A review on mechanical properties of epoxy nanocomposites

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ABSTRACT

Epoxy resins have highly appreciable design flexibility, good mechanical, thermal, chemical properties and also compatible with a wide variety of reinforcement materials. These excellent properties make epoxy resin as a choice resin for many high-performance engineering applications. Despite their high performances, there are challenges and opportunities to improve further the performance and durability of epoxy composites. This paper presents a survey of the literature on epoxy nanocomposites and the influences of nanofillers on the mechanical properties of epoxy composites. Herein, various pivotal parameters affecting their mechanical properties including their morphology are discussed. This review will have a great impact on the field and will assist researchers in enhancing the mechanical properties of epoxy polymer composites by reinforcing nanofillers.

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1. Introduction

The performance of constituent materials decides the structural integrity, durability, and efficiency of engineered structural components. High performance and cost-effective designs for structural components are indelible top criteria of aerospace, automobile, civil and other energy industries. These critical requirements of industries have led engineers to give high priority in designing high strength materials with reduced weight. The need for lightweight and strong materials has paved the way for the industries to composite materials. Among such composite materials, polymer-based composite materials have attracted the material's scientists and engineers because of their deep-rooted advantage of high strength to weight ratio. Most of the advanced polymer composites are made up of epoxy, a thermosetting resin [1]. Epoxy composites are used for adhesives, automobile, aerospace, wind energy and civil applications due to epoxy resin's outstanding characteristics like good adhesion to fiber reinforcements, compatibility with variety of curing systems, better thermal, mechanical, electrical, and chemical properties [2–3].

However still, a lot of investigations are going on in the direction of enhancing the epoxy's mechanical properties, damage resistance, extreme environmental resistance, and high-temperature performance. Performances of the epoxy-based composites are improved by dispersing second phase material in epoxy resin systems [4]. Efforts have been made during the last few decades towards enhancing the performance of epoxy-based composites by the incorporation of second phase fillers [5–6]. Graphite, silicon carbide, alumina, rubber particles, and elastomers when used these microfillers (second phase) found to improve the mechanical performance of epoxy composites through interfacial attachments with the matrix [7–8]. By reducing the particle's size, the properties of composites have been remarkably improved. Thus researchers [8–10] have observed that the mechanical properties are influenced by the particle size of fillers. The interfacial interactions between particles with a matrix have a significant correlation with the cross-linking network of the polymer [11]. As the particle size reduces, interfacial area (phase) increases in the composite due to increased surface area per unit volume. The symbolic representation shows that when the particle size is reduced the surface area per unit volume increases. By using the second phase material (fillers) at the nanoscale (10^{-9} m) as reinforcement to the epoxy matrix, a lot of enhancements in the composite's properties are observed which is mainly due to the improved interface which results in improved load transferring ability.

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An effective method to fabricate advanced composites is the incorporation of nanofillers in the epoxy matrix combining the benefits of both epoxy and nanomaterials [1,12]. Thus epoxy nanocomposites developed as a novel field of research, to enrich the mechanical properties of the polymeric matrix composites. In the past few decades particularly nanocomposites of the epoxy polymer have attained much attention with more scientists searching for techniques to enrich the composite properties while holding their structural integrity. Unlike epoxy composites that are traditionally filled, this requires dispersant addition at the relatively low amount to accomplish significant improvements in its property, thus creating it appropriate for applications of aerospace. Some of these improvements include an increase in strength values over the flexural, tensile, impact, interlaminar shear test and glass transition temperature [1].

Historically, it is clear from the research on nanomaterials reinforced polymer composites that mostly spherical nanomaterials (isotropic) are focused more on structural based applications. At present, nanomaterials with a high aspect ratio (HAR) like clays, graphene, and nanotubes have received more attention as they possess elongated geometry in one or more directions, which alters chemical, optical, electrical, and mechanical properties anisotropically. State of Isotropy (or anisotropy) and shape have been recognized as an influential tool for engineering properties (thermal, mechanical, electronic, chemical and magnetic) of polymer nanocomposites. In contrast to macrofillers, at the surface of nanofillers, a larger number of constituent atoms or molecules lie, thus resulting in large interfaces, which can influence their mechanical, thermal, electrical and chemical properties, with the resultant attractive feature of enhanced properties. Based on the morphology of nanofiller reinforcements, epoxy nanocomposites can be classified as isotropic nanofillers reinforced epoxy nanocomposites and anisotropic nanofillers reinforced epoxy nanocomposites.

2. Isotropic nanofillers reinforced epoxy nanocomposites

Isotropic nanofiller means a material having identical dimensions in all directions. Here in our discussion, nanofillers, mostly spherical shape, wherein the diameter size of the nanoparticle is considered as one dimension.

Epoxy nanocomposites reinforcing titanium dioxide (TiO$_2$, ~32 nm) nanoparticles have been prepared [9]. Enhancement in modulus and % elongation was reported at the 10 wt% level of nanoTiO$_2$. Epoxy nanocomposite showed % elongation of about 15% higher than plain epoxy. Epoxy nanocomposites were prepared by reinforcing various amounts of nanoalumina (13 nm) up to 10 wt% and studied their effects on mechanical properties [13]. Studies on the effect of alumina nanoparticles demonstrated their ability to enhance stiffness and impact energy. Importance of strength and stiffness of the interface between the epoxy polymer and nanofiller, quality of nanofiller dispersion was reported. Epoxy nanocomposites have been fabricated by incorporation of TiO$_2$ nanofillers (300 nm) into epoxy and studied the effect on flexural and impact properties [14]. Mechanical test results indicated that incorporation of 4 vol% of TiO$_2$ nanofillers have improved both the impact strength and flexural strength by 50% and 13% respectively in comparison to pure epoxy. It was concluded that the TiO$_2$ particles are able to block and deviate the cracks propagation in the composite. The reinforcing effects of TiO$_2$ nanoparticles (5–40 nm) have been investigated and it was established the increase of tensile modulus and flexural modulus for 5 nm size TiO$_2$ (1 wt%) [15]. Reinforcement of TiO$_2$ nanoparticles of various sizes (17 nm, 50 nm, and 220 nm) and at varied addition levels (1%, 3%, 5%, and 10%) investigations have been carried out [16]. Results indicated the intensification epoxy composite' properties as a result of the

adding of a little fraction of TiO$_2$ particles. Maximum strength was achieved in tensile at 3 wt% whereas flexural at 1 wt%. It was established that the quantity of particles existing and its size alter the quality of the interface and ultimately affect the matrix deformation. It was found that the particles of smaller size yield higher properties than bigger ones. Reinforcing influences of varying percentages of titanium dioxide (TiO$_2$) nanofillers to epoxy resin have reported [17]. Reinforcing TiO$_2$ nanoparticles enhanced the tensile properties of the epoxy composite. They observed a 48% improvement in modulus with 10 vol% of TiO$_2$ and strength around 10% at 6 vol% of TiO$_2$. The failure strain of the composites showed the linear trend rise with increasing particle content. These reinforcing effects are ascribed to the presence of the TiO$_2$ nanofillers in the epoxy, which leads to energy dissipation through different mechanisms such as crack deflection, crack pinning at particle, or shear yielding of the matrix.

TiO$_2$ spherical nanoparticles (10 nm) reinforced epoxy nanocomposites have prepared using ultrasonication dispersion technique with different addition levels of fillers up to 10 wt% [18]. Maximum enhancement in flexural strength by 18% and flexural modulus by 27% was observed at 10 wt% addition level. The maximum impact strength enhancement reported was up to 76% at 2 wt% of nanofiller. They attributed this reinforcing effect to homogeneously distributed TiO$_2$ nanoparticles which have led to the toughening mechanisms like shear yielding, ridging of the crack by the nanoparticles, and particle debonding. Epoxy nanocomposites with silica nanoparticles of 60–70 nm size functionalized (f-silica) and as received (u-silica) conditions at different addition levels were prepared [19]. Study on reinforcing effects of both unmodified-silica and functionalized-silica nanoparticles on tensile properties of epoxy composites was carried out and the increased tensile strength and stiffness in comparison to pure epoxy was reported. The failure in silica/epoxy nanocomposites was ascribed to the ductile mode and for the functionalized -silica/epoxy nanocomposites a brittle failure. It was observed that after the addition of the functionalized -silica, polymer chains have become stiffer than that of the unmodified epoxy and u-silica epoxy nanocomposites. The influences of TiO$_2$ nanofiller (50 nm) on properties of epoxy composites at varied addition levels of TiO$_2$ up to 20 vol% were studied [20]. A steady increase in flexural strength and modulus was observed with respect to nanofiller additions up to 4 vol%, thereafter flexural strength was reduced and irregular behaviour in flexural modulus was observed. These reinforcing influences at different nanofiller addition levels were attributed to the nature of the interface between nanofiller and polymer, the constrained movement of polymer chains at nanofillers and agglomeration of nanofillers. Impact properties of nanocomposites reinforced with SiO$_2$ (~17 nm) and Al$_2$O$_3$ (~47 nm) nanofillers up to 3 wt% were reported [21]. Maximum enhancement in impact energy reported with Al$_2$O$_3$ nanofiller was 92% and SiO$_2$ nanofiller was 81%. It was concluded that the physicochemical interplay among the nanofillers and the matrix shows a significant lead in refining the mechanical performance of the composites.

Al$_2$O$_3$ nanofiller reinforced epoxy nanocomposites with different nanofiller addition levels up to 5 wt% and reported the maximum enhancements achieved in impact strength, flexural modulus, and flexural strength as 84%, 52%, and 20% respectively [22]. Reinforcing effects were attributed to the better dispersion of nanofiller and substantial interface among epoxy polymer and the nanofiller. The influence of TiO$_2$ nanoparticles (25–35 nm) on the mechanical performance of the epoxy composite was reported [23]. It was observed that the TiO$_2$ nanoparticles (0.5 wt%) improved tensile strength and toughness. Using different addition levels of 25 nm size ZnO nanoparticles (NPs) epoxy/ZnO nanocomposites have prepared [24]. The observation states that all

nanocomposites exhibit a rise in the tensile properties in comparison to pure epoxy. Strength, stiffness and maximum strain increased with ZnO. Uniform dispersion of the nanofillers was noticed especially at low content (0.8 wt%). Toughness, tensile strength, modulus, and elongation at break (EAB) were improved by 105%, 70%, 69%, and 27%, respectively.

The influence of alumina nanofillers (100 nm) on the impact strength of epoxy nanocomposites have examined with different hardeners up to 5 wt% [25]. Maximum enhancements in impact strength achieved were 89% and 82% with two different hardeners. They attributed this effect to the uniform dispersion nanofiller in the epoxy. The effect of TiO$_2$ nanofillers (up to 20 wt%) on the tensile strength of epoxy composites improved on the increase of nanoparticles' addition up to 10 wt% and then decreased [26]. Compared to pure epoxy, $\sim$26% enhancement in the tensile strength was achieved for 10 wt% TiO$_2$/epoxy nanocomposite, which confirms the efficient interfacial interactions which improve the stress transfer thereby increasing the strength. With up to 20 wt% increase of nanofiller, the moduli of the nanocomposite enhance.

3. Anisotropic nanofillers reinforced epoxy nanocomposites

Anisotropy is the means of materials to show variations in physical properties along different axes which signify different properties in different directions. One of the appealing aspects of nanotechnology is that the size and shape-dependent contributions for properties. After the discovery of carbon nanotubes [27] and nanoclays, the shape of nanofillers is found to have a prominent role in influencing the enhanced performance of nanocomposites. In the literature, a diverse spectrum of few anisotropic nanofillers such as nanorods [28], nanowires [29], nanotubes [30] belonging to 1D; plates and sheets [31–32], belonging to 2D; and pyramids [33–34], stars [35–36], flowers [37], multi-pods [38–39], nanourchins [40], tadpole [41], nanocages [42], nanorice [43–44], nanocorns, nanocubes, nanoboxes, triangular nanoframes, nanodumbbells, belonging to nanostructures were reported by [40]. Distinctive structure and physical properties associated with anisotropic nanostructures have played a significant part in an explosion of research in their reinforced epoxy composites. The research works can be classified as clay-based 2D layered nanofillers, carbon-based nanofillers and metals and metal oxides, carbides based nanofillers.

3.1. Clay-based 2D layered nanofillers reinforced epoxy composites

Clays are the most favourable 2D nanofillers due to their abundant natural availability and their ability to extract in a large scale. Clay minerals are a subdivision of silicates with clay silicate layers of less than 2 μm particle size and 1 nm thick. Clay nanofillers thus contribute to marvellous mechanical properties at relatively low cost. Detailed studies have resulted in the incorporation of different types of nanoclays in epoxy to improve properties [45–47]. The reinforcement effects of nanoclay at 1–10 wt% on the epoxy composites were studied [48], it was observed that with a rise in clay %, the elongation at break decreased and the modulus of the composites increased continuously. Thus 80% enhancement was obtained at 10 wt%. The increased elastic modulus was credited to the exfoliation and good distribution of nanoclay resulting in better interfacial adhesion which hinders the movement of polymer chains under loading conditions. It was concluded that the positioning of clay platelets and the direction of polymer chains concerning the direction of loading determines the reinforcement effects. On mixing nanoclay in epoxy resin, it was observed that the modulus of the epoxy/clay improved linearly by clay addition,

and for the addition of 5 wt%, 40% improvement in modulus was seen [49]. A similar trend in modulus was reported elsewhere [10].

The effect of nanosilicate clay up to 5 wt% on epoxy polymer was studied [50] and shown that for 3% nanofillers flexural strength was increased by 13% and for 5 wt% impact strength increased by 23%. On the whole, high addition levels of nanolayered clay were required to have an appreciable increase in strength. Investigation on the effects of nanoclay up to 5 wt% on the performance of the epoxy polymer was reported and achieved the enhancement by 12.5% and 13.3% in tensile and flexural moduli [51]. This increase was attributed to the transfer of load between matrix and clay, having a higher modulus in comparison to plain epoxy. Up to 4% of addition levels increase the modulus. Further additions lead to improper dispersion, causing agglomerations, resulting in increased viscosity of the mixture and probable creation of air-traps and intensification of microvoids. Thus during the test agglomerations and microvoids increase the stress concentrations and lead to premature specimen failures. The dependence of strain at failure on the interfacial interaction between epoxy and clay layers also identified.

The tensile test was conducted on epoxy-nanoclay composites of clay additions for 1–10 wt% [52]. The tensile strength increased by 7% for 1% of clay and decreased beyond 2%. Similar trends were stated [53]. The addition of nanoclay also resulted in a decrease in the strain at failure linearly with an increase up to 5 wt%; after which, it had a negligible effect. The reduction in tensile strength and strain at failure higher than 1 wt% was ascribed to growth in the number and size of entangled clay clusters. These clusters acted as stress raisers caused to decrease tensile strength and strain at failure. Thus the agglomerated clay clusters were favoured areas for crack initiation, resulting in early failure. Since the nanofiller has a higher modulus than pure epoxy, the possibility of stress concentrations existing at the interfaces is highly probable. Hence while specimens were subjected to tension tests, cracks can begin at these weak areas causing the failure to occur at a lower strength and lower strains at failure [54]. One reason for such reduction was the struggle to degas appropriately due to the increased viscous mixture at high nanofiller levels (5 to 10%), which leads to the initiation of a crack. Lei et al., 2006 and Ha et al., 2007 observed that for nanoclay levels up to 5%, the modulus increased linearly and then got flattened subsequently was observed [55–56]. The elastic modulus enhancement was ascribed to the fine distribution of clay nanolayers. This curbed the movement of polymer chains during loading and also contributed to better interfacial adhesion. Thus the reduction in the strain at failure and improvement in elastic modulus are standard characteristics for polymer–clay nanocomposites. The enhancement of a 20% rise in the tensile modulus of the reinforcing nanoclay (3 wt%) was achieved [57]. In the case of ultrasonically mixed nanocomposites [48], the amount of exfoliation of the large aspect ratio nanoplatelets and greater bond of the exfoliated/intercalated nanoclay with the epoxy yielded pronounced stiffness increase. It was concluded that when submicron-sized particles are homogeneously dispersed gets intercalated contributes to the further influence of the stiffness. Tensile strength values remained almost unchanged. It was presumed that nanoclay collections existing in the epoxy and acted as stress raisers resulting in the composite to break at much lower loads [58–59]. Strain at failure values reduced enormously with the nanoclay addition. The lessening of tensile strength and elongation was supposed to hail from an embrittlement effect initiated by the stiffer clay nanoparticles [53,59]. The properties of plain epoxy and 3 wt% nanoclay epoxy composites have compared, which were prepared using sonication and mechanical mixing methods, resulted in enhanced modulus of the composite [60]. This improvement could be elucidated by the stiffening effect of nanofillers which were sharing a partial load and at the same time

restricted the movement of polymer chains through stress transfer and thereby paving way for deformation failure by shear. The internal stress imposed by dissimilar rates of curing in the epoxy matrix and at epoxy-silicates interfaces reduced the tensile strength of nanocomposites [61]. Epoxy/clay prepared by sonication process showed improved tensile properties in contrast to that fabricated by mechanically mixing process that contributed to the increased aspect ratio of distributed clay layers.

The reinforcing influences of modified clay with fish Deoxyribonucleic acid (D-clay) and Nanomer organoclay (M−clay) on the performance of epoxy composites at 2.5 wt% and 5 wt% were explored [62]. Noteworthy enhancements of 26%, 14%, and 6% fracture toughness, tensile strength and tensile modulus of epoxy composites, respectively, was accomplished with the addition of D-clay at 2.5 wt%. They have noticed that D-clay addition to epoxy resulted in a significant increase in properties as compared to M−clay additions. This phenomenon was the result of the improved clay-matrix interfacial bond, improved dispersion and superior part of D-clay in consuming crack energy by way of several mechanisms such as crack arresting, and crack deviation. A similar trend of enhanced fracture toughness of epoxy composites (Fig. 1) reinforced with 0.06 wt% of silver clusters was reported [63].

[Fig. 1]

Inorganic-organic nanohybrid of clay-chitosan nanoparticles (QCn) was taken as a reactive strengthening agent in the fabrication of toughened epoxy nanocomposites [47]. Thus QCn was incorporated into an epoxy matrix to fabricate EP-Q nanocomposites and commercially modified nanoclay was reinforced into epoxy to prepare EP-M epoxy nanocomposites. Composites up to 5 wt% nanofillers were prepared and were compared with pure epoxy (EP). The 2.5 wt% M−clay addition showed improvement in tensile strength. A decline in tensile strength was noticed for

5% M−clay, whereas for 5% QC-clay the tensile strength increased. Considering the modulus in comparison to pure epoxy, the reinforcement of 2.5 and 5 wt% of M−clay increased up to 17% and 26%, whereas QC-clay addition of the same amounts enhanced modulus up to 54% and 74%, respectively.

3.2. Carbon based nanofillers reinforced epoxy composites

Carbon-based nanomaterials (CBN) are getting attention worldwide with their versatile superiority in flame retardancy, thermoelectrical conductivity, mechanical stability, and biocompatibility. The performance of epoxy-based composites would get enormously improved if carbon nanofillers are homogeneously dispersed in the matrix, which makes consequences in strong interfacial bonding. On the contrary bonding with weak interfacial curbs transfer of load between the fillers and epoxy. Hence, good uniform dispersion along with interfacial bonding of fillers is crucial for improving the properties. Carbon-based nanofillers [64] reinforced epoxy composites are preferred to meet the high mechanical properties demands in aerospace, automobile, and marine applications. The addition of CBN to epoxy is an efficient technique to enhance epoxy composites concerning its mechanical properties [64–66]. The purpose of this section is to furnish an ample understanding of epoxy nanocomposites based on carbon nanomaterials. Attention has been paid to the performance of different anisotropic carbon nanomaterials. A collection of different carbon nanomaterials' structures and their nomenclature are presented.

3.2.1. Carbon nanotubes (CNTs) reinforced epoxy composites

Among the new materials discovered in the last three decades, CNTs are most exciting [27] and have initiated enormous research in supreme areas of science and engineering because of their
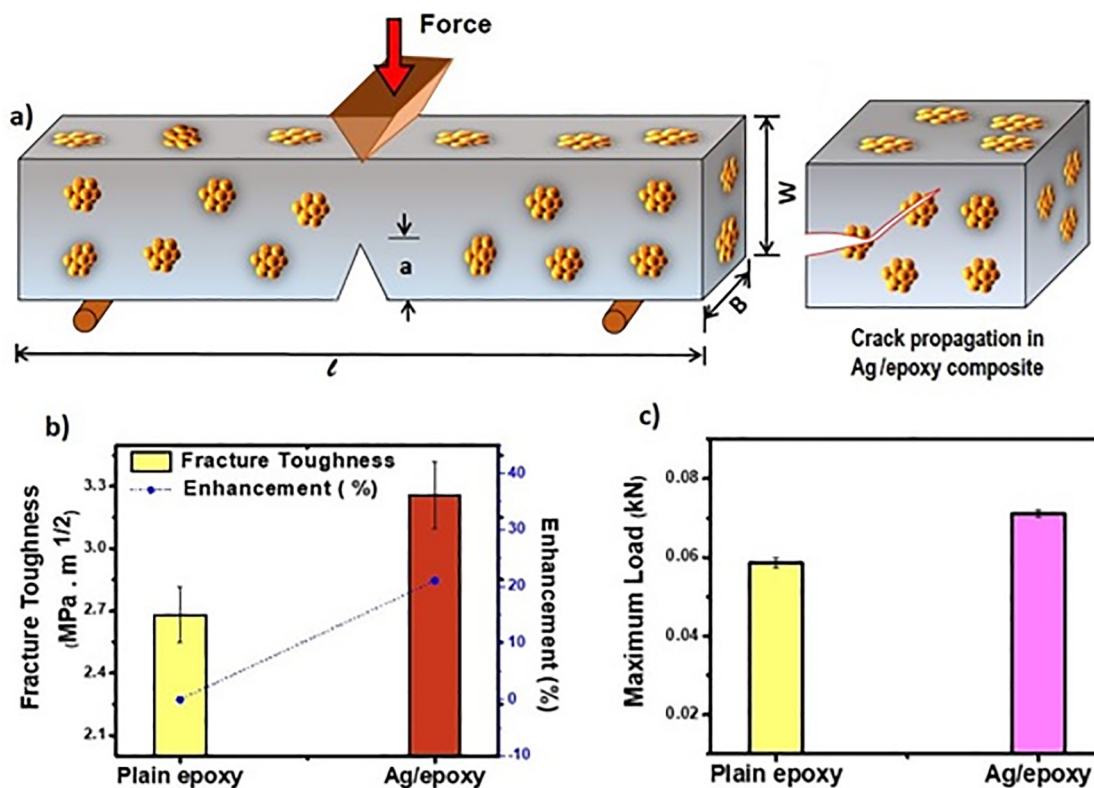

Fig. 1. a) Scheme representing load application and crack resistance offered by Ag clusters; b) Fracture toughness (K_{IC}) values c). Maximum load (P_Q) values of plain epoxy and Ag QCs/epoxy Composites [63].

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superior mechanical, electronic and thermal properties. Recently, great potential reinforcement of CNTs in composites has been shown. The CNT's abilities to carry the load in nanocomposites have been established using experiments [67–68]. As remarkably, CNTs great thermal conductivity has been conveyed, and it leads to the discovery of silicon wafer coated with the graphene layer which yields a super-efficient heating film.

Only low addition levels (< ~5 wt%) of CNTs as reinforcements to polymer composites were identified most suitable, because of the swift increase in viscosity and other difficulties in processing. This was because even though nanotubes were uniformly distributed, it could lead to the rigid gel generation in solvent simply because of their aspect ratio which was high and resultant ability in network forming. MWCNTs are usually tied with the formation of curved agglomerates which was seen in bundles. In best properties enhancement in CNTs/polymer composites, there are numerous fundamental problems to be resolved, i.e., CNTs surface functionalization for good adhesion results in improved dispersion, interfacial adhesion and better configuration of CNTs within the polymer. Chemical functionalization improves the covalent coupling between the matrix and CNTs, and the amino-functionalized MWCNTs usage in epoxy outcomes in increased mechanical properties [69]. Recent investigations suggest that interfacial bonding showed a crucial role in load transfer between CNTs and polymer [70]. Thus controlling the interfacial interactions among the polymer and CNTs and is a good technique in preparing the nanocomposites for improved mechanical characteristics of the composite [71]. A good CNT/matrix interfacial interactions resulted in an increase in the fracture strength by confirming a shear stress transfer to the nanofiller [72]. Thus novel crystalline carbon form, carbon nanotubes, single graphene layer or single-walled CNTs (SWCNTs) or several graphene layers in-folded upon themselves are known as multi-walled CNTs (MWCNTs) have been thought of [73]. MWCNTs/epoxy nanocomposites have been prepared and were investigated [73] after introducing CNTs up to 4% by weight. With the incorporation of 1 wt% of CNTs, the yield strength and modulus were doubled and quadrupled at 4 wt% CNTs, in comparison with the pure epoxy samples. They have additionally established that the uniform distribution of nanofillers in the composite was a crucial point for better mechanical performance.

On investigating the reinforcing effects of functionalized SWCNTs on epoxy polymer composite, achieved 25% enhancement in tensile strength and 30% enhancement in modulus and 30% enhancement in % elongation with 1 wt% of nanofiller (SWCNTs) reinforcement [74]. They attributed these reinforcing effects to the strong interfacial bonding of functionalized SWCNTs at the molecular level with epoxy polymer chains. Nanocomposites consisting of very low additions of (0.1 wt%) amino-functionalized double-walled carbon nanotubes (DWCNTs) were prepared [75]. The modulus and % elongation was improved with nanotubes whereas no effect on tensile strength was noticed. This behaviour was explained by their improved dispersability and ability to form agglomerates, improved stiffness under retention of the ductility. The van der Waals attractive forces of intrinsic nature and large aspect ratio, dictate that CNTs usually exist in the form of ropes and bundles. This makes the distribution of CNTs in the media a difficult task. As CNTs are mixed with the polymer, it would further aggravate as it usually aggregates in base matrices. As the rise in viscosity is expected, it is to be ensured that CNTs are uniformly distributed in the polymer. Hence much care required to be taken to evade any such concerns in processability. The poor CNTs dispersion cause slip easily over the other when the composites are exposed to force [76]. On the application of load weakly adhered CNTs are removed from the matrix thereby restraining their effect of reinforcement.

Marvellous research has been focused to rectify the difficulties mentioned above. Many methodologies, like the use of surfactants, high shear mixing, ultrasonication, CNTs encapsulation, surface functionalization, and some above combination, have been attempted [76–77]. At 1 wt% addition level of CNTs with open-end oxidation as well as sidewall fluorination, achieved a 30% increase in the modulus and 14% increase in tensile strength [78]. Normally epoxy and nanofillers are mixed, and subsequently curing agent is added for polymerization to take place. Whereas [79], curing agents have embedded on top of the surface of reinforcements namely CNTs. Thus at 0.5 wt% addition of functionalized CNTs 25% increase in elastic modulus obtained. As we compare the modulus improvements achieved between CNTs reinforced thermoplastic and thermoset polymers, the latter gave lesser values.

Among the many approaches, surface functionalization of SWCNTs is preferred, as this solves the mixing problem and meets adhesion needs. Few chemical functional groups added to CNTs surfaces helps to increase the adhesion among CNTs and the neighbouring polymer, as a consequence reducing the accumulation of the nanotubes. To further research, the various combinations of chemical functional groups on the CNTs be able to be used as predecessors for the successive reaction to an extensive variety of polymers. The effects of SWCNTs, DWCNTs, and MWCNTs with functionalization and pristine CNTs on tensile properties of the epoxy polymer were reported [69]. They achieved the highest tensile strength improvement by 8% and modulus by 15% with functionalized DWCNTs at 0.5 wt%.

Composites have prepared by first well-dispersing SWCNTs in epoxy by SWCNTs surfaces functionalization and oxidization using polyamido-amine generation O (PAMAM-O) dendrimer [80]. To have an association, epoxy/PAMAM-O, plain epoxy, and epoxy/pure-SWCNTs composites were fabricated. It was concluded that the functionalization of a surface increases bonding effectively with SWCNTs and the mixing in epoxy. To be precise, the addition of pure-SWCNTs could increase the epoxy's tensile strength and modulus by 16% and 18%, respectively. Whereas for the functionalized –SWCNTs, it gave the highest effect of reinforcement in strength and modulus by 17% and 27%, respectively. The desired increase in strength was not accomplished that is why researchers have contemplated de-bundling SWCNTs and enabling them to become conventional in epoxy to maximize the SWCNTs benefits.

The reinforcing influences of CNTs on epoxy composites were investigated and enhancement in tensile strength of the composite attributable to CNTs [81]; SWCNTs improved the tensile strength by 11% whereas MWCNTs improved by 14% at 0.1 wt% reinforcement level. The effects of two different aspect ratios (l/d) of MWCNTs on the properties of epoxy composites were studied [82]. Even at 1 wt% of nanofiller reinforcement, there was no change in tensile strength, but lower aspect ratio (MWCNTs-L) filler could improve % elongation by 57% while the higher aspect ratio filler (MWCNTs-H) improved only 33%. But the higher aspect ratio nanofiller improved the impact strength by 84% while the lower aspect ratio filler could improve by 64%. The reinforcing influences of MWCNTs on flexural properties of epoxy composites up to 0.4 wt% reinforcement levels were investigated [83]. They achieved relatively better improvement in overall flexural properties at 0.3 wt%, flexural strength improved by 29%, modulus by 8% and %elongation improved by 89%. As the filler reinforcement level increased to 4 wt%, they observed that the dispersion of filler was not uniform. The reinforcing influences of MWCNTs on the properties of epoxy composites have been investigated [84]. They have reported that nanofillers improved the properties at 0.5 wt% MWCNTs addition improved the tensile strength of 8% and at 1 wt% level the tensile modulus of 17% is achieved. These effects were credited to the improved distribution level of nanofillers in

the epoxy. The tensile modulus of epoxy composites strengthened with MWCNTs up to 0.5 wt% was reported [85]. They achieved the enhancement in tensile modulus by 12% with 0.5 wt% of nanofiller. The reinforcing influences of pristine and functionalized MWCNTs as nanofillers on tensile properties of epoxy composites were studied [86]. They found that functionalized nanofiller enhanced the properties better than a pristine one. Functionalized MWCNTs at 1 wt% filler level improved the %elongation by 23% and tensile modulus by 3%. To have a precise view of all effects of carbon nanotubes (CNTs) reinforced epoxy composites on the performance of epoxy composites is summarized below (Table 1).

3.2.2. Graphene reinforced epoxy composites

The influence of graphene platelets on the properties of epoxy composites was studied [81]. Improvement of the tensile strength (40%) of the composite due to graphene nanofiller was attributed to the improved interfacial properties resulting from the large surface and surface nature of graphene platelets. Epoxy nanocomposites strengthened with graphene platelets with and without functionalization and have reported that graphene platelets increased the flexural properties of epoxy composites [87]. The enhancement in the performance was attributed to the improved interfacial interaction of graphene platelets with epoxy due to their wrinkled large surface. Graphene oxide strengthened epoxy composites were fabricated and it was concluded that the nanoreinforcements because of its higher surface area, surface nature, and better interfacial properties enriched the tensile, flexural, and impact properties of epoxy composites [88]. Different multi-layered graphene nanosheets reinforced epoxy nanocomposites were prepared by dispersing graphene nanofillers in three different mediums acetone (MA), an epoxy (ME), and a hardener (MH) to achieve better dispersion of nanofiller to get optimum mechanical properties [89]. Variations in improvements in tensile strength were around 16%, 20%, 31%, flexural strength around 15%, 17%, 30%, impact strength around 22%, 27% and 89% were reported. These enhancements in properties to the reinforcing effects of the graphene sheet have been attributed to the interfacial properties and the crack path deviation mechanisms. The strengthening influence of amine functionalized expanded graphene nanoplatelets (AE-Graphene) on the flexural modulus of epoxy composites was reported [90]. Graphene nanofiller had improved the flexural modulus of composites; the improvement in flexural modulus was ascribed to considerable load transfer from the matrix to the fillers when stress is being applied.

Maximum enhancement in tensile strength by 36% with reduced graphene oxide (GO) reinforcement at 0.25 wt% on comparing with pristine epoxy was achieved [65]. They observed that by modifying the epoxy, improved tensile strength along with maintaining toughness was achieved. The reinforcing influence of 0.5 wt% graphene on epoxy composites was presented with the conclusion that the tensile strength was improved by 18% due to improved interfacial and adhesion between nanofiller and the epoxy [23]. Hyperbranched epoxy nanocomposites were prepared with different graphene addition levels up to 0.5 wt% and investigated the performance of the nanocomposites. Results revealed that graphene oxide improved the tensile strength by 61% and % elongation by 59%. Reinforcing effects were attributed to graphene interactions with epoxy and stress distribution between the filler and the epoxy [66].Graphene oxide reinforced epoxy composites with different additions of graphene oxide up to 3 wt% were prepared and examined the effects of nanofiller on properties of epoxy composites [91]. The work has shown that the tensile, flexural and impact properties of epoxy composites' were increased by the presence of nanofillers in the epoxy matrix, most significant enhancements were obtained at 1 wt% and 1.5 wt % of nanofillers.

Table 1
Effect of carbon-based nanofillers reinforcement on the mechanical the mechanical properties of epoxy composites.

Nanofiller	Reinforcement fraction (wt.%)	Name of the Property	Improvement Reported (%)	Reference
DWCNTs	0.5	Tensile strength	8	71
		Tensile Modulus	15	
MWCNTs	1	Tensile strength	100	75
		Tensile Modulus	100	
	4	Tensile strength	150	
		Tensile Modulus	294	
SWCNTs	1	Tensile strength	25	76
		Tensile Modulus	30	
		% Elongation	30	
	4	Tensile strength	23	
		Tensile Modulus	68	
DWCNTs	0.1	Tensile modulus	6	77
SWCNTs	1	Tensile strength	30	81
		Tensile Modulus	14	
SWCNTs	0.5	Tensile Modulus	25	82
SWCNTs	1	Tensile strength	16	83
		% Elongation	25	
f-SWCNTs		Tensile strength	17	
		% Elongation	27	
SWCNTs	0.1	Tensile strength	11	84
MWCNTs		Tensile strength	14	
MWCNTs-L	1	%elongation	57	85
		Impact strength	63	
MWCNTs-H	1	%elongation	33	
		Impact strength	84	
MWCNTs	0.3	Flexural strength	29	86
		Modulus	8	
		% Elongation	89	
MWCNTs	0.5	Tensile strength	8	87
	1	Tensile Modulus	17	
MWCNTs	0.5	Tensile Modulus	12	88
MWCNTs	1	% Elongation	23	89
		Tensile Modulus	3	

The properties of epoxy nanocomposites that were strengthened by the graphene and graphene oxide addition with and without functionalization at different addition of nanofiller levels till 1 wt% were reported [92] . Results exposed that the presence of the nanoparticles had improved the tensile strength along with modulus of an epoxy composite. The nanocomposites reinforced with functionalized graphene (f-graphene) nanoparticles at 1 wt% showed the highest improvement in the tensile modulus, 14%, indicating a significant impact of functionalization on the stiffness of composites. The nanocomposites' tensile strength was improved by 38% at 0.5 wt% of nanoparticle addition level. They stated that the functionalization of nanofillers improved the interfacial strength and the dispersion efficiency in the matrix. The strengthening influences of graphene oxide (GO) nanosheets on the performance of epoxy composite through tensile and flexural tests were investigated [93]. It was observed that graphene oxide nanofiller, irrespective of functionalization enriched the tensile and flexural properties of epoxy composites. The improvement in performance was attributed to graphene sheets in epoxy and their interaction with the epoxy polymer under different loads. Epoxy nanocomposites were prepared by the addition of GO as nanofiller were prepared and reported that the nanofiller improved tensile and flexural strengths and stiffness of epoxy composites [94]. Ascribed the reinforcement effects to improved interfacial properties among epoxy and GO sheets. To have a precise view of all the effects of graphene and graphene oxide reinforcement on the properties of epoxy composites it is summarized hereunder (Table 2)

[TABLE 2]

4. Metals, metal oxides, and carbides based anisotropic nanofillers reinforced epoxy composites

Nickel nanowires reinforced polymer nanocomposites have been studied [95] and found that the high aspect ratio of nanowires has a noteworthy influence on the elastic modulus of the composite, and contributes greatly, similar reinforcing effects of nanowires was reported [96–97]. A systematic investigation of properties of TiO_2 nanotubes incorporated epoxy composites has been executed [98] which yields improved mechanical properties. This reinforcing effect was credited to the hindered motion of polymer chains of epoxy by the presence of TiO_2 nanotubes.

The reinforcing influences of ZrO_2 nanotubes on flexural properties of a polymer matrix were reported [99], found that the nanotubes as fillers improved flexural strength by 21% at 0.5 wt% addition of ZrO_2 nanotubes, and attributed the reinforcing effects to good interaction of polymer chains and the nanotubes. The reinforcing effects of alumina nanorods of 10 nm length and 50 nm diameter on the flexural properties of epoxy composites containing nanofillers up to 1.5 wt% were investigated [100]. Results indicate that the strength and modulus values obtained from the flexural test on the nanocomposites improved up to 1% increase by weight with nanorods of alumina and then the values declined with more accumulation of nanorods. The maximum enhancement of 14% in flexural strength and 28% in flexural modulus was reported and it was ascribed to the restricted motion of polymer chains by nanorods.

Table 2
Effect of graphene and graphene oxide reinforcement on the mechanical the mechanical properties of epoxy composites.

Nanofiller	Reinforcement fraction (wt.%)	Name of the Property	Improvement Reported (%)	Reference
Graphene	0.5	Tensile strength	18	23
Graphene oxide	0.25	Tensile strength	36	66
Graphene oxide	0.1	Tensile strength	25	67
	0.1	% Elongation	38	
	0.25	Tensile strength	46	
	0.25	% Elongation	70	
	0.5	Tensile strength	62	
	0.5	% Elongation	59	
Graphene	0.1	Tensile strength	40	84
Graphene	0.1	Flexural strength	10	90
		Flexural modulus	7	
Graphene oxide	0.25	Tensile strength	32	91
		Flexural strength	85	
		Flexural modulus	65	
		Impact strength	103	
Graphene-MH	0.1	Tensile strength	31	92
Graphene-ME	0.1	Tensile strength	20	
Graphene-MA	0.1	Tensile strength	16	
Graphene-MH	0.3	Impact strength	89	
Graphene-ME	0.3	Impact strength	27	
Graphene-MA	0.3	Impact strength	22	
Graphene-MH	0.1	Flexural strength	15	
Graphene-ME	0.1	Flexural strength	16	
Graphene-MA	0.1	Flexural strength	30	
AE-Graphene	2	Flexural modulus	15	93
Graphene oxide	1	Tensile strength	16	94
	1	Flexural strength	38	
	1.5	Tensile strength	46	
	1.5	Flexural modulus	48	
f-Graphene	0.5	Tensile strength	38	95
	1	Tensile modulus	14	
f-Graphene	0.1	Tensile strength	51	96
	0.25	Tensile strength	48	
Graphene	0.1	Tensile strength	35	
Graphene oxide	0.5	Tensile strength	6	97

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Epoxy nanocomposites reinforced with cubic shaped Fe_2O_3 nanoparticles of size ~ 40 nm were fabricated and observed the nanofillers influences on epoxy composites' mechanical properties [101]. The outcomes of investigations showed that Iron oxide nanofillers improved mechanical properties. They observed the maximum enhancement in the tensile strength by 50% with modified Fe_2O_3 nanoparticles. Similar reinforcing effects of Fe_2O_3 nanomaterials were also reported elsewhere [102]. The influence of the cuprite structure and nanoparticles of Copper oxide (CuO) on properties of epoxy composite was studied [103]. It was perceived that the matrix strength from tensile test rises with enrichment of CuO content and attains a peak value at addition in 5 wt% with a resulting increase by 47%. Thus the higher interaction levels between matrix-filler enable the transfer of stress to the phase of filler [104]. The improvement in strength value from the tensile test was ascribed to the effect of CuO as reinforcement, which aids in the effective transfer of stress.

The influence of irregular (anisotropic) shape nano-alumina (maximum size of 100 nm) reinforcement at different weight fractions on properties of epoxy composites was reported [105]. It was observed that 1 wt% was the optimum addition level of nano-alumina, at which flexural strength increased by 59%, and flexural modulus increased by 27%. However, beyond 1 wt% nanofiller addition levels, reduced mechanical properties were obtained due to agglomerations of nanoparticles.

5. Conclusion

Epoxy-based composites have been used extensively in aerospace, naval, automobile, civil, wind energy and electronic industries due to their attractive properties. Large-scale research has been done since the last few decades on epoxy composites to improve their performance, especially by modifying epoxy with fillers. This review shows that modifying with rubbers, elastomers, and inorganic particles improved the mechanical properties of epoxy composites. Later it is found that particle size has an enormous effect on the mechanical properties of epoxy composites and reducing the size of the particle benefit the composite due to improved interface area between epoxy and the filler. Modifying the epoxy by reinforcing with fillers at the nanoscale has a significant effect on mechanical properties of epoxy composites. From the review of the literature, it is found that reinforcing effects of anisotropic nanofillers other than CNTs, Graphene, Clays and 3D nanostructures on epoxy mechanical properties of composites are very limited. There is so much need for developing lightweight and strong epoxy nanocomposites with cost-effective methods.

CRediT authorship contribution statement

Praveen Kumar Balguri: Investigation, Data curation, Writing - original draft, Formal analysis. **D.G. Harris Samuel:** Supervision, Writing - review & editing. **Udayabhaskararao Thumu:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Further Reading

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