

Review Research

A REVIEW OF EPOXY-NANOCOMPOSITE PROPERTIES

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Abstract: Epoxy resins have been the subject of many studies as a consequence of their extensive usage in recent years. The brittleness and low resistance to propagation and crack initiation of epoxy resins are well-recognized characteristics. Therefore, in recent years, experts have concentrated on increasing epoxy resin's fracture resistance. Adding inorganic nanoparticles like titanium dioxide (TiO₂), silica (SiO₂), carbon black, alumina (Al₂O₃), and others to the polymer matrix is one of the most investigated techniques in polymer science. Despite having a modest nanofiller content, the resulting nanocomposites may enhance their thermal, mechanical, rheological, electrical, and optical characteristics. These nanocomposites are an alternative to metal-based materials. They have great promise as multifunctional materials in a range of applications, including optoelectronic devices, semiconductor devices, civil engineering, automotive, and aerospace. To show potential future directions and market prospects for polymer nanocomposites reinforced with TiO₂ nanoparticles, current results, and trends have been examined and highlighted. In addition, the current review surveys many studies that highlighted using nanoparticles as reinforcement, their different structure, the interface, and the geometry and structure of the resulting nano-materials reinforced resin.

Keywords: Carbon-Nanofillers; metal oxide; nanofiller; polymer; resin

1. Introduction

Epoxy resins are thermosetting polymers with exceptional mechanical qualities (strength and stiffness), resistance to stability, chemicals, and

corrosion, and durability when exposed to a wide range of environmental agents, as well as minimal shrinkage throughout the curing process and excellent adhesion to a wide range of materials. They are widely employed in a variety of applications and industries as electrical components, insulators, matrices for fiber-reinforced composites, coatings, and adhesives. Epoxy resins' characteristics may be enhanced by including one or more nano-sized phases, creating a nanocomposite [1-3]. The system comprises an organic (epoxy) phase closely coupled to an inorganic phase at the nanoscale level, creating organic-inorganic hybrid systems. Hybrid materials are often characterized as nanoscale-scale structures that switch between organic and inorganic phases. One of the shortcomings of epoxy resins is their lack of durability. Similar to other thermosetting polymers, they are brittle by nature [2, 4-6]. Their application in prefabricated nano-sized elements, i.e., nanofillers, is limited by high thermal expansion coefficients, thermal/electrical conductivity, and other faults. These attributes may be altered, enhanced, or modified as necessary to meet demands. Nanofillers are materials with at least one

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dimension in the range of 1-100 nm that come in a variety of chemical forms [4-7].

2. Nanoparticles as Reinforcements

Fillers made of Different nanoparticles are being tested for the first time to modify/improve the epoxy resin's characteristics and properties. They come from a variety of chemical families, including metal oxides, and clay carbon-based fillers, nanoparticles.

2.1 Carbon-Nanofillers

Carbon nanofillers have two-dimensional crystals with an average of 1-10 m thickness and 0.5-5 m diameter. Because of its distinctive structure and exceptional electrical and thermal characteristics, grapheme which is shown in Fig. 1 was the first compound of this large family suggested to produce high-efficiency nanocomposites [8-9].

Al Sheheri et al. [10] focused on the synthesis and composite creation of CNTs. Also highlighted are how these fillers may be included in polymer nanocomposites and the effects they can have on the final product's qualities.

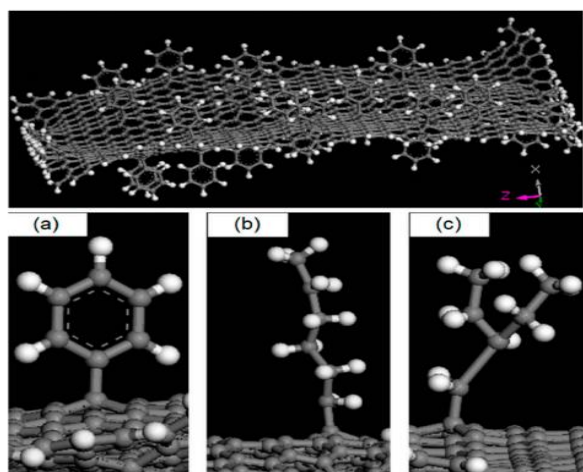


Figure 1. Graphene with various functionalized groups (a) phenyl groups (b) $-C_6H_{13}$ and (c) $-C_2H_4 (-C_2H_5)_2$ [3].

Shukla and Sharma [11] looked at the synergistic impact of hybrid nanofillers in epoxy resin and then compared the mechanical characteristics of two and three-phase composites made by adding graphene and carbon nanotube nanofillers in epoxy separately. Numerous characterization strategies are explained, including Fourier transforms infrared spectroscopy (FTIR), transmission electron microscopy, scanning electron microscopy, and X-ray diffraction to validate the outcomes and gain knowledge of the effect of filler materials on the interfacial characteristics of composites.

Kumar et al. [12] investigated how carbon nanomaterials, including graphene, carbon nanotubes (CNTs), and carbon black, can be used as nanofillers to enhance the characteristics of rubber composites. These nanofillers have been helpful for a variety of applications, including strain sensing, and can greatly improve the characteristics of silicone rubber (SR) nanocomposites. Therefore, the review includes developments in this field of study as well as carbon-nanofiller-reinforced SRs. The microstructures, defect densities, and crystal structures of carbon nanofillers for silicone rubber nanocomposites are investigated. Their processing and dispersion are also detailed.

2.2 Metals Oxide and Other Nanooxides

Nano- Al_2O_3 is one of the other metal oxides that are the most often utilized to create polymer nanocomposites with enhanced thermal and mechanical effectiveness. When combined with nano titania and carbon-based nanofillers, the reduced manufacturing costs of alumina nanoparticles provide an additional legitimate benefit. This nanofiller's typical size (diameter), available as nanorods or nanospheres, ranges from 10 to 80 nm [13-14].

Tomer et al. [15] studied the effects of the high aspect ratio of the montmorillonite and the high permittivity of the (BaTiO₃) nanoparticles on epoxy resin composites based on these materials. In addition, they investigated the synergistic effects of combining epoxy with montmorillonite and (BaTiO₃) particles, which might have beneficial effects on the whole system. It was found that the nature of the organic-inorganic interfaces strongly influences the glass transition temperature and the dielectric characteristics of these composites. In particular, they investigated the polymer's local dynamics at the interfaces through dielectric relaxation spectroscopy.

Siddabattuni et al. [16] used a bifunctional interfacial coupling agent to modify the inorganic oxide particle surface. The composite maintains the glass transition temperature of pure polymer. As a result, the Maxwell-Wagner relaxation of the composite polymer and particles is reduced. Compared to particle epoxy composites, which fail to form an interfacial contact between the composite filler and polymer matrix, this material shows far lower sensitivity to dielectric breach.

Das et al. [17] demonstrated that metal ions located in metal-organic frameworks with a reduction reaction of 0.27 volts or above invariably produce pure metal nanoparticles throughout thermolysis in N₂. This was done by using the rationalized synthesis technique of a broad variety of metal oxide and metal nanoparticles, such as Cu/CuO, CO/CO₃O₄, ZnO, Mn₂O₃, MgO, and CdS/CdO. Metal ions having reduction potentials lower than 0.27 volts, however, result in the formation of metal oxide nanoparticles when heated in N₂. The relationship between the nanoparticle size and the separation between the secondary building units found within the MOF precursors is

another intriguing observation. It's interesting to note that the N₂ and air in the atmosphere have a considerable influence on the crystallinity of the carbon matrix during thermolysis.

The effect of metal and metal oxide nanoparticles on plant metabolism was studied by Rastogi et al. [18]. They demonstrated how the size, concentration, and exposure technique of nanoparticles affected the effects on plants. Furthermore, they proposed oxidative burst as a generic mechanism by which plant damage caused by nanoparticles spreads.

Dizaj et al. [19] examined metal oxide and metal nanoparticles comprise a category of materials. In terms of their antibacterial activities, they concentrated on the most recent research on the antibacterial properties of metal oxide and metal nanoparticles as well as their mechanisms of action. The critical factor influencing the metal nanoparticles' effectiveness against microbes was their particle size. Combination therapy using metal nanoparticles is one potential method to combat bacterial resistance to antibacterial drugs.

2.3 Nano clays

Halloysite (Al₂Si₂O₅(OH)₄) nanotubes (HNTs) with an inner/external diameter of 12–15/50–60 nm and a length of 0.5–10 μm. They are made of aluminosilicate clay. These nanofillers may be used to build epoxy-based nanocomposite materials for a variety of purposes, including biocompatibility, thermal stability, and mechanical strength [20].

Horsch et al. [21] investigated The use of supercritical carbon dioxide to scatter nanoclays as a new processing technique. Nanocomposites are analyzed using a mix of wide-angle XRD, SEM, TEM, and rheology to determine the structure and characteristics of the clays and their nanocomposites.

Rajaei et al. [22] used ammonium polyphosphate and two nano-clays to compare epoxy composites' fire and mechanical characteristics based on halloysite nanotube and layered double hydroxide. According to the data, an 87% reduction in epoxy resin's peak heat release rate was obtained by combining ammonium polyphosphate and nano-clay. According to the comparison investigation, an 18% reduced heat release was found in the halloysite nanotube-based composite compared to the layered double hydroxide-based composite.

Yang et al. [23] demonstrated how the distinct reactions of the layered nano clay and the stiff SiO₂ to shear flow in the processing of phenylene sulfide melts yield the desired result of a significant interaction between the two materials. This allows for the simultaneous realization of the exfoliation structure of nanoclay and well-dispersed nano-SiO₂. This efficient morphological control enhances the strengthening effect of nanofillers in phenylene sulfide with just a small quantity of extra filler. Moreover, the mobility of PPS molecular chains is constrained with the help of exfoliated clay and nano-SiO₂ particles, resulting in a notable shift in the crystalline properties of phenylene sulfide.

2.4 Phosphorus Nanofillers

Aluminum hypophosphite nanoparticles, that have a 60 nm diameter or less, are phosphorus-base substances that could be added to epoxy resins in very small concentrations (up to 0.5 weight percent epoxy) without causing any surface alteration as a flame retardant. The 2D nanofiller phosphorene material has a strong flame retardant efficiency even at low concentrations.

Xie et al. [24] propose a novel composite made of shape memory polymers (SMP). The

composite is constructed of a thermo-responsive SMP formed of piperazine-based polyurethane and sheets of black phosphorus used as NIR photothermal nanofillers. Only 0.08 weight percent of BP sheets in the mixture enables rapid temperature rise over PU's glass transition temperature. Under 808 nm light irradiation, it causes the composite to change shape with a 100% shape recovery rate. The in vitro and in vivo toxicity tests show that the PU/BP composite has high biocompatibility. In addition to non-toxic phosphate from black phosphorus, it naturally breaks down into non-toxic carbon dioxide and water from polyurethane.

Novak et al. [25] synthesized a cheap technique of synthesis to produce high-quality black phosphorus, which was then incorporated into a PEDOT: PSS film to make the first BP composite thermoelectric material. The film power factor, with 2 wt% black phosphorus ($36.2\mu\text{Wm}^{-1}\text{K}^{-2}$), represents a 109% improvement over the pure PEDOT: PSS film ($17.3\mu\text{Wm}^{-1}\text{K}^{-2}$). This indicates that the inclusion of black phosphorus considerably improves thermoelectric capabilities. Boosting the black phosphorus wt% is discovered to enhance the Seebeck coefficient and the electrical conductivity by increasing mobility and decreasing the carrier concentration simultaneously. These findings demonstrate the possible use of this cheap black phosphorus in energy-related applications.

Gnanasekar et al. [26] showed that it is possible to create bio-based composite resins that are durable, heat-resistant, and safe for the environment. For usage as a fire-resistant glue, By using a two-step process, a novel bio-based phosphorus-containing vanillin epoxy resin was created.

3. Preparation of Epoxy Nanocomposites

The final performance of these materials is significantly influenced by the processing techniques. Given their simplicity and adaptability, high-shear mechanical mixing and solution blending using traditional mechanical stirring and/or sonication techniques are two of the most often used techniques to create epoxy nanocomposites. Epoxy impregnation has been mentioned as another technique to help further improve the homogenous distribution and/or customized network of 2D nanofillers for creating epoxy nanocomposites, see Table 1.

3.1. Solution Blending

Due to their simplicity and versatility, high-shear mechanical mixing and solution blending through mechanical stirring and/or sonication are among the most frequently used procedures to produce epoxy nanocomposites. Additional methods have aided in the uniform distribution and/or customized network of 2D nanofillers.

3.2. Mechanical Mixing

Epoxy nanocomposites are frequently made using the mechanical mixing processing technique, which uses high shear pressures to disseminate and/or exfoliate 2D fillers in the resin. The three-roll milling method, which uses shear forces between rollers, may mechanically spread two-dimensional fillers inside epoxy resins, such as graphene or hexagonal boron nitride. There were no chemicals or solvents utilized. Li et al. [27] successfully produced epoxy/graphene nanocomposites by exfoliating natural graphite to graphene nanoplatelets in situ during the three-roll milling process. Graphene nanoplatelets with diameters between 5 and 17 nm and an aspect ratio between 300 and 1000 were created directly from natural graphite. The epoxy nanocomposites displayed better

mechanical and electrical properties without separation or purification procedures.

Table 1. Contrasting several techniques for creating epoxy nanocomposites.

Methods	Advantages	Disadvantages
1. Solution blending	*Simple *Effective *Versatile	*difficult to regulate filler orientation *At high filler contents, there is poor dispersion *When organic solvents are utilized in significant quantities, there may be potential environmental risks.
2. Mechanical mixing	*Solvent-free *Easy operation *precise filler orientation	*decreased filler lateral size *At high filler contents, there is poor dispersion *High filler amounts are necessary to see noticeable changes
3. Epoxy impregnation	*Easy operation *regulated orientation of filler *high filler fractions are allowed *Cost-effective * large-scale size	* time and energy-consuming * challenging to scale up * Controlling the layered structure is challenging.

3.3. Epoxy Impregnation

Vacuum filtration [28], freeze-drying [29], or other directed assembly processes [30] are used to form 2D nanosheets into aligned 2D or 3D structures before epoxy impregnation. Epoxy

resin is impregnated into the constructed components to produce epoxy nanocomposites.

Before epoxy impregnation, two-dimensional nanosheets are shaped into aligned two-dimensional or three-dimensional structures using vacuum filtration, freeze drying, or other directed assembly processes. Epoxy nanocomposites are created by impregnating the built components with epoxy resin.

4. Size, Shape, Interfacial Region

The properties of materials change dramatically at the nanoscale and differ significantly from their bulk counterparts. The specific surface area of a material increases as its size decreases. (Because of electrostatic attraction, nanoparticles attract one another. Van der Waals forces). Due to particle-particle interactions in the interfacial region (IR), which increase reactivity and turn the materials into highly reactive catalysts for basic catalytic activities with surface atoms and the polymer matrix, the new properties of the materials are primarily controlled by these interactions [31]. By carefully choosing nanoparticles throughout the synthesis process and manipulating their size and form, one may influence the final qualities of the particles (optical, magnetic, electronic, and mechanical). The water-to-titanium molar ratio significantly influences all three dimensions (size, stability, and shape) of the resulting alkoxide sol. ($r=[\text{H}_2\text{O}]/[\text{Ti}]$) [32]. Additionally, the poetization procedure did not affect the properties of a powder form created utilizing the sol-gel technique. The solution may be heated, or a poetization agent can be used to carry out the reaction at the molecular level. TiO_2 nanoparticles' ultimate size is shown to be significantly impacted by the pH of the produced solution [33]. TiO_2 nanocrystals of different shapes and sizes were produced in an

aqueous medium or alkaline solution of 8–100nm diameter and 20–200nm length. It includes elongated, pseudocubic, and ellipsoidal. Nanoscale oxides have their characteristics modified by chemisorbed and physisorbed water. It has been reported that needle-shaped TiO_2 crystals with a diameter of 8 nm and a length of 100 nm may be produced by chemically treating TiO_2 powders or precursors with a 5-10 M NaOH aqueous solution. However, the complex titanates, such as $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$, were formed as a result of the chemical reaction[33] rather than the desired TiO_2 . Therefore, regulating the morphology of anatase TiO_2 remains difficult. Matrix, reinforcement, and IR are the three primary components of any composite. Because of its closeness to the filler's surface, the IR has different characteristics than the bulk matrix and is responsible for the "communication" between the matrix and filler (the static adhesion strength and IR stiffness). The ability of a material to transfer stresses and elastic deformations from the matrix to the fillers is indicated by its IR spectra. The particles cannot support a portion of the external tension applied to the composite if the IR spectrum is weak. The brittle-to-ductile transition occurs when the yielding mechanism of glassy amorphous polymers switches from cavitation to shear. As a result, there is no way to make the material stronger than the matrix polymer already is. However, a larger IR spectrum facilitates efficient stress transmission from the matrix to the nanoparticles, leading to higher composite yield strength.

5. Dispersion of Nanoparticles

Maximizing interactions among the polymer and inorganic fillers seems to enhance the electrical and mechanical characteristics of nanocomposites. To avoid dielectric behavior changes, Calobrese et. al. [34] Established that

the processing parameters that induce particle dispersion must be strictly maintained. Surface functionalization improves dielectric function and breakdown strength, and it is recommended based on the findings. In addition to the more traditional silane coupling agents, using surface ligands containing electron traps [35] offers intriguing possibilities that should be researched further. All of the aggregated nanoparticles might not be capable of being broken apart by high shear mixing. Thus, other mixing processes should be used to improve dispersion quality. Kurimoto et. al. [36] Demonstrated Ultrasonication and centrifugal mixing to reduce agglomeration size. However, after processing, this method lacks control over the filler content. Quantitative techniques are strongly recommended for analyzing the state of dispersion instead of making decisions based on a qualitative evaluation. There are benefits and drawbacks to the different quantitative metrics of dispersion. Combining several quantitative analysis methods could be the best choice in certain circumstances. While removing human judgment, a quantitative evaluation may provide criteria for characterizing the dispersion state and enable comparison of the dispersion quality across different materials. A quantitative examination will also enable determining how different preparation and processing techniques will affect dispersion and, in turn, the properties of the material, simpler.

6. Epoxy Nanocomposites Structure

6.1 Epoxy Resins

In contrast to thermoplastics, epoxy is a thermoset substance; after it has cured, the network polymer formed by its covalent crosslinks between monomers has a permanent hardness (e.g., polyethylene). Thermosets do not soften when heated, which makes them stronger

but more brittle. The monomer's molecular weight and chain length affect how strongly it interacts with nanoparticles. In most investigations of epoxy's dielectric properties, the epoxy resin utilized is diglycidyl ether of bisphenol-A (DGEBA). Some cycloaliphatic epoxies (3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanecarboxylate) may also be appropriate.

6.2 Filler Materials

6.2.1 Oxide Filler

For high-voltage insulation, inorganic oxides are often used as fillers in epoxy nanocomposites. The review will focus on epoxy nanocomposites that include oxides such as titanium dioxide, silicon dioxide, and aluminum oxide are the three most prominent nanoparticles in the literature. TiO₂, which has a large band gap and several polymorphs, is an ionic semiconductor. The rutile, anatase, and Brookite phases are among the most crucial. In high numbers, the rutile phase is more stable. For nanoparticles smaller than 30 nm, anatase is more stable than rutile due to its lower surface energy [37]. However, Between 30 and 200 nm, rutile or anatase can develop with equal probability. The difference between rutile and anatase may become significant in nano dielectrics due to their respective permittivity (dielectric constant) due to a polaron effect. Rutile has more ionic TiO bonds and structure distortion, causing more excellent ionic screening and a greater effective electron mass, leading to a higher relative permittivity. Silicon oxide is usually an amorphous insulator for electricity when employed as a nanofiller to improve composite properties. The structure, which comprises tetrahedral SiO₄ units connected by Oxygen atoms, lacks the long-range order in crystalline forms. Al₂O₃ is a familiar insulator in corundum

structures ($\text{-Al}_2\text{O}_3$). However, Because the surface energy of nano-sized Al_2O_3 is lower than that of $\text{-Al}_2\text{O}_3$ when the surface area exceeds $370 \text{ m}^2 \text{ g}^{-1}$, it can exist in an amorphous phase [38].

6.2.2 Non-Oxide Filler

The review will concentrate on inorganic oxide Nano fillers used in epoxy nanocomposites. Because of their ubiquity in the literature, while inorganic oxides are the most commonly applied to the study of epoxy nanocomposites' dielectric properties, other nanoparticles have also been researched. Non-oxide nanofillers such as aluminum nitride and boron nitride are used because of their high thermal conductivities. Adding cubic boron nitride to epoxy modified with polyhedral oligomeric silsesquioxanes improves the material's dielectric breakdown strength, thermal conductivity, and glass transition temperature [39]. For low filler contents, Epoxy nanocomposites, including hexagonal boron nitride and aluminum nitride, have also demonstrated low permittivity [40]. Another non-oxide alternative nanofiller in epoxy is silicon carbide (SiC), which has better partial discharge resistance [41].

7. The Nanoparticle Interface

Their size and surface chemistry govern the organization and structure of the nanoparticles inside the polymer matrix. Believe that the interaction between the nearby polymer strands and the nanoparticles is what gives the nanocomposite its unique features. Because there are more surface atoms on smaller particles, the surface area to volume ratio is higher [42]. As a result, Clustering and aggregation is an expected behavior among nanoparticles since their surface energy is much larger than that of micrometer-sized particles.

The vast difference in surface energy between hydrophilic inorganic particles and hydrophobic organic polymer chains makes them chemically incompatible and contributes to agglomerate formation. Compared to micrometer-sized counterparts, composite materials with well-dispersed nanoparticles would have a wider surface accessible where the polymer chains and inorganic particles interact. The interfacial area around the particle polymer chain is believed to be modified due to these interactions between the particle and the polymer. As expected, the permittivity of epoxy-TiO₂ micro composites (10 wt%) increased dramatically, given TiO₂'s much higher permittivity than epoxy. On the other hand, the permittivity of an epoxy-TiO₂ nanocomposite dropped. This decline prompted the hypothesis that the interfacial region's dielectric characteristics differ vastly from the polymer on the inorganic filler. The loss in permittivity of the nanocomposite is due to a huge interfacial region.

The interface model between nanoparticles and polymer chains was put out by Tsagaropoulos and Eisenberg [43], in which particle-chain interactions result in zones of constrained chain mobility. A glass transition that is different from the rest of the polymer may be seen in this region. It might be the location of the split between a weakly bound layer and a strongly bound layer, the latter of which does not contribute to the glass transition. Weakly connected layers between adjacent nanoparticles can cross. Danikas and Tanaka et al. [44] provided a multicore model for the interface that included an inside bonded layer, an inside bound layer, and lastly an outside free layer. Additionally, they imply that when Coulombic contact is added on top of the other three layers, an electric double layer exists that spans all four. The bound layer, a transition zone 1 nm

thick, is used by coupling agents to chemically bond polymer chains to the surface of nanoparticles. Only when such coupling agents are used to functionalize the nanoparticle surface does this layer arise. It could have an indirect impact on the nanocomposite's properties. The initial layer of the bound layer, which is 2–9 nm thick, interacts heavily with polymer chains. Only little interactions with polymer chains are present in the second layer of the loose layer, which is >10 nm thick. At different levels of the interfaces, the chain mobility, conformation, and crystallinity in the polymer matrix change. These models create bound, bonded layers like the electrical double layer in colloidal dispersions [36]. The Stern layer and diffuse Guoy-Chapman layers both serve as examples of bound layers. Bonded layers, on the other hand, represent the Stern layer.

8. Epoxy Nanocomposites Structure-Property Relations

8.1 Electrical Properties

The dielectric breakdown strength is one of the crucial electrical characteristics for high voltage insulating materials. Complex permittivity and electrical conductivity are further crucial factors. The breakdown strength of the material reveals how much electric field it can withstand before its insulating qualities collapse.

8.1.1 Complex Permittivity

As micrometer-sized particles are utilized as fillers, the dielectric losses and relative permittivity of the finished composite are improved when compared to ordinary epoxy.

8.1.2 Breakdown Strength

Since it determines the maximum permitted voltage that may be supplied to the insulation

system by the electrical field, the strength of dielectric breakdown for electrical insulation materials is crucial. In addition to material characteristics, breakdown strength is also influenced by the kind of insulation used, the type of applied voltage (alternating or direct current), and ramp rates [45]. Because dielectric breakdown is a random event, statistical approaches are commonly employed to describe and forecast breakdown values.

8.2 Mechanical Characteristics

Polymer composite insulation materials are susceptible to cracking and delamination under constant abrasion and high shear pressures, which ultimately leads to electrical discharge and failure. Epoxy's brittleness is one of its well-known drawbacks, limiting its use where high impact and fracture resistance are required. To solve these issues and improve the mechanical properties, inorganic or metallic filler particles are typically utilized to reinforce polymer matrices. Traditionally, filler particles were micrometer-sized, but nanoparticles have become more popular in the recent decade. Nanoparticles can enhance the mechanical properties of composites when compared to micrometer-sized particles. When utilizing smaller particles at a given filler load, improved physical and chemical interactions between polymer chains and filler particles result in improved mechanical performance [46]. Table 2 lists the mechanical properties of several epoxy nanocomposites that have changed as filler levels have increased. The modified Equation (1) of mixtures can be used to characterize the Young's modulus of bulk nanocomposites, E_c , as follows:

$$E_c = \eta_o \eta_l E_{eff} V_f + E_m V_m \quad (1)$$

Where V_f and V_m ($V_f + V_m = 1$) are the filler and matrix volume fractions, The length efficiency factor, η_l , depends on the aspect ratio of the nanoplatelets, and η_o is the Krenchel orientation factor ($\eta_o = 1$ for aligned nanosheets and $8/15$ for randomly oriented ones). E_m is the matrix's modulus, while E_{eff} is the filler's effective modulus.

8.2.1 Changes in the Strength and Elastic Moduli

as seen in Table 2, Adding nanoparticles to epoxy increases its flexural and tensile strengths and fracture toughness. Particle-matrix interactions that provide uniform stress transmission from the polymer matrix to the nanoparticles are credited with increased strength and toughness[47, 48]. Excess filler loads (typically greater than 5–10 wt percent) have been proven to reduce mechanical performance in some experiments. The decrease with increased filler loading is typically attributed to increased particle-particle interactions and particle clustering as a result of shorter average interparticle distances. These interactions between particles could lead to uneven stress concentrations close to agglomerates, which would lead to material failure. Elastic moduli of nanocomposites are anticipated to rise because of inorganic nanoparticles' much higher elastic moduli than epoxy. Many investigations compare the anticipated and actual values of tensile modulus using the Halpin-Tsai and Lewis-Nielsen models [47]. The data indicate good agreement with both models at lower filler loading (utilizing the Lewis-Nielsen model's "no slip" assumption). However, agglomeration effects cause bigger discrepancies at higher filler loads [49].

Table 2. Modifications in epoxy nanocomposites' mechanical characteristics.

Measured properties	Filler	Properties changes	Ref.
Flexural modulus	Al ₂ O ₃	Improved Increased (up to 5 wt%)	[48]
	TiO ₂	Rise	
	SiO ₂	Rise	
Flexural strength	Al ₂ O ₃	Improved rise (up to 5 wt%)	[48]
	TiO ₂	Improved	
	SiO ₂	Slightly decreased	[50]
Flexural strain-to-break	Al ₂ O ₃	rise (up to 2 wt%)	[48]
	TiO ₂	Decreased	
	SiO ₂	Decreased	[50]
Tensile modulus	Al ₂ O ₃	rise rise both without and with surface modifications. The increase was more significant without surface modification.	[51]
	TiO ₂	Improved Improved Improved	
	SiO ₂	rise (up to 3 wt%) Improved	
Tensile strength	Al ₂ O ₃	Rise (up to 2.5 wt%) Rise for unmodified nanoparticles No change (up to 15 wt%) for surface-modified nanoparticles), followed by a large lower	[51]
	TiO ₂	Rise (up to 10 wt%) Rise (up to 2.5 wt%) rise	
	SiO ₂	Rise (up to 2 wt%). Greatly rise at lower temp. Rise (up to 3 wt%)	
Fracture	SiO ₂	Improved	[50]

toughness		Improved	
		Improved	
		Improved	
Impact energy and wear resistance	Al ₂ O ₃	Rise (up to 6.7 wt%)	[48]
Tensile toughness	TiO ₂	Rise (up to 5 wt%)	[52]
Impact strength	SiO ₂	Rise (up to 3 wt%)	[47]
Fracture energy		Improved	
		Improved	

8.2.2 Strain-to-Break Changes

It increases the strain-to-break, fracture toughness, and tensile strength of nanocomposites since neat epoxy is brittle.

8.2.3 Toughening Mechanisms

Adding fillers may make the epoxy more challenging, and many processes have been suggested. The amount of energy necessary for a crack to spread increases as a result of crack pinning and deflection, both of which entail nanoparticles changing the crack's path. The fracture front is bent outward between the strong epoxy filler particles, acting as pinning centers. For nanoparticles, the particles needed for crack pinning must be greater than the fracture opening displacement [49].

8.3 Thermal Properties

The structure and behavior of polymer nanocomposites can dramatically affect temperature and thermal stability. When choosing materials for different applications, especially high-voltage insulation, where dielectric losses cause heat dissipation and raise the material's temperature, these effects should be taken into consideration. Given that high temperatures inevitably cause material properties to decrease owing to thermal

decomposition, the materials' extraordinary thermal resilience is impressive. Two changes can take place:

- Variations in Thermal Conductivities and Thermal Stabilities;
- Variations in the Glass transition temperature

when the matrix in which the fillers are placed lacks an inter-filler network. The series model (Equation 2) describes the composite thermal conductivity,

$$k_c = \left[\frac{V_m}{k_m} + \frac{V_f}{k_f} \right]^{-1} \quad (2)$$

Where k_c , k_m , and k_f are the thermal conductivities of the composites, matrix, and filler, respectively. The parallel model gives the composite thermal conductivity,

$$k_c = V_m k_m + V_f k_f \quad (3)$$

When fillers accumulate to a critical loading the inter-filler network forms in a matrix. For the majority of the experimental results, these two models established the lower bound and upper bound.

8.4 Flame retardancy

Epoxyes were first used in a variety of high-tech applications, and this led to the creation of materials with lower flammability. It is challenging to quantify the contributions of many system components to one dominant mechanism in flame retardant materials; nonetheless, the effective mechanism of flame retardancy can be split into two actions: the gas phase and the condensed phase actions. The flame zone, the char layer, the thermal decomposition (or molten polymer), and the underlying polymer zones are all engaged in the flame retardancy mechanism when the flame is directed to a polymer. Volatiles are produced in

the thermal decomposition zone and then mitigate toward the flame zone, where the char layer controls heat and mass transmission between the condensed and gas phases. By preventing flammable volatiles from diffusing and protecting the polymer from air and heat, the char layer that forms on the surface of the condensed phase regulates heat and mass transmission between the gas phase and the condensed phase. As particular radicals combine with highly reactive species to create less reactive halogen atoms, the gas phase mechanism also includes the stoppage of the combustion process by radical absorption. To increase the flame retardancy of epoxy resins, various techniques such as chemical functionalization and the addition of flame retardant chemicals have been used. Since 2D materials can make it easier for a protective char layer to form in the condensed phase, they have been investigated as flame-retardant additives. Furthermore, 2D materials can prevent combustion during the gas phase mechanism.

8.5 Anticorrosive Properties

Epoxy resins are appropriate for anti-corrosion coatings spanning from heavy industry to everyday life because of their outstanding chemical resistance, strong adherence to substrates, and great mechanical strength. To prevent corrosion, an epoxy coating can be applied to the desired metal. Epoxy coatings, for instance, have long been used to safeguard ships and other marine structures. Epoxy resins are frequently used to cover metal cans and containers to stop rusting. Additionally, epoxy resins have been used to coat items like laminate table tops, sculptures, statues, and paintings. Epoxy coatings can create a physical barrier effect and prevent corrosive fluids from penetrating metal surfaces.

9. Fracture Surface

SEM may be used to study nanocomposites' fracture surfaces, while FE SEM can examine the morphology of nanocomposites' fracture surfaces near the crack tip. The fracture surface of tidy EP is well known for being smooth and featureless, showing the brittle nature of firmly crosslinked EP. On the other hand, the fracture surface of nanocomposites has various morphologies. It suggests that several toughening processes are to blame for the previously observed increase in fracture toughness and energy (void nucleation interface debonding, inelastic shear matrix deformation, and crack deflection). SEM micrographs of the fracture surfaces of untoughened and toughened EP resins after impact and tensile testing, for example, revealed unmodified EP [53]. A smooth fracture surface was seen in cracks in various planes. These findings point to the EP's unaltered version having a brittle fracture pattern, which explains its low impact strength. The fracture surface of the EP-submicron composite demonstrated considerable shear deformation when filled EP resin composites were utilized. This finding suggests that when exposed to mechanical stress, the submicron particles' stress concentration appears to exacerbate EP interlayer shear yielding at the propagating crack's tip, which persists throughout the volume. On the fracture surface, there were additional thumbnail-like marks. Due to the toughening particles and crack trapping, this most likely signals the onset of crack pinning. These findings suggest that thumbnail markings are linked to a more dominant sort of toughening mechanism in impact testing. The fractures intersect, revealing a brittle river fracture pattern similar to that seen in metal cleavage fractures, according to Al-Turaif [52]. This shows that the specimens were fractured

with only a little energy. According to Chatterjee and Islam's [53], SEM visual examination of the fracture surfaces of nanocomposites for the clean epoxy matrix resin system, brittle behavior is characterized by wide, smooth patches, significant hyperbolic markings, ribbons, and fracture steps in the direction of the crack propagation. The nanocomposite surfaces, on the other hand, are rougher structured and show multiple hyperbolic marks that open in the direction of fracture development.

10. Application of Nanofilled/nanostructured epoxy resins

A wide range of experimental nanoepoxies' remarkable chemical and physical qualities enable a broad range of implementations, from structural adhesives to coatings, from FRP matrix to Materials 2020, 13, 3415 15 of 24 electrical/electronic components. Numerous industries have used epoxy nanocomposites [54]. These applications include aerospace, aircraft, automotive, buildings, electronic devices, antistatic materials [55], anti-corrosive coatings abrasive tools, (for instance, in pipes or maritime environments), and structural applications with self-sensing qualities are all examples of self-sensing uses. Improved characteristics frequently enable more efficient multipurpose use. As for another test, in general, and according to earlier studies, the XRD and FTIR examination results likewise revealed a uniform distribution of nanoparticles in the epoxy and a rise in the number of peaks with an increase in the weight percentage of the particles.

11. Classification of Nanoparticles

As shown in Fig. 2, based on a variety of factors, nanomaterials can be divided into

numerous groups. NMs are typically divided into categories based on their dimensionality, morphology, condition, and chemical makeup.

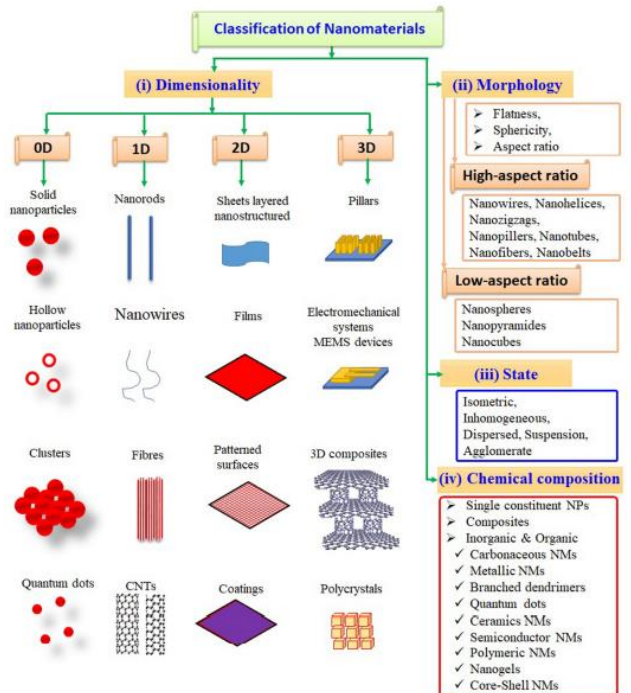


Figure 2. Schematic representation of the various criteria used to classify nanomaterials[56].

12. Synthesis of Nanoparticles

There are various methods for creating nanomaterials, including as top-down and bottom-up methods (Fig. 3). In the bottom-up method, the desired material is first synthesized at the atomic level, followed by the synthesis of nanoparticles. In the top-down method, a bulk macroscopic material is trimmed down to the desired nanoparticles using several techniques.

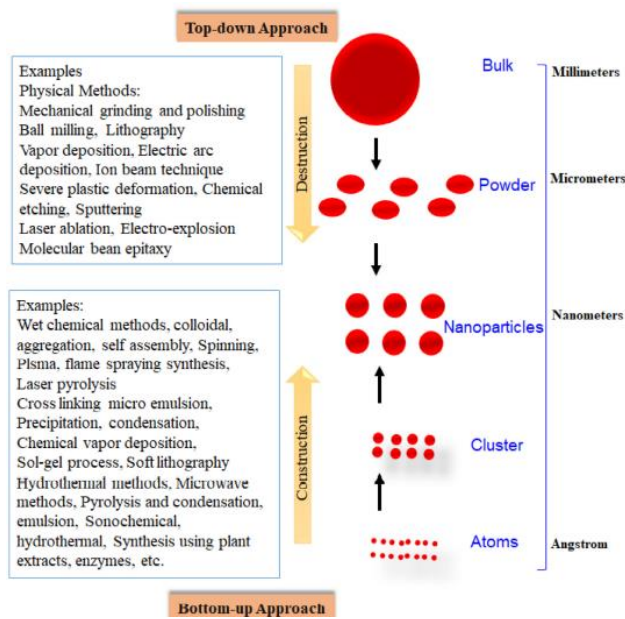


Figure 3. Diagram showing the top-down and bottom-up approaches to creating nanoparticles[56].

13. Limits of the Production

In the manufacture of polymer-based nanocomposites, different technological restrictions can be encountered. The resin matrix has widely explored the significance of achieving fine and homogeneous nanofiller dispersion. Spreading the nanofiller in liquid resin is the most popular and economical approach to creating a nanocomposite, however, it is not always successful. Furthermore, conventional techniques for creating and using the nanocomposite may still be employed when very minute quantities of nanoparticles are introduced to the epoxy. At large nanoparticle loadings, however, the viscosity of the nanofiller/resin combination considerably rises, necessitating more time-consuming and costly techniques for the synthesis of nanocomposites. It is necessary to review the cost-to-performance ratio of such nanocomposites and compare it to the economic benefit of the intended application. In a similar vein, the advised experimental methods for functionalizing the nanofiller surface often need to utilize highly

specialized or well-crafted chemicals or solvents.

In contrast, the industry prefers cheaper commercially available chemical products, accelerating scale-up manufacture. Last but not least, according to life cycle analysis (LCA) ideas, various problems are related to the health risks and environmental repercussions of such nanomaterials throughout their "life." Toxic substances, acid/basic chemicals, and organic solvents are commonly used in manufacturing nanofillers.

14. Conclusions

Focusing on the important recent developments and advancements in the area of epoxy-based nanocomposites, a review of the most recent research in the literature has been provided. The various nanofillers can improve epoxies' properties or mitigate some of their well-known flaws. It highlights the important roles performed by the nanoparticles' chemical makeup, their dimension and aspect ratio, and their presence in the epoxy (alone or in combination with other nanomaterials). It has also been shown that organic epoxy may be used as a coupling agent between the nanoscale inorganic phase and the organic polymer phase in organic-inorganic hybrid systems, the third form of nanocomposite. The reviewed papers show that nanoparticles' uniform dispersion and interactions with the epoxy matrix are required to develop an excellently performing nanocomposite based on epoxy resin. Additionally, the surface of the nanofillers may be chemically altered to achieve similar objectives for any other polymeric matrix [57]. However, they can also change the epoxy resin's curing kinetics. The type of nanofiller, quantity, and dimensional features influence the crosslinking reaction rate, the final Tg, and the

crosslinking degree. Epoxy-based nanocomposites have a tremendous amount of promise, and many applications, including some likely industrial ones, have been explored. The main technical barriers to the production of epoxy-based nanocomposites and their impact on the environment and human health have finally been revealed. The literature reviewed indicated that when using inorganic oxide fillers as fillers in epoxy nanocomposite systems, low nanofiller loadings show certain beneficial dielectric characteristics. In comparison to micro composites and empty systems, the permittivity and tan delta values in nanocomposites are found to be lower (for a few filler loadings). Further research is required to fully understand the internal interaction dynamics of nanocomposites, which are difficult because of the influence of multiple factors.

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Author Contribution Statement

Author Samer Saad wrote the research paper, and researchers Raouf Mahmood and Harith Hasson reviewed and gave some comments that would show the research at its current value.

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