

CRANFIELD UNIVERSITY

DANNING LI

Investigation of the General Properties and Field-induced
Electromechanical Response of Polymer Nanocomposites with
Surface-functionalised Dielectric Nanoparticles

School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

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Academic Year: 2018 - 2022

Supervisors:
Dr. David Ayre
Dr. Hamed Yazdani Nezhad
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This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy at the Faculty of Manufacturing,
Cranfield University

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ABSTRACT

For the past several decades, polymer composite materials have become increasingly popular in various industrial sectors owing to their advantageous properties, such as light weight and high mechanical performance. Most of the failure modes of composite materials are initiated by the coalescence of microcracks in the matrix. Therefore, matrix toughening is one of the most popular approaches to improve the overall fracture toughness of polymer composite materials. The most widely known approach for matrix toughening is the addition of a second phase, such as rigid or/and rubber particles, to dissipate the fracture energy. Several studies have focused on another approach, known as 'active toughening', involves introducing a thermal-induced strain from the fillers to its surrounding matrix, but this approach could only deliver slow and irreversible toughening due to the polymer's poor thermal conductivity. In this study, a new approach is presented that involves an instantaneous extrinsic strain field activated by remote electromagnetic radiation. Quantification of the real-time field-induced strain evolution with microwave radiation is conducted via fibre optic sensing technology (FBGs). Theoretical expressions correlating the field-induced strain with microwave power level and exposure time have been developed, with the theoretically calculated solution validating the experimental data and describing the underlying physics. This study has introduced functionalised ferroelectric barium titanate nanoparticles (BaTiO_3) as a second phase dispersed into an epoxy matrix. The embedded nanoparticles are capable of introducing electro-strains to their surrounding rigid epoxy when subject to an external electric field, which result from the domain wall movements due to polarisation orientation. A diglycidyl ether of bisphenol A epoxy with the hardener Aradur 3487 were modified with the BaTiO_3 nanoparticles embedment. The silane coupling agent for the nanoparticles' surface functionalisation was 3-glycidoxypropyl trimethoxysilane (3-GPS). Ultrasonication and solvent-aided mixing (ethanol, $\text{C}_2\text{H}_6\text{O}$, 99.9%) are employed to facilitate the dispersion of BaTiO_3 nanoparticles. Firstly, the crystal microstructure of the functionalised BaTiO_3 nanoparticles and the mechanical, thermal, and dielectric properties of epoxy nanocomposite materials have been characterised via various conventional techniques. It has

been observed that the addition of the nanoparticles only has an insignificant impact on the curing extent of the epoxy. After that, the surface-bonded fibre grating sensors have been employed to investigate the variation of strain and temperature change of the epoxy nanocomposite materials simultaneously in the microwave oven at 2.45GHz with different power levels. The strains developed in the nanocomposite, adhesive used for FBG bonding, and the holding fixture are then studied via FBG sensors to distinguish the strains induced by domain wall movement from thermally induced strains. Repeated compressive strain fields are observed as a decline in the FBGs strain measurements of epoxy nanocomposite samples with negligible temperature change when placed horizontally in the oven cavity. Raman spectra are used in this study to observe the post-microwave effect of the internal stress state. The blueshift of the characterisation peaks of BaTiO₃ has been identified, thus suggesting a residual stress field experienced by the nanoparticles. The multi-functional nanocomposite development and qualifications presented in this study proposed a novel active toughening technology for high-performance composite applications in numerous sectors.

Keywords:

Multifunctional nanocomposites; Matrix toughening; Ferroelectrics; Barium titanate; Domain wall movement.

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LIST OF ABBREVIATIONS

3-GPS	3-glycidoxypropyl trimethoxysilane
CSR	Core-shell rubber
CTBN	Carboxyl terminated butadiene-acrylonitrile
CTE	Coefficient of thermal expansion
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential scanning calorimeter
DW	Domain wall
FBG	Fibre Bragg gratings
FCC	Federal Communications Commission
FRP	Fibre-reinforced polymer
FTIR	Fourier-transform infrared spectroscopy
PEEK	Polyether ether ketone
PMC	Polymer matrix composite materials
PMMA	Polymethyl methacrylate
PTFE	Polytetrafluoroethylene
PZT	Lead zirconate titanate
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
UV	Ultraviolet
VNA	Vector network analyser
XRD	X-ray diffraction
TMA	Thermal Mechanical Analysis

LIST OF NOMENCLATURE

P_0	Spontaneous polarization
d	Domain width
Δl	Domain wall displacement
E	Electric field strength
Δp	Electric dipole moment
Δv	Elastic dipole moment
S_0	Spontaneous deformation
T_{ij}	Induced internal mechanical stress
A	Area of the domain wall
k	Force constant per unit domain wall area
V_{DW}	The volume occupied by domain walls without external fields
w	Thickness of a 90° domain wall
$\delta(V_{DW})$	Dirac delta function for the volume V_{DW}
c_{klmn}	Elastic stiffnesses of a medium
$S_{i^*j^*}^0$	Spontaneous deformation of the crystal lattice
G_{ik}	Dynamic Green's tensor
V'	Overall surfaces of the nanoparticle
$u^T(r, t)$	The total geometric displacement of a unit cell
r'	Original equilibrium position without the microwave field
t'	Original equilibrium time without the microwave field
G	Shear modulus

δ_{km}	Kronecker delta
Δl_m	The maximum displacement of the DWs under microwave
ε_0	The permittivity of the free space
E_m	The amplitude of the electric component of the microwave field
$\varnothing$	Phase lag of DW motion with the oscillating microwave field
g	Grain size
Y	Young's modulus
e_{ij}	Elastic strain
ε_{ij}^*	Eigenstrain
u_i	Displacement
σ_{ij}	Stress
C_{ijkl}	Effective stiffness tensor
S_{ijkl}	Compliance tensor
n_j	Outward unit normal vector to the boundary
T_i	Traction force on the boundary
δu_i	Virtual displacement
$\delta \varepsilon_{ij}$	Virtual strain
ε_{kl}^0	Equivalent eigenstrain
Ω	Inhomogeneous problem
Ω^0	Virtual homogeneous problem
ε_{kl}^*	Real residual strain in the inhomogeneous Ω
ε_{kl}^0	Equivalent eigenstrain in the homogeneous Ω^0

r	Radius of the nanoparticle
λ	Lame constants
μ	Lame constants
ν	Poisson's ratio
H	Varying magnetic field strength
E	Varying electric field strength
ω	Angular frequency
ε	Complex relative permittivity
μ	Complex relative permeability
ρ	Charge density
f	Frequency of the applied microwave field
E_{rms}	The root-mean-square value of the local electric field strength
C	Specific heat capacity of the material
d_p	The penetration depth of microwave in the material
c	Velocity of light
ε'	The real part of the complex dielectric permittivity
$\tan \delta$	Tangent loss
ξ	Absorption coefficient
Γ	Transmission coefficient
$P_{incident}$	Incident power at the surface
a	Thickness of the sample
n	Refraction index

1 INTRODUCTION

Among their high-performance engineering applications, the most extensively used ones are fibre-reinforced polymer (FRP) composite materials with the advantages of high specific strength and modulus, facile fabrication, good thermal resistance, and economic efficiency [1]. High-performance FRP composites have two major damage initiation modes when exposed to dynamic events, which are intra-laminar damage (e.g., matrix cracking, fibre fracture and fibre-matrix debonding) and inter-laminar damage (e.g., delamination). The intra-laminar damage is mainly dominated by matrix, fibre, and fibre-matrix interphase properties. However, it is challenging to tailor the properties of the fibre during the fabrication process. Therefore, the most widely adopted approach is matrix toughening owing to the feasibility of manufacturing.

High-performance FRP material is mainly made of thermoset resin, such as epoxy, due to their highly cross-linked structure which provides great mechanical properties and thermal stability. However, despite these advantageous properties, epoxy has its drawbacks of having inherent brittleness that tends to break, especially under transversal direction when subjected to high strain rate or impact loading [2]. Alternatively, thermoplastic-based FRP materials could avoid this problem and are also widely used for engineering applications within the aeronautical and automotive sectors [3]. Thermoplastic-based FRP materials are better at avoiding microcracks and hence display a relatively higher fracture toughness [4]. However, they exhibit a softening behaviour under elevated temperatures and also come with a much higher manufacturing cost and lower stiffness compared to thermoset-based materials [3].

To overcome these property-driven drawbacks in polymer-based composites, researchers have explored different approaches, such as modifying epoxy with the inclusion of various micro-, and nano-fillers as a second phase. Rubber tougheners [5], silica particles [6], carbon nanoparticles [7, 8], clay [9] and fibre coating method [10] are some examples of these fillers. Among these, rubber tougheners have shown to be the most effective in improving fracture toughness [11]. However, the toughness enhancement achieved through the addition of a

second phase is only performed before service. When the epoxy matrix is exposed to mechanical loading during the fabrication, storage and service, microcracks may form, which are extremely difficult to detect and repair due to techniques limitation. Consequently, these internal micro-defects not only decrease the composite's performance but also propagate and lead to disastrous structural failure. Therefore, intensive research has focused on developing bio-mimetic self-healing techniques that can perform a self-repairing operation against cracks during service. However, this technique still faces huge challenges with the cost penalty, and it is also only a one-time event healing [12]. Apart from aforementioned toughening techniques, a few studies also explored the use of an 'active' and reversible toughening approach by introducing an internal residual compressive stress field in the epoxy resin through heating. Such toughening mechanism is mainly attributed to the discrepancy in filler/matrix thermal expansion. However, the drawback of this approach is also apparent that the control of the toughening process is extremely challenging due to the poor thermal conductivity of the polymer, which slows down the material's response. More details on the various toughening methods and their drawbacks are discussed in detail in Section 2.1.

Thus far, most 'active' toughening methods are mainly focused on using external heating and there are no attempts made to date that investigate the strain behaviour of embedded fillers in rigid polymer composites under electromagnetic field exposure. Therefore, in this project, a study on electromagnetic field-induced strain behaviour of embedded fillers is carried out and presented, by incorporating dielectric fillers that demonstrate an electro-strain under an applied electric field. Dielectric materials have been extensively used as actuators and transducers, showing potential for huge electric field-induced strain which is attributed to intrinsic mechanisms from lattice deformation and extrinsic mechanisms due to domain wall movement [13]. The background theory of field-induced strain of ferroelectric materials under an electromagnetic field is explained in Section 2.1.3 and Section 2.3. By incorporating such material in rigid epoxy composite materials, a compressive stress field can be imposed in its surroundings matrix when domain wall movements are activated by external electric field stimulation.

The hypothesis of this project is based on suggesting that the microcrack propagation during damage events would be suppressed under such compressive field activated by microwave field and hence more energy would be required to create new fracture surfaces which ultimately leads to the toughening effect.

Therefore, the first objective of this study is to develop a modified epoxy resin with uniformly distributed dielectric nanomaterials that exhibit electro-strain. A modified epoxy system with uniformly distributed barium titanate (BaTiO_3) nanoparticles is developed, and details about the material properties, functionalisation, and fabrication methods are described in Section 4.1. The effects of incorporated fillers on the thermal, mechanical, and dielectric properties of such epoxy nanocomposite material are studied and presented in Section 5.1.

The second objective of this study is to quantify the strain response of the modified epoxy system in-situ under an electromagnetic field exposure (e.g. microwave). However, the primary limitation of the experiment design is that mechanical tests cannot be performed simultaneously under microwave radiation to evaluate the toughening effect. The major problem in the observation of the mechanical properties of modified epoxy resin under microwave exposure is the requirement to design a testing rig with all components made of non-metal materials that exhibit the least interaction with the microwave field. To experimentally measure the perceivable strain effect induced by the agitation of embedded barium titanate particles under microwave stimulation, fibre optic sensors with fibre Bragg gratings (FBG) are employed onto the surface of the modified epoxy specimens. Specimens are then placed in a domestic microwave oven of 2.45 gigahertz (GHz) frequency with different power levels. The experiment setup and procedure are explained in Section 4.2 and the results of in-situ measurements of the strain effects are presented in Section 5.2. Raman spectroscopy is employed to observe the residual internal stress field after microwave exposure. Results are presented and discussed in Section 5.2.3.

The third objective is to establish a theoretical constitutive equation underpinning the correlation between the induced mechanical field and the microwave field in Section 3.

Finally, the experiment and theoretical results are discussed in Section 6 and the contribution of this research and recommendations for future work are summarised subsequently.

2 LITERATURE REVIEW AND THEORY BACKGROUND

2.1 Fracture Resistance of Polymer composites

For the past several decades, polymer matrix composite materials (PMC) are one of the most commonly used materials for engineering applications in many sectors from marine [14], automobile [15], aerospace [16] and defence [17] to orthopaedics [18] and dentistry [19]. PMC materials in industrial applications nowadays are usually reinforced with various types of fibres with enhanced properties like specific strength and elastic modulus, accessible fabrication process, flexible design ability, and economic efficiency [20]. The damage of FRP composites under loading initiates and propagates as a combination of interactions from a series of individual events [21]. Damage initiation modes of high-performance fibre-reinforced polymer (FRP) laminated composites are identified to be fibre breakage, fibre-matrix debonding, matrix cracking, and delamination as illustrated in Figure 2-1, below [22, 23].

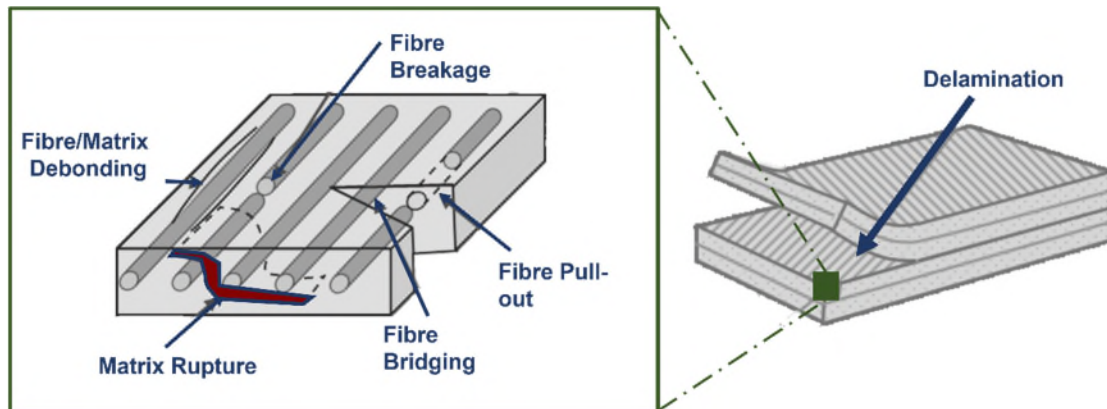


Figure 2-1 Fracture modes of FRP laminated composites, recreated from [23].

Overall, these damage modes of FRP laminated composites except fibre fracture, are mainly dependent upon the matrix and interphase properties between fibre and matrix [24, 25]. To prevent the failure of FRP laminated composites from the aforementioned damage events, composites with toughened matrices attract much attention and different approaches to increase the fracture toughness of the polymer matrix are proposed to improve the ability to dissipate the fracture energy via different deformation mechanisms. Some studies employed

thermoplastics with inherently higher toughness such as polyether ether ketone (PEEK) [26]. Although the toughness of fibre reinforced PEEK composites is increased by nearly ten times compared with FRP composites with epoxy matrix [21], the extremely high processing temperature at around 440°C results in a higher fabrication cost that restrain its further application in industry. In the meantime, others began to seek an alternative way of modifying epoxies by incorporating rubber or inorganic fillers like silica and alumina particles. Among all polymeric materials, epoxy is the most popular matrix used in FRP composites owing to its highly beneficial properties such as enhanced elastic modulus and strength, resistance to heat, and facile processability, which is a result of its highly crosslinked microstructure after curing [27]. However, the highly cross-linking structure also brings unwanted drawbacks of lower fracture toughness, which might be attributed to the internal stresses induced during curing as reported in previous research [21, 28, 29]. The poor fracture toughness leads to insufficient suppression of initiation and propagation of the crack. Previous research [30-34] successfully demonstrated that these problems can be overcome by introducing a second phase at the micro- and/or nano-scale in the epoxy matrix. There are various types of methods developed for modifying epoxy matrices such as the inter-penetrating network [35], polymer plasticisation [36], the addition of rubber [37] and/or rigid inorganic particles like glass [38] volume dilation [39], and self-healing [40]. A brief review of some of the above methods and their limitations are summarized in the sections below.

2.1.1 Toughening with Filler

It has been well established by numerous researchers for several decades that the incorporation of carbon nanoparticles [41, 42], clay [43], rubber [1] and/or rigid inorganic particles such as nano-silica [44] and metallic oxide nanoparticles (aluminium oxide and titanium oxide) [45] with the epoxy matrix can significantly improve fracture toughness, tensile strength, and breakage elongation while preserving the inherently advantageous stiffness and specific strength.

Carbon nanotube (CNT) and graphene have been extensively studied due to their extraordinary mechanical performance, electrical and thermal properties, and

high aspect ratio. The main toughening mechanisms involved in carbon nanotube epoxy nanocomposites are crack pinning, crack bridging, crack deflection, nanotube-matrix debonding, and nanotube breakage [7, 46]. It is found by Wichmann *et al.* [47] that the fracture toughness increased up to 77% in 0.3 wt% CNT and amine-modified CNT. It is also found by researchers that graphene exhibits more effectiveness in preventing interlaminar crack propagation due to its unique two-dimensional (2D) structure [48]. The toughening mechanisms involved in graphene and graphene oxide in epoxy nanocomposites are crack pinning, crack bridging, crack deflection, and separation of graphene layers [8]. By comparing the toughening performance of epoxy matrix with various kinds of nanoparticles, Rafiee *et al.* [42] found out that graphene is the most effective one among all fillers as the fracture toughness increased 125% in 0.1 wt% of graphene nanoplatelets epoxy nanocomposites.

Other than graphene, clay is also one of the unique 2D nanomaterials that attract numerous attention due to its excellent mechanical strength and relatively low cost [49]. The toughening mechanisms proposed by studies in clay/epoxy nanocomposites are crack deflection and plastic deformation [50]. Siddiqui *et al.* found out the fracture toughness of 7 wt% octadecylamine-modified montmorillonite epoxy composites increased by 100% [51].

Rubber is also one of the earliest candidates selected for epoxy toughening. To satisfy the compatibility requirement with the epoxy resin as well as reacting with the epoxy resin during the curing process, carboxyl terminated butadiene-acrylonitrile (CTBN) rubber is chosen and commonly selected as the toughening filler [52]. Except for the CTBN rubber toughener that reacts with epoxy resin, core-shell rubber (CSR) with a glassy shell surrounding a rubber core also attracts many interests as a non-reactive rubber toughener [53, 54]. The rubber core is capable of providing sufficient toughness while the glassy shell ensures compatibility with epoxy resin [55]. There exist some debates in earlier studies on the work-dissipating mechanisms over whether the energy is dissipated via the rubber filler or the epoxy matrix [21]. It has been concluded by most studies that the primary toughening mechanisms in epoxy toughened with rubber are plastic

shear yielding in the polymer matrix surrounding the rubber particles and the following particle cavitation that further accelerates the shear yielding behaviour by relieving hydrostatic stress the crack tip [56-58]. In spite of the evident results from other studies proving the inclusion of rubber improves the fracture toughness of brittle epoxy by multiple orders of magnitude, reductions in strength and stiffness are also observed [21]. It has been noted that in recent development, rigid organic particles like silica are utilised solely or together with rubber tougheners to toughen epoxies. An increase in fracture toughness of the glass/epoxy composites by up to 82% is achieved by incorporating both CSR particles and silica nanoparticles [59]. Furthermore, fracture energy of 965 J/m² is obtained from an epoxy polymer containing 9 wt.% rubber particles and 15 wt.% silica particles while the measurements for the neat epoxy used is 77 J/m². The identified toughening mechanisms in this 'hybrid' composite materials are plastic shear yielding from rubber particles and debonding of the silica particles from the matrix, following a plastic void growth in the epoxy matrix [60].

Meanwhile, it is also discovered that the elastic modulus increased gradually with the increasing weight loading of silica particles and the addition of silica particles always leads to an improved toughness of the modified epoxy resin [61]. Possible toughening mechanisms are observed and suggested for epoxy modified with rigid particles: (i) plastic deformation in the polymer matrix and initiation of localised yielding caused by the stress concentration at the particle region. This effect also results in crack tip blunting which also prevents crack propagation. (ii) crack pinning, which could be identified as a 'tail' surrounding the rigid particles on the fracture surfaces as rigid particles served as obstacles to crack propagation [21]. (iii) debonding of the rigid particles and the following plastic void growth of the epoxy matrix [61]. However, it has been observed experimentally by others that the particle debonding did not occur in some particles, which indicates a less effective toughening performance compared with rubber particles [60].

The properties of the particle-modified epoxy depend on many factors such as the type, size, content loading, surface treatment of the included particles, strain

rate, and also environmental conditions [21, 62]. The elastic modulus of modified epoxy increases only when the particle size drops below the micron-scale to the nano-scale [32]. Furthermore, it is shown that the mechanical performance has increased dramatically with the increasing weight percentage of the filler [63, 64]. However, it is also observed by many studies that a threshold exists above which the particles tend to agglomerate and cause a degradation in mechanical properties [65, 66]. The quality of particle/matrix interfacial bonding is another crucial factor that determines the mechanical properties of a modified epoxy matrix. Thus the application of coupling agents for the surface treatment of particles is introduced to achieve a better interfacial bonding between particles and matrix [31]. A notably increased fracture toughness is observed in a study of epoxy toughened with rubber and surface-modified silica nanoparticles [30].

Despite the excellent performance of particle-toughened epoxy composites, loss in elastic modulus, tensile strength, and glass transition temperature are also reported by other studies [55]. The curing process, which is when cross-linking occurs, is significantly affected by the existence of particles. The addition of particles into the epoxy matrix often leads to a higher viscosity, and shear thinning behaviour [29, 67]. Optimal uniform dispersion of the particles in the epoxy resin is also a critical factor that requires to be achieved. The structural performance of modified epoxy increases significantly when a uniform dispersion is attained due to a better load transfer between epoxy and fillers [29]. Although the modified epoxy with particles exhibits a promising future with excellent toughening performance, microcracks still formed in fibre-reinforced composites when subject to mechanical loadings and under extreme environmental conditions during the manufacturing and also service [12]. It is tremendously challenging to detect and repair the FRP composite materials during service due to techniques limitation. Consequently, these hidden internal micro-defects not only deteriorate their mechanical properties but also could cause catastrophic structural failure during service. Apart from matrix toughening, extensive research also focused on bio-mimetic self-healing composite materials, which are briefly introduced in the following Section 2.1.3.

2.1.2 Toughening by Residual Stress

The toughening via volume dilation of embedded fillers is first proposed in a study by Ho Sung *et al.* It is achieved by prestressing the epoxy matrix via the expandable hollow microspheres under heating [68]. This concept is based on a mimicking of the toughening effect of the phase-changing ceramics in the vicinity of the crack. Phase-transition toughening is extensively studied for past years and it is also one of the most effective toughening mechanisms for ceramics [69]. It has been observed experimentally that the stress-induced martensitic phase transition of a second phase at the crack tip, such as a tetragonal Zirconium dioxide change to a monoclinic phase, can result in volume expansion and forming a compressive stress field around the crack tip to prevent further crack propagation [70].

Ho Sung *et al.* [68] studied the specific fracture energy of microsphere modified epoxy with and without heat treatment to isolate the toughening effect and it is observed that the fracture toughness with and without heat treatment increases with the increasing content of microspheres. It is also worth noting that the maximum improvement in fracture toughness in heat-treated samples is 13 times the neat epoxy while the unheated sample is only six times of the neat epoxy. It is identified under a transmission optical microscope that a residual compressive stress field is introduced around the microspheres to the matrix and consequently, the stress intensity factor is reduced when the cracks are under loading [68]. Further studies [71] using graphical analysis in conjunction with the test results described above confirm that the toughening effect in the heat-treated modified epoxy is mainly attributed to the residual compressive stress rather than a post-cure shrinkage effect of the epoxy.

A Similar toughening mechanism is also discovered in modified epoxy with particles, which is the mismatch of coefficients of thermal expansion between fillers and the epoxy matrix [72]. The compressive stress field introduced in the epoxy matrix under certain conditions due to the thermal expansion mismatch might contribute to improved fracture energy. It is presented in the above paragraph that the induced compressive residual stress by the volumetric

expansion of phase transforming zirconium dioxide particles can be utilised to improve the fracture toughness in brittle ceramics and composites [73].

The differential thermal expansion plays an important role in all composite systems as it determines the distributions of residual stress/strain in the material and consequently affects the mechanical and fracture toughness after fabrication. The toughening effect may only be introduced when the thermal expansion of the matrix is smaller than that of the fillers of composite materials with sufficient strong filler/matrix interfaces to support the resulting radial tensile stresses during cooling after the curing process. In the meantime, tangential compressive stress fields are introduced to the surrounding matrix and lead to an increase in the strain required for crack initiation and propagation, thus a toughened epoxy composite [39].

It has been widely accepted that the toughening of brittle materials can be achieved by introducing a compressive stress field within the material, such as toughened glass [74] and prestressed concrete [75]. The predominant damage mode in brittle materials initially starts with the crack formation and subsequently crack propagation. When a tensile load is applied to the material, the stress concentration at the crack tips leads to a much higher local tensile stress at the tips than in the bulk material, which eventually accelerates crack propagation [76]. However, a higher tensile load is required for crack propagation in a material with compressive residual stress as the fracture energy of the initial crack is increased due to the extra work of overcoming the existing compressive stress. Therefore, a controlled compressive stress field is desired in the application of brittle materials toughening [68].

For the past decades, various approaches are proposed and extensively researched in previous studies to introduce the toughening effect in brittle materials via an internal compressive stress field activated by external stimulators. However, these approaches are limited to ceramics such as transformation toughening via the phase transition of crystals at the crack-tip. Research on the subject of activated toughening in polymer matrix like epoxy has only been carried out in a small number of studies and restricted only in the area of utilising

mismatch in filler/matrix thermal expansion coefficient activated by heating. To the best of my knowledge, there are no attempts made to date to investigate the mechanical behaviour of embedded fillers in polymer composites under other stimulators such as the electromagnetic field. Therefore, a more interesting proposition of active toughening effect in polymer matrix composite materials is presented in this study by incorporating a second phase of ferroelectric crystals that demonstrates an electro-strain under an applied electric field.

2.1.3 Active Toughening to Extend Service Life: Self-healing

As discussed in the above sections, polymer composites are susceptible to the cracks and microcracks formed during material handling and their service life. Different varieties of approaches are presented and discussed. However, these proposed methods are mainly focused on improving the damage tolerance via enhanced fracture toughness before the damage happens. Once the cracks are developed during the service time, the detection and repair are extremely costly in order to extend the lifespan of polymer composite materials. Consequently, the propagation of cracks and microcracks could lead to catastrophic failure of the composite structure. Therefore, in recent years, tremendous efforts went into the development of multifunctional composite materials with structural enhancement including structural properties like strength, elastic modulus, and fracture toughness [77] as well as non-structural performance such as electrical conductivity [78], sensing and actuation [79], and self-healing [40]. Self-healing composites are developed that could trigger a healing process automatically to restore their original performance and prolong their service life when damage occurs [68]. The idea of self-healing in composites is developed from the biological process of wound healing, which mimics the way bleeding is stopped. For the past years, self-healing composites have become an extensively studied field as traditional repair approaches could not deal with inaccessible damages during the service. The key feature of self-healing is that no external aids such as repairing tools or inspection facilities are needed. There are two major groups of self-healing methods based on their mechanisms of toughening in response to an event of damage, whether it is extrinsic or intrinsic. The damages are repaired

by the releasing of healing agent sequestered by the embedded container in the matrix. Sometimes heating is needed to expedite the healing process. Unlike the extrinsic mechanism, the intrinsic approach, the toughening in the event of damage relies on the response of the polymer themselves under an external stimulus via chemical and physical interactions such as ultraviolet (UV) light, heat, and chemicals [80]. The most common approaches for self-healing epoxy-based composites are extrinsic. The self-healing agents are prepacked in a brittle vessel and the vessel is embedded into the epoxy matrix subsequently. An applied load triggers the fracture of the vessel and low viscosity healing agents are released to the damage region following a curing process and finally seal the microcracks as illustrated in Figure 2-2, below [81].

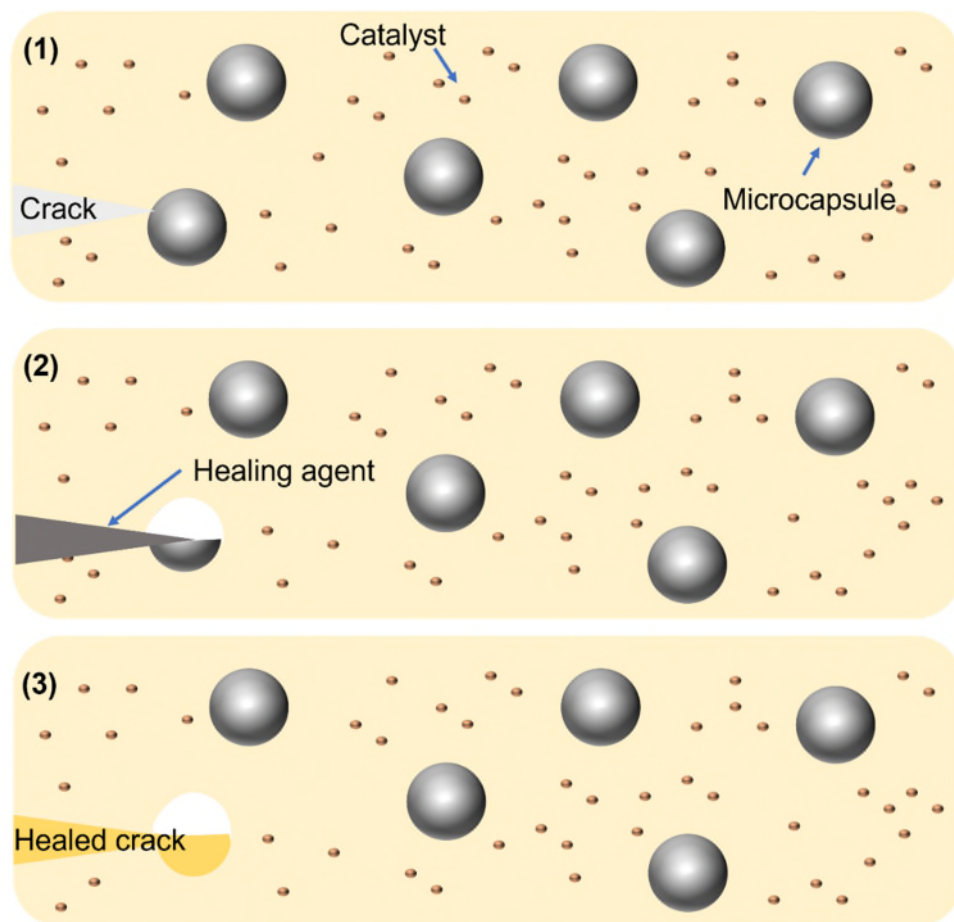


Figure 2-2 Schematic illustration of self-healing process using microcapsules, (1) crack initiation in the polymer matrix, (2) crack intersect microcapsules and the released healing agent starts to react with catalyst, (3) crack is self-healed and propagation stop [81].

The most commonly used in the epoxy matrix are hollow fibre and microencapsulation [40]. Healing efficacy tests on specimens containing hollow glass fibres embedded in an E-glass/epoxy laminate [82] show successfully completed healing of matrix cracking and delamination of the laminates. In the case of microencapsulation, healing efficiencies are characterised by an improved fracture toughness of up to 90% [83] for neat epoxies and up to 66% for fibre-reinforced epoxy composites [84]. However, concerns still exist regarding the deficient compatibility of the embedded vessel with the epoxy resin which limited their potential industrial application. It is also noteworthy that multiple repairs in the same region from the vessels are not possible as the healing agent consumed during the healing process could not be recovered when the quantity is insufficient.

The rigidity of the thermal stability of epoxy materials limited their utilization of intrinsic self-healing approaches, therefore most intrinsic methods are designed for thermoplastic materials due to their inherent repeatable reform ability [80]. As no healing agent or catalyst is required during the intrinsic healing process, different types of external stimuli are carefully selected to trigger self-healing. A study focused on crack healing employing thermoplastics chain mobility with a minimum amount of heat applied in polymethyl methacrylate (PMMA) reveals that the tensile strength can be fully restored to that of the pristine material [85]. Moreover, a flexible organo-silicon polymer coating is developed that is capable of starting the self-healing process under exposure to UV radiation, oxygen, and atomic oxygen in low earth orbit environment. The silicon from the polymer reacts with the oxygen from the environment to form silicon-oxide compounds that could condense on the defects, and subsequently fill the microcracks [40, 86]. Although extensive research has been carried out and significant progress are made in recent years, it is still a challenging concept for practical application and commercialisation due to the increased manufacturing cost and other factors, such as the incompatibility with existing manufacturing procedures. Furthermore, the outcome of the self-repairing process is hard to control and validate. Overall, the developed self-healing materials nowadays usually exhibit a weaker performance compared to their original version [80].

Another toughening method is presented in the following Section 2.1.2, which is similar to a combined version of particle modification and intrinsic self-healing. The toughening is accomplished through volume dilation of embedded particles under external stimulation like heating.

2.2 Electric Field-Induced Strain in Ferroelectric Materials

2.2.1 Ferroelectric Materials

Ferroelectric materials attract numerous interests owing to their distinctive behaviour of correlated physical properties (permittivity, polarisation etc.) and external stimulus (temperature change, electric, and mechanical fields), especially when the phase transition takes place. Ferroelectric materials are dielectric crystals that display spontaneous polarisation at their polar phase that could be switched by applying an external electric field [87]. The term 'ferroelectric' is chosen due to the similarity of properties with a ferromagnetic material, which exhibits a spontaneous magnetization and hysteresis behaviour between magnetization and magnetic field [88]. Like ferromagnetic materials, this ferroelectricity phenomenon is usually discovered at certain temperature ranges and the transition temperature is denoted as Curie Temperature. Above the Curie Temperature, the crystals no longer exhibit ferroelectricity and become paraelectric material [89]. The ferroelectric behaviour was first revealed in Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) in 1921 by Valasek [90]. Other examples of typical ferroelectrics including lead titanate, PbTiO_3 , potassium di-hydrogen phosphate KH_2PO_4 and barium titanate BaTiO_3 . The relationship between ferroelectric materials and dielectric materials is illustrated in Figure 2-3, below [91].

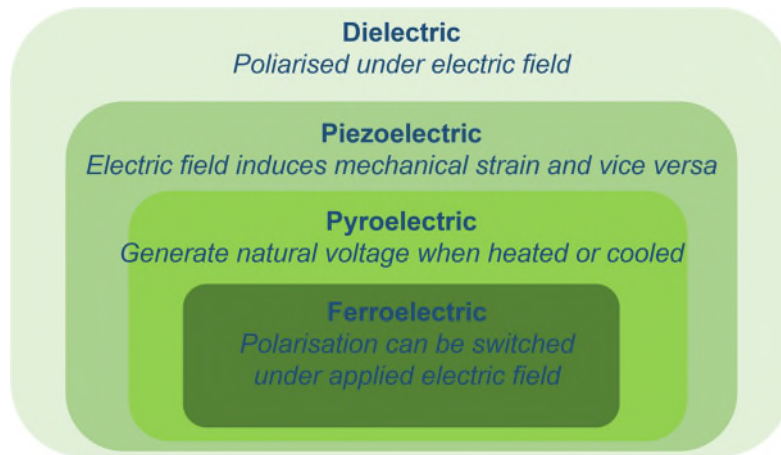


Figure 2-3 Relationships between the dielectric, piezoelectric, pyroelectric and ferroelectric materials, recreated from [91].

Spontaneous polarisation

Spontaneous polarisation is determined by the dipole moment per unit volume. When a particle with a positive charge $+q$ and a particle with a negative charge $-q$ is separated with distance r , the dipole moment has a magnitude of qr and a direction from negative charge to positive charge as shown in Figure 2-4, below.

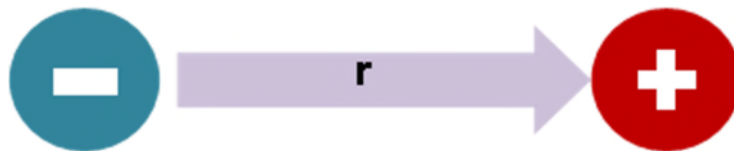


Figure 2-4 A dipole with a positive charge and a negative charge separated by a distance r .

Ferroelectric crystals have a net permanent polarisation which is the vector sum of all the dipole moments in the unit cell [92]. It is due to the absence of a centre of symmetry that makes the crystals in this class have one or more polar axis. The axis of spontaneous polarisation is usually a crystal axis [88]. For example, barium titanate belongs to the perovskite oxides group which is the most studied ferroelectric material. The general form of the compounds categorised in this group is ABO_3 . The separation of positive ion A, negative ion B and the Oxygen ions result in a spontaneous polarisation in the ABO_3 structures [90]. For instance, the crystal structure of barium titanate (perovskite-type ferroelectrics) is cubic above the Curie temperature (120°C), with the Ba^{2+} ions at the corners, the Ti^{4+}

ion at the cube centre and the O^{2-} ions at the face centres as shown in the left Figure 2-5. Any dipole moment in this structure is forced to be zero due to the centrosymmetric structure and hence has non-polar behaviour [93].

When the temperature is below 120°C , the cubic structure on the left deforms into a tetragonal polar structure with a shifting centre atom Ti^{4+} as shown in the right Figure 2-5. A dipole moment is created by the displaced Ti^{4+} ion and hence the spontaneous polarisation in the structure. The Ti^{4+} ion in the tetragonal barium titanate can be displaced in six different directions therefore the corresponding dipole moment can have six types of directions along these crystallographic axes.

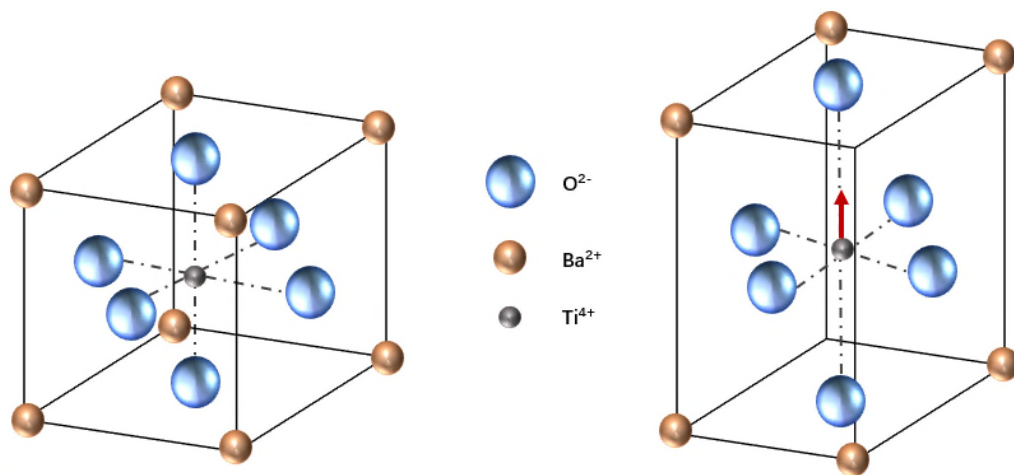


Figure 2-5 Barium Titanate with (left) cubic phase above 120°C and (right) tetragonal phase under 120°C , recreated from [93].

Switching of polarisation under electric field

In an electric field, the electric dipoles that lie parallel to the field direction have the lowest free energy while the ones that are perpendicular to the field direction have higher free energy. Furthermore, the unparallel ones have the highest free energy. This phenomenon results in a torque on the electric dipoles that align all dipole moments to the direction of the applied electric field in order to minimise the free energy [94]. The typical spontaneous polarisation and the hysteresis behaviour of the ferroelectric material with an applied electric field are presented in Figure 2-6, below.

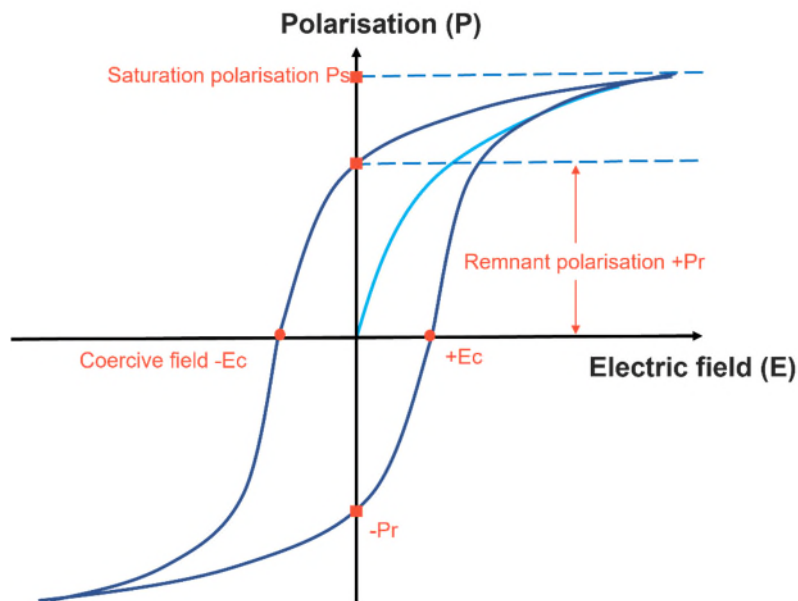


Figure 2-6 A ferroelectric hysteresis loop of Polarisation (P) as a function of Electric field (E), recreated from [95].

As shown schematically in Figure 2-6, above, when an electric field is applied in the positive direction, while the strength of the field increases, the polarisation increases and reaches a saturation state where all dipoles are aligned with the field direction. When the external field is removed, the polarisation is not going back to zero and the crystals display a remnant polarisation P_r . The extrapolation of the linear region to the polarisation axis corresponds to the value of the spontaneous polarisation P_s . The value of the electric field strength that could orient all the polarisation to zero is called the coercive field E_c as illustrated in Figure 2-6, above [93].

Curie temperature and phase changes

Another unique character of ferroelectric materials is the temperature of phase transition, the temperature at which the ferroelectric phase transformed into the paraelectric phase happens is called the Curie point. Under this temperature, the ferroelectric crystal goes through a structural deformation that transfers from a non-polar paraelectric phase to a polar ferroelectric phase [96]. For example, the Curie point of barium titanate is 120°C , and there are also three different ferroelectric phases in barium titanate below 120°C as shown in Figure 2-7, below

[97]. When the temperature decreased from the Curie temperature, its structure changes from a symmetric state (cubic) to a non-symmetric state (tetragonal, orthorhombic, and rhombohedral) as presented in Figure 2-7, below. This symmetry lowering transition results in spontaneous polarisation and become ferroelectric material [98]. The phase transition temperature between two different non-symmetric ferroelectric phases is called a transition temperature [99]. There are two reasons for this general temperature-dependent behaviour of ferroelectric materials (excluding KNO_3). The first one is the randomisation of dipole moments. When the temperature gets higher, the direction of the dipole moments randomises from an ordered state and leaves a disordered material without net polarisation. The other reason is that the phase transitions create possibilities for the formation of new dipole moments as illustrated in Figure 2-7 [93].

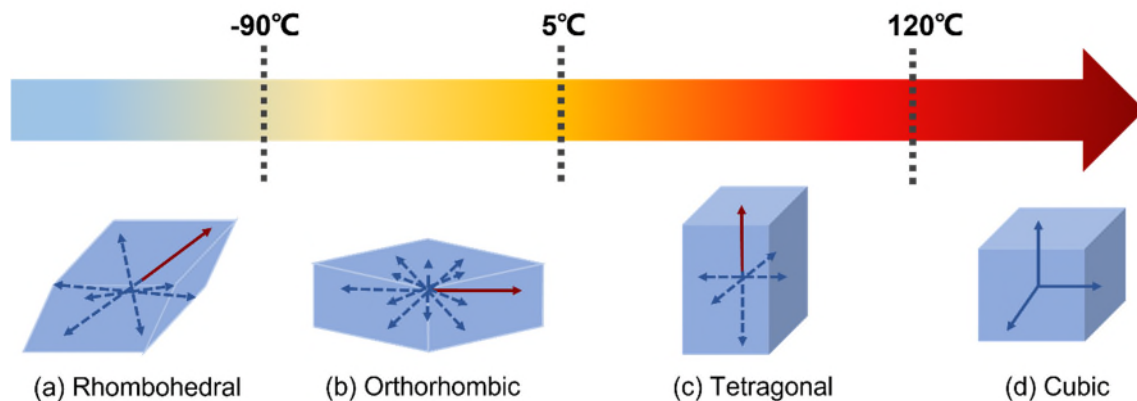


Figure 2-7 Phase transitions of barium titanate with red arrow showing the polarisation direction (a) rhombohedral structure with 8 crystallographic axes; (b) orthorhombic structure with 12 crystallographic axes; (c) tetragonal structure with 6 crystallographic axes; (d) cubic structure, recreated from [100].

2.2.2 Ferroelectric Domains

Domain

In ferroelectric materials, there exist domains that are defined as a finite regions in which all the spontaneous polarisations within this region are in the same direction as shown in Figure 2-8, below. The domain configurations in ferroelectric materials are discovered during the investigation of spontaneous

birefringence [101]. The origin of the ferroelectric domains is not fully understood, but possible explanations have been raised by previous researchers. From a phenomenological view that the polydomain structure has the minimum free energy [102]. From a microscopic viewpoint that two explanations have been proposed, one is that when the spontaneous polarisation occurs during the crystal transformation from paraelectric to ferroelectric, the difference of electrostatic force on the crystal's faces results in different polarisation to minimise the energy state and hence domains form. The other explanation is that there exist many defects and internal stress in a crystal and domains are formed due to these imperfections [93].

Domain wall

The boundary that separates two neighbouring domains is called the domain wall as shown in Figure 2-8, below. A domain wall is characterised by the angle of polarisation axes between two adjacent domains, such as 180° and 90° domain walls in barium titanate (BaTiO_3) crystals [102]. Types of domain walls are determined by the angles between all crystallographic axes. For example, 90° and 180° domain walls exist in a tetragonal phase BaTiO_3 and 71° or 109° domain walls in the rhombohedral phase due to the different angles between their possible crystallographic axes as shown in Figure 2-7, above [103]. Generally speaking, 180° domain walls are only responsive under electric fields while the other non- 180° domain walls are responsive under both electric, and mechanical stress fields [102]. The thickness of the domain wall is taken as infinitesimally small in most theoretical analyses, however, the thickness, in reality, is about the scale of a few lattice cells. Monte Carlo simulations [104, 105] theoretically predicted that the thickness of 180° domain walls in tetragonal barium titanate and lead titanate is the order of two lattice constants or less. Also, the thickness of the 90° domain walls of lead titanate was calculated to be $5 \pm 0.5 \text{ \AA}$ [106]. However, the thickness of domain walls observed from a high-resolution transmission electron microscopy (TEM) study shows a larger value and the reason for this wide difference may be the existence of defects in materials [107-109].

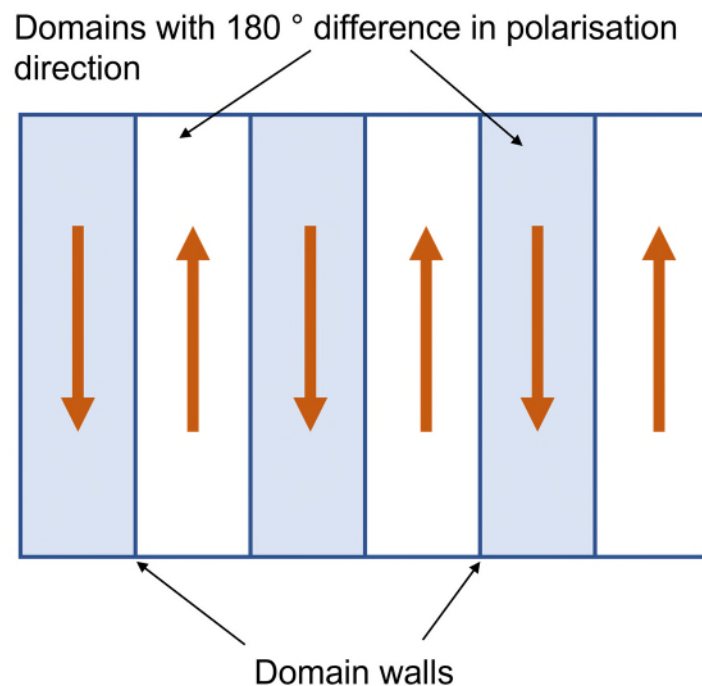


Figure 2-8 Domains with 180° difference in polarisation direction.

Ferroelectrics are crystalline materials and have a rather complex structure. All bulk ferroelectric crystals are polycrystals when they are first grown with the current level of fabrication. Ferroelectric polycrystal contains many grains that are randomly oriented, and each grain is a single monocrystal. There exist several domains in each grain as presented in Figure 2-9, below [110].

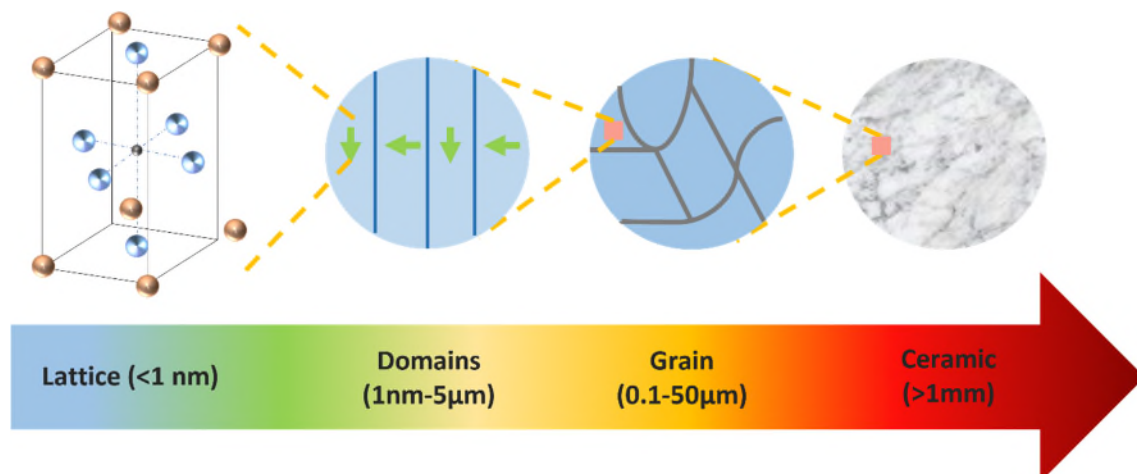


Figure 2-9 A schematic diagram describing the structure of BaTiO₃ at different scales.

The mono-domain crystal could be obtained by applying a strong strength external electric field to the polydomain crystal and aligning the direction of the spontaneous polarisation in all domains. This process is called 'domain switching' or 'poling' as illustrated in Figure 2-10 [111].

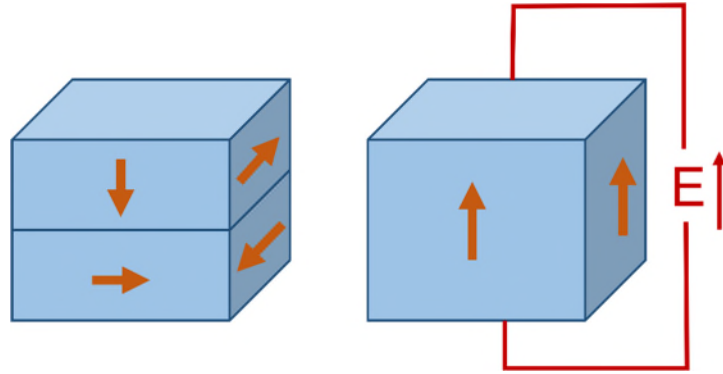


Figure 2-10 A schematic image of the domain switching process, before (left) and after (right), recreated from [112].

Hysteresis loop

The domain configuration of each ferroelectric crystal is defined by its own structure, and it could be changed by domain wall displacements under an electric field or mechanical loading. The hysteresis behaviour of ferroelectric materials could be mostly attributed to the domain wall motion. The ferroelectric hysteresis loop is observed using a Sawyer-Tower Circuit shown below [113].

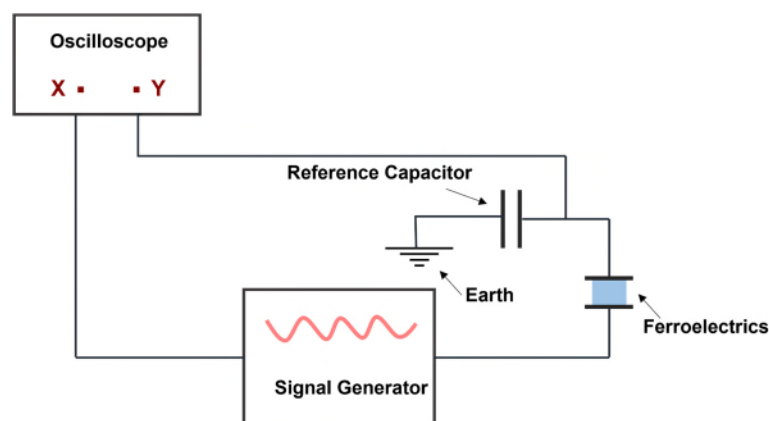


Figure 2-11 A Sawyer-Tower circuit to measure the hysteresis behaviour of ferroelectric materials, recreated from [114].

An alternating voltage at a high frequency is applied by the signal generator across the reference capacitor and ferroelectric sample. Since they are connected in series, the surface charge of the ferroelectric material could be calculated by the capacitance and measured voltage of the capacitor. Therefore, the polarisation of the ferroelectric sample in an oscillating electric field could be represented by the applied voltage as the x-axis and the calculated surface charge as the y-axis. As shown in Figure 2-12, below, grey, and white parts indicate domains with different polarisation.

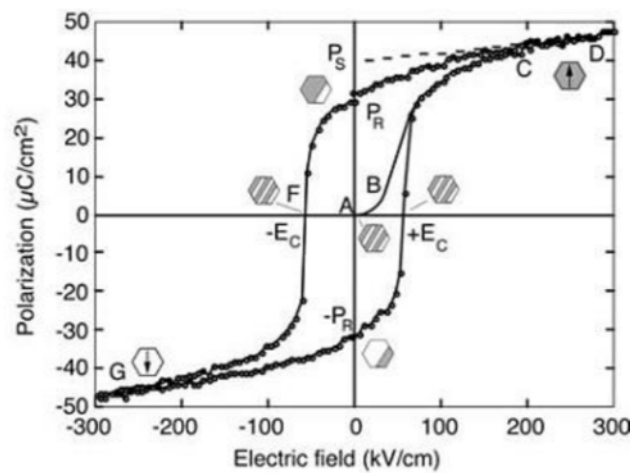


Figure 2-12 Hysteresis loop of Polarisation (P) versus electric field (E) of a (111)-oriented sol-gel Lead zirconate titanate (PZT) film [115].

In the beginning, the applied electric field is not sufficient enough to induce a switch of polarisation directions in domains. When the electric field strength starts to be able to cause rotation of unparallel domains, the polarisation increases until all domains are switched to the field direction in the end. If the electric field is dropped to zero, some domains still remain switched, and the remanent polarisation exists.

2.2.3 Current Understanding of Field-induced Strain Mechanisms

Electric field-induced strain is one of the most well-known characteristics of ferroelectric crystals and it has been widely used for electromechanical applications. However, most lead-based piezoelectric materials with a higher dielectric constant are restricted due to health and environmental issues.

Therefore, lead-free ferroelectric materials with higher electromechanical performance have attracted great interest [116].

For example, when an electric field is applied to the ferroelectric crystals with a perovskite structure, there are mainly three representative deformation behaviours that contribute to this mechanical strain response [117]. The intrinsic strain comes from the electrostriction and piezoelectric effects of the materials while the extrinsic strain is mainly attributed to the domain wall movement in the polydomain materials as presented in Figure 2-13, below.

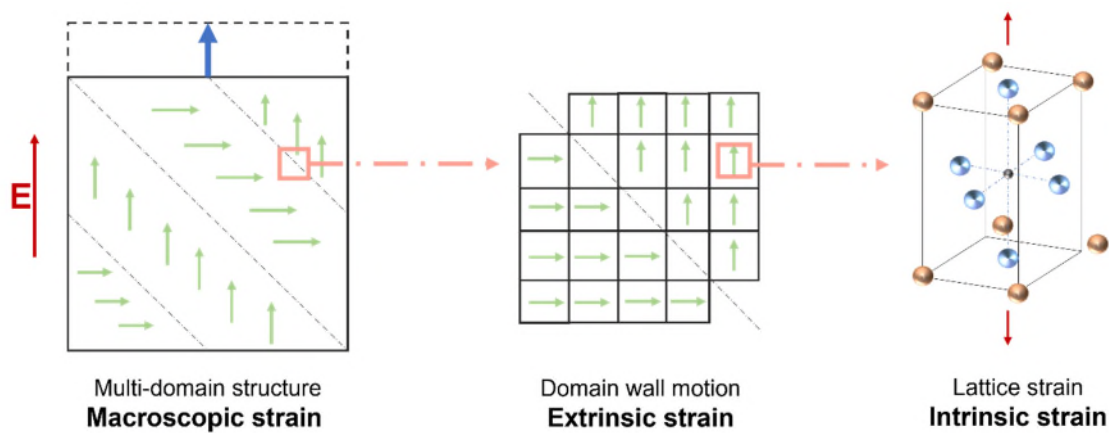


Figure 2-13 Schematic diagram of the extrinsic strain and intrinsic strain that contributes to macroscopic strain in a tetragonal crystal.

It is rather difficult to separate each component from the experiment data, but it is still possible to find which one is predominant [118].

Intrinsic: electrostrictive and piezoelectric

Electrostriction behaviour exists in materials with centrosymmetric and non-centrosymmetric crystal structures, including amorphous solids and fluid. This behaviour is due to the displacement of the ion under an electric field, which is very small. When the electric field is removed, the strain effect disappears accordingly. It has been measured that the electrostriction effect results in an elongation along the field direction [119]. The electric field dependence of the electrostriction is a quadratic function, therefore the direction of the

electrostrictive strain remains positive in spite of the field direction due to the symmetric structure [120].

Piezoelectricity is a property only to be found in materials with non-centrosymmetric structures. Under an applied electric field, the polar distortion of the material is either extended or contracted and mechanical strain manifests (converse effect). External mechanical stress also induces a charge displacement in the material (direct effect). The converse effect has a linear relationship between induced strain and applied electric field. It could be either elongation or contraction according to the field direction and material polarity [121].

Extrinsic: domain wall movement

In a mono-domain ferroelectric crystal, the electric field-induced strain is generated by the intrinsic electrostriction and piezoelectric effect. This intrinsic effect is linear and also highly anisotropic as it could be measured with respect to the angle between the applied field and polarisation direction. However, in both poly-domain single crystal and polycrystalline ferroelectric materials, the domains that contain spontaneous polarisation in various directions can be aligned in the same direction by applying an external electric field that is sufficiently strong.

In a poly-domain ferroelectric crystal, the macroscopic strain is significantly dominated by the contribution of extrinsic strain [122]. Extrinsic effects occur at longer length-scales and the main contributor is domain wall motion. While the strain effect and electric field strength present a linear relationship in mono-domain single crystals, the field-induced strain effect exhibits a non-linear response in poly-domain materials [123]. In contrast with the materials without domains, it is generally accepted that the irreversible domain wall motion is the main reason for the non-linear response (e.g., strain or polarisation), even measured under weak amplitudes of the external stimulator (e.g. electric field, and mechanical stress) [124-126].

As discussed earlier, the domain wall motion under an electric field or mechanical stress can be characterised as 180° and non- 180° motion based on their change in orientation of the polarisation.

The non- 180° domain wall motion is the primary but not the only contribution of the extrinsic strain effect. Non- 180° domain wall motion is dependent on the crystallographic symmetry of the material. Among all non- 180° domain wall motions, 90° domain wall motion in tetragonal systems draws the most attention as this domain wall motion exhibits both ferroelectric and ferroelastic properties as it has differences in both the orientation of polarisation and the spontaneous strain as shown in Figure 2-14, below. In certain materials, 180° domain reorientation has been observed as a process with the intermediate non- 180° domain switching process [127].

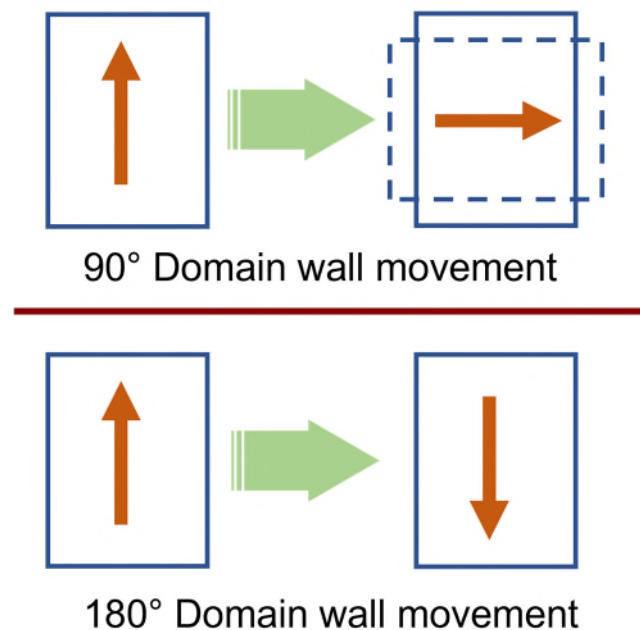


Figure 2-14 90° domain wall movement (up) with changes in both polarisation direction and strain and 180° domain wall movement (below) with only changes in polarisation direction, recreated from [126].

Ferroelectric ceramics and polycrystals that contain many grains that each consist of domains with their own spontaneous polarisation orientation are the most commonly used form of ferroelectrics. In polycrystalline ferroelectric materials, the macroscopic response is a collection of the responses of individual

grains. Each grain contains various crystallographically oriented domains which are distributed at all possible angles to the applied external field. Therefore, the response incorporates the full anisotropy to the single crystal response. Also, the domain wall motion and interphase boundary motion between neighbouring grains may further raise the complexity of the response mechanism. Domain wall motion in polycrystal structure is a more complicated and collective process therefore It has not been experimentally measured and fully understood, i.e., how these components interfere with each other.

2.2.4 Common Ferroelectric Materials: Barium Titanate

Barium titanate (BaTiO_3) is first discovered by Wul, B [128] in 1945 and it is one of the most renowned lead-free ferroelectric materials owing to its exceptional dielectric and ferroelectric properties [98]. After that, studies have been focused on developing variations of BaTiO_3 with different dopants due to its relatively simple perovskite structure. Nowadays, they have become one of the largest families of ferroelectrics for applications in capacitors, transducers, and actuators [98, 129]. BaTiO_3 displays five different phase transitions with changing temperatures as illustrated in Figure 2-15, below.

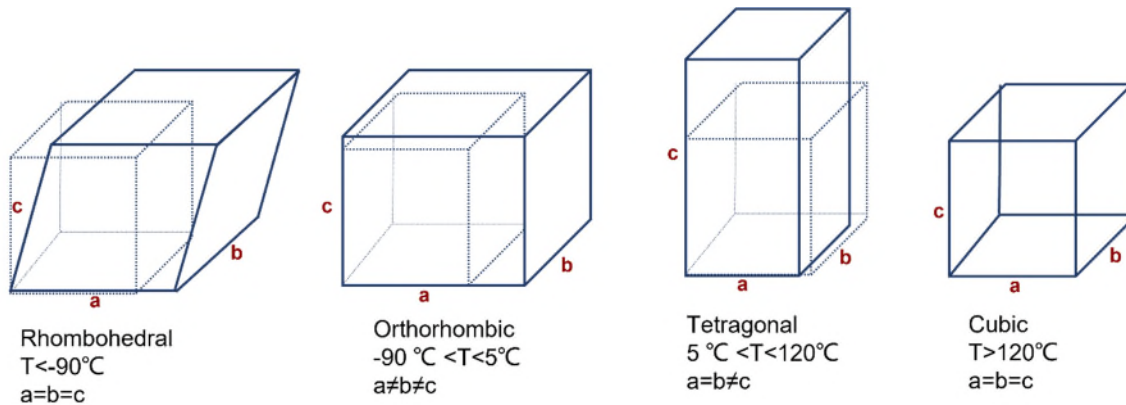


Figure 2-15 Crystallographic changes of BaTiO_3 from a cubic structure above 120°C , recreated from [130].

Its structure is tetragonal at room temperature with a ferroelectric nature. There are six equivalent directions for the polar axis in the crystal when cubic barium titanate transforms to a tetragonal structure below the Curie temperature (120°C),

therefore only 180° and 90° domain walls can be observed. However, as the temperature goes below room temperature, it transforms into another two non-symmetrical phases, at first the orthorhombic structure between 0°C and -90°C , then the rhombohedral structure below -90°C . The tetragonal BaTiO_3 is of particular interest in this study as it exhibits a spontaneous polarisation hence higher dielectric properties at room temperature due to its non-symmetrical structure.

The dielectric permittivity of BaTiO_3 in its non-cubic phase is strongly dependent on the material structures. In a poly-domain single crystal or polycrystal BaTiO_3 , the measured dielectric permittivities along different axes are different and the dielectric measurement of BaTiO_3 powers obtained is only a mean value due to the presence of different polarisation directions in each poly-domain powder [131]. A dielectric measurement of a single crystal tetragonal BaTiO_3 is carried out by Matthias and Von Hippel [132] and a strong electric field is applied to orient all the domains to the field direction prior to the dielectric measurements. It is found that a dielectric real permittivity of 500 along the c-axis and 1700 along the a-axis by applying a small a.c. field as shown in Figure 2-16, below. Another dielectric measurement carried out by Mason and Matthias [133] of a single domain crystal of tetragonal BaTiO_3 shows a dielectric real permittivity along the a-axis of the order of 10^5 through over frequency range of 0.001-10 megahertz (MHz).

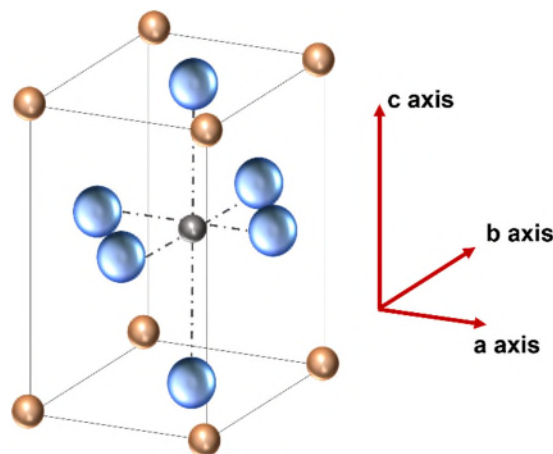


Figure 2-16 Crystal structure of tetragonal phase of BaTiO_3 .

It is found by many studies that the BaTiO₃ ceramics and polydomain single crystals exhibit a drop in the real permittivity and a peak in the loss tangent at lower microwave frequencies (up to 24 GHz), which are ascribed due to the dielectric relaxation behaviour [134, 135]. For instance, Powles observed a drop of real permittivity from 1500 at 1.5 MHz to 300 at 9.45 GHz while the tangent loss increased from 0.015 to 0.53 [136]. However, investigations of BaTiO₃ single crystals conducted by Benedict *et al.* [137] and Lurio *et al.* [135] demonstrate no observation of relaxation at 24 GHz. Furthermore, no relaxation behaviour seems to be identified in the BaTiO₃ single crystal below a frequency of 50 GHz and the drop of real permittivity might be attributed to the piezoelectric resonance of the domain walls [89, 137]. On the other hand, the relative permittivity of BaTiO₃ polycrystalline ceramics drops from 1500 to approximately 150 when the frequency reaches 30 GHz. The centre of the relaxation process is at 3 GHz and the tangent loss reaches its peak value. [89, 138]. The mechanisms of this drop are not fully understood and explanations are proposed by various studies [134] that this behaviour is attributed to the piezoelectric resonance of grains and domains [90], and the oscillation of the domain walls under the oscillating electric field component of the microwave [139].

The dielectric properties of BaTiO₃ are strongly dependent upon the crystal size and structure as described below.

Size and shape effect

Up to the present time, BaTiO₃ crystals are produced either in bulk form or at nano-scale [140-142] with various crystalline phases [143, 144] via different methods [145, 146]. Particularly, the nanostructure BaTiO₃ such as nanowires [147] and nanoparticles [148], attract increasing interest and their enhanced properties in many aspects have been intensively demonstrated by studies [149-151]. The mechanisms of the unique 'nano-effect' introduced are still not fully understood, however, it is suggested that it is attributed to the 'quantum effect' [152] and might also be due to a larger surface area compared with larger-scale BaTiO₃ crystals at the same mass [149]. In nanostructure BaTiO₃ materials, there exists a strong correlation between the size and shape of the structures and

properties. It is widely accepted by studies [153] that grain size and particle size are the two most important factors that affect the behaviour of dielectric relaxation and resonance. It is first detected using x-ray diffraction that the tetragonality of the BaTiO₃ powders decreases when the particle sizes are below 5 μm [154]. More studies focused on the size-dependent tetragonality of BaTiO₃ crystals using transmission electron microscopy and other methods demonstrated the existence of a critical size for barium titanate crystal structure to transform from tetragonal to cubic, which is around 120-150 nm [155-157]. A possible explanation suggested by others is that the wall energy could not be restored from the volume term as particle size decreases hence a simpler domain structure with fewer types of walls [153]. It is also suggested by Uchino *et al.* [158] that the Curie temperature drops with a decrease in the particle size and the Curie temperature also affects the crystal structure of BaTiO₃ at room temperature hence the dielectric properties. Thus far, it is not possible to distinguish the size effect from other factors that also change with the size [159]. Moreover, the grain size of polycrystalline BaTiO₃ also affects the dielectric properties as identified by many studies. It is found that the dielectric constant increases with decreasing grain size and reaches a maximum value at a critical size. However, further reduction in grain sizes leads to a decrease in dielectric properties after the peak [160, 161]. The grain size effect might be due to the increase in domain wall density and build up internal stress with a decreased grain size [153]. Furthermore, Hsiang *et al.* [162] observed a transition from a tetragonal polydomain structure to the cubic single domain structure when the particle size decreased below 80 nm.

Among all crystal structures, zero-dimensional (0D) BaTiO₃ nanoparticles are the most widely used type due to their facile synthesis process. Compared with 0D nanoparticles, the dielectric properties of 1D nanowires are considerably affected by the extrinsic strains introduced during the fabrication process [98]. Furthermore, a recent study [163] also found that the unique morphology of BaTiO₃ nano-torus exhibits an enhanced loss of 120% compared with that of BaTiO₃ nanoparticles which could result from an additional response of dipoles due to a hollow structure.

Field-induced strain effect in bulk BaTiO₃

Over past decades, extensive research interests are drawn to the development of lead-free ceramics-based actuators that display electric field-induced strain due to environmental concerns of lead toxicity [116, 117]. To date, only three candidates attract the most attention and are considered to be the most promising replacement of lead-free ceramics for practical application owing to their large electromechanical response, i.e. BaTiO₃, K_{0.5}Na_{0.5}NbO₃, and (Bi_{0.5}Na_{0.5})TiO₃ [164, 165]. BaTiO₃ in particular with a simple fabrication process and better electromechanical properties is the most popular one and studies focusing on their electromechanical behaviour increased dramatically in past decades [166]. The three mechanisms that contribute to the electric field-induced strain are discussed in 2.2.3, which are the piezoelectric effect, electrostriction and domain wall movement.

It is found that the piezoelectric coefficients of BaTiO₃ single crystal [167] and the polycrystalline ceramics, which indicate the volume change under applied electric field, are relatively low compared with PZT ceramics [168]. However, the intrinsic anisotropy electromechanical effect due to polar axes and the extrinsic domain wall contributions are the most crucial two factors that result in the enhanced electromechanical properties of BaTiO₃ [166]. It is noted that the electromechanical properties of tetragonal BaTiO₃ single crystals are strongly dependent upon the polar axis of crystal structure as a larger electro-strain is obtained along the <111> direction [13, 169]. Moreover, the extrinsic domain wall movement and carefully engineered domain configurations also play important roles in further improving the electromechanical performance of BaTiO₃ [166]. Wada *et al.* discovered that the electro-strain induced increased dramatically with reducing domain size [170]. Furthermore, the 90° domain wall movement also contributes to enhanced electromechanical performance in tetragonal BaTiO₃ single crystals with nanodomain configurations [166, 171]. The 90° domain switching in BaTiO₃ introduces a large electro-strain due to the exchange of two different crystallographic axes as illustrated in Figure 2-16 in 2.2.3 and the field induced-strain is one or two orders of magnitude larger than the linear electro-

strain of piezoelectric materials. After the removal of the electric field, the domain structure cannot be restored to its original form due to lack of energy and a remnant polarisation appears. Therefore, the 90° domain switching is a one-time process [166].

Domains in BaTiO₃ crystals

BaTiO₃ crystals exhibit more complex domain structures due to different crystallographic axes in the tetragonal phase at room temperature as shown in Figure 2-5 in 2.2.1. Apart from the normal parallel 180° domains, there also exist adjacent domains that are polarised at 90° to each other. Domain structures of BaTiO₃ crystals at different sizes are observed using different methods such as surface etching techniques, polarised light microscopy, X-Ray diffraction (XRD), and transmission electron microscopy (TEM) [172]. It is observed by Hsiang *et al.* [162] that the 40-80 nm BaTiO₃ powders display a single-domain structure while powders with sizes larger than 80 nm are polydomain tetragonal structures. Moreover, Dudhe *et al.* also clearly observed the 90° and 180° nanodomains of 80 nm BaTiO₃ nanoparticles using TEM. Furthermore, another study focused on the polydomain structure of BaTiO₃ nanoparticles with grain size 50-70 nm found that the domain size is in the range of 10-12 nm [173]. It is also found by many studies that the complexity of domain configurations decreases with reducing the grain size. As the grain size further decreases, the BaTiO₃ crystals change from polydomain structure to single-domain structure and the domain configurations drastically affect the dielectric properties [174, 175].

Besides the intrinsic contribution of the electro-strain effect, the existence of 90° domains in BaTiO₃ crystals is capable of introducing a large strain that is attributed to the crystallographic axes exchange under an alternating electric field and the field-induced strain could be one or two orders of magnitude larger than the piezoelectric strain in poled BaTiO₃ crystals [176]. Due to the lack of driving force to restore the original domain configuration after removing the field, the domain wall movement is irreversible and consequently the macroscopic strain [176]. However, it is extremely difficult to distinguish the contributions from intrinsic and extrinsic (domain wall movement) contributions and conventionally,

the single-domain crystals are considered to be only affected by the intrinsic properties while the contributions of the extrinsic domain wall movement are investigated in the polydomain crystals [102].

2.2.5 Polymer Matrix Nanocomposites with embedded Barium Titanate

In recent years, there is an increasing need for materials that possess both high dielectric and mechanical performance in electronic and electrical industrial sectors [177-179]. However, ferroelectric ceramics or polymer dielectrics on their own could not meet these requirements. Therefore, numerous works have been carried out to investigate polymer matrix nanocomposite materials with embedded inorganic dielectric fillers [178, 180]. Apart from ferroelectric fluoropolymers such as Polyvinylidene fluoride (PVDF) and PVDF-based copolymers [181], the dielectric properties of epoxy-based nanocomposites have also been extensively studied due to better mechanical properties and low-cost processing ability [182, 183]. Among various kinds of fillers with high dielectric permittivity, Barium Titanate (BaTiO_3) [184-186] and Lead Titanate (PbTiO_3) [187] have been widely accepted to be the most popular and effective ones to disperse into epoxy to form a composite. The traditional approach of incorporating such fillers is solvent-aided dispersion, by mixing the powders with solvents to help better dispersion with viscous epoxy resin. In general, a large amount of fillers (vol.% > 50) are required to achieve the highest possible dielectric permittivity values [188], and the properties exhibited are significantly affected by the presence of porosity and filler distribution [189]. Other approaches to achieve a better dispersion quality are physical mixing e.g. ultrasonication, and surface functionalisation of the ceramic fillers [188]. In order to enhance the compatibility between the inorganic fillers and organic polymer matrix, researchers start with surface hydroxylation via hydrogen peroxide treatment, followed by modification with surface active agents, e.g., silane coupling agents [190-192]. Such coupling agents added functional groups onto the BaTiO_3 particles' surface that formed covalent bonds with the epoxy matrix [188]. It has been widely accepted that the dielectric permittivity increases in nanocomposites with surface functionalised BaTiO_3 due to the uniform dispersion and fewer voids content [190, 193].

Most studies found that dielectric permittivity increases with increasing filler content, and decreases with increasing frequency due to decreased dipole polarisation of BaTiO₃ at a lower frequency (< 1MHz) [194-196]. The main polarisation mechanisms that exist in BaTiO₃ epoxy nanocomposites are spontaneous dipole polarisation originating from BaTiO₃ and interfacial polarisation. The interfacial polarisation is correlated with BaTiO₃/epoxy interphases that are highly dependent on the loading of BaTiO₃ nanoparticles [194]. On the other hand, dielectric loss in BaTiO₃ epoxy nanocomposites at low frequencies up to MHz is primarily attributed to epoxy as BaTiO₃ shows no significant dielectric loss within this frequency range [188]. It is found by Yang *et al.* that the dielectric permittivity drops as the frequencies increase to a higher range (> 1GHz). At the same time, the dielectric loss increases [197]. It is well known that BaTiO₃ exhibits a very strong dielectric relaxation at higher frequencies (200MHz-5GHz), which is characterised as a decrease in the dielectric constant and a peak in the dielectric loss [135, 136, 198]. Due to the lossy nature of BaTiO₃ at the GHz range, it has been widely served as a lossy filler in polymer nanocomposite materials for microwave absorption applications [184, 199, 200]. The majority of the existing literature mainly focused on the influence of BaTiO₃ fillers on electrical performance as a function of dielectric permittivity. Therefore, there is a limited understanding of how the BaTiO₃ impacts the mechanical behaviour of epoxy at higher frequencies.

2.3 Interaction of Ferroelectric Materials with the Microwave Field

2.3.1 Introduction of Microwave

Microwaves are on the electromagnetic spectrum and have the speed of light with a wavelength in the range of 1 m to 1 mm, which is equivalent to the frequency range of 300 MHz to 300 GHz as shown in Figure 2-17, below [201].

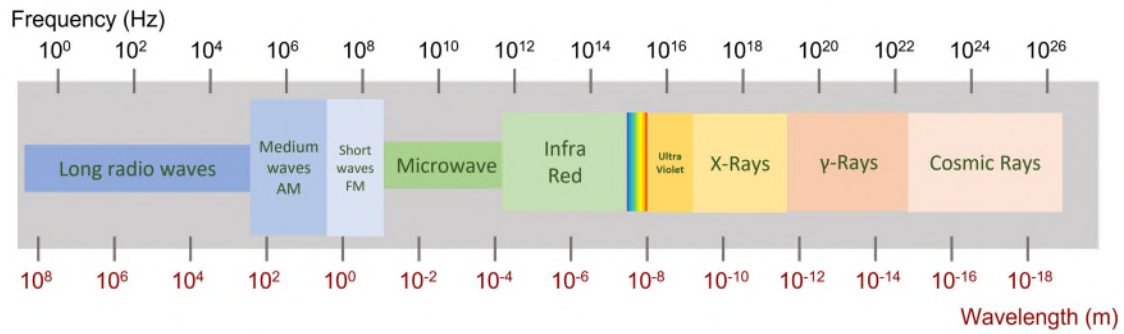


Figure 2-17 Schematic diagram of the electromagnetic radiation spectrum, recreated from [201].

Microwaves are originally developed for application in the telecommunication industry. It has also been widely used in domestic food cooking and industrial material processing due to its uniform heating ability [202, 203]. Unlike conventional heating, energy is directly transferred into the material via the field/material interaction at the molecular level under microwave radiation. The ability to generate heat from the inside lead to a volumetric heating pattern inside the material. Other than the benefit of volumetric heating, microwave also offers many other advantages in comparison with conventional heating, e.g. rapid, non-contact, and selective heating [204]. Nowadays, microwaves at 2.45 GHz and 0.915 GHz are selected to be used in material processing for industrial, scientific and medical applications by the Federal Communications Commission (FCC) [202]. The microwave is a coupling of an oscillating electric field and a magnetic field [205]. Different materials under microwave radiation n interact with either one of these two fields or both of them. It is first discovered by Cheng *et al.* [206, 207] that some materials such as ferrites and some conductive powders have a stronger interaction with the magnetic field than the electric field by comparing their heating efficacy.

2.3.2 Material-microwave Interactions

When a material is under microwave radiation, various responses could happen depending on its composition and structure. The mechanism of the material and microwave interaction is particularly complex and it involves the orientation of dipoles, free-to-move electrons, domain wall movement and electron spins, which

are activated by the electric and/or magnetic field components [208]. Materials are usually categorized into four groups based on the response of the material to microwave radiation as shown in Figure 2-18, below [209]. The incident microwaves pass the materials in the transparent group (e.g., Quartz) completely without any energy loss. In the case of a lossy insulator, the materials have relatively high dielectric loss tangents and absorb all the microwaves, also known as absorber materials, such as water. When the microwaves get reflected by a material (e.g., conductors) without any or negligible energy absorption, it belongs to the opaque group with no penetration at all. The last group is mixed absorbers which are composite materials that at least consist of one or more phases that are lossy insulators like polymer matrix. Materials in this group interact with microwaves via the localized lossy phase.

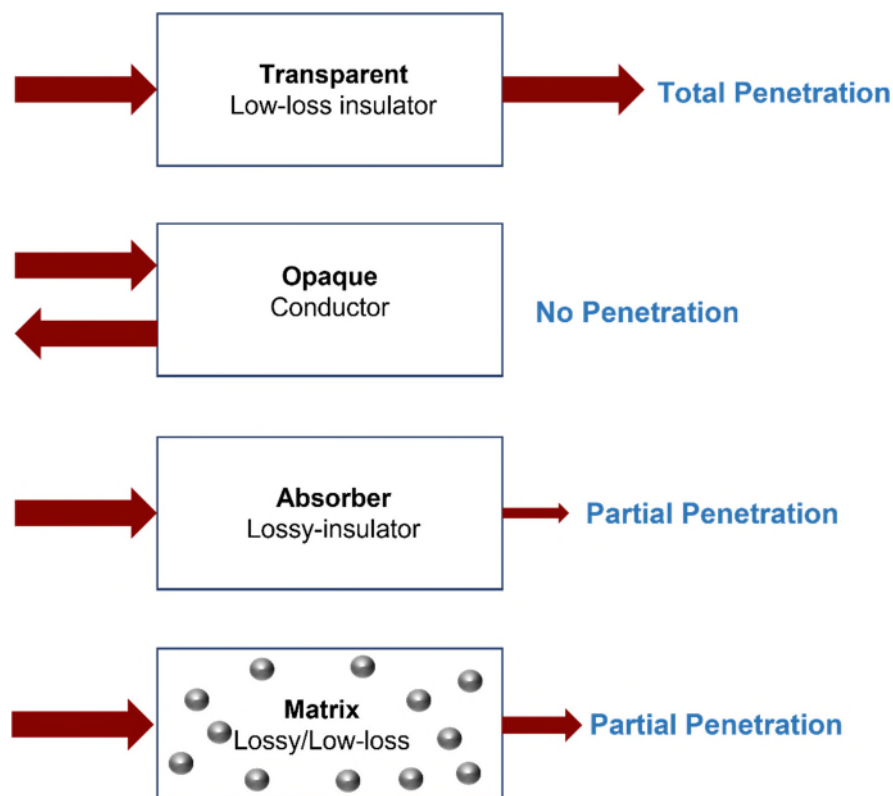


Figure 2-18 Microwave interaction with different types of materials. Red arrows indicate the incident and reflected/transmitted microwaves, recreated from [209].

A magnetic material, e.g., Iron, Nickle, etc., interact with both electric and magnetic components of the microwave field. The electric field triggers the movement of the free electrons while the magnetic field initiates the electron spin

and magnetic domain wall movement. The mechanisms of the materials interacting with the magnetic component of the microwave field are intensively studied by other researchers and the major ones involved are hysteresis losses, eddy current losses, and magnetic resonance losses due to domain wall resonance and electron spin [210, 211]. On the contrary, non-magnetic materials such as water, polymers and ceramics interact solely with the electric component of the microwave field. The two main mechanisms of energy loss in microwaves are dipolar losses and conduction losses. In non-magnetic conductors (e.g., Cu and Al), semiconductors and metal matrix composites, movements of free electrons are imparted by the electric component of the microwave along its field direction and an electric current emerges. A magnetic field in the opposite direction to the external magnetic component of microwaves is then induced and a force is then applied to the free-moving electrons in the opposite direction. The oscillating microwave field repeats this process rapidly and the flow of electrons heats up the material through resistive heating [212]. In an insulator or dielectric material, electrons do not flow freely like conductors, therefore, dipolar loss is the dominant effect [213]. However, the applied electric field component of microwaves introduces reorientation or distortion of permanent dipoles to align with the field direction and this process leads to dielectric heating as shown in Figure 2-19, below [214]. Figure 2-19 schematically described the molecular dipoles in dielectric materials like water (with positive H^+ and negative O^{2-}), and the process of dipoles reorienting themselves to be in the same direction as the oscillating electric field component of microwaves. Inertial, elastic, and frictional forces are against this rapid reorientation behaviour hence kinetic energy of the molecule is increased and leads to volumetric heating [215].

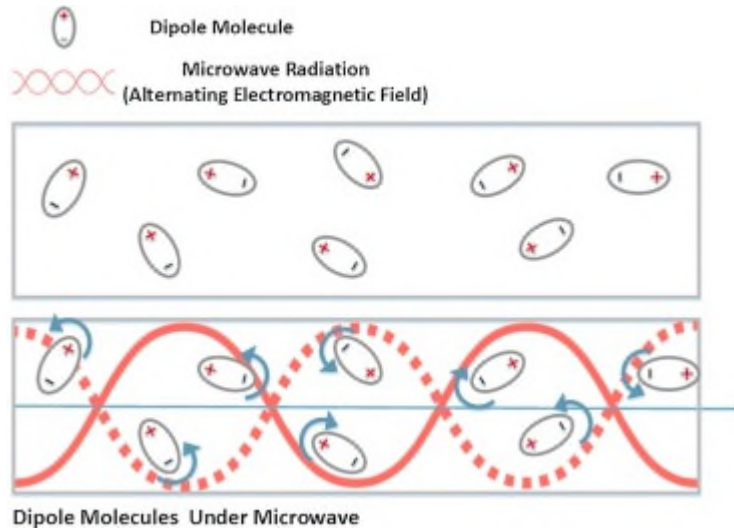


Figure 2-19 A schematic diagram of the material that consists of dipole molecules under an alternating electromagnetic field with arrows indicating the reorientation of dipoles to align with the field direction, recreated from [214].

The essence of the interaction between the dielectric material and the electromagnetic field is energy transformation at the molecular level. Therefore, the dielectric properties of a material, which is measured as the complex permittivity quantifies the ability of a dielectric material to absorb and store electrical potential energy when exposed to a microwave field [216]. The complex permittivity that represents the microwave-material interactions is expressed by Equation 2-1, below:

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad 2-1$$

Where ε' is the real part of the permittivity that indicates the ability to store microwave energy of the material while ε'' is the imaginary part of the permittivity that indicates the ability to dissipate the microwave energy [216], and the dielectric loss tangent is expressed by Equation 2-2, below:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad 2-2$$

The loss tangent is the measure of the material to convert absorbed energy into other forms of energy like heat [205].

There exist several different mechanisms that contribute to the dielectric response of dipoles and charges depending on the frequency of the applied electromagnetic wave, including electronic polarisation, ionic polarisation, dipole polarisation and interfacial polarisation. Furthermore, the interphase polarisation manifests in composite materials, which rise from the accumulation of mobile charges at the interface of different phases [202]. For each polarisation mechanism, there is a critical frequency above which the oscillations of charges/dipoles induced by the electromagnetic field become infinitesimal and negligible as presented in Figure 2-20, below [217]. As described in Figure 2-19, above, the dipoles in an alternating electric field will reorient themselves to align with the new field direction. However, this process cannot happen instantaneously thus some time is required to fulfil the reorientation of dipoles. The time for the dipoles to reorient themselves under a switching field is called relaxation time. This characteristic relaxation time for dipole reorientation is 10^{-12} seconds (s) [218]. Therefore, the orientations of dipoles are not capable of keeping up with an alternating field with a frequency above 10^{12} Hz and the dipole polarisation mechanism will stop contributing to the polarisation of the dielectric material hence the real permittivity ε' drops accordingly due to vanished interaction configurations as the frequency increases [212]. At microwave frequencies, dipole polarisation is commonly taken to be the most dominant one for energy transfer at the molecular level as shown in Figure 2-20, below.

The physical origin of dielectric loss ε'' is the delay between the motion of the polar molecules and the applied alternating electromagnetic field. The lost energy is a result of the combination of different loss mechanisms trying to establish an equilibrium between the changing charges and/or dipoles and the switching electromagnetic field. As illustrated in Figure 2-20, the dielectric loss ε'' is particularly high around the relaxation or resonance frequencies of each polarisation mechanism due to the interaction between the polarisation and applied field caused by the phase lag [218].

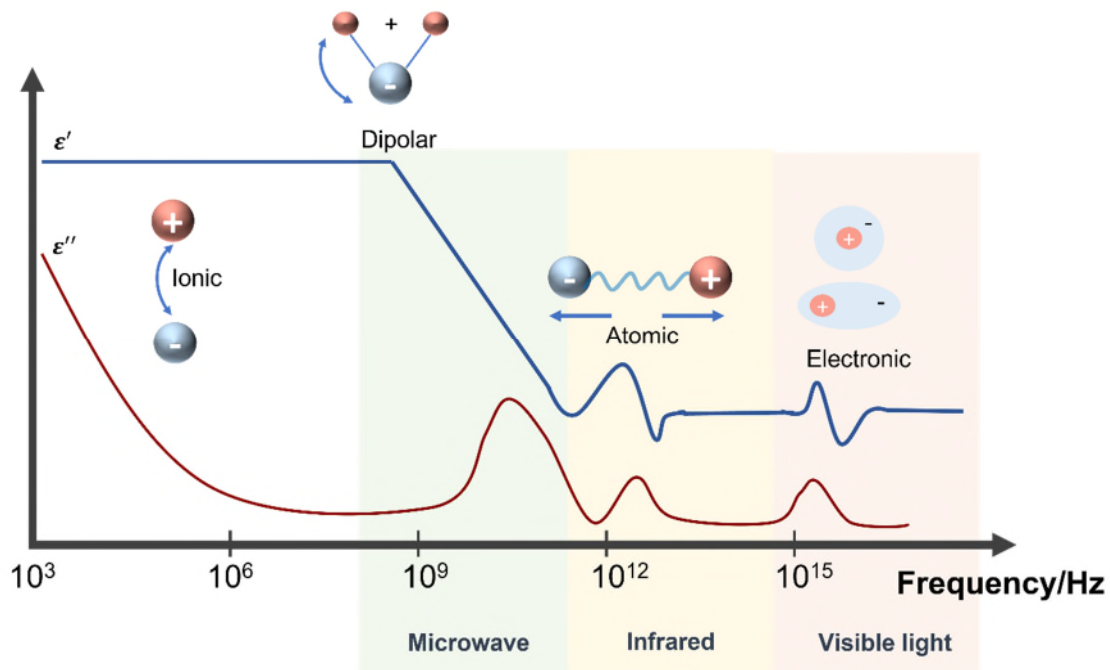


Figure 2-20 Schematic diagram of different polarisation mechanisms as a function of frequency in the dielectric material, recreated from [217].

All materials that lack a centre of symmetry contain permanent dipoles, e.g., water. The temperature changes have a significant effect on their dielectric real permittivity due to the thermal effect on the orientational polarisation. The dipole polarisation drops drastically with increasing temperature due to the less oriented state of dipoles owing to the induced thermal effect. However, it does not represent a continuous increase in the real permittivity as the temperature is lowered as sometimes the temperature change also induces a phase change in several materials (e.g. BaTiO_3) and the dielectric permittivity is strongly dependent on the structure of the material as discussed previously in 2.3.1 [218, 219].

As mentioned in 2.2.5, the BaTiO_3 /epoxy nanocomposite materials exhibit a peak in the dielectric loss at high frequencies range and the mechanism proposed by Kittle [220] is due to the resonance behaviour of the domain wall motion. Owing to their unique dielectric properties within the microwave frequency range, BaTiO_3 /epoxy nanocomposites are often served as microwave absorber materials due to rapid development in electronic and telecommunication industries. Although no studies till today have been focused on the performance

of BaTiO₃-modified epoxy matrix with carbon fibre under microwave radiation, there are numerous investigations on interactions of fibre reinforced polymer with microwave radiation for applications such as microwave-assisted curing [214], composites recovery by microwave pyrolysis [221], microwave non-destructive testing [222] and microwave absorbing composite materials [223]. When exposed to microwave radiation, carbon fibre itself reflect most incident radiation like metals due to its high conductivity. On the contrary, epoxy is considered to be nonconductive and hence transparent to microwave radiation as it presents a relatively low dielectric loss which is negligible [224, 225]. When the carbon fibres are included in epoxy resin, the heating pattern is selected by microwave radiation and generates hot spots due to the huge difference between fibres and epoxy matrix. In general, the fast heating phenomenon in carbon fibre epoxy composite materials is originated from the high-frequency motion of electrons on the carbon surface [226]. The heating pattern is also determined by the orientation of the fibres with incident microwave, and the thickness of the materials due to prevented penetration due to extremely high dielectric loss at GHz frequencies. It is found by *Yichen et al.* that the loss tangent of carbon fibre is approximately 2.5 [227], which is significantly higher than that of BaTiO₃ at 0.5 [228]. When the BaTiO₃ nanoparticles are introduced to the epoxy resin with the existence of carbon fibres, the interaction between carbon fibres and microwave becomes prominent compared to that of BaTiO₃ nanoparticles and hence rapid heating in the areas surrounding carbon fibres would be induced. As a consequence, precise and accurate temperature control plays an important role in future applications of carbon fibre reinforced polymer composites with a modified matrix with BaTiO₃ nanoparticles.

As in the above sections, numerous studies have been carried out to overcome the catastrophic failure initiated due to the inherently brittle nature of polymer composites. Despite the excellent mechanical performance provided by introducing a second phase into the polymer matrix, microcracks could still occur during the service time under various extreme environments. Apart from the various types of filler that could improve the over toughness, the inclusion of microcapsules is also studied to trigger local self-healing around the crack tip

when it occurs during service time. Thus far, previous studies only focused on these 'one-time' toughening methods and no attempts are made on investigating the strain behaviour of dielectric polar fillers in rigid polymer composites under electromagnetic field radiation. Therefore, an investigation on field-induced strains in the polymer matrix is carried out in this study by introducing ferroelectric ceramic nanoparticles that exhibit an electro-strain phenomenon.

3 THEORETICAL ANALYSIS

In this chapter, the theoretical analysis of the strain field of embedded BaTiO₃ nanoparticles in epoxy resin under microwave exposure is presented. Firstly, the theory of dynamic elastic response of tetragonal BaTiO₃ nanoparticles under alternating electric field at the microwave frequencies proposed in previous studies is presented and discussed in Section 3.1 [229]. The displacement of the DW could be used employed as the eigenstrain for the estimation of the stress and strain field in the BaTiO₃/epoxy composite material. A novel approach of the equivalent eigenstrain for inhomogeneous inclusion employing the principle of virtual work [230] is incorporated into the calculation. Based on this approach, a theoretical framework of microwave activated dynamic elastic response of the BaTiO₃ nanoparticles to the surrounding epoxy matrix is discussed in Section 3.2. Finally, the non-uniform distribution of the microwave field and the interaction with the samples are presented in Section 0

3.1 Deformation in a Representative Crystallite of BaTiO₃ under the Microwave Field.

As mentioned in Section 2.2.3, the 90° domain wall movement is the major contribution to the extrinsic field-induced strain. Therefore, the tetragonal BaTiO₃ nanoparticle is assumed to be formed by several multi-domain crystallites that contain a laminar 90° domain structure. A conceptual schematic view of a crystallite is shown in Figure 3-1. The domain wall movement in such crystallites is assumed to be not affected by that in other crystallites.

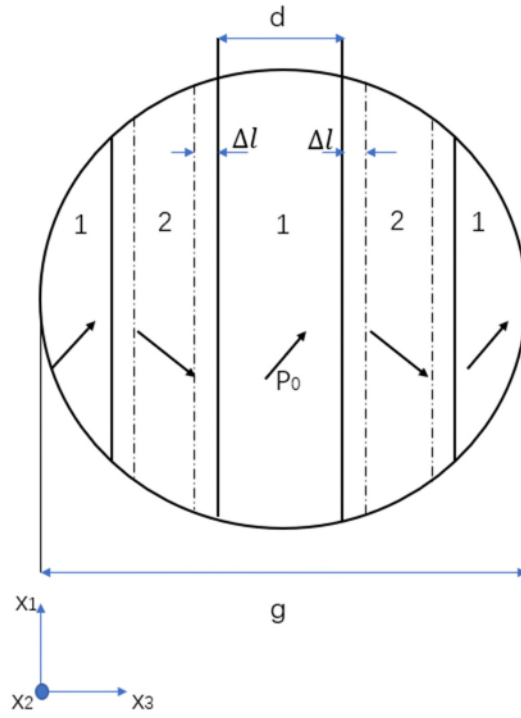


Figure 3-1 Schematic illustration of a spherical nanoparticle (simplified as a crystallite) with a laminar 90° domain structure with spontaneous polarisation P_0 and domain size d , recreated from [231].

Before the application of the microwave field, it is assumed that the DWs are in an equilibrium state and all the domains are of the same size, dielectric properties and elastic properties. Therefore, the interactions between adjacent domains are not included as it is neglectable compared with other factors as suggested in a previous study [232]. Moreover, the internal electric and mechanical fields are assumed to be negligible hence no forces act on the DWs before the microwave exposure [233].

When the microwave field is applied, the interactions with the magnetic component are negligible as the BaTiO_3 nanoparticles are a non-ferrite material. Therefore, the alternating electric component of the microwave field is considered, and it is assumed to be homogenous across the whole nanoparticle in this study. The spontaneous polarisations in the 90° domains reorient themselves with the direction of an applied alternating electric field as demonstrated in Section 2.2.2. Consequently, a driven force $f_A(t)$ as the function

of time is introduced on the DWs that enables the DW motion due to polarisation change as illustrated in Figure 2-14 [234]. The displacement of DW movement is denoted as Δl in Figure 3-1. Due to the ferroelectricity that of BaTiO_3 nanoparticles, the DW movement also introduce an internal electric field E in the nanoparticle due to the change in the polarisation direction. As a result, the internal stress field is also no longer negligible due to the newly developed internal electric field and DW movement from its equilibrium position. An additional force f_l on the DWs is developed subsequently due to the change in internal electric and stress field from zero, and it is calculated in previous studies [232, 235] as presented below.

Due to the displacements in DWs, the electric dipole moment Δp induced by the internal electric field, and the elastic dipole moments Δv induced by the internal mechanical stress field are given by [236] :

$$\Delta p = \sqrt{2}P_0\Delta l \quad 3-1$$

$$\Delta v = 2S_0\Delta l \quad 3-2$$

Where P_0 is the spontaneous polarization, and S_0 is the spontaneous deformation.

The correlation between Δl and the dipole moments is assumed to be linear, and their internal energy W_{electric} under the internal electric field E , and W_{elastic} under the mechanical stress field T_{13} are:

$$W_{\text{electric}} = -\sqrt{2}P_0\Delta l E \quad 3-3$$

$$W_{\text{elastic}} = -2S_0\Delta l T_{13} \quad 3-4$$

Where E is the internal electric field, and T_{13} is the internal mechanical stress T_{ij} ($i, j=1,2,3$) as illustrated in the coordinate system (x_1, x_2, x_3) in Figure 3-1.

The expression of the DW motion is [234]:

$$kA_{DW}\Delta l = -\left(\frac{\partial W_{electric}}{\partial \Delta l} + \frac{\partial W_{elastic}}{\partial \Delta l}\right) \quad 3-5$$

By derivation of Equation 3-3 and Equation 3-4, the force f_I due to the internal fields per unit area $k\Delta l$ is obtained,

$$k\Delta l = \sqrt{2}P_0E + 2S_0T_{13} \quad 3-6$$

Where k is the force constant per unit DW area, and A_{DW} is the area of the DW.

The displacements of all DWs from their equilibrium positions under the microwave field are assumed to have the same magnitude, $|\Delta l(t)|$. The force f_I per unit DW area at a random point r , and time t can be expressed by Equation 3-6, as below:

$$f_I(r, t) = \sqrt{2}P_0E_1(r, t) + 2S_0T_{13}(r, t) \quad 3-7$$

The correlated DWs motions are then described by Newton's second law of motion in the following Equation 3-8:

$$m\Delta \ddot{l} = \bar{f}_I(t) + f_A(t) \quad 3-8$$

where m is the mass of a DW per unit area, $\bar{f}_I(t)$ is the mean value of the DWs-driven force f_I from the internal fields, $f_A(t)$ is the aforementioned exerted force on the DWs by the applied microwave field. The $\bar{f}_I(t)$ is then calculated by averaging the $f_I(r, t)$ over the summation Σ of all DWs surfaces in the nanoparticle as presented below [229].

$$\bar{f}_I(t) = \frac{1}{\Sigma} (2S_0 \int_{\Sigma} T_{13}(r, t) d\Sigma + \sqrt{2}P_0 \int_{\Sigma} E(r, t) d\Sigma) \quad 3-9$$

The DW displacements induced internal electric field $E(r, t)$ and internal mechanical field $T_{13}(r, t)$ in Equation 3-9 must be calculated first to get a value for $\bar{f}_I(t)$. The internal electric field was evaluated in a quasi-static approximation under microwave field and $E(r, t)$ were considered to be proportional to the DW displacement $\Delta l(t)$. The internal mechanical stress field T_{ij} was considered as a

dynamic problem as the DW motions lag behind the 2.45 GHz microwave frequency [229]. In this study, only the extrinsic effect, i.e., DW motions, is considered as they are commonly accepted to be the primary contributor to the electro-strain compared with the intrinsic effect such as piezoelectric effect and electrostriction as considered in Section 2.2.3.

To get the value of the internal mechanical stress field, the change of the spontaneous deformation S_0 caused by the DW displacements in Equation 3-9 was calculated, and the $\Delta S_{13}^0(r, t)$ and $\Delta S_{31}^0(r, t)$ were approximated as [229]:

$$\Delta S_{13}^0(r, t) = \Delta S_{31}^0(r, t) = S_0 \frac{\Delta l(t)}{w} \delta(V_{DW}) \quad 3-10$$

Where w is the thickness of a 90° DW, V_{DW} is the volume of DWs without an applied microwave field, and $\delta(V_{DW})$ is the Dirac delta function for V_{DW} .

The thickness w is around 100 Å and is much smaller compared with the domain width d and the particle size [231], therefore, Equation 3-10 was simplified to Equation 3-11 [229].

$$\Delta S_{13}^0(r, t) = \Delta S_{31}^0(r, t) = S_0 \Delta l(t) \delta(\Sigma) \quad 3-11$$

Where Σ represents the midplanes of DWs when $\Delta l = 0$, $\delta_3(\Sigma)$ is the Dirac delta function of the Σ with a unit normal directed along the x_3 axis [237].

The internal mechanical stress field that introduces the change of $\Delta S_{mn}^0(r, t)$ was then approximated as follows [229]:

$$p_k = -c_{klmn} \Delta S_{mn,l}^0, \quad 3-12$$

Where c_{klmn} is the elastic constant tensor of the nanoparticle, and the index l in the subscript denotes the differentiation with respect to the coordinate x_l ($l = 1, 2, 3$). Based on the dynamic elasticity theory [238], the total displacement $u_i^T(r, t)$ ($i = 1, 2, 3$) of a unit cell was expressed in the following Equation [229]:

$$u_i^T(r, t) = \int dV' \int_{-\infty}^t G_{ik}(r - r', t - t') p_k(r', t') dt' \quad 3-13$$

Where G_{ik} is the dynamic Green's tensor, V' represents the overall surfaces of the nanoparticle, the r' and t' is the original equilibrium position and time before the microwave field application. Substitute Equation 3-12 into Equation 3-13:

$$u_i^T(r, t) = -2GS_0(\delta_{k1}\delta_{l3} + \delta_{k3}\delta_{l1}) \int_{\Sigma} d\Sigma' \times \left(\int_{-\infty}^t G_{ik}(r - r', t - t') \Delta l(t') dt' \right)_{,l} \quad 3-14$$

Where G is the shear modulus of the nanoparticle, δ_{km} is the Kronecker delta, and the expression of G_{ik} used in this calculation was taken from [238].

The total deformation was expressed as follows [229]:

$$S_{ij}^T(r, t) = \frac{1}{2} [u_{i,j}^T(r, t) + u_{j,i}^T(r, t)] \quad 3-15$$

The electric component of the oscillating microwave field is a sinusoidal function of time and the DW displacement $\Delta l(t)$ is written as

$$\Delta l(t) = \Delta l_m \sin \omega t \quad 3-16$$

Where Δl_m is the maximum displacement of the DWs under the microwave field. Substituting Equation 3-14, and the expression of $G_{ik}(r, t)$ into Equation 3-15, the internal mechanical stress field $T_{13} = T_{31} = G(S_{13} + S_{31})$ was expressed with dimensionless functions $h_s(r)$ and $h_c(r)$ (presented at the end of this section due to the lengthiness of the equations) as [229]:

$$T_{13}(r, t) = T_{31}(r, t) = -GS_0 \frac{\Delta l_m}{d} [h_s(r) \sin \omega t + h_c(r) \cos \omega t] \quad 3-17$$

The nanoparticle is assumed to be a homogeneous and isotropic dielectric medium, and the internal electric field $E(r, t)$ is proportional to $\Delta l(t)$,

$$E(r, t) = -\frac{P_0}{\epsilon_0} \frac{\Delta l_m}{d} h_e(r) \sin \omega t \quad 3-18$$

Where ϵ_0 is the permittivity of the free space ($\epsilon_0=8.8542 \times 10^{-12}$ F/m), d is the width of the DW, and $h_e(r)$ are approximated as [229]:

$$h_e(r) = \frac{\sqrt{2}}{\epsilon_{11} + 2\epsilon^*} \quad 3-19$$

Where ϵ_{11} is one of the dielectric permittivity tensor ϵ_{ij} ($i, j = 1, 2, 3$) that represents the dielectric permittivity of the crystallite as illustrated in Figure 3-1, and ϵ^* is the dielectric permittivity of the nanoparticle.

The force $\bar{f}_l$ was then calculated with the internal mechanical stress field $T_{13}(r, t)$ from Equation 3-17 and the internal electric field $E(r, t)$ from Equation 3-18 and Equation 3-19.

The field-induced force f_A is due to the effective electric field in the x_1 the direction of the applied microwave field as illustrated in Figure 3-1. The electric field component E_{A1} is a function of time as follows:

$$E_{A1}(t) = E_m \sin (\omega t + \phi) \quad 3-20$$

Where E_m is the amplitude of the electric component of the microwave field, and ϕ is the phase lag of DW motion with the oscillating microwave field.

Substitute Equation 3-20 into Equation 3-6 with the second part equals zero as $f_A(t)$ is only introduced by an electric field

$$f_A(t) = \sqrt{2}P_0E_m \sin (\omega t + \phi) \quad 3-21$$

Substitute Equation 3-9, Equation 3-17, Equation 3-18, and Equation 3-21, into Equation 3-8,

$$\begin{aligned}
\frac{\Delta l_m}{d} & \left[\left(2GS_0^2 \bar{h}_s(\omega) + \sqrt{2} \left(\frac{P_0^2}{\varepsilon_0} \right) \bar{h}_e - md\omega^2 \right) \sin \omega t \right. \\
& \left. + 2GS_0^2 \bar{h}_c(\omega) \cos \omega t \right] \\
& = \sqrt{2}P_0E_m(\cos\phi \sin \omega t + \sin \phi \cos \omega t)
\end{aligned} \tag{3-22}$$

Where $\bar{h}_s$, $\bar{h}_c$, and $\bar{h}_e$ are the average of $h_s(r)$, $h_c(r)$ and $h_e(r)$ over DW surface Σ .

From Equation 3-22, it could be seen that the DW displacement Δl_m is a function of the strength of the electric component of an applied microwave field E_m , dielectric permittivity of the nanoparticle, ε_r . The value of DW displacement $\Delta l_m(\omega)$ could be obtained by numerical computations of the $\bar{h}_s(\omega)$ and $\bar{h}_c(\omega)$.

To get a rough value from a simplified model, a further assumption is made that the nanoparticles are small enough to be considered as a multi-domain single crystal, namely a crystallite. Therefore, the crystallite as illustrated in Figure 3-1 could be considered as a single BaTiO₃ nanoparticle without any adjacent crystallite and hence no corresponded internal electric and stress field. Consequently, Equation 3-8 could be simplified to:

$$m\Delta \ddot{l} = f_A(t) = \sqrt{2}P_0E_m \sin(\omega t + \phi) \tag{3-23}$$

For further simplicity of calculation, it is assumed that the DW movement under the oscillating microwave field is a simple harmonic motion with a driven force of $f_A(t)$. Assuming the lagging of the reorienting dipoles is neglected, the DW motion becomes in phase with the oscillating field. The driving force at the maximum electric field strength f_m is:

$$f_m = \sqrt{2}P_0E_m \tag{3-24}$$

The amplitude Δl_m is:

$$\Delta l_m = \frac{\sigma L}{k} = \frac{f_m L}{Ak} = \frac{f_m L}{d^2 k} \tag{3-25}$$

Where k is the force constant per unit DW area of the BaTiO₃ nanoparticle and d is the domain width where the area of the domain is approximated to be d^2 .

Dimensionless function $h_s(r)$, $h_c(r)$:

The internal stresses T_{13} and T_{31} induced by DW displacements in a crystallite, is determined by the functions $h_s(r)$ and $h_c(r)$. The dynamic Green's function $G_{ik}(r, t)$ of an isotropic elastic medium is employed in the study and the analytical expression is presented below [229].

$$G_{ik}(r, t) = \frac{1}{4\pi\rho r} \left[\frac{n_i n_k}{c_l^2} \delta\left(t - \frac{r}{c_l}\right) + \frac{\delta_{ik} - n_i n_k}{c_t^2} \delta\left(t - \frac{r}{c_t}\right) \right] \quad 3-26$$

$$+ \frac{t - (\delta_{ik} - 3n_i n_k)}{4\pi\rho r^3} \left[\Theta\left(t - \frac{r}{c_t}\right) - \Theta\left(t - \frac{r}{c_l}\right) \right]$$

$$\Theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases} \quad 3-27$$

The $h_s(r)$ and $h_c(r)$ can be rewritten as follows:

$$\begin{aligned}
h_s(r) = \frac{d}{2\pi} \Bigg\{ & \oint_L \frac{\Delta x_2}{R^3} dL'_1 + 2 \oint_L \frac{\Delta x_1}{R^3} \left[\cos \frac{\omega R}{c_t} - 1 \right. \\
& + \frac{\omega R}{c_t} \sin \frac{\omega R}{c_t} + 2 \frac{\Delta x_3^2}{R^2} \frac{\omega R}{c_t} \left(\frac{c_t^3}{c_l^3} \sin \frac{\omega R}{c_l} - \sin \frac{\omega R}{c_t} \right) \\
& - 2 \left(1 - 6 \frac{\Delta x_3^2}{R^2} \right) \left(\frac{c_t^2}{c_l^2} \cos \frac{\omega R}{c_l} - \cos \frac{\omega R}{c_t} \right) \\
& + 6 \left(1 - 5 \frac{\Delta x_3^2}{R^2} \right) \left(\frac{\omega R}{c_t} \right)^{-2} \left(\cos \frac{\omega R}{c_l} - \cos \frac{\omega R}{c_t} \right. \\
& \left. + \frac{\omega R}{c_l} \sin \frac{\omega R}{c_l} - \frac{\omega R}{c_t} \sin \frac{\omega R}{c_t} \right) \Big] dL'_2 \\
& + \int_{\Sigma} \frac{(\Delta x_3^2 - \Delta x_1^2)}{R^5} \left[3 \left(\cos \frac{\omega R}{c_t} - 1 + \frac{\omega R}{c_t} \sin \frac{\omega R}{c_t} \right) \right. \\
& \left. - \left(\frac{\omega R}{c_t} \right)^2 \sin \frac{\omega R}{c_t} \right] d\Sigma' \Bigg\}
\end{aligned}$$

$$\begin{aligned}
h_c(r) = \frac{d}{2\pi} \left\{ \oint_L \frac{\Delta x_1}{R^3} \left[-\sin \frac{\omega R}{c_t} \right. \right. \\
+ \frac{\omega R}{c_t} \cos \frac{\omega R}{c_t} + 2 \frac{\Delta x_3^2}{R^2} \frac{\omega R}{c_t} \left(\frac{c_t^3}{c_l^3} \cos \frac{\omega R}{c_l} - \cos \frac{\omega R}{c_t} \right) \\
+ 2 \left(1 - 6 \frac{\Delta x_3^2}{R^2} \right) \left(\frac{c_t^2}{c_l^2} \sin \frac{\omega R}{c_l} - \sin \frac{\omega R}{c_t} \right) \\
+ 6 \left(1 - 5 \frac{\Delta x_3^2}{R^2} \right) \left(\frac{\omega R}{c_t} \right)^{-2} \left(-\sin \frac{\omega R}{c_l} + \sin \frac{\omega R}{c_t} \right. \\
+ \left. \frac{\omega R}{c_l} \cos \frac{\omega R}{c_l} - \frac{\omega R}{c_t} \cos \frac{\omega R}{c_t} \right) \left. \right] dL'_2 \\
+ \int_{\Sigma} \frac{(\Delta x_3^2 - \Delta x_1^2)}{R^5} \left[3 \left(-\sin \frac{\omega R}{c_t} - 1 + \frac{\omega R}{c_t} \cos \frac{\omega R}{c_t} \right) \right. \\
+ \left. \left(\frac{\omega R}{c_t} \right)^2 \sin \frac{\omega R}{c_t} \right] d\Sigma' \left. \right\}
\end{aligned}$$

Where, $R = |r - r'| = (\Delta x_1^2 + \Delta x_2^2 + \Delta x_3^2)^{\frac{1}{2}}$, $\Delta x_i = x_i - x'_i$, d is the domain width, ω_{DW} is the frequency of DW vibrations, c_t and c_l are the phase velocities of transverse and longitudinal DW vibrations generated in the nanoparticle.

3.2 Epoxy Embedded with a BaTiO₃ Nanoparticle.

Eshelby's inclusion approach is employed in this study to compute the effective stress field within an epoxy matrix with the embedded BaTiO₃ nanoparticle. General Eshelby's inclusion problem involves ellipsoidal inclusions in an infinite linear elastic medium [239, 240]. Therefore, the embedded BaTiO₃ nanoparticle is an inhomogeneous spherical inclusion as it has different elastic properties compared with the surrounding epoxy matrix. This method is widely accepted by many studies to solve problems involving thermal expansion, reinforced composite materials, phase transformation, etc [241, 242]. For an inhomogeneous spherical inclusion that displays nonuniform eigenstrain, a generalised adaption of Eshelby's inclusion method proposed based on the principle of virtual work is employed in this study and presented below [230]:

First, equations based on the elastic theory to solve the eigenstrain of Eshelby's inclusion are presented.

The total strain of infinitesimal deformations is expressed as follows:

$$\varepsilon_{ij} = e_{ij} + \varepsilon_{ij}^* \quad 3-30$$

Where e_{ij} is the elastic strain, and ε_{ij}^* is the eigenstrain.

The compatibility condition of total strain ε_{ij} is expressed in terms of displacement u_i

$$\varepsilon_{ij} = \frac{u_{i,j} + u_{j,i}}{2} \quad 3-31$$

The stress σ_{ij} is expressed by Hooke's Law,

$$\sigma_{ij} = C_{ijkl}e_{kl} = C_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^*) = C_{ijkl}(u_{k,l} - \varepsilon_{kl}^*) \quad 3-32$$

Where C_{ijkl} is the effective stiffness tensor, $C_{ijkl} = C_{ijlk}$ and $C_{ijkl}u_{k,l} = C_{ijkl}u_{l,k}$.

In the region where $\varepsilon_{kl}^* = 0$, Equation 3-32 is:

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} = C_{ijkl}u_{k,l} \quad 3-33$$

The inversed Equation 3-32 is

$$\varepsilon_{ij} - \varepsilon_{ij}^* = C_{ijkl}^{-1}\sigma_{kl} = S_{ijkl}\sigma_{kl} \quad 3-34$$

Where S_{ijkl} is the compliance tensor that has the same symmetries as the stiffness tensor.

The equation of equilibrium is expressed as follows:

$$\sigma_{ij,j} + f_i = 0, (i = 1,2,3) \quad 3-35$$

Where f_i is the body force, and the boundary condition is:

$$T_i = \sigma_{ij}n_j \quad 3-36$$

Where n_j is the outward unit normal vector to the boundary.

The corresponding stress and strain field of a homogeneous inclusion in an infinite medium could be obtained using Green's function method with the profile of the inclusion [243]:

The Eshelby inclusion problem is applied here in this study as illustrated in Figure 3-2, below. It is assumed that the inclusion has a dynamic deformation of the eyestrain $\varepsilon(t)$ as a function of time under the microwave field. A fictitious load T is applied to the inclusion in order to maintain the original shape. The inclusion is then put back into the hole within the infinite epoxy matrix with the original shape and size. After removing the applied T , the inclusion exerts a traction force F on the matrix, which equals $-T$.

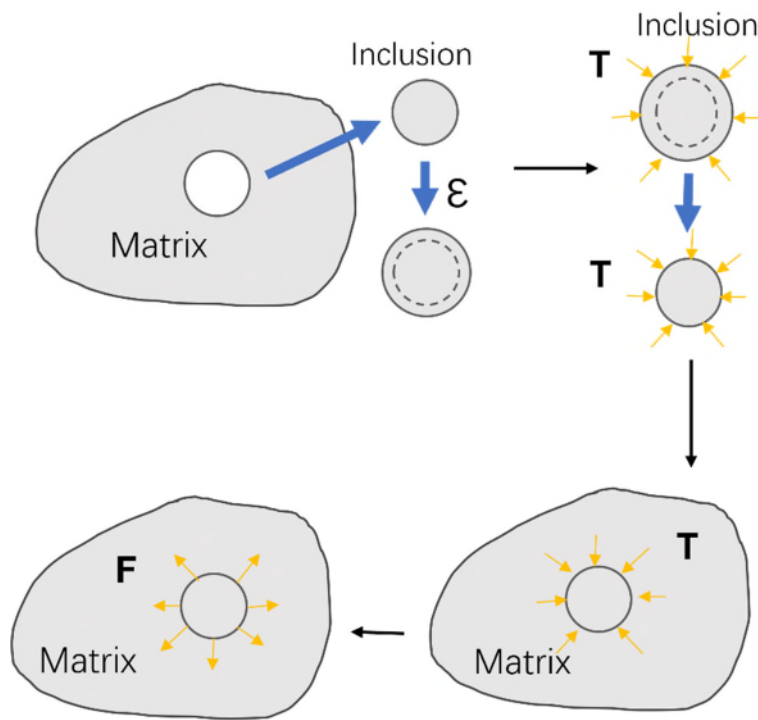


Figure 3-2 Schematic diagram of Eshelby's inclusion.

However, several assumptions made in this method are that the inclusion is in ellipsoids shape and has identical elastic properties with the matrix. Furthermore, the eigenstrain in the inclusion is uniform. Therefore, the inhomogeneous inclusion of embedded BaTiO₃ nanoparticles could only be solved by transforming the inhomogeneous inclusion into a homogenous inclusion. The

nanoparticle with residual strain embedded within the epoxy was transformed into a homogenous inclusion problem with a distribution of equivalent eigenstrain.

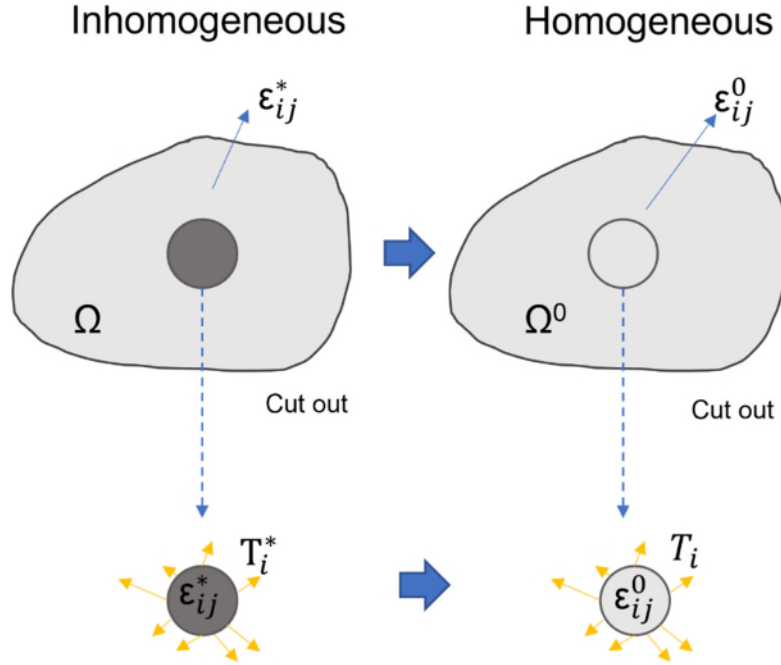


Figure 3-3 Schematic diagram of the principle of equivalent eigenstrain of transforming an inhomogeneous problem to a virtual homogeneous problem.

The transformation illustrated in Figure 3-3 based on the principle of virtual work is presented below [230]:

First, the inclusions in both inhomogeneous and homogeneous cases in Figure 3-3 are imaginarily cut from the matrix and the virtual works of both processes are expressed as Equation 3-37 in Ω of the inhomogeneous problem and Equation 3-38 in Ω^0 of the virtual homogeneous problem.

$$\int_v f_i^* \delta u_i dv + \int_s T_i^* \delta u_i ds = \int_v \sigma_{ij}^* \delta \epsilon_{ij} dv \quad 3-37$$

$$\int_v f_i \delta u_i dv + \int_s T_i \delta u_i ds = \int_v \sigma_{ij} \delta \epsilon_{ij} dv \quad 3-38$$

Where δu_i is the virtual displacement, $\delta \epsilon_{ij}$ is the virtual strain, f_i is the body force, T_i is the traction force on the boundary, and σ_{ij} is the stress of the nanoparticle.

Equation 3-38 minus Equation 3-37,

$$\int_v (f_i - f_i^*) \delta u_i dv + \int_s (T_i - T_i^*) \delta u_i ds = \int_v (\sigma_{ij} - \sigma_{ij}^*) \delta \epsilon_{ij} dv \quad 3-39$$

As the stress states in both conditions are identical, therefore, $f_i = f_i^*$, and $T_i = T_i^*$. The $\delta \epsilon_{ij}$ can have any value and Equation 3-39 is expressed as follows:

$$\sigma_{ij} = \sigma_{ij}^* \quad 3-40$$

From Equation 3-32 based on Hook's Law, the stress states are expressed as Equation 3-41 for Ω , and Equation 3-42 for Ω^0 :

$$\sigma_{ij}^* = C_{ijkl}^* (\epsilon_{kl} - \epsilon_{kl}^*) \quad 3-41$$

$$\sigma_{ij} = C_{ijkl} (\epsilon_{kl} - \epsilon_{kl}^0) \quad 3-42$$

Where C_{ijkl} and C_{ijkl}^* are the elastic constant of the homogeneous and inhomogeneous inclusion, respectively, ϵ_{kl} is the total strain, ϵ_{kl}^* is the real residual strain in the inhomogeneous Ω , and ϵ_{kl}^0 is the equivalent eigenstrain in the homogeneous Ω^0 .

As $f_i = f_i^*$, and $T_i = T_i^*$, the deformation of the nanoparticle in the epoxy matrix in Ω is equivalent to that of the virtual homogeneous inclusion in Ω^0 by incorporating an equivalent eigenstrain ϵ_{kl}^0 .

Substitute Equation 3-40 with Equation 3-41 and Equation 3-42:

$$C_{ijkl}^* (\epsilon_{kl} - \epsilon_{kl}^*) = C_{ijkl} (\epsilon_{kl} - \epsilon_{kl}^0) \quad 3-43$$

The equivalent eigenstrain in Ω^0 is:

$$\epsilon_{kl}^0 = (1 - C_{ijkl}^* S_{ijkl}) \epsilon_{kl} + C_{ijkl}^* S_{ijkl} \epsilon_{kl}^* \quad 3-44$$

Therefore, with the equivalent eigenstrain ϵ_{ij}^0 , the stress and strain field in the nanoparticle of Ω could be calculated using Green's function method as presented as follows [230, 243]:

The displacement field for a 3-D inclusion is:

$$u_i(\mathbf{X}) = \int_{-\infty}^{\infty} C_{jlmn} \varepsilon_{mn}^*(\mathbf{X}') G_{ij,l}(\mathbf{X} - \mathbf{X}') d\mathbf{X}', \mathbf{X}, \mathbf{X}' \in \Omega \quad 3-45$$

Where $G_{ij,l}(\mathbf{X} - \mathbf{X}')$ is the Green's function, and

$$G_{ij,l}(\mathbf{X} - \mathbf{X}') = \frac{\partial}{\partial x_l} G_{ij}(\mathbf{X} - \mathbf{X}') - \frac{\partial}{\partial x_l'} G_{ij}(\mathbf{X} - \mathbf{X}') \quad 3-46$$

The strain field is:

$$\varepsilon_{ij}(\mathbf{X}) = -\frac{1}{2} \int_{-\infty}^{\infty} C_{klmn} \varepsilon_{mn}^*(\mathbf{X}') \{G_{ik,lj}(\mathbf{X} - \mathbf{X}') + G_{jk,li}(\mathbf{X} - \mathbf{X}')\} d\mathbf{X}' \quad 3-47$$

The total strain in Equation 3-44 is expressed as a function of the equivalent eigenstrain ε_{ij}^0 according to Equation 3-47:

$$\varepsilon_{pq}(\mathbf{X}) = -\frac{1}{2} \int_{-\infty}^{\infty} C_{klij} \varepsilon_{ij}^0(\mathbf{X}') \{G_{pk,lq}(\mathbf{X} - \mathbf{X}') + G_{qk,lp}(\mathbf{X} - \mathbf{X}')\} d\mathbf{X}' \quad 3-48$$

Therefore, the corresponding deformation field in the inclusion and the matrix can be calculated using the Green's function method with the equivalent eigenstrain ε_{ij}^0 .

As illustrated in Figure 3-4, below, A BaTiO₃ nanoparticle is embedded in the epoxy matrix and the epoxy is assumed to be infinite. The BaTiO₃ nanoparticle and the epoxy are assumed to be isotropic. A nominal eigenstrain ε_{ij}^* , due to DW movement is prescribed as shown in Figure. It is assumed that the eigenstrain is the collective displacements of all the domains that exhibit different polarisation in all possible directions.

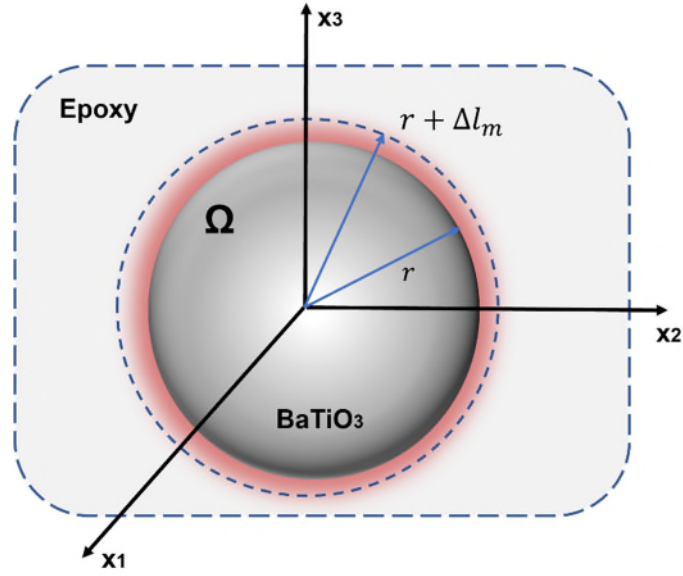


Figure 3-4 Schematic illustration of An inhomogeneous sphere embedded in an infinite solid with nominal interference fit strain ε_{ij}^* .

The nominal eigenstrain is denoted as ε_{ij}^* :

$$\varepsilon_{ij}^* = \Delta l_m / r \quad 3-49$$

From Equation 3-44, the equivalent eigenstrain ε_{kl}^0 in Ω is:

$$\varepsilon_{kl}^0 = (1 - C_{ijkl}^* S_{ijkl}) \varepsilon_{kl} + C_{ijkl}^* S_{ijkl} \varepsilon_{kl}^* \quad 3-50$$

The anisotropic elastic constants of isotropic materials are C_{ijkl} , and C_{ijkl}^* for Epoxy and BaTiO₃ respectively:

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad 3-51$$

$$C_{ijkl}^* = \lambda^* \delta_{ij} \delta_{kl} + \mu^* (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad 3-52$$

$$\mu = \frac{Y}{2(1 + \nu)} \quad 3-53$$

$$\lambda = \frac{Y\nu}{(1 + \nu)(1 - 2\nu)} \quad 3-54$$

Where $\lambda(\lambda^*)$ and $\mu(\mu^*)$ are Lamé constants, [244], ν is the Poisson's ratio, and δ_{ij} is Kronecker delta.

Insert Equation 3-51 Equation 3-52 into Equation **3-50**:

$$\begin{aligned} & \lambda \delta_{ij} \varepsilon_{kk}^0 + 2 \mu \varepsilon_{ij}^0 \\ &= [(\lambda - \lambda^*) \delta_{ij} \varepsilon_{kk} + 2(\mu - \mu^*) \varepsilon_{ij}] + (\lambda^* \delta_{ij} \varepsilon_{kk}^* + 2\mu^* \varepsilon_{ij}^*) \end{aligned} \quad 3-55$$

The equivalent eigenstrain ε_{kl}^0 and total strain can be written as ε_{kl} :

$$\varepsilon_{kl}^0 = \delta_{kl} \varepsilon_0, \quad \varepsilon_{kl} = \delta_{kl} \varepsilon \quad 3-56$$

Where ε is a function of ε_0 [243]:

$$\varepsilon = \frac{1 + \nu}{3(1 - \nu)} \varepsilon_0 = \alpha \varepsilon_0 \quad 3-57$$

Therefore, Equation **3-55** is:

$$(3\lambda + 2\mu) \varepsilon_0 = [3(\lambda - \lambda^*) + 2(\mu - \mu^*)] \varepsilon + (3\lambda^* + 2\mu^*) \varepsilon^* \quad 3-58$$

And the equivalent eigenstrain ε_0 of the inclusion is solved by Equation **3-58**:

$$\varepsilon_0 = \frac{3\lambda^* + 2\mu^*}{(3\lambda + 2\mu)(1 - \alpha) + (3\lambda^* + 2\mu^*)\alpha} \varepsilon^* \quad 3-59$$

Therefore, the strain ε_{kl} in the epoxy is solved by substituting Equation **3-56** with **3-56** and Equation **3-59** :

$$\varepsilon_{kl} = \varepsilon - \varepsilon_0 = \frac{(3\lambda^* + 2\mu^*)(\alpha - 1)}{(3\lambda + 2\mu)(1 - \alpha) + (3\lambda^* + 2\mu^*)\alpha} \varepsilon^* \quad 3-60$$

3.3 Theory of Material-microwave interaction.

As previously described in Section 2.3.2, the major interaction between the dielectric material and the microwave field is the polarisation of the dipoles. Under an oscillating microwave field, the dipoles try to reorient themselves with the external electric field component of the microwave field. Therefore, the BaTiO₃ nanoparticles interact with the electric field component of the microwave field and the magnetic field effect is negligible. The main contribution of microwave power loss in the multi-domain BaTiO₃ nanoparticles originates from the piezoelectric domain wall movement [134]. A significant dielectric loss of the BaTiO₃ nanoparticles occurs at the frequency range of GHz to terahertz (THz) [136]. Compared with the BaTiO₃ nanoparticles, the dielectric loss tangent of epoxy represents the ability to dissipate the absorbed energy is relatively smaller (in the range of 10⁻³ to 10⁻⁴) [245]. The origin of the power loss in most polymers is associated with the dipolar loss due to polar segments of the polymer chain and it is highly dependent upon the temperature and the frequency [245]. The mobility of the polar segments decreased significantly when the frequency reaches the GHz range [246]. Therefore, the dielectric loss in BaTiO₃/epoxy nanocomposites observed at a higher frequency is mainly attributed to the BaTiO₃ nanoparticles.

The behaviour of the electric and magnetic components of the microwave field is governed by Maxwell's equations coupled with boundary conditions [247].

$$\nabla \times \mathbf{H} = j\omega\epsilon\mathbf{E} \quad 3-61$$

$$\nabla \times \mathbf{E} = j\omega\mu\mathbf{H} \quad 3-62$$

$$\nabla \cdot \mu\mathbf{H} = 0 \quad 3-63$$

$$\nabla \cdot \epsilon\mathbf{E} = \rho \quad 3-64$$

Where $\mathbf{H}$ and $\mathbf{E}$ are the varying magnetic (A/m) and electric field strength (V/m), respectively, ω is the angular frequency (rad/s), ϵ is the complex relative permittivity, μ is the complex relative permeability, and ρ is the charge density. The first two equations, namely Ampere's law and Faraday's law, relate the changes in the electric or magnetic field with each other. The last two equations are Gauss's laws, which represent the net magnetic flux out of a region must be zero while the net electric flux out of a region is related to the charge density within the region [248].

The power absorbed by the material in the microwave field is dependent on many factors such as the shape, size, and location of the material. For a thin material that is fully penetrated by the microwave field, the power dissipated P (W/m³) as heat in the material under the microwave field is expressed based on Maxwell's Equations as follows [215]:

$$P = \omega(\mu_0\mu''H_{rms}^2 + \epsilon_0\epsilon''E_{rms}^2) \quad 3-65$$

Where the first term $\mu_0\mu''H_{rms}^2$ described the dissipation of power due to magnetic field and can be neglected for a non-ferrite material, $\omega = 2\pi f$, f is the frequency of the applied microwave field (2.45 GHz), ϵ_0 is the dielectric permittivity of the free space, ϵ'' is represents the imaginary part of the complex dielectric permittivity, and E_{rms} is the root-mean-square value of the local electric field strength (V/m). Therefore,

$$P = \omega\epsilon_0\epsilon''E_{rms}^2 \quad 3-66$$

However, the explicit value of the absorbed power by the material inside the oven cavity is extremely difficult to obtain due to the non-uniformity of the microwave

distribution and hence a varying electric field strength. The power absorbed by the material P_{absorb} , is expressed as follows:

$$P_{absorb} = P_{input} - P_{reflected} - P_{oven} \quad 3-67$$

Where P_{input} is the input power from the magnetron, $P_{reflected}$ is the power reflected and attenuated, and P_{oven} is the power absorbed by the cavity wall, waveguide, and magnetron.

It is apparent that direct measurements of the values from Equation 3-67 are extremely challenging. Furthermore, the increased temperature due to microwave heating also has a significant impact on the dielectric properties of the material, which in turn affects the degree of interaction of the material with the microwave field. In previous studies, an empirical approach is proposed to estimate the absorbed power. It is assumed that the amount of microwave energy absorbed by the material/field interaction is converted into heat during the exposure, and is expressed as follows [210, 249]:

$$\sum mC\Delta T = 2\pi f \varepsilon_0 \varepsilon'' E_{rms}^2 Vt \quad 3-68$$

Where m is the mass of the material, C is the specific heat capacity of the material, ΔT is the temperature change, V is the volume of the material, and t is the microwave exposure time.

The energy transferred into the material is also significantly determined by the depth up to which the microwave field travels into it. The degree of microwave penetration in the material is defined by a factor, 'Penetration depth, d_p ', which is the distance between the surface of the material and the place inside the material where the magnitude of the field strength drops to e^{-1} (36.8%) of that at the surface. The penetration depth d_p neglecting the effects from the magnetic field for a non-ferrite material is expressed as follows [210]:

$$d_p = \frac{c}{\omega \sqrt{2\varepsilon'} \left[\left(\sqrt{1 + (\tan \delta)^2} - 1 \right) \right]^{1/2}} \quad 3-69$$

Where c is the velocity of light, ε' is the real part of the complex dielectric permittivity, and $\tan \delta$ is the tangent loss of the material, $\tan \delta = \varepsilon'' / \varepsilon'$. Generally speaking, microwave power decays more quickly in lossy materials with higher $\tan \delta$ due to energy dissipation hence a lower penetration depth.

Many attempts have been made in past years to measure the magnitude of the electric field in free space and material media under the microwave field using an electric field probe [250]. Indirect measurements are also conducted in another study by measuring the temperature rise in liquids in a microwave oven [215, 251]. From Maxwell's equation, it is noted that the energy of the microwave field is proportional to the square of the amplitude, which represents the maximum strength of its electric and magnetic components. For a continuous sinusoidal microwave field in the air of an empty cavity, the average intensity I is the power carried by the microwave field per unit area, and is expressed as follows [252]:

$$I = \frac{c \varepsilon_0 E_m^2}{2} \quad 3-70$$

Where E_m is the maximum electric field strength, and the root-mean-square value of the electric field is:

$$E_{rms} = \sqrt{E_m^2/2} \quad 3-71$$

Equation 3-70 and Equation 3-71 above could only be used to calculate the electric field strength in an empty oven. When a sample is placed in the multimode microwave oven, the electromagnetic field is considered to be a superposition of multiple plane waves penetrating the material from different directions. Regardless of the differences in each mode, the superposition of all the waves could be assumed to have an approximately uniform and constant distribution pattern in the material within the localised region [253]. Assumptions are made that the absorbed microwave energy is converted to heating in the material with neglected surface heat loss, thermal diffusion, and energy absorbed

by the oven (e.g., magnetron, cavity wall). Therefore, the energy absorbed by the material is corresponding to the temperature rise of the material, and it is expressed by rewriting Equation 3-68:

$$E_{internal} = \sqrt{\frac{mC\Delta T}{2\pi f \epsilon_0 \epsilon'' \Delta t}} \quad 3-72$$

It should be noted that the internal electric field is only localised in the material and is different from that in the surrounding cavity.

Under the same assumption that the material is surrounded by a uniform microwave field, incident microwaves are mostly transmitted and absorbed by the material while some are reflected. It is also assumed that no reflected wave at the interface. An expression is presented as follows [254]:

$$Q_{absorb}V = P_{absorb} = \rho C \frac{\Delta T}{\Delta t} V = \epsilon_0 \cdot E_{rms,external}^2 \cdot c \cdot A \cdot \xi \cdot \Gamma \quad 3-73$$

Where V is the volume of the material, ρ is the density of the materials, c is the phase velocity of the microwave (3×10^8 m/s) [255], A is the surface area, ξ is the absorption coefficient that represents the fraction of the absorbed power that generates heat, and Γ is the transmission coefficient.

By solving Equation 3-73, the time-averaged strength of the external electric field $E_{rms,external}$ obtained:

$$E_{rms,external} = \sqrt{\frac{\rho C a \Delta T}{3 \Delta t c \epsilon_0 \xi \Gamma}} \quad 3-74$$

The power absorption coefficient ξ is expressed as follows [256]:

$$\xi = \frac{P_{absorb}}{P_0} = 1 - e^{-2a/d_p} \quad 3-75$$

Where P_0 is the incident power at the surface, and a is the thickness of the sample.

The transmission coefficient, Γ , is the energy fluxes per unit of time and unit area at the interface. It is assumed that the microwave incident is normal to the material surface as the energy flux comes from all directions within the cavity, and the transmission coefficient Γ is simplified as [255]:

$$\Gamma = \frac{4(n_1/n_2)}{[(n_1/n_2) + 1]^2} \quad 3-76$$

Where n_1 and n_2 are the refraction index of air and the material, respectively.

The refraction index n for non-magnetic material is:

$$n = \sqrt{\varepsilon'} \quad 3-77$$

Although the exact electric field outside and inside the material is difficult to be measured due to effects from many factors that are described above. The above equations are employed in Section 6.2 to obtain a simple evaluation of the average and peak electric field strength of the incident microwave with a given cavity size. The absorbed microwave power by the BaTiO₃ sample could be estimated subsequently.

The principle of virtual work is utilised in this study to theoretically describe the strain introduced by the BaTiO₃ nanoparticle as an inhomogeneous spherical inclusion to its surrounding epoxy matrix as an infinite linear elastic medium. In order to solve the equation, the inhomogeneous inclusion of embedded BaTiO₃ nanoparticles is transformed into a homogenous inclusion problem with a distribution of an equivalent eigenstrain. It is assumed that the eigenstrain in the inclusion is uniform in all directions. It is assumed that the inclusion (BaTiO₃) has a nominal eigenstrain activated by microwave stimulation as a function of exposure time. A simplified model is proposed that the nanoparticles are small enough to be considered as a multi-domain single crystal, namely a crystallite. It is also assumed that the microwave-driven DW movement is a simple harmonic motion and the in phase with the microwave field. The nominal eigenstrain in the BaTiO₃ nanoparticle is solved with the estimated electric field strength at different power levels and exposure time in Section 6.2 with acquired temperature change data from FBG measurements in Section 5.2.2.

4 MATERIALS AND EXPERIMENTS

4.1 Material and Manufacturing

This section describes the raw material and formulation used to manufacture the developed epoxy nanocomposites. The characterisations of the developed epoxy nanocomposites are presented in Section 5.1.

The epoxy used in this study is, Araldite LY1564, a diglycidyl ether of bisphenol A (DGEBA) and the curing agent is Aradur 3487, an amine hardener. This two-part epoxy system is selected as a well-documented general base matrix material for the nanocomposites. Although using different ratios of resin and hardener could result in variation in cross-linking, this work adopted a single standard mix ratio to ensure consistent and repeatable results. They are purchased from Huntsman, UK. This epoxy resin system has relatively low viscosity and high flexibility mainly for aerospace and industrial structural composite parts.

It is extremely difficult to reach a uniform dispersion of nanoparticles in the polymer blend. It is widely observed that when the nanoparticles are added to the polymer, the nanofillers cluster and aggregate due to the “nano” effect [257]. Particle agglomeration has been observed in many studies when the inorganic BaTiO₃ nanoparticles are mixed with an organic epoxy matrix. Such phenomenon is attributed to their high surface area and the existence of van der Waals forces among them. Nowadays, the most widely used methods for nanoparticle dispersion in the organic epoxy matrix are physical mixing and surface functionalisation [29]. Therefore, apart from the physical mixing approach, a coupling agent is also applied to the particle surface via covalent bonds [188]. Various investigations have been carried out on BaTiO₃ nanoparticle surface modification with surface active modifiers, such as silane coupling agents [190, 258, 259]. Such silane coupling agent consists of two functional groups that form covalent bonds with hydroxyl groups on the particle surface and the epoxy, respectively [188]. Many studies have concluded that a uniform dispersion, decrease in voids and defects, and improved dielectric properties are achieved with the applied particle surface functionalisation process with a silane coupling

agent [192, 260, 261]. 3-GPS is one of the most widely used silane coupling agents and its ability to enhance the nanoparticles' dispersion quality has been approved in many studies [190, 262-265].

The coupling agent for surface functionalisation selected in this study is 3-glycidoxypropyl trimethoxysilane (3-GPS) purchased from Sigma-Aldrich, US. Hydrogen peroxide (H₂O₂, 30%) and acetic acid (C₂H₄O₂, 99.9%) used as functionalisation aids are purchased from Sigma-Aldrich, US. The ethanol (C₂H₆O, 99.9%) used for BaTiO₃ dispersion is purchased from Fisher Scientific International, Inc., UK.

BaTiO₃ powders are purchased from Nanostructure & Amorphous Materials Inc., US. The general properties of purchased BaTiO₃ powders measured by the manufacturer are detailed in Table 4-1, below [266]. All the chemicals except BaTiO₃ powders are used as received without any further treatments.

Size	200 nm
Phase	Tetragonal
Specific surface area (SSA)	6-7 m ² /g Spherical
Density	5.85 g/cm ³

Table 4-1 General properties of BaTiO₃ nanoparticles measured by the manufacturer [266].

The phase composition of BaTiO₃ powders is confirmed by X-Ray diffraction (XRD) using a Siemens D5005 X-Ray Diffractometer with Cu-K α radiation (wavelength λ of 1.54 Å, at 40 kV and 30 mA). The scanning speed is 0.5 °/s in the range of 20° to 90°. The peaks analysis is performed by data analysis software Origin using a Lorentzian curve fit function.

Figure 4-1, below displays a well-defined perovskite structure of BaTiO₃ without a noticeable second phase. The split peaks between 44°-46° of the 2 θ angle correspond to reflections (002) and (200) as shown in the inset confirm that the

tetragonal phase of BaTiO₃ while a cubic lattice only gives one peak (200) in this range [267].

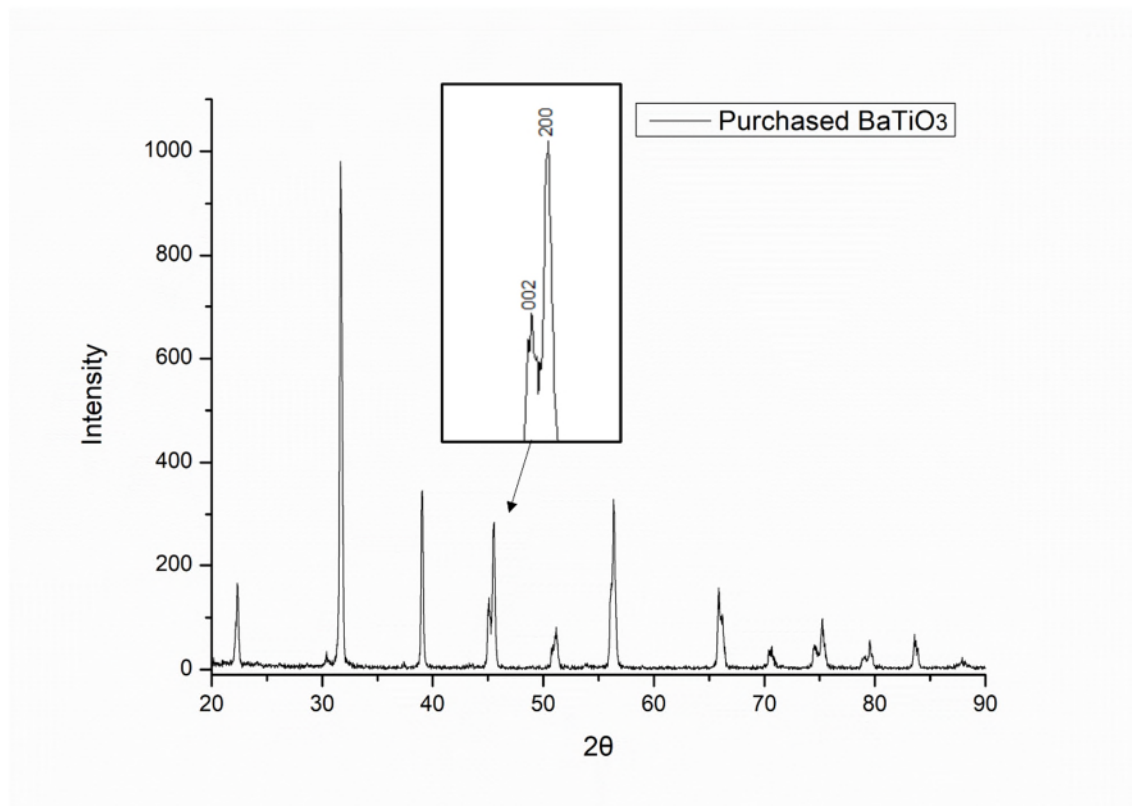


Figure 4-1 X-ray diffraction patterns of purchased BaTiO₃ powders. The inset shows the split peaks of (002) and (200) indicating the tetragonal phase.

4.1.1 Surface Functionalisation of BaTiO₃ and Characterisation

Purchased BaTiO₃ powders were prepared with the combustion method, therefore firstly they needed to be pre-treated in H₂O₂ for the hydroxylation process to add hydroxyl group (-OH) to the surface [260].

Hydroxylation Process

10g of BaTiO₃ nanoparticles are added into a 230mL solution of H₂O₂ in a round bottom flask. The mixture is then sonicated in an ultrasonic bath for 30 minutes (mins) and then refluxed at the boiling temperature of 30% H₂O₂ solution at 108°C [268] at 100 revolutions per minute (rpm) using a mechanical stirrer for 6 hours to facilitate the process by heating without losing any H₂O₂. The nanoparticles were retrieved by centrifuging the resulting solution at 4500 rpm for 15mins and

washed three times with deionized water. The obtained BaTiO₃ nanoparticles are dried in an oven at 80°C for 24 hours. The reflux and particle retrieving processes are similar as in the surface functionalisation with 3-GPS as presented in Figure 4-2, below.

Surface Functionalisation with 3-GPS

3-GPS is then applied to BaTiO₃ nanoparticles in this study to improve the processability and filler dispersion in nanocomposites as shown in Figure 4-2, below. First, the solution of 1 wt.% of 3-GPS with respect to BaTiO₃ is prepared. 150mL aqueous solution of ethanol and deionized water (9:1) is first mixed in a beaker. Adding the acetic acid drops using a pipette and stir vigorously after each drop until the pH value of 3.5-4 measured by a METTLER TOLEDO pH meter is reached. Stir vigorously again for 3mins to form a clear solution. The low pH values of the solution facilitate the silane functionalisation process [269]. After the addition of the 0.1g 3-GPS solution to the acidified solution using a pipette, leave the mixture in an ultrasonic bath for 30mins to form a homogenous solution. 10g hydroxylated BaTiO₃ powders are then added to the silane solution and mixed under an ultrasonic bath again for 10mins for better filler wetting. Finally, the mixture is refluxed at the boiling temperature of ethanol 78°C [270] at 100 rpm using a mechanical stirrer for 6 hours using a silicone oil bath over a hotplate as shown in Figure 4-2, below. After refluxing, the BaTiO₃ is washed three times with deionized water and retrieved using centrifugation at 4500 rpm. The silane-treated BaTiO₃ (Si-BaTiO₃) powders are dried at 110°C for 24 hours to avoid any condensation of silanol groups at the surface. In the end, the powders are crushed in a mortar and pestle for nanocomposite preparation. The size distribution of Si-BaTiO₃ particles is analysed in its epoxy nanocomposite form in the following Section 4.2.1.

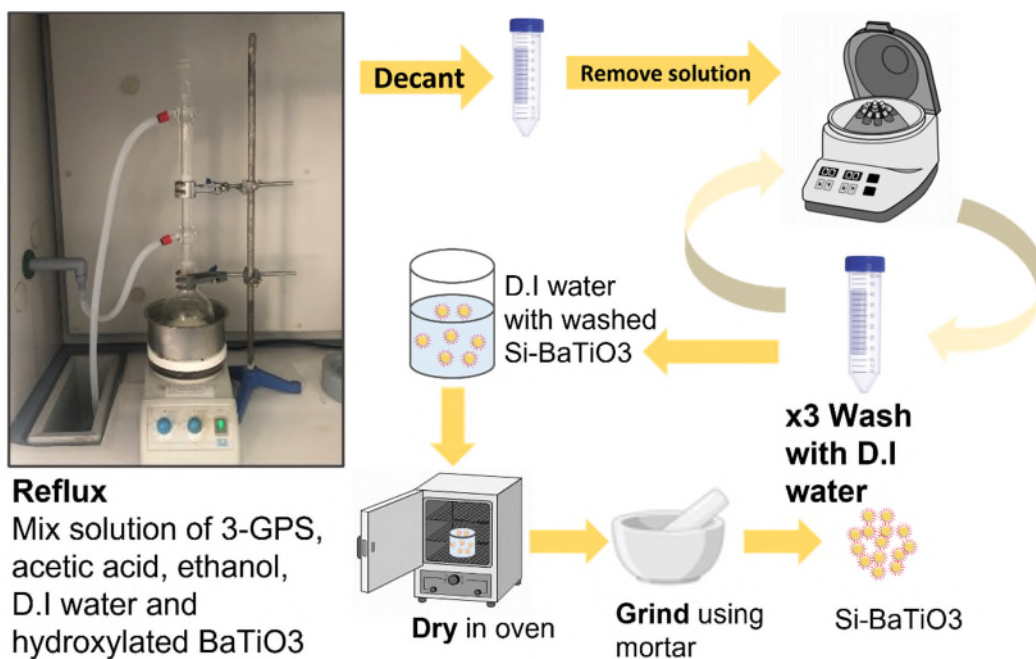


Figure 4-2 Schematic diagram of the functionalisation process of BaTiO₃ with 3-GPS.

The silane-treated powders are then characterised by Thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectrometry to confirm the existence of the functional group in the following sections.

4.1.1.1 Fourier Transform Infrared Spectrometry (FTIR)

FTIR is performed to detect the silane functional groups on the modified BaTiO₃ powders in transmission mode using a Jasco FT/IR-6200 in the range of 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹ at room temperature. The nanoparticles are mixed with Potassium Bromide (KBr) pellets and then pressed into small flakes for FTIR measurements. The FTIR spectra of Si-BaTiO₃ and untreated powders are presented in Figure 4-3, below. The peaks at 1437 cm⁻¹ and 1630 cm⁻¹ are due to the small trace of BaCO₃ and physically absorbed water on BaTiO₃ powders from the combustion fabrication process according to the manufacturer [191]. The broad band peaked at 3435 cm⁻¹ is attributed to hydroxyl groups -OH (from Si-OH group) stretching vibrations at the surface of the nanoparticles. The 574 cm⁻¹ band is attributed to the stretching vibrations of Ti-O bonds. The bands between 850 cm⁻¹ and 1250 cm⁻¹ are representations of Si-O, Si-O-C₂H₅, and Si-

O vibrations. These appeared new peaks confirm that the silane group are successfully grafted onto the surface of BaTiO₃ powders [188].

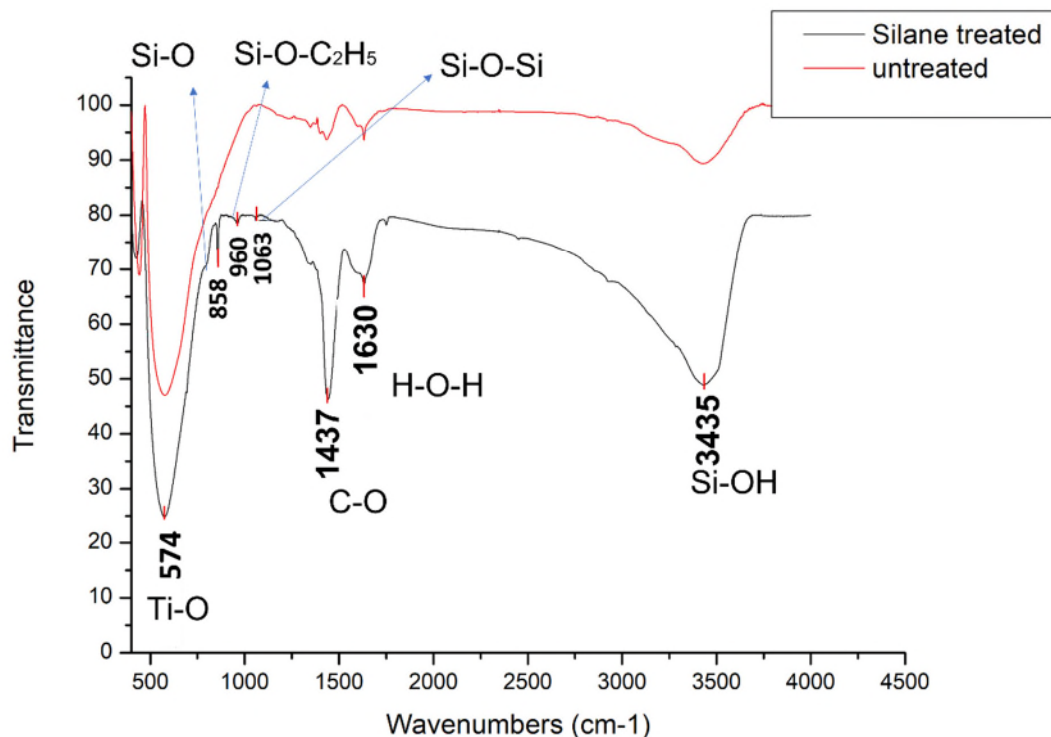


Figure 4-3 FTIR spectra of Si-BaTiO₃ (black) and untreated (red) BaTiO₃ powders.

4.1.1.2 Thermogravimetric Analysis (TGA)

The amount of organic silane group grafted onto the surface of BaTiO₃ powder was obtained by TGA using a TA instrument Q-500 at a rate of 20°C/min under a dry nitrogen gas flow rate of 100 ml/min to 700°C. Figure 4-3, below shows the TGA curves of untreated and Si-BaTiO₃ powders. The weight loss percentage indicated as the lowest point of the green line is 0.35% for untreated BaTiO₃ and 1.2% for treated. Therefore, the amount of 3-GPS grafted onto the BaTiO₃ surface is calculated to be about 0.85%, which is close to the previously designed 1% in the surface functionalisation process. The weight curve of 3-GPS treated BaTiO₃ powders showed three well-defined degradations as labelled in Figure 4-3, below. Based on the results presented in the previous FTIR Section 4.1.1.1, the absorbed water is removed between 50°C to 150°C labelled as 1 and 2 in Figure 4-3. The degradation step from 240°C to 450°C represents the free hydroxyl

groups (-OH) and/or silane molecules that remained on the surface labelled as 3. The pyrolysis of surface silane compounds is observed at around 565°C labelled as 4 [191, 271].

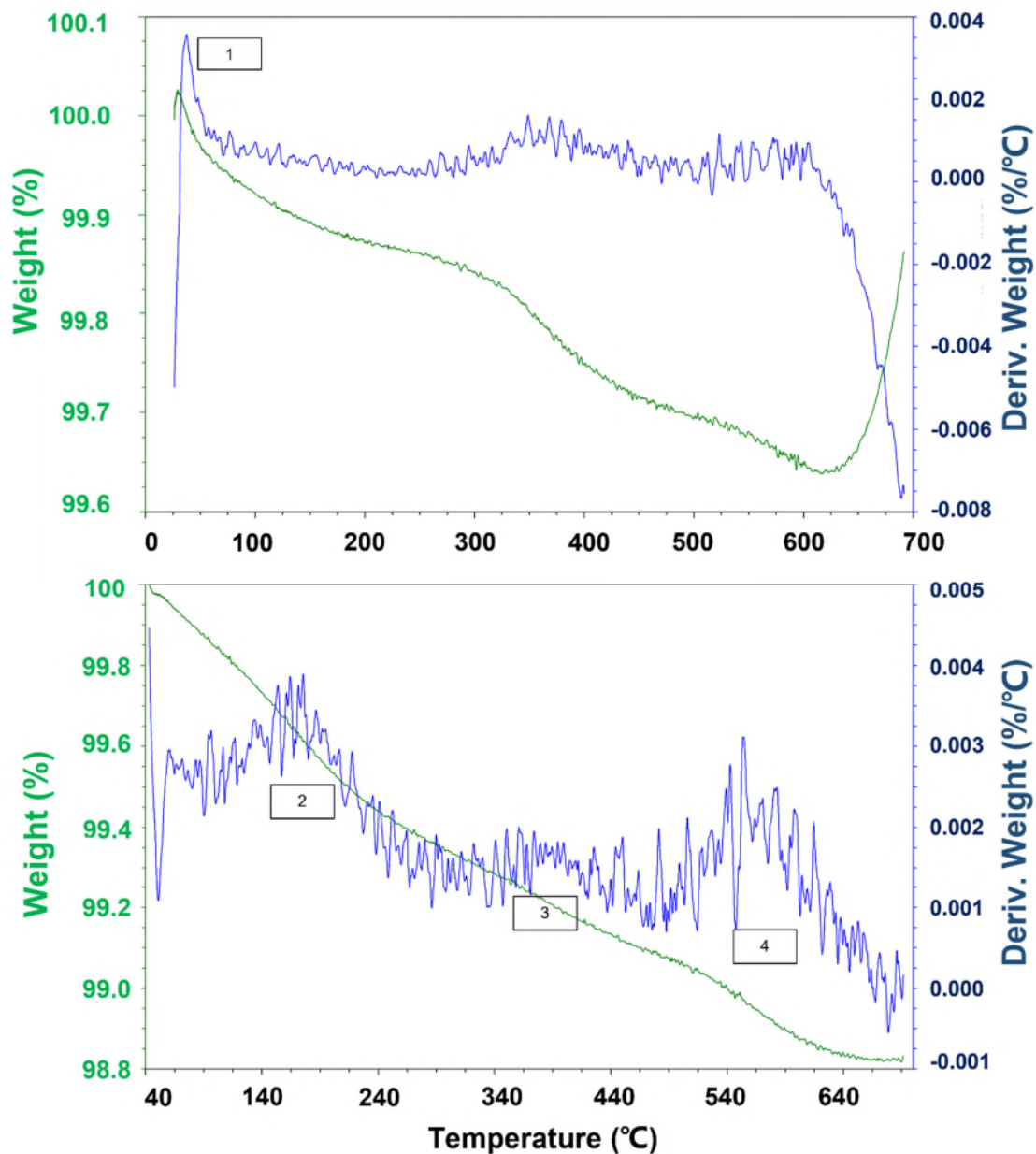
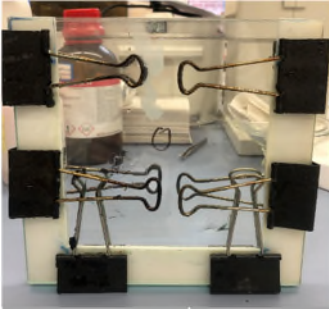


Figure 4-4 TGA curves of untreated (above) and Si-BaTiO₃ powders. Green lines are the weight percentage of the powders versus temperature and blue lines are the rate of change of the weight percentage versus temperature.

4.1.2 Sample Preparations of BaTiO₃ Nanocomposites

The epoxy nanocomposite fabrication process including Si-BaTiO₃ functionalisation is schematically illustrated in Figure 4-6, below. Although the extra epoxy-ended groups are introduced by the silane coupling agent, the mixing ratio of epoxy and hardener remains the same for all neat epoxy and nanocomposite samples. Previous studies have demonstrated improved dielectric properties with an increasing weight loading of BaTiO₃ particles [148, 272-274]. However, degradation of the mechanical properties of BaTiO₃/epoxy nanocomposites is also observed when the weight loading goes over 10 wt.% due to the prominent particle agglomeration [196]. Therefore, the epoxy resin nanosuspension with 1, 5, 10, 15 wt.% Si-BaTiO₃ nanoparticles and 5, 10, 15 wt.% untreated BaTiO₃ nanoparticles are prepared as follows. Firstly, the weighed amount of BaTiO₃ powders are added to ethanol and sonicated with an ice water bath for 2mins using an ultrasonic horn (Branson Digital Sonifier S-450D) with a 10s pulse to form a homogenous solution. Then a weighed amount of epoxy and the previous mixed solution are blended together in a beaker using a mechanical stirrer at 300 rpm and 80°C overnight under the fume hood to gradually remove the ethanol without precipitation of the particles. The mixture is weighed before and after the previous step to ensure the complete removal of ethanol. The curing agent is then added to the mixture with a weight ratio recommended by the company and stirred for a further 3mins. Finally, the mixture is placed in the vacuum oven at 30°C for 1 hour to remove bubbles at 98kPa and achieve complete removal of ethanol. The whole mixture is poured into a mould made of two pieces of glass clamped with a 3 mm silicone gasket in-between as shown in Figure 4-5, below. A uniform thickness of each sample is achieved with the help of this type of glass mould. They are then cured in the oven for 8 hours at 80°C as prescribed by the manufacturer and then cooled naturally to room temperature. The final samples are of size 160x140x3 mm, and they are cut to different sizes using a precision cut-off machine BRILLANT 220.




	Epoxy/g Hardener/g	Ethanol/mL	BaTiO ₃ /g
Neat Epoxy	40 13.6		
1 wt.% Si-BT		15	0.536
5 wt.% Si-BT		15	2.68
10 wt.% Si-BT		15	5.36
15 wt.% Si-BT		15	8.04
10 wt.% BT		15	5.36
15 wt.% BT		15	8.04

Figure 4-5 Picture of glass mould used for nanocomposite fabrication and the cured nanocomposite samples.

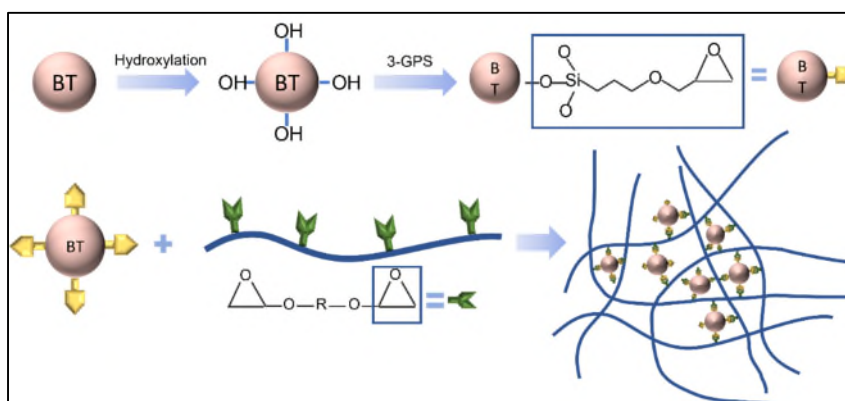


Figure 4-6 Schematic illustration of the hydroxylation and silane functionalisation process for the BaTiO₃ nanoparticles.

4.2 Experiment Methods

4.2.1 General Material Characterisations

Morphology Characterisation

The morphological characterisation of cured nanocomposites with different weight loading between 0 and 15 wt.% are carried out. The morphologies of fracture surface from tensile test specimens are characterised with a field emission scanning electron microscope TESCAN Vega 3 with a secondary electron detector under acceleration voltage 10kV. A thin layer of gold of 10nm is coated on each sample before testing to enable better conductivity. ImageJ (Version 1.53) is used to identify the number and area of the nanoparticles. The SEM images are first calibrated by setting the scale with a known distance. The Fast Fourier Transform (FFT) bandpass filter is then applied to flatten the images. Afterwards, the modified monochrome images are further enhanced to outline most nanoparticles before size distribution analysis by adjusting the colour threshold and erasing unnecessary noises with drawing tools [275]. ImageJ is used to identify the number and area of the nanoparticles. The SEM images are initially calibrated using a known distance to set the scale. The Fast Fourier Transform (FFT) bandpass filter is then applied to flatten the images. Afterwards, the modified monochrome images are further enhanced to outline most nanoparticles before size distribution analysis by adjusting the colour threshold and erasing unnecessary noises with drawing tools [275]. Finally, the data was exported from ImageJ, and Origin software was used to calculate the diameter of the nanoparticles, which was then used to generate histograms of the nanoparticles' size distribution.

Thermal Characterisation

The thermal characterisation of the cured nanocomposites is studied by a differential scanning calorimeter (DSC Q200, TA Instruments). The DSC measurements are performed in a nitrogen flow (50 mL/min). Samples of size 5x3x1 mm are prepared using a Buehler ISOMAT low-speed saw. The samples are first heated from 40°C to 220°C at a ramp rate of 20°C/min. The measured DSC curves of all epoxy nanocomposites present a distinct exotherm peak. Thereafter, the second run at a heating rate of 20°C/min with each sample is scanned again to 220°C after cooling down from the first scan. The glass-transition temperature (T_g) is determined using the inflection-point method following the IS/DIS 11357-2. A tangent is drawn at the point of inflection in the

DSC spectra from the second run and the T_g is the midpoint between the onset and the endset of the drawn tangent.

Tensile Test

The tensile test is one of the most widely used methods to obtain the mechanical properties of polymer nanocomposite with inorganic fillers. Young's modulus, tensile strength, and morphology analysis of fracture surface are obtained. Rectangular-shaped samples with weight loading 5%, 10%, and 15% of silane-treated and untreated barium titanate powders of dimension 85x10x3 mm are cut from the prepared nanocomposites specimens in 4.1.2 with the help of a precision cutter. Samples are tabbed with aluminium of size 25x1 mm at both ends to counter the stress concentration at the grips as shown in Figure 4-7. Tensile tests are carried out at a crosshead speed of 1.0 mm/min using a 5/100 kN Instron 5500R following BS2782-3 and a laser extensometer is used to obtain the actual strain in the sample during the test. Six specimens are prepared in each loading category.

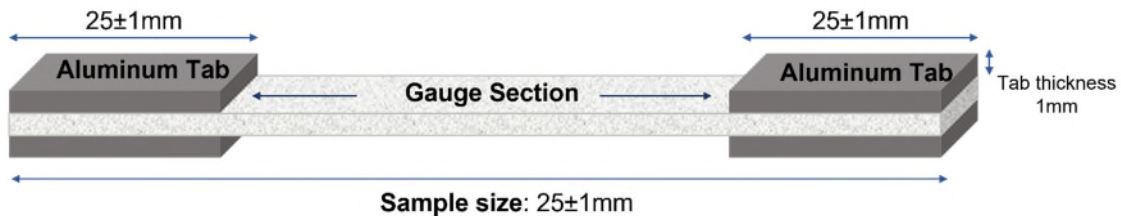


Figure 4-7 Schematic diagram of an aluminium tabbed sample for tensile test.

Dielectric Characterisation

The complex relative permittivity and permeability of neat epoxy and nanocomposites of different weight loading with increasing frequency from 0.25 GHz to 4.50 GHz at a 0.25 step increment are measured using a vector network analyser (VNA) with microstrip methods [276] in collaboration with the Institute of Radioelectronics and Multimedia Technology, Warsaw University of Technology. The microstrip line configuration is one of the most frequently used methods for dielectric measurements in the high-frequency range up to tens of GHz owing to its relatively simple fabrication process. Flat plate samples of size 50x50x3 mm

are prepared as substrates for conductive lines as shown in Figure 4-8. They are then attached on top with a ground metal plate at the bottom as presented in the Figure below. The dielectric constants of the samples are then measured using a VNA connected to the configuration shown below.

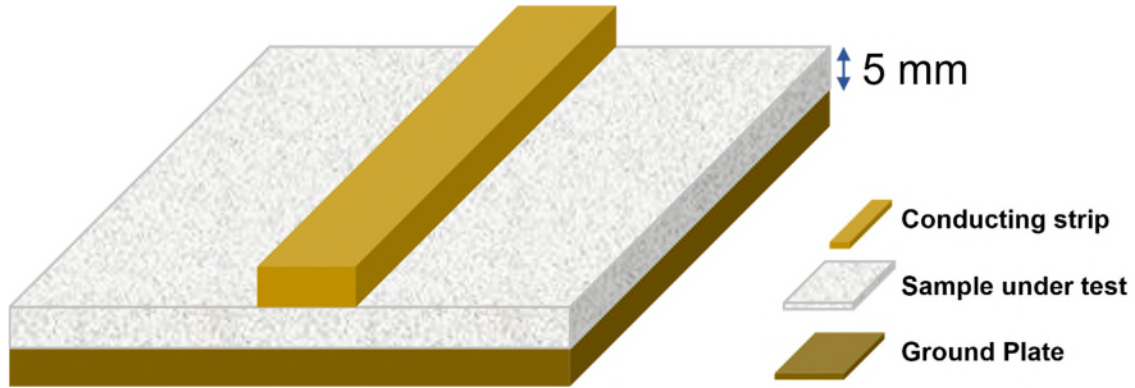


Figure 4-8 Schematic illustration of the layout of the sample for microstrip line methods.

The resonant approach is capable of providing a more accurate value of the dielectric properties compared with the transmission line method. However, the resonant methods could only measure the dielectric properties at a single frequency instead of measuring through the frequency range [277].

4.2.2 Field-induced Strain Measurements

The microwave field is selected to be the external stimulator as BaTiO₃ exhibit a peak in a dielectric loss at the microwave frequency range. The dielectric loss indicates the loss of microwave energy due to the material/field interaction. The microwave energy is dissipated within the material due to several mechanisms as mentioned in Section 2.2.4 and Section 2.3.2. Most importantly, the design of the experiment becomes more feasible with remote stimulation from the microwave field owing to the spacious cavity. The mechanical response of the modified epoxy system is investigated under a microwave field within a domestic microwave oven Panasonic NN-SF464MBPQ running at 2.45 GHz and cavity size 354x338x230 mm. The conventional microwave oven has a transformer that operates at constant power and the power level can only be changed by turning it on and off repeatedly. In contrast with the conventional one, this oven equipped

with inverter technology has a circuit board that replaces the transformer hence the output power can be adjusted linearly by varying the pulse width to ensure a more precise and continuous microwave exposure [278]. The unique flat-bed design of this model is equipped with a stationary ceramic plate that allows more space to place the sample and its holder.

One major limitation of this approach is not being able to perform mechanical tests simultaneously to evaluate the mechanical property enhancement triggered by microwave radiation. Alternatively, any strain field introduced by the BaTiO₃ nanoparticles to the surrounding epoxy that is activated by microwave field is studied by measuring strain response on the surface of epoxy nanocomposite samples with the incorporation of Fibre optic sensor with fibre Bragg gratings (FBG) in collaboration with the Centre for Engineering Photonics, Cranfield University. FBGs were fabricated by a periodic intense laser light applied onto the core of an optic fibre. The laser light exposure introduced a permanent increase in the refractive index of the fibre's core and a fixed modulation was created subsequently. Each FBG is around 5 mm long with a grating period of 1 micron. Two arrays with 3 FBGs for each sample are fabricated. FBG arrays are then adhesively bonded to the surface of two geometrically identical 135x10x3 mm samples of 15 wt.% Si-BaTiO₃ epoxy nanocomposites. The strain array is bonded to the surface by adhesives at the FBG regions while the temperature array is firstly packaged into a capillary glass tube and then glued parallel to the strain array. The arrays are placed in the same location with the same distance in-between on each sample. The strain experienced by the samples is transferred to the FBG sensors and the measurements are also affected by the temperature. Therefore, the temperature array only measures the temperature change and compensates for the strain measurements accordingly.

A preliminary test via a FLIR One Pro LT Smartphone Thermal Camera is carried out to inspect the temperature change of different samples under different power levels. Samples are placed at a designed location as schematically illustrated in Figure 4-9, below. The exposure time is then carefully selected based on the heating profiles of each sample to control the temperature of samples below T_g

during the microwave test to avoid any interference in strain measurements from the post-cure shrinkage.

The sample is clamped on one end by a designed sample holder made of polytetrafluoroethylene (PTFE) to ensure minimum interaction with the microwave field owing to its extremely low dielectric loss. The size and location of the load inside the cavity are two primary factors that affect microwave field distribution [278]. To control the microwave field distribution, the sample and the holder are placed at the designed location shown in Figure 4-9, below for all tests. The power level of 100W and 440W are first selected to avoid temperature surges in samples within a short period. Exposure time is set to be 650s for 100W and 148s for 440W to limit the temperature of samples below T_g (80°C) based on the preliminary test results obtained by the thermal camera mentioned above.

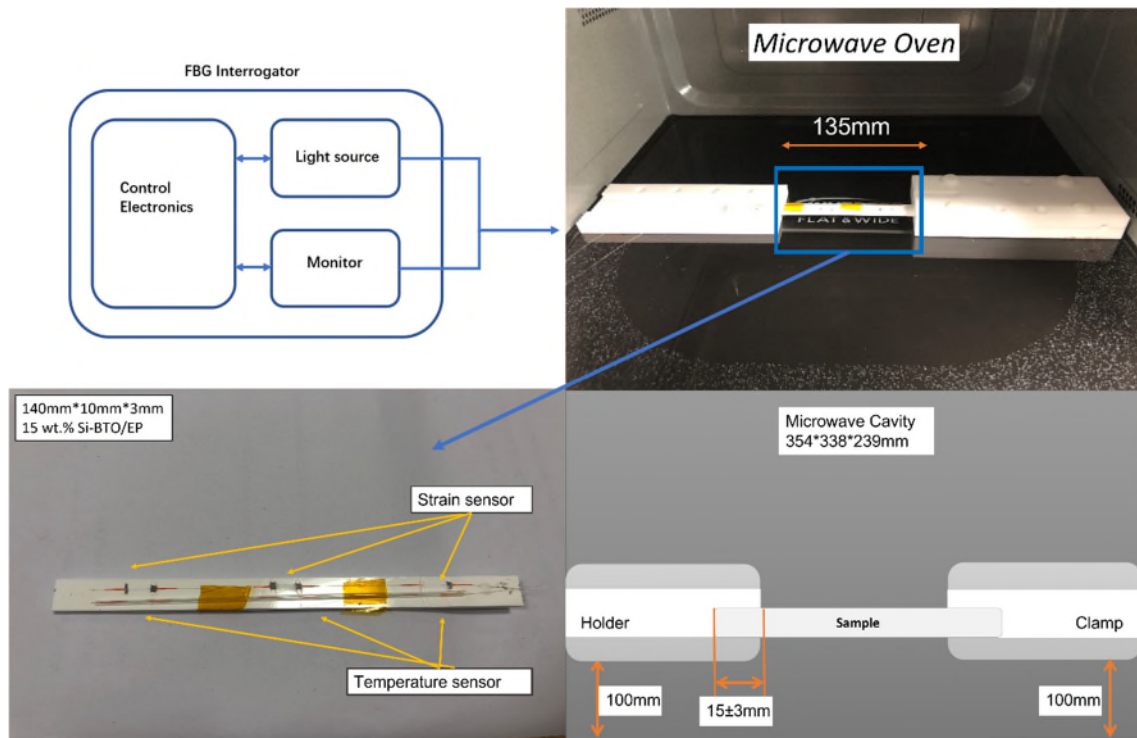


Figure 4-9 Schematic illustration of the sample of epoxy nanocomposite with BaTiO₃ on the PTFE holder in the microwave oven with surface-bonded FBG arrays connected to an interrogator.

Neat epoxy, BaTiO₃ nanoparticles, and adhesive used for bonding FBGs have different thermal expansion coefficients (CTE) and microwave heating patterns.

Microwave field interaction with the neat epoxy and adhesive is investigated thereafter. Two arrays with 5 FBGs of 5 mm long and 1 micron grating period are fabricated for each test. First, the adhesive response under microwave radiation is studied by two arrays of FBGs adhesively bonded to the surface of a PTFE block as shown in Figure 4-10, below. Measured strain and temperature change are solely due to the microwave heating of adhesive as PTFE has neglectable heating effects under the microwave. The PTFE block is placed in the microwave oven at the designed location in order to locate the first FBG sensor on the left end at the same location as the one in the previous test of 15 wt.% nanocomposites. The tests are performed under 100W for 650s and 440W for 110s from room temperature at 21°C. Data starts to be recorded on the interrogator 10s prior to the microwave exposure for each run to ensure no data is missing after the microwave starts.

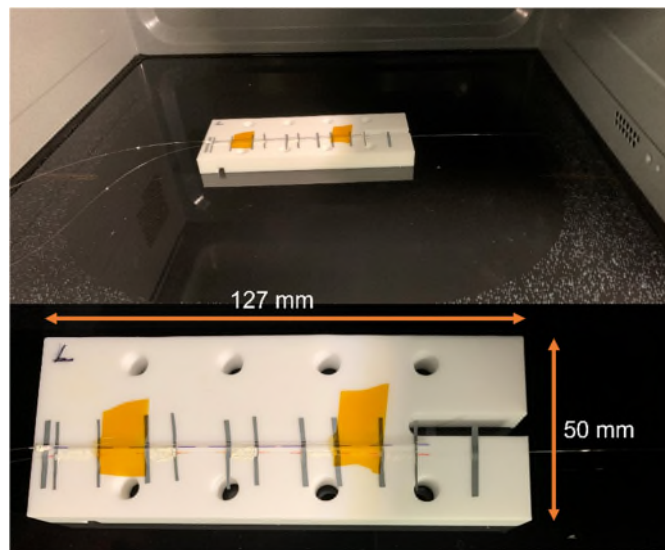


Figure 4-10 Illustration of FBG arrays bonded to a PTFE block using Permabond 920.

The effect of neat epoxy with FBG sensors bonded to its surface is investigated as a controlled group to the test of 15 wt.% nanocomposites at 10 W for 600s and 440W for 60s. The neat epoxy sample geometrically identical to 15 wt.% nanocomposites in the previous test is placed in the designed location with surface-bonded arrays of FBGs. The whole measurements from the adhesive and the neat epoxy are compared with the results from the previously performed

test on nanocomposites to achieve a better understanding of BaTiO₃ modified epoxy response under microwave exposure.

4.2.3 Raman Spectroscopy

Raman characterisation is carried out to investigate if any residual stress or crystal structure change in BaTiO₃ nanoparticles inside epoxy after microwave exposure. Neat epoxy samples and samples of 15 wt.% BaTiO₃ epoxy nanocomposites with the identical geometric dimension of 135x10x3 mm as samples in the above microwave test are characterised before and after 440 W microwave radiation of 110s first to investigate any crystallography changes introduced by microwave radiation. The Raman spectra are obtained using a Raman spectroscope Horiba Scientific LabRAM HR with a 514 nm excitation wavelength laser for all samples at room temperature.

5 RESULTS

5.1 General Material Characterisations

5.1.1 Scanning Electron Microscope (SEM)

The BaTiO₃ nanoparticles as the second filler in an epoxy nanocomposite tend to agglomerate and degrade the desired properties due to their large surface area and nano-scale dimension. It has been commonly accepted by other studies that a good filler/matrix interfacial bonding enables a uniform dispersion and assures an improved mechanical and dielectric performance [191, 258, 279]. As previously described in Section 4.1.1, a silane coupling agent 3-GPS is introduced to modify the BaTiO₃ particles in this work to achieve a finer dispersion in epoxy. In order to evaluate its effectiveness, the dispersion and distribution of barium titanate nanoparticles in epoxy with different loadings are characterised using the SEM.

Different levels of aggregation events due to increased weight fraction of particles and enhancement of distribution due to surface functionalisation are presented and reported below.

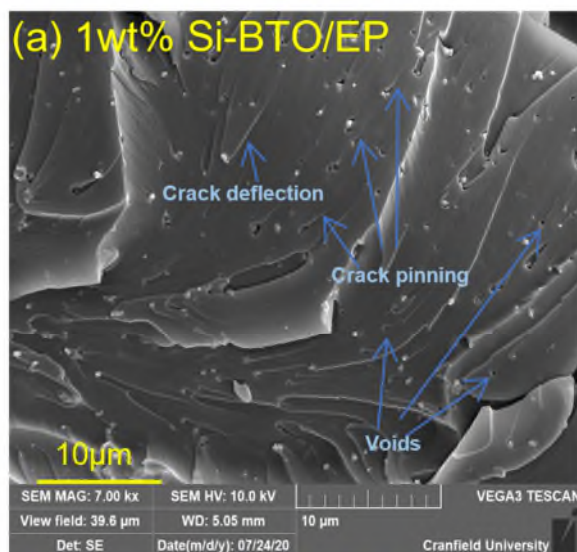
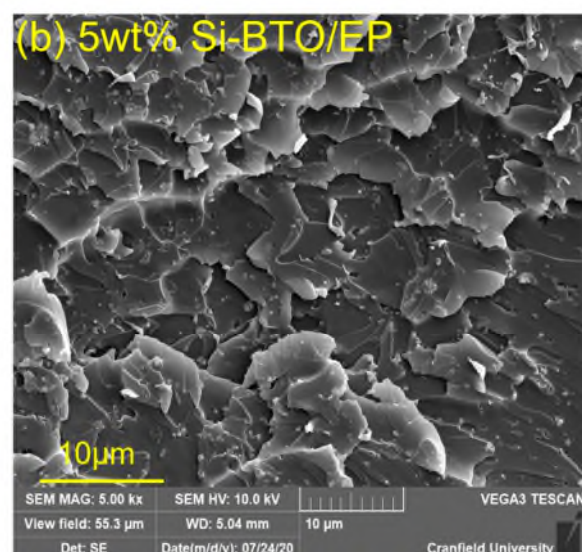
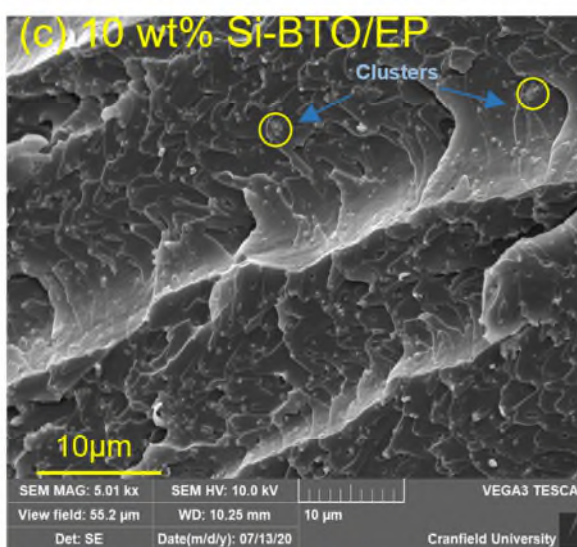
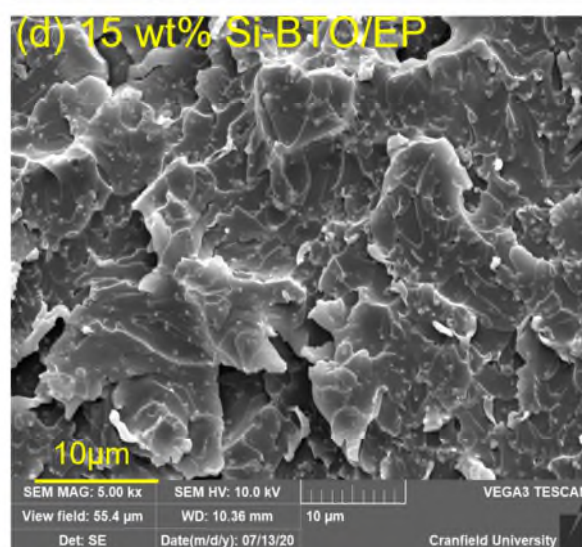
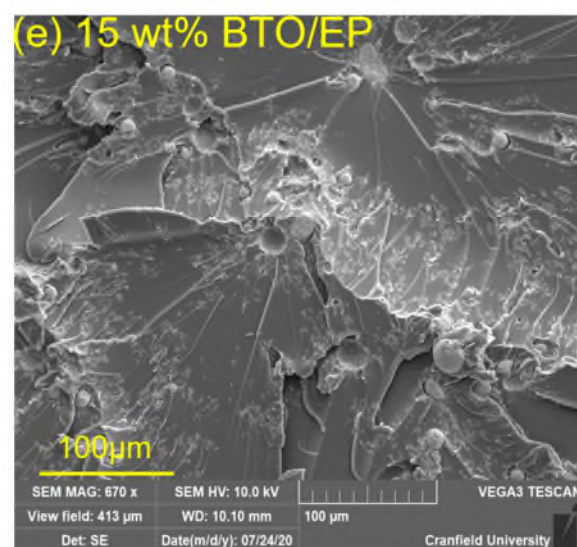
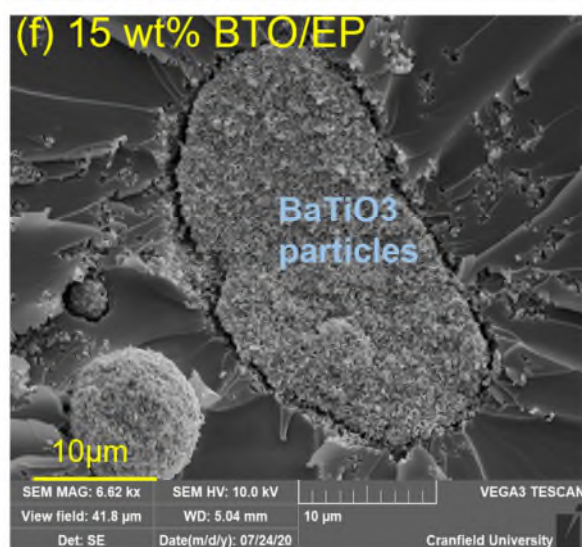


Figure 5-1 SEM images of fracture surfaces (centre area) of epoxy nanocomposites with BaTiO₃ at different weight loading, (a)-(d) are images of 1 wt.%, 5 wt.%, 10 wt.% and 15 wt.% Si-BaTiO₃/epoxy nanocomposite samples. (e) and (f) are 15 wt.% untreated-BaTiO₃/epoxy nanocomposite samples at lower (670x) and higher (6620x) magnification.

Figure 5-1(a)-(f) presents the SEM images of the fractured cross-section of the silane functionalised and non-functionalised BaTiO₃ epoxy composites of various weight loadings. It is shown that the nanoparticles are generally uniformly dispersed with the aid of surface functionalisation. As can be observed from Figure 5-1(a), the silane-treated particles are of a similar size of 200 nm as pristine BaTiO₃ particles. There is no obvious aggregation of Si-BaTiO₃ particles until small-scale clusters become visible as illustrated in Figure 5-1(c) and Figure 5-1(d) when the amount of BaTiO₃ reaches 10 wt.% and over which is due to nanofillers agglomeration as circled in Figure 5-1(c) and Figure 5-1(d). Overall, the majority of the Si-BaTiO₃ particles are still finely dispersed at an acceptable level compared with untreated ones. Figure 5-1(e) and Figure 5-1(f) are images of the composites with 15 wt.% non-functionalised BaTiO₃ particles at different magnifications. In contrast with functionalised BaTiO₃ at the same weight loading of 15 wt.% shown in Figure 5-1(d), the 15 wt.% untreated BaTiO₃ particles in Figure 5-1(e) and Figure 5-1(f) agglomerate to form enormously large clusters and leave large-scaled lamellar structures which are neat epoxy as anticipated. According to the experiments carried out by other researchers [258, 279, 280], the dispersion and distribution of nanofiller which is an indication of the quality of interface property between the fillers and matrix would have a significant effect on the properties of the composites. The SEM images presented above revealed a considerably finer dispersion of silane-treated BaTiO₃ particles compared with untreated ones. The efficacy of the silane functional group is in good agreement with works carried out by others [190, 264, 281].

In Figure 5-1(a), the regions where epoxy resin is not occupied by BaTiO₃ particles are smooth cleavage surfaces indicating a brittle fracture compared with higher loading composites in Figure 5-1(b)-(d). As the addition of BaTiO₃ particles increases, the fracture surfaces become much rougher and exhibit river patterns.

These features represent a switch of the dominating damage mode from brittle fracture to plastic deformation and it is also observed in other epoxy nanocomposites with rigid particles [282, 283]. Features representing cracking pinning and crack deflection are observed in silane-treated BaTiO₃ particles as shown in Figure 5-1(a) and similar features could also be observed in Figure 5-1(b)-(d). Voids with the size of individual nanoparticles or small clusters are also presented in Figure 5-1(a)-(d) indicating the debonding of nanoparticles. These features stated above are also toughening mechanisms for particle-filled epoxy proposed by other researchers [21, 284]. For untreated BaTiO₃ /epoxy composites in a lower magnified SEM image Figure 5-1(e), the particles form large aggregates and leave unoccupied epoxy with similar brittle fracture surface features as in Figure 5-1(a). It could also be observed in a large-magnified image in Figure 5-1(f) from Figure 5-1(e) that significant gaps are formed around the BaTiO₃ aggregates that indicating a relatively weaker interfacial bonding between the particles and epoxy.

The particle size distribution is performed using ImageJ with acquired SEM images of fracture surfaces of Si-BaTiO₃/epoxy composites at different weight loadings. The analysis is performed on nanocomposites with up to 15 wt.% weight loading of nanoparticles, therefore, noise in the data is experienced. The results of the particle size distribution are presented in Figure 5-2.

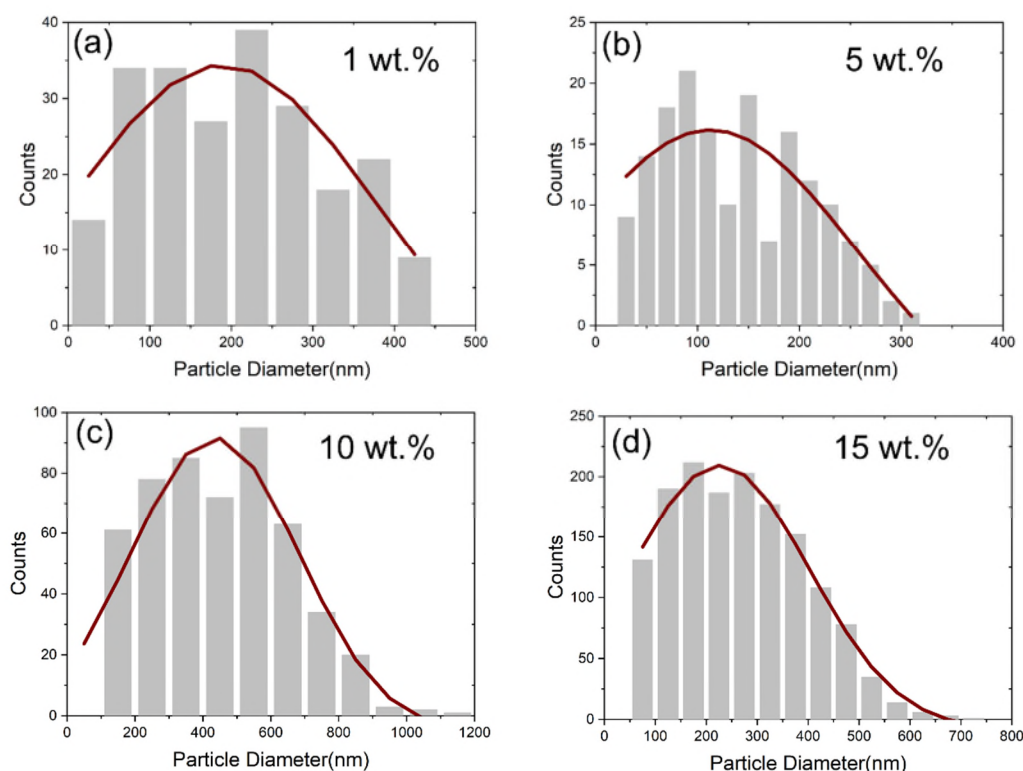


Figure 5-2 Particle size distribution calculated by ImageJ of Si-BaTiO₃ at different particle loadings (a) 1 wt.%, (b) 5 wt.%, (c) 10 wt.%, and (d) 15 wt.%.

The colour threshold is applied to remove unnecessary features, increasing the accuracy of the particle size and location detection. The data is then modulated by a gaussian distribution to display a particle size distribution with a smooth line. Processed data from ImageJ displayed in Figure 5-2 shows that the particle size distribution shift towards larger sizes with increasing particle loading. When the weight loading reaches 10 wt. %, the presence of maximum sizes exceeding 1000 nm could be observed, which directly indicates the start of particle agglomerations that form large clusters. Overall, it could be concluded that the particles up to 15 wt.% are reasonably well-dispersed in the epoxy matrix and the trace of particle agglomerations is negligible.

5.1.2 DSC

The cross-linking process of polymer chains during the curing of epoxy is disturbed by introducing a second phase in it. In polymer resin, there exist free spaces named 'free volume', which can be defined as the volume of the total

mass that is not occupied by polymer chains themselves and hence diffusing molecules can be situated there [285]. After the curing process, the free volume around the particles will also be changed. The Differential scanning calorimetry (DSC) is conducted to examine the effect on the glass transition temperature (T_g) of cured epoxy nanocomposites with varying weight fractions of Si-treated and untreated BaTiO₃ nanoparticles.

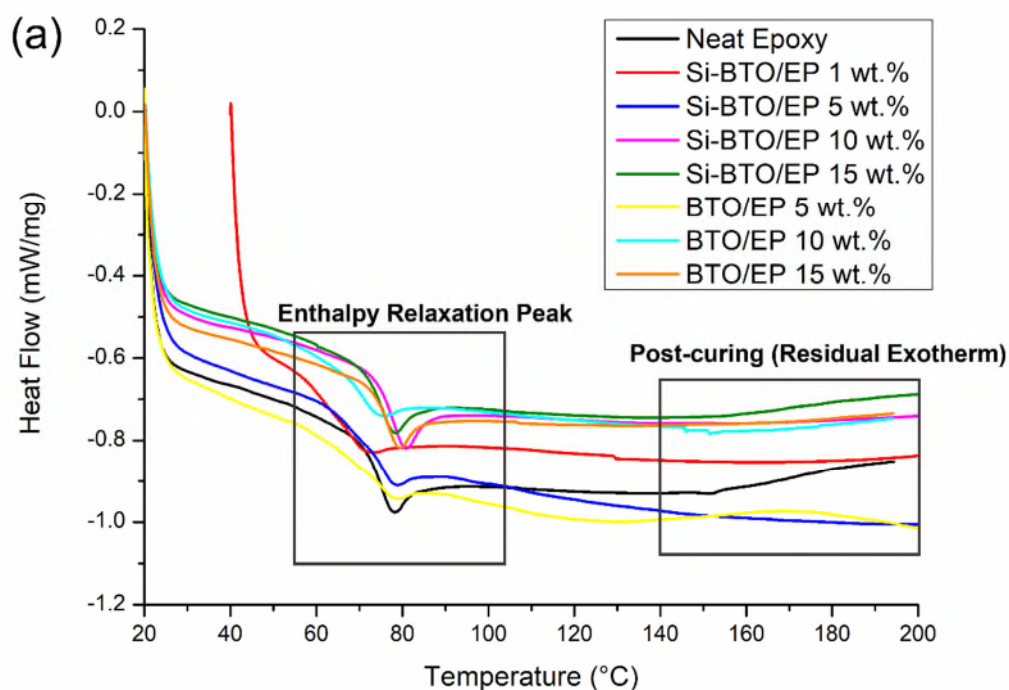
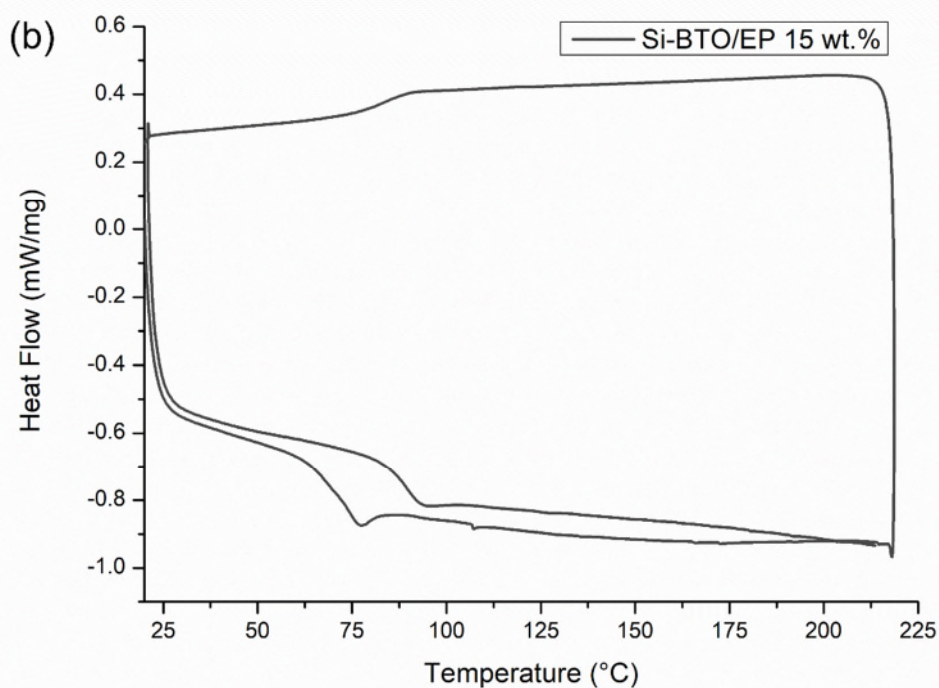


Figure 5-3 (a) DSC spectra of neat epoxy and nanocomposites with untreated BaTiO_3 and Si- BaTiO_3 . Enthalpy relaxation peak around T_g and weak exothermic

peak from 140°C -220°C. (b) DSC spectra of the heat-cool-heat cycle of 15 wt.% Si-BaTiO₃/epoxy nanocomposite.

Figure 5-3(a) above shows the DSC spectra of neat epoxy and epoxy nanocomposites with various BaTiO₃ content at different weight loadings. The epoxy resin and its nanocomposites are prepared and cured according to the datasheet at 80°C for 8 hours. As can be observed from the insets in Figure 5-3(a) above, the DSC spectra of all samples display small “bumps” denoted as exothermal peaks representing the post-curing process at 140°C-220°C. The post-curing process happens when a cured epoxy resin is exposed to a temperature at or above the curing temperature for a period of time [286]. Furthermore, enthalpy relaxation peaks that emerge on the spectra represent the relief of the stress introduced during processing and handling or the thermal history. When the material is heated through glass transition temperature, the rigid molecules become more flexible and stress can be relieved [287]. A second scan is performed on all samples and the results all presented similar transitions of T_g. The spectra of the 15 wt.% BaTiO₃/epoxy sample are presented in Figure 5-3(b) as an example, and it could be observed that T_g is shifted to higher temperatures indicating higher crosslink density due to the post-cure effect. The endothermic peaks around the glass transition region have a negative impact on the interpretation of the T_g. Therefore, a second scan is then performed for each sample to relieve the internal stresses through a heating-cool-heat cycle. Therefore, a new batch of samples is heated to 100°C first to relieve the internal stress built up during processing and avoid post-curing above 140°C. The samples are then cooled down to room temperature and start a second heat ramp to 100°C to investigate the true T_g of each sample.

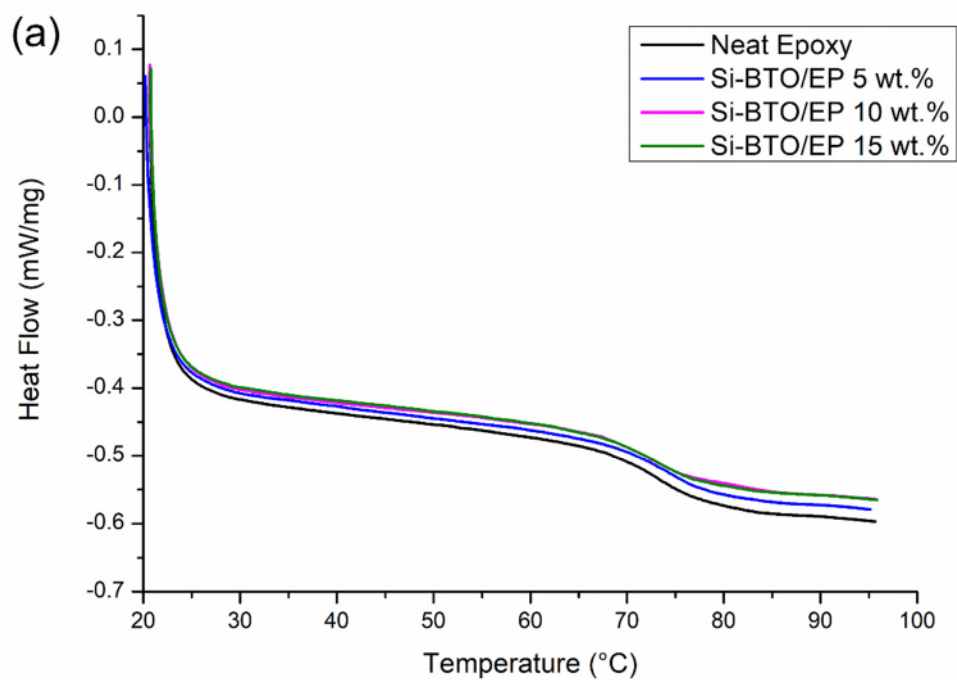
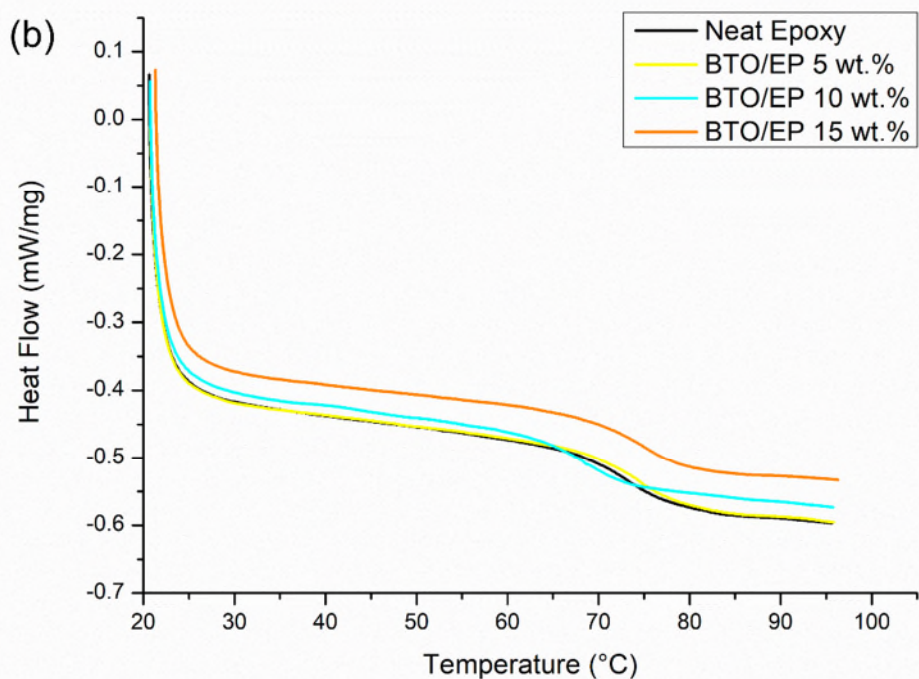


Figure 5-4 DSC spectra of the (a) neat epoxy (black) and Si-BaTiO₃/epoxy nanocomposite samples at 5 wt.% (Blue), 10 wt.% (Pink), and 15 wt.% (Green), (b)

BaTiO₃/epoxy nanocomposite samples at 5 wt.% (Yellow), 10 wt.% (Cyan), and 15 wt.% (Orange)

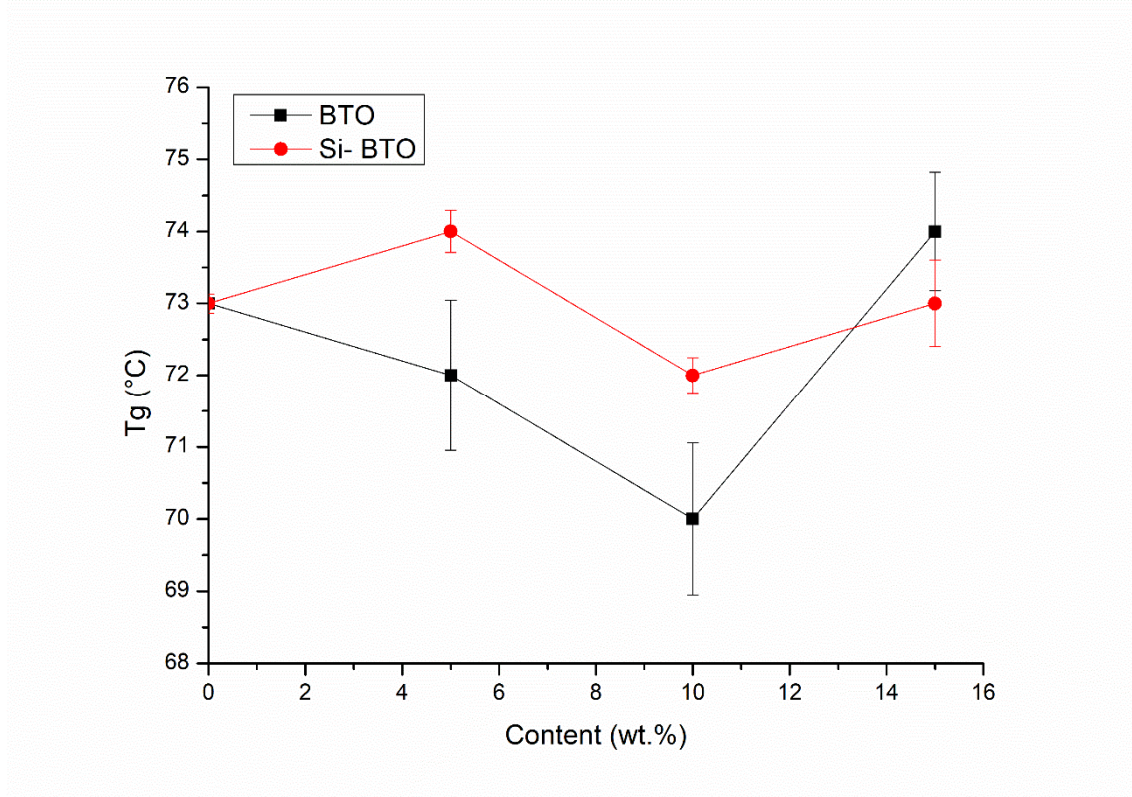


Figure 5-5 Tg temperature as a function of weight loading of Si-BaTiO₃ (Red) and untreated BaTiO₃ (Black) of the epoxy nanocomposites samples.

Figure 5-4(a) and Figure 5-4(b) present the DSC spectra of a second heating scan for neat epoxy and epoxy nanocomposite specimens with functionalised and non-functionalised BaTiO₃ after cooling down from 100°C from the first scan. The internal stresses are relieved as no perceptible exothermal peak is presented and the mid-points could be easily determined from the glass transition region. The red and black lines in Figure 5-5 are drawn as a demonstration of Tg variation along with the weight fraction of the nanofiller. At 5 wt.% and 10 wt.% particle loading, the Tg values of non-functionalised BaTiO₃/epoxy are more spread than functionalised BaTiO₃/epoxy as presented by the error bars. It is shown in the SEM images of fracture surfaces that the non-functionalised particles aggregate and form clusters that lead to different distributions in each specimen hence significant variations in the Tg values. The values of Tg at different loadings of

functionalised BaTiO₃ particles lie in the range of 72.0°C -74.5°C and they barely showed any significant change compared with the T_g of neat epoxy (73°C). These findings could suggest that the existence of functionalised BaTiO₃ particles has a negligible impact on the cross-linking structures of the epoxy matrix. However, in previous research conducted by *Phan et al.* [196], the T_g of epoxy nanocomposites increased by incorporating functionalised BaTiO₃ particles at lower weight loading up to 10 wt.% and reached a plateau at 10 wt.%. The highest increase in the T_g is at 5 wt.% by 20°C compared with neat epoxy at 100°C. It is suggested by *Phan et al.* that the increase in the T_g is attributed to the decrease of the epoxy chain mobility resulting from an enhanced particle-epoxy interaction via the functional group. However, the dispersion of silane functionalised BaTiO₃ nanoparticles presented a relatively uniform dispersion, which suggests a good interfacial interaction between the nanoparticles and epoxy resin as presented in Section 5.1.1. Therefore, the difference between the current work and the previous study might be caused by the inclusion of nanoparticles with different sizes as *Phan et al.* selected particles with 70nm, which is considerably smaller than the 200nm nanoparticles used in this work. At the same particle loading, larger size nanoparticles could introduce more free volumes within the epoxy resin and make it easier for polymer segments to move around at lower temperatures, thereby, lower T_g as less energy is required. On the other hand, the T_g values of non-functionalised BaTiO₃ /epoxy at 5 wt.% and 10 wt.% (as shown in the black line) exhibit a decreasing trend compared to neat epoxy. However, the decrease in the T_g values in the current work is within 4°C, which is insignificant compared to the T_g of nanocomposites at the same weight loading reported in previous literature. In a study carried out by *Xi et al.*, the T_g values drop from 108.31°C to 79.78°C with the addition of non-functionalised BaTiO₃ reaching 10 wt.% [288]. The decrease in the T_g with the inclusion of non-functionalised BaTiO₃ is ascribed to the enhanced mobility of polymer chains at a lower temperature within the extra spaces provided by the enlarged free volumes arising from the particle surface and epoxy matrix. Additionally, the nanoparticle agglomerations could also have a negative impact on the formation of cross-linking structure, which ultimately results in reduced T_g values. It could

be noted that in *Xi's* work, the nanoparticles were only dispersed in epoxy via mechanical stirring without further ultrasonication or solvent aiding, which may lead to lower dispersion quality. Therefore, the difference between the current work and the previous one could be attributed to the inhibited cross-linking structure resulting from increased nanoparticle agglomeration.

It is also noteworthy that the T_g increases when the non-functionalised BaTiO_3 particles reach 15 wt.% as shown in the black line in Figure 5-5. The glass transition process is influenced by various factors, including free volume, polymer chain mobility, and cross-linking density. The increased T_g represents that more energy is needed from higher temperatures to complete the glass transition process, which indicates that the movement of polymer chains under heating is hindered by the increasing amount of non-functionalised BaTiO_3 nanoparticles. Similar observations have been reported by other researchers that the T_g increased from 54.10°C to 82.77°C by increasing the loading of 500nm BaTiO_3 particles to 10 wt.% from 1 wt.% and it is proposed that the enlarged free volumes before curing by the nanoparticles contribute to the T_g increase at higher loading ones [288]. Although the T_g decreases with increasing free volumes existed in the cured epoxy, it is also proposed in several studies that the free volumes in uncured epoxy could have a positive impact on the T_g in the cured epoxy resin. During the curing process, the mobility of the polymer chains decreases, and the T_g increases under elevated temperatures. The vitrifying process ends when the T_g reaches the curing temperature, and the polymer chains stop moving. After the curing process finishes, the free volume around the nanoparticles will also be changed. *Xi et al.* suggested that the enhanced mobility of the polymer chains during curing via enlarged free volumes favours the curing process as the uncured polymer chain could move freely more easily, eventually cease to move at a higher temperature, leading to a higher T_g .

5.1.3 Tensile Test

It is a commonly used approach nowadays to toughen epoxy via the inclusion of an inorganic rigid filler such as silica particles [289, 290] and titanium dioxide particles [64]. In this study, the surface morphology of epoxy nanocomposites

demonstrated a relatively uniform dispersion of Si-BaTiO₃ in epoxy resin. Therefore, the mechanical properties of modified epoxy nanocomposites with functionalised nanoparticles are characterised using tensile tests to investigate the impact on the mechanical behaviour of Si-BaTiO₃/epoxy at varying weight loadings. The fracture strain (elongation at break) and modulus of elasticity are measured. The fractured surfaces are observed under SEM to gain a better understanding of the fracture behaviour in the bulk epoxy nanocomposite systems.

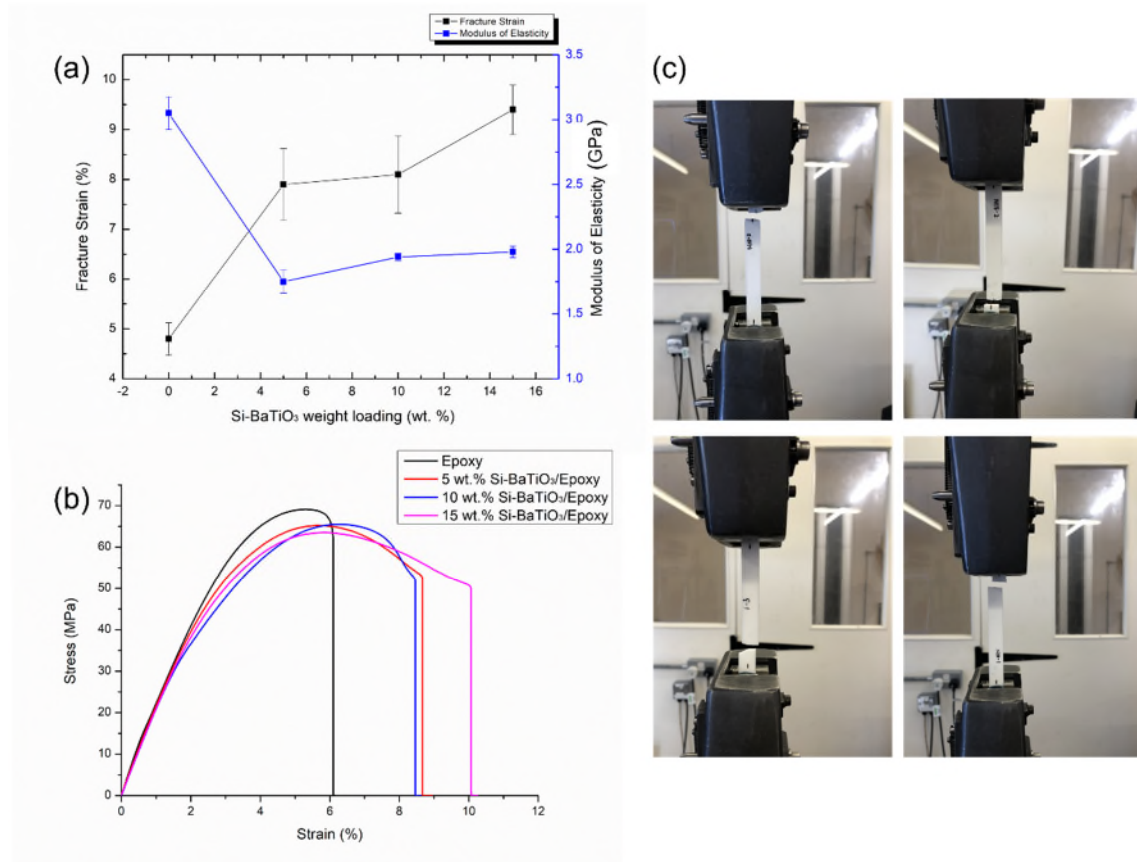


Figure 5-6 (a)Fracture strain (black symbols) and modulus of elasticity (blue symbols) of epoxy and its nanocomposites with silane-treated BaTiO₃, (b) Stress-strain curves of pure epoxy and Si-BaTiO₃/epoxy nanocomposites at various weight loadings, and (c) Images of several specimens failed near the grip ends.

The fracture strain and modulus of elasticity as a function of weight loading of Si-BaTiO₃ are shown in Figure 5-6 (a) above. It can be observed from the blue line that the modulus of elasticity is decreased by introducing Si-BaTiO₃ nanoparticles

to epoxy resin. Nevertheless, the moduli of these epoxy nanocomposites exhibit a gradual rise with an increasing weight loading of Si-BaTiO₃. Furthermore, the increased elongation at break with increasing weight loadings of Si-BaTiO₃ could arise due to the reduction of internal triaxial stresses caused by defects introduced by nanoparticles. When stress is applied to the nanocomposite, these defects act as stress concentrations, causing particle debonding and subsequent plastic void growth in epoxy, which ultimately leads to an increase in elongation at break [21].

Studies have shown that for any given epoxy polymer, the elastic modulus steadily increased as a function of the weight fraction of rigid particles like silica [289]. Unfortunately, there are not as many investigations of mechanical properties change by incorporating BaTiO₃ particles with epoxy. Chandradass, J and Bae, D. S. [291] demonstrated that the tensile stress and elastic modulus of 20 nm BaTiO₃/epoxy nanocomposites keep rising until the weight loading of untreated BaTiO₃ goes over 3 wt.%. Another study of the flexural modulus of functionalised 70 nm BaTiO₃ modified epoxy shows an increase in modulus until the amount of particles goes over 10 wt.% [196]. Furthermore, a study of 500 nm BaTiO₃ conducted by Zhang, X. *et al.* [288] confirms the tendency of increasing tensile stress and elastic modulus with an increasing amount of added BaTiO₃. The main explanations suggested by others of the enhanced tensile properties with increasing content of BaTiO₃ particles or any other rigid particles are attributed to: (i) reinforcement from the intrinsic high elastic modulus of BaTiO₃, and (ii) better interfacial bonding between BaTiO₃ particles and the epoxy matrix via surface functionalisation [32, 288]. Although the test results of the Si-BaTiO₃/epoxy nanocomposites presented above do not follow the expected trend seen in other studies, the elastic modulus still exhibits a gradual increase as presented in the research discussed above when more nanoparticles are included. It is important to note that the results from a tensile test could vary depending on many factors. However, the most possible reason could be a slightly affected data reported due to the misalignment of the specimens during testing. As could be observed from Figure 5-6 (c), in this case, most specimens break near the grip ends instead of the central gauge section. This type of failure

is due to significant stress concentration at the grip, despite the modification of tabbed sample ends to mitigate this effect [292]. A dog-bone shaped sample might be necessary for the tensile test in the future to reduce the excessive stress and local breakage caused by the clamping force from the grip.

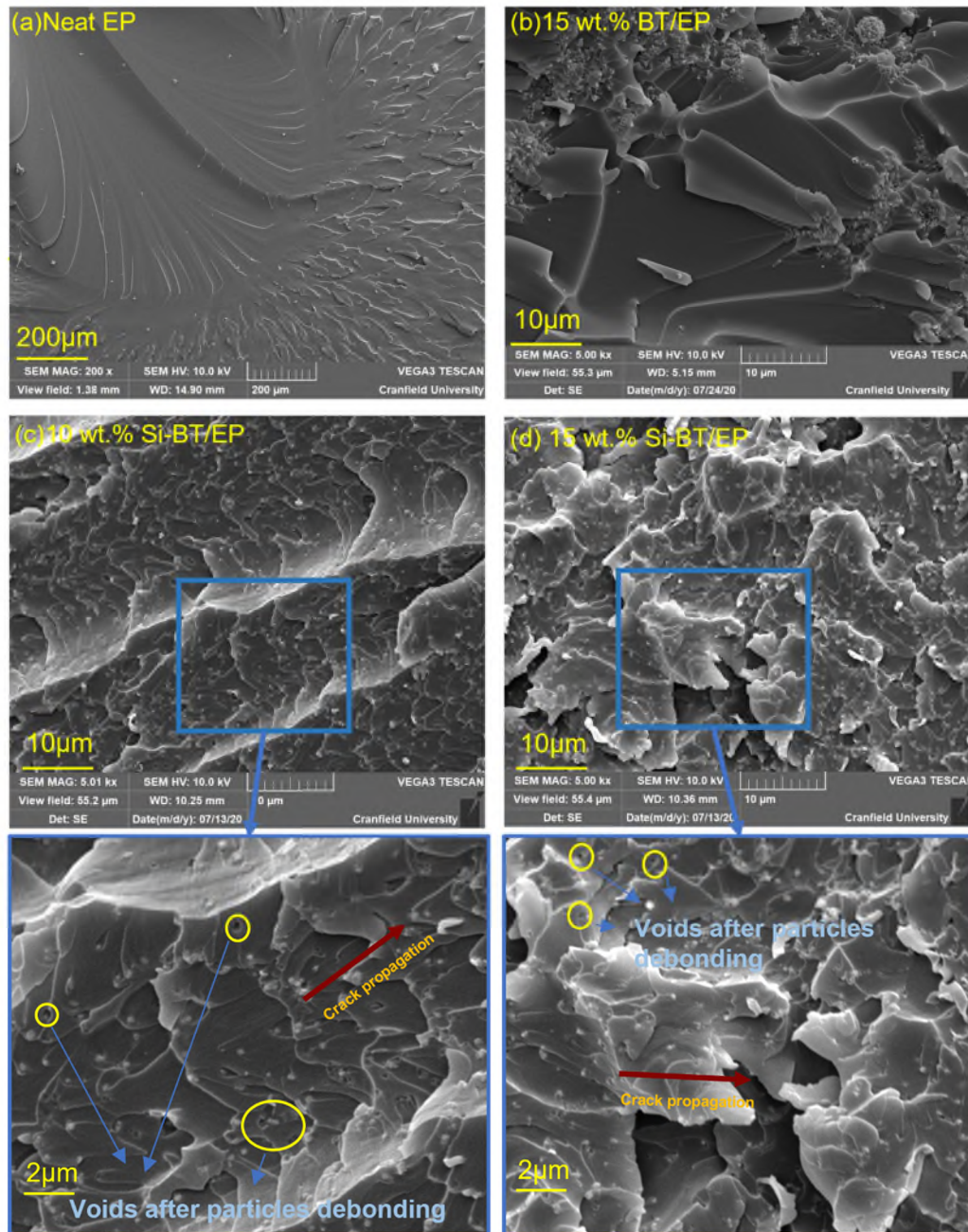


Figure 5-7 SEM images of (a) neat epoxy (b)-(d) fracture cross-section of epoxy nanocomposites with BaTiO₃ at different weight loading

The SEM images in Figure 5-7(a)-(d). showing the fracture surface of neat epoxy and nanocomposites after the tensile test. It is evident that neat epoxy has a very smooth lamellar surface as presented in Figure 5-7(a) which is a direct indication of its inherent brittleness. Large-scaled aggregations of non-functionalised BaTiO₃ nanoparticles are observed in Figure 5-7(b), leaving surrounding areas as neat epoxy with mirror-like fracture surfaces [64]. Despite the lamellar-like fracture surface in Figure 5-7(c), the increased amount of uniformly distributed BaTiO₃ nanoparticles leads to randomly oriented deformation trails around the nanoparticles. The deformation trails are attributed to the load transfer from weak epoxy to nanoparticles with higher strength. The deformation trails became more prominent in Figure 5-7(d) at 15 wt.% and it is also a sign of a brittle fracture that turns into ductile tearing. The observed fracture surface is significantly rougher than the neat epoxy. Plastic void growth of the epoxy matrix is initiated by debonding of nanoparticles and round shape craters without nanoparticles are also presented in the insets of Figure 5-7(c), which will either be in the opposite fracture surface or have fallen out during fracture. The subsequent plastic void growth of epoxy after particle debonding is also one of the major mechanisms proposed by previous studies for enhanced mechanical properties like crack resistance and elongation at break [21].

The surface morphology studies in other research discussed above of modified epoxy with rigid particles like silica or BaTiO₃ at the nano-scale suggested two toughening mechanisms that could be observed on the fracture surface. The first one is localised shear bands caused by the stress concentration around the rigid particles. The other one is the debonding of the silica nanoparticles with subsequent plastic void growth of the epoxy matrix [61]. The indication of both mechanisms can be directly identified in the SEM images in Figure 5-7. Characteristic features of crack pinning mentioned in section 5.1.1 could also be observed around nanoparticles in Figure 5-7. The cracks are pinned and bowed out by the nanoparticles as the crack front does not carry the required energy to penetrate through the particle and matrix with enhanced bonding quality [293]. These deformation features also contribute to the energy absorption during crack propagation which indicates more energy is required for breaking and hence a

higher fracture strain with increasing particle loadings. This finding is also in agreement with previous findings that failure strain under tensile test increase with increasing particle loadings [294].

5.1.4 Dielectric Properties of BaTiO₃/epoxy Nanocomposites

The microwave dielectric properties of the epoxy nanocomposites are investigated from 0.25 GHz to 4.50 GHz at a 0.25 step increment using a Vector network analyser PNA-X N5245A via a stripline technique at room temperature. The real permittivity ϵ' and dielectric loss tangent $\tan \delta$ at room temperature are presented below.

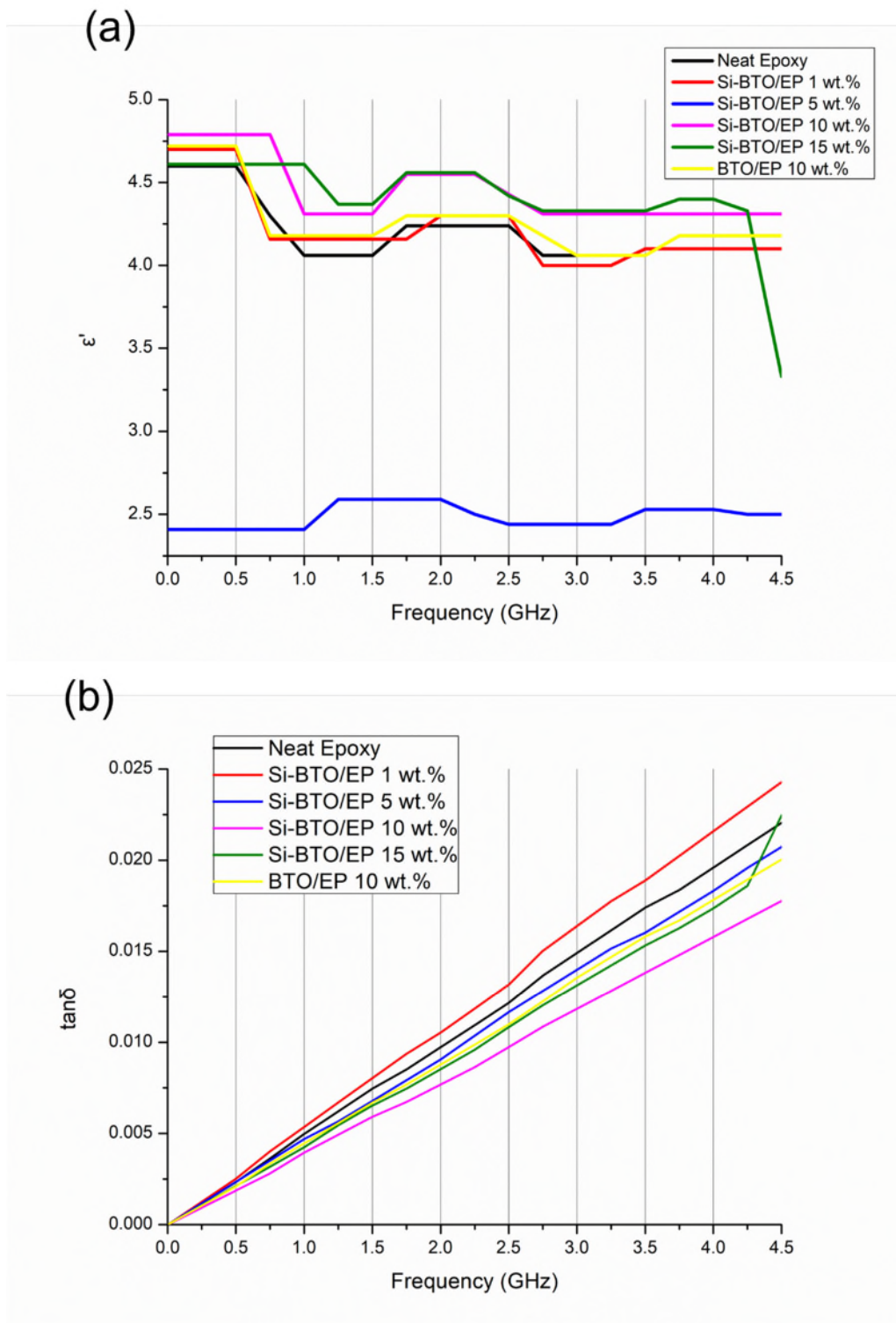


Figure 5-8 Dielectric measurements (a) real permittivity ϵ' , (b) loss tangent $\tan\delta$ from 0 to 4.5 GHz at room temperature of neat epoxy and BaTiO₃/epoxy nanocomposites at different weight loading.

The dielectric constant of a material is in a complex form that measures the interaction of materials and the electric field as presented in Equation 5-1.

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad 5-1$$

The real part of permittivity ε' represents the lossless interaction between the wave and the material, which indicates how much polarisation can be induced within the material by the electromagnetic field. The built potential energy by polarisation will dissipate as thermal energy if there is no releasing mechanism. If the material has an imaginary permittivity ε'' which quantifies how much the material passes on the energy, the energy dissipates due to the frictions of the agitated atoms displaced from its equilibrium position, then generate heat subsequently [205]. The loss tangent is expressed as the imaginary permittivity ε'' divided by the real part of permittivity ε' .

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad 5-2$$

The loss tangent is a ratio of energy stored and lost in a material under an electromagnetic field as shown in Equation 5-2. It measures the loss due to the inherent dissipation of the material.

BaTiO₃ particles only exhibit a maximum value of loss tangent when the frequency reaches the GHz frequency range. Hence, the dielectric loss of most BaTiO₃ polymer nanocomposites is mainly originated from the particles [295]. It is discovered by *Cheng et al.* that the real permittivity ε' and tangent loss both increased with particle loading at 1 GHz. The real permittivity ε' reached 3.9 from at 25 wt.% loading from that of neat epoxy of 3.2 while it peaked at 13.1 when the particle loading is 80 wt.%. The increase in loss tangent is less significant than real permittivity within the range from 0.022 to 0.028 [184]. For higher frequencies above 1 GHz, *Wenhu et al.* found that the real permittivity and tangent loss are stable without notable variation in values from 2GHz to 20GHz by adding 200nm tetragonal BaTiO₃ particles into epoxy resin [197].

In Figure 5-8(a), the ε' values of all samples over the measured frequency range have slight decrease trends with increasing frequency due to the dipoles in the

material that cannot follow the speed of the alternating field and reorient themselves with the field direction [288]. Compared with neat epoxy, the inclusion of Si-BaTiO₃ nanoparticles at 10 wt.% and 15 wt.% give a perceptible rise to the value of ε' through the frequency range, which are similar results as reported in other studies [184, 192, 296]. In the meantime, the 1 wt.% and non-treated 10 wt.% BaTiO₃/epoxy samples present similar values of ε' with the neat epoxy due to little amount of BaTiO₃ of 1 wt.% and aggregations of unfunctionalized 10 wt.% [192]. The silane treated samples have higher values in ε' due to a more uniform dispersion of BaTiO₃ nanoparticles [184, 295, 296]. However, there are no huge differences between the values of ε' at 10 wt.% and 15 wt.%. As discussed previously in Section 2.2.1, the ferroelectricity character of tetragonal BaTiO₃ enables a spontaneous polarisation that can be reversed by an applied field [89]. Therefore the ε' of epoxy is enhanced due to the addition of BaTiO₃ nanoparticles, which agrees with the findings in other research [184, 197, 295, 296]. Generally speaking, a substantial increase in the dielectric properties of modified epoxy is only to be achieved by a generous amount of BaTiO₃ content as high as 90 wt.% [297]. However, expected degraded mechanical properties occur of modified epoxy with a higher loading with BaTiO₃ particles. Therefore, one of the critical requirements in this study is an optimized balance between the dielectric and mechanical properties. The blue line represents the dielectric response of 5 wt.% silane-treated BaTiO₃ epoxy nanocomposite and presents a significantly lower value of real permittivity ε' below the neat epoxy. This drastic decline in the value of ε' could be attributed to testing errors from air gaps between the sample and conductive line [298]. Therefore, the reported data of 5 wt.% silane-treated BaTiO₃ epoxy nanocomposite is considered to be erroneous and excluded from the analysis. Only one sample per category is characterised due to limited access to the facilities and care should be taken in the future characterisation on the elimination of the testing errors.

Figure 5-8(b) illustrates that the loss tangent of all samples increases with increasing frequency. On the contrary with the real permittivity, the loss tangent has slightly decreased with adding BaTiO₃ powders except from 1 wt.% content. The loss tangent of a composite system has contributions from dipole orientation,

conduction loss and interfacial polarisation as previously described in Section 2.3.2 [299]. Silane treatment of the BaTiO₃ powders introduces a reduction of the concentration of ionizable hydroxyl groups (-OH) on the BaTiO₃ surface and hinders the mobility of the charge carriers on the surface. The lowered conduction loss could be the primary reason for lowered loss tangent [188]. The results of the loss tangent of Si-BaTiO₃ particles are extensively lower than reported by Yang, W. H. *et al.* [197], which is approximately 0.06 (high $\tan \delta > 0.03$ [300]) of 200 nm tetragonal Si-BaTiO₃/epoxy nanocomposites. Although the reported sample contains more BaTiO₃ nanoparticles up to 40 vol.% and it is also suggested by other studies that a correlation between the increased dielectric loss and BaTiO₃ addition [200]. The resonant techniques are the most precise methods to measure dielectric properties [301]. Nonetheless, limitations still exist as the measurement is conducted on the sample configuration rather than using a cavity perturbation technique due to a simpler and cost-effective fabrication process. The configuration is able to fit samples with relatively large dimensions but only produces accurate measurements with low-loss materials (loss tangent $< 3 \times 10^{-4}$) [302]. It is advised to perform the cavity perturbation approach and the transmission line technique in the future to achieve more precise and accurate dielectric measurements.

5.2 In-situ Strain Response under Microwave at Different Power Levels.

5.2.1 Microwave exposure under 100W and 440W

FBG labelling of strain and temperature arrays for both conditions are illustrated in Figure 5-9, below. As stated in the hypothesis, the proposed strain field is expected to be introduced by the inclusion of nanoparticles. In order to achieve an optimal strain effect from each individual nanoparticle, a balance between the uniform dispersion and particle loadings need to be considered carefully. According to findings in previous sections, the properties and structure of epoxy resin are not significantly altered by adding 15 wt.% of Si-BaTiO₃ particles. Meanwhile, nanoparticles at 15 wt.% present a relatively uniform dispersion within the epoxy resin as shown in the SEM images in Section 5.1.1. Therefore,

15 wt.% epoxy nanocomposite samples are selected to investigate the field-induced strain under microwave exposure. In contrary to the conventional microwave ovens constantly switching on and off at a single power level, the inverter-equipped oven used in this research can control the power output by varying the pulse width. Therefore, the power level determines how much energy the microwave carries per second, which is also equivalent to the amplitude of the electric wave component when the microwave oven is on. To avoid phase transition by overheating the sample to the curie temperature of BaTiO₃ particles, the field-induced strain effect of epoxy nanocomposites of 15 wt.% BaTiO₃ is investigated using FBG sensors within a domestic microwave oven starting with the lowest two power levels at 100W and 440W for the preliminary attempt. Since FBG sensors have sensitive responses to both strain and temperature, temperature compensation becomes necessary to avoid errors during strain measurements under microwave exposure. The simplest frequently used method for temperature compensation is to arrange two FBG arrays next to each other. Field response in strain and temperature change of the materials are measured by two arrays with one array measuring the strain and temperature while the other one only measures the temperature by detaching it from the sample surface as illustrated schematically in Figure 5-9, below. The microwaves bounce back and forth within the cavity of the microwave oven. The waves reflected each time and eventually could be considered as standing waves. Since microwaves have peaks and troughs, there exist regions with high microwave intensity overlapping with a distance of half wavelength (60mm) between each other. For a 135mm sample, the area at both ends must exhibit different strain and temperature responses compared with that of the middle area. Therefore, three sensors are placed at different regions along the sample respectively as presented in Figure 5-8 to get a full picture of the strain response under the complex microwave heating patterns.

Part of the absent data and sudden drastic fluctuations presented in both Figure 5-10 and Figure 5-11 below are due to Bragg wavelengths moving into adjacent spectral windows that were set up on the sensor interrogator as stated by the manufacturer.



Figure 5-9 Schematic illustration of surface-bonded FBG arrays measuring temperature and strain.

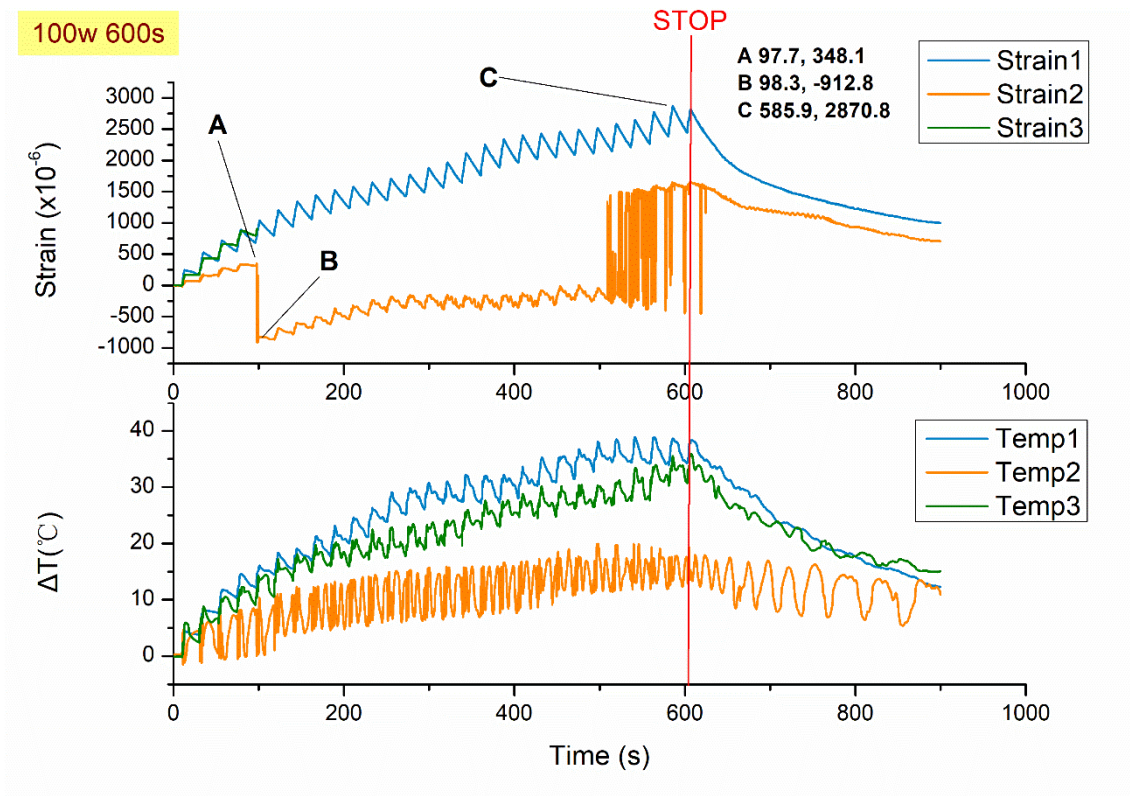


Figure 5-10 Strain and temperature change measurements of 15 wt.% Si-BaTiO₃/epoxy samples under 100W for 600s.

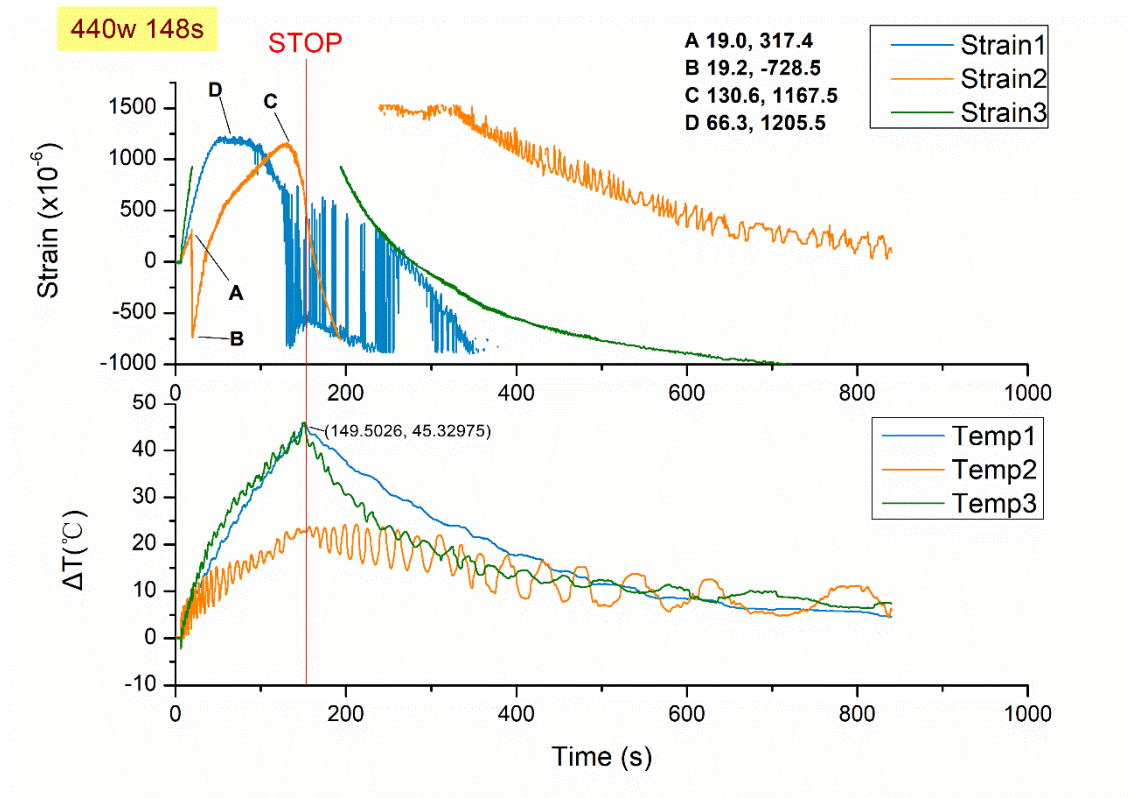


Figure 5-11 Strain and temperature change measurements of 15 wt.% Si-BaTiO₃/epoxy samples under 440W for 148s.

As demonstrated in Figure 5-10 and Figure 5-11, above, the strain and temperature measurements have a general trend of increasing with the exposure time. The measured temperature in both cases showed a steady increase with time under the microwave heating effect and started to drop gradually immediately after the microwave stopped due to the ceased material-microwave interaction and the remaining heat transferred to the air via convection as expected.

The temperature appeared to be higher at both ends of the specimen (sensor 1 and 3) compared to the middle (sensor 2), which is in accordance with the 'hot spot' theory due to microwave nonuniformity as illustrated in Figure 5-12, below.

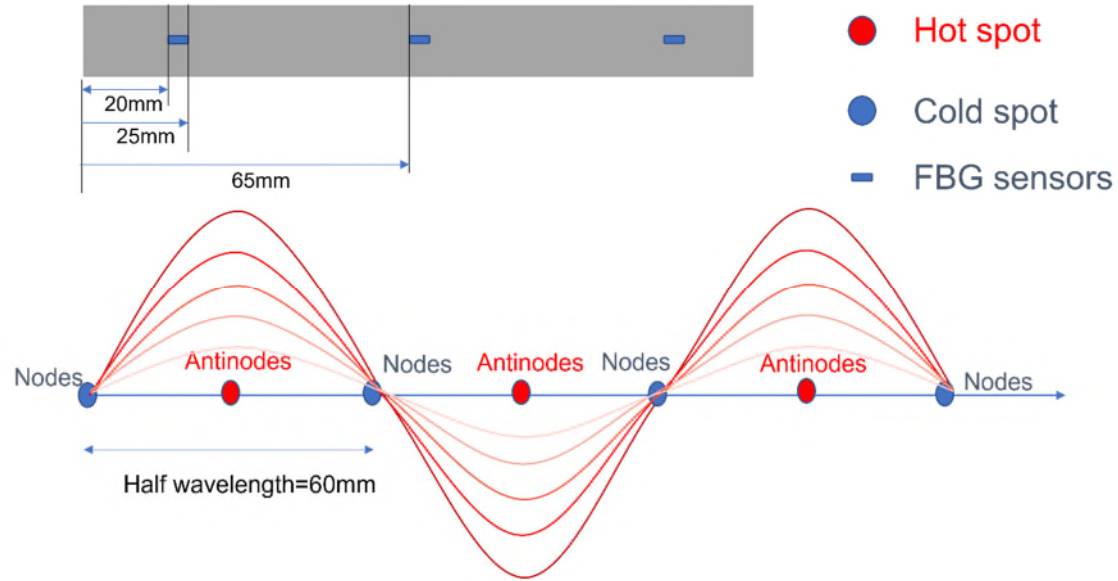


Figure 5-12 Schematic illustration of (above) the location of FBGs on the sample surface, and (below) standing waves formed in a microwave oven showing hot spots (antinodes) and cold spots (nodes).

The microwave oven cavity is designed to be a multimode resonant cavity, similar to a closed waveguide. The microwaves generated by the magnetron are reflected back and forth by the metal walls inside the cavity and eventually form standing waves throughout the cavity's volume as illustrated in Figure 5-12 [303]. Under microwave exposure, the distance between the area with higher temperature (antinodes) and the cold spot with lower temperature (nodes) is a quarter of the wavelength, which is approximately 31 mm in the air [204]. The sensors have a 40 mm distance between each other and accordingly, they fell in different temperature zones under the standing waves.

The strain measured from a stretched FBG sensor is derived from the change in wavelength of reflected ultraviolet light due to grating period change. The wavelength changes with strain and temperature are expressed in Equation 5-3 below [304].

$$\frac{\Delta\lambda}{\lambda_0} = k \cdot \varepsilon + \alpha_\delta \cdot \Delta T \quad 5-3$$

Where $\Delta\lambda$ is wavelength shift, λ_0 is the base wavelength, $k = 1 - p$, p is the photo-elastic coefficient, $p = 0.22$, ε is the strain due to both mechanical and

thermal factors, ΔT is the temperature change, and α_δ is the change in the refraction index.

As expressed in Equation 5-3, above, the measured results from the strain sensor are a combination of two factors. The first part is the actual strain of the material including any mechanical strain and strain due to temperature changes. The second part is the wavelength shift due to a change in the glass-refraction index of optical fibre with temperature. According to the manufacturer of FBG sensors, the 1°C temperature change induced strain of optical fibre itself is approximately equivalent to 8 microstrain. Under microwave exposure, FBG sensors in both arrays start the measurements by recording the change in the reflected spectrum received by the interrogator. Afterwards, the temperature compensation process is completed by subtracting the temperature introduced strain calculated from the wavelength shift data of strain-free sensors.

Under both 100W and 440W, the strain measured at the beginning of microwave radiation in strain sensors 1 and 3 have similar trends of increasing as predicted when the temperature sensors 1 and 3 measurements have close gradients. However, a sudden drop in the strain measurements of the middle sensors (strain 2) can be observed in both cases soon after the first climb. A decline in the strain measurements could be evidence of the existence of a compressive strain field. As shown in the DSC spectra in Section 5.1.2, post-cure shrinkage could lead to a compressive strain field within the specimen when the temperature exceeds 140°C. However, the temperature change is approximately 12°C and 5.7°C from room temperature 19°C when the sudden drop happens at point A, which is remarkably lower than the temperature around 140°C as indicated by the exotherm peaks in the DSC spectra Figure 5-3. Different FBG arrays are adhesively bonded at the same location on the surface of two specimens of 15 wt.% with identical geometric dimensions and the placements of the two specimens are at the exact location within the microwave cavity. Accordingly, the distribution of microwaves in both cases is considered to be identical. Such sharp decline in the strain measurements in both cases could be an indication of a developed compressive strain field by the nanoparticles under the stimulation of

the microwave exposure as described hypothetically in section 1. However, in order to prove the reproducibility of such unexpected behaviour and distinguish the possible effect with experimental faults, repeated microwave exposures on two more 15 wt.% Si-BaTiO₃/Epoxy samples are performed for a second attempt in the following Section 5.2.3.

The strain and temperature change measurements of sensor 2 under 100W and 440W before and after the 'sudden drop' is presented in Figure 5-13(a)-(d), below. It can be observed from Figure 5-13(a) and Figure 5-13(b) that the measured strain demonstrated a steady step-wise increase with the increasing temperature that fluctuated within a constant range of approximately 8°C. The fluctuations in temperature change exhibit a periodic pattern that is in phase with each step of the increment in strain. Under 440W as shown in Figure 5-13(c) and Figure 5-13(d), the increase in the measurements of strain and temperature change follows a similar trend as under 100W but at a higher rate.

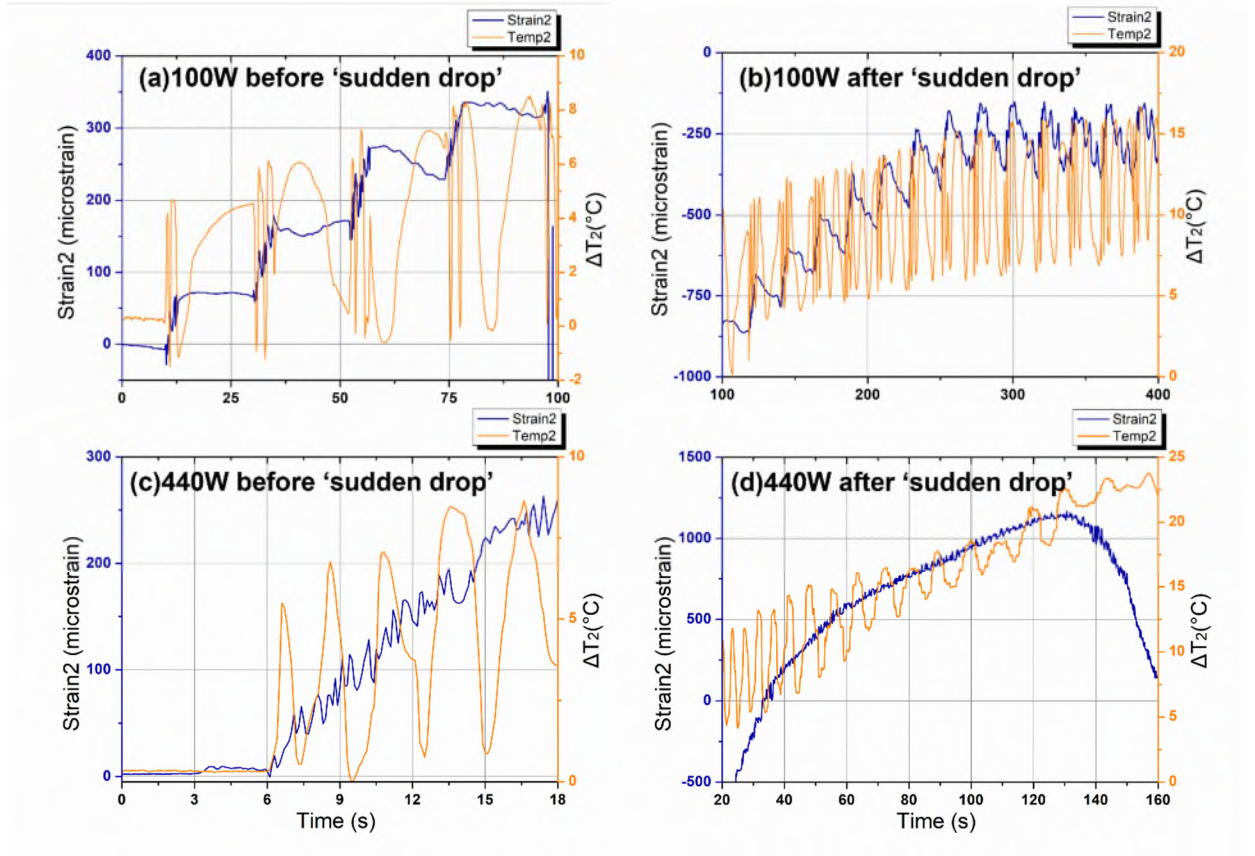


Figure 5-13 Strain and temperature change from sensor 2 before and after the 'sudden drop' at 100W (a) and (b), and 440W (c) and (d).

In contrast with the middle sensors, the steps of increment of strain and temperature from sensor 1 under 100W and 440W are predominately synchronized as presented in Figure 5-14, below. It could be observed from Figure 5-14(a) and Figure 5-14(c) that the cycle time for each step is approximately 20s and each step is approximately 100 microstrain. A similar trend is also observed in the first 50s of microwave exposure under 440W from Figure 5-14(b). However, the cycle time for each step as shown in Figure 5-14(d) falls sharply to 2s accompanying a higher step increment of 300 microstrain compared with 100W test results. These noise steps in the strain measurements could be related to the discrepancy between the thermal expansions of the adhesive and the host material of strain FBGs. Moreover, the noise in the temperature FBGs could be caused by the interrogator while trying to record the signals of the reflected wavelength spectrum. The rapid variation in strain and

temperature under higher microwave power levels is considered to be the main reason for the shorter noise step time at 440W.

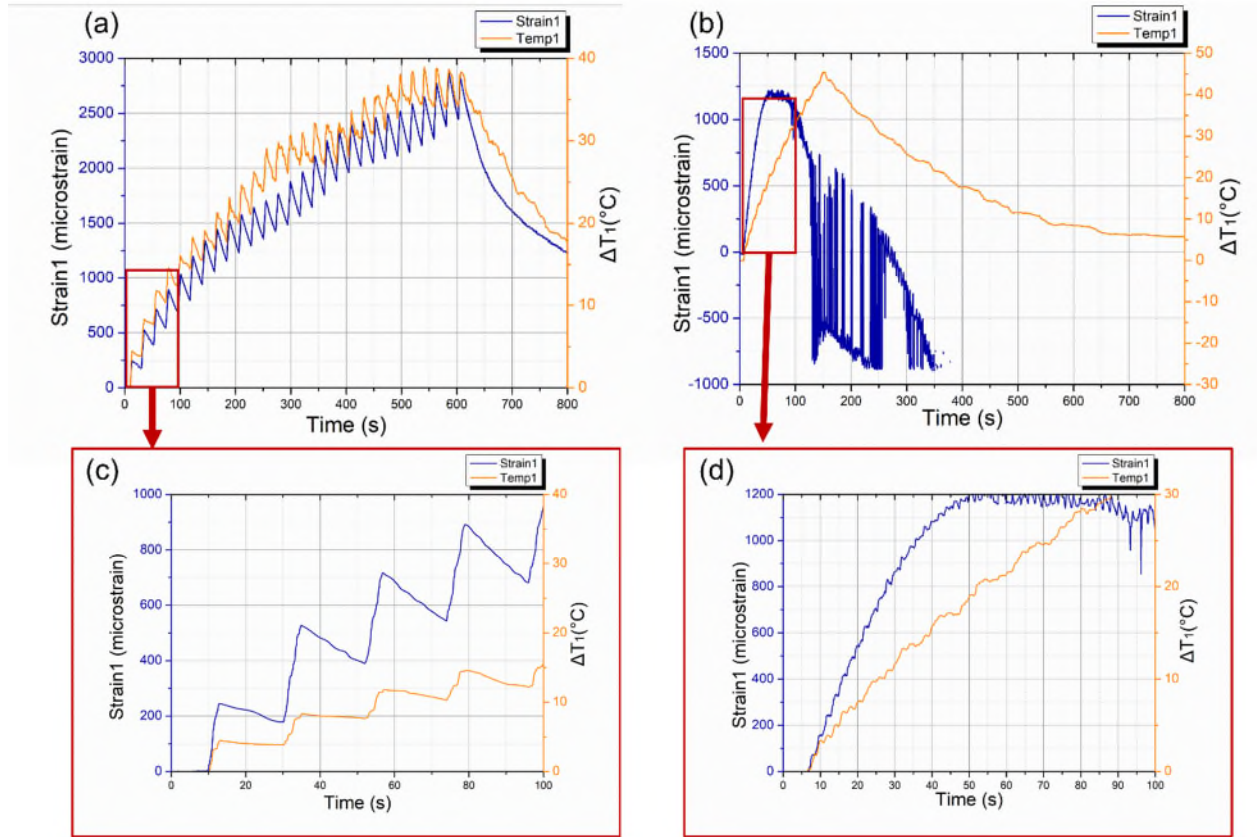


Figure 5-14 Strain and temperature measurements of FBG sensor 1 of (a) and (c) 15 wt.% Si-BaTiO₃/epoxy nanocomposite sample under 100W for 600s, (b) and (d) 15 wt.% Si-BaTiO₃/epoxy nanocomposite sample under 440W for 148s.

Despite the widely known utilisation of FBG as strain sensors, there still exists a layer of adhesive and protective coating that could introduce a negative impact on the accuracy of the strain measurements [305]. Therefore, the thermal effect in the adhesive and neat epoxy due to microwave heating is investigated in Section 5.2.2 below.

5.2.2 Adhesive and Neat Epoxy Effect

This Section investigated the possible effect on strain measurements induced by adhesive and neat epoxy due to temperature rising. The strain array of FBG sensors is adhesively bonded to the surface of the specimens and the selection of adhesive could perceivably have an impact on the accuracy of the FBG

measurements. Therefore, a widely used glue, PERMABOND 920 Cyanoacrylate, is suggested by the manufacturer, which is compatible with epoxy resin under elevated temperatures. The real permittivity, loss tangent, and CTE of PTFE, adhesive and neat epoxy are listed in Table 5-1, below.

	Real Permittivity	Loss Tangent	Coefficient of Linear Thermal Expansion (CTE) microstrain/°C
PTFE	2.1[306]	0.0004[306]	124[307]
Adhesive	2.5[308]	<0.02[308]	90[308]
Epoxy	4.25	0.01*	75[309]

Table 5-1 Dielectric properties and coefficient of linear thermal expansion of PTFE, Adhesive and neat epoxy. *Measured values in Section 5.1.4

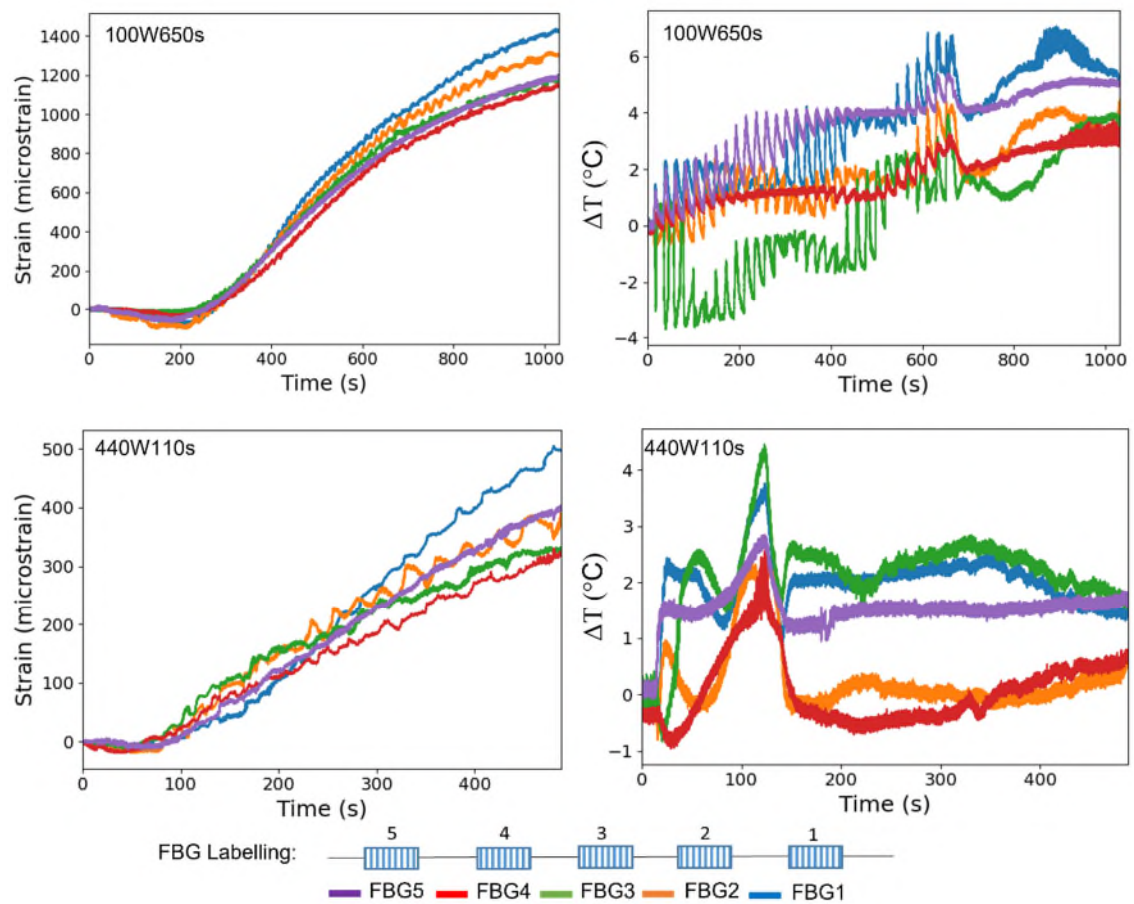


Figure 5-15 Strain and Temperature change measurements via FBG sensors of adhesive (Permabond 50) adhesively bonded on the surface of the PTFE holder under 100W for 650s and 440W for 110s.

Arrays with 5 FBG sensors 20 mm apart are employed in this study to better understand the field response distribution. Figure 5-15 above presents the strain, and temperature change measured via sensors bonded to a PTFE block with adhesive under 100W and 440W. It can be observed from Figure 5-15 that temperature increases with microwave exposure time at both power levels as predicted while the temperature rise has a higher rate under 400W. The maximum temperature changes right before the microwave stopped are around 7°C and 4.5°C for 100W and 440W accordingly. The insignificant amount of temperature rise is direct evidence of relatively less interaction between adhesive and microwave. The strain measurements steadily increase with rising temperature in both cases due to the thermal expansion of PTFE and adhesive. The calculated thermal strain of PTFE based on Figure 5-15 in Table 5-1 under

100W is approximately 868×10^{-6} when the temperature change is 7°C . The calculated value is almost consistent with the measured value of strain sensor 1 which is approximately 960 microstrain at the same temperature change. Unlike 100W, the measured strain of sensor 1 in 440W shown as the blue line when microwave stops is approximately 10 microstrain, which is much lower than 458 microstrain, the calculated thermal strain of PTFE at the same temperature change (3.7°C). When the microwave starts to radiate, the adhesive solely interacts with the microwave and is heated up owing to its higher dielectric loss compared with the PTFE holder. However, the PTFE have a higher CTE than the adhesive. Consequently, it could be concluded that the measured strain under 100W is mainly attributed to the thermal expansion of PTFE from the conduction of heat. The strain sensors of 100W only started to have strain measurements after around 200s also proves a substantial amount of time is required to initiate the heating conduction between adhesive and PTFE holders. On the contrary, 440W has a higher rising rate of temperature within 110s microwave radiation, which leads to a remarkable discrepancy between the measured and calculated strain of thermal expansion from the PTFE as the heat conduction is not initiated immediately between the heated adhesive and PTFE holder. Based on the above analysis of the calculated and measured strain, the strain under 100W is mainly attributed to PTFE thermal expansion while the strain under 440W is dominated by the thermal expansion of the adhesive.

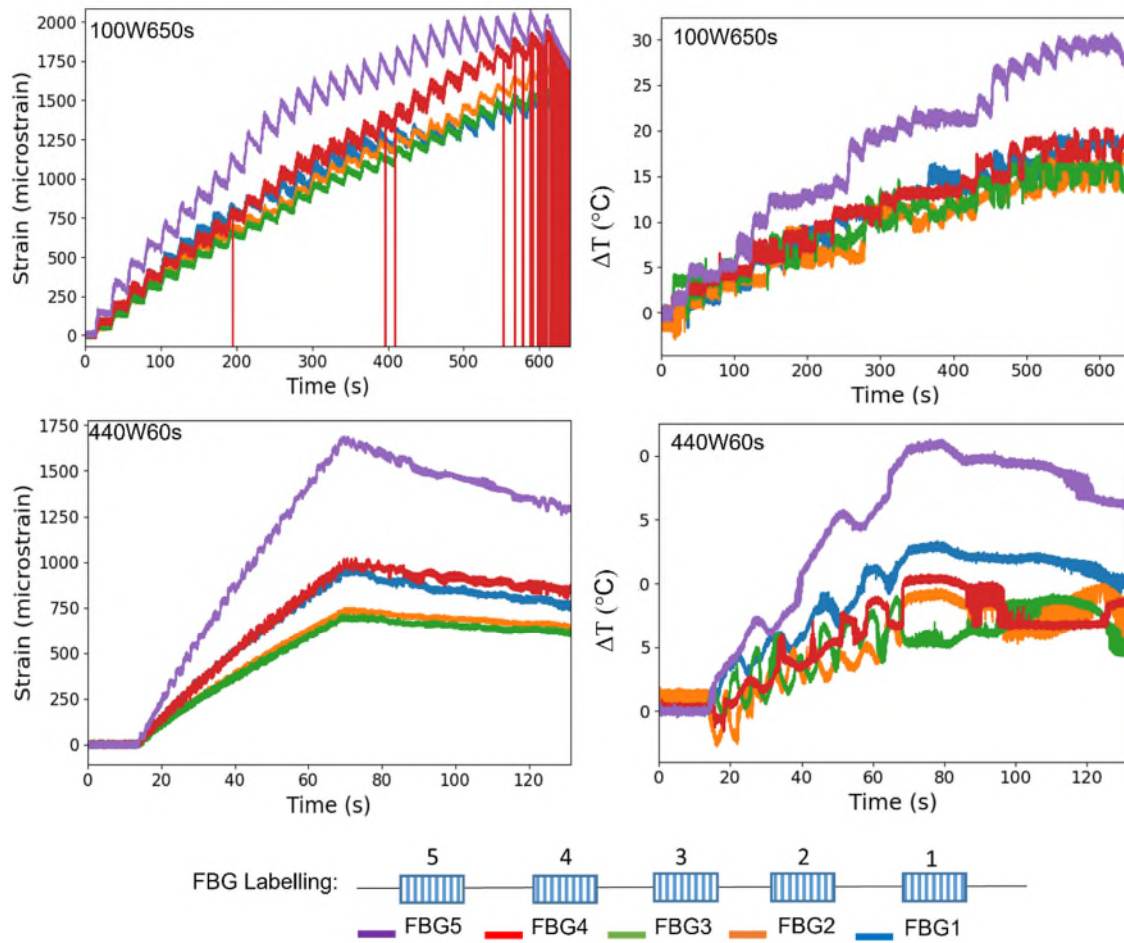


Figure 5-16 Strain and Temperature change measurements via FBG sensors bonded to the surface of the neat epoxy sample under 100W for 650s and 440W for 60s.

Strain and temperature response of neat epoxy with adhesively bonded arrays together under microwave are investigated and results are presented in Figure 5-16 above. The temperature increases as a function of microwave exposure time and starts to drop as soon as the microwave stops as predicted. The FBG sensors 5 present a higher rate of temperature change compared with other FBG sensors which confirms the 'hot spot' theory discussed previously in 5.2.1. The region in which FBG sensor 5 locates falls in the zone with a higher rate of temperature rising that is denoted as a 'hot spot' zone as presented in Figure 5-17 below hence the next hot spot as shown in Figure 5-17 (red square symbol) are half (60 mm) of the microwave wavelength (120 mm) away between sensor 3 and sensor 2. As schematically demonstrated in Figure 5-17, the rest of the

FBG sensors locate out of the hot spot region and therefore they develop similar rates of temperature change under microwave radiation.

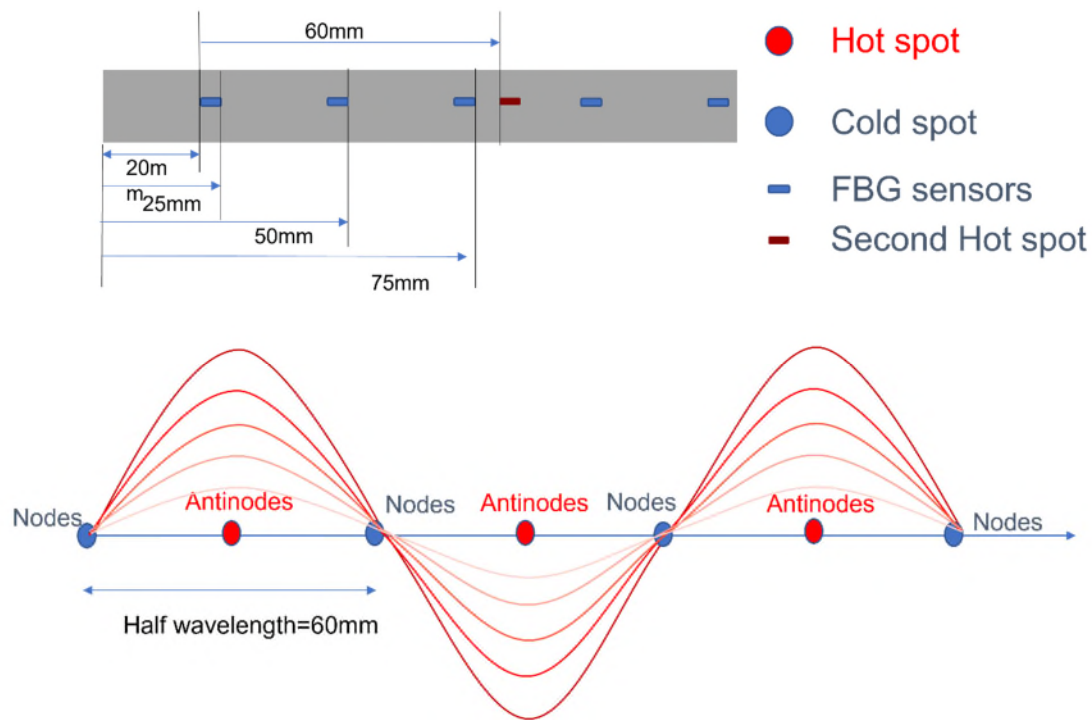


Figure 5-17 Schematic illustration of (above) the location of FBGs on the sample surface with 20 mm distance in between, and (below) standing waves formed in a microwave oven showing hot spots (antinodes) and cold spots (nodes).

The temperature change in both cases reached a higher value of up to 30°C compared with measurements of adhesive only. The measured strain follows a similar increasing trend with temperature change, which is a result of the thermal expansion of adhesive and neat epoxy. The measurements of strain at the different temperature change from the sensor at the left end of three different samples: adhesive on PTFE holder (sensor 5), adhesive on epoxy (sensor 5), and adhesive on epoxy nanocomposites (sensor 1) are tabulated in Table 5-2, below.

100W	100W	100W	440W	440W	440W
Strain/ $\times 10^{-6}$	$\Delta T/^{\circ}\text{C}$	Exposure Time/s	Strain/ $\times 10^{-6}$	$\Delta T/^{\circ}\text{C}$	Exposure Time/s
Adhesive+PTFE					
790	5.0	650	70	2.8	110

Adhesive+Epoxy					
375	5.0	40	320	5.0	14
2080	30.0	600	1700	21.0	60
Epoxy+ BaTiO₃+ Adhesive					
203	5.0	31	290	5.0	15
1990	30.0	445	1057	21.0	58

Table 5-2 Strain and temperature change measurements under 100W and 440W of three categories: FBG sensors bonded by adhesive to PTFE, FBG sensors bonded by adhesive to the neat epoxy, and FBG sensors bonded by adhesive to the epoxy nanocomposite with BaTiO₃.

Power level: 100W

The measured strain of adhesive on PTFE holders is mainly attributed to the thermal expansion of PTFE as discussed previously. When the FBG arrays are adhesively bonded to a neat epoxy sample, the measured strain drops almost 52% from 790 microstrain to 375 microstrain at the same temperature change of 5°C. The reason for the decline in strain measurements could be due to lower CTEs of epoxy and adhesive. Furthermore, at this temperature change of 5°C, the measured strain in 15 wt. % Si-BaTiO₃/epoxy nanocomposite drops 56% compared with that of the neat epoxy, which could be attributed to a compressive strain introduced by the nanoparticles. However, as temperature change rises to 30°C, the measured strain in the neat epoxy and Si-BaTiO₃/epoxy nanocomposites tend to be similar. The explanation for the asymptotic values could be the domination of the thermal expansion effect over the compressive strain field.

Power level: 400W

At the beginning of the microwave exposure, slightly lower values of the strain measurements in the Si-BaTiO₃/epoxy nanocomposite sample could be observed than that of the neat epoxy when the temperature changes are at 5°C and 10°C. Furthermore, the strain declined from 1700 microstrain of the neat epoxy sample to 1057 microstrain of the Si-BaTiO₃/epoxy nanocomposite sample

when the temperature change reaches 30°C. Such differences between the strain measurements of the neat epoxy and the Si-BaTiO₃/epoxy nanocomposite could also represent the existence of the introduced compressive strain field by the BaTiO₃ nanoparticles.

5.2.3 Si-BaTiO₃/epoxy Nanocomposites and Neat epoxy Under 440W

In order to further investigate strain measurements of such nanocomposite material and justify the origin of the compressive strain field, additional 15 wt.% Si-BaTiO₃/epoxy and neat epoxy samples are placed in the microwave oven under 440W in different locations. FBG sensor labelling is identical to the preliminary 440W test in Section 5.2.1 as presented below in Figure 5-18. There are certain missing data in the measurements which is due to a fault in the interrogator software.

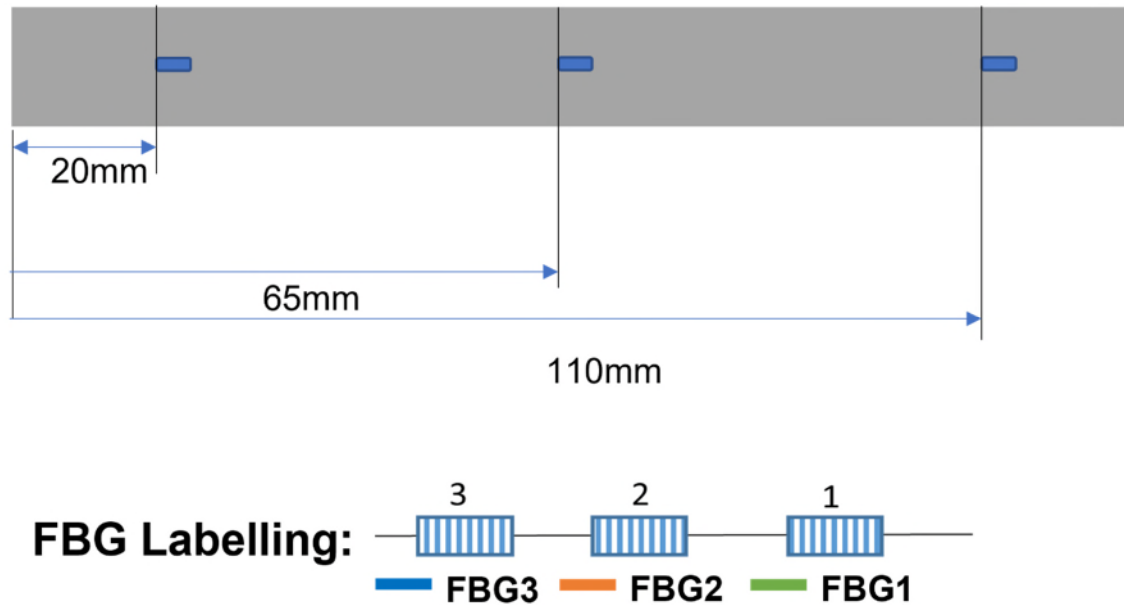


Figure 5-18 Schematic illustration of surface-bonded FBG sensors

15 wt.% Si-BaTiO₃/epoxy Nanocomposites Sample 1(Horizontal)

The first sample of 15 wt.% Si-nanocomposite is placed horizontally to the microwave oven door using FBG sensors as schematically illustrated in Figure 5-19. The field-induced strain and temperature change under 120s microwave

exposure at 440W are presented in Figure 5-20. The data recording starts 10s prior to the microwave exposure.

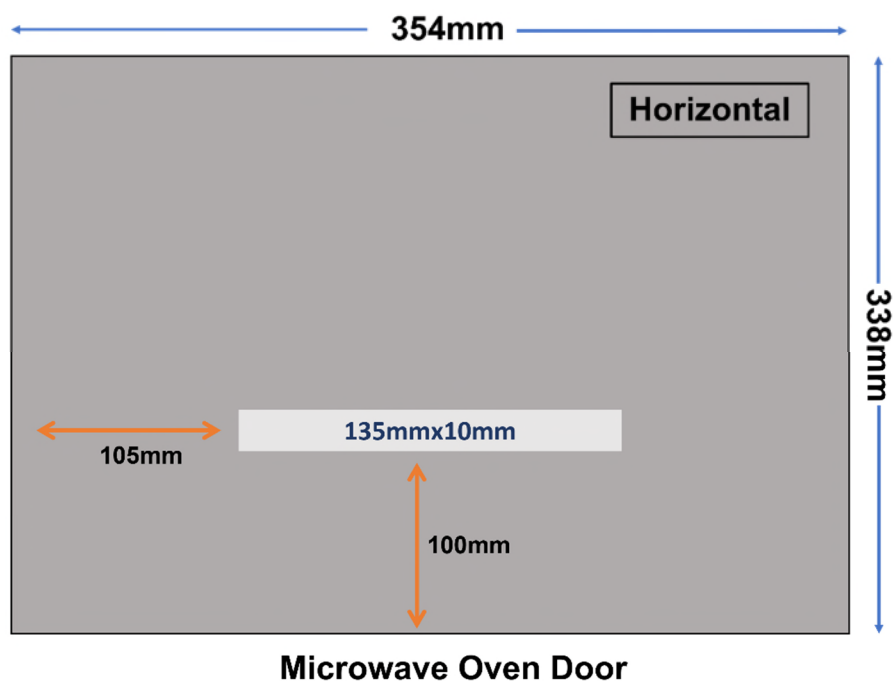


Figure 5-19 Schematic illustration of the sample location (horizontal) in the microwave oven.

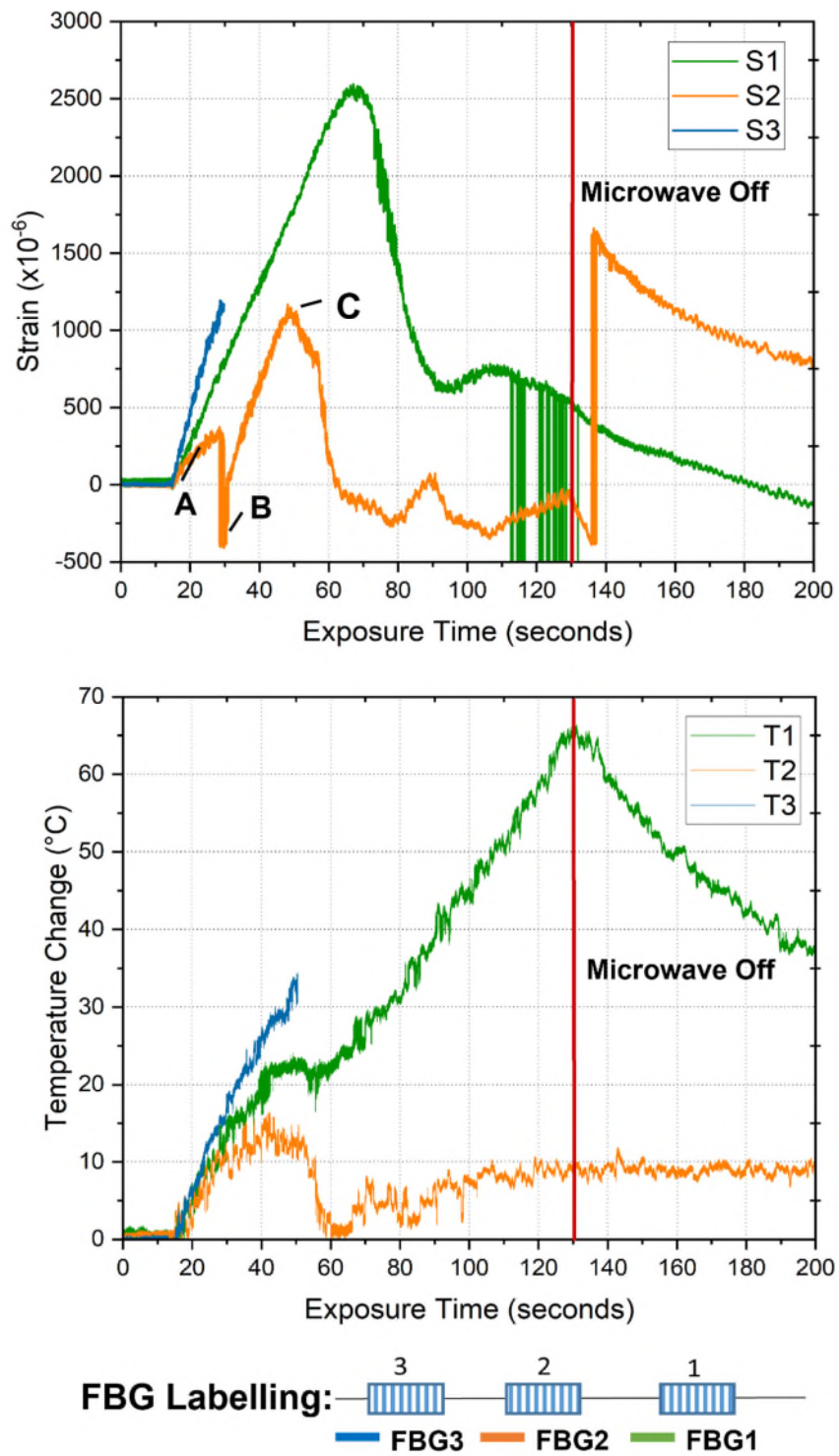


Figure 5-20 Strain and temperature change measurements of 15 wt.% Si-BaTiO₃/epoxy sample 1 (horizontal) under 440W for 120s.

It is apparent that the strain and temperature change under microwave exposure presents a similar increasing trend to the preliminary test under 440W as shown in Figure 5-11. Initially, the temperature rises in all three sensors are stable at the beginning and start to drop gradually as soon as the microwave is stopped. The temperature at both ends of the specimen as indicated in sensor 1 and 3 exhibit a higher increasing rate compared to the middle sensor 2, which is consistent with the 'hot spot' theory in Figure 5-12 discussed in previous Section 5.2.1. However, it should also be noted that a considerable amount of decline in temperature change from sensor 2 (orange) is observed from 40s to 60s. At the same time, a slight impact on the temperature change in sensor 1 (green) could also be observed. After the test, a sample size reduction of approximately 2mm and notable fibre bending of FBG arrays could be observed. These observations could be owing to the sample shrinkage in overheating spots with the evolution of the superpositioned microwave field. Although the highest temperature change is reported to be 26°C (room temperature at 19.2°C) in sensor 3 at 40s, there might exist localised hot spots close to sensors and both ends that already triggered the post-curing process, thereby fibre bending due to post-curing shrinkage as the temperature FBG array is fixed at sample ends with tapes. As point 'C' displayed in Figure 5-20, strain measurements from sensor 2 drop sharply from 1169 microstrain to -255 microstrain while the temperature change in sensor 2 also presents a sharp drop from 12.5°C to 0°C. It is evident that from this point 'C', the negative impact on the accurate measurements from sensor 2 become significant due to the deformation in the FBG arrays. As a consequence, the data captured from both strain and temperature change sensors after 40 seconds are excluded from further analysis. To avoid the possible influence of overheating, the exposure time of Si-BaTiO₃/epoxy nanocomposites sample 2 is controlled to ensure the overall temperature change not exceeding 25°C.

Despite the serious impact of sample shrinkage on the data obtained after 40 seconds, there is still another sudden drop of the strain measurements from middle sensor 2 could still be observed from point 'A' to point 'B' as labelled in Figure 5-20 after the stable increasing at the beginning of the microwave exposure at approximately 30s. It should be noted that the temperature change

at point 'A' when the sudden drop occurs is approximately 10°C and the changing rate of the temperature is the lowest compared with that from sensors 1 and 3. Under such circumstances, the compressive strain field could not be related to the local temperature changing as the temperature is not high enough to activate thermally induced compressive strain due to sample shrinkage. Although the sudden drop appeared again which is similar to the previous attempt, it should still be noted that there exist many unavoidable noise data scattered around point 'B' that make it difficult to study. Thus, further investigations are conducted on the neat epoxy sample 1 and results are presented in the following sections.

Neat epoxy Sample 1(Horizontal)

Neat epoxy sample 1 is placed in the same location as 15 wt.% Si-BaTiO₃/epoxy sample 1 in the microwave oven and measurements from FBG sensors are presented in Figure 5-21. The data recording starts 10s prior to the microwave exposure.

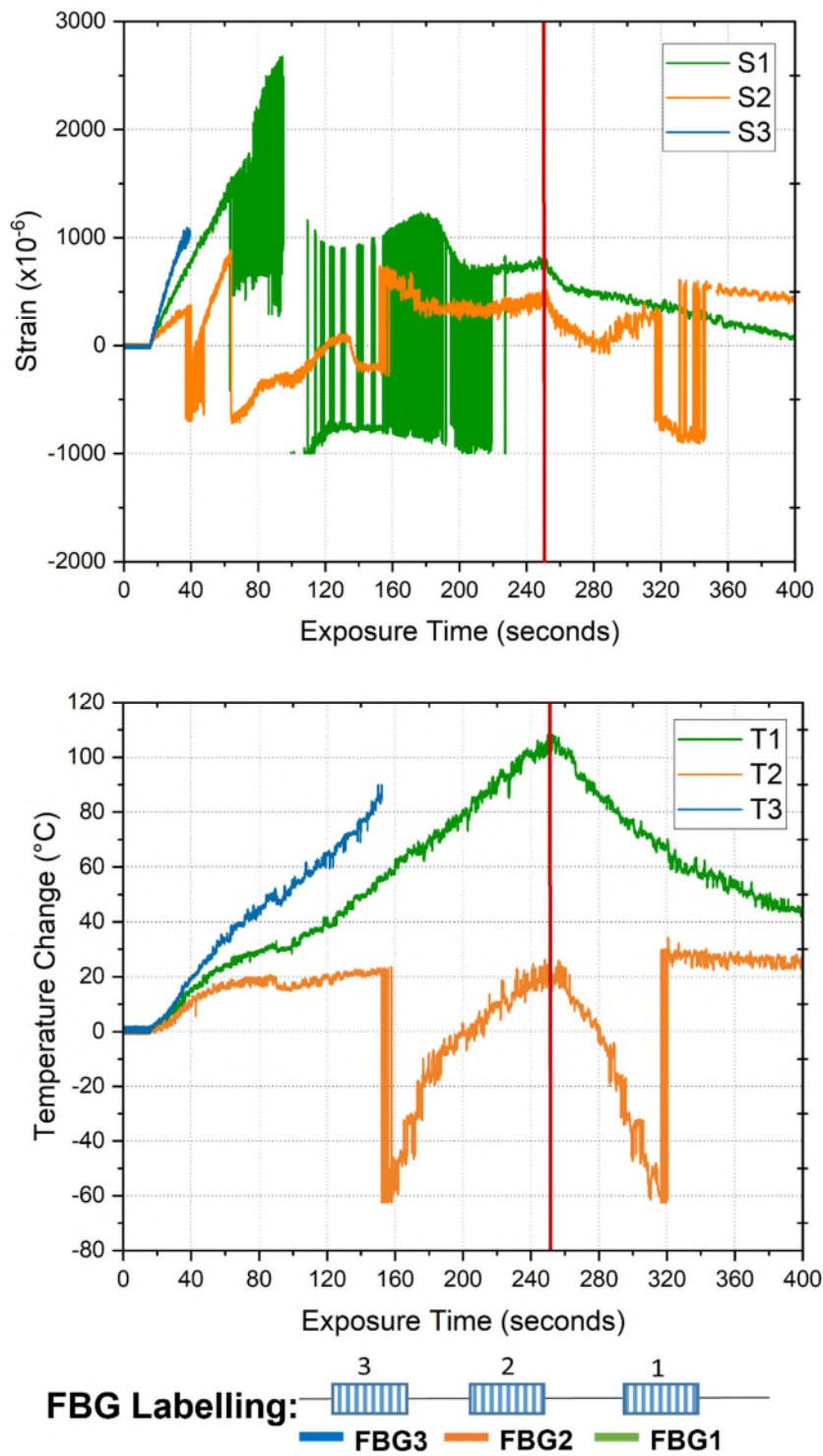


Figure 5-21 Strain and temperature change measurements of neat epoxy sample 1(horizontal) under 440W for 240s.

From Figure 5-21, it can be seen that the temperature change in sensor 1 goes up to 100°C. Consequently, sample shrinkage and fibre bending are also observed after the test. The strain measurements in sensor 2 almost present a similar trend as in Figure 5-20. A sharp drop in strain is observed at around 40s after a stable increase at the beginning, followed by a second sharp drop at 62s. Nevertheless, the temperature change only presents a slight impact from the sample shrinkage as the temperature change plateaus at around 62s and starts to drop gradually at 88s. Therefore, it implies that the impact on data measurements from sample shrinkage starts to become effective from 62 seconds as the temperature change in sensor 3 already reaches 36°C at the same time. The second strain drop could be associated with fibre bending due to sample shrinkage. When the sudden drop of strain happens in sensor 2 at 40s, the highest temperature change measured at this point is from sensor 3 at 20°C. The strain measurements as shown in Figure 5-21 are also affected by scattered unexpected noise data masking the real strain behaviour and it is still not completely clear to draw a conclusion on whether the sudden drop in strain is caused by the stimulated particle or thermal effect. The fibre bending caused by sample shrinkage makes it impossible for surface-bonded FBG arrays to provide accurate measurements after 62s. The data after 62s could not be used for further analysis. Figure 5-21 also shows that sensor 2 undergoes an abrupt decline and increase in temperature change between 160s to 320s of exposure time. This drastic temperature fluctuation is attributed to a signalling error caused by fibre bending. Despite being placed above the sample, the strain-free temperature FBG array is tape-fixed at both ends of the sample to ensure close contact with the strain sensors for more accurate temperature measurements. After the microwave exposure, the bending of the temperature FBG array during the sample shrinkage could also be easily observed. Therefore, the sample shrinkage at elevated temperature during microwave exposure lead to inaccurate wavelength signals and the erroneous data is excluded from the analysis. Therefore, a second group of samples, namely Si-BaTiO₃/epoxy sample 2 and neat epoxy sample 2 are then investigated at first with the same horizontal placement under 440W microwave exposure in the previous attempt. After that, the samples are also placed vertically and diagonally in the microwave oven as schematically illustrated in Figure 5-24. In the end, the 15 wt.% Si-BaTiO₃/epoxy

sample 2 is placed in the horizontal position again for a final run to investigate the possible post-microwave effect after the Curie point of 120°C.

15 wt.% Si-BaTiO₃/epoxy Nanocomposites Sample 2(Horizontal)

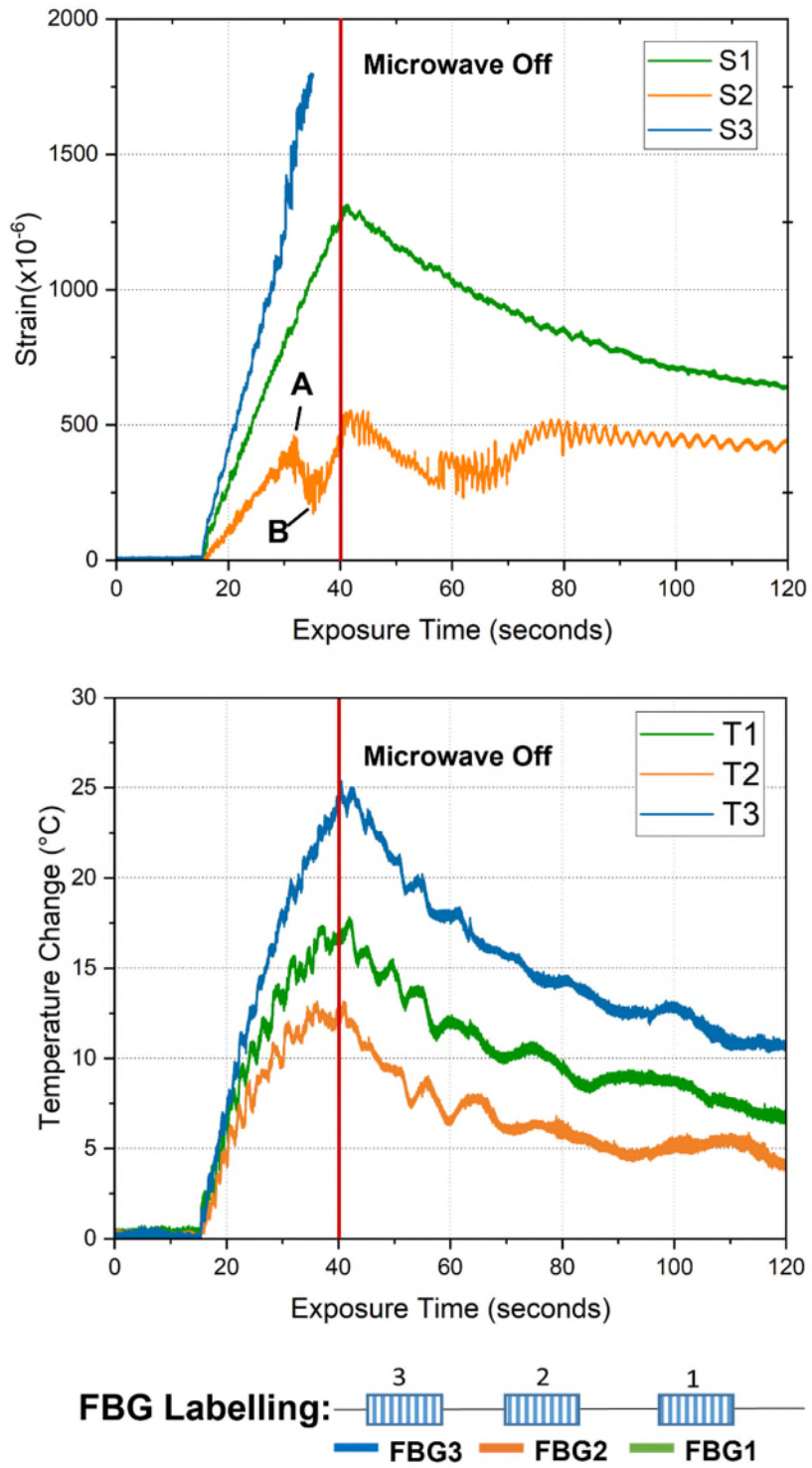


Figure 5-22 Strain and temperature change measurements of 15 wt.% Si-BaTiO₃/epoxy sample 2 (horizontal) under 440W for 30s.

Si-BaTiO₃/epoxy sample 2 is located horizontally in the oven as illustrated in Figure 5-19 under 440W for 30s. The data recording starts 10s prior to microwave exposure. The highest temperature change monitored is controlled below 25°C from sensor 3. As can be seen from Figure 5-22, the strain and temperature change presented a similar overall increasing trend with exposure time compared with the results from sample 1 in Figure 5-20. The 'hot spot' theory could also be applied to the measurements of temperature change from sensors at different locations. It could also be identified in Figure 5-22 that a clear sudden drop in strain measurements occurs at point 'A' to 'B' after the initial stable increase in temperature from middle sensor 2. At point 'A', the temperature change in middle sensor 2 is 11°C with an exposure time of 32s, while at point 'B', the strain declines by approximately 290 microstrain within 3s. Moreover, the change in temperature between points 'A' and 'B' is only 1°C from 11°C to 12°C. As discussed in the above sections, the field-induced compressive strain field via nanoparticles could be accounted for the decline in strain measurements from middle sensor 2. It is difficult to correlate the compressive strain with temperature change as it is only 1°C from 11°C, which is extremely low to cause any noticeable thermal strain effect and hence negligible. In order to further investigate the origin of the compressive strain field, neat epoxy sample 2 is placed horizontally in the microwave oven as illustrated in Figure 5-19. Results from strain and temperature change are presented in the subsection below.

Neat epoxy Sample 2(Horizontal)

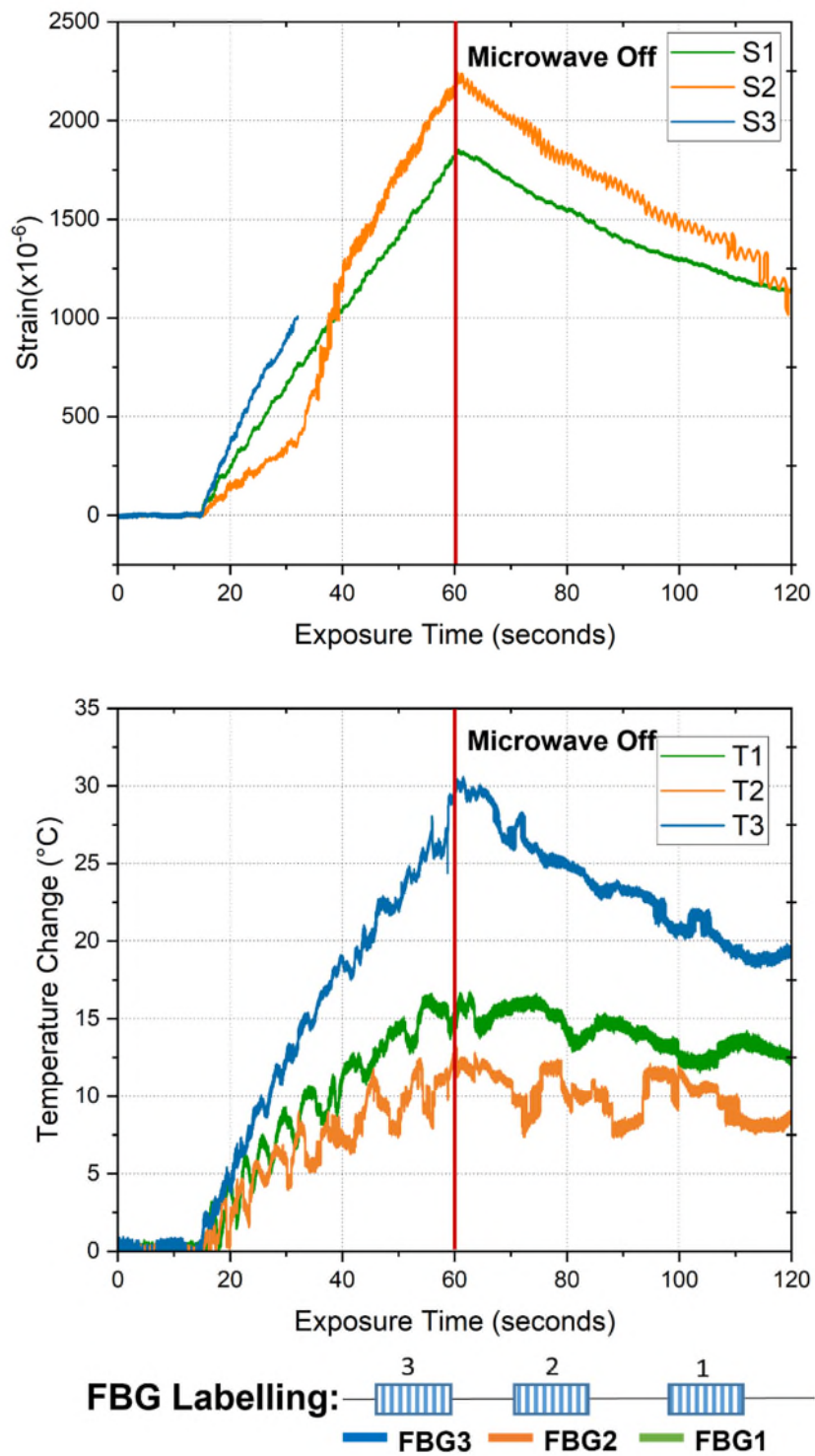


Figure 5-23 Strain and temperature change measurements of neat epoxy sample 2(horizontal) under 440W for 50s.

Neat poxy sample 2 is exposed to the microwave at 440W for 50s and measurements are presented in Figure 5-23. The data recording starts 10s prior to microwave exposure. As can be seen from Figure 5-23, the strain and temperature change shows a similar overall increasing trend with exposure time compared with the results from sample 1 in Figure 5-21. The temperature change in sensor 3 has the highest increasing rate while the middle sensor 2 has the lowest. The strain measurements in all sensors display a general rising trend with the increased exposure time hence the temperature. The strain and temperature change in all sensors start to decrease gradually immediately after the microwave exposure stopped. It could be concluded that the strain introduced in the neat epoxy sample is solely dependent on the thermal change resulting from the heat generated during epoxy and microwave interaction. These findings further prove that the compressive strain field introduced in Si-BaTiO₃/epoxy samples is attributed to the incorporation of the BaTiO₃ nanoparticles. Further studies on Si-BaTiO₃/epoxy and neat epoxy samples are carried out by placing the samples at different locations as illustrated in Figure 5-24.

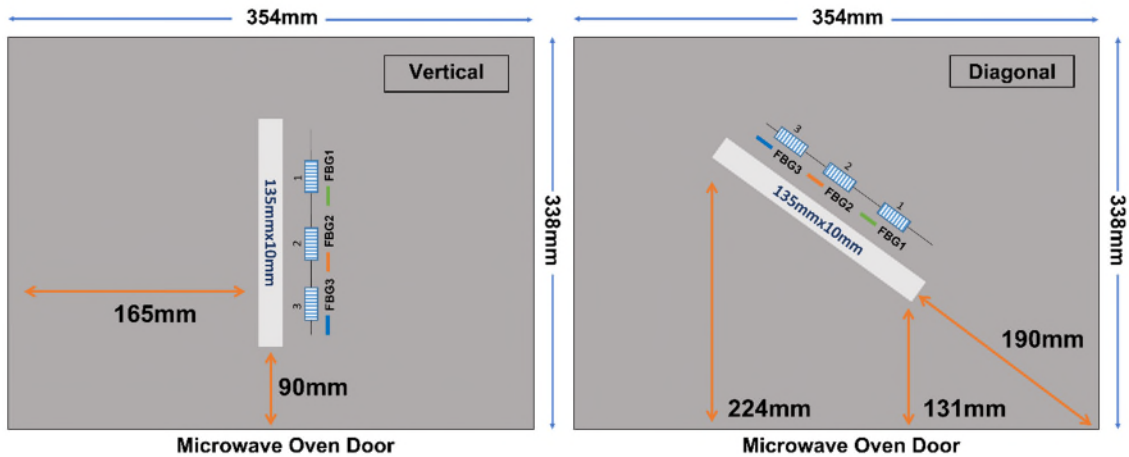


Figure 5-24 Schematic illustration of the sample locations in the microwave oven: vertical position (left) and diagonal position (right).

15 wt.% Si-BaTiO₃/epoxy Nanocomposites Sample 2 and neat epoxy Sample 2 (Vertical)

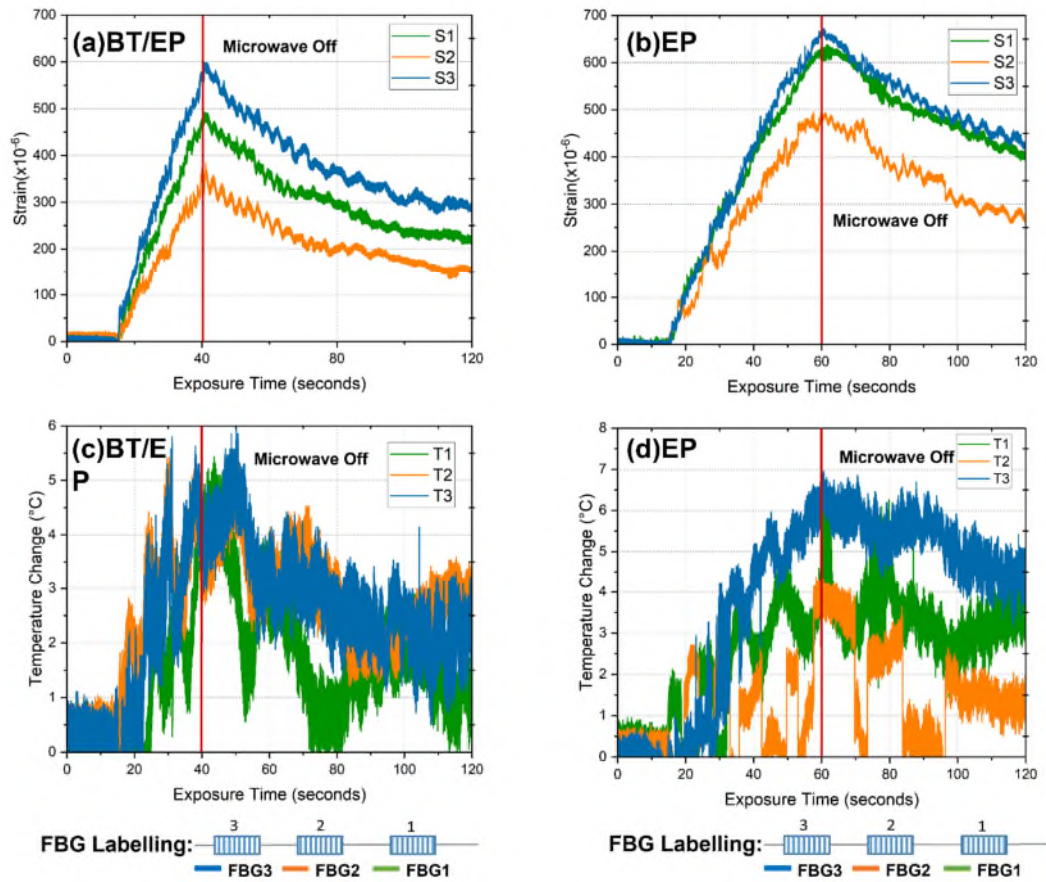


Figure 5-25 Strain and temperature change measurements of (a)(c)15 wt.% Si-BaTiO₃/epoxy sample (vertical) under 440W for 30s and (b)(d) neat epoxy sample (vertical) under 440W for 50s.

After the horizontal test presented in the above subsections, Si-BaTiO₃/epoxy sample 2 and neat epoxy sample 2 are placed vertically in the microwave oven for 30s and 50s, respectively. Measurements of strain and temperature change are presented in Figure 5-25 above. The data recording starts 10s prior to microwave exposure. It could be observed from Figure 5-25 (c) and (d) that the maximum temperature change is recorded by sensor 3 without exceeding 7°C for the sample exposure time as in the previous attempt. The small variation in temperature change indicates limited microwave interaction with samples when placed in this location vertically to the oven door. In the meantime, the strain measurements display a steady increase with the exposure time and the increasing temperature. The difference in strain measurements between each sensor can be identified from Figure 5-25 (a) and (b) and it is approximately up

to 100microstrain at the highest point right before the microwave stopped. The change in strain is relatively small compared to that of the previous attempt (approximately 750 microstrain) as shown in Figure 5-22. The imperceptible variation in both measurements implies that the sample size is not big enough to cover the 'hot spots' along the longitudinal direction at this location.

15 wt.% Si-BaTiO₃/epoxy Nanocomposites Sample 2 and neat epoxy Sample 2 (Diagonal)

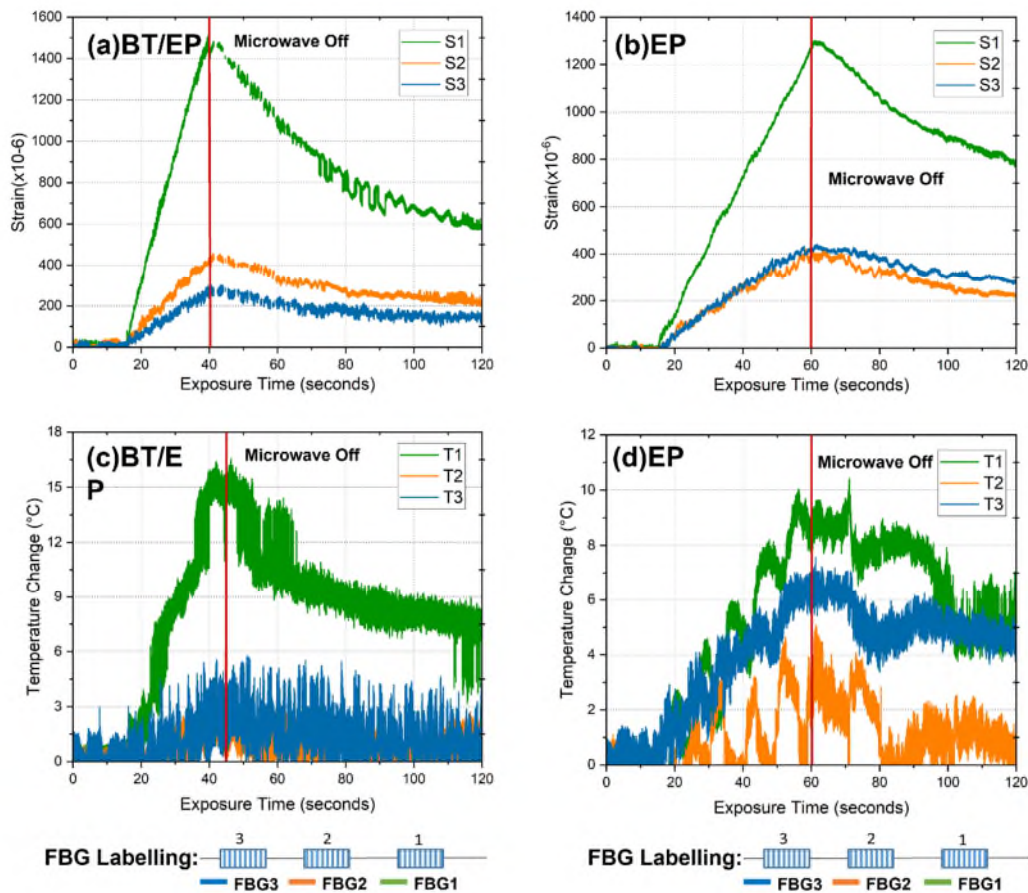


Figure 5-26 Strain and temperature change measurements of (a)(c)15 wt.% Si-BaTiO₃/epoxy sample (diagonal) under 440W for 30s and (b)(d) neat epoxy sample (diagonal) under 440W for 50s.

After the vertical test presented in the above subsection, Si-BaTiO₃/epoxy sample 2 and neat epoxy sample 2 are then placed diagonally to the microwave oven door for 30s and 50s, respectively. Measurements of strain and temperature

change are presented in Figure 5-26 above. The data recording starts 10s prior to microwave exposure. It could be observed from Figure 5-25 (c) and (d) that, for the sample exposure time as in previous attempts, the maximum temperature change for Si-BaTiO₃/epoxy sample 2 and neat epoxy sample 2 are 15°C and 10°C, respectively. These temperature changes are almost half of the values of horizontally placed samples. It could also be found from Figure 5-25 that the measurements of strain and temperature change exhibit remarkable differences compared with the other two sensors. The substantial difference could be an indication of a 'hot spot' fell in or near the region of sensor 1. In comparison with results from 'horizontal' and 'vertical' attempts, it seems plausible that the sensor located close to the door with distances of 100mm (horizontal), 90mm(vertical), and 131mm (diagonal), reported the maximum temperature change. The reason behind this could be attributed to the distribution of the microwave field within the microwave oven, which is relatively more uniform in accordance with the 'hot spot' theory along the horizontal direction.

A final microwave exposure is conducted for 180s to investigate the strain measurements and following post-microwave effects that are characterised with the sample overheating above the phase change temperature at 120°C.

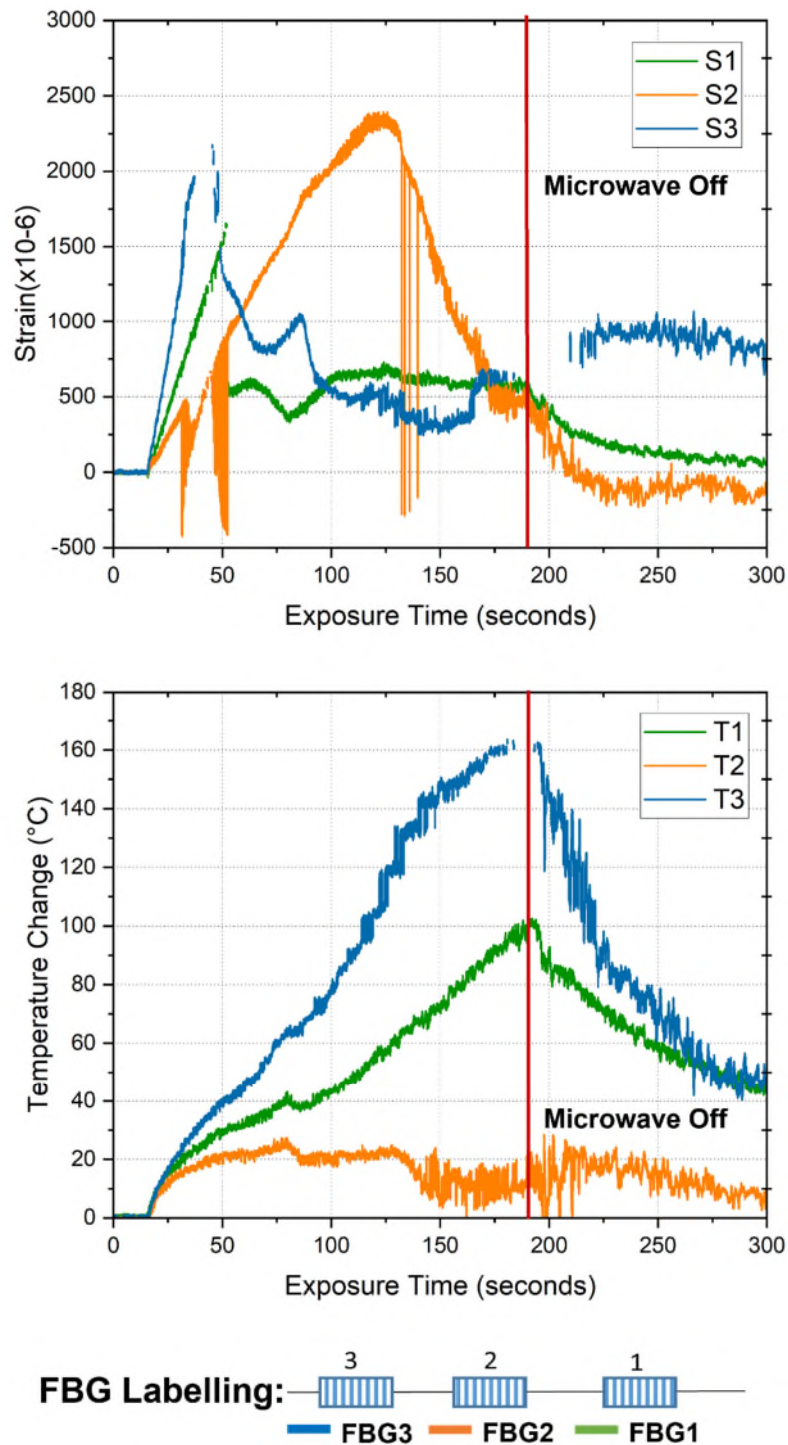


Figure 5-27 Final strain and temperature change measurements of 15 wt.% Si-BaTiO₃/epoxy sample 2 (horizontal) under 440W for 180s.

Si-BaTiO₃/epoxy sample 2 is located horizontally in the oven again as illustrated in Figure 5-19 under 440W for 180s. The data recording starts 15s prior to

microwave exposure. It can be observed from Figure 5-27 that the highest temperature change monitored goes up to 160°C from sensor 3. At the beginning of the exposure, the strain and temperature change presented a similar overall increasing trend with exposure time compared with the results in Figure 5-22. Suppression in the temperature change measurements from the middle sensor 2 could also be observed, which is consistent with the results from the 15 wt.% Si-BaTiO₃/Epoxy sample 1 due to the fibre bending with overheated spots. Two sudden drops in strain measurements could be observed after the initial stable increase in temperature from middle sensor 2. However, remarkable outliers in data are presented in the results and make it difficult to distinguish any field-strain effect from the measurement errors due to fibre bending. Post-microwave effects of samples with such overheating thermal history are characterised by Raman spectroscopy in the following section.

5.3 Raman Characterisation

Raman spectroscopy is one of the most powerful techniques to probe the local residual stress in crystalline materials by observing a shift of scattering frequency due to changes in the interatomic spacing under stress. However, this method is also proven to be applicable to polymer matrix composites by many other researchers [310]. For instance, the Raman peaks on the spectrum of a polyetheretherketone (PEEK) prepreg with carbon fibre shifted from 2660 cm⁻¹ to approximately 2670 cm⁻¹ under a compressive strain of 0.65% [311]. Raman spectroscopy is also widely used for the confirmation of BaTiO₃ phases based on the change in the crystal structure as presented in Section 2.2.4 [312, 313]. For these reasons, Raman spectroscopy is employed in this study to examine any possible residual strain induced by the particles to the surrounding epoxy matrix, and the crystal structure transformation of BaTiO₃ particles that might be introduced by the microwave exposure. The middle region of the samples where the ‘sudden drop’ of strain measurements is of particular interest hence it is the region where the laser is focused to obtain the Raman spectra. Three random points are selected within this region for each sample under test.

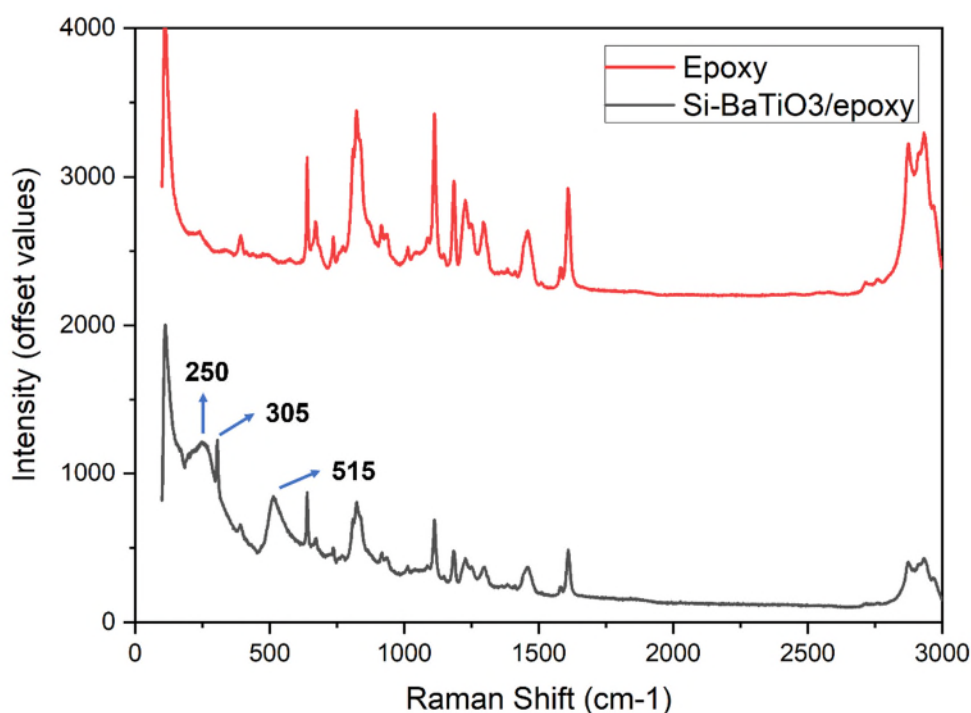


Figure 5-28 Raman spectra of neat epoxy (red) and 15 wt.% epoxy nanocomposites with Si-BaTiO₃ without microwave exposure.

Raman characterisations are first performed with the neat epoxy and Si-BaTiO₃/epoxy nanocomposite samples without microwave radiation to establish baseline curves to correlate any possible change in the position of Raman peaks for the samples with microwave exposure. Raman spectra of neat epoxy and Si-BaTiO₃/epoxy nanocomposite samples all delivered fair consistency of the peaks at all three random points. Therefore, the spectra of neat epoxy and Si-BaTiO₃/epoxy nanocomposite samples are presented in Figure 5-28. The peak at 250 cm⁻¹ and 515 cm⁻¹ are characteristic peaks of BaTiO₃ which are assigned to mode A₁(TO₂) and B₁(TO) respectively. Meanwhile, the 305 cm⁻¹ is a characteristic of the tetragonal phase of BaTiO₃ representing the out-of-phase and axial motion of the two oxygen atoms facing oppositely as illustrated in Figure 2-16 [199, 312].

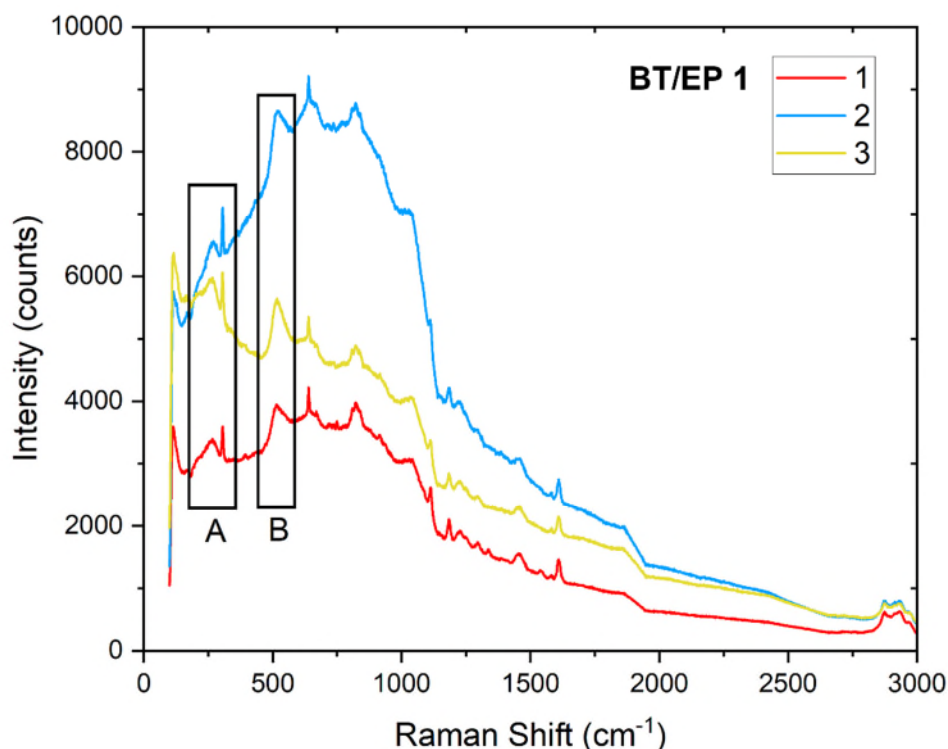


Figure 5-29 Raman spectra of three random points on the 15 wt.% Si-BaTiO₃/epoxy nanocomposite sample 1 after the microwave exposure.

The Raman spectra of three random points in the region of middle sensor 2 on the Si-BaTiO₃/epoxy nanocomposites sample 1 in the second attempt are presented in Figure 5-29. It could be seen that the background consists of multiple humps and broad peaks compared with Figure 5-28 which could be attributed to the fluorescence interference. However, the characteristic peak of represents the tetragonal phase of BaTiO₃ nanoparticles at 306 cm⁻¹ could still be observed from the spectra in the box 'A'. The highest temperature change measured for Si-BaTiO₃/epoxy nanocomposite sample 1 is approximately 65°C hence the temperature of the sample is well below the Curie temperature of 120°C for phase transformation. By comparing the peaks of 250 cm⁻¹ in Figure 5-28 with the peaks in the box 'A' of Figure 5-29, the position of the peak is shifting up by 19 cm⁻¹ to 269 cm⁻¹ in the spectrum of point 2. In addition, a blueshift in peak 515 cm⁻¹ to 522 cm⁻¹ could also be identified from the spectrum of point 2.

The characteristic Raman peaks of BaTiO₃ nanoparticles are 250 cm⁻¹ and 515 cm⁻¹, and they are not overlapping with any peaks from the epoxy resin. Therefore, the blueshift in these two peaks might be due to a compressive residual strain experienced by the nanoparticles after microwave exposure. Unlike spot 2, there is insignificant variation in the characterisation Raman peaks at spot 1 and spot 3. Following the cessation of microwave radiation, the sample cools down and residual stress starts to build up due to the mismatch in CTEs between the matrix and nanoparticles. However, the temperatures could be different at each point due to non-uniform microwave heating patterns and could be the cause for the unnoticeable shift in Raman peaks in spot 1 and spot 3.

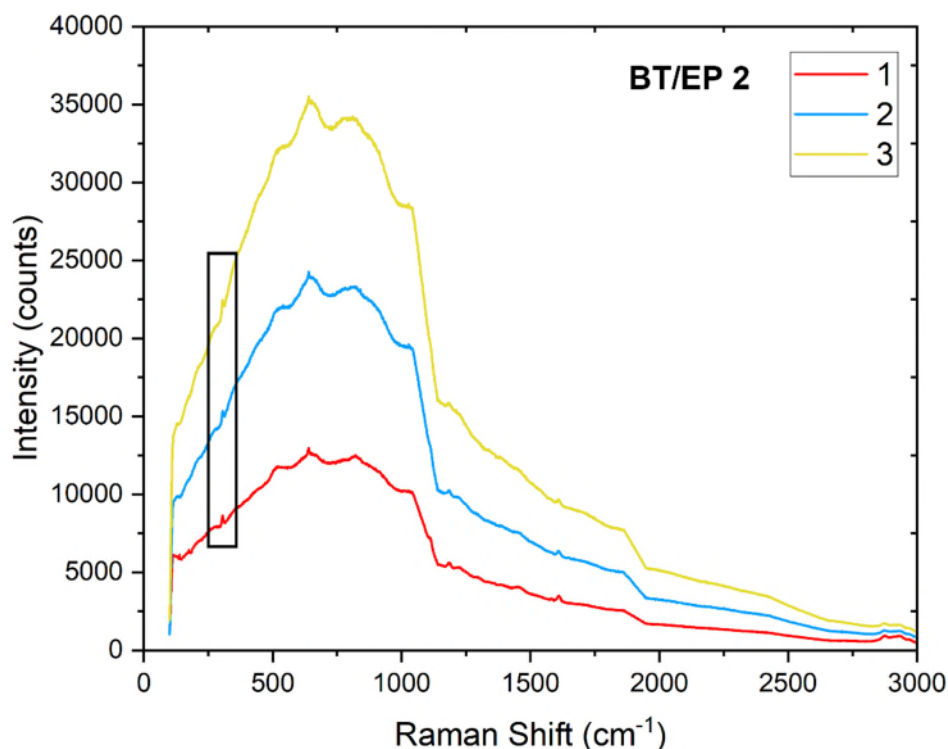


Figure 5-30 Raman spectra of three random points on the 15 wt.% Si-BaTiO₃/epoxy nanocomposites sample 2 after the microwave exposure.

The Raman spectra of three random points in the region of the middle sensor 2 on the Si-BaTiO₃/epoxy nanocomposite sample 2 in the second attempt are presented in Figure 5-30. The background also consists of multiple humps and

broad peaks similar to Figure 5-29 and could also be attributed to the fluorescence interference. However, the characteristic peak of represents the tetragonal phase of BaTiO₃ nanoparticles at 306 cm⁻¹ could barely be observed from the spectra. The highest temperature change measured for Si-BaTiO₃/epoxy nanocomposite sample 2 is approximately 160°C as shown in Figure 5-27 hence the temperature of the sample went above the Curie temperature of 120°C for phase transformation. The crystal structure of BaTiO₃ nanoparticles transformed from tetragonal to cubic under such heating and caused the weakening of the 305 cm⁻¹ peak. Unfortunately, the peaks could hardly be detected due to interferences from the background. It could be seen from both Figure 5-29 and Figure 5-30 that the characteristic peaks representing epoxy at 639 cm⁻¹ (C-H out-of-plane deformation), 824 cm⁻¹ (C–H vibrations) and 1609 cm⁻¹ (C=C stretching) are barely shifted [314].

The blueshift of the characteristic peaks of BaTiO₃ nanoparticles could be an indication of the residual compressive strain field introduced by the nanoparticles during microwave exposure. However, further studies need to be carried out to get a deeper understanding of the quantification of the residual strain as a function of peak shift. Results of the real-time strain measurements during microwave exposure by FBGs and the post-microwave Raman spectra are then discussed in the section below.

6 DISCUSSION

6.1 Overview of the General Properties

Epoxy is one of the most widely used thermosetting polymers in industrial applications including adhesives and structural parts. The growth of interest in developing epoxy nanocomposites by incorporating a second phase to enable a toughening effect has emerged in recent years. Different types of fillers are proposed to improve the toughness of modified epoxy systems and prior studies have documented the effectiveness of enhanced mechanical performance as previously presented in Section 2.1.3. However, most of these studies are facing the problem of not being able to maintain consistent performance during service due to the difficulties in detection and repair. Therefore, this study is proposed to investigate the mechanical response of a multifunctional epoxy composite material with embedded BaTiO₃ nanoparticles under an applied microwave field.

The 200nm BaTiO₃ nanoparticle is selected to be the dielectric filler due to its unique tetragonal structure as presented in 2.2.4. It has been discovered by previous studies that the tetragonality of such crystals is considerably dependent on particle size. It is found that the ferroelectricity behaviour in the particles reduced with decreasing particle size and would eventually disappear with crystal structure switching from tetragonal to cubic below a critical size that falls in the range of 100nm-150nm depending on the particle fabrication method [315, 316]. Therefore, tetragonality that determines the impressive interactive ability with microwave is retained by incorporating nanoparticles with a size of 200nm in this study. As previously discussed in Section 4.1.2, it has been demonstrated that the dielectric property is improved with an increasing amount of BaTiO₃ particles in the epoxy matrix. Nevertheless, undesired particle agglomerations also become prominent at the same time, which leads to the degradation of the overall mechanical properties of Si-BaTiO₃/epoxy nanocomposites when the weight loading is over 10 wt.% as presented in other studies[196]. The ultimate goal for future applications of such nanocomposite materials is to achieve perceivable field-induced compressive strain with only a sufficient amount of nanoparticles to avoid the negative impact on the mechanical properties. Therefore, in addition to

agitation exerted during ultrasonication mixing by an ultrasonic horn, the silane coupling agent (3-GPS) is also applied to increase the compatibility between nanoparticles and epoxy matrix. Various kinds of silane coupling agents are available and used in different studies and their abilities to uniformly disperse the nanoparticles within the epoxy matrix have been approved via enhanced mechanical and dielectric properties [190, 262-265]. Unfortunately, there are limited studies comparing the possible impact of different silane coupling agents on the overall properties. Moreover, limited work has been done on providing a standard functionalisation procedure including solvent types and silane coupling agent quantities that should be used. Although much work could be carried out on this topic, the focus of applying a silane coupling agent is only on avoiding particle agglomeration and achieving better dispersion. The evidence of better dispersion has been presented by comparing the SEM images of fracture surfaces from functionalised and non-functionalised Si-BaTiO₃/epoxy samples in Figure 5-1. The fair uniform dispersion presented in these images is not only attributed to the ultrasonication and silane functionalisation. Solvent-aided mixing is also used by mixing the nanoparticles firstly with ethanol solvent before mixing with epoxy resin with the intention to lower the viscosity and ease the manufacturing process. Any increase in viscosity due to nanoparticle addition is unlikely to interfere with solvent-aided mixing, and solvent-aided mixing is used to reduce the initial viscosity of the epoxy and facilitate mixing. The final blends of epoxy resin and nanoparticles became extremely easy to handle with the aid of ethanol and the ethanol is gradually removed overnight with heating under a fume hood. Mechanical stirring of the mixture is also non-stop overnight to avoid precipitation of the particles. Although the solvent decreased the viscosity during the mixing of epoxy and BaTiO₃, the uncured blend of BaTiO₃ and epoxy remains viscous after the solvent is removed. The air might be trapped while pouring the uncured modified epoxy system into the mould. Therefore, the degassing process is performed under the vacuum before the curing and no voids could be observed in the cured samples with the naked eye.

The thermal, mechanical, and dielectric properties are first examined prior to the investigation of the performance of the epoxy nanocomposites under the

electromagnetic field. The results are presented and discussed in Section 5.1. Polymer nanocomposites consisting of the BaTiO₃ particles at nanoscales are extensively studied for applications like sensors, actuators, and capacitors in the electronic industry. Prior work has documented that the enhanced properties of developed polymer nanocomposites depend on the following factors: (i) sizes and shapes of the BaTiO₃ crystals [98, 317, 318]; (ii) quality of BaTiO₃/Polymer interfacial bonding via various functionalisation methods [191, 260, 288]; (iii) dispersion quality of the BaTiO₃ [189]; and (iv) types of the solution used in BaTiO₃ dispersing during fabrication [319]. However, the majority of studies on BaTiO₃/polymer carried out by others focused on a relatively high content of fillers (>50 wt.%) to achieve higher permittivity and breakdown strength. Results on the mechanical properties of the nanocomposites are also absent due to the rare concerns about their structural performance. Generally speaking, the increasing content of BaTiO₃ could induce deterioration in mechanical properties as a result of particle agglomeration. Therefore, an overview of the thermal, mechanical, and dielectric performance of Si-BaTiO₃/epoxy nanocomposites is presented in this study to provide a better understanding of optimizing the balance between mechanical and dielectric properties.

It is noted from the DSC results presented and discussed in Section 5.1.2 that the addition of functionalised BaTiO₃ has negligible impact on the curing process as the variations in T_g are insignificant. On the contrary, the non-functionalised Si-BaTiO₃/epoxy exhibit reduced T_g up to 10 wt.% and it might be attributed to the interfered cross-linking result from particle agglomeration. It should also be noted that the tensile test results of the Si-BaTiO₃/epoxy nanocomposites presented in Section 5.1.3 are not following other studies as expected. The elastic modulus decreased with the addition of Si-BaTiO₃ nanoparticles. The reason for the unexpected data is highly likely due to the misalignment of the specimens during the tensile test as indicated in Figure 5-6(c). It could be identified that most specimens break at the grip end instead of the central gauge section. A dog-bone shaped sample needs to be prepared for the tensile test in future work to reduce the excessive stress and local breakage due to the clamping force from the grip.

The results from the SEM images in Section 5.1.1 infer that the particles are well dispersed owing to the strong interfacial interaction between the surface functionalised BaTiO₃ and the epoxy matrix. Strong interfacial bonding between the filler and the epoxy matrix is highly desirable so that the stress transfer between the dispersed phase and the matrix could be maximised. The strength of the reinforcing filler could not be fully transmitted to the matrix with weak interfacial bondings[62]. However, the hydroxyl groups on the nanoparticle surfaces due to absorbed water molecules are hydrophilic and make them incompatible with the hydrophobic epoxy [320]. As a result, the agglomerations of the particles are formed in the epoxy nanocomposites as presented in Figure 5-1(f). In order to overcome such challenges, a silane coupling agent is introduced to add functional groups onto the surface of the nanoparticles via covalent bonds and subsequently reduce their surface energy, thereby less agglomeration. Furthermore, the silane coupling agent also consists of another epoxied-end functional group that could react with the epoxy chain of the resin during the polymerization during curing, which has been studied and proved for the similar process of silane functionalisation for carbon nanotubes and graphene oxide [262, 321, 322]. As a result, the improved interfacial bonding via the covalently-bonded BaTiO₃-silane-epoxy system could enable a more efficient stress transfer of the compressive stress field introduced by the BaTiO₃ nanoparticles to their surrounding matrix [323]. In addition, by comparing the T_g of modified epoxy with functionalised and unfunctionalised nanoparticles in Section 5.1.2, the unaffected T_g for samples with functionalised nanoparticles could also be a validation for the increased interfacial bonding quality, which is also consistent with findings in other studies [322, 324, 325].

Due to the lack of studies on the Si-BaTiO₃/epoxy nanocomposites at a lower content level (<50 wt.%), future works could therefore be carried out on the characterisation of samples at slightly higher weight loadings. The field-induced strain response is considered to be a collective result of each nanoparticle hence it is reasonable to predict that the strain effect might also be dependent on the amount of BaTiO₃ incorporated. In addition, the fabrication process also needs to be optimized by investigating the effects on samples prepared by different

methods, such as the solution used for dispersing particles as the solution might have an adverse interaction with epoxy [190, 319]. Furthermore, the minimum quantity of silane coupling agent that can achieve a successful surface functionalisation needs to be studied as the condensation of excessive silane might introduce a harmful effect to the epoxy matrix.

6.2 Compressive Strain Field-induced in Epoxy Nanocomposites with BaTiO₃ under the Microwave radiation

As previously described in Section 2.1.3, extensive studies carried out over the past several decades demonstrate the large electric-field-induced strain due to domain switching, and the domain wall piezoelectric resonance under the oscillating electric field at a higher frequency discovered in BaTiO₃ crystals. However, all studies are focused on the application in electronic devices such as actuators, sensors and transducers owing to its high dielectric constant (real permittivity) and tunability due to the reversible spontaneous polarisation under an electric field. To the best of my knowledge, there is no such development that employs the distinct electromechanical properties of ferroelectric materials (e.g., BaTiO₃) into developing multifunctional materials that not only introduce the advantageous structural performance due to the inherent rigidity of BaTiO₃ ceramics but also achieve a toughening effect remotely under an applied electromechanical field.

Due to the limitations of techniques and resources in the in-situ measurement of the electromechanical response of the BaTiO₃ nanoparticles in the modified epoxy matrix simultaneously with the microwave field exposure, the mechanical response of the Si-BaTiO₃/epoxy nanocomposite samples under the radiation in the microwave oven is examined in terms of the strain measured on the sample surface via adhesively bonded FBG arrays. The size of each FBG sensor conducts strain measurements from a 5 mm x 0.5 mm area from the sample surface and it is hypothesised that an overall phenomenologically compressive strain could be introduced and detected as it is a resultant of the compressive strain response from each BaTiO₃ nanoparticle activated by the microwave exposure at the micro-scale.

As discussed in Section 2.1.3, the strain behaviour measured via FBG sensors is resultant of coupling fields between the stress field, the electric component of the microwave and the thermal field due to microwave dielectric heating and as illustrated in Figure 6-1 below. A small change in any of the fields introduces a corresponding change in others via dielectric heating, thermal expansion, and electromechanical effects. The aim is to find the compressive electro-induced strain in the surrounding matrix of the BaTiO₃ particles. When the sample is placed in the microwave, the dielectric heating process begins instantaneously, and the temperature starts to increase as labelled process '2' in Figure 6-1. Consequently, the thermal expansion of the sample introduces a thermal strain labelled as process '3' in Figure 6-1 and contribute to the total strain measurements from the FBG results. In the meantime, another contributor is the microwave-triggered compressive stress field within the elastic limit labelled as process '1'. Therefore, it is important to find a difference between the strain measurements from the FBGs and the theoretically calculated strain induced by the linear thermal expansion of samples to confirm the existence of the compressive stress field introduced by the BaTiO₃ particles. Therefore, the discussion on the results that indicate the discrepancy between the theoretical thermal expansion of the sample due to non-microwave heating events and the actual strain measurements of the 15 wt.% Si-BaTiO₃/epoxy samples from FBGs under microwave exposure are presented below.

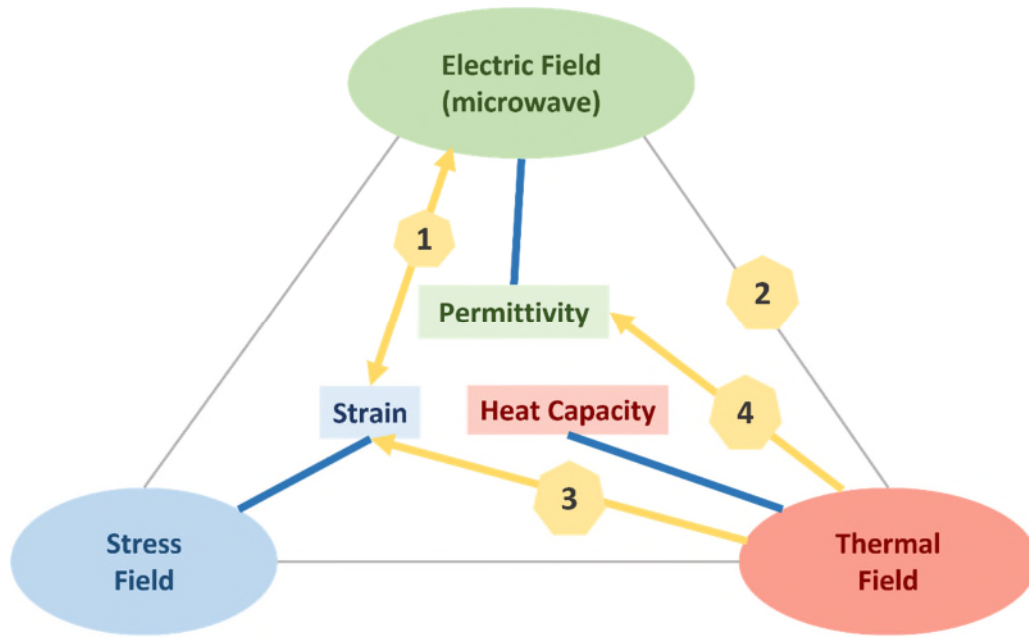


Figure 6-1 Heckmann diagram, schematically depicting the coupled electric, mechanical, and thermal field of ferroelectric crystals, recreated from [326].

It is observed from the FBG test results in Section 5.2 that the overall strain measurements of the 15 wt.% Si-BaTiO₃/epoxy nanocomposites are relatively smaller compared with those of the neat epoxy under 100W. The strain measurements of Si-BaTiO₃/epoxy nanocomposite samples of the first attempt from the beginning of the microwave exposure ($\Delta T=5^{\circ}\text{C}$) to a later stage ($\Delta T=30^{\circ}\text{C}$) from FBG sensor 1 are presented as blue triangle symbols in Figure 6-2. Strain measurements of the neat epoxy sample are also presented as red circle symbols to evaluate the mechanical strain induced by dielectric heating under microwave exposure. The corresponding theoretical thermal expansion of the adhesive was calculated with the CTE of the adhesive (90 microstrain/ $^{\circ}\text{C}$ [308]) multiplied by the temperature change and presented as black square symbols in Figure 6-2. In Figure 6-3, the strain measurements include data from sensor 1 of 15 wt.% Si-BaTiO₃/epoxy sample from the first attempt, 15 wt.% Si-BaTiO₃/epoxy samples 1 and 2 from the second attempt under 440W microwave exposure and the data are presented with an error bar indicating the standard deviation between these samples.

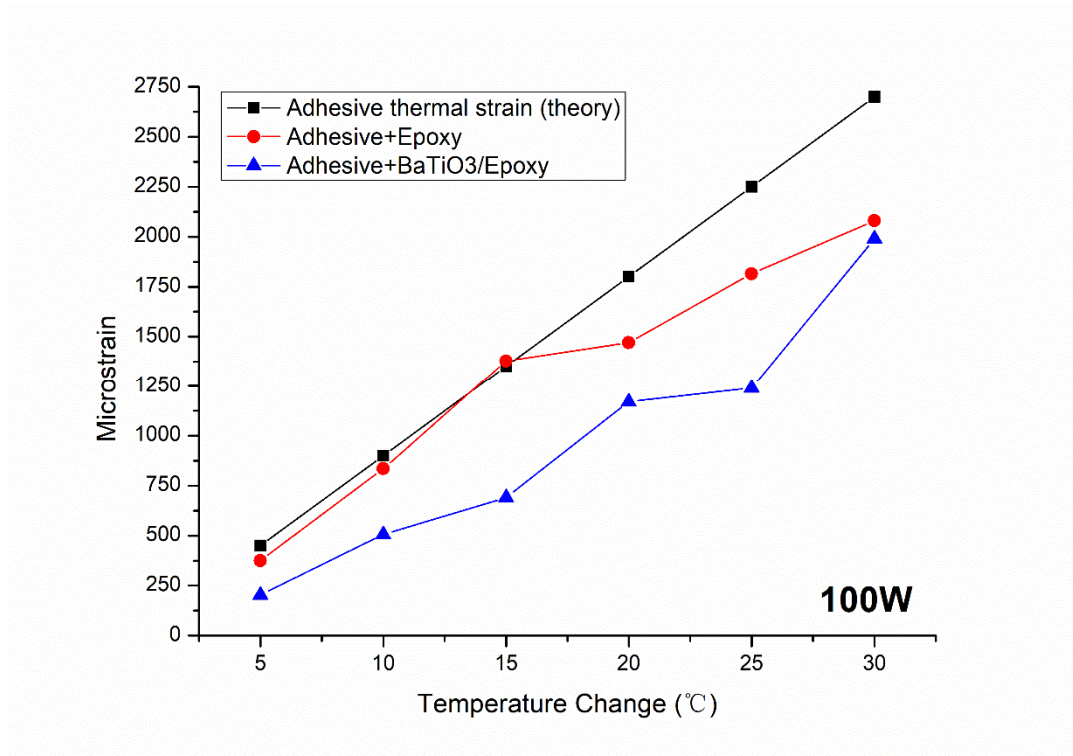


Figure 6-2 Theoretically calculated thermal expansion of adhesive (black), strain measurements of FBG sensor 5 in the first attempt that adhesively bonded to the neat epoxy sample (red), and strain measurements of FBG sensor 1 in the first attempt of adhesively bonded to the 15 wt.% Si-BaTiO₃/epoxy sample (blue) under 100W at 5, 10, 15, 20, 25, and 30°C.

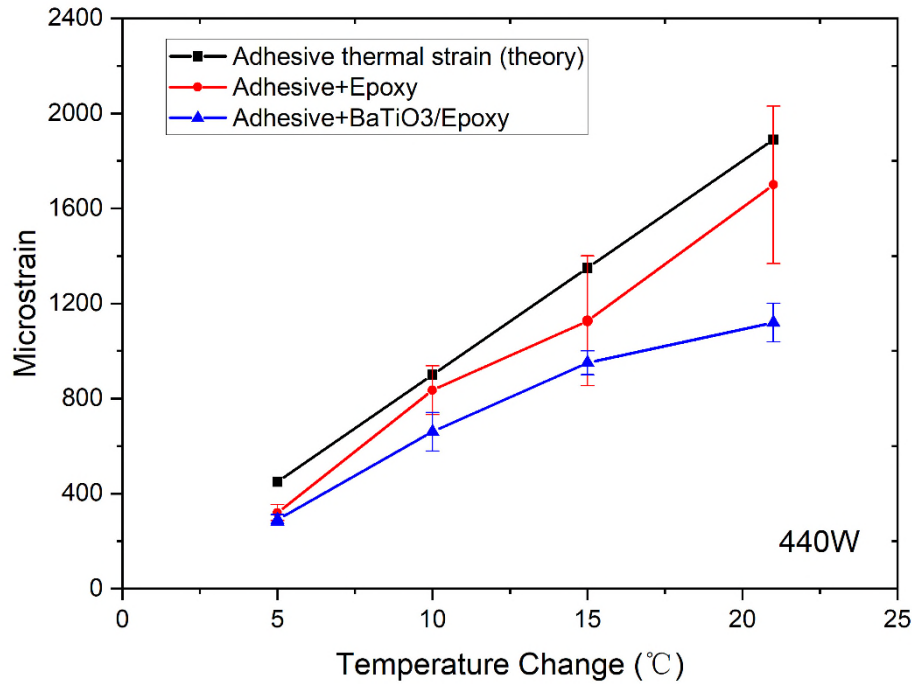


Figure 6-3 Theoretically calculated thermal expansion of adhesive (black), strain measurements of FBG sensor 5 from first and second attempts that adhesively bonded to the neat epoxy sample (red), and strain measurements of FBG sensor 1 from the first and second attempt that adhesively bonded to the 15 wt.% Si-BaTiO₃/epoxy sample (blue) under 440W at 5, 10, 15, and 21°C.

It could be observed from both Figure 6-2 and Figure 6-3 that the strain measurements of Si-BaTiO₃/epoxy nanocomposites (blue triangle symbols) are generally smaller than that of the neat epoxy (red circle symbols). Notably, the differences became more evident with increasing temperatures under 440W while the difference is smallest at the highest temperature change (30°C) under 100W. Such differences between strain measurements in the neat epoxy and epoxy nanocomposites could be considered as an indication of suppressed thermal expansions within modified epoxy samples with BaTiO₃ nanoparticles given the same temperature change. Over the past years, the impact of the existence of microcracks on the properties of composites are studied extensively. The mechanical properties such as elastic modulus, Poisson's ratio, shear modulus [327-329] and coefficient of thermal expansion (CTE) [330-333] are

strongly dependent upon the microcracks in the matrix. Camahort *et al.* [334] correlated a reduction of the CTEs of thermal cycled composite laminates in the specimens with microcracks identified under the microscope. Furthermore, a theoretical study of the CTEs of cracked laminates demonstrated that CTEs change as a function of the internal stress field [332]. This discrepancy in CTEs under different internal stress fields is due to the fact that the internal stresses induced by thermal cycling could be either tensile or compressive. Therefore, this correlation between the microcracks under the impact of field-induced compressive strain and CTEs might provide an explanation for the reduced strain measurements of Si-BaTiO₃/epoxy samples presented in Figure 6-2 and Figure 6-3. During the microwave exposure, the domain wall movements in the BaTiO₃ nanoparticles could be triggered by microwave radiation, thereby the internal stress fields around the microcracks might be altered as illustrated in Figure 6-4, below.

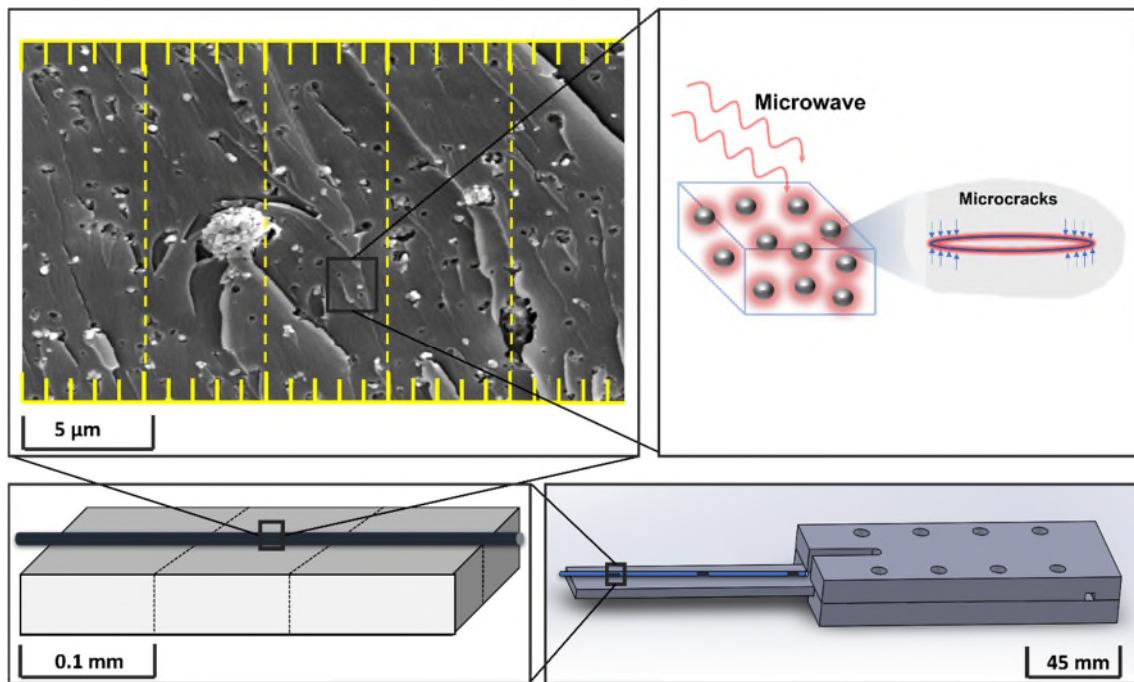


Figure 6-4 Schematic illustration of the 15 wt.% Si-BaTiO₃/epoxy sample in the microwave oven at different scales.

It is clear that the strain measurements in the FBGs on the host material are predominately due to the thermal expansion with increasing temperature resulting from the microwave heating effect. To distinguish between the thermal

strain and microwave field-induced strain arising from the inclusion of nanoparticles, the contribution of the thermal expansion under the same temperature change needs to be determined through conventional heating. Previous research has demonstrated that the CTE of composite material is highly dependent upon its constituents as they possess different CTEs under heating [335, 336]. For instance, the CTE of a modified epoxy system with silica nanoparticles presents a noticeable decrease with increasing loadings of silica nanoparticles and it is attributed to a relatively lower CTE of the fillers in comparison with the epoxy matrix [337]. Therefore, the impact of the addition of 15 wt.% BaTiO₃ nanoparticles on the CTE of the epoxy matrix is then studied by the Thermal Mechanical Analysis (TMA) for temperature range up to 100°C according to ASTM Standards E831-19 [338]. The results of neat epoxy and epoxy nanocomposite samples all presented linear thermal expansion with temperatures up to the T_g. It could also be derived from the results that the variation in the mean CTEs is insignificant between the neat epoxy and epoxy nanocomposite samples, which is approximately 59±2 microstrain/°C. By multiplying the measured CTE of the Si-BaTiO₃/epoxy samples with different temperature changes, the corresponding theoretical values of thermal expansion at different temperature changes and the strain measurements from sensor 1 of the Si-BaTiO₃/epoxy samples from both attempts are obtained and presented below in Figure 6-5. The missing value of the strain measurements for 15 wt. % Si-BaTiO₃/epoxy sample 2 is due to the highest measured temperature change being below 20°C. It is noteworthy that most of the measured strains are smaller than the theoretically calculated thermal expansion. Such findings could also be a validation of the presence of a consecutive compressive strain field introduced by the addition of BaTiO₃ nanoparticles at lower temperature ranges.

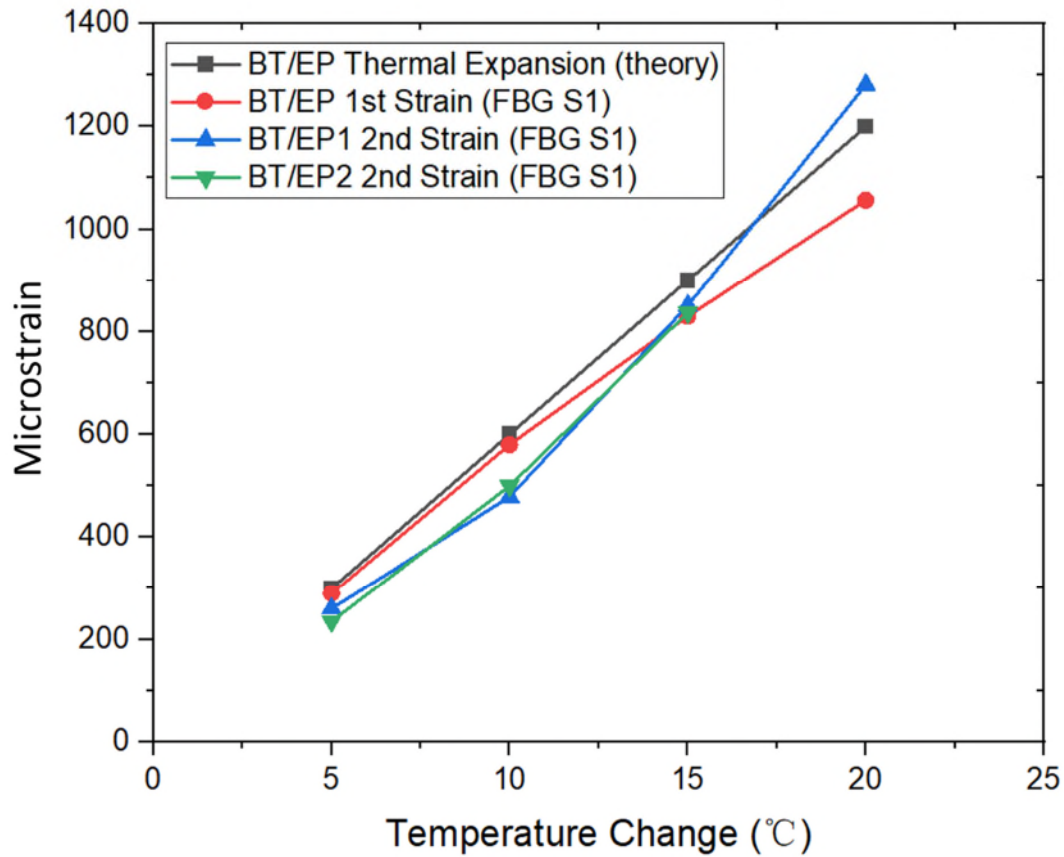


Figure 6-5 The theoretical calculated thermal expansion of 15 wt.% Si-BaTiO₃/epoxy sample based on the measured CTE of 60 (Black), strain measurements from FBG sensor 1 of 15 wt.% Si-BaTiO₃/epoxy sample 1 (blue), and sample 2(green) of the second attempt of FBG test.

The average crystallite size of the purchased BaTiO₃ nanoparticles is determined by XRD results using Scherrer's equation [339]:

$$\text{Crystallite size} = \frac{k\lambda}{B(2\theta)\cos(\theta)} \quad 6-1$$

Where k is the dimensionless shape factor of the crystallite, λ is the X-ray wavelength, 2θ is the peak position, $B(2\theta)$ is the half-width of the maximum intensity of the peak and θ is the Bragg diffraction angle. Although there has been constant discussion for the values of shape factor k , and it is in the range of 0.8-1.2. A round-up value of 1.0 is selected in this study. The mean crystallite size is

35.9 nm, and it indicates that the corresponding grain size is 35.9 nm in the 200 nm BaTiO₃ nanoparticles as presented in Figure 6-6, below.

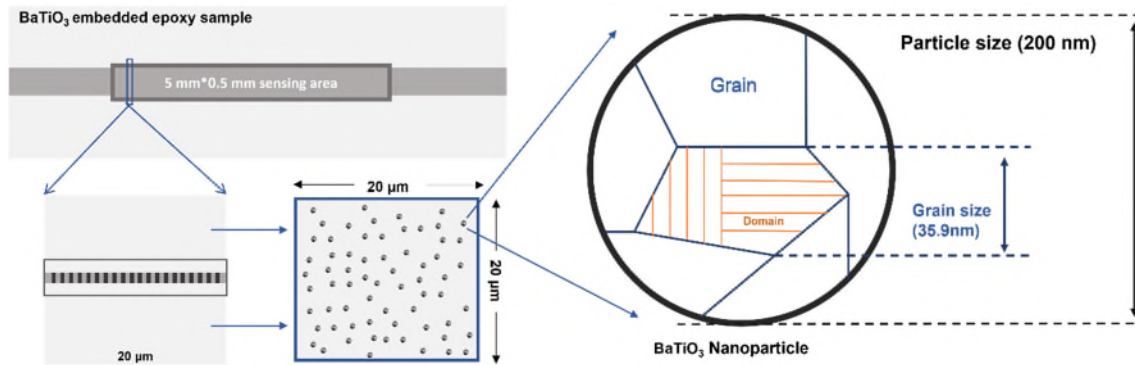


Figure 6-6 Nanocrystalline structure of Si-BaTiO₃ nanoparticles well-dispersed within the area over which the extrinsic strains are measured by the FBG sensors.

The difference in the grain size and particle size is an implication of the polycrystal structure in the particles. As illustrated in Figure 6-6, above, each grain consists of many domains that have different orientations in six possible directions as shown in Figure 2-16. Therefore, it is difficult to have an explicit prediction of the strain field induced by the domain wall movements from an individual nanoparticle experimentally in this study. However, it could also be seen from Figure 6-6 that the strain measured by each sensor is averaged over a 5 mm x 0.5 mm region, which is the size of the fibre gratings. For a 15 wt.% Si-BaTiO₃/epoxy sample, there could be approximately 70 200 nm particles over a 20 x 20 µm² area. Therefore, the strain measured from each surface-bonded FBG sensor could be interpreted as a collective resultant from the compressive strain field introduced by all the BaTiO₃ nanoparticles covered within this region under microwave stimulation at the micro-scale.

Moreover, the interparticle distance as shown in the schematic illustration in Figure 6-4 could be another factor that poses an impact on the overall field-induced strain by the BaTiO₃ nanoparticles, as demonstrated in numerous studies that the interparticle distance plays an important role in the mechanical and dielectric properties of composite materials [340, 341]. However, achieving precise control over the interparticle distance would be very challenging, and

smaller interparticle distances could only be attainable via much higher weight loadings of the nanoparticles. It could be speculated that in a hypothesised 1D linear situation involving two nanoparticles with relatively short interparticle distance, the compressive strain field in the overlapping area of epoxy between the nanoparticles could be the summation of the compressive strain exerted by each nanoparticle. Nevertheless, it remains unclear how 3D conditions might affect this, and further investigations could be carried out to study the strain response under microwave field stimulation with different weight loadings.

It is well known that the embedded FBG sensors would be able to provide more sensitive real-time measurements of the strain response under microwave stimulation without any interference with the field. However, it has been found that the waveform monitoring of embedded FBG sensors would be significantly affected by the curing shrinkage, resulting in a great compressive strain and waveform monitoring could be significantly changed [342, 343]. Therefore, the surface-bonded FBG could perform a more accessible and accurate temperature compensation by incorporating two separate FBG arrays close to each other to measure strain and temperature change, respectively. Since the FBG sensors are adhesively bonded to the sample, the strain measurements from the adhesive and neat epoxy under microwave radiation are investigated to distinguish the nanoparticle-induced strain and thermal-induced strain in the epoxy and adhesives. The black square symbols in Figure 6-2 and Figure 6-3 represent the corresponding theoretically calculated linear thermal expansion of the adhesive used for surface bonding of FBG arrays at different temperature changes. It can be observed that most strain measurements of the neat epoxy exhibit an overall close and slightly lower value compared with the thermal expansion of the adhesive at the same temperature. It could be attributed to the difference in CTEs of the two materials as indicated in Table 5-1. A schematic diagram of the cross-section of an FBG array bonded to the sample surface via adhesives is presented in Figure 6-7 below. As discussed in Section 5.2.2, the adhesive exhibits a relatively lower interaction with the microwave hence a poorer dielectric heating effect. Thus, when the microwave radiation started, as illustrated in Figure 6-7, the neat epoxy sample is firstly heated up due to the microwave selective heating

based on different dielectric loss values. The energy is then transferred to the adhesive via heating conduction from the epoxy sample and the thermal expansion effect in the adhesive is also initiated. However, the epoxy possesses a relatively lower CTE in comparison with that of the adhesive. Consequently, the thermal expanding rates are different due to the mismatched CTEs. As a result, the strain measurements in the FBGs are originated from the thermal expansion of the adhesive that constrained by the epoxy. As demonstrated in Figure 6-7, the CTE mismatch causes the FBG arrays to bend with increasing temperature and bend back when the temperature drops. The interrogator system directly read the wavelength of reflected spectra from FBG sensors consecutively for the period with microwave exposure. Any outliers in the data recording process would appear as isolated data with drastic changes without influencing the next data reading. Therefore, this cyclic behaviour might be an explanation for the 'zig-zag' step-wise increment observed in Figure 5-14. When the temperature ramping rate is slow at 100W, the heat transfer between the epoxy sample and the adhesive is relatively steady compared to that under 440W. As a consequence, the strain measurements display a clearer step-wise increment under 100W. A similar trend could be also observed in Figure 5-14, Figure 5-15 and Figure 5-16. However, in contrast with the strain measurements, the FBG sensors for temperature change measurements are strain-free with no direct contact with the host sample hence no constraints from adhesives. It could also be observed that the step-wise increment in temperature change is displayed in all attempts under both power levels. The only difference is that with the lower temperature ramping rate at 100W, the steps become more clearly visible compared to 440W. In addition, when the temperature change is small with limited microwave interaction with the samples placed vertically and diagonally in the oven, clear steps could also be observed in Figure 5-25 and Figure 5-26. Although the temperature change FBG sensors are free from adhesives, there still exists air between the FBGs and host material. The observation of a 'zig-zag' increment in temperature change measured by FBGs could be attributed to the heat conduction process from the host material to air, then finally FBGs.

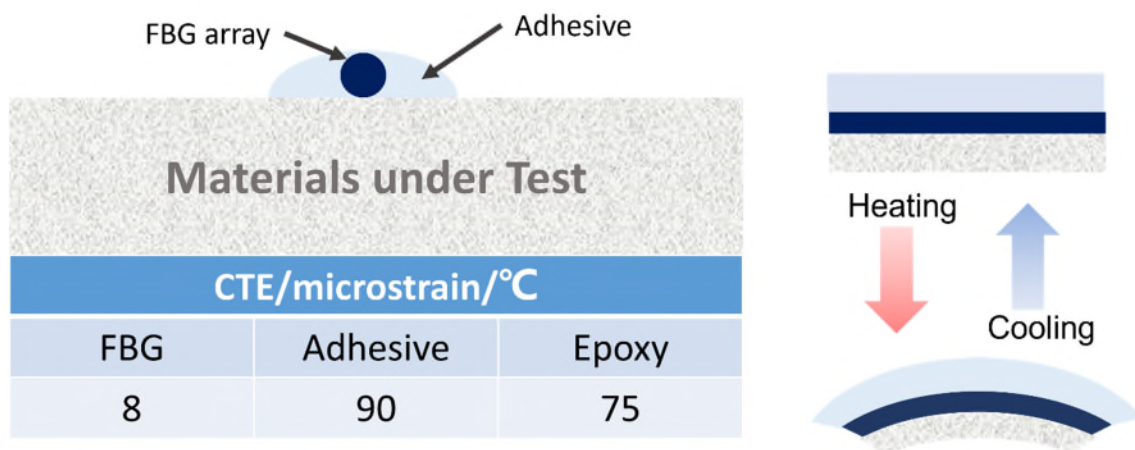


Figure 6-7 Schematic diagram of adhesively-bonded FBG arrays to the sample's surface and nonuniform thermal expansion due to mismatch in CTEs.

It is also noteworthy that the unanticipated finding of a 'sudden drop' in strain measurement of the middle FBG sensors is presented in Figure 5-10 and Figure 5-11 under both power levels. The sharp changes in strain measurements could imply the onset of significant anomalies in the samples. In the first attempt, this surprisingly sudden drop happens at the beginning of the microwave exposure at 1045 microstrain under 100W and 1261 microstrain under 440W, which could be an implication of existing compressive strain around the middle FBG sensor. It is discussed in Section 5.2.2 that the temperature when this unusual phenomenon happens is under 31°C, hence the possible thermal effects could be ruled out. Such phenomenon could not be observed in the adhesive and neat epoxy when they are solely interacting with the microwave field as shown in Section 5.2.2. Also, the FBG arrays for strain measurements on each sample are adhesively bonded to the surface and disposable. If this phenomenon is caused by an error in the interrogator during data collecting, it is highly unlikely that this happens in both cases in the FBG sensor at the same region in different FBG arrays. However, the reason for the drastic strain change under both power levels from the first attempt could not be fully justified as multiple erroneous data are displayed, especially under 440W. Therefore, in order to rule out the error from the data reading from the interrogator, a second attempt has been made to investigate the strain measurements under 440W for two groups of the neat epoxy and the Si-BaTiO₃/epoxy samples. Similar phenomena are observed in the

strain measurements from Si-BaTiO₃/epoxy sample 1 and sample 2 when placed horizontally like in the first attempt. The strain measurement results only showing the ‘sudden drop’ events in different samples are presented in Figure 6-8 below.

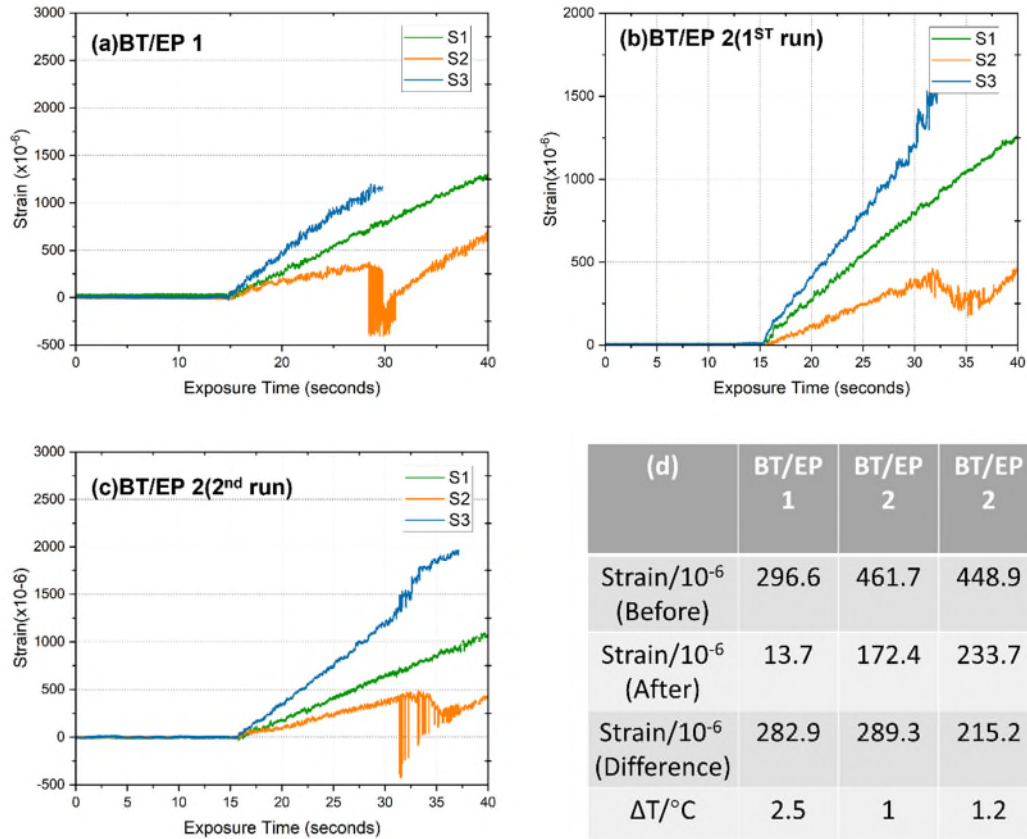


Figure 6-8 Strain measurements of the second attempt at 440W of (a) Si-BaTiO₃/epoxy sample 1, (b) Si-BaTiO₃/epoxy sample 2 first horizontal run, (c) Si-BaTiO₃/epoxy sample 2 second horizontal run, and (d) strain and temperature change data before and after the ‘sudden drop’ from the FBGs.

It could be seen from Figure 6-8 that the decline in strain measurements occurred in all three microwave tests with different samples and FBG sensors. As presented in Figure 6-8 (d), the changes in strain measurements indicate that the compressive strain fields have fairly close values while the temperature change is only up to 2.5°C with insignificant thermal effect introduced. It is also worth noting that there is a clear trace of data outliers due to the fault in the interrogator in Figure 6-8 (a) and (c), which only displayed as isolated data without affecting other neighbouring readings. Therefore, the erroneous data could be ignored and

excluded from the analysis hence didn't affect the results. In comparison with the data from the first attempt at 100W, the declines in measured strain are considered to be more evident and reliable under 440W. It has been discussed in Section 2.2.1 that there is a critical value of electric field strength for all ferroelectric materials, namely coercive field, and it is significantly dependent on the temperature and crystal structure. When the applied electric field strength reaches this critical value, all the polarisations that exist in the ferroelectric domains could be oriented in the same direction as the electric field. Under 440W, the effective strength of the electric component from the microwave at the region of the middle sensor could be sufficient enough at the start of the 'sudden drop' events, and it could introduce the compressive strain field by the ferroelectric BaTiO₃ nanoparticles due to the DW movement result from the polarisation orientation in the domains. The temperature ramping rate is slow enough in the middle sensor and such phenomenon is not masked by the strain induced by thermal expansion. According to the data from the temperature change of middle sensor 2 (orange) as presented in Figure 6-8 (d), the temperature changes at these onsets of such strain drop events fell in the range of 11.2°C to 16.3°C, which might be a critical temperature change for the compressive strain to manifest without masked by the thermal expansion. Unlike epoxy nanocomposite samples placed horizontally in the microwave oven, both vertically and diagonally placed samples failed to show any observable event with field-induced compressive strain field. It could be seen from Figure 5-25 that the overall temperature is below 7 °C due to the lack of microwave interaction, therefore the microwave energy absorbed by the sample might not be sufficient to trigger a notable difference in the strain measurements during microwave exposure. Also, under the diagonal placement as presented in Figure 5-26, only sensor 1 presented a notable increase in the temperature change. It could be speculated that the temperature ramping rate is too high hence the strain measurements could be dominated by the thermal expansion effect due to microwave heating.

In general, these experimental findings raise intriguing questions regarding the mechanical response of ferroelectric materials in a polymer composite material and the extent of the effects it introduced in its surrounding matrix. The existence

of the compressive strain field is experimentally investigated and discussed in this study. It is also an important first step to build an understanding of the mechanical behaviour of the BaTiO₃ nanoparticles embedded in epoxy under microwave radiation. These findings could be employed for the future development of a multi-functional nanocomposite with self-adjusting properties in response to an externally applied electromagnetic field. Such composite material has particular advantages over other multi-functional composite materials owing to its ability to tailor the material properties remotely with varying electromagnetic field strength and these advantages make it particularly valuable for engineering applications in various fields.

Nonuniformity of the Microwave Oven.

The non-uniformity of the microwave field distributed in the oven and the samples during exposure and the effect that could be imposed on the results are discussed in this section. When a material is placed in a microwave oven, the energy is transferred directly into the material via different mechanisms of the material/microwave interaction at the molecular level. This process is highly dependent on the nonuniformity of the microwave field distribution, and it is also a critical factor that affects the behaviour of the BaTiO₃ nanoparticles embedded in the epoxy resin. However, the spatial distribution of the varying microwave field is difficult to measure and no studies to date have ever managed to provide precise quantification of such nonuniformity. Various computational models are employed to visualise the variation of microwave field with changing parameters from the loaded material (e.g., shape, volume, and dielectric properties), and the microwave oven (e.g., size, frequency, and power level) [344, 345]. As the microwave travels through the material, the microwave power decays due to the absorption by the material as it goes deeper and finally diminishes to zero. As a result, the distribution of the microwave field within the material is nonuniform. For the 15 wt.% Si-BaTiO₃/epoxy samples, the penetration depth calculated by Equation 3-69 is approximately 0.86m, based on the measured dielectric properties in Section 5.1.4 at 2.5 GHz. This value indicates that approximately 63% of the energy from the incident microwave is lost at this distance under the

sample surface. Therefore, for a Si-BaTiO₃/epoxy sample with 3 mm thickness in the microwave oven, it is a reasonable assumption that the microwave fully penetrates the sample in Section 5.2. Apart from the nonuniformity caused by the penetration depth of the microwave, there is also another factor that affects the nonuniform electric field distribution in the material, which is the standing waves formed in the microwave oven and it is extensively studied in previous studies [346-348]. When the microwave field transmits and reflects within the cavity of the microwave oven, the standing waves form and the 'hot spot' phenomenon manifests. The distance between two 'hot spots' is half of the wavelength of the incident microwave, which is approximately 60mm. Therefore, the temperature change measured by FBG sensors in Section 5.2.1 exhibit different heating rates along with the 130 mm sample. Therefore, a computational model should be developed in the future study to simulate the varying electric field within the microwave oven cavity and investigate the effect of different oven parameters such as different frequencies and powers.

Theoretical Calculations

To build a further understanding of the field-induced strain by comparing the theoretical and experimental work, the theoretical value of the nominal eigenstrain within the BaTiO₃ nanoparticle when triggered under microwave radiation is first calculated with data acquired from the first attempt at different power levels in the subsection below.

The theoretical power absorbed by the material is evaluated by the method of the energy balance of the microwave heating effect. At power setting 100W, the average power per unit area in the 354x338 mm microwave oven is calculated as follows:

$$I = \frac{P}{A} = \frac{100}{0.354 * 0.338} \approx 835.8 \text{ W/m}^2 \quad 6-2$$

From Equation 3-70 and Equation 3-71, the peak electric field strength E_m and root-mean-square E_{rms} of the incident microwave field is:

$$E_m = \left(\frac{2I}{c\epsilon_0} \right)^{1/2} = 793.5 \text{ V/m} \quad 6-3$$

$$E_{rms} = \sqrt{E_m^2/2} = 561.1 \text{ V/m} \quad 6-4$$

Similarly, for the 440W microwave power level, the peak electric field strength E_m is $1.67 \times 10^3 \text{ V/m}$, and the E_{rms} is $1.18 \times 10^3 \text{ V/m}$.

The estimated electric field is the power absorbed by the air. However, it is assumed that when the microwave field generation is initiated by the magnetron, the electric field strength within the microwave oven is assumed to be equivalent to the value of the E_{rms} as the dimension of the sample (4 cm^3) is relatively smaller than the cavity size (27520 cm^3). The energy absorbed as a function of time is calculated based on the E_{rms} calculated above is estimated as follows:

$$P_{estimated} = 2\pi f \epsilon_0 \epsilon'' E_{rms}^2 V t \quad 6-5$$

The strain and temperature measurements as a function of energy absorbed in Joules are presented below.

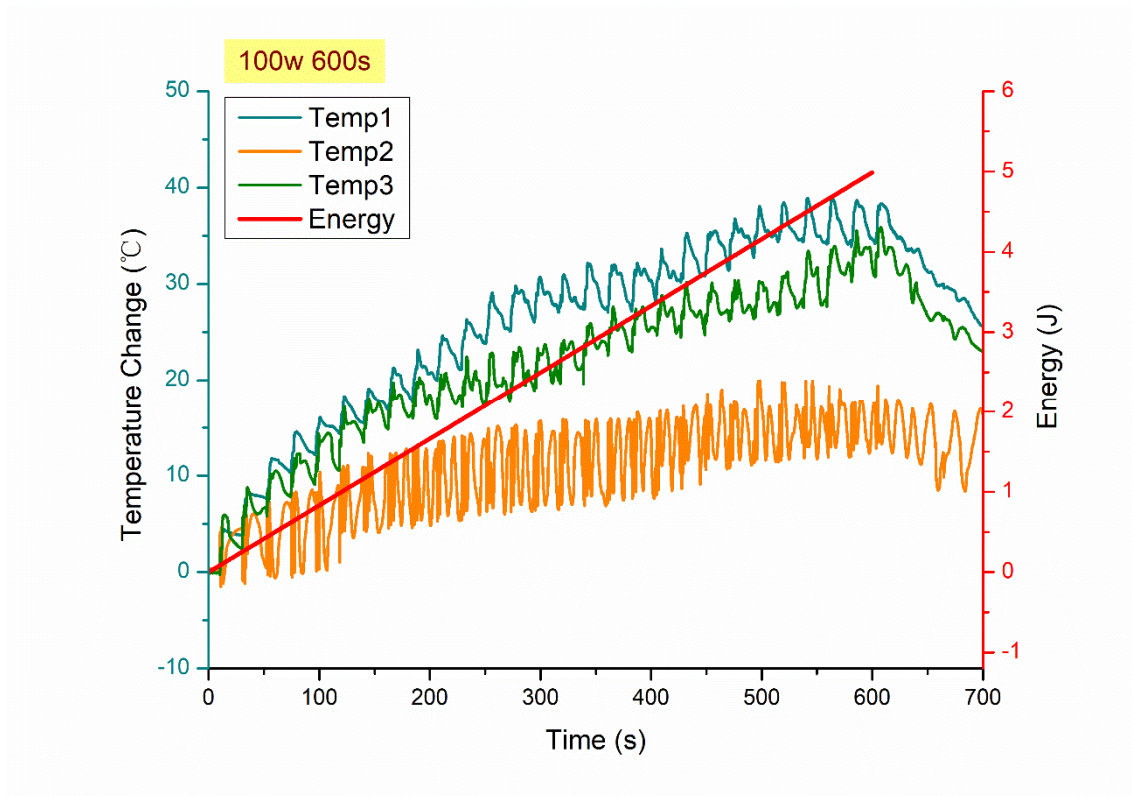


Figure 6-9 Temperature change measurements (microstrain) by FBG sensors (left), and energy absorbed (right) versus time (s) under 100W.

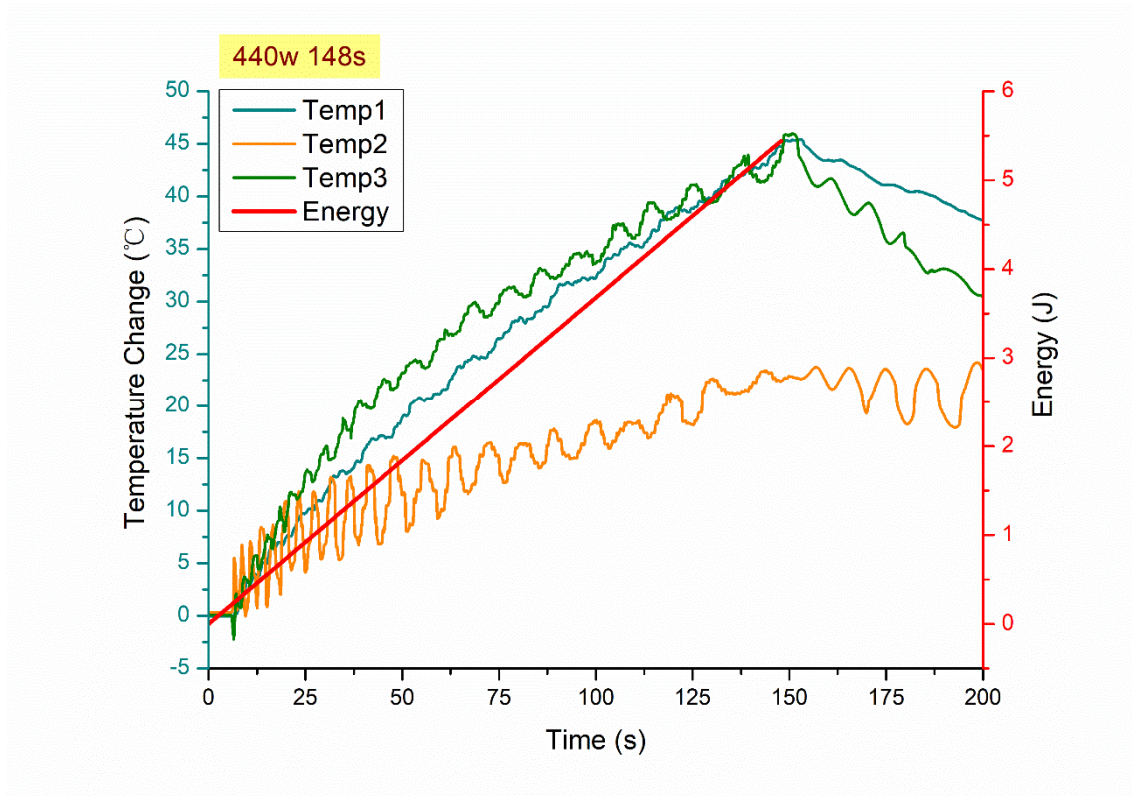


Figure 6-10 Temperature change measurements (microstrain) by FBG sensors (left), and energy absorbed (right) versus time (s) under 440W.

The $P_{estimated}$ is not a validated estimation of the energy absorbed for the given microwave exposure time as the value of E_{rms} is only valid for an empty cavity. However, it could be observed from Figure 6-9 and Figure 6-10 that, the energy absorption rate is close to the rate of temperature rising in FBG sensors. At the beginning of the microwave exposure, the temperature rising exhibits a similar rate compared with the energy absorption rate. As the exposure time increases, the temperature rising rate becomes significantly slower as illustrated in Figure 6-9 and Figure 6-10. The 'hot spot' theory due to the non-uniformity of microwave fields is proposed to be the possible explanation of this phenomenon as described in Section 5.2.

The internal electric field inside the sample could only be estimated based on the assumption that 100% of energy transfers into heat. Therefore, the external electric field of the incident microwave at the surface of the Si-BaTiO₃/epoxy

sample, $E_{rms,external}$ is solved by Equation 3-74, and employed to be the E_{rms} to solving the Equation 3-25 to estimate the eigenstrain of the BaTiO₃.

$$E_{rms} = \sqrt{\frac{\rho C a \Delta T}{3 \Delta t c \varepsilon_0 \xi \Gamma}} \approx 12.1 \times \sqrt{\frac{\Delta T}{\Delta t}} \quad 6-6$$

Where calculated ρ by given weight and volume is 1.3 g/cm³, C calculated from the DSC spectra is 1.238 J.g⁻¹.°C⁻¹, a is sample thickness 3 mm, c is the speed of microwave (3x10¹⁰ cm/s), ε_0 is the permittivity of the free space (8.85x10⁻¹⁴ F/cm), and ξ and Γ are calculated by Equation 3-75, Equation 3-76, and Equation 3-77 as follows:

$$\xi = 1 - e^{-\frac{2a}{d_p}} \approx 0.007 \quad 6-7$$

$$\Gamma = \frac{4(n_1/n_2)}{[(n_1/n_2) + 1]^2} \approx 0.874 \quad 6-8$$

Where d_p is calculated to be 850 mm, n_1 is 1 for air and $n_2 = \sqrt{\varepsilon'} = \sqrt{4.42}$.

At the beginning of the exposure when the microwave incident the sample at $t = 10s$ under 100W, the rate of temperature rise $\frac{\Delta T}{\Delta t}$ is obtained using the linear fit of the temperature change measurements from FBG sensor 1, which is 0.05.

$$E_{rms} = 2.71 \text{ V/cm} \quad 6-9$$

The eigenstrain of BaTiO₃ nanoparticle movements based on the simplified model of Equation 3-24 and Equation 3-25 at 100W, ε_{BaTiO_3} is:

$$\varepsilon_{100} = \frac{\Delta l_m}{L} = \frac{f_m}{d^2 k} = \frac{\sqrt{2} P_0 E_m}{d^2 k} = 65 \times 10^{-6} \quad 6-10$$

Where P_0 is 0.26 C/m², k is the force constant per unit DW area of BaTiO₃, which is 13.6x10⁸ N/cm² [236].

The domain width d is highly dependent on the grain/crystallite size, therefore, it is estimated to be 4x10⁻⁵ cm with the crystallite size assumed to be equal to the nanoparticle size 200 nm based on the measurements in previous studies [349].

And the strain ε_{440} at $t = 7s$ under 440W with the rate of temperature rise of 0.3, is 144×10^{-6} followed by the same calculation process.

Therefore, for the calculations of the strain in the epoxy matrix, the nominal residual stress of a nanoparticle could be assigned by the strain ε_{440} . Therefore the $\varepsilon^* = \varepsilon_{440} = 144 \times 10^{-6}$.

The Lamé constants of the BaTiO₃ nanoparticle and the epoxy matrix are solved by Equation 3-53 and Equation 3-54,

$$\mu = \frac{Y}{2(1+\nu)} = 1152.7 \text{ N/mm}^2, \mu^* = \frac{Y^*}{2(1+\nu^*)} = 25769.2 \text{ N/mm}^2$$

$$\lambda = \frac{Y\nu}{(1+\nu)(1-2\nu)} = 1880.7 \text{ N/mm}^2, \lambda^* = \frac{Y^*\nu^*}{(1+\nu^*)(1-2\nu^*)} = 38653.8 \text{ N/mm}^2$$

Where the Y is the Young's modulus of the epoxy of 3020MPa, Y^* is the Young's modulus of the BaTiO₃ nanoparticles of 67000MPa, ν is the Poisson's ratio of the epoxy of 0.31, and ν^* is the Poisson's ratio of the BaTiO₃ nanoparticles of 0.30 [350, 351].

By substituting the values of $\lambda, \lambda^*, \mu, \mu^*, \varepsilon^*$, and Equation 3-57, Equation 3-60 could be solved as

$$\varepsilon = \frac{(3\lambda^* + 2\mu^*)(\alpha - 1)}{(3\lambda + 2\mu)(1 - \alpha) + (3\lambda^* + 2\mu^*)\alpha} \varepsilon^* = -85.7 \text{ microstrain}$$

Therefore, the theoretically calculated value of the strain exerted by a BaTiO₃ nanoparticle to its surrounding matrix via DW movements activated by the microwave field is approximately -86.75 microstrain.

This value is derived from the theoretical equations from Section 3 and could only serve as an estimation of the strain field exerted by one nanoparticle that is assumed small enough to be considered as a multi-domain single crystal. The interparticle interactions between the dispersed nanoparticles are not considered in this study. Also, for a simplified model of the DW movements with the oscillation of the electric component of the microwave field, the lag between the polarisation in the domains and the field oscillation is ignored. The actual values could be computationally modelled in the future and could be much smaller than the

theoretically calculated value, thereby a smaller ε . The strain measurements from the FBGs are taken within a region of 5 mm x 0.5 mm as can be seen in Figure 6-6. Therefore, the strain measured from the FBGs consists of the thermal expansion from the host material and the sum of the compressive strain effect introduced by all the nanoparticles in this area. Therefore, in this study, the theoretically calculated value only provides an understanding of the strain level that could be introduced by a single nanoparticle with a perfect DW harmonic movement with the microwave field.

6.3 Post-microwave Residual Effect in the Si-BaTiO₃/epoxy Nanocomposites.

It is discussed in Section 2.1.3 that the electric field-induced strain is predominately attributed to the irreversible domain wall movement in multi-domain ferroelectric crystals. Therefore, when the microwave field is removed, a residual stress field or a crystal structure change due to internal stress might appear in the sample, and Raman spectroscopy is employed in this study to probe any possible residual stress fields that originate from microwave-activated BaTiO₃ nanoparticles. Raman spectroscopy has been widely used in many studies to understand the chemical structure as well as the mechanical properties of materials [352, 353]. The shift of corresponding Raman peaks could be an indication of the changes in the molecular vibration energy due to displaced atomic spacing of the atoms during deformation, namely the strain information [352]. Therefore, the determination of the strain field in the material could be achieved by identifying the peak shifts in the Raman spectra [354-356]. In the meantime, it is also discovered that the changed stress state surrounding the BaTiO₃ could introduce a crystal structure change due to the piezoelectricity effect exhibited in ferroelectric materials as demonstrated in Section 2.2.1. Many studies showed the phase change phenomenon of BaTiO₃ crystals under applied stress field due to a crystal structure change [357, 358], and the Raman spectra are capable of detecting the differences of sharpness according to characteristic Raman peaks of each phase [313].

Raman spectra of the neat epoxy sample and 15 wt.% Si-BaTiO₃/Epoxy nanocomposite samples without microwave exposure have established consistent peaks in the spectra of all three random points as shown in Figure 5-28. Clear characterisation peaks of the BaTiO₃ nanoparticle could be identified from the spectra. It could also be found in the Raman spectra in Figure 5-29 that the blueshift of the characteristic Raman peaks of BaTiO₃ at 250 cm⁻¹ and 515 cm⁻¹ are observed to be 19 and 7, respectively. Such peak shifts could imply the existence of a residual compressive strain field within the nanoparticles in certain regions. Furthermore, the temperature in the Si-BaTiO₃/epoxy sample 1 measured in Figure 5-20 is 85°C (Room temperature at 19°C) where the peak shifts are detected in Figure 5-29, which is far below 140°C when the post-curing shrinkage occurs. The observed Raman peak shifts suggest the presence of a residual compressive stress field within the nanoparticles. This could be a result of the mismatch in CTEs between the matrix and the nanoparticles during cooling off after microwave radiation. In contrast, the characteristic peaks of epoxy show minimal variation. The compressive strain field resulting from the microwave-nanoparticle interaction, as hypothesized in the previous section, is likely to disappear soon after the microwave radiation stopped. Therefore, the Raman results could suggest a reversible strain introduction mechanism. It could also be found that the tetragonality of the BaTiO₃ nanoparticles in Si-BaTiO₃/epoxy sample 2 is significantly reduced due to the elevated temperature over the Curie point at 120°C. No notable residual stress fields are presented in the spectra as the characteristic peaks of BaTiO₃ are lost in the background. Laser with a longer wavelength could be performed in the future with a controlled temperature rising to avoid fluorescence interference in the background of the spectrum. In addition, the temperature in the sample during microwave exposure must be controlled under the phase-transforming temperature to avoid any additional stress introduced by phase change. More Raman spectra should be carried out in the future on different samples with microwave exposure at different power levels to validate the appearance of the peak shifts.

7 CONCLUSIONS

In recent decades, the development of multi-functional materials has been a popular research topic in the field of polymer composite materials. Significant progress has been made in high-performance polymer composite materials with enhanced mechanical properties and self-repairing abilities. However, most of the research in this field focuses on preventing damage before going into service and current repair techniques still heavily rely upon damage detection and inspection. To the best of my knowledge, there has been no previous research that explores the use of ferroelectric materials, which display electro-strains as a second phase in the polymer matrix composite material. Furthermore, little is known about the mechanical behaviour of embedded ferroelectric materials under external electromechanical fields and their potential impact on the stress state of microcracks within their surrounding matrix. Therefore, this study examined the mechanical, thermal, and dielectric properties of ferroelectric filler (BaTiO_3) modified polymer (epoxy) matrix at a lower weight loading up to 15 wt.% and subsequently investigated the internal stress state induced by the BaTiO_3 nanofillers in their surrounding matrix. Silane surface functionalisation of BaTiO_3 nanoparticles is utilised to enable a uniform dispersion and improved interfacial filler/matrix bonding quality. Furthermore, the effect of the incorporated BaTiO_3 nanoparticles in the epoxy resin on mechanical, thermal, and dielectric properties is investigated. FBG sensors are employed in this study to monitor the strain and temperature response of such composite materials simultaneously in a microwave oven and the post-microwave effect is investigated using Raman microscopy. From a short review above, the key findings from the demonstrated results in Chapter 5 emerge:

1. A time-dependent strain field is introduced in the multi-domain BaTiO_3 nanoparticles under the stimulation of a microwave field. The strain is theoretically described with expressions of the deformation from a nanoparticle simplified as a multi-domain crystallite based on an estimated electric field strength introduced by the microwave field at the geometric boundary of the Si- BaTiO_3 /epoxy nanocomposite. The principle of virtual work

is used to estimate the strain introduced within the epoxy matrix by one field-stimulated BaTiO₃ nanoparticle when subject to microwave exposure.

2. In order to achieve the full benefit from the electro-strain behaviour of the BaTiO₃ fillers, uniform dispersion of the nanoparticles in the epoxy matrix is considered to be the primary determinant factor. Large agglomerates are observed in non-functionalised BaTiO₃/epoxy samples due to the attraction between nano-scale particles, and their intrinsic incompatibility with hydrocarbon epoxy matrix. Uniform dispersion of surface functionalised BaTiO₃ nanoparticles ensures a uniform application of the domain wall movements triggered strain field to their surrounding epoxy matrix. Furthermore, it also avoids the negative attributes from large agglomerations to mechanical performances, as the aggregation of nanoparticles might act as a weak spot compared with uniformly dispersed nanoparticles. The efficiency of silane functionalisation on uniform dispersion of BaTiO₃ nanoparticles is demonstrated and it provides more opportunities in the development of composite materials at higher filler content in the future.
3. The curing process of the modified epoxy resin is not affected by the addition of functionalised BaTiO₃ nanoparticles as the change in T_g is insignificant.
4. Sudden drops in strain measurements were observed in different 15 wt.% Si-BaTiO₃/epoxy nanocomposite samples during the microwave exposure at different power levels. To the best of my knowledge, such a phenomenon has not yet been studied and reported in the existing literature. The drop in strain measurements within a short periods of time provides direct evidence of the instantaneous introduction of a compressive strain field. Furthermore, a blueshift of the characteristic peaks of BaTiO₃ is also observed in the Raman spectra after microwave exposure, which is an implication of the residual compressive internal stress field experienced by the nanoparticles. No arcing during the microwave exposure or damage in the FBG sensors could be observed after the microwave stopped. Such strain effect could be interpreted as a compressive strain field introduced by the mismatch in CTEs between the matrix and the nanoparticles during cooling off after microwave radiation.

Our results suggest that there is still much to be done to observe and study this self-tailoring effect in this composite material under a remote field, both qualitatively and quantitatively. Nonetheless, the primary contribution of this study is that it serves as a solid starting point for future research and discussion of such polymer composite materials with embedded ferroelectric materials that could be piezoelectric activated by external electromagnetic fields. The limitations and potential future directions of such research are discussed in the following subsection.

Limitations and Future Works

It is clear that the approach taken in this study to investigate the mechanical response of embedded BaTiO₃ nanoparticles is subject to several limitations, with the primary one stemming from the FBG measurements of the strain and temperature. More works are certainly necessary to further explore this novel idea by employing various other characterisation techniques.

Due to the lack of appropriate characterisation equipment, it was not possible to investigate the behaviour of BaTiO₃ nanoparticles in the epoxy simultaneously under microwave exposure. Therefore, the limitations here of the method used in this study are apparent. The mechanical effect of BaTiO₃ nanoparticles on the surrounding epoxy matrix could not be obtained using a conventional mechanical test simultaneously during microwave exposure. Hence, FBG sensors were employed, owing to their negligible interference with microwave radiation, and a more straightforward approach of using surface-bonded FBG arrays was selected over embedding them into the cured epoxy matrix. One major concern of FBGs is the accuracy of strain measurements. It is expected that the surface-bonded FBG strain sensors are perfectly integrated with the host sample so that the measured strain values are equivalent to those obtained from embedded FBG sensors. Overall, while the use of FBG sensors provides a convenient and non-invasive way to measure strain and temperature in the composite samples under microwave exposure, there are limitations to the accuracy of the measurements. The strain transfer from the host material to the fibre core is affected by the adhesive, and the mismatch in the CTEs of the adhesive and host material as

illustrated in Figure 6-7 can introduce deviations between actual strain and FBG measurements. As a result, the surface-bonded FBG strain sensors often produce underestimated strain values [359]. Therefore, the key problem to be solved regarding surface-bonded FBG sensors is the 'strain transfer'. In this study, the adhesive was sprayed over the top of the FBG arrays that are tape-fixed to the sample surface to improve accuracy by increasing the coverage area over FBG [359]. Furthermore, accurate strain measurements in the host sample also rely on the essential correcting model implemented by the FBG sensors manufacturer. To address this, future investigations could explore the use of FBG sensors with a shorter grating length, which is suggested in other studies to enhance the accuracy to infer the true strain in the sample under measurement [359]. Another limitation in this approach, involving the FBG sensors, is in the temperature measurements. The temperature FBG sensors not only monitor the in-situ heating effect in the microwave oven but also plays an important role in enabling more accurate strain measurements by temperature compensation. The temperature FBG arrays are pre-packed into a capillary glass tube and elevated from the sample surface and the measured temperature is a result of heat transfer firstly from the sample to the air, and eventually to the FBG sensors. Therefore, the accuracy of the temperature measurements is affected by the heat transfer process, which is dependent on the distance between the temperature FBG arrays and the strain FBG arrays. It could be observed from Figure 4-9 that a considerable distance exists between the two FBG arrays and this distance could generate errors in the temperature measurements due to uniform heating from the microwave radiation. To address this limitation, future works involving surface-bonded FBG sensors with temperature compensation could place two arrays closely next to each other to ensure a more accurate measurement of temperature change in the region where the strain is measured.

In addition, future works could further explore the mechanical response of embedded BaTiO₃ nanoparticles. For example, FBG sensors could be embedded into the polymer matrix along different directions to get a three-dimensional investigation of the internal stress field under microwave exposure and possibly achieve closer contact with the embedded ferroelectric particles. Epoxy

nanocomposite samples with larger sizes that cover a certain amount of hot spots could be incorporated with embedded FBGs in different directions to gain a better understanding of the effect of microwave distribution on the field-induced strain field.

While this study provides valuable insights into the mechanical behaviour of BaTiO₃ nanoparticles in a polymer matrix under microwave exposure, it is important to note that several factors were not considered due to the inherent complexity of incorporating ferroelectric crystal nanofillers into the polymer matrix. Assumptions are made and many factors are not taken into consideration at this preliminary stage of investigations. For instance, the influence of the grain boundary effect in BaTiO₃ nanoparticles is not investigated in this study, which could potentially have a strong influence on the mechanical behaviour of the embedded BaTiO₃ nanoparticles. Future studies could address this limitation by incorporating multi-domain single ferroelectric crystals into the polymer matrix as a control group.

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