

Epoxy-Based Fibre Reinforced Nanocomposites: Current Status

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Abstract

The modification of epoxy resins with nanoparticles could endow the materials with some superior properties such as broadening of the glass transition temperatures, modest increases in the glassy modulus, low dielectric constant, and significant increases in key mechanical properties. In the last 15 years, some studies have shown the potential improvement in properties and performances of fibre reinforced polymer matrix materials in which nano and micro-scale particles were incorporated. From the existing literature, considerable effort has been given to the synthesis and processing of these unique polymers, but relatively little work has focused on the fibre reinforced epoxy composites. The purpose of this work, therefore, is to review the available literature in epoxy-fibre reinforced composites manufactured using carbon nanotubes, carbon nanofibre and nanoclays for reinforcement.

Keywords: Fibre-reinforced epoxy composites, carbon nanotubes, nanofibres, nanoclay

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1. Introduction

Epoxy resins are widely used in fibre-reinforced composites due to their superior thermal, mechanical, and electrical properties. Depending on the chemical compositions and curing kinetics, it is possible to vary their mechanical properties ranging from extreme flexibility to high strength and hardness, and physical properties such as adhesive strength, chemical resistance, heat resistance and electrical resistance. The widespread use of the epoxy thermosets, however, is limited in many high-performance applications because of their inherent brittleness, delamination and fracture toughness limitations. The development of improved high performance composites based on thermosetting polymers can only be achieved by simultaneously improving resin, fibre and interface properties. Significant property improvements are currently made possible by (i) using resins, curing agents and co-monomers with new backbone chemistries, which provide networks with reduced moisture absorption, (ii) modification of the thermoset resins with thermoplastic polymer, and (iii) incorporating tough thermoset or thermoplastic films in the form of interpenetrating network systems. The most successful strategies concerning the toughening of epoxy resins involve the incorporation of dispersed elastomeric and thermoplastic phases into the resin matrix, which results in a multiphase polymeric system [1-4]. Unfortunately, such methods generally do not provide adequate improvements in toughness for highly crosslinked, high glass transition temperature (T_g) epoxies and their composites for *e.g.* aerospace and automotive applications. Other successful toughening processes such as through-the-thickness reinforcements or Z-pinning are upcoming and commercially available but they generally require special robotic machines that result to extra manufacturing costs.

A newly developed approach offering promising results and a unique level of mechanical properties enhancement and/or control involves the use of nano-sized organic and inorganic particles. During the past 15 years, a lot of fundamental and applied researches have been carried out in the field of polymer nanocomposites. Due to the molecular size of their reinforcement, polymer nanocomposites offer the possibility to develop new materials with unusual properties. Nano-particles are presently considered to be high-potential filler materials for the improvement of mechanical and physical polymer properties. The nanometric size, leading to huge specific surface areas of up to more than 1000 m²/g, and their unique properties (of at least some of these nano-particles) have caused intensive research activities in the fields of natural and engineering sciences. Candidates in the collectivity of nano-particles with a high-potential for the enhancement of mechanical and physical properties of polymers are carbon nanotubes, nanofibres and nanoclays.

Carbon nanotubes (CNT) were first observed by Ijima [5] in 1991. This new allotropic form of carbon is built up of carbon atoms arranged in hexagons and pentagons, forming cylinders. Typically, carbon nanotubes consist of single-walled tubes (SWNTs) or multi-walled nanotubes (MWNTs) where several nanotubes of decreasing diameter are interlocked. They are flexible and resistant to an applied stress. They have potential applications in various fields such as in field emission devices, electrical and thermal conductivity, hydrogen storage and molecular sieves. Since the beginning of the research on CNT/polymer composites, scientists and engineers were

able to utilise the potential of CNTs as conductive filler already at an early state. The production of some polymer-based composite materials containing carbon nanotubes is described in the literature [6-9]. Nevertheless, major difficulties are found to get the homogeneous dispersion of the nanotubes in the polymer matrices, most often limiting the performances of the recovered composite materials. Another main issue in the realisation of mechanically reinforced CNT/polymer composites is the tuning of interfacial adhesion between the CNTs and the polymer. An experimental determination of the interfacial strength is still a difficult procedure, however, some progress has been made in this field, but most of the potential arises from theoretical predictions [9-11]. The stress-transfer from the matrix to the reinforcements has to be performed via the interface, which can be influenced by a chemical functionalisation of the CNT surface. A tailored functionalisation can lead to the formation of covalent bonds and/or additional dipole-dipole-interactions between CNTs and the polymeric matrix, resulting in a strengthened interface and an improved wettability of the CNTs. Manufacturing of resins with nanotube contents of more than 0.5 wt.% is still a challenge, due to the enormous surface area of CNTs and the resulting increase in viscosity. The methods published to present on the improvement of mechanical properties of polymer composites have mainly focused on the optimization of the manufacturing process of the composites, i.e. with the use of prepared nanotubes.

From the nanofiller reinforcement family of materials, carbon nanofibres (CNF) are one of the most promising mechanical reinforcing materials for polymeric composites. This is attributed to their high axial Young's modulus, high aspect ratio, large surface area, and excellent thermal and electrical properties. The most promising current approaches towards increasing the orientation of nanoscale reinforcements within a matrix include optimisation of the extrusion die [12] and stretching the composite melt to form films [13, 14] and fibres [15, 16]. One complication is that the microstructure of semicrystalline polymer matrices is influenced not only by the processing history but also by the presence of nanoparticles. The addition of various types of carbon nanotubes and nanofibres to polymers has already been observed to influence the crystallisation kinetics and resulting morphology [17, 18]. Such changes in matrix morphology need to be considered when evaluating the nanocomposite performance with regard to the intrinsic filler properties. The effects of carbon nanotubes or nanofibres on such oriented polymer systems, although significant, have not yet been fully established. Finally, it should be noted that the presence of additives such as colouring pigments has been shown to influence matrix morphology during fibre spinning [19], whilst there is the whole technology of nucleating agents which are deliberately added to influence crystalline microstructure.

The other promising nanomaterials are polymer-layered silicate nanocomposites. The layered silicates were first introduced by researchers from Toyota [20] in the 1990s who discovered the possibility to build a polymer-layered silicate nanocomposite from polyamide 6 and an organophilic clay. Their new materials presented significant improvements of their mechanical and physical properties. Following this new approach, other researchers synthesised polymer-layered silicate nanocomposites based on epoxies [21-24], unsaturated polyesters [25], polyurethanes [26, 27], polyimides and polyethers [28], polystyrene [29], poly(ethylene) terephthalate [30] and polycarbonate [31] among many others. There are essentially three different approaches

that may be used to synthesize polymer/clay nanocomposites: the melt intercalation, solution, and in situ polymerization methods [32-34]. In the melt intercalation process, a polymer is mechanically mixed with organophilic clay at elevated temperatures. The polymer chains are then intercalated directly between layers of clay. In the solution method, the organoclays and the polymer are dispersed and dissolved in a polar organic solvent, respectively. The dissolved polymer chains are able to penetrate into the clay layers. A uniform mixing of polymer and layered clay is achieved after the solvent has evaporated. In the in situ method, monomers are used to intercalate directly into the clay layers. Then the monomers are polymerized in the presence of the layers. Although the high aspect ratio of silicate nanolayers is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to face stacking in agglomerated tactics. Dispersion of the clay into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic engineering plastics. The homogeneous dispersion of inorganic layered silicates in an organic medium like a polymer on a molecular scale is realised by treating layered silicates with organic ions in order to make them organophilic. Indeed, layered silicates such as fluorohectorite or montmorillonite have a remarkable ability to exchange ions. Their structure consists of two fused silica tetrahedral sheets sandwiching an edge shared octahedral sheet. Isomorphous substitutions in the tetrahedral and the octahedral sheets cause an excess of negative charges within the layered silicate. These negative charges are counterbalanced by cations situated between the layers and can be exchanged for organic onium ions with long alkyl chains to render the layered silicate organophilic and therefore more compatible with the polymer-matrix. Alkylammonium ions reduce, also, the Van der Waals interactions between the silicate layers, which favours the penetration of the polymer or polymer precursors between these layers and therefore the formation of an exfoliated nanocomposite. So far, most of the scientific work has been focussing on the synthesis of polymer-layered silicate nanocomposites and on the study of their physical and mechanical properties.

A replacement of FRPs by nanocomposites can be regarded as unrealistic, due to the highly developed and well-established conventional fibre-reinforcement of polymers and their still unmatched level of material properties. The rapid development of nano science and technology not only stimulates the research work rigorously, but also accelerates the potential applications in many fields. While most research concerning nanocomposites has been confined only to two-phase nanocomposites (for example, carbon nanotubes-dispersed epoxy), the incorporation of nano-fillers into the polymers is expected to improve the mechanical properties such as fracture toughness and the compressive strength of three-phase composites (for example, glass/carbon fibre reinforced epoxy with carbon nanotubes), as shown in Figure 1 [35].

Figure 1

It is also believed that an addition of small amount of nanoclays into the fibre reinforced epoxy composite system can improve the mechanical properties through the reinforcement of clay particles in the matrix rich region in order to bring the improvement in interfacial and impact properties. A number of studies have been

carried out on either fibre or clay reinforced systems. However, in this present work we are only concerned with a small part of engineering application, *i.e.*, adding nanoparticles in epoxy fibre reinforced composites to make a significant improvement in mechanical properties. Thus, the survey of literature will be limited to the related experimental research in various nanoparticles (nanotubes, nanofibres and nanoclays) and their corresponding properties.

2. Laminated carbon nanotubes (CNT) and carbon nanofibres (CNF) fibre reinforced composites

Nano-scaled fillers such as carbon nanotubes (CNT) and carbon nanofibres (CNF) offer new possibilities towards low-weight composites of extraordinary mechanical, electrical, and thermal properties. Taking into consideration their high axial Young's modulus, high aspect ratio, large surface area, and excellent thermal and electrical properties, these filler can be used as modifiers for the polymer matrices of the fibre-reinforced composites (FRPs) leading to advanced mechanical behaviour [36, 37]. The size scale, high aspect ratio, low density, and other exceptional properties of nanotubes are generally advantageous when they are applied in a variety of applications. However, in the case of nanotube-reinforced polymer composites, there has only been a moderate strength enhancement that is significantly below the theoretically predicted potential [38]. To achieve the full reinforcing potential of nanotubes, there remains two critical issues that have to be firstly solved, (i) the dispersion of nanotubes in a polymer matrix and (ii) the interfacial bonding between the nanotubes and the polymer matrix. In general, weakly interacted nanotube bundles and aggregation of nanotubes would result in a poor dispersion state that significantly reduces the aspect ratio of the reinforcement [39]. The reason for the weak interfacial bonding behaviour lies in the atomically smooth, non-reactive surface of the nanotubes that cannot ensure efficient load transfer ability from the polymer matrix to the nanotube lattice. To solve this problem, a number of methods have been developed to maximize the benefits of nanotubes in polymer composites, *i.e.* surfactant assisted dispersion [40], sonication with high power [41], in situ polymerization [42], electric field or magnetic-induced alignment of nanotubes [43, 44], plasma polymerization [45], and surface modification such as inorganic coating [46], polymer wrapping [47], as well as protein functionalization [48].

One key area where nanocomposites can make a significant impact is in addressing interlaminar toughness in the fibre reinforced composites. Interlaminar toughness improvement of fibre reinforced composites has been in the research focus for a considerable time, since it is directly related to the dynamic as well as the damage tolerance performance of the composite. The problem has been addressed in various ways; stitching [49], Z-pinning [50, 51] or interleaving [52] with a notable increase in toughness while also providing improvement in mechanical properties, such as fatigue life. Other approaches focus on tailoring the matrix or interface properties in order to provide the necessary interlaminar fracture toughness. Notably, matrix toughening may be performed through chemical modification or, more recently with the incorporation of fillers in the matrix material. Interface modification can also be performed by grafting in order to tailor the chemical compatibility between the fibres and the matrix [53].

One of the applications of CNT reinforced polymer for filament wound carbon fibre-reinforced composites (CFRP) was demonstrated by Spindler-Ranta and Bakis [54]. 1 wt.% SWNT was added epoxy to the polymer matrix. However, this study concluded that SWNT did not produce any noticeable affect in the CNT reinforced composites and filament wound CFRP rings. In contrast, Veedu *et al.* [55] reported significant improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping, thermoelastic behaviour, and thermal and electrical conductivities. They presented an approach to the three dimensional (3D) through-the-thickness reinforcement, without altering the two dimensional (2D) stack design, on the basis of the concept of interlaminar CNT forests that provided enhanced multifunctional properties along the thickness direction. The CNT forests allowed the fastening of adjacent plies in the 3D composite. They grew MWNT on the surface of micro-fibre fabric cloth layouts, normal to the fibre lengths, resulting in a 3D effect between plies under loading. These nanotube-coated fabric cloths served as building blocks for the multilayered 3D composites, with the nanotube forests providing interlaminar strength and toughness under various loading conditions.

Gojny *et al.* [56] investigated on interlaminar shear strength of nano-reinforced FRPs and also reported about an efficient technique (mini-calendering) to disperse carbon-based nano-particles in epoxy resins. The application of a mini-calander to disperse carbon nanotubes (and carbon black) proved to be an efficient approach to reach a good state of dispersion and enabled to manufacture high volumes of nanocomposites. (This method is an established and common technique to disperse micro-particles in different matrices, *e.g.* colour pigments for cosmetics or lacquers). A major advantage of the calendaring method is, besides the improved dispersion results, the efficiency in manufacturing of larger amounts of nanocomposites. The produced nanotube/epoxy composites exhibit a significant increase in fracture toughness, as well as an enhancement of stiffness already at low nanotube contents. Later on, Gojny *et al.* [57] investigated the influence of CNTs on the interlaminar shear strength of a glass-fibre-reinforced composite (GFRP). They reported an increase of +19% in interlaminar shear strength with a weight fraction as low as 0.3 wt.% of amino-functionalised double wall CNTs (DWCNT-NH₂) in the epoxy matrix, Figure 2.

Figure 2

It was claimed that the nanometre size of the particles enabled their application as modifiers in fibre-reinforced polymers. The composites were produced via the resin-transfer-moulding process (RTM) and the particles were not filtered by the glass-fibre bundles. A follow-up work by the same research team reported that the interlaminar shear strengths of the nanoparticle modified GFRP were significantly improved (+16%) by adding only 0.3 wt.% of CNTs [58]. The interlaminar toughness (G_{Ic} and G_{IIc}) was not affected in a comparable manner. The laminates containing CNTs exhibited a relatively high electrical conductivity at very low filler contents.

Zhao *et al.* [59] fabricated CNTs and continuous carbon fibre (T300) reinforced unidirectional epoxy resin matrix composites. They prepared CNTs by catalytic decompose of benzene using floating transition method at

1100-1200 °C. Benzene was used as carbon source and ferrocene as catalyst with thiophene. The CNTs used were straight with diameter 20-50 nm, internal diameter 10-30 nm and length 50-1000 µm. The volume fraction of continuous carbon fibre (first filler) in the composites without second filler (CNT) was 60%. The flexural strength of the composites reached the maximum value of 1780 MPa when the weight percent of CNT in epoxy resin matrix was only 3%. The study concluded that flexural strength and modulus of the composites increased firstly and then decreased with the increasing of CNT contents in epoxy resin matrix.

For the concept of non-destructive evaluation, damage sensitivity and reinforcing effect of carbon nanocomposites could be obtained from the electrical volume and contact resistivity measurement with acoustic emissions techniques. Adding conductive particles to an isolating polymer can result in an electrically conductive composite, if the particle concentration exceeds the percolation threshold, which is the particle volume fraction required to form a conductive network through the bulk polymer. Because of their high aspect ratio and strong tendency to reaggregate, CNTs are very effective fillers concerning the implication of electrical conductivity into polymeric matrices. Percolation thresholds as low as 0.0025 wt.% have been reported using MWNTs in an epoxy matrix [60]. The percolation threshold for the materials and the dispersion process used in this work was found to be below 0.1 wt.% [57]. Conductivities of up to 2×10^{-2} S/m could be achieved with unfunctionalised CNTs. The functionalisation of CNTs with amino-groups usually increases the percolation threshold and decreases the maximum achievable conductivity, because the graphitic structure of the nanotubes becomes more defected during the functionalisation process. Furthermore, the average nanotube length is reduced, which explains the increasing percolation threshold [57, 61]. Park *et al.* [62] explored this concept by applying electro-micromechanical technique to obtain the fibre damage and the reinforcing effect of carbon nanocomposites with their content. The sensitivity for fibre damage such as fibre fracture, matrix deformation and fibre tension was highest for 2.0 vol.% CNT composites. They suggested that damage sensitivity by electrical resistance measurement might be related to closely three-dimensional network structure, percolation structure. For CNT composites, mechanical properties and apparent modulus indicating the reinforcing effect increased with CNT content. The researchers confirmed that, apparent modulus measurement by electro-micromechanical test could be applied to evaluate mechanical properties of fibre reinforced composites. Reinforcing effect of 2.0 vol.% CNT obtained from mechanical properties and apparent modulus measurements was highest. In 2.0 vol.% CNT case, percolation structure was observed when compared to 0.1 and 0.5 vol.% CNT cases. Morphological trends were found consistent with the result of damage sensitivity based on electrical properties.

Hsiao *et al.* [63] and Meguid and Sun [64] investigated the tensile and shear strength of nanotube-reinforced composite interfaces by single shear-lap testing. They observed a significant increase in the interfacial shear strength for epoxies with contents between 1 and 5 wt.% of MWNT when compared to the neat epoxy matrix. In particular, instead of processing and characterizing CNT/polymer composites, Hsiao *et al.* [63] explored the potential of CNT to reinforce the adhesives in joining two composite structures. In the study, different weight fractions of MWNT were dispersed in epoxy to produce toughened adhesives. The reinforced adhesives were

used to bond the graphite fibre/epoxy composite adherends. This experimental study showed that by adding 5 wt.% MWNT in the epoxy adhesive, effectively transferred the shear load from the adhesive to the graphite fibre system in the composite laminates and improved the average shear strength of the adhesion by 46% ($\pm 6\%$). Significant enhancement of the bonding performance was observed as the weight fraction of CNTs was increased. As shown in Figure 3(left), the 5 wt.% MWNT effectively transferred the load to the graphite fibres in the adherends and the failure was in the graphite fibre system. On the other hand, for epoxy adhesives containing no MWNT (see Figure 3(right)), the failure occurred at the epoxy along the bonding interface and no significant graphite fibre fracture was observed.

Figure 3

Despite the promising results, the researchers concurred that further experiments involving increasing MWNT weight fractions and more detailed SEM observations are required in order to understand and model the role of the MWNT in enhancing adhesion.

Kim *et al.* [65] directed their work to design radar absorbing structures (RAS) with load-bearing ability in the X-band. Glass/epoxy plain-weave composites of excellent specific stiffness and strength, containing MWNT to induce dielectric loss, were fabricated. The fabrication involved impregnation of glass/epoxy plain-weave composites by the mixture of the matrix and the MWNTs. Then, the MWNT-filled fabric composites were dried for 5–7 min at 100 °C. Drying times increased with MWNT contents. As the viscosity of the premixture increased rapidly over the 3.0 wt.%. The researchers reported that they found it difficult to maintain the uniformity of MWNTs in the matrix. Specimens were cured at stabilized pressure of 3 atm and vacuum-bagged in an autoclave first for 30 min at 80 °C and then for 2 h at 130 °C. The observation of the microstructure of the composites revealed that the uneven distribution of MWNTs could induce a high dielectric loss, which was confirmed through the measurement of permittivity. The optimal design of two-layered RAS, consisting of the MWNT-added glass/epoxy fabric composites, was performed by linking a genetic algorithm with a program for the reflection/transmission of electromagnetic waves in a multi-layered RAS. As a result, a two-layered RAS was designed having 90% absorption of electromagnetic (EM) energy for the entire X-band. An RAS fabrication process was proposed that considered the nonlinearity of thickness per ply with MWNT contents and the number of plies. The comparison between the theoretical and experimental reflection loss confirmed that the process is applicable to the fabrication of multi-layered RAS. However, the authors commented, further studies directed to broadening the absorbing bandwidth of a RAS which is composed of a multi-layered RAS and a frequency selective surface are required.

Various studies can be found in the literature regarding the incorporation of CNFs in polymeric matrices and the final mechanical and/or electrical properties of these materials [66-69]. As in all cases where nano sized fillers are involved, the development of high performance CNF/polymer composites requires homogeneous dispersion of CNFs in the polymeric matrix is crucial to the composite performance. The quality of the stress transfer

between the nanofibers and the matrix material is also reported to play an important role in the composite properties interface quality in order to achieve efficient load transfer from the matrix to the CNFs. Early studies by Hussain [70] reported that matrix reinforcement with nanowhiskers can damage the fibres in composite materials. As such, he incorporated micro and nano scale Al_2O_3 particles in filament-wound carbon fibre/epoxy composites. He observed an increase in modulus, flexural strength, interlaminar shear strength, and fracture toughness when the matrix was filled at 10 vol.% with alumina particles (25 nm diameter). This effect stemmed largely from the large surface area of the filler and the ability of the particles to mechanically interlock with the fibres. Hybrid reinforced composites consisting of two or more different types of reinforcing fibres have also been studied in the polymer matrix composite systems. It was also reported that hybridization by incorporating whiskers into the matrix causes fibre damages resulting in a decrease in ultimate strength. However, the work claimed that the incorporation of rigid spherical filler, especially fine or nano-sized filler, did not cause serious damages to the fibre surfaces.

Further, Mahfuz *et al.* [71] studied the tensile response of carbon nanoparticle/whiskers reinforced composites and observed 15–17% improvement in the tensile strength and modulus. On the other hand, Iwahori and Ishikawa [67] reported that compressive strength improvements in CFRP laminates by using cup-stacked type carbon nano-fibre (CSNF) dispersed epoxy as three-phase composites. Later on, Iwahori and coworkers [68] went a step further and employed two types of CSNF in the difference of aspect ratios, i.e. fibre length of 500 nm to 1 μm (AR10) and fibre length of 2.5 to 10.0 μm (AR50), respectively. These two types of CSNF were dispersed to epoxy resin. At the first trial stage, a manual fabrication process of the composite plates by impregnation of the diluted compound by the same epoxy into dry carbon fibre fabrics was employed followed by the hot-press curing. The compression strength improvements around 15% in the three-phase composites by a loading of CSNF were attained in comparison with the control case of no CSNF. Stimulated by the promising mechanical properties results, they additionally manufactured cup-stacked carbon nanotubes (CSCNTs)-dispersed CFRP fabrics in order to obtain more stable mechanical properties than manual fabrication processes. (Figure 4 illustrates the CSCNTs manufactured).

Figure 4

They evaluated the mechanical properties of the CSCNT-dispersed CFRP and found the improvement in stiffness and strength (*e.g.* compressive strength) in two-phase and three-phase nanocomposite materials. The researchers accepted that another key issue in the prepreg development is an optimization of the aspect ratio of CSNF. Although the details of this process were not disclosed, it is noteworthy that one advantage for a good dispersion is many numbers of edges of graphene sheets appearing on the CSNF surface. Such edges may help to increase interaction between CSNF and polymer due to this cup-stack nature. A good dispersion of CSNF was suggested in the microscopic micrographs for the three phase composites through the prepreg route. Major compression strength improvement in these three phase composites by the prepreg was greater than manually

impregnated cases. In this T-700 CF UD prepreg case, the compression strength in the fibre direction was improved by 25% in comparison with the control (no CSNF) case. However, the elastic modulus in compression of this composite was not affected as naturally expected. More recently, Yokozeki *et al.* [35] investigated the damage accumulation behaviours in carbon fibre reinforced nanocomposite laminates under tensile loading. The nanocomposite laminates used in the study were manufactured from prepregs consisting of traditional carbon fibres and epoxy resin filled with CSCNTs. Thermo-mechanical properties of unidirectional carbon fibre reinforced nanocomposite laminates were evaluated, and cross-ply laminates were subjected to tension tests in order to observe the damage accumulation behaviours of matrix cracks. As shown in Figure 5, the number of matrix cracks in CSCNT-dispersed CFRP is much less than that in the conventional CFRP.

Figure 5

A clear retardation of matrix crack accumulation in the CSCNT-dispersed CFRP laminates (both 5 wt.% and 12 wt.%) can be observed compared to that in the laminates without CSCNT. Fracture toughness associated with matrix cracking was evaluated based on the analytical model using the experimental results. It was suggested that the dispersion of CSCNT resulted in fracture toughness improvement and residual thermal strain decrease, which was considered to cause the retardation of matrix crack formation.

In Wichmann *et al.* [58], different nanoparticles, as fumed silica and carbon black, were used to optimise the epoxy matrix system of a glass-fibre-reinforced composite. Their nanometre-size enabled their application as particle-reinforcement in FRPs produced by a modified-RTM, without being filtered by the glass-fibre bundles. Figure 6 illustrates the schematic drawing of the modified RTM-device.

Figure 6

An electrical field was applied during curing, in order to enhance orientation of the nanofillers in *z*-direction. The interlaminar shear strengths of the nanoparticle modified composites were significantly improved (+16%) and an increase in fracture toughness of 42% by adding only 0.3 wt.% of CNTs. The interlaminar toughness was not affected in a comparable manner. (Only the fumed silica nanocomposites exhibited a negligible decrease in Young's modulus. However, with 0.5 vol.% of epoxy-functionalised fumed silica nanoparticles, K_{Ic} increased by 55%). The laminates containing CNTs exhibited a relatively high electrical conductivity at very low filler contents, which allowed the implication of functional properties, such as stress-strain monitoring and damage detection. It should be acknowledged that traditional fibre-reinforced composite materials with excellent in-plane properties perform poorly when out-of-plane through-thickness properties are important. Composite architectures with fibres designed orthogonal to the 2D layout in traditional composites could alleviate this weakness in the transverse direction, but the efforts so far have only produced limited success. Nevertheless, the combination of a nanotube-modified matrix together with conventional fibre-reinforcements (e.g. carbon-, glass-

or aramid-fibres), could lead to a new generation of multi-functional materials [10]. Besides electrical conductivity, which can be induced by the carbon nano-particles, an additional z -reinforcement can be expected. The fibre-orientation in structural components is usually in plane (x - and y -direction), leading to fibre-dominated material properties in these directions, whereas the z -direction remains matrix dominated. With regard on the nanometric size, carbon nano-particles allow an infiltration between the micro-scaled fibres. The application of CNTs as reinforcing phase should increase the matrix properties, especially in z -direction, equivalent to improved interlaminar properties.

3. Laminated nanoclay-epoxy FRP nanocomposites

Early research reported that nano-fillers-dispersed polymers become brittle compared with the original polymers [72], [73]. Using nanoreinforcements in epoxy matrix, Rice and co-workers [74, 75] found no major improvements of the mechanical properties of carbon fibre-reinforced laminates, even though 2 wt.% of organosilicate induced a modulus improvement of 12% of the nanocomposite as compared with the pure epoxy [76]. However, recent sophisticated studies indicated that fracture toughness of the nanocomposites is higher than that of the neat polymers. It should be emphasised that their work was preliminary and many variables were not explored.

For example, Haque *et al.* [77] using a similar manufacturing process as used by Rice *et al.* [74, 75], (*i.e.* vacuum assisted resin infusion method (VARIM)) showed large improvement of the mechanical properties of their S2-glass fibre laminates and at very low layered silicate content. They showed that by dispersing 1 wt.% nanosilicates, S2-glass/epoxy-clay nanocomposites exhibited an improvement of 44%, 24% and 23% in interlaminar shear strength, flexural strength and fracture toughness, respectively. Similarly, the nanocomposites exhibit approximately 26 °C higher decomposition temperatures than that of conventional composites. The increased properties at low loading were associated to several factors:

- (i) enhanced matrix properties due to lamellar structures,
- (ii) Synergistic interaction between the matrix, clay and fibres, and,
- (iii) Enhanced matrix–fibre adhesion promoted by the clay.

The clays were also presumed to decrease the coefficient of thermal expansion mismatch, significantly reducing residual stresses and leading to higher quality laminates. An increased interfacial bonding, matrix agglomeration and coarse morphology were observed from the fractured surface of low loading nanocomposites. The degradation of properties at higher clay loadings was believed to be caused by phase-separated structures and also by defects in the cross-linked structures. However, the authors acknowledged that further work is necessary in order to achieve fully exfoliated structure in clay–epoxy nanocomposites.

Similarly, Chowdhury *et al.* [78] employed VARIM process to manufacture woven carbon fibre reinforced polymer matrix composites. They investigated the effects of nanoclay particles on flexural and thermal

properties. Different weight percentages of a surface modified montmorillonite mineral were dispersed in SC-15 epoxy using sonication route. The nanophased epoxy was then used to manufacture 6000 fibre tow-plain weave carbon/epoxy nanocomposites using VARIM technique. Flexural test results of thermally post cured samples indicated a maximum improvement in strength and modulus of about 14% and 9%, respectively. Dynamic mechanical analyses (DMA) results of thermally post cured samples showed a maximum improvement in storage modulus by about 52% and an increase in glass transition temperature of about 13 °C. A 2 wt.% nanoclay seems to be an optimum loading for carbon/SC-15 epoxy composites in terms of mechanical and thermal properties. Micro-structural studies revealed that nanoclay promotes good adhesion of fibre and matrix thereby increasing the mechanical properties.

Li *et al.* [79] successfully prepared layered silicate/glass fibre/epoxy hybrid composites using a vacuum-assisted resin transfer moulding (VARTM) process. Figure 7 shows a schematic of the experimental set-up for the closed-mould VARTM process.

Figure 7

They focused on such issues by selecting clay and short length glass fibres to reinforce an epoxy resin. To study the effects of the fibre direction on the clay distribution in the hybrid composites, unidirectional glass fibres were placed in two directions: parallel and perpendicular to the resin flow direction. The intercalation behaviour of the clay and the morphology of the composites were investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The complementary use of XRD and TEM techniques revealed an intercalated clay structure in the composites. Dispersion of clay in the composites was also observed using scanning electron microscopy (SEM); the observed clays were dispersed between both the bundles of glass fibres and within the interstices of the fibre filaments. The mechanical properties of the ternary composites were also evaluated. The results indicated that introducing a small amount of organoclay to the glass fibre/epoxy composites enhanced their mechanical and thermal properties, confirming the synergistic effects of glass fibres and clays in the composites. Elsewhere, Aktas *et al.* [80] developed a novel approach for characterisation of nanoclay dispersion in polymeric composites using electron microprobe analysis (EMPA). Dispersion analysis was performed on three sets of centre-gated discs fabricated by RTM. The first set was neat epoxy polymer without reinforcement, whereas the second set comprised 17 vol.% randomly oriented chopped glass fibre preforms. The last set, in addition to the glass fibre reinforcement, contained 1.7 wt.% Cloisite 25A nanoclay. Upon completion of curing, a sample along the radius of a nanoclay reinforced disc was analysed on a electron microprobe analyser. The results from scanning electron micrographs indicated that nanoclay exists in clusters of various sizes ranging from over 10 μ m down to submicrometre scale. Nanoclay clusters larger than 1.5 μ m, were analysed by digital image processing on the scanning electron micrographs taken along the part's radius. The dispersion of nanoclay smaller than 1.5 μ m was quantified by compositional analysis via wavelength dispersive spectrometry (WDS).

Distribution of nanoclay clusters larger than $1.5 \mu\text{m}$ was found to be approximately constant along the radius with an average value of 1.4% by volume. Similarly, nanoclay clusters smaller than $1.5 \mu\text{m}$ were found to be distributed evenly with an average value of 0.41 wt.%. In addition, the glass transition temperature improved by 11% with the addition of nanoclay.

Gilbert *et al.* [81, 82] and Timmerman *et al.* [83] demonstrated that fracture toughness and mechanical properties are increased by incorporation of metal and inorganic particles. In these studies, they have been developing the concept of La PolynanoGrESS (Layered Polynanomeric Graphite Epoxy Scaled System) which utilizes the nanoparticle effect in an epoxy matrix and scales to a continuous carbon fibre reinforced composites systems. Typically, Timmerman *et al.* [83] modified the matrices of carbon fibre/epoxy composites with layered inorganic clays and a traditional filler to determine the effects of particle reinforcement, both micro and nano scale, on the response of these materials to cryogenic cycling. The mechanical properties of the laminates studied were not significantly altered through nanoclay modification of the matrix. The incorporation of nanoclay reinforcement in the proper concentration resulted in laminates with microcrack densities lower than those seen in the unmodified or macro-reinforced materials as a response to cryogenic cycling. Lower nanoclay concentrations resulted in a relatively insignificant reduction in microcracking and higher concentrations displayed a traditional filler effect. In a recent development, Brunner *et al.* [84] exploited Timmerman *et al.* [83] work on use epoxy with a relatively small amount of nano-size filler as matrix in fibre-reinforced laminates. They [84] focused on investigating whether a nano-modified epoxy matrix yields improved delamination resistance in a fibre-reinforced laminate compared to a laminate with neat epoxy as matrix material. To start with, neat and nano-modified epoxy specimens without fibre reinforcement were prepared for a comparison of the fracture toughness of the matrix material itself. Additional properties of the neat and nano-modified epoxy were also determined (partly taken from Timmerman *et al.* [83]) and compared. The study reported fracture toughness improvement up to about 50% and energy release rates increased by about 20% were observed for addition of 10 wt.% of organosilicate clay.

Several other studies have reported on properties enrichment due to addition of nanoclay in the composite matrices. For instance, Schmidt [85], Mark [86] and Hussain *et al.* [70] demonstrated the possible technology of dispersing Al_2O_3 particles in the matrix and investigated their effect on the mechanical properties of CFRP. The incorporation of the filler particles resulted in higher fracture toughness by improving significantly the toughness of the matrix and the crack deviation. Studies on carbon/SiC-epoxy nanocomposites reported a 20–30% improvement in mechanical properties [87]. Mohan *et al.* [88] evaluated the tensile performance of S2-glass epoxy composites dispersed with alumina nanoparticles up to 1.5% weight fraction and found an increase of 12% in tensile modulus and 8% in tensile strength. Kornmann *et al.* [89] successfully synthesised epoxy-layered silicates nanocomposites based on diglycidyl ether of bisphenol A and an anhydride-curing agent. A manufacturing process using hand lay-up, vacuum bagging, and hot pressing techniques was also developed to produce glass fibre-reinforced laminates with this nanocomposite matrix. Transmission electron microscopy

indicated that silicate layers dispersed in the epoxy matrix present a long-range order with an interlamellar spacing of about 9 nm. X-ray diffraction analysis confirmed this nanostructure both in the nanocomposites and in the fibre-reinforced composite based on the same matrix. Scanning electron micrographs of the laminate with a nanocomposite matrix showed that nanolayers stacked at the surface of the glass fibre, improving possibly in this manner the interfacial properties of the fibres. Flexural testing of the laminates showed that the nanolayers improved the modulus and the strength, respectively, by 6% and 27%. Dynamic mechanical analyses (DMA) of the epoxy and nanocomposite plates and their corresponding laminates showed a systematic glass transition temperature decrease of the nanocomposite based materials. This, the researchers suggested, explained the larger water uptake observed at 50 °C in the plate and the laminate based on a nanocomposite matrix as compared with those based on the pristine epoxy.

Karaki *et al.* [90] incorporated layered clay, alumina, and titanium dioxide into an epoxy matrix and fabricated continuous carbon fibre-reinforced polynanomeric matrices to study tension–tension fatigue behaviour. They found that the number of microcracks in each layer depended on the type of particles and their concentration. Wang *et al.* [91] demonstrated that the exfoliated clay with only 2.5 wt.% in epoxy showed a significant improvement in fracture toughness and concluded that an increase of the microcracks and the fractured surface due to crack deflection resulted in the toughness increase. Siddiqui *et al.* [92] investigated the mechanical properties of nanoclay-dispersed CFRP, and showed that the interlaminar fracture toughness of nanoclay-dispersed CFRP is higher than that of the conventional CFRP. Ragosta *et al.* [93] showed that critical stress intensity factors of epoxy-silica nanocomposites increased with the increase of silica content. Work by Seferis *et al.* [94] demonstrated the ability to incorporate nanosized alumina structures in the matrix and interlayer regions of prepreg-based carbon fibre/epoxy composites. Subramaniyan *et al.* [95] observed that addition of 5 wt.% of nanoclay increased elastic modulus of epoxy resin under compression by 20% and the compressive strength of glass fibre composites with nanoclay when made by wet lay-up technique increased by 20–25%. A proceeding work by Subramaniyan and Sun [96] showed that polymers can be toughened significantly using a relatively small amount of nanoclay particles based on the three-point bending tests of the edge-notched specimens with sharp crack tips. A parallel study by the same authors [97] reported that compressive strength of unidirectional GFRP with nanoclays increased compared to the conventional GFRP.

Hackman and Hollaway [98] studied the potential applications of clay nanocomposite materials to civil engineering structures. They concluded that the materials ability to increase service life of materials subjected to aggressive environments could be utilized to increase the durability of glass and carbon fibre composites. Liu *et al.* [99] demonstrated the improvement of fracture toughness and the reduction of water diffusivity of epoxy/nanoclay composites. Ogasawara *et al.* [100] investigated helium gas permeability of silicate clay (montmorillonite) particles/epoxy nanocomposites. They reported that incorporation of increasing amounts of montmorillonite particles reduced the helium gas permeability. With the increase of montmorillonite loading, gas diffusivity decreased, while gas solubility increased. Helium diffusion behaviour was found to be in agreement to the numerical results based on the Hatta–Taya–Eshelby theory [101, 102]. They revealed that

dispersion of nanoscale platelets in polymer is effective in improving gas barrier property. The study appreciated the fact that surface modified clays are amenable to make organic/clay nanocomposites because of the weak bonding force between layers of montmorillonite [100]. In the study, a typical less viscous epoxy of Epikote 807 base resin was used for better dispersion. It was shown that a loading of the nano-clay of about 4 vol.% (about 6 wt.%) reduced the diffusion coefficient to 1/10, and that the theoretical predictions based on the aspect ratio of 0.001 agreed well with the experimental results.

In an interesting development, Miyagawa *et al.* [103] studied the influence of biobased epoxy organo-montmorillonite clay and PAN-based carbon fibre composites. A sonication technique was utilized to process the organically modified clay into glassy biobased epoxy networks. This process resulted in clay nanoplatelets being homogeneously dispersed and completely exfoliated in the matrix. Carbon fibre reinforced composites were processed by compression moulding, shown on Figure 8, using the biobased epoxy/clay nanocomposites as the matrices.

Figure 8

The study found that the flexural strength and modulus did not change with the use of nanoclay. It was, however, observed that the interlaminar shear strength of CFRP improved by adding 5 wt.% intercalated clay nanoplatelets. Dynamic mechanical analysis conducted yielded an increase of 0.9 GPa for the storage modulus of biobased epoxy at 30 °C with the addition of 5 wt.% exfoliated clay nanoplatelets. The glass transition temperature, however, decreased with addition of the organo-clay nanoplatelets. The CFRP having a neat epoxy resin matrix (diglycidyl ether of bisphenol F (DGEBF)) yielded the highest interlaminar shear strength as shown on Figure 9.

Figure 9

The interlaminar shear strength of the CFRP having neat biobased ELO epoxy matrix clearly showed a lower response than that with neat DGEBF, although the fracture toughness of the neat ELO epoxy was the same as that of DGEBF. The researchers attributed this weaker property to the result of inferior compatibility with the surface treatment of the carbon fibres that caused weaker adhesion at the ELO epoxy/carbon fibre interfaces. When 2.5 wt.% exfoliated clay nanoplatelets were added to the biobased epoxy, the ILSS decreased. In contrast, when 5.0 wt.% intercalated clay nanoplatelets were added to the biobased ELO epoxy, higher interlaminar shear strength was observed versus the neat biobased ELO epoxy. It was concluded that the result of short beam shear tests with intercalated clay nanoplatelets yielded similar trends as the fracture tests. It is appropriate to add on that petroleum-derived epoxy/clay nanocomposites have splendid characteristics, i.e. remarkably increased elastic modulus [11, 104-106] and fracture toughness [107, 108]. The incorporation of biobased glassy epoxy resins reinforced by clay nanoplatelets would be one of the best combinations for developing environmentally

friendly nanocomposites. It can be expected that these developed biobased nanocomposites would be widely used in industrial and structural applications, where they are used as the matrix with high-performance fibres, *e.g.* carbon fibres. Thus, the blend of nanoscale reinforcements, such as organically modified clay, and biobased epoxy resin could result in new advanced materials to satisfy the demanding requirements in different applications.

4. Concluding remarks

Fibre-reinforced composites are a type of engineering material that has exhibited high strength–weight and modulus–weight ratios, even compared with some metallic materials. In the last two decades, some studies have shown the potential improvement in properties and performances of fibre reinforced polymer matrix materials in which nano and micro-scale particles were incorporated. This technology of nano and micro-scale particle reinforcement can be categorized into inorganic layered clay technology, single walled and multi-walled carbon nanotube, carbon nanofibre technology, and metal particle technology. To date, nanoparticle reinforcement of fibre reinforced composites has been shown to be a possibility, but much work remains to be performed in order to understand how nanoreinforcement results in major changes in material properties. The understanding of these phenomena will facilitate their extension to the reinforcement of more complicated anisotropic structures and advanced polymeric composite systems.

One of the technology drawbacks is that the mechanical reinforcement by the application of nano-particles as a structural element in polymers is more difficult to realise and still remains a challenging task. An efficient exploitation of the nanoparticles properties in order to improve the materials performance is generally related to the degree of dispersion, impregnation with matrix and to the interfacial adhesion. The advantage of nano-scaled compared to micro-scaled fillers is their enormous surface area, which can act as interface for stress-transfer. The methods published so far on the improvement of mechanical properties of polymer composites have mainly focused on the optimization of the manufacturing process of the composites, *i.e.* with the use of prepared nanoparticles. The property and performance enhancements made possible by nanoparticle reinforcement may be of great utility for carbon or glass fibre-epoxy composites that are used for the high performance and high temperatures applications such as aerospace engine components and nacelle, storage of cryogenic liquids, and motorsports. Then again, precautionary measures should be observed in high temperatures since the structure and properties of these materials can change radically when they are exposed to extreme temperatures, especially in a cyclical fashion.

Better dispersion of nano-sized, silicate-based filler in epoxy resin is expected to yield improved materials properties in several areas. Various mechanical properties, specifically improved fracture toughness, as well as improved flame-retardant effects are of interest. A key objective of the on going worldwide research is investigating whether a nano-modified epoxy matrix yields improved delamination resistance in a fibre-reinforced laminate compared to a laminate with neat epoxy as matrix material. It is necessary, however, to

evaluate the damage resistance characteristics of three-phase nanocomposite laminates for the enhancement of their applicability to the structural elements. Further, as lamented earlier on, another complication is that the microstructure of semicrystalline polymer matrices is influenced not only by the processing history but also by the presence of nanoparticles. The addition of various types of carbon nanotubes nanofibres or nanoclays to polymers has already been observed to influence the crystallisation kinetics and resulting morphology. Such changes in matrix morphology need to be considered when evaluating the nanocomposite performance with regard to the intrinsic filler properties. The effects of nanoparticles on such oriented polymer systems, although significant, have not yet been fully established. In addition, as mentioned earlier on, it should be noted that the presence of additives such as colouring pigments has been shown to influence matrix morphology during fibre spinning, whilst there is the whole technology of nucleating agents which are deliberately added to influence crystalline microstructure.

Further, through nanoparticles reinforcement, an electrically conductive matrix could provide enhanced feasibilities including stress-strain monitoring or damage detection. The application of an electrical field is known to orient the nanoparticles in the in-field-direction, which may result in an increased efficiency of the *z*-reinforcement of the laminates. As a further benefit, the electrical conductivity in *z*-direction should be increased with this approach. Nanoparticles and especially CNTs provide a high potential for the modification of polymers. They are very effective fillers regarding mechanical properties, especially toughness. Besides, they allow the implication of functional properties, which are connected to their electrical conductivity, into polymeric matrices. The electro-micromechanical technique had been studied as an economical non-destructive evaluation method for damage sensing, characterization of interfacial properties, and non-destructive behaviour because conductive fibre can act as a sensor in itself as well as a reinforcing fibre.

It should be emphasized that the importance of environmentally friendly natural products for industrial applications has become radically crucial in recent years with increasing emphasis on environmental issues, waste disposal, and depleting non-renewable resources. Renewable resource-based polymers can replace petroleum based polymers, and hence, compete or even surpass the existing petroleum-based materials on cost-performance basis and eco-friendliness. There is a growing urgency to develop and commercialize new biobased products that can unhook widespread dependence on petroleum. Functionalized vegetable oils such as epoxidized linseed oil and epoxidized soybean oil are now commercially available as coatings and plasticizer additives. More valuable applications of such functionalized vegetable oils will ultimately reduce the needs of petroleum-based products. In particular, the chief drawback petroleum derived epoxy resins is their high cost. Currently, the price of a general-purpose epoxy resin is higher than the price of functionalized vegetable oils - therefore, modifying epoxy resins with functionalized vegetable oils is beneficial to not only eco-friendliness but also economical. As a result, nanoparticles induction into biobased epoxy materials will possibly be of intense research interest in future.

In conclusion, it is clear from the perusal of the literature that epoxy systems reinforced with nanoparticles fillers is at its infancy and has not been fully explored, and hence, there is a need to explore these aspects. In short,

though the vision of the development of nanocomposite increases more challenges and potentials, there is still a lot of space to advance in the integration of nano science and technology, such as in the combination of research and application.

5. References

- [1] J. Kong, R. Ning, Y. Tang, *J. Mater. Sci.* **2006**, 41, 1639.
- [2] Sritima Kar, A. K. Banthia, *J. Appl. Polym. Sci.* **2005**, 96, 2446.
- [3] A. R. Siebert, in: *Rubber-Modified Thermoset Resins. Based on a symposium held at the 186th Meeting of the American Chemical Society*. Washington, DC, **1984**, 179.
- [4] Dodiuk, H. Kenig, S. Blinsky, I. Dotan, A., A. Buchman, *J. Adhesion and Adhes.* **2005**, 25, 211.
- [5] S. Iijima, *Nature*. **1991**, 354, 56.
- [6] T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Awad, J. Douglas, *Macromol. Rapid Comm.* **2002**, 23, 761.
- [7] J. Njuguna, K. Pielichowski, *Adv. Eng. Mater.* **2004**, 6, 193.
- [8] J. Njuguna, K. Pielichowski, *Adv. Eng. Mater.* **2004**, 6, 204.
- [9] R. Andrews, D. Jacques, M. Minot, T. Rantell, *Macromol. Materials Eng.* **2002**, 287, 395.
- [10] E. T. Thostenson, Z. Ren, T. Chou, *Compos. Sci. Technol.* **2001/10**, 61, 1899.
- [11] J. Njuguna, K. Pielichowski, *Adv. Eng. Mater.* **2003**, 5, 769.
- [12] R. J. Kuriger, M. K. Alam, D. P. Anderson, R. L. Jacobsen, *Composites Part A*. **2002**, 33, 53.
- [13] L. Jin, C. Bower, O. Zhou, *Appl. Phys. Lett.* **1998**, 73, 1197.
- [14] B. Safadi, R. Andrews, E. A. Grulke, *J. Applied Polym. Sci.* **2002**, 84, 2660.
- [15] R. Haggemueller, H. H. Gommans, A. G. Rinzier, J. E. Fischer, K. I. Winey, *Chemical Phys. Lett.* **2000/11/10**, 330, 219.
- [16] S. Kumar, H. Doshi, M. Srinivasarao, J. O. Park, D. A. Schiraldi, *Polymer*. **2002**, 43, 1701.
- [17] A. R. Bhattacharyya, T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge, R. E. Smalley, *Polymer*. **2003**, 44, 2373.
- [18] B. Safadi, R. Andrews, E. A. Grulke, *J. Applied Polym. Sci.* **2002**, 84, 2660.
- [19] A. Marcincin, *Progress in Polymer Science*. **2002/6**, 27, 853.
- [20] A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigaito, *Mater. Res. Soc. Proc.* **1990**, 171, 45.
- [21] T. J. Pinnavaia, T. Lan, Z. Wang, H. Shi, P. D. Kaviratna, *ACS Symposium Series*. **1996**, 622, 250.
- [22] X. Kornmann, H. Lindberg, L. A. Berglund, *Polymer*. **2001**, 42, 1303.
- [23] C. Zilg, R. Thomann, J. Finter, R. Mulhaupt, *Macromol. Mater. Eng.* **2000**, 280-281, 41.
- [24] X. Kornmann, R. Thomann, R. Mulhaupt, J. Finter, L. A. Berglund, *Polym. Eng. Sci.* **2002**, 42, 1815.
- [25] X. Kornmann, L. A. Berglund, J. Sterte, E. P. Giannelis, *Polym. Eng. Sci.* **1998**, 38, 1351.
- [26] C. Zilg, R. Thomann, R. Muelhaupt, J. Finter, *Adv Mater.* **1999**, 11, 49.
- [27] Z. Wang, T. J. Pinnavaia, *Chem. Mater.* **1998**, 10, 3769.
- [28] T. J. Pinnavaia, T. Lan, P. D. Kaviratna, M. S. Wang, *MRS Symp. Proc.* **1994**, 346, 81.

- [29] A. Moet, A. Akelah, A. Hiltner, E. Baer, in: *Proceedings of the 1994 MRS Symposium*. Apr 4-8 1994; San Francisco, **1994**, 91.
- [30] Y. Ke, C. Long, Z. Qi, *J. Applied Polym. Sci.* **1999**, 71, 1139.
- [31] X. Huang, S. Lewis, W. J. Brittain, R. A. Vaia, *Macromolecules*. **2000**, 33, 2000.
- [32] S. Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, 28, 1539.
- [33] L. Jiankun, K. Yucai, Q. Zongneng, Y. Xiao-Su, *J. Polym. Sci. Part B*. **2001**, 39, 115.
- [34] Y. Ke, J. Lu, X. Yi, J. Zhao, Z. Qi, *J. Appl. Polym. Sci.* **2000**, 78, 808.
- [35] T. Yokozeki, Y. Iwahori, S. Ishiwata, *Composites Part A*. **2007**, 38, 917.
- [36] S. Tsantalis, P. Karapappas, A. Vavouliotis, P. Tsotra, V. Kostopoulos, T. Tanimoto, K. Friedrich, *Composites Part A*. **2007**, 38, 1159.
- [37] T. Ishikawa, *Adv. Compos. Mater.* **2006**, 15, 3.
- [38] A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted, A. Hirsch, *Nature Materials*. **2002**, 1, 190.
- [39] A. Kis, G. Csányi, J. -. Salvetat, T. -. Lee, E. Couteau, A. J. Kulik, W. Benoit, J. Brugger, L. Forró, *Nature Materials*. **2004**, 3, 153.
- [40] X. Gong, J. Liu, S. Baskaran, R. D. Voise, J. S. Young, *Chem. Mater.* **2000**, 12, 1049.
- [41] M. S. P. Shaffer, A. H. Windle, *Adv. Mater.* **1999**, 11, 937.
- [42] C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, J. Smith, S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison, T. L. S. Clair, *Chemical Phys. Lett.* **2002**, 364, 303.
- [43] C. A. Martin, J. K. W. Sandler, A. H. Windle, M. -. Schwarz, W. Bauhofer, K. Schulte, M. S. P. Shaffer, *Polymer*. **2005**, 46, 877.
- [44] D. Shi, P. He, J. Lian, X. Chaud, S. L. Bud'ko, E. Beaunon, L. M. Wang, R. C. Ewing, R. Tournier, *J. Appl. Phys.* **2005**, 97, 64312.
- [45] D. Shi, P. He, J. Lian, X. Chaud, E. Beaunon, L. Wang, R. Ewing, R. Tournier, *JOM*. **2004**, 56, 129.
- [46] M. Olek, K. Kempa, S. Jurga, M. Giersig, *Langmuir*. **2005**, 21, 3146.
- [47] A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S. -. Chung, H. Choi, J. R. Heath, *Angew. Chemie - Inter. Ed.* **2001**, 40, 1721.
- [48] S. Bhattacharyya, C. Sinturel, J. P. Salvetat, M. -. Saboungi, *Appl. Phys. Lett.* **2005**, 86, 113104.
- [49] L. A. Mignery, T. M. Tan, C. T. Sun, *ASTM Special Technical Publication*. **1985**, 371.
- [50] D. D. R. Cartie, I. K. Partridge, in: *Proc. of 44th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*. Apr 7-10 2003; Norfolk, **2003**, 1,707.
- [51] A. I. Marasco, D. D. R. Cartie, I. K. Partridge, A. Rezai, *Composites Part A*. **2006**, 37, 295.
- [52] W. S. Chan, C. Rogers, S. Aker, *ASTM Special Technical Publication*. **1986**, 266.
- [53] L. R. Xu, V. Bhamidipati, W. Zhong, J. Li, C. M. Lukehart, E. Lara-Curzio, K. C. Liu, M. J. Lance, *J. Composite Mater.* **2004**, 38, 1563.
- [54] S. Spindler-Ranta, C. E. Bakis, in: *Proc. of 47th International SAMPE symposium*. **2002**, 1775.

- [55] V. P. Veedu, Anyuan Cao, Xuesong Li, Kougen Ma, C. Soldano, S. Kar, P. M. Ajayan, M. N. Ghasemi-Nejhad, *Nature Materials*. **2006**, 5, 457.
- [56] F. H. Gojny, M. H. G. Wichmann, U. Köpke, B. Fiedler, K. Schulte, *Compos. Sci. Technol.* **2004**, 64, 2363.
- [57] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, W. Bauhofer, K. Schulte, *Composites Part A*. **2005**, 36, 1525.
- [58] M. H. G. Wichmann, J. Sumfleth, F. H. Gojny, M. Quaresimin, B. Fiedler, K. Schulte, *Eng. Fract. Mech.* **2006**, 73, 2346.
- [59] D. L. Zhao, R. H. Qiao, C. Z. Wang, Z. M. Shen, in: *Proc. of the Asian International Conference on Advanced Materials (AICAM 2005)*, 3-5 Nov. 2005. Beijing, China: **2006**, 517.
- [60] J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer, A. H. Windle, *Polymer*. **2003**, 44, 5893.
- [61] F. H. Gojny, M. H. G. Wichmann, B. Fiedler, I. A. Kinloch, W. Bauhofer, A. H. Windle, K. Schulte, *Polymer*. **2006**, 47, 2036.
- [62] J. M. Park, D. S. Kim, J. R. Lee, T. W. Kim, in: *Current Trends in Nanoscience - From Materials to Application Symposium A, E-MRS Spring Meeting 2003*, 10-13 June 2003. Strasbourg, 2003, 971.
- [63] K. Hsiao, J. Alms, S. G. Advani, *Nanotechnology*. **2003**, 14, 791.
- [64] S. A. Meguid, Y. Sun, *Materials & Design*. **2004**, 25, 289.
- [65] Chun-Gon Kim, Sang-Eui Lee, Ji-Ho Kang, *Composite Structures*. **2006**, 76, 397.
- [66] J. Xu, J. P. Donohoe, C. U. Pittman, *Composites Part A*. **2004**, 35, 693.
- [67] Y. Iwahori, T. Ishikawa, *Proceedings of the third Japan–Korea joint symposium on composite materials*. **2002**, 191, .
- [68] Y. Iwahori, S. Ishiwata, T. Sumizawa, T. Ishikawa, *Composites Part A*. **2005**, 36, 1430.
- [69] B. A. Higgins, W. J. Brittain, *European Polymer Journal*. **2005**, 41, 889.
- [70] M. Hussain, A. Nakahira, K. Niihara, *Materials Letters*. **1996**, 26, 185.
- [71] H. Mahfuz, A. Adnan, V. K. Rangari, S. Jeelani, B. Z. Jang, *Composites Part A*. **2004**, 35, 519.
- [72] L. S. Schadler, in: *Nanocomposite Science and Technology* (Eds. P.M. Ajayan, L.S. Schadler, P. Braun). Wiley-VCH, Weinheim **2004**, 77.
- [73] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito, *J. Mater. Res.* **1993**, 8, 1185.
- [74] B. P. Rice, C. Chenggang, L. Cloos, D. Curliss, in: *46th International SAMPE Symposium and Exhibition*, 6-10 May 2001. Long Beach, **2001**, 355.
- [75] C. Chen, D. Curliss, *Proc. of SAMPE 46th International Symposium and Exhibition*. **2000**, 1, 362.
- [76] C. Chen, D. Curliss, *SAMPE Journal*. **2001**, 37, 11.
- [77] A. Haque, M. Shamsuzzoha, F. Hussain, D. Dean, *J. Compos. Mater.* **2003**, 37, 1821.
- [78] F. H. Chowdhury, M. V. Hosur, S. Jeelani, *Mater. Sci. Eng A*. **2006**, 421, 298.
- [79] L. Lin, J. Lee, C. Hong, G. Yoo, S. G. Advani, *Compos. Sci. Technol.* **2006**, 66, 2116.
- [80] L. Aktas, Y. K. Hamidi, M. C. Altan, *Plastics, Rubber and Compos.* **2004**, 33, 267.

- [81] E. N. Gilbert, B. S. Hayes, J. C. Seferis, *Polym. Compos.* **2002**, 23, 132.
- [82] E. N. Gilbert, B. S. Hayes, J. C. Seferis, *J. Compos. Mater.* **2002**, 36, 2045.
- [83] J. F. Timmerman, B. S. Hayes, J. C. Seferis, *Compos. Sci. Technol.* **2002**, 62, 1249.
- [84] A. J. Brunner, A. Necola, M. Rees, P. Gasser, X. Kornmann, R. Thomann, M. Barbezat, *Eng. Fract. Mech.* **2006**, 73, 2336.
- [85] H. Schmidt, *J. Non-Crystal. Solids.* **1985**, 73, 681.
- [86] J. E. Mark, *Poly. Eng.Sci.* **1996**, 36, 2905.
- [87] N. Chisholm, H. Mahfuz, V. K. Rangari, A. Ashfaq, S. Jeelani, *Compos. Struc.* **2005**, 67, 115.
- [88] R. V. Mohan, A. D. Kelkar, O. Akinyede, in: *Proc. of 50th International SAMPE Symposium and Exhibition*, May 1-5 2005. Long Beach, **2005**, 2425.
- [89] X. Kornmann, M. Rees, Y. Thomann, A. Necola, M. Barbezat, R. Thomann, *Compos. Sci. Technol.* **2005**, 65, 2259.
- [90] T. Karaki, J. P. Killgore, J. C. Seferis, *International SAMPE Symposium and Exhibition (Proceedings)*. **2004**, 49, 2195.
- [91] K. Wang, L. Chen, J. Wu, M. L. Toh, C. He, A. F. Yee, *Macromolecules.* **2005**, 38, 788.
- [92] N. A. Siddiqui, R. S. C. Woo, J. Kim, C. C. K. Leung, A. Munir, *Composites Part A.* **2007**, 38, 449.
- [93] G. Ragosta, M. Abbate, P. Musto, G. Scarinzi, L. Mascia, *Polymer.* **2005**, 46, 10506.
- [94] B. S. Hayes, M. Nobelen, A. K. Dharia, J. C. Seferis, J. Nam, in: *Proc. of 33rd International SAMPE Technical Conference -Advancing Affordable Materials Technology*. Nov 5-8 2001; Seattle, **2001**, 1050.
- [95] Subramaniyan AK, Bing Q, Nakima D, Sun CT, in: *Proc. of 18th Annual Technical Conference of American Society for Composites*. Gainesville, **2003**, Paper 194.
- [96] A. K. Subramaniyan, C. T. Sun, *Composites Part A.* **2007**, 38, 34.
- [97] A. K. Subramaniyan, C. T. Sun, *Composites Part A.* **2006**, 37, 2257.
- [98] I. Hackman, L. Hollaway, *Composites Part A.* **2006**, 37, 1161.
- [99] W. Liu, S. V. Hoa, M. Pugh, *Compos. Sci. Technol.* **2005**, 65, 2364.
- [100] T. Ogasawara, Y. Ishida, T. Ishikawa, T. Aoki, T. Ogura, *Composites Part A.* **2006**, 37, 2236.
- [101] H. Hatta, M. Taya, *J. Appl. Phys.* **2006**, 58, 2478.
- [102] T. Mori, K. Tanaka, *Acta Metal. Mater.* **1973**, 21, 571.
- [103] H. Miyagawa, R. J. Jurek, A. K. Mohanty, M. Misra, L. T. Drzal, *Composites Part A*, **2006**, 37, 54.
- [104] P. C. LeBaron, Z. Wang, T. J. Pinnavaia, *Appl. Clay Sci.* **1999**, 15, 11.
- [105] J. M. Brown, D. Curliss, R. A. Vaia, *Chem. Mater.* **2000**, 12, 3376.
- [106] H. Miyagawa, M. J. Rich, L. T. Drzal, *J. Polym. Sci, Part B.* **2004**, 42, 4391.
- [107] C. Zilg, R. Mülhaupt, J. Finter, *Macromol. Chem. Phys.* **1999**, 200, 661.
- [108] H. Miyagawa, L. T. Drzal, *J. Adhes. Sci. Technol.* **2004**, 18, 1571.

Caption of Figures

Figure 1 Scenario of mechanical properties improvement of CFRP by incorporation of nano-fillers [35].

Figure 2 Interlaminar shear strength (ILSS) of the (nano-reinforced) GFRPs (EP-epoxy, CB- carbon black and DWCNT – double wall carbon nanotubes) [57].

Figure 3 SEM picture (left) of the fracture surface of the bonding area of the 5 wt.% MCNT + epoxy case; failure at the graphite fibre of the adherends was observed. SEM picture (right) of the fracture surface of the bonding area of the epoxy-only case; failure occurred at the epoxy surface of the adherends and no significant graphite fibre fracture was observed [63].

Figure 4 Schematic view of cup-stacked carbon nanotube (left) [68], (right) typical TEM image [35].

Figure 5 Comparison of accumulation behaviours of matrix cracks in cross-ply laminates; ε refers to applied strain [35].

Figure 6 Schematic of the modified RTM-device. The electrical field can be applied between the brass plates (z-direction). [58]

Figure 7 Schematic of the preparation of nanoclay/glass fiber/epoxy composites using VARTM [79].

Figure 8 Schematic drawing of processing CFRP by compression moulding [103].

Figure 9 Interlaminar shear strength of unidirectional CFRP containing different epoxy matrix [103].

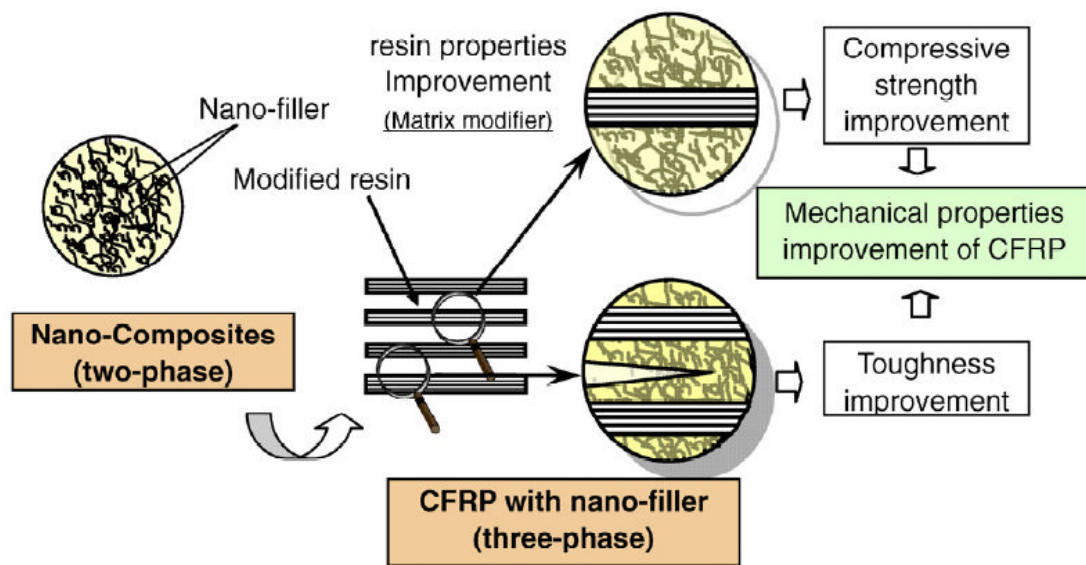


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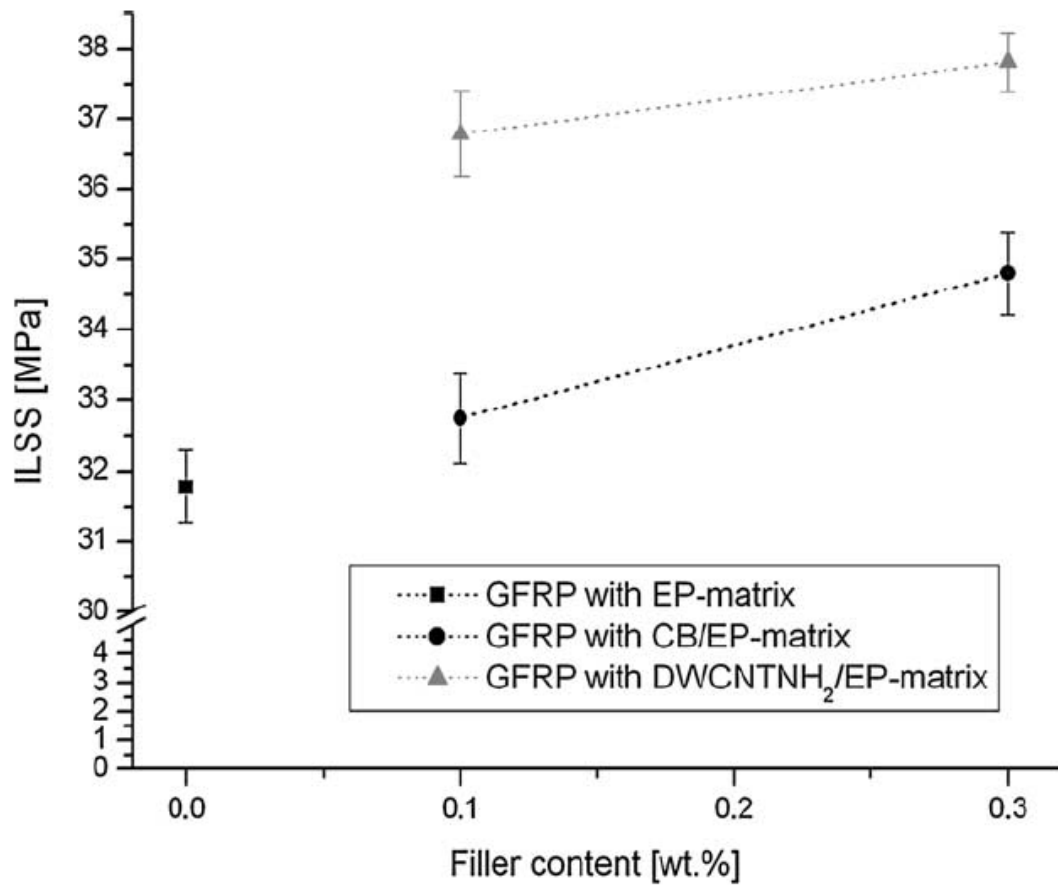


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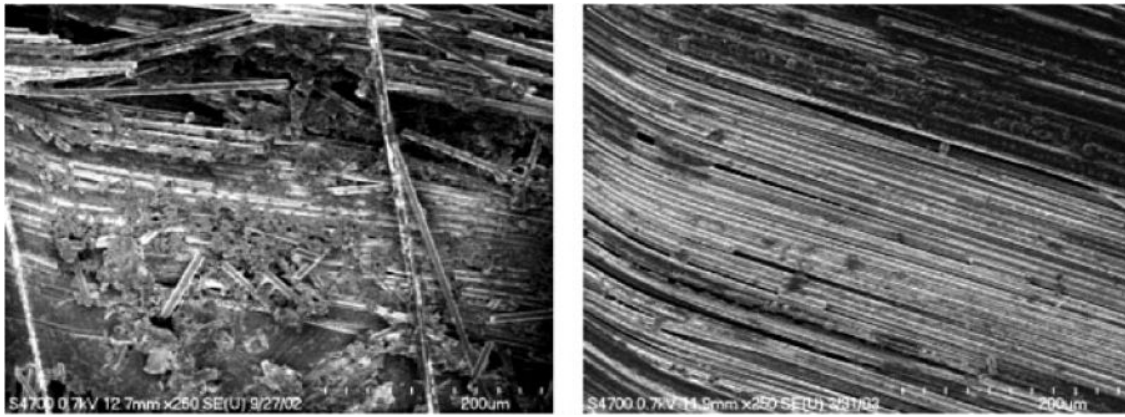


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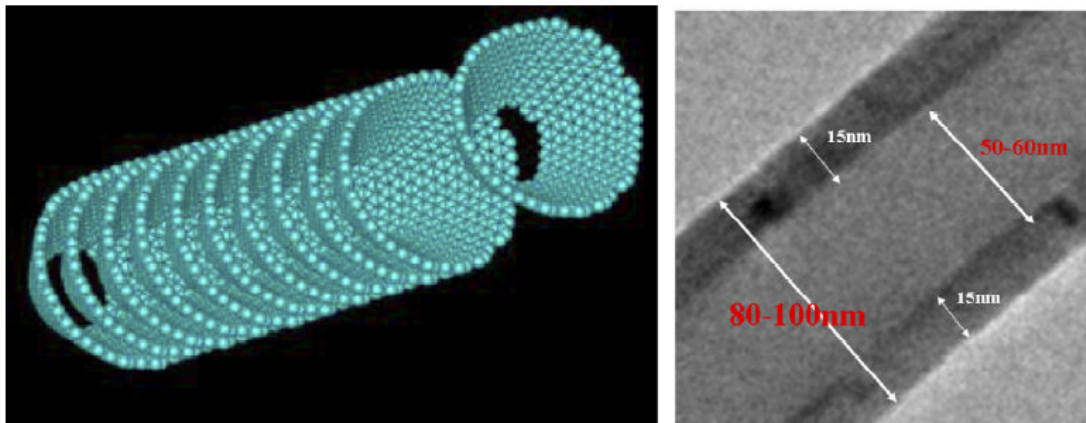
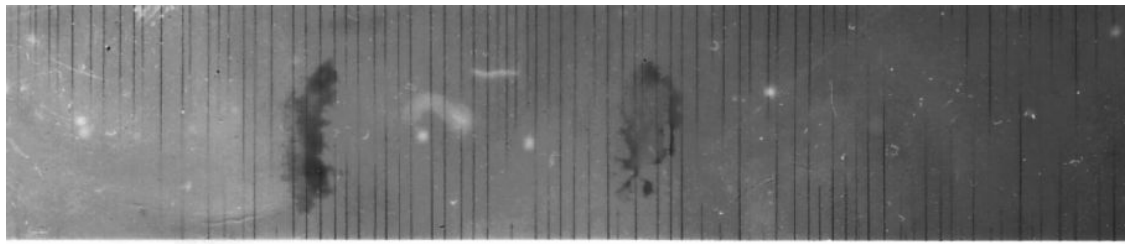
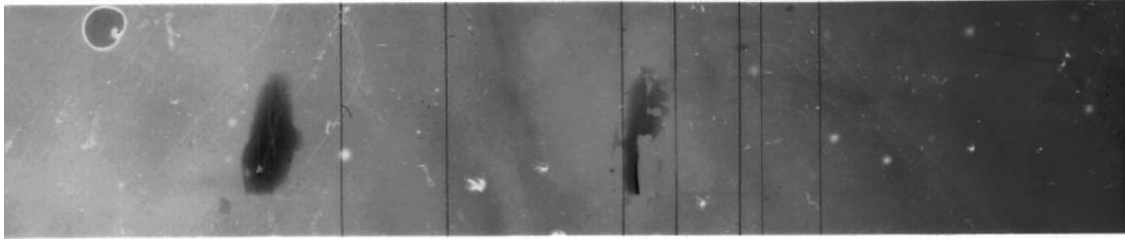


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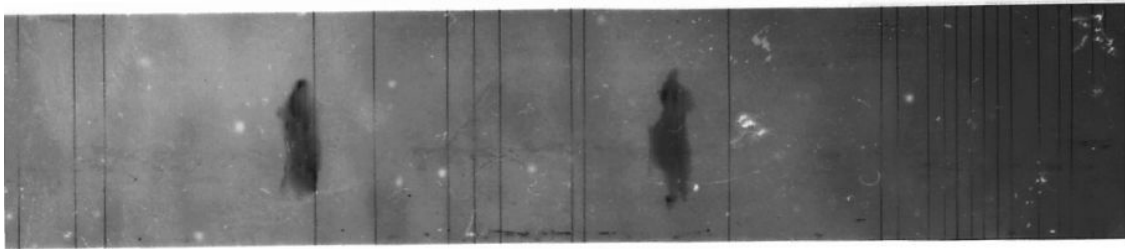


(a) 0wt%, $\epsilon = 0.49\%$

10mm



(b) 5wt%, $\epsilon = 0.50\%$



(c) 12wt%, $\epsilon = 0.55\%$

Figure 5 Comparison of accumulation behaviours of matrix cracks in cross-ply laminates; ϵ refers to applied strain [35].

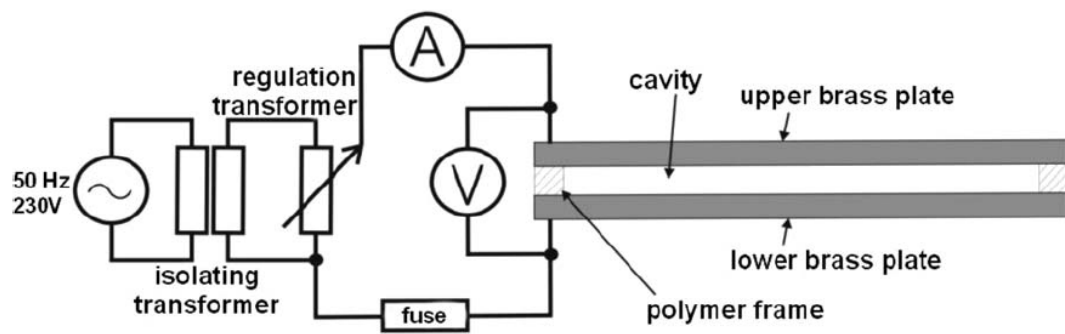


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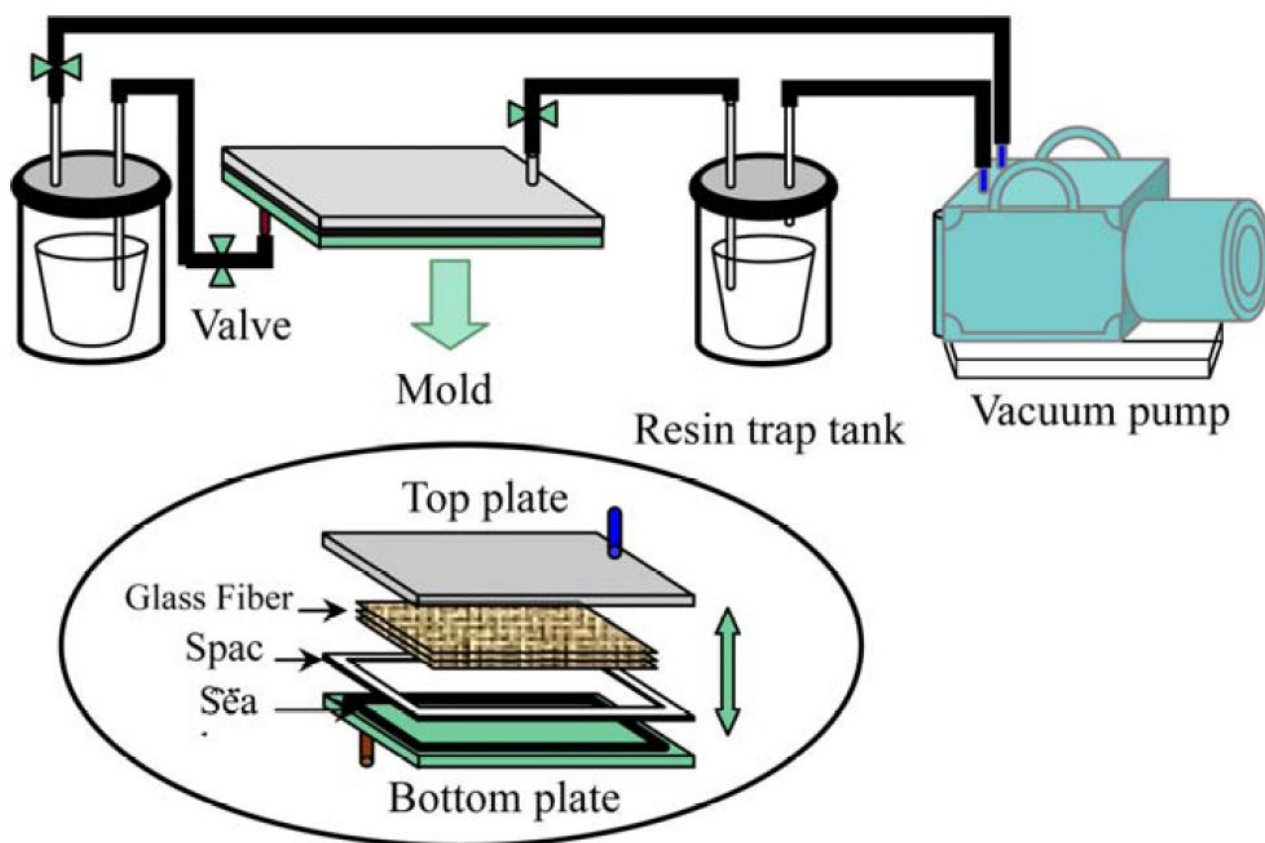


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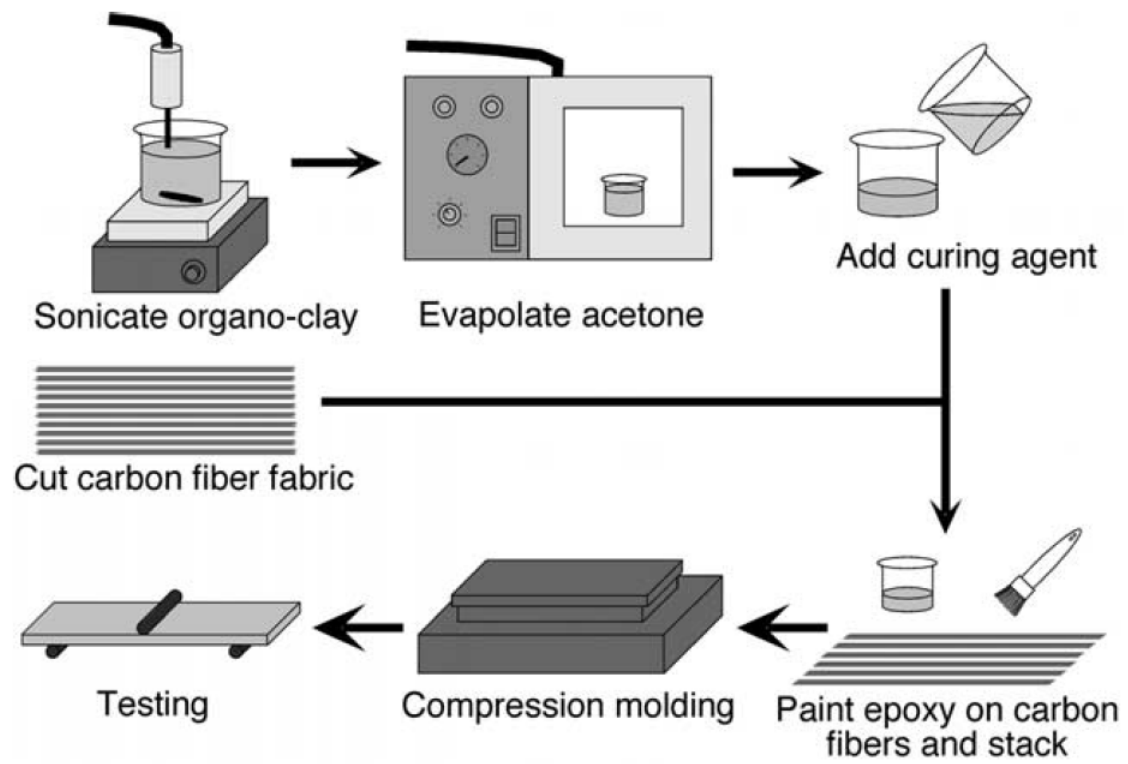


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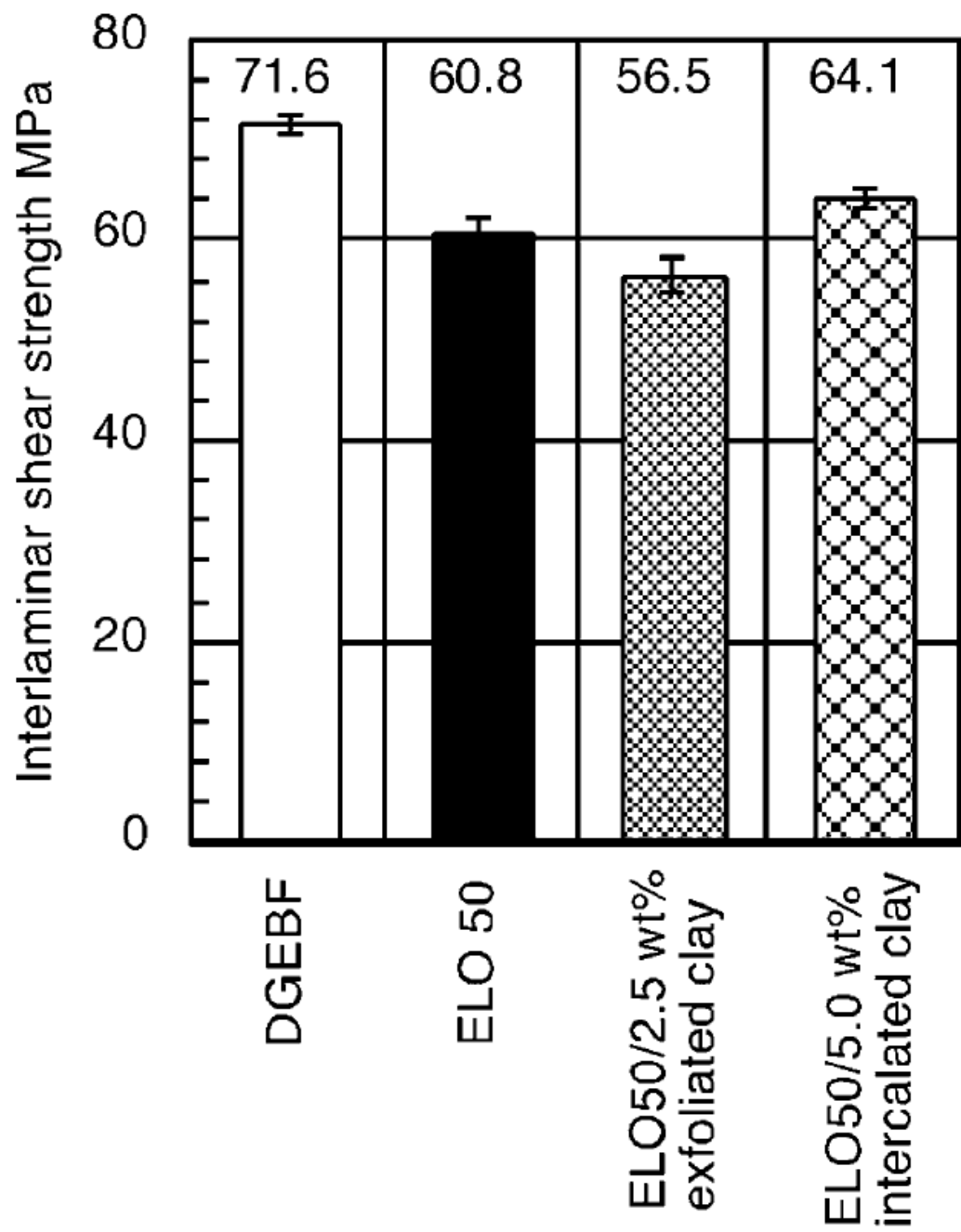


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Epoxy-based fibre reinforced nanocomposites

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