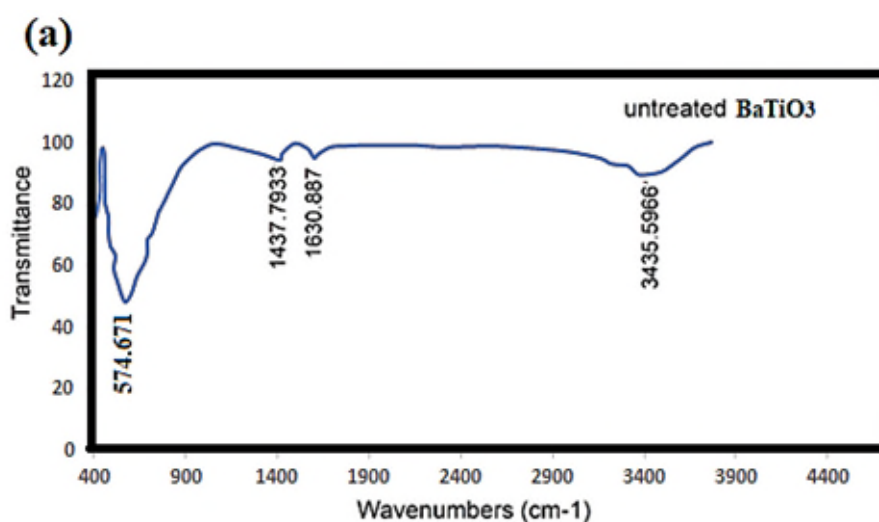
5.4 Results and discussion

The investigation aimed to understand the dispersion of BaTiO₃ particles in the epoxy matrix by examining the microstructure of samples prepared with both modified and unmodified BaTiO₃. This study followed the FTIR characterisation of Si- BaTiO₃ particles to gain deeper insights into their distribution within the epoxy material. The research aimed to assess how Si-BaTiO₃ particles within an epoxy matrix respond to electro-induced stress and strain at different voltage levels. This evaluation focused on understanding the material's behaviour under varying electrical conditions.

5.4.1 Characterisation of Si- BaTiO₃ by FTIR

Fourier transform infrared (FTIR) spectroscopy is a technique used to analyse the chemical composition and functional groups in a material by measuring the absorption or emission of infrared light. In this case, FTIR spectroscopy was used to confirm the presence of functional groups on the surface of BaTiO₃ nanoparticles that had been treated with silane (S- BaTiO₃). BaTiO₃ nanoparticles and silane were prepared separately. The nanoparticles were treated with the silane to functionalise their surface. FTIR spectroscopy involves shining infrared light on a sample and measuring the absorption or emission of the light at different wavelengths. The resulting data is called an FTIR spectrum. The obtained FTIR spectra for both untreated BaTiO₃ (Figure 5.8a) and silane-treated BaTiO₃ (S- BaTiO₃, Figure 5.8b) were analysed. The spectra provide information about the chemical bonds and functional groups present in the samples. By comparing the spectra of untreated and silane-treated BaTiO₃, researchers could confirm the presence of specific functional groups introduced by the silane treatment. These functional groups are important for improving the compatibility of the nanoparticles with the epoxy matrix in the nanocomposites. A Jasco FTIR-6200 spectrometer was employed for the FTIR measurements. The measurements were conducted in transmission mode. In this mode, the sample is placed between two transparent windows, and the FTIR spectrometer measures the absorption of infrared light as it passes through the sample. The characterisation was performed at room temperature, indicating that the measurements were conducted under typical laboratory conditions. The spectrometer operated with a spectral resolution of 2 cm⁻¹. Spectral resolution refers to the ability of the instrument to distinguish between closely spaced wavelengths in the infrared spectrum. The FTIR measurements covered a spectral range from 400 cm⁻¹ to 4000 cm⁻¹. This range encompasses a wide portion of the infrared spectrum, allowing for the detection of various functional groups and chemical bonds. Peaks at 1437 cm⁻¹ and 1630 cm⁻¹ are present in both Figure 4-8a and b. They indicate traces of BaCO₃ and physically absorbed water on the BaTiO₃ (and Si- BaTiO₃) particles, respectively. BaCO₃ can be a byproduct of the combustion manufacturing process. Peak at 858 cm⁻¹, 960 cm⁻¹, and 1063 cm⁻¹ correspond

to various vibrations related to silicon-oxygen (Si-O) bonds. They are strong indicators of the successful silane modification of the BaTiO₃ nanoparticles. The peak at 858 cm⁻¹ represents Si-O vibrations. In this context, it signifies the presence of silicon-oxygen bonds, which are characteristic of the silane molecules. The peaks at 960 cm⁻¹ and 1063 cm⁻¹ are associated with Si-O-C₂H₅ (Si-O-ethyl) vibrations. These vibrations specifically indicate the attachment of ethyl groups from the silane molecules to the nanoparticle surfaces. The presence of these bonds signifies that the silane molecules have successfully bonded with the surface of the BaTiO₃ nanoparticles, as shown in Figure 5.8b. In Figure 5-8b, the bands in 3200-3700 cm⁻¹ range reveal the existence of hydroxyl groups (OH) stretching vibrations. These hydroxyl groups are a result of the silane functionalisation process. They are derived from Si-OH groups, indicating that the surface of the BaTiO₃ nanoparticles has been modified with silane molecules containing hydroxyl groups. The successful silane modification of the BaTiO₃ nanoparticles is crucial in the context of nanocomposite fabrication. It enhances the compatibility between the nanoparticles and the epoxy matrix, improving their dispersion within the matrix. This, in turn, contributes to the overall performance of the nanocomposite material, including properties like mechanical strength, electrical conductivity, and thermal stability.



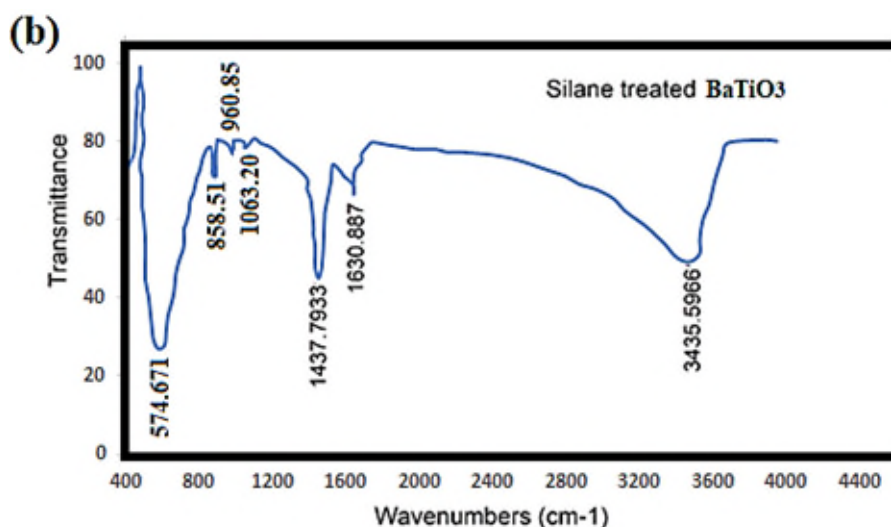


Figure 5-8. FTIR spectra of unmodified BaTiO₃ and modified BaTiO₃, a) unmodified BaTiO₃, b) modified BaTiO₃ (Si-BaTiO₃).

5.4.2 Scanning electron microscope (SEM)

BaTiO₃ nanoparticles were initially treated with a silane coupling agent called 3-GPS (3-glycidoxypropyl trimethoxy silane). This treatment aimed to modify the surface properties of the BaTiO₃ particles. The purpose of this treatment was to achieve a finer dispersion of BaTiO₃ nanoparticles within the epoxy resin. Finer dispersion leads to a more uniform distribution of nanoparticles in the epoxy matrix. SEM (Scanning Electron Microscopy) was then used as an analytical tool to characterise and examine the dispersion and distribution of these treated nanoparticles. The SEM analysis was conducted at various loadings of BaTiO₃ nanoparticles in the epoxy resin. Different loadings might include different concentrations or weight percentages of nanoparticles. The goal of this analysis was to determine whether the silane treatment successfully improved the dispersion and distribution of BaTiO₃ nanoparticles in the epoxy resin. Achieving a finer and more uniform dispersion can have significant implications for the mechanical, electrical, and thermal properties of nanocomposite materials. In the case of unmodified BaTiO₃ nanoparticles, higher weight fractions and poor dispersion resulted in noticeable aggregation at various levels within the epoxy

resin. Aggregation refers to the clumping together of nanoparticles, which can lead to uneven distribution within the material. Silane functionalisation of BaTiO₃ nanoparticles was performed to make them compatible with the epoxy resin. This treatment aimed to improve the dispersion of the nanoparticles. The SEM images depicted in Figures 5-9a-c show cracked cross-sections of epoxy composites containing silane-functionalised or modified BaTiO₃ nanoparticles (Si- BaTiO₃) at different weight percentages. These images illustrate that even at higher concentrations of modified BaTiO₃ (Si- BaTiO₃), better dispersion was maintained compared to unmodified BaTiO₃. The key observation here is that surface functionalisation through silane treatment resulted in a more uniform distribution of nanoparticles within the epoxy matrix. Notably, the size distribution of silane-treated particles with a high content of nanoparticles was found to be similar to that of Si- BaTiO₃ particles with low content. This suggests that the silane functionalisation process was successful in achieving consistent particle distribution, regardless of the concentration of Si- BaTiO₃. In contrast, untreated particles (unmodified BaTiO₃) showed uneven distribution in the epoxy matrix, as shown in Figure 5-9d. The SEM images and observations indicate that there was no visible aggregation of Si- BaTiO₃ particles, whether at low or high Si- BaTiO₃ content. This absence of aggregation is a positive outcome, as it contributes to a more homogeneous distribution of nanoparticles in the epoxy resin. In conclusion, the surface functionalisation of BaTiO₃ nanoparticles with silane was shown to be beneficial in achieving improved dispersion and uniform distribution within the epoxy matrix. This uniform distribution is crucial for enhancing the mechanical, electrical, and thermal properties of nanocomposite materials. These findings underscore the effectiveness of silane functionalisation in maintaining consistent nanoparticle dispersion and preventing aggregation within the epoxy resin, ultimately contributing to the quality and performance of the nanocomposite material[95,412].

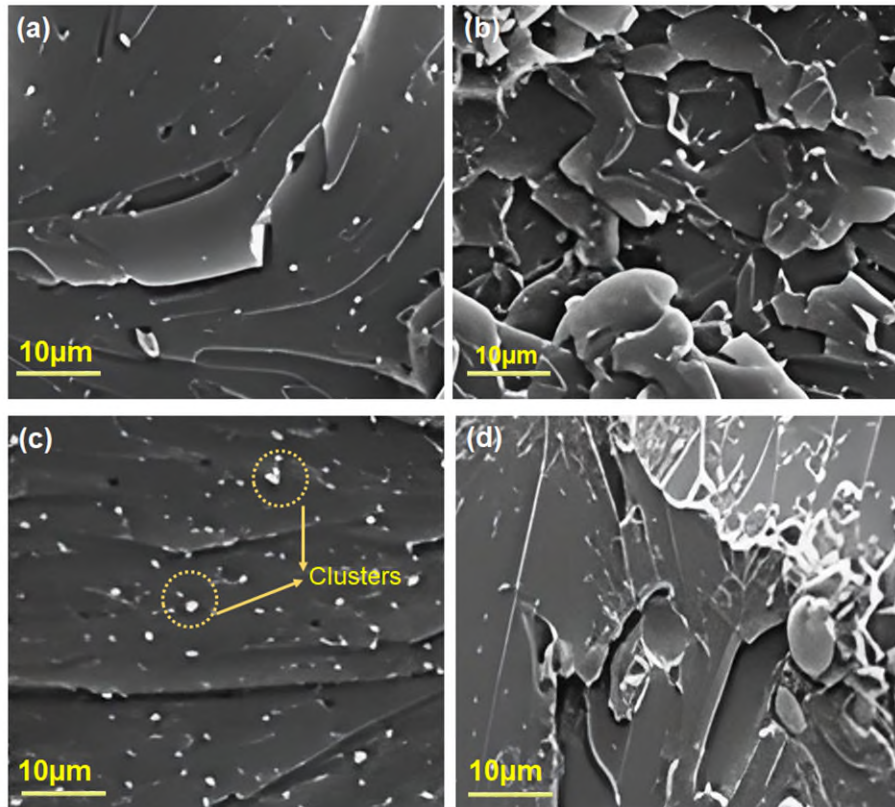


Figure 5-9. SEM images of fractured cross-sections of epoxy nanocomposites with BaTiO₃ at different weight loading, (a)-(c) images of 1 wt.%, 5 wt.% and 10wt%Si- BaTiO₃/epoxy nanocomposite, (d) unmodified 10wt% BaTiO₃ /epoxy nanocomposite.

5.4.3 Electric field induced tensile test

The study focused on evaluating the mechanical properties of Si- BaTiO₃ epoxy composites with varying Si- BaTiO₃ concentrations (ranging from 1% to 10% by weight) under the influence of different in-situ voltages (0V, 6V, 9V, and 24V). The primary goal was to investigate how electrical conditions, represented by these voltages, impact the mechanical behaviour of these composites. The evaluation involved measuring three important mechanical properties: tensile strength, elongation, and modulus. These properties provide insights into the material's response to tensile (pulling) forces and its ability to withstand deformation. Figure 5-10 provides a observations related to the influence of voltage on the mechanical properties of nanocomposites. Figures 5-10a-c in the study's illustrations demonstrate that increasing the applied voltage led to

enhancements in both tensile strength and elongation in the nanocomposites. Notably, the study found that composites containing a 1 wt.% BaTiO₃ concentration exhibited a significant decrease in tensile strength and elongation when subjected to applied voltage conditions (0V, 6V, 9V, and 24V). In contrast, composites with higher Si- BaTiO₃ concentrations (5 wt.% and 10 wt.%) were less affected by the applied voltages. This suggests that the electrical conditions, represented by the applied voltages, had a more pronounced impact on the mechanical properties of composites with lower BaTiO₃ content (1 wt.%). To ensure the reliability of these findings, the study conducted three tests per category, including extreme conditions of 0V (no electrical field) and 24V applications, at different Si- BaTiO₃ concentrations (1%, 5%, and 10%). The results are presented in Figure 5-11. Figure 5-11 provides evidence of the reproducibility of measurements across multiple tests. In general, the results show that as the quantity of Si- BaTiO₃ nanoparticles and applied voltage levels increased, both tensile strength and elongation consistently improved. The study attributes the substantial influence of voltage on the mechanical properties to the ferroelectric polarisation of Si- BaTiO₃ molecules at intrinsic strain levels. This ferroelectric polarisation leads to the immediate application of extrinsic stresses on the surrounding polymer, resulting in interfacial compressive strain, which contributes to the observed improvements in tensile strength and elongation. In summary, the research highlights the differential impact of applied voltages on nanocomposites with varying BaTiO₃ concentrations, emphasising the substantial effect on composites with lower BaTiO₃ content (1 wt.%). The study also underscores the reproducibility of results and provides insights into the mechanism by which voltage influences mechanical properties. Further investigation is suggested to fully understand the reasons behind this differential impact.

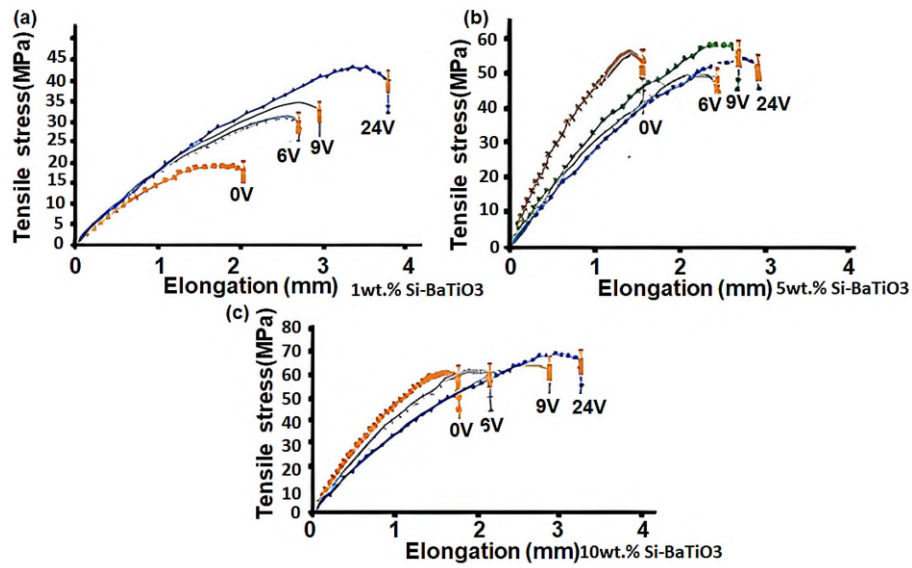
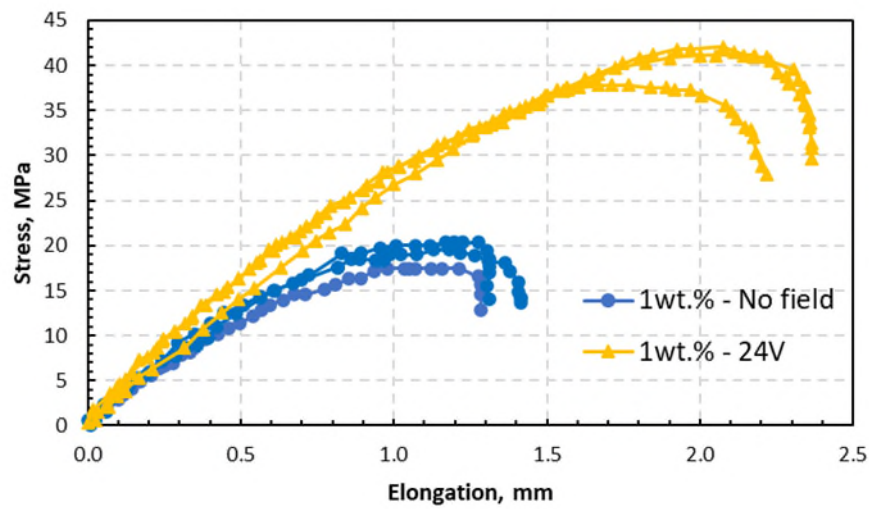


Figure 5-10. The tensile stress vs. elongation trends in Si-BaTiO₃-epoxy nanocomposites under increasing electrical voltage and varying content of Si-BaTiO₃.



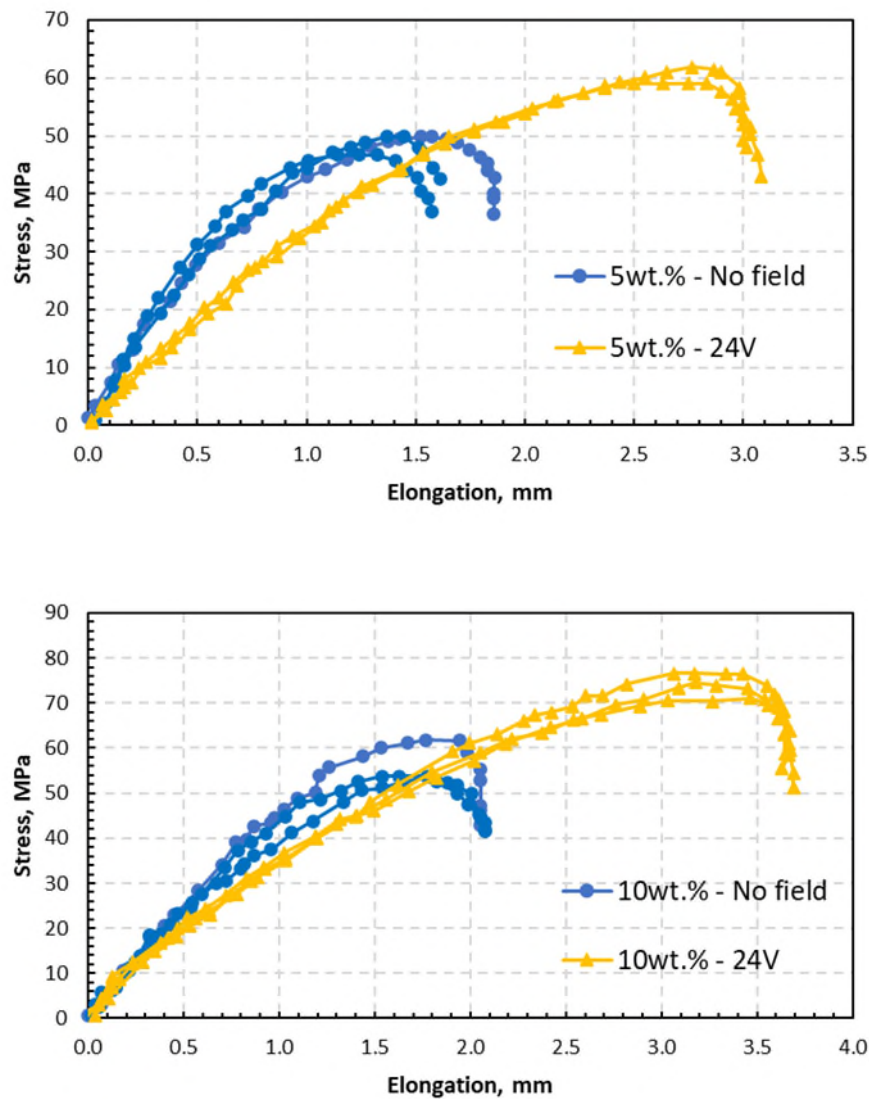


Figure 5-11. The tensile stress vs. elongation data in 1wt.%, 5wt.% and 10wt.% Si-BaTiO₃-epoxy nanocomposites under 0V and 24V electrical voltage.

Elastic modulus is known to be significantly affected by the concentration of nanofillers and the matrix. Tensile tests were conducted on epoxy composites with increasing Si- BaTiO₃ content (ranging from 1% to 10% by weight) while applying various in-situ voltages (0V, 6V, 9V, 24V). Results indicate that elongation and the point of fracture increase with rising Si- BaTiO₃ content and voltage application. For 1 wt% BaTiO₃, the tensile strength increased significantly with increasing voltage, as shown in Figure 5-10 and 5-11, while the tensile

modulus showed only a slight change (Figure 5-12a). In the case of 5 wt% and 10 wt% Si-BaTiO₃, tensile strength showed minor fluctuations with increasing voltage (Figures 5-12b and c). However, there was an evident decline in the tensile modulus with increasing electric fields. The increase in elongation and strength is attributed to the introduction of a compressive field. The application of an electric field at higher Si- BaTiO₃ content led to the softening of the nanocomposite material. This softening or toughening effect was more pronounced at higher filler contents (e.g., Si- BaTiO₃) compared to lower filler contents, as it was not as significant in the 1 wt% Si- BaTiO₃/epoxy nanocomposites. The softening effect could be related to the polarisation of epoxy nanocomposites and domain wall displacement under the electric field. Further experiments would be required to provide a complete explanation for the decreasing trend in modulus caused by the presence of an electric field in the cases of 5% and 10% wt.% Si- BaTiO₃. However, it is evident that the application of an electric field at higher Si- BaTiO₃ content levels has a softening effect on the nanocomposite material. This information highlights the complex interplay between nanofiller concentration, applied voltage, and the mechanical properties of these composites, providing valuable insights for further research and applications.

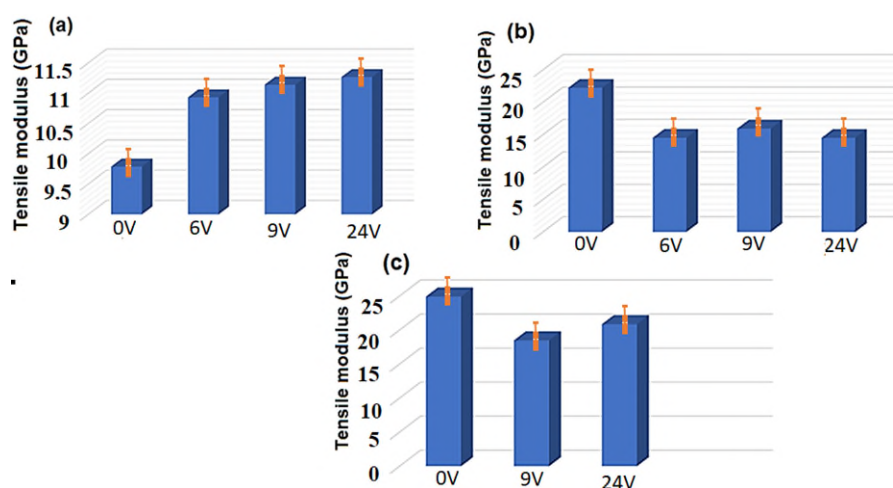
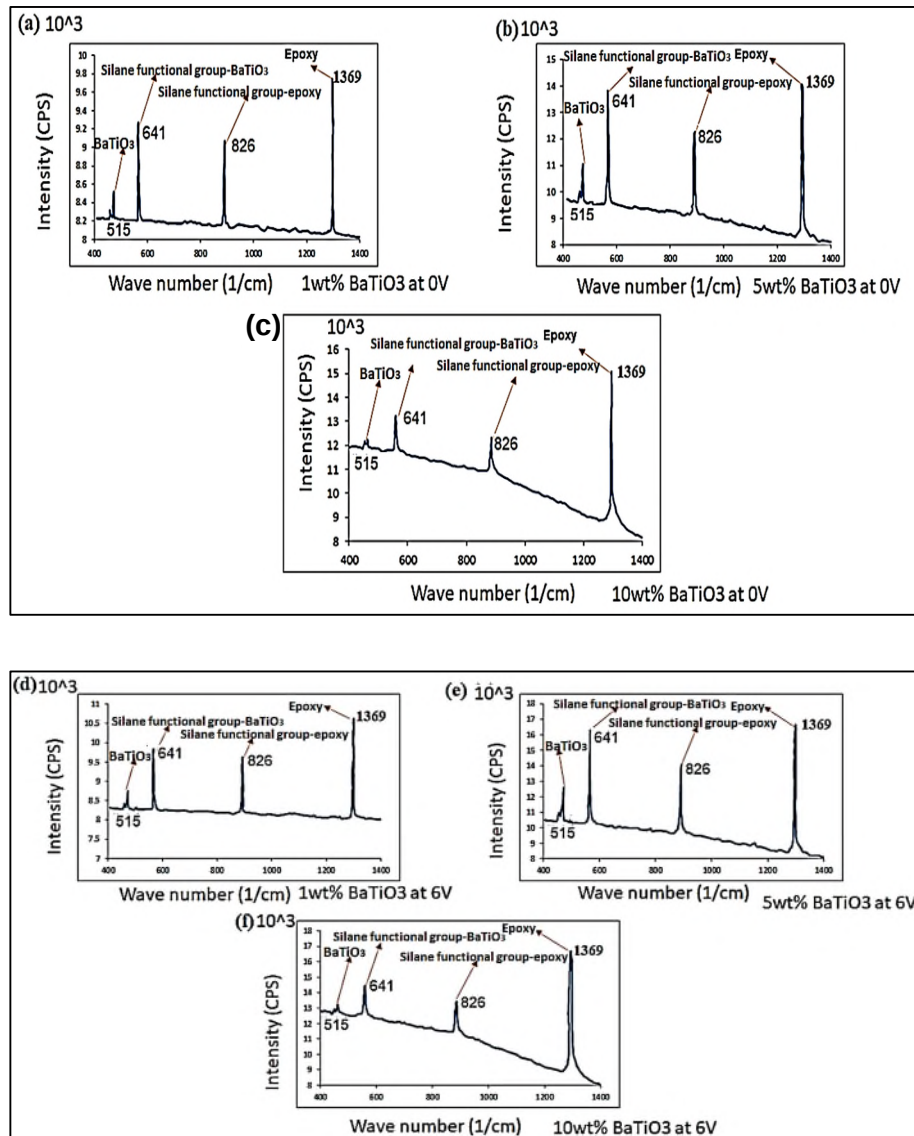


Figure 5-12. The tensile modulus of Si-BaTiO₃-epoxy nanocomposites at different electrical voltage with varying content of 1 wt.%, 5 wt.% and 10wt%.

5.4.4 Electric field induced raman spectroscopy

Raman spectroscopy, which studies a shift in scattering frequency as a function of inter-atomic spacing fluctuation, is one of the most effective methods for examining local residual stresses in crystalline materials. Nonetheless, this method has been demonstrated for polymer matrix composites. Raman spectroscopy is also used to verify changes in the Si- BaTiO₃ crystal structure. As seen in Figure 5-13, such characterisations were initially performed on Si- BaTiO₃/Epoxy nanocomposite samples comprising 1, 5, and 10% wt.% while applying electric fields with voltages of 0, 6, 12, and 24 V. The Raman sharp peaks with no electric field (Figure 5-13a-c) are identified as 515, 641, 826, and 1369 cm⁻¹, showing the usual peaks of BaTiO₃, Si- BaTiO₃, Si- epoxy, and amorphous epoxy, accordingly. By increasing the amount of Si- BaTiO₃, the peak's intensity has been somewhat increased. Since Raman peak intensity represents molecule polarisability and active molecular group density, a minor rise in intensity suggests a slight increase in the polarisability of Si- BaTiO₃-epoxy nanocomposites and an increase in active species with increasing Si- BaTiO₃ content. The Raman spectra of Si- BaTiO₃-epoxy nanocomposites at 1, 5, and 10% Si- BaTiO₃ in a 6V field (Figure 5-13d-f) show a significant increase in intensity when relative to samples measured in absence of electric field (0). In higher field strengths of 12V and 24V, this trend of rising intensity is reproduced (Figure 5-13g-i and Figure 5-13j-l, respectively). Additionally, it was observed that the higher the voltage the broader the peaks. Such a result supports the idea that polarisability is influenced not only by Si- BaTiO₃ concentration but also by the applied voltages. The peak's enlargement and intensity imply bond stretching and structural change because of field-induced dipolar displacement at the intrinsic level and polarisation in such a field. With this intrinsic straining/stretching effect for Figure 5-13 data, it can be interpreted that such stretch at the interatomic crystalline level (under a simplified assumption of full crystalline Si- BaTiO₃

structure) would contribute to softening and thus decrease in tensile modulus at larger extrinsic scales.



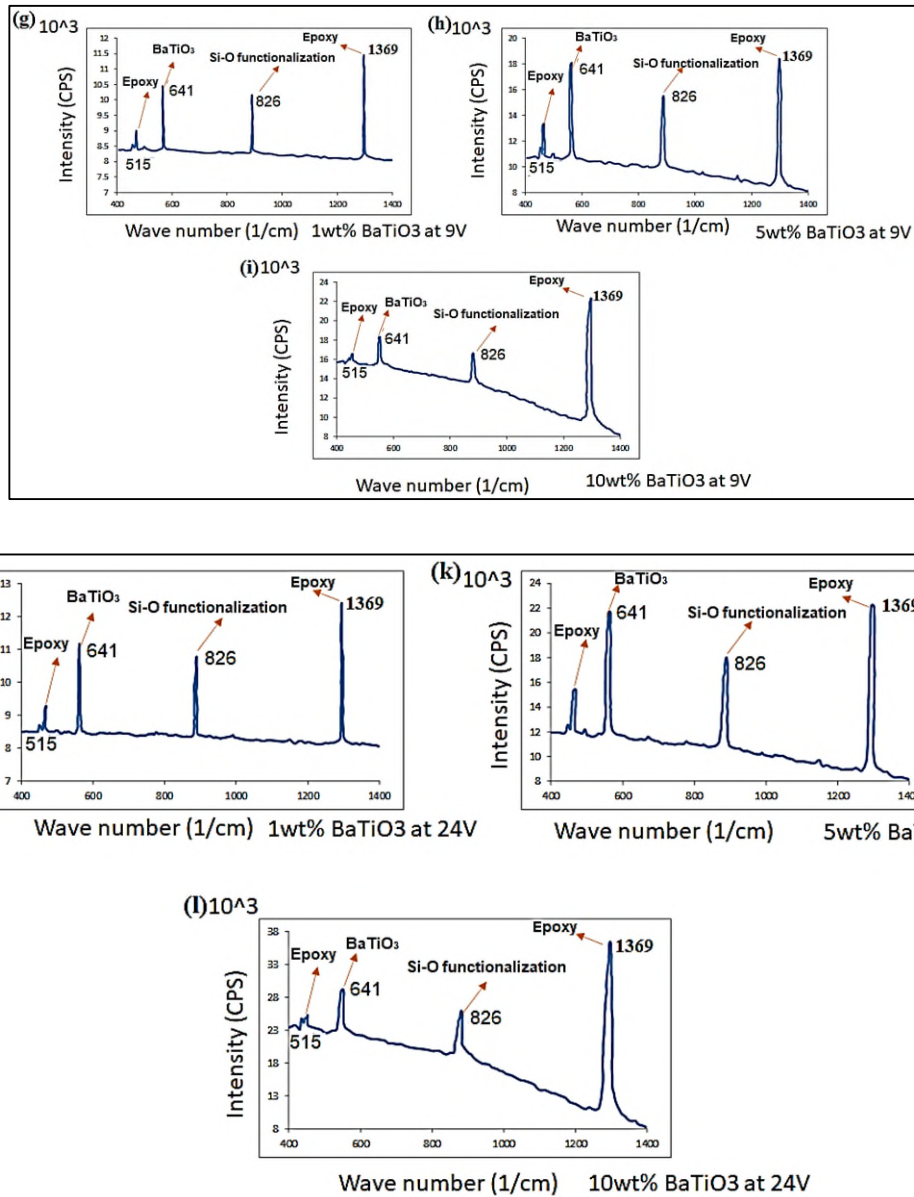


Figure 5-13. Measurement of intensity and broadening of Raman peaks with respect to the wave number at different Si-BaTiO₃ content and under electric fields of a-c) 0V (no field), d-f) 6V, g-i) 12V and j-l) 24V.

5.4.5 Electric field induced tensile testing with digital image correlation (DIC)

Tensile testing with digital image correlation (DIC) was conducted to evaluate the mechanical behaviour of epoxy composites containing different concentrations of Si- BaTiO₃ (5% and 10% wt%) under the influence of in-situ electric fields with varying voltages (0 V and 24 V). The primary measurement focused on tracking

the total displacement per millimeter (mm) of the specimens during tensile testing, as illustrated in Figure 5-14. This approach allowed for a detailed analysis of how the electric fields and Si- BaTiO₃ content affected the deformation and mechanical response of the epoxy composites. The observed relationship between Si- BaTiO₃ concentration and total displacement per millimeter in the epoxy composites suggests a complex and likely nonlinear interaction. This interaction is influenced not only by the Si- BaTiO₃ content but also by the applied voltage. Several factors contribute to this complexity, including the particle size and distribution of BaTiO₃ in the composite, the properties of the epoxy matrix, and the electrical characteristics of Si- BaTiO₃-epoxy nanocomposites. These findings highlight the intricate nature of the mechanical behaviour in these materials and the need for further investigation to fully understand the underlying mechanisms. The relationship between applied voltage and total displacement per millimeter can be affected by various factors, including the duration of applied voltage and the testing environment. The statement likely refers to the ferroelectric and piezoelectric effects observed in BaTiO₃ ceramics. The ferroelectric effect is a property where certain materials exhibit reversible spontaneous electric polarisation when subjected to an external electric field. This effect can play a significant role in the behaviour of materials like BaTiO₃ in response to electrical stimuli, further contributing to the complexity of their mechanical response. The ferroelectric effect is associated with the asymmetrical arrangement of electric dipoles within a material, leading to the presence of spontaneous polarisation. This effect arises due to the disparity in the arrangement of positive and negative charges within the crystal lattice. Crystals like barium titanate and lead zirconate titanate are well-known for exhibiting the ferroelectric effect, and they find applications in capacitors, memory devices, sensors, and other technologies. The piezoelectric effect involves the generation of an electric potential when a material experiences mechanical stress or deformation. This property is valuable in various applications, including sensors, actuators, and energy harvesting devices. Both the ferroelectric and piezoelectric effects demonstrate the intricate interplay between electrical and mechanical phenomena in certain materials. According to the results, the displacement per

millimetre (displacement/mm) in ceramics such as BaTiO₃ is proportional to the strength of the applied electric field. Increasing the strength of the electric field or mechanical stress result in an increase in displacement/mm. The polarisation state of the material has a significant effect on the displacement/mm, as demonstrated by the results of in-situ electric field-induced tensile testing. This means that the magnitude and direction of the BaTiO₃ ceramic's polarisation can influence the amount of displacement caused by an applied electric field or mechanical stress. This is evidence that electric fields might have a positive effect on the elongation of epoxy/Si- BaTiO₃ nanocomposites, and this improvement in elongation leads to improved toughness. The study of the relationship between electrical stimuli and the mechanical response of polymeric materials is known as electroactive polymers. In the case of epoxy, increased elongation is likely to result in increased toughness because it allows the material to absorb more energy before breaking. This is an exciting area of research that could lead to the development of advanced materials for a variety of industries.

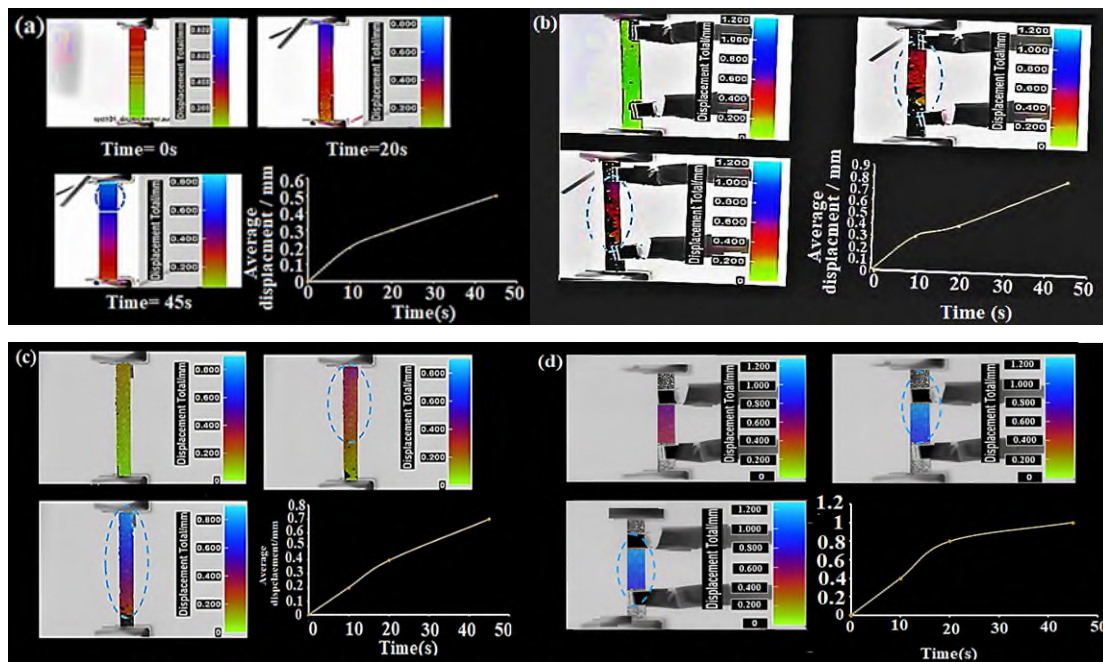


Figure 5-14. Electric field Induced mechanical properties with digital image correlation (DIC), a) average displacement 5wt% Si-BaTiO₃/epoxy nanocomposite at 0V during the test, b) average displacement 5wt% Si-BaTiO₃/epoxy nanocomposite at 24V during the test, c) average displacement 10wt% Si-BaTiO₃/epoxy nanocomposite at 0V during the test, d) average displacement 10wt% Si-BaTiO₃/epoxy nanocomposite at 24V during the test.

5.4.6 Electric field induced different electrical properties by COMSOL 5.5 Multi-physics

The measurement of electrical displacement field, dielectric polarisation, and volumetric power dissipation density is essential for understanding how different factors, including the voltage (0 V and 24 V) and the concentration of Si- BaTiO₃ in the epoxy composites, affect the electrical properties of the material. These measurements provide valuable insights into how the material responds to applied electric fields, which is crucial for various applications in electronics and materials science. Figure 5-15 likely illustrates the results of these measurements, showing the relationship between the parameters mentioned and the experimental conditions. Dielectric nanocomposites are unique materials composed of components with distinct electrical and mechanical properties. They possess the capacity to store significant energy, primarily attributed to the presence of an electrical displacement field (EDF). This field characterises the behaviour of electric charge within an electric field, enabling the measurement of polarisation in these materials. Understanding EDF and polarisation is essential for comprehending how these nanocomposites respond to electric fields, particularly in terms of energy storage and electrical properties. The electric displacement field, denoted as D , is a vector field featured in Maxwell's equations. It takes into account the impact of both bound and free charges within materials. The term "displacement" in D signifies its role in describing the displacement current in dielectrics. Electrical displacement fields find application in the fields of physics and electrical engineering to model and understand electric charge behaviour in various materials. Electrical displacement fields are essential in

numerous electronic applications, such as data transmission, signal amplification, and the functioning of capacitors. Studying the electrical displacement fields of these materials is crucial for understanding how they respond to electric fields. In classical electromagnetism, the density of induced electric dipole moments within a dielectric material is represented by polarisation density. This parameter helps characterise the material's response to an external electric field. The electric polarisation of a dielectric is the electric dipole moment generated per unit volume of the dielectric material. In systems containing Si- BaTiO₃ (strain-induced barium titanate), increasing the concentration of this material can enhance electrical properties like the electrical displacement field, dielectric polarisation, and volumetric power dissipation density, as illustrated in Figure 4-15. This suggests that higher Si- BaTiO₃ content leads to improved electrical characteristics in the composite material. The increase in Si- BaTiO₃ content in the system leads to higher overall electrical polarisation, resulting in elevated electrical displacement field, dielectric polarisation, and volumetric power dissipation density. This effect is primarily attributed to the ferroelectric nature of BaTiO₃, allowing for reversible electric polarisation when exposed to an electric field. This enhances the energy storage capacity of the system, resulting in increased volumetric power dissipation density. BaTiO₃ possesses a high dielectric constant, enabling the storage of substantial electrical energy per unit volume. This underscores the critical role of material selection in determining a system's electrical properties, as supported by simulation results. These findings emphasise the material's potential for industrial applications, showcasing its significance in electrical engineering. Increases in tensile strength, elongation, and modulus signify improved material strength and resistance to stress-induced fractures. Greater ductility and elasticity suggest enhanced flexibility and energy absorption capacity without material failure. The heightened Raman intensity indicates a more ordered and organised molecular structure, contributing to improved material properties. These findings hold valuable insights for researchers and engineers seeking to enhance material properties across diverse applications. Additional research may be necessary to comprehensively elucidate the underlying mechanisms driving these improvements and explore the broader

spectrum of potential applications for this material. Alignment with experimental observations further strengthens the validity of these observations.

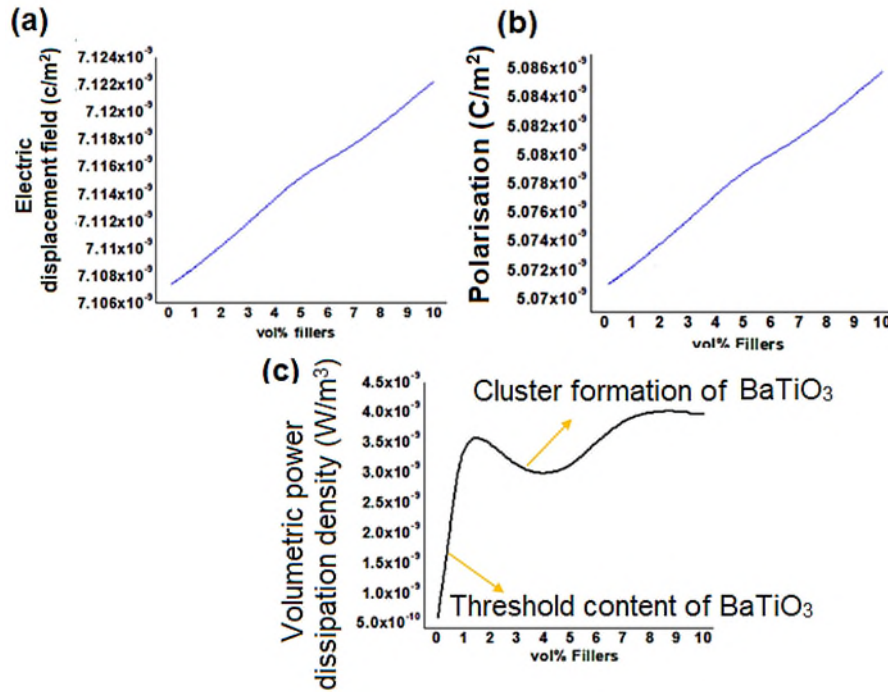


Figure 5-15. Electric field Induced Electrical properties of Si-BaTiO₃/epoxy nanocomposite by COMSOL 5.5 Multi-physics at 24V, a) Electrical displacement field (c/m²), b) Dielectric Polarisation, c) Volumetric power dissipation density.

5.5 Conclusions

The study distinctly uncovered the substantial influence of integrating ferroelectric Si- BaTiO₃ nanoparticles into the epoxy matrix, leading to noteworthy enhancements in mechanical properties. Under the influence of an in-situ electric field, these nanocomposites exhibited pronounced improvements in tensile strength, elongation, and modulus compared to their non-electrically stimulated counterparts. This observation strongly suggests that ferroelectric materials possess the potential to dynamically bolster the mechanical performance of nanocomposites, perfectly aligning with the thesis objective aimed at investigating their impact on material properties. Another pivotal aspect of this research focused on employing surface functionalisation with silane. This

process significantly augmented the quality of bonding between the nanoparticles and the epoxy matrix. Strengthening the interfacial bonding is crucial for optimising nanocomposite effectiveness, ensuring better load transfer between the filler and matrix. This directly fulfills the objective of understanding how ferroelectric nanoparticles impact the material matrix and provides valuable insights into methods for enhancing nanocomposite performance. The study extensively deliberated on the potential implications of these enhanced mechanical and electrical properties across various industries such as aerospace, automotive, and electronics. These sectors heavily depend on advanced materials to achieve lighter, stronger, and more efficient components. For instance, the application of nanocomposites with superior properties in aerospace can lead to lighter aircraft and enhanced fuel efficiency. These findings align seamlessly with the broader objective of exploring the potential applications of ferroelectric materials in enhancing material performance across different sectors. The research also underscored the highly sensitive response of ferroelectric materials to electric fields. This notable sensitivity opens avenues for developing smart materials capable of adapting to changing conditions—a critical aspect for industries requiring adaptable and responsive materials. This observation distinctly relates to the objective of investigating the influence of ferroelectric nanoparticles, shedding light on their dynamic behaviour under the influence of electric fields. Finally, the chapter emphasised the significance of this research as a foundational basis for future investigations in the field. It hinted at potential future directions, including exploring different ferroelectric materials, optimising processing conditions, and varying the strength of electric fields. These proposed directions harmonise perfectly with the objective of paving the way for deeper exploration into the influence of ferroelectric nanoparticles on nanocomposite properties. In summary, the chapter elegantly provides detailed evidence illustrating how the work and findings intricately answer the specific thesis objective of investigating the influence of ferroelectric nanoparticles on the mechanical, electrical, and thermal properties within high-performance epoxy nanocomposites, aligning with the predefined research objectives.

CHAPTER 6

Concluding Insights and Future Directions

6.1 Summary of findings

This research has been dedicated to unravelling the impact of electric fields on the electrical and mechanical characteristics of conductive and dielectric nanocomposites. It has employed a comprehensive approach that marries computational modelling with experimental characterisation, delving into a wide array of properties, including thermal, mechanical, electrical, viscoelastic, and crystallisation responses. The goal was to gain a profound understanding of multifunctional nanocomposites' behaviour, which carries significant implications for practical applications such as energy storage, sensors, and electronic devices. The research was centred on the characterisation of modified epoxy and thermoplastic nanocomposites filled with evenly distributed dielectric and electrically conductive nanomaterials while subjecting them to in-situ electric and electromagnetic fields. To achieve this, the study has exploited several approaches: computational modelling and Bayesian statistical analysis to scrutinise the influence of filler materials on properties, experimental assessments of electrical and mechanical properties under the influence of electric fields, and theoretical modelling combined with experimental validation of GNPs/ BaTiO₃/thermoplastic/epoxy-based nanocomposites. By utilising these approaches, the research has aspired to construct a robust knowledge framework. This framework is intended to serve as a guide for designing superior materials tailored to specific applications, marking a significant stride in advancing the field of materials science and engineering. The ultimate ambition is to contribute to the creation of materials that can address complex challenges across various industries. The current emphasis on multifunctional materials is a response to the desire to exploit the advantages of combining diverse and complementary properties. This focus is driven by the ambition to achieve heightened performance in critical sectors such as aerospace, automotive, and energy. Multifunctional materials offer the potential to revolutionise various industries by endowing them with superior attributes that result from the synergistic combination of distinct properties. This trend has gained momentum in response to the growing demand for materials capable of addressing multifaceted challenges and fulfilling diverse requirements. One of the primary

objectives is to enhance overall performance and efficiency in critical applications by harnessing the remarkable versatility of multifunctional materials. Scientists and researchers are actively exploring innovative approaches to create materials that can seamlessly integrate a range of properties to enhance efficiency, strength, and versatility. The pursuit of multifunctional materials underscores their pivotal role in driving technological advancements and fostering innovation across industries. This drive is motivated by the need to develop materials that excel in diverse applications, offering enhanced performance across various domains. The goal is to harness the full potential of multifunctional materials to unlock new possibilities and capabilities, thereby pushing the boundaries of what technology can achieve. Researchers are dedicated to exploring novel methods to design and fabricate materials capable of meeting the complex and evolving demands of modern industries, ultimately leading to more efficient and adaptable solutions. Graphene-based materials, renowned for their remarkable surface area, mechanical strength, and electrical conductivity, have the capacity to bring about a revolution in the realm of composite materials. Similarly, Barium Titanate (BaTiO_3), characterised by its status as a ferroelectric ceramic with a high dielectric constant and exceptional piezoelectric properties, holds the promise of enabling the creation of composites boasting superior properties, potentially even including self-repairing capabilities.

This comprehensive research endeavours spans five chapters, each meticulously examining the properties of materials and their responses when subjected to electric and electromagnetic fields. Its overarching objective has been to provide profound insights into the transformative potential of Polymer Nanocomposites (PNCs), which are poised to reshape the landscape of materials science by surmounting long-standing limitations. Through this research, the aim has been to unlock the secrets of PNCs, unveiling their capacity to overcome traditional barriers and revolutionise the development of materials. This transformation has the potential to impact diverse industries and applications, offering innovative solutions and enhanced performance across the board. Researchers are dedicated to exploring the intricate interplay of material

properties and electric fields to harness the full potential of PNCs and open new frontiers in materials science and technology.

Chapter 1 has served as an exploration into the profound influence that PNCs exert on the expansive field of materials science. It has underscored the transformative potential of PNCs, ushering in a fundamental shift from traditional materials. These innovative materials empower researchers with an unprecedented degree of control, achieved through the meticulous integration of nanoparticles into polymers. This heralds a new era in materials design, granting precision control over vital attributes such as stiffness, strength, thermal conductivity, and electrical conductivity. The chapter has positioned PNCs at the vanguard of materials innovation, poised to reshape entire industries and propel technological advancement. Chapter 1 has laid the groundwork for a deeper understanding of the pivotal role played by PNCs in reshaping materials science and fuelling technological progress. The enhanced versatility that PNCs offer has the transformative potential to surmount longstanding limitations, instigating innovation across diverse industries. PNCs are positioned as a solution to revitalise polymers like polypropylene and polyethylene terephthalate, which, while essential, have been hampered by inadequate mechanical properties. Through the intervention of PNCs, these polymers can gain newfound mechanical robustness, rendering them adaptable and dependable across an array of applications. This highlights the indispensable role of PNCs in meeting the evolving demands of industries and propelling them towards heightened performance and innovative breakthroughs. This research has probed deeply into the transformative capabilities of PNCs within the realm of materials science. PNCs emerge as a catalyst for engineering materials endowed with bespoke properties, elevated mechanical attributes, and amplified performance across a spectrum of industries. It is worth noting that epoxy, a ubiquitously used thermosetting polymer, has been grappled with constraints rooted in brittleness and low toughness, yet PNCs offer a pathway to fortify its capabilities. Through the infusion of nanoparticles into epoxy, its strength and versatility witness significant augmentation. Chapters 1 and 2 provide a sturdy foundation, setting forth the research's significance and alignment with the existing corpus of

knowledge. Subsequent chapters delve into the intricacies of research methodologies, divulging findings, and their implications, ensuring a structured and all-encompassing approach. The overarching aim has been to kindle innovation and proffer solutions to critical sectors by harnessing the inherent adaptability of PNCs. This research promises to redefine the boundaries of composite materials' capabilities and unfurl fresh avenues for materials engineering and innovation spanning diverse industries.

Chapter 3 of this research study represents a significant dive into the realm of theoretical modelling and empirical validation concerning GNPs/BaTiO₃/thermoplastic-based nanocomposites. Its primary objective has been to establish a robust comprehension of how these nanocomposites perform across a spectrum of properties, bridging the theoretical and experimental aspects. This chapter meticulously has scrutinised the influence of diverse filler materials on electrical, thermal, mechanical, and electromagnetic behaviours, offering profound insights into their potential for enhancing material properties. Through a harmonious amalgamation of computational modelling and real-world experimentation, Chapter 3 contributes a wealth of valuable insights into the intricate world of nanocomposite materials. It has effectively demystified how different filler materials, such as GNPs and BaTiO₃, impact the properties of thermoplastic polymer matrix composites. The spotlight here has been on the electrical, thermal, mechanical, and electromagnetic aspects of mechanically stimulated composites, with an eye towards optimising their performance. Notably, Chapter 3 underscores the viability of GNPs and BaTiO₃ as alternative filler materials, expanding the repertoire of choices in thermoplastic polymer composites. An essential highlight of this chapter is its emphasis on reinforcement geometry's pivotal role in moulding composite properties. It has also accentuated the profound impact of filler quantity and mechanical stimulation on morphology, particularly how they contribute to enhancing electrical and thermal characteristics in nanocomposites. The comprehensive insights garnered in Chapter 3 offer a rich understanding of how distinct fillers influence composite behaviours, empowering material designers with the knowledge needed for precise optimisation. In essence, Chapter 3 acts as a bridge between theory and

practice, providing invaluable data and observations that guide the design and enhancement of nanocomposite materials. It serves as a critical foundation for the subsequent chapters, where the exploration of these materials' properties continues, further illuminating their transformative potential in materials science and industry applications.

Chapters 4 and 5 of this research have delved into a comprehensive exploration of the electrical, thermal, mechanical, and electromechanical properties of epoxy nanocomposites reinforced with graphene and BaTiO₃. These chapters represent the culmination of a multidimensional investigation that seamlessly has integrated theoretical modelling with practical experimentation, offering a holistic understanding of the studied nanocomposites. Chapter 4 has focussed on the computational analysis of critical electrical and thermal characteristics in epoxy nanocomposites reinforced with graphene and BaTiO₃. This thorough examination has employed computational modelling and Bayesian statistical analysis to assess how various filler materials, including GO, RGO, GNP, and BaTiO₃, can impact the properties of epoxy polymer matrix composites. Key properties under scrutiny have encompassed direct current (DC) conductivity, dielectric constant, and thermal behaviour. The findings spotlight the potential of GO and RGO as alternative filler materials in epoxy composites, shedding light on the pivotal role of filler geometry in shaping composite properties. Moreover, Chapter 4 has evidenced the influence of GNPs' quantity and thickness, with thinner GNPs demonstrating superior electrical conductivity and thermal characteristics, opening doors to applications in energy storage and thermal management. Additionally, the study has emphasised the significance of considering size and shape when incorporating BaTiO₃ nanoparticles into energy-efficient electrical devices. The tantalising prospect of phase transitions facilitated by electric fields adds a layer of innovation, hinting at non-volatile information storage and the possibilities of neuromorphic computing. Chapter 5 has delved into the mechanical response of epoxy composites infused with varying concentrations of Si- BaTiO₃ under diverse electric field conditions. It has scrutinised key mechanical properties, including tensile strength, elongation, and modulus, in the context of applied electric fields. The findings have revealed

intriguing fluctuations in mechanical properties tied to Si- BaTiO₃ concentration and voltage levels. These observations suggest the potential for both softening and toughening effects, particularly at higher filler concentrations, driven by ferroelectric polarisation and domain wall displacement. Furthermore, the incorporation of Raman spectroscopy in Chapter 5 has provided valuable insights into structural changes induced by electric fields. This analytical tool has uncovered how applied voltages influence polarisability and molecular structure, offering explanations for alterations in mechanical properties. In essence, Chapter 5 has unravelled the intricate interplay between electric fields and mechanical behaviour in nanocomposites, adding depth to the understanding of their behaviour. Together, Chapters 4 and 5 constitute a pivotal segment of the research, shedding light on the multifaceted behaviours of nanocomposite materials under varying conditions. They offer a treasure trove of insights with implications for practical applications and the optimisation of these versatile materials across various industries.

This final chapter plays a crucial role in this research by offering a synthesis of the study's vital discoveries and providing a glimpse into potential avenues for future investigations. It serves as a summative reflection of the research's achievements and offers guidance for further exploration in the field. In essence, this chapter underscores the profound importance of multifunctional materials across a spectrum of industries. It reinforces the idea that materials capable of seamlessly integrating a diverse range of properties hold the key to unlocking enhanced performance and innovation. These materials are positioned to address the evolving challenges and demands in critical sectors. A central theme of this chapter is the pivotal role of polymer nanocomposites (PNCs) in elevating material properties. PNCs are acknowledged as a driving force behind the enhancement of various attributes in materials. Specifically, the potential of graphene-based materials and barium titanate as reinforcement agents in polymer composites are underscored. Graphene, renowned for its impressive surface area, mechanical strength, and electrical conductivity, is identified as a game-changer in the realm of composite materials. Its incorporation has the potential to revolutionise a wide array of industries by enhancing mechanical,

electrical, and thermal properties. Moreover, the tantalising prospect of self-repair capabilities adds an extra layer of innovation. Barium titanate, a ferroelectric ceramic with a high dielectric constant and remarkable piezoelectric properties, is recognised for its potential to elevate the performance of polymer composites. When integrated into polymer matrices, it holds the promise of creating composites with superior mechanical, electrical, and thermal properties. Ultimately, the research described in this thesis radiates optimism regarding the future of research in this field. It envisions a landscape where multifunctional materials, empowered by PNCs and the contributions of graphene-based materials and barium titanate, could usher in transformative changes across various industries and applications. The potential to elevate performance, enhance material properties, and even achieve self-repair capabilities paints a bright picture of innovation on the horizon. This work encapsulates the spirit of discovery and the promise of revolutionising industries through materials science.

6.2 Implications and significance

This research journey has delved into the intricate world of nanocomposites, where the fusion of diverse materials, including thermoplastic polymers like polypropylene and poly(ethylene terephthalate), and epoxy, with cutting-edge nanofillers like graphene oxide (GO), reduced graphene oxide (RGO), graphene nanoplatelets (GNPs), and barium titanate (BaTiO_3), leads to remarkable advancements in material science. The research methodology employed in this study represents a groundbreaking approach that integrates computational modelling, experimental techniques, and advanced analysis methods to investigate the properties and behaviour of various nanocomposites. Each chapter of the research contributes significantly to our understanding of these materials and their potential breakthrough applications. These thermoplastic polymer blends are celebrated for their exceptional toughness, rendering them invaluable in industries spanning packaging, automotive, and energy. This research seeks to unlock the potential of nanofillers in these polymers, potentially revolutionising their properties and expanding their utility. Epoxy polymer composites have carved out their niche, especially in aerospace and electronics.

However, their intrinsic brittleness has limited their applicability. This study has ventured into the realm of nanofillers, such as GNPs and BaTiO₃, with the aim of enhancing the mechanical characteristics of epoxy, potentially paving the way for novel applications. The inclusion of nanofillers like GO, RGO, GNPs, and BaTiO₃ represents a paradigm shift in material science. Integrating these nanomaterials into polymers, both thermoplastic and epoxy, holds the promise of redefining their properties, spanning electrical and thermal conductivity, mechanical strength, and more. This research has adopted a holistic approach, leveraging state-of-the-art analytical tools like Scanning Electron Microscope (SEM), Differential Scanning Calorimetry (DSC), 4-probe electrical conductivity measurement, Atomic Force Microscope (AFM), polarised microscopy, tensile testing, and a vector network analyser. These tools have been used to dissect these ingeniously engineered materials, probing their microstructure, crystallisation behaviour, thermal properties, surface characteristics, transcrystallisation phenomena, electrical conductance, mechanical responses, and Electromagnetic Interference (EMI) shielding capabilities. This comprehensive exploration has been carried out to unearth the fundamental principles governing these materials, addressing the intricate questions of why, what, where, and how. Chapter 4 has showcased the research's computational prowess, bolstered by Bayesian statistical analysis. This potent combination has enabled the evaluation of diverse filler materials' effects on the direct current (DC) conductivity, dielectric constant, and thermal properties of epoxy polymer matrix composites. Through simulations, it has unravelled the underlying mechanisms dictating these properties, offering critical insights. The findings stemming from computational modelling have been elevated to scientific significance through empirical validation. Aerospace-grade epoxy resin fortified with tetragonal barium titanate (BaTiO₃) nanoparticles have been subjected to rigorous testing, with the results revealing remarkable tensile properties that open exciting research avenues. Electric field simulations have introduced a novel dimension, studying the intricate response of BaTiO₃ nanoparticle-infused epoxy under varying content loadings. Real-time Raman spectroscopy, conducted in the presence of electric fields, has facilitated a quantitative analysis, uncovering the complex interplay between electric fields

and material behaviour. In conclusion, this research presents groundbreaking implications for the realm of material science and engineering. It not only provides a roadmap for enhancing the properties of nanocomposites but also illuminates the underlying mechanisms governing these materials. These findings transcend the laboratory, offering real-world applications across diverse industries, pushing the boundaries of technological possibilities.

6.3 Future research directions

Nanocomposite materials, amalgamating nanoparticles into polymer matrices, have emerged as promising contributors to enhanced material properties in diverse industries. This proposed study was aimed to deepen the understanding of nanocomposites and unravel their multifunctional capabilities through the integration of advanced materials and innovative techniques. The primary focus was in augmenting electrical, thermal, mechanical, and electromagnetic properties of nanocomposites. The overarching goal was to advance our understanding of how nanocomposites respond to external stimuli, with a particular focus on applications such as sensors and energy harvesting devices. Whereas in this study we have investigated GNP and BaTiO₃, in future research, alternative by important ferroelectric materials such as zirconate titanate (PZT) and bismuth ferrite (BiFeO₃) will be explored to delve deeper into their properties and applications. This will involve a comprehensive investigation to understand the structural, electrical, and mechanical characteristics of these materials, considering their suitability for integration into nanocomposites. The study will focus on elucidating the ferroelectric behaviours of PZT and BiFeO₃, examining their response to varying conditions such as temperature, pressure, and electric fields. Additionally, the research will explore the synthesis methods and fabrication techniques to optimise the incorporation of these materials into nanocomposite matrices, ensuring enhanced compatibility and performance. The outcomes of this future work aim to provide valuable insights into the potential of PZT and BiFeO₃ as alternative ferroelectric materials, thereby expanding the range of options for nanocomposite formulations and advancing the field towards novel applications in various industries. In future investigations, the optimisation

of processing conditions for nanocomposites will be a key focus. This entails a systematic exploration of various processing parameters, such as temperature, pressure, mixing duration, and precursor concentrations, to fine-tune the fabrication process. The goal is to achieve enhanced control over the electrical, thermal, and mechanical characteristics of the nanocomposites. Experimental methodologies, including statistical design of experiments, will be employed to systematically vary processing conditions and analyse their impact on material properties. The research will also delve into novel processing techniques, such as advanced mixing methods or innovative curing processes, to further refine nanocomposite structures. This future work aims to establish comprehensive guidelines for tailoring processing parameters to achieve specific material outcomes, facilitating the reproducibility and scalability of nanocomposite fabrication processes for various applications across different industries. In future research endeavours, the investigation of the impact of various stimuli on nanocomposite performance (including graphene based and BaTiO₃ epoxy nanocomposites) will be expanded beyond electric fields. This extension involves exploring the influence of different stimuli, including but not limited to electric field strengths, temperature variations, mechanical stress, and humidity fluctuations. The study will systematically analyse how these external factors affect the electrical, thermal, and mechanical properties of nanocomposites, providing a holistic understanding of the material's responsiveness to multiple stimuli, contributing to the development of adaptable and multifunctional nanocomposites. Experimental protocols will be designed to subject nanocomposites to controlled conditions mimicking real-world scenarios, and advanced analytical tools will be employed to quantify and assess the material responses. The outcomes of this future work are expected to broaden the potential applications of nanocomposites, paving the way for advancements in self-regulating systems and adaptable structures across various industries. The outcomes will facilitate the development of nanocomposites with enhanced dynamic properties, opening avenues for innovative solutions in various industries. This research will extend its focus to external stimulation of nanocomposites, exploring their responses to factors such as temperature

changes, mechanical stress, and humidity variations. This comprehensive exploration aims to broaden the potential applications of nanocomposites, leading to advancements in self-regulating systems and adaptable structures. Sustainability and environmental impact will also be considered, aligning with global efforts toward greener technologies.

6.4 Conclusions

This thesis was meticulously developed to explore how nanocomposites respond to mechanical and electrical stimuli. The objectives were effectively attained through a well-organised methodology, ensuring a coherent and progressive analysis from the research's inception to a thorough exploration of nanocomposite properties. The selection of materials, particularly graphene-based nanomaterials (GNPs) and barium titanate (BaTiO_3), was not only pertinent but also executed with ethical considerations in line with the research objectives. This material selection significantly contributed to advancing materials science and engineering, showcasing the potential for creating innovative and sustainable materials from recycled sources. The intentional choice of materials aimed to address critical environmental concerns while seamlessly aligning with the research's focus on exploring the potential applications and properties of these materials. This thesis represents a crucial milestone in the progression, understanding, and application of nanocomposite materials. It surpasses mere expansion of our understanding, holding immense promise in shaping the future of materials science and engineering, paving the way for innovative and sustainable solutions across industries. The journey through this thesis involved a comprehensive exploration of Polymer Nanocomposites (PNCs), GNPs, and BaTiO_3 . Chapters 1 and 2 provided a foundational understanding by highlighting the disruptive impact of PNCs in material design and emphasising the revolutionary potential of GNPs and BaTiO_3 across scientific domains. These chapters acted as a springboard for a deeper investigation into the properties and potential applications of these materials. Successive chapters laid out a robust framework for examining the behaviour of GNPs/ BaTiO_3 /thermoplastics-based nanocomposites. Chapter 3's theoretical modelling and experimental validation

were pivotal in unravelling how these materials influence various properties. Chapter 4 further advanced the analysis through computational modelling and Bayesian statistical analysis, discerning the distinct impact of different filler materials on epoxy polymer matrix composites. Chapter 5 introduced cutting-edge real-time evaluation techniques using the COMSOL Multiphysics platform. This chapter served as a critical juncture, shedding light on the intricate behaviour of aerospace-grade epoxy resin embedded with BaTiO₃ nanoparticles under electric fields, significantly advancing our understanding of their dynamic responses to external stimuli. This concluding Chapter not only has reaffirmed the significance of multifunctional materials and polymer nanocomposites but also has offered a visionary perspective. It vividly showcased the potential of GNPs and BaTiO₃ in fortifying material properties, leading to advancements in mechanical, electrical, and thermal characteristics. Moreover, it hinted at the prospect of self-repair capabilities, indicating a transformative era across diverse industries. In summary, this thesis stands as a significant accomplishment in unravelling the potential of nanocomposite materials. It does not merely expand our understanding; it holds the promise of transforming the landscape of materials science and engineering, heralding a new age of innovation and sustainability across a multitude of industries.

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