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Review

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A Comprehensive Review on the Role of Nanosilica as a Toughening Agent for Enhanced Epoxy Composites for Aerospace Applications

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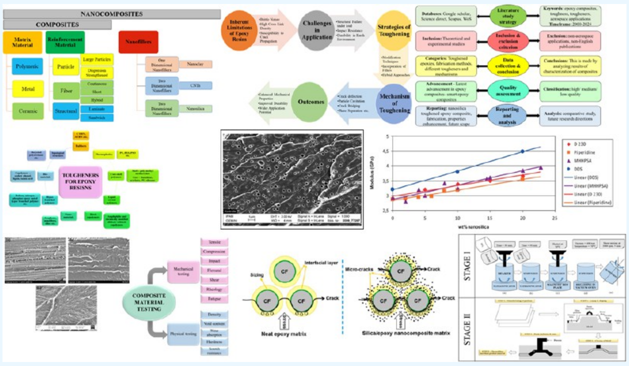
ABSTRACT: This review provides a thorough review on nanosilica as a strengthening component in epoxy composites, with a specific emphasis on its suitability for use in aerospace applications. The study commences by examining the distinctive characteristics of nanosilica, encompassing its methods of synthesis as well as its efficacy in augmenting the mechanical and thermal properties of epoxy-based composites. A substantial part of the review focuses on assessing the efficiency of nanosilica-reinforced glass fiber composite laminates, particularly in the field of aerospace structural applications. The issue of low toughness in epoxy composites, specifically the occurrence of crack growth and propagation when subjected to stress, is tackled through the investigation of different toughening techniques. These techniques involve the addition of nanosilica and liquid rubber tougheners such as ETBN. In addition, this review presents the techniques used to distribute nanosilica particles within epoxy resins and offers a detailed examination of the mechanical testing and characterization methods employed for these nanocomposites. The study determines that nanosilica, owing to its substantial surface area and mechanical durability, greatly improves the resilience and overall mechanical efficacy of epoxy composites, rendering it a highly promising material for the aerospace sector. This study suggests that addition of nanosilica in epoxy-based composites until 5% by weight gives the best possible outcomes with respect to increment in mechanical properties like modulus, strength, and toughness.



1. INTRODUCTION

Conventional materials along with advanced materials are being used in mechanical and structural applications; on the other hand, composite materials are capable of resisting fatigue and corrosion, which are the main reasons that these composites are now being used in several applications, such as in the aerospace industry. Apart from this, these polymer-based composites are light in weight and are reliable as compared to contemporary materials.[1] The field of nanocomposites is that typical field of materials that deals with the incorporation of nanosized materials into composites during manufacturing, with the motive to achieve some enhanced properties, like strength, toughness, impact energy, etc.[2] The primary distinction between composites and nanocomposites lies in the size of the filler used. The evolution of composite materials has been marked by a gradual reduction in filler size—from several millimeters in traditional composites to microscale.[3] An aircraft has to face an environment in space which consists of vacuum, micrometeoroids, space debris, and very large temperature variation because of sunlight. So, materials used to construct aerospace components should possess good thermal properties so that they can sustain high temperature variations.[4] But the main challenge of epoxy-based composites is their low toughness, which leads to crack growth and propagation.[5] Epoxy resin is a low-molecular-weight thermosetting polymer material, which has many reactive epoxide groups in it. Epoxy composites with high durability and high strength are in high demand in engineering applications because of their size-to-strength ratio, versatility, and cost-effectiveness.[6] Despite their excellent mechanical properties and chemical resistance, epoxy composites are highly flammable, which limits their use in safety critical applications. To address this drawback, flame retardants are introduced to enhance thermal stability and reduce the material's flammability during exposure to fire or high heat. These additives help meet fire safety standards required in industries such as aerospace, automotive and construction.[7]

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Recent developments on multiwalled nanotubes and epoxy composites on improved dispersion techniques and surface functionalization of nanotubes to enhance interfacial bonding have been achieved. These advancements have significantly boosted electrical conductivity, enabling their use in sensors, electromagnetic shielding and energy storage applications.[8] Industries like the automotive, structural, and aerospace sectors rely heavily on composites with high durability for a variety of engineering applications.[9] The automotive sector is shifting toward lightweight design to reduce energy consumption and environmental impact, with a 10% weight reduction leading to a 6−8% drop in energy use. Composite materials, especially fiber reinforced polymers, offer high strength-to-weight ratios, making them ideal for electric vehicle components.[10] Exceptional tensile, flexural, and impact properties of fiber-reinforced epoxy composites are the result of the fiber matrix interface adhesion.[11] Fiber reinforced polymer composites are widely used for their excellent mechanical properties, with recent efforts focusing on ecofriendly alternatives like natural and hybrid fibers. Enhancing fiber matrix bonding through chemical treatments and nanoparticles has significantly improved their performance.[12] Chemically modifying the surface of the fiber to increase adhesion, as is done in surface treatment, improves the overall fiber properties.[13] Carbon fibers are widely used in polymer composites but suffer from poor adhesion due to their inert surface. Many surface treatment methods are available like acid oxidation, plasma and gamma irradiation that enhance fiber−matrix bonding by improving surface area and chemical reactivity.[14] The aerospace industry is continually evolving, driven by the need for materials that are exceptionally high performance under extreme weather conditions.[15] Recent advancements in aircraft materials have led to the development of high-performance composites and metal based alloys for enhanced strength and durability. Despite their benefits, issues like corrosion and wear persist, prompting ongoing research to improve mechanical properties and longevity.[16] Epoxy composites have garnered significant attention and are valued for their high strength-to-weight ratio, excellent adhesion properties and resistance to environmental degradation.[17] Natural fibers are gaining attention as sustainable, low-cost reinforcement materials in composites due to their availability and environmental benefits. Research is focused on enhancing the mechanical, thermal and rheological properties of these biocomposites for diverse applications, including biomedical fields.[18] However, the critical challenge with epoxy-based composites is their inherent brittleness, which limits their applicability in aerospace structures, where toughness and durability are paramount.[19] Carbon based nanomaterials like graphene are widely studied for their exceptional mechanical, thermal and electrical properties. There are recent advancements in graphene-epoxy nanocomposites, particularly their enhanced fracture toughness due to mechanisms like crack pinning and deflection. It provides valuable insights for developing tough, high-performance composites for applications in the aerospace, automotive, biomedical and energy sectors.[20] To overcome this limitation, various toughening strategies have been explored in this study, including incorporation of nanosilica, liquid rubber-based tougheners, etc.[21] Epoxy was modified using liquid CTBN and nanosized nanosilica particles to create binary and ternary composites, revealing changes in particle size and morphology through SEM and TEM analysis. The addition of CTBN/nanosilica to an epoxy system significantly enhanced mechanical strength and fracture toughness. Toughness was primarily attributed to rubber particle cavitation and shear-induced void growth, especially within the stable crack propagation zone.[22] Nanosilica toughened epoxy composites represent a cutting-edge advancement in material science, combining superior mechanical properties of epoxy resins with the remarkable reinforcement capabilities of nanoscale silica particles.[23] Epoxy resins are widely used across industries for applications like coatings, adhesives, and high-performance composites. Understanding the curing process and network formation is key to tailoring their properties, though challenges arise due to their infusibility and insolubility.[24] These nanocomposites exhibit enhanced toughness, improved impact resistance, and superior fracture mechanics, making these composites ideal for aerospace composites.[25] The study highlights the significant impact of incorporating various nanoparticles—such as CNTs, graphene, nanoclay and nanosilica—on the mechanical properties of epoxy resins. Enhancement in fracture toughness, strength and stiffness is closely tied to nanoparticle type, dispersion quality and matrix adhesion. The role of surface functionalization is also discussed in various studies.[26] The unique properties of nanosilica, including its high surface area, excellent thermal stability, and mechanical robustness, contribute significantly to the overall performance of the epoxy matrix.[27] The introduction of nanosilica into the epoxy resin facilitates the formation of a more homogeneously and densely packed microstructure, which is crucial for improving the material's toughness.[28] This enhancement is primarily attributed to mechanisms like crack deflection, energy dissipation through particle−matrix debonding, and plastic deformation of the matrix around the nanoparticles.[29] These mechanisms collectively contribute to the improved resistance to crack propagation and the ability to absorb and dissipate energy under impact, which are critical attributes for materials used in the aerospace sector.[30] In aerospace applications, materials are subjected to a variety of stresses and environmental conditions, including thermal cycling, mechanical vibrations, and exposure to aggressive chemicals.[31] Nanosilica-toughened epoxy composites not only meet the mechanical and thermal requirements but also offer significant advantages in terms of weight reduction, which is a crucial factor in the aerospace industry.[32] The reduction in weight without compromising structural integrity leads to improved fuel efficiency and overall performance of the aircraft component. Moreover, the use of nanosilica in epoxy composites aligns with the growing trend toward nanotechnology in material science. The ability to manipulate the material at nanoscale permits design of composites with tailored properties with flexibility to meet special requirements for aerospace components. Despite the promising potential of nanosilica-toughened epoxy composites, there are still some challenges that needed to be rectified to realize their full capabilities, like uniform dispersion of nanosilica into the epoxy matrix, optimization of loading levels of nanoparticles, and understanding of the long-term performance under service conditions.[33] These are critical areas for ongoing research. Advances in these areas will pave the way for the broader adoption of nanosilica-toughened epoxy composites in the aerospace industry.

Nanocomposites are composite materials which incorporate nanoscale materials like nanoparticles, nanotubes, etc. into the matrix material, offering several distinguishable features and advantages over conventional composites. These enhance-

Table 1. Comparison of Conventional Composites and Nanocomposites:

Property	Conventional Composites	Nanocomposites	Refs
Significance	These are made up of fibers or particulates in macro-/microform reinforced in a matrix material.	Composites with nanometer scale fillers like nanoparticles, nanotubes, nanoclay etc. dispersed in a matrix along with the reinforcement material.	49−53
Mechanical Strength	Moderate to high, it depends upon type of reinforcement and matrix material.	It possesses superior strength, due to high surface area and better load transfer at nanoscale.	
Stiffness	Good stiffness value but limited by fiber-matrix adhesion.	Higher stiffness due to strong nanoscale interactions.	
Weight Reduction	Light in weight as compared to metals, but still dependent on matrix material.	Even lighter in weight with enhanced properties due to matrix interaction at nano level.	
Thermal Stability	Moderate, degrades at high temperature.	Higher thermal resistance due to nanoscale dispersion and heat dissipation.	
Electrical properties	Generally insulating unless conducting fillers are introduced.	These can be engineering for conductivity by introducing CNTs, graphene etc.	
Barrier Properties	Limited resistance to gas and moisture diffusion.	Excellent gas and moisture barrier properties due to nanofiller alignment.	
Processing	Well established techniques like hand lay-up, VARIM etc.	Complex processing as nanofiller dispersion is a challenge.	
Cost	Relatively lower.	Higher cost, as it requires advanced materials and processing techniques.	
Applications	Aerospace, automotive, marine and construction industries.	High performance applications in aerospace, electronics, biomedical and energy storage.	

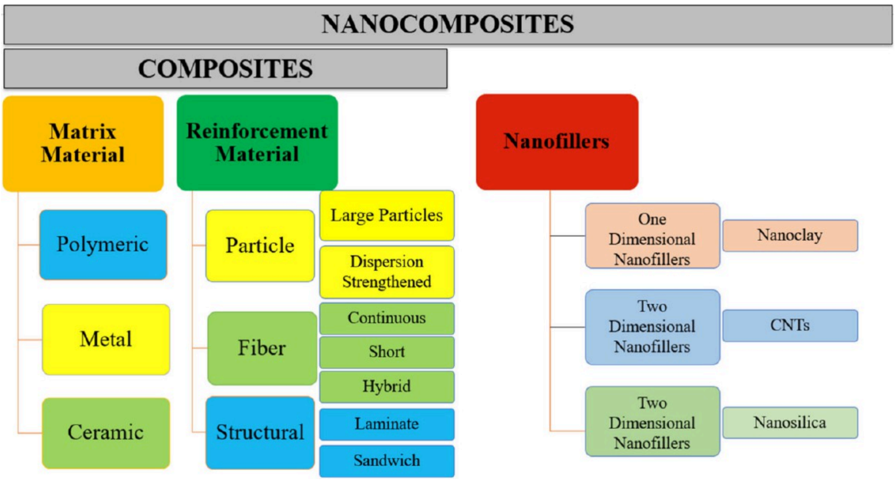

Figure 1. Components of composites and nanocomposite materials.

ments in properties arise from the nanoscale dimensions of the reinforcing materials, which provide a high surface area to volume ratio and unique physical, mechanical and chemical characteristics.[34] Due to the high surface to volume ratio, there is a large interface between the reinforcement and the matrix material which allows better load transfer and interfacial adhesion.[35] Effective load transfer ensures that stress applied to the nanocomposite is distributed efficiently across the nanoreinforcement, increasing overall strength.[36] Nanoparticles and nanofibers are capable of enhancing the mechanical properties like tensile strength, modulus, flexural strength, impact resistance, and toughness, as the nanoscale materials tend to dissipate energy more effectively as compared to composite materials.[37] The uniform dispersion of nanoscale materials creates a network that resists deformation and failure. The small size of the reinforcement materials helps them fill microscopic voids and defects in the matrix, which would otherwise act as stress concentrators and weaken the material.[38] The thermal stability of the nanocomposites refers to their ability to maintain their structural integrity and resist degradation at elevated temperatures. This property is significantly enhanced compared to conventional composites due to the inclusion of nanofillers with high thermal resistance and specific interaction with the matrix.[39] Nanofillers such as graphene, carbon nano tubes (CNTs), nanoclays, and ceramic nanoparticles inherently possess high thermal stability and melting points.[40] Additive manufacturing or 3D printing is gaining interest for structural applications, but improvements in materials are needed. The study highlights how carbon nanofillers like graphene and CNTs enhance the mechanical and thermal properties of additive manufacturing parts, making them more viable for load-bearing uses. Print orientation and nanofiller dispersion that influence performance are also discussed.[41] Recent focuses have been on lightweight, ecofriendly kenaf-fiber reinforced nanomodified epoxy composites for enhanced mechanical performance. The addition of graphene improves strength and barrier properties without sacrificing toughness. Among various tested combinations, a nanocomposite with 75 nm salinized fillers and kenaf fibers showed the highest mechanical performance, boosting tensile strength by 16% though some microlevel flaws that reduced structural stability.[42] Nanoclays and nanosilica exhibit exceptional resistance to decomposition and help with thermal insulation. In polymer matrices, nanofillers can act as barriers that prevent the diffusion of heat and gases. This inhibits the escape of volatile decomposition products, delaying thermal degradation.[43] By restricting oxygen permeability, nanofillers reduce the oxidative degradation of the polymer at high

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temperatures. Nanomaterials also help to improve the thermal conductivity, which helps dissipate localized heat more effectively. This prevents hotspots and uneven temperature distribution, reducing thermal stress and degradation in specific regions.[44] Nanofillers in a way provide structural reinforcement at high temperatures. At elevated temperatures, many materials tend to get weakened due to softening and thermal expansion. Nanofillers strengthen the matrix by forming a rigid network that resists deformation and thermal expansion.[45] Nanoparticles can induce cross-linking in polymer matrices or enhance crystallinity during processing. Cross-linking raises the materials glass transition temperature and decomposition temperature, improving thermal stability. Higher crystallinity improves resistance to thermal softening by increasing the percentage of ordered regions in the polymer.[46] Table 1 shows a brief comparison of conventionally used composite materials and nanocomposite material. Figure 1 gives a representation of constituents from which composites and nanocomposites are being made. The composite material structure utilizes carbon nanotubes microhierarchy and skeleton lattices mesohierarchy to enhance rigidity and dampen excitation, achieving a loss modulus of up to 1.54 GPa.[47] A new composite printing strategy has been proposed, allowing for the direct fabrication of composite parts by using composite powders. This method eliminates the need for a complex premade filament process, resulting in excellent mechanical properties. This study fabricated hydroxyapatite reinforced composite specimens with the highest flexural and compression strengths. The composites were also successfully fabricated with different reinforcement fillers.[48]

This present study gives a brief idea about toughened epoxy-based composites. The main challenges of using such types of composites are discussed in detail with a motive to provide benefit to young researchers and scientists. The need for using nanosilica in epoxy composites is discussed in detail, including the basics of nanosilica with its properties, key source, and synthesis methods. Epoxy resins which are used in the construction of aerospace components are being discussed with challenges and morphology which will give a clear vision to researchers who are working on the same subject. Toughening of the epoxy composite is required because of its brittleness; this is discussed in detail, along with different tougheners and toughening mechanisms observed in epoxy resin. Incorporating tougheners into epoxy resin results in enhancement of mechanical properties like modulus, tensile strength, impact energy, fracture toughness, interlaminar shear strength, etc. Toxicological aspects of silica nanoparticles are studied in this review paper to understand their effect on health and environmental conditions. The method of incorporating nanosilica into epoxy resin is represented in a very good manner, so that it can be understood effectively. Preparation techniques of nanosilica toughened epoxy-based composites are also discussed. Various characterization techniques are discussed, including tensile test, fatigue test, fracture test, water absorption test, etc. Smart epoxy composites are discussed, which are capable of self-healing, retaining their original shape and size, and inhibiting undesirable properties, along with their applications. The paper concluded by depicting that nanosilica is capable of increasing the toughness of epoxy composites, as it possesses high surface area, which allows better interaction with the matrix material and thus better stress transfer is observed. Other mechanical properties of the overall composite are also increased because nanosilica itself has a high modulus.

This review is conducted specifically with the following objectives:

- To study epoxy-based composites, on the basis of their suitability and limitations for aerospace applications.
- To study the effect of nanosilica on the mechanical properties of epoxy-based composites.
- To obtain an understanding of the different toughening mechanisms observed during addition of liquid rubber tougheners and nanosilica into epoxy resin.

2. REVIEW PAPER METHODOLOGY

This review follows the Preferred Reporting Items for Systematic Reviews and Meta Analyses (PRISMA) guidelines, ensuring a systematic and comprehensive approach for conducting the literature review and selecting relevant articles. The methodology adopted in this review consists of the following steps:

2.1. Formulation of Research Questions. The main objective of this research is to evaluate the capabilities of tougheners to enhance the mechanical properties of epoxy-based composites for aerospace applications. The key research questions include the following:

- Can nanosilica be used as a toughener in epoxy-based composites?
- What is the procedure to incorporate nanosilica into epoxy resin?
- What is the significance of toughening in epoxy-based composites?
- What is the fabrication method to prepare silica-epoxy nanocomposites?
- What are the current challenges and future scope of this field?

2.2. Literature Search Strategy. A comprehensive literature search was conducted using databases such as Google Scholar, Science Direct and Scopus. Keywords used in this search included “epoxy composites”, “tougheners”, “aerospace applications”, “nanosilica”, “liquid rubber tougheners”, “impact resistance”, “fracture toughness”, “flexural strength”, etc. Research articles published during 2000−2023 were considered to record the most recent work on the subject.

2.3. Inclusion and Exclusion Criterion. Inclusion criteria:

- Peer reviewed journal articles, conference papers, reviews focused on epoxy-based composite applications in aerospace components.
- Studies that involved experimental and theoretical analysis of toughened nanocomposites.
- Studies involving properties of nanosilica as a reinforcing agent.
- Articles involving the fabrication procedure of such composites and nanosilica-epoxy resin, their mechanical properties, enhancement of toughness, and their characterization.

Exclusion criteria:

- Studies not related to aerospace applications.
- Publications in languages other than English.

2.4. Data Collection and Conclusions. Data were collected on the basis of the predefined categories involving toughened epoxies, fabrication methods, different tougheners and mechanisms, mechanical properties, and performance outcome. Conclusions were drawn from analysis and comparison of various SEM and TEM images and mechanical test results of the composites.

2.5. Quality Assessment. The quality of each included study was assessed on the basis of knowledge shared about the key research question, the validity of the results, and methodological study of the topic. This review paper includes high-, medium-, and low-quality studies based on these criteria.

2.6. Reporting and Analysis. The studies under consideration were organized in keynote areas including nanosilica toughened epoxy composite, fabrication, properties enhancement, and future scope. A comparative study was created to highlight advantages against traditional materials. The methodology is shown in Figure 2.

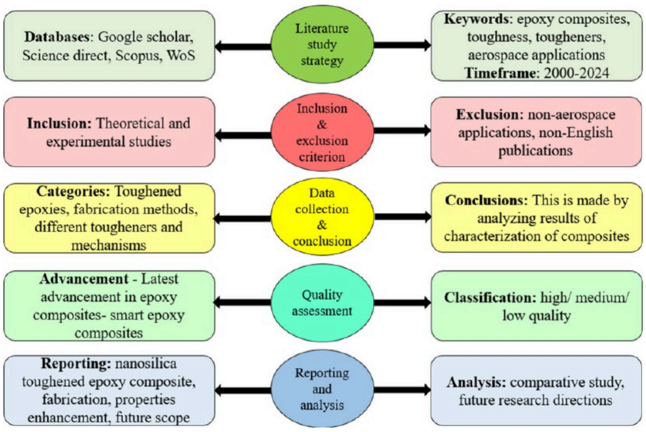

Figure 2. Review paper methodology.

3. NANOSILICA: SYNTHESIS AND APPLICATION

Pure silicon (Si) is a natural nonmetallic element, which is found in rocks, sand, clays, and soils. As it is too reactive, it is generally found in the form of silicon dioxide (SiO_2) or silicates.[54] It serves as the primary glass-former in ceramic glazes, contributing significantly to their structure and properties.[55] Nanosilica size is extremely small, ranging from 1 to 100 nm, and because of these nanoscale dimensions, it exhibits some unique properties compared to bulk silica particles. Such properties include enhanced reactivity, increased surface area, and also different optical, electronic, and mechanical characteristics. Nanosilica is used as an additive, in cement and other construction materials, to improve their strength and durability;[56] in rubbers and plastics, to enhance their hardness and tensile strength; and in coatings and paints, to enhance scratch and wear resistance. Nanosilica is found to be compatible in various biomedical applications like drug delivery systems and imaging agents[4,5] Nanosilica possesses the high surface area 653 m^2/g, which is a helpful property for applications like adsorption, catalysis and as a reinforcement agent in composite materials.[58,59] Due to its high surface area and increased number of surfaces, nanosilica is more reactive than its bulk material. Hence, it is a useful component in catalysis and a functional component in chemical processes. When nanosilica is incorporated into composites, it enhances the mechanical properties like tensile strength, hardness and abrasive resistance, which makes it a useful advanced material for aerospace structures.[60] Table 2 shows such properties' enhancement compared to epoxy resin. Also, nanosilica is thermally stable and is used in applications where a variation of temperature is observed. Nanosilica possesses high surface area, because of which good interaction of nanosilica and the epoxy matrix has been noticed by various researchers.[61] This improved interaction leads to better stress transfer between them, and so the toughness and other mechanical properties increase.

Table 3 gives an idea of particle size and raw material used in the synthesis of nanosilica. Hydrogen bonded silanol groups (-Si-OH) are found on the surface of nanosilica, which allows it to bond with polar molecules, which eventually helps in the surface modification and functionalization process.[64] The siloxane group (-Si-Si-) is also present in amorphous and crystalline nanosilica, which are capable of making 3-D networks and a regular lattice, respectively, contributing to better stability and mechanical properties.[65] Amorphous nanosilica was synthesized from rice husk using an ecofriendly method and combined with ferrites and PVDF to form a magnetic nanocomposite via injection molding. Characterization confirmed the nanosilica's amorphous structure, small particle size and diamagnetic nature, while the composite exhibited ferromagnetic behavior due to ferrite content.[66] These groups are responsible for better adhesion in composite systems, coatings, and adhesives.

Nanosilica is synthesized using various techniques, with the sol−gel method being the most common. In this method, a silica precursor such as Tetraethyl Orthosilicate (TEOS) or sodium silicate undergoes hydrolysis and condensation in a controlled environment, leading to the formation of silica nanoparticles. Other techniques of nanosilica synthesis along with its advantages and limitations are discussed in Table 4. The advantages of nanosilica include high surface area, improved mechanical and thermal stability, and enhanced chemical reactivity, making it suitable for applications like coatings, catalysts, drug delivery, and concrete reinforcement.

4. EPOXY RESINS IN AEROSPACE APPLICATIONS

Amorphous, highly cross-linked epoxy resins have long been the focus of research and development due to their high modulus toughness and hardness, low creep, and exceptional chemical and heat resistance, among other desirable properties, in the field of structural engineering, and affordable cost.[87] Epoxy resins are susceptible to cracking owing to their dense three-dimensional molecular network structure.[24] The material

Table 2. Enhanced Properties of Epoxy Resin after Incorporating Nanosilica[62]

Sr. No.	Material	Modulus (GPa)	Strength (MPa)	Toughness (kPa/m^2)	Energy (J/m^2)	Key Findings
1.	Epoxy resin	2.76	86	1381	606	Nanosilica is capable of increasing toughness of epoxy resin, because of its high surface area (≈400 m^2/g)[63]
2.	Epoxy resin +10% wt. nanosilica	3.45	86	1916	1016	Nanosilica is capable to increase mechanical properties of epoxy resin, because of its high modulus of elasticity.

Table 3. Nanosilica: Properties and Synthesis Method

Sr. No.	Particle Size (nm)	Key Source	Synthesis Method	Key Findings	Ref
1.	13 to 24 nm	Agricultural waste rice husk ask	Precipitation method, sol gel method	Presence of hydrogen-bonded silanol group and siloxane groups in silica, which helps in surface modification and functionalization processes	67
2.	20 to 50 nm	Rice husk	Pyrolysis method	Obtained nanosilica: Specific surface area = 204.3−352.6 m^2/g Purity = 95.85−99.62%	68
3.	-	Coal fly ash	Impregnation method	Application − for selective adsorption of CO_2	69
4.	1−100 nm	Tetraethyl orthosilicate	Stober process	Uniform spherical particles, controllable size	70
5.	22 nm	Rice husk	Sol−gel method	High surface area, good for drug delivery and catalysts	59
6.	304 nm	Sodium silicate	Precipitation method	Cost-effective, applicable in composites and coatings	71
7.	10 nm	Silica fume	Flame synthesis	High purity, used in high-performance concrete	72
8.	4 to 50 nm	Silane precursor	Wet chemical method	Minimum impurity is found Unable to control the particle size and morphology	57
9.	10−12 nm	Sand	Hydrothermal synthesis	Environment friendly, used in ceramics and polymers	73

Table 4. Nanosilica Synthesis Techniques: Advantages, Limitations

Nanosilica Synthesis Technique	Advantages	Limitations	Ref
Sol−gel method	High control over property size and morphology Purity and uniformity of nanosilica are excellent Allows functionalization during synthesis like dopings	Requires expensive precursors Slow reaction rates Sensitive to process parameters	74,75
Precipitation method	Cost effective and scalable Simpler and faster as compared to sol−gel method Yields larger quantity of nanosilica	Particle size control is less precise Impurities removal is a challenge Higher chances of particle aggregation	67
Pyrolysis	High purity and small particle size Continuous production process Produces nonporous particles with high specific surface area	High energy consumption Requires specialized equipment and safely measures Limited control over porosity and particle shape	76
High pressure autoclave method	Control over crystalline structure Uniform particle size Enhance reaction rates Ability to use water as solvent	High initial investment Energy intensive Complex process control Limited choice of precursors Longer reaction times	77,78
Stober	Produces monodispersed spherical particles Excellent control over particle size Suitable for surface functionalization	Higher cost Limited scalability	79,80
Biogenic synthesis	Environmental friendly and sustainable Cost effective as agricultural waste is used Functionalized particles can be synthesized directly	Quality and yield depends on the biological source Requires optimization for reproducibility Potential impurities from biological materials	81,82
Flame spray pyrolysis	Rapid production of nanoparticles High purity and consistent particle size Scalable	High energy cost Limited control over porosity Requires specialized equipment	83,84
Microwave assisted synthesis	Faster reaction times as compared to other methods Enhanced uniformity and smaller particle size Energy efficient	Requires microwave compatible equipment Limited scalability for large scale production	85,86

matrix for composites of fiber-reinforced polymers and reinforced adhesives are two examples of reinforced materials, where this limitation has hampered their use in engineering fields that require high resistance to fracture.

4.1. Challenges and Limitations. Epoxy cracking is a common problem.[88] So, scientists have spent decades producing and researching novel and innovative techniques to prevent it. To improve the toughness of epoxy resin, the matrix material can be fortified by incorporating soft rubber particles or rigid silica particles throughout the polymer matrix.[89] It has been found that particle cavitation, matrix plastic deformation and matrix void expansion are the primary toughening mechanisms in micronized rubber-epoxy systems.[90] Micronized silica/epoxy systems, on the other hand, have been linked to shear banding, as a mechanism for toughening matrix dilation and particle debonding followed by void growth.[91] The study explored the impact of mixed micro- and nanosilica particles on the dynamic properties of epoxy composites using split Hopkinson pressure bars. Results showed that while dynamic stiffness increased with silica content, it decreased with glass transition temperature. An optical particle mix improved energy absorption and reduced stress transmissibility, offering a balanced design approach for high performance epoxy/silica adhesives.[92,93] Epoxy composites reinforced with nanosized fillers have garnered a lot of attention from scientists and consumers alike. The tensile strengths of epoxies typically increase with decreasing filler size.[20,95,96] Epoxy resin is significantly toughened by the addition of nanosized particles and nanosilica, nanorubber in particular.[97,98] Result showed a significant change in GIC at

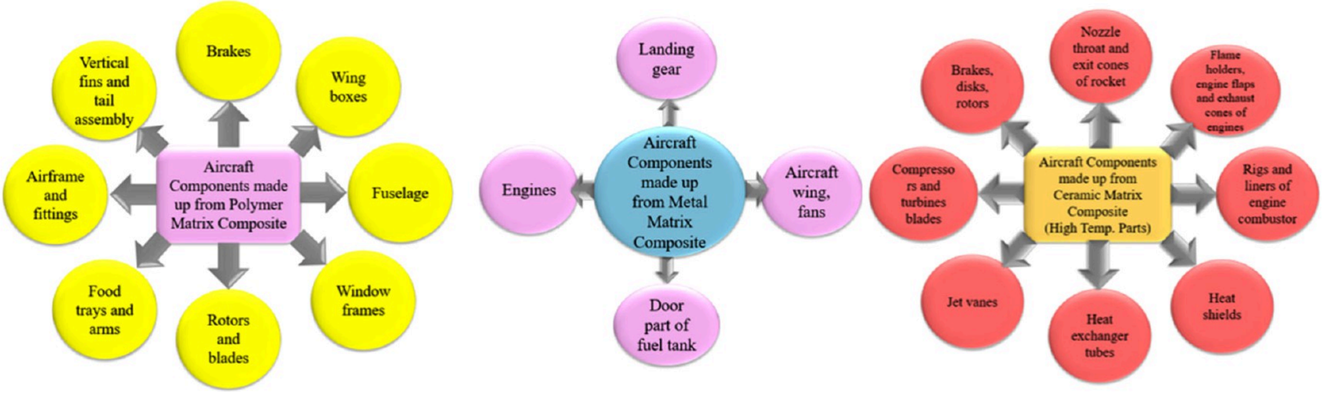

Figure 3. Various aircraft components made up from different composites: PMC, MMC, and CMC.[16]

high strain rates, attributed to notch tip blunting from adiabatic heating. A proposed model explains this behavior and offers practical insights for accurate impact testing.[99] Results for the toughness of epoxies modified with rubber or silica particles were typically obtained under a static loading at room temperature. The aforementioned statement fails to provide an accurate depiction of the performance of the composite under specific environmental circumstances, including impact loading and extreme temperature fluctuations ranging from subzero to high levels.[100] Epoxy resin are sensitive to high temperature; they degrade at high temperatures, which leads to loss of mechanical properties.[101] This limits the use of epoxy composites in high temperature environments such as engine components or areas exposed to direct sunlight in space. Another challenge of using epoxy resin is that it is brittle in nature as compared to other metal materials, which results in cracking under impact or sudden stress conditions.[102] This reduces the durability and impact resistance of the component. Besides, epoxy resin requires precise processing conditions which include controlled temperature and curing time to achieve the optimal properties.[103] This complexity increases manufacturing costs and time, and it also requires specialized equipment and skilled professionals. Vacuum environments are common in space. One more common issue with epoxy resin in aerospace components is that, when these are subjected to a vacuum environment, they release volatile gases.[104] This limits their use in sensitive components and systems. Although epoxy resin is resistant to chemicals, it is susceptible to many aggressive chemicals and solvents.[105] Repairing epoxy resin is difficult, and it does not store or retain the original mechanical properties.[106] This increases maintenance complexities and requires specialized techniques and equipment for effective repair.

4.2. Importance of Epoxy Composites in Aerospace Structure. By replacing traditional heavy metallic parts with lightweight epoxy composite structures, aircraft weight is significantly reduced, which increases fuel efficiency. Use of epoxy-based composites enables aircraft designers to achieve the goals of reducing carbon emissions and other operating costs. These materials can withstand harsh environmental conditions like vibrations encountered during flight, temperature variation, corrosion, etc. Figure 3 shows the aircraft components, which are made up of different composites. Epoxy-based composites play a very crucial role in structures used in aerospace vehicles, because of their lightweight, high strength and excellent mechanical properties and also their ability to be tailored to meet specific requirements. Polymer matrix composites are typically favored because of their exceptional strength-to-weight ratio, fatigue resistance, corrosion resistance, and design flexibility. Metal matrix composites (MMC) are suitable for such components because they consist of high strength materials like ceramics, carbon/glass fibers, etc. These possess high strength, stiffness, and thermal resistance, which make MMC suitable candidates for extreme temperature conditions. The hydrophobicity of graphene-based nanocomposite films was seen to improve with increasing exposure to ultraviolet light; these films demonstrated promise for use in long-term space missions. For the structural health monitoring of a morphing aircraft, these nanocomposites are used to create stretchable sensors.[107] For the superior aerospace qualities, nanocomposite systems have also made use of high strength elements like titanium. Graphene oxide was employed to strengthen titanium nanopowders, creating a matrix system with exceptional hardness—a key requirement for many structural aerospace components.[108] Among the several nanocomposite technologies utilized in aircraft applications, use of carbon nanotubes (CNT) predominates.[109] The combination of recycled polyethylene terephthalate (PET) and high density polyethylene (HDPE) in carbon nanotubes formed a maximum load pressure of 24.9 MPa, making them suitable in advanced structural design.[110] A nanocomposite material consisting of silica nanoparticle dispersed in epoxy polymer matrix was used to evaluate surface degradation caused by UV light. The International Space Station (ISS) travels in a lower earth orbit around the sun and is exposed to intense UV light, which causes erosion. Silica nanoparticles decreased the atomic oxygen induced erosive yield of the polymer matrix. A thermally resistant substance called nanosilica ethylene propylene diene monomer (EPDM) nanocomposite was utilized to safeguard the structural components of a spacecraft during lift off.[111] The addition of nanosilica improved erosion resistance, while maleic anhydride grafting enhanced matrix polarity. Characterization confirmed good dispersion and improved thermal, mechanical and ablative performance, indicating strong potential for commercial aerospace applications.[112]

5. NEED FOR ENHANCEMENT OF TOUGHENING OF EPOXY RESINS

Epoxy resin toughening has been shown to no longer require the addition of toughening chemicals; instead, modifications to

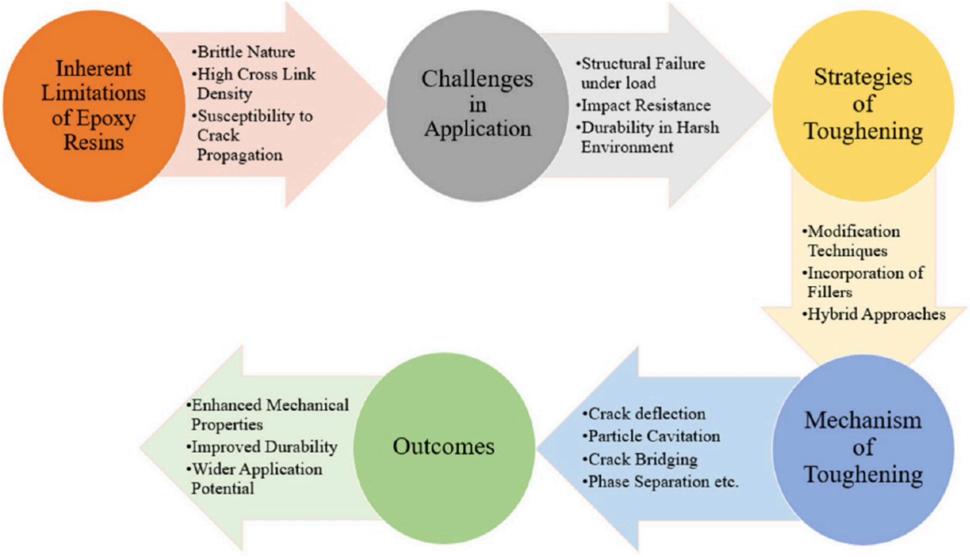

Figure 4. Necessity of improving toughness of epoxy resin

the subatomic structures of the resin are responsible for the desired effect.[113] Toughened epoxy is widely used in scientific fields due to its ability to increase the composite strength. The main benefits of epoxy resins are their antislip coating, rigid structure, and application as glue in composites. Epoxy toughness can be improved with the help of MG30 (liquid rubber), in-situ-produced rubber nanoparticles, core−shell rubber, and other liquid rubber products.[114] The material's overall ductility and mechanical properties were improved through the incorporation of 30% poly(methyl methacrylate) liquid rubber (LMG30).[115] Plant-based natural rubber has garnered attention in the past due to the application of cured epoxy. Epoxy composites toughened with liquid natural rubber have better mechanical properties, as found by Tan et al.[116] The optimal results for the bending test required 3 wt % liquid natural rubber (LNR), while the impact test required 5 wt % LNR. Both studies found mechanical improvements in response to external force loading, whether slow or fast. The use of a toughening chemical typically increases the polymer's overall ductility across a broad temperature range in addition to improving water absorption, thickness, toughness, and resistance to notch sensitivity reduction.[117] Polymer electrolytes such as the MG30 polymer matrix have been the focus of a lot of research.

Figure 4 gives the need for increasing toughness and other properties of the cured epoxy resin. Epoxy resins, including heavy-duty protective coatings, have long been utilized in a variety of industrial systems, electrical and electronic applications, high-performance fiber-reinforced composites, structural automotive adhesives, and many more. However, they are very fragile, so tougheners are typically included in commercial formulations to make them more robust. Epoxy resins toughened with the help of reactive liquid rubbers have become increasingly popular since the 1970s and 1980s. Epoxy-rubber epoxy terpolymers are formed when an excess of epoxy resin reacts with carboxyl terminated butadiene nitriles (CTBNs). Their solubility in epoxy resins distinguishes them from pure rubber. After the three-dimensional network has been formed and the rubber has cured, the rubber molecules undergo phase separation, revert to an insoluble state, and develop into rubber domains or particles within the cured polymer matrix. Rubber particles, chemically bonded together, make up the polymer. Since the initial research of Kinloch and associates, the mechanisms of rubber toughening have been thoroughly examined. However, the conditions of phase separation and domain formation are sensitive to changes in curing rate, curing temperature, and curing agent. The particle dimensions are additionally impacted by the acrylonitrile concentration within the copolymer. The fact that not all long-chain rubber molecules participate in phase separation is also worth mentioning. The epoxy polymer matrix is cross-linked with a random selection of these molecules. As the network density decreases, the strength, modulus, and glass transition temperature (Tg) all decrease as well. Epoxy resins having reactive liquid rubber become highly viscous, which makes them inappropriate for applications requiring low viscosities. To overcome these limitations, core−shell elastomers were created in the 1980s and 1990s. Rubber particles were initially integrated, in contrast to the formation of a second phase during curing. The structural elements consist of a roughly 90-nm-diameter rubber-like elastomeric core that is usually made of a Butadiene homopolymer or a Butadiene-Styrene copolymer. The goal of an outer copolymer layer, which ranges in thickness from 10 to 20 nm, is to determine compatibility with the epoxy resin. When compared to epoxy resin modified with reactive liquid rubbers, epoxy resin containing these core−shell particles is substantially less viscous. Toughening has an effect regardless of the type or length of treatment. The strength and modulus of solid rubbers can occasionally be reduced, but these reductions are not as substantial as those of liquid rubbers. The cured polymer's strength and modulus significantly decrease as a result of the shell's tendency to soften at higher temperatures, greatly restricting the polymer's use in high-temperature applications. A second high-temperature-capable material was created by CSR innovation in the middle of the 1980s. This was made possible by the reduction of the shell thickness to a molecular monolayer; the material that was produced is more similar to a core−skin than a core−shell. Epoxy-functional CSR are good tougheners over a broad temperature range, featuring a polysiloxane core and an average diameter of roughly 500−700 nm. The official designation for CSRs will be Type III.

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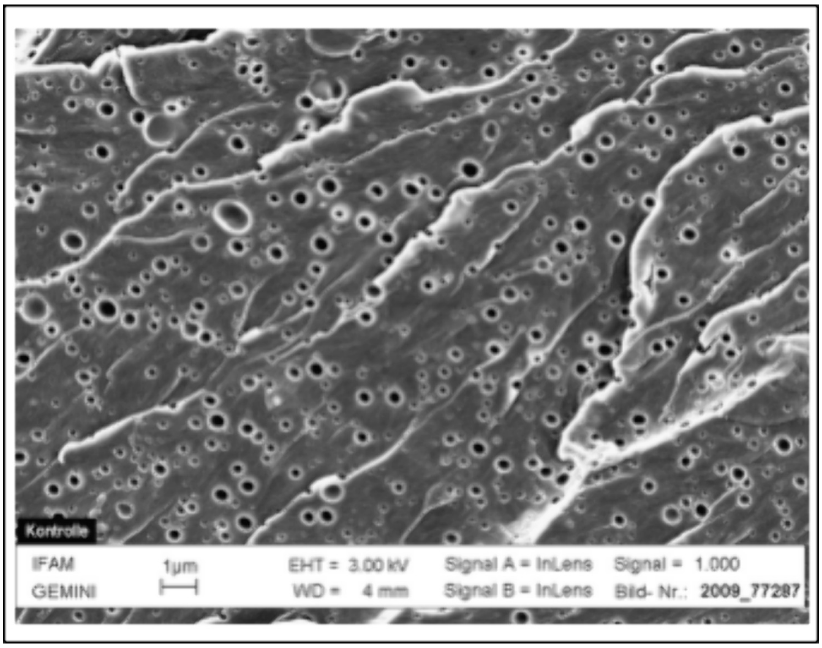


Figure 5. SEM image of an epoxy polymer containing 5.5%wt Type III CSR. Reprinted in part with permission from ref 118. Copyright [2013], [Elsevier].

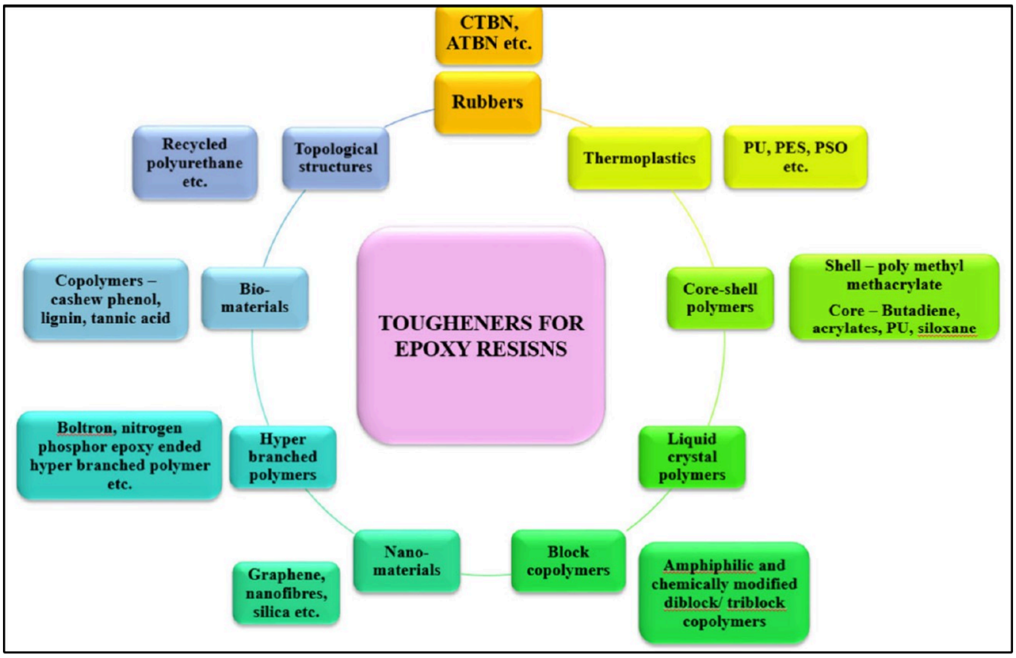


Figure 6. Different tougheners used in epoxy resins.[127]

The fracture surface of an anhydride-cured epoxy resin containing 5.5% by wt of CSR Type III is shown in Figure 5 as an unstained SEM image. The morphology of these images is similar to that of polymers treated with reactive liquid rubbers. It can be observed clearly from the SEM image that the epoxy resin toughened with liquid rubber suggests a decent level of particle dispersion, as a lack of agglomerated particles are there. These liquid rubbers will act as stress concentrators there by increasing the strength of the resin. Since the first commercial grades of surface-modified silica nanoparticles were introduced in 2002−2003, their use has made it easier to create remarkably uniform rubber domains. The particles have a median size of 20 nm and a narrow particle size distribution. They are produced by utilizing an upgraded sole gel method in the epoxy resin.

5.1. Different Tougheners Used in Epoxy Resins. One of the most traditional ways to enhance the toughness properties of epoxy resins is by using liquid rubbers, which is a heterogeneous method of toughening. Basically, there are two types of rubber-toughening of epoxy resin; one is by using liquid rubber and another is by using rubber particles. Reactive liquid rubber has less molecular weight, so these are capable of dissolving completely in the epoxy matrix, but as soon as curing happens, they lose their compatibility, phase separation occurs, and there is formation of a second phase; in this way, heterogeneous toughening occurs. Besides, core−shell rubber particles are used to enhance the toughness of epoxy resin. When core−shell rubber was added until 38% by volume, its fracture energy gets increased to 3750 J/m^2.[119] Thermoplastics like PU, PES, PSO, PC, PEEK, etc. are used as a second phase material to increase the toughness of cured epoxy resin. When thermoplastics get cured with epoxy resins, slowly they tend to separate, and a different phase is likely to be formed which gives a better toughening effect as compared to spherical rubber. Among the thermoplastics, Polyethersulphone (PES) gives the best results in context to the maximum fracture toughness at 5% weight of toughening agent.[120] Core−shell polymer tougheners are made up from emulsion polymerization of multiple monomers and have a soft (rubber) core and rigid (plastic) shell. The rigid plastic shell makes it compatible with the epoxy resins, and soft rubber helps in enhancing the toughness of the epoxy resin without compromising modulus and tensile strength.[121] Liquid crystal polymers are toughening agents which consist of microcrystalline elements having high strength, modulus, and other excellent properties. In this, toughening is done in two ways. The first way is to add the liquid crystal copolymer or curing agent into the epoxy system through blending; the ordered structure of the polymer is then embedded into the epoxy resin during curing, which results in toughening of the composites.[122] With 10 phr liquid crystalline polymer, impact strength was improved by 30%, along with increased fracture toughness and reduced dielectric constant and loss.[123] Another way is by synthesizing liquid crystal epoxy resin.[124] Block copolymers are made into different nanoscale morphologies like rod shaped, spherical shaped, etc. There are two types of block copolymers: one is reactive and another is nonreactive. When nonreactive block copolymers come into contact, these tend to make self-assemblies and form nanostructures, while reactive copolymers tend to react and form cross-links which gives the maximum increment in fracture toughness.[125] A triblock polymer significantly improves mechanical properties, impact strength and fracture toughness, due to nanoparticle formation during blending, without notably affecting glass transition temperature.[126] Detailed representations of tougheners used in epoxy resin with examples are shown in Figure 6.

5.2. Toughening Mechanisms in Epoxy Resins.

Over the past decades, extensive research has been carried out on the addition of different tougheners into the polymer matrix with the purpose to enhance its mechanical properties. In recent years, a theoretical understanding regarding the mechanisms involved in toughening of epoxy resins has been explored. Figure 7 shows all of the toughening mechanisms observed. Crack pinning is a phenomenon where the crack front bows out between the filler particles and stays trapped at the particles as it travels through the resin.[132] Microcracks are observed where there is incorporation of rubber particles as tougheners. Microcracks lead to tensile deformations, because of tensile yielding. Because of this mechanism, the modulus decreases as there is an increase in deformation strain.[133] Table 5 gives a description of toughened epoxies with different fillers along with the key findings. The use of nanosilica and nanocupric oxide, two nanomaterials with limited thermal expansion, has led to a novel approach to reinforcing carbon fiber composites. To improve their bonding with epoxy resin, these functionalized nanoparticles are coated with polydopamine and are tiny. Both at ambient and cryogenic temperatures, the mechanical and fracture characteristics of epoxy nanocomposites are enhanced when PDA-coated nano-copper oxide is used. Stripping the matrix, debonding the fibers, and fiber peel-off are the toughening mechanisms observed.[134]

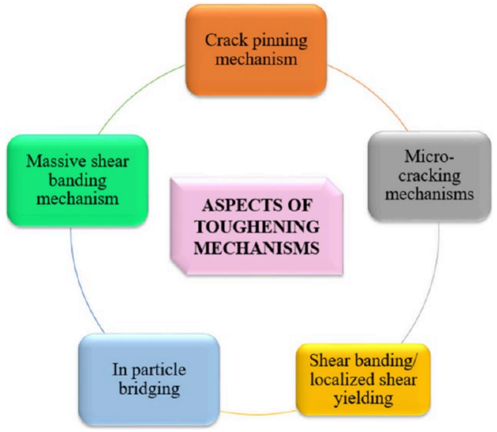


Figure 7. Toughening mechanisms in epoxy resins.

5.3. Impact of Nanosilica on Mechanical and Thermal Properties of Epoxy Resin.

Epoxy resin will be called more efficient if it requires a large amount of applied stress and the capability to absorb more energy before failure. The toughness of the specimen is basically the total energy required to make the specimen fail. Failure may be breakage in the case of brittle materials and plastic deformations or yielding in ductile materials. To improve the energy absorption capacity of epoxy resins, toughening is done to increase the energy absorption capacities by adding the appropriate tougheners. This addition, apart from increasing toughness, also enhances properties like impact resistance, elongation, and crack propagation. Elastomer modification, particulate modification, and thermoplastic modification are different ways to carry toughness enhancement in epoxy resin. Elastomeric materials like polysiloxane, fluoro elastomers, acrylated elastomers and reactive butadiene acrylonitrile liquid rubbers are used for this purpose.[135] Toughening is achieved by dispersing a small percent by weight of elastomer into the epoxy resin, while simultaneously rotating it in the stirrer. It is rotated until the suspension is homogeneous and clear. The suspension is then degassed in vacuum at about 60 °C. Hardener or curing agent of definite proportion is then added and mixed gently into the toughener−epoxy suspension, followed by the pouring of suspension into the molds with appropriate sample size. The curing time and temperature of these molds are dependent upon their chemical structure. Figure 8 shows the flowchart of the procedure to incorporate liquid rubber-based tougheners like CTBN and ETBN into epoxy resin, followed by making samples of appropriate size in molds. Table 6 gives a brief idea of different filler materials with variable weight percentages used to increase the properties of epoxy resin.

Mechanical properties of epoxy resin increase due to several synergetic effects at molecular and structural level when it is reinforced with nanosilica. Figure 9 gives a quick layout of such parameters. When nanosilica is uniformly dispersed into epoxy resin, these act as stress concentrators, which help in transferring and distributing applied loads more efficiently across the materials. This prevents stress localization, reducing the likelihood of crack initiation and propagation, thereby enhancing tensile strength.[62] The surface of nanosilica is

Table 5. Toughened Epoxies

Sr. No	Material	Toughener	Result	Key findings	Ref.
1.	Material A - DGEBA, Diethyltoluene diamine	CTBN, Siloxane based TP, HBP	For material A - With 10% wt. Siloxane, Max. KIC = 1.05 MNm3/2 With 15% wt. CTBN, Max. KIC = 0.98 MNm3/2 With 10% wt. HBP, Max. KIC = 0.8 MNm3/2	For material A - After 10% wt. of Siloxane toughener, KIC ↓, while CTBN & HBP keeps on ↑ For material B - After 5% wt. of Siloxane and CTBN toughener, KIC ↓. CTBN is capable to increase the toughness significantly Material B as highly cross linked epoxy resins, did not undergo plastic deformation and so not capable to ↑ KIC.	[128]
	Material B - TGDDM, TGAP, Diethyltoluene diamine, cyclohexylmethylene diamine		For material B - With 5% wt. Siloxane, Max. KIC = 0.87 MNm3/2 With 5% wt. CTBN, Max. KIC = 0.69 MNm3/2 With 0% wt. HBP, Max. KIC = 0.7 MNm3/2		
2.	Epoxy resin, Araldite MY721	CTBN – liquid rubber	CTBN toughener gave highest flexural storage modulus = 13.1 GPa PESOH toughener gave maximum GIC = 1183 J/m2, compression strength = 27% ↑ = 600 MPa, failure strain = 46% ↑ Phenoxy toughener gave maximum ILSS = 36% ↑ = 55 MPa	Tougheners have improved the mechanical properties of epoxies. Impact damage resistance has improved. Ductility of the matrix is improved by TP-epoxy miscibility.	[129]
		Polyethersulfone with hydroxyl end-groups (PESOH) - TP			
		Phenoxy - TP			
3.	Bisphenol-A epoxy	Core shell rubber particles	Increased impact strength at 5% CSR = 65kJ/m2 Elastic modulus and yield strength decreases	CSR particles enhances toughness and flexibility	[130]
4.	Bisphenol F and cycloaliphatic epoxy resin	nanosilica	(↑) Modulus = 4.25 GPa – Bisphenol F, (↑) Modulus = 3 GPa – cycloaliphatic Max. KIC = 1.2 MPa*m1/2 for Bisphenol F Max. KIC = 1.12 MPa*m1/2 for cycloaliphatic	Mechanical properties were increased due to better crosslinking of toughener and epoxy resins.	[131]

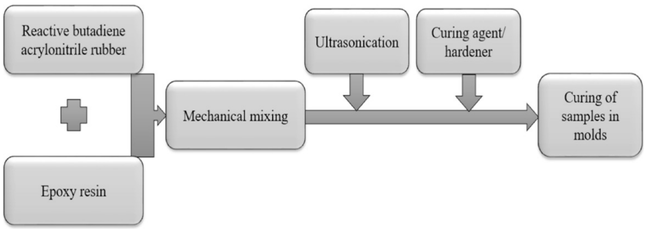


Figure 8. Procedure of adding liquid rubber toughener into epoxy resin.

functionalized with silane coupling agents to improve adhesion between the nanosilica and the epoxy matrix.[136] Strong interfacial bonding ensures better mechanical reinforcement as the stress applied to the matrix is effectively transferred to the rigid nanosilica particles.[137] Nanosilica particles create a

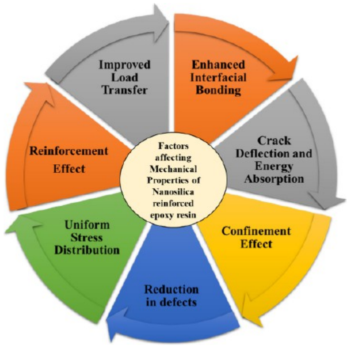


Figure 9. Factors affecting mechanical properties of nanosilica reinforced epoxy resin.

Table 6. Enhanced Properties of Epoxy with Different Fillers of Variable Loadings

Sr. No.	Filler Material	Weight Percentage	Improved Properties	Observations	Ref
1.	Nanoclay	(0% to 4%)	Tensile strength, impact strength and hardness	Dispersion technique − ultrasonication, homogenization Optimum wt. − 1.5% Superior mechanical properties because of mechanisms like crack deflection, crack pinning, crack arresting Tensile strength ↑ 48%, impact strength ↑ 22% and hardness 44.5% ↑	155
2.	MWCNT	(0.06%, 0.1%)	Impact strength	Impact strength ↑ 338.8%, 165.2% respectively	156
3.	Nanosilica	(1%, 1.5%, 2%)	Tensile strength, flexural strength and impact strength	Optimum wt. − 1.5% Because at this wt., voids and balanced with fillers Tensile strength ↑ 31%, impact strength ↑ 22.65% and flexural strength 42.36% ↑	157
4.	Graphene oxide	1%	Flexural strength, flexural modulus, impact strength, storage modulus	Flexural modulus = 2.94 GPa, ↑ by 10.11% Flexural strength = 130.46 GPa, ↑ by 14.67% Impact strength = 5.83 kJ/m2 ↑ by 45.39% On ↑ beyond 1.5% wt., properties degrades because of agglomeration of GO sheets	158

torture path for cracks to propagate through the matrix. This increases the energy required for crack growth, thereby enhancing the mechanical strength of the polymer. These particles also help to dissipate energy during deformation, further improving the material's resistance to tensile failure. Nanosilica also restricts the movement of the chain in the polymer, which in-turn increases the properties like stiffness and strength.[138] Epoxy resins typically contain microvoids and imperfections which act as weak points under the tensile loading conditions. The incorporation of nanosilica fills these voids, reducing the overall defect density and enhancing the overall mechanical properties.[139] Nanosilica particles improve the homogeneity of the stress distribution in epoxy resin. This minimizes the stress concentration areas, which would otherwise cause premature failure. Due to the high surface area-to-volume ratio of nanosilica, these provide a larger interface for interaction with epoxy resin as compared to microscale fillers. This increased surface area amplifies the reinforcing effect, improving the mechanical properties.

There is an enhancement in thermal properties when nanosilica is being incorporated into epoxy resin. This can be attributed to several factors related to physical and chemical interactions between the nanosilica particles and the epoxy matrix. Figure 10 gives a quick layout of such parameters.

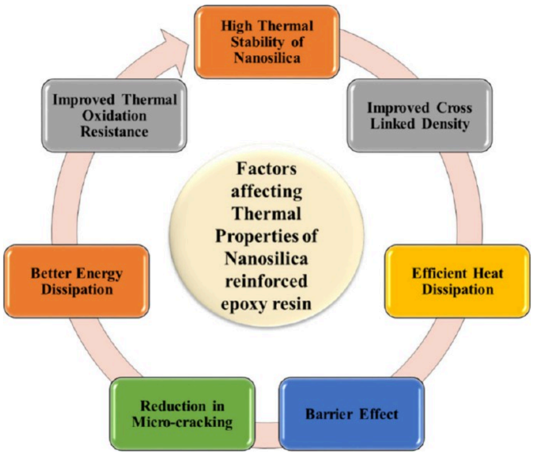


Figure 10. Factors affecting thermal properties of nanosilica reinforced epoxy resin.

Nanosilica particles possess higher thermal conductivity as compared to other nanoparticles.[140] When dispersed well, these tend to enhance the overall thermal conductivity of the epoxy matrix. Nanosilica acts as a filler that interacts with the matrix, potentially increasing the cross-link density of cured polymer. This denser network structure restricts molecular motion, which contributes to higher thermal stability and heat resistance.[141] Nanosilica possesses a low coefficient of thermal expansion, and so the nanosilica reinforced epoxy matrix possesses a low coefficient of thermal expansion.[142] This means that it reacts less in terms of contraction or expansion when there is temperature variation. This makes the material more stable under the temperature change conditions. By limiting matrix expansion, nanosilica reduces internal stresses caused by thermal cycling.[143] Nanosilica particles acts as a barrier that hinders the diffusion of heat and volatile degradation products during thermal decomposition.[144] This delay in thermal degradation enhances the thermal stability of the epoxy resin. The strong interaction between the nanosilica surface and polymer chains further protects the matrix from thermal breakdown; the high surface area of nanosilica particles allows for uniform heat distribution throughout the composite. This reduces localized thermal stresses and hotspots, improving the overall thermal endurance of the material. Since more than two decades ago, the primary aim of integrating silica nanoparticles into epoxy resin applications has been to offer a functional reinforcement that does not induce any modification to the viscosity of the epoxy resin. Conventional, large-scale additives significantly elevate the viscosity, which eliminates their viability for integration into a wide range of formulations. SiO_2 nanoparticles exhibit transparency and lack any discernible interference with visible light as a result of their infinitesimal dimensions. Cycloaliphatic epoxy polymers, which are utilized in stereolithography, are among the radiation-cured systems that require this. Furthermore, transparency regarding the structure of the fabric employed is of utmost importance in applications involving fiber-reinforced composites, such as carbon fiber automotive components, which are not painted but rather intended to be so. The utilization of silica nanoparticles in infusion or injection processes is frequent, owing to their capacity to pass through tightly woven fabrics without enduring filtration, in contrast to conventional filler particles that have a diameter of microns. The dimension is crucial in many electrical and electronic applications including chip underfill, encapsulation, and flip-chip. Regardless of the enormous size of the generators, the results suggest that electrocorrosion of encapsulated generators could be prevented by the ability of nanoparticles to pass through the spaces between the copper wires. As a result, the generator will be able to stay in service for a lot longer. When added at

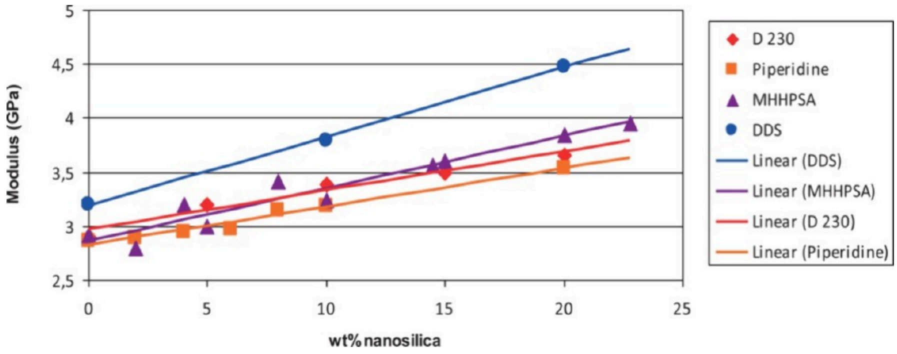


Figure 11. The modulus of DGEBA epoxy resin under varying curing agents in relation to the concentration of silica nanoparticles. Reprinted in part with permission from ref 94. Copyright [2013], [WILEY].

concentrations below 10 wt %, silica nanoparticles have a negligible effect on the glass transition temperature (Tg). However, as addition levels rise, a modest drop in temperature (between 2 and 50 °C) is seen. The modulus of cured epoxy resin always rises with the size of the infill. Figure 11 shows the correlation between the concentration of silica nanoparticles and the increase in the modulus of a diglycidyl ether bisphenol A DGEBA standard epoxy resin. The modulus of unmodified cured DGEBA inherently varies in accordance with the curing agent's chemical composition and its impact on network formation. Polyether amine (D 230), piperidine, and methylhexahydrophthalic acid anhydride (MHHPSA) have the greatest values. The cured resin's modulus rises linearly with the amount of silica nanoparticles added. Studies indicate slight improvements in tensile strength, but nanosilica does not seem to increase it.[94] More than the modulus, the curing agent's chemical makeup will most likely affect the tensile strength. Every 10% increase in weight caused by the addition of nanoparticles can result in a 30% increase in compressive strength and compressive modulus. Increases in compressive strength, tensile strength, tensile modulus, and compressive modulus were observed by Jumahat et al.,[145] along with a linear relationship between property improvement and nanosilica addition level. Zhang et al.[121] investigated the relationship between strain rate and compressive properties of a toughly cross-linked tetrafunctional epoxy resin called tetra glycidyl ether of methyl dianiline that was cured with diaminodiphenyl sulfone.[146] A 10% concentration of the commercially available nanosilica 40% solution was used to fortify the DGEBA. They came to the conclusion that silica's significantly higher modulus than epoxy resin's was the cause of the increase in compressive modulus. The uniform dispersion of nanoparticles throughout the resin is thought to be responsible for the strength increases because it may lead to a reduction in local stress concentrations, which could otherwise result in premature component failure. The benefits were more pronounced at lower strain rates and less pronounced at higher strain rates due to the decreased interactions between the nanosilica and the epoxy resin matrix. Dmitriev et al.[147] employed an amine-cured DGEBA with an uncommonly low cross-link density to replicate the behavior observed under stress and strain. They achieved a high degree of concordance between theoretical predictions and empirical data, presuming that the addition of nanosilica enhanced the strength. They asserted that the increase in strength was attributable to higher cross-linking Tg values, but they offered no substantiating evidence. The incorporation of nanosilica resulted in significant improvements in stiffness, as meticulously modeled by Thorvaldsen et al.[148] They discovered that their theoretical models corresponded well with empirical data obtained from the curing of DGEBA with an anhydride hardener and an amine curing agent. The stiffness can be anticipated in relation to the concentration of the nanosilica. According to Zhang et al.,[149] the addition of nanosilica allowed for the improvement of additional intriguing properties. The friction and wear properties of a DGEBA containing nanosilica and wax microcapsules cured in anhydride were investigated. The ideal tribological properties were achieved by combining wax microcapsules at a weight percentage of 10% with silica nanoparticles at a weight percentage of 23%. The coefficient of friction was 10-fold reduced as a result, and the wear rate was reduced by an order of magnitude. The wear characteristics of amine-cured DGEBA with 2% weight percentage SiO_2 nanoparticles were investigated in a marine environment by Zhang et al.'s study.[150] The epoxy containing nanosilica did not lose its fracture toughness after 30 days in salt water, in contrast to the neat epoxy. The inclusion of silica nanoparticles improves the fatigue performance of cured bulk epoxy resin systems when subjected to cyclic stress. Mai et al.[151] observed a 1.5-fold enhancement in the quality of amine-cured DGEBA at a 2-wt % addition level. However, as the addition level increased, the quality declined significantly. Research conducted by Kinloch et al.[152] on anhydride-cured DGEBA indicates that fatigue performance can be enhanced by augmenting the nanosilica content. Applications involving epoxy resin, such as adhesives and fiber-reinforced composites, have undergone additional fatigue testing to determine the underlying mechanisms in this study. This helped to find the mechanisms like crack initiations, crack propagation, and material's abilities to sustain repeated and continuous stresses. Epoxy resins' coefficient of thermal expansion can be significantly decreased by replacing organic components with inorganic ones, like nanosilica. Experiments using various epoxy resins and hardeners revealed that the CTE (coefficient of thermal expansion) decreased as the concentration of SiO_2 increased. The cost-effectiveness of manufacturing techniques for fiber-reinforced composite components is significantly influenced by the rate of curing. The high volume of production makes them suitable for automotive applications. The mechanical properties and exothermic rates of epoxy resins containing silica nanoparticles are enhanced. In addition to demonstrating that the curing reaction remained unaffected, Taylor et al.[152153] demonstrated that the reaction's total heat could be decreased. A theological and kinetic model was devised to facilitate the fabrication of significant components and the prediction and regulation of rapid cure cycles. In order to compare the effects of carbon nanotubes (CNTs) and nanosilica on the mechanical characteristics of polyethylene fiber-reinforced cementitious composites, seven sets of specimens with varying content of nanomaterials were made. The results state that both materials improve mechanical characteristics. Nanosilica helped in improving compressive strength and early tensile crack strength, whereas CNTs helped in improving compressive and tensile strain.[154]

5.4. Toxicological Aspects of Silica Nanoparticles in Epoxy Resins.

It is crucial to do further research on the toxicological effects of silica nanoparticles. The amorphous nature of silica nanoparticles made by using sol−gel techniques has been established by small-angle neutron scattering studies; this must be taken into account before moving forward. There is currently no evidence of amorphous silica causing harm to humans, despite decades of manufacturing and use in industry. Toxic effects from ingesting amorphous silica are negligible, and colloidal silica sols have several uses in the food industry, including the clarity of fruit beverages. The aspect ratio also plays a significant role. Silica nanoparticles available for commercial use typically take a spherical shape. They are not seen as dangerous by macrophages due to their larger size when compared to rod-like structures with a high aspect ratio, like asbestos and carbon nanotubes. The genotoxicity of ultrafine particulate matter in the lungs was investigated by the German Federal Institute for Occupational Safety and Health, or BAUA. Analysis of nanoparticles included fullerenes, titanium dioxide, amorphous silica, carbon black, and crystalline silica. There is no evidence that amorphous silica nanoparticles cause cancer. used T3T cell systems and discovered that amorphous nanoparticles of varying sizes (21–240 nm) were not genotoxic. The same degree of toxicity was found in both in vitro and in vivo studies by Fruijtier-Pölloth on amorphous silica nanoparticles.[159] There were no documented cases of bioaccumulation or biopersistence of silica nanoparticles in living organisms, as they were rapidly eliminated by physiological excretion systems. Crystalline and amorphous silica nanoparticles were both evaluated in-depth by Hoet et al.[160] Data from a wide range of in vitro and in vivo experiments was used to conduct a thorough evaluation of the various possible toxicological action mechanisms. Since synthetic amorphous nanosilica is free of crystalline silica, proponents claim it is more secure for human consumption.[161] Regretfully, it was determined that insufficient data currently available justifies waiving the requirement for a waiver for all silica nanomaterials. A recent analysis of studies conducted in Europe and the United States on the safety of nanoparticles[162] confirmed the importance of continuing research in this field. As a result, protecting yourself from airborne or contact-deposited silica nanoparticles is paramount. The available industrial particles have been designed to prevent the creation of isolated particles at any stage of the production, use, or disposal process. The current sol–gel manufacturing techniques trap nanoparticles in a matrix consisting of water, solvents, and epoxy. Commercial offerings feature silica nanoparticle concentrates in liquid epoxy resins that are compatible with conventional epoxy resins. Safe handling of epoxy compounds requires only the usual attention to detail. Using nanoparticle detectors, the air in the office was examined but no particles were detected. After curing, the epoxy resin forms covalent bonds with the particles, rendering them immovable in the resin. Nanomaterials were not detectable in the waste products produced by mechanically treating nanosilica-cured epoxy resins using various abrasives. Instead, researchers uncovered larger polymer fragments that contained nanosilica particles.

The subsequent inquiry is about what happens to the nanoparticles inside the cured epoxy resin if it is exposed to high temperatures, such as those produced by a fire or thermal decomposition. It is possible that the smoke, ashes, and residue from the fire include isolated silica nanoparticles. Larger formations or agglomerates resembling fumed silica were seen but no single nanoparticles. Standard air filtration systems are well-suited to trapping agglomerates on the micron scale. The thermal degradation of the cured epoxy resin matrix appears to cause an almost instantaneous change in the organic coating of the particles, resulting in the formation of larger agglomerates that resemble fumed silica. Since most materials based on epoxy resin are currently thermally recycled in the production of steel and glass, this is important not only to prevent unintentional fires but also to ensure safety. The study examines the potential of graphene as a nanoadsorbent due to its enormous surface area, π-π interaction, and accessible functional groups. The research targets aromatic chemicals like trypan blue (TB) and Bisphenol-A (BPA) from water. Silica nanoparticles are functionalized on graphene oxide nanosheet for adsorption using a simple, cheap, and efficient manufacturing technique. The hybrid nanocomposites with oxygen containing functional groups demonstrated improved adsorption capacity, having the highest surface area of 1768 m^2/g. This study revealed that the hybrid nanocomposite GO/SiO_2 could remove aromatic compounds from wastewater efficiently and cheaply.[163]

6. UNIFORM DISPERSION OF SILICA NANOPARTICLES INTO EPOXY RESIN

Silica particles are normally a white, fine amorphous powder. They outperform as compared to all other nanoparticles because of their most important property of having very large surface area and a smooth nonporous surface. This promotes them as a very compatible reinforcing agent when they are embedded into a polymer matrix. The high surface area leads to better surface interactions of both the filler and matrix material. This further leads to improvement in mechanical properties.[164] Table 7 gives the process parameters that are followed while dispersing nanosilica into the epoxy resin matrix. Table 8 gives an idea about nanosilica as a reinforcing agent to composite materials. Achieving uniform dispersion of nanosilica in epoxy resin is crucial for optimizing the mechanical, thermal, and electrical properties of the composite material. The steps described in Figure 12 are used to achieve uniform dispersion.

Table 7. Specific Dispersion Process Parameters

Parameters	Range
Nanosilica loading	1–5 wt %
Solvent	Ethanol
Solvent-to-epoxy resin ratio	1:1 to 1:5
Mixing speed	500–1000 rpm
Mixing time	10–30 min
Ultrasonic power	100–500 W
Ultrasonic time	10–30 min
Degassing time	10–120 min

6.1. Methods of Evaluating Dispersion Effects.

Achieving the nanosilica dispersion in epoxy resin requires not only the proper dispersion process but also effective evaluation techniques to verify the quality of dispersion. Given below are various methods categorized into qualitative and quantitative approaches:

6.5.1. Microscopic Analysis. Microscopic methods offer direct visualization of a nanosilica dispersion within the epoxy matrix.

Scanning Electron Microscopy (SEM):

This technique provides high-resolution images to observe the distribution of nanoparticles and detect agglomerations. Cross-sectional analysis of cured resins is performed to evaluate bulk uniformity.

Transmission Electron Microscopy (TEM):

This technique is used to observe very small nanoparticles individually and their interaction with the epoxy matrix. It is useful for identifying nanosilica clustering at the nanoscale.

Optical Microscopy:

This technique is suitable for lower magnifications to examine the general distribution of nanosilica. Polarized light microscopy highlights dispersion uniformity, especially in transparent or semitransparent epoxy systems.

6.5.2. Particle Size Analysis. Quantifying the particle size distribution indicates the effectiveness of deagglomeration and dispersion.

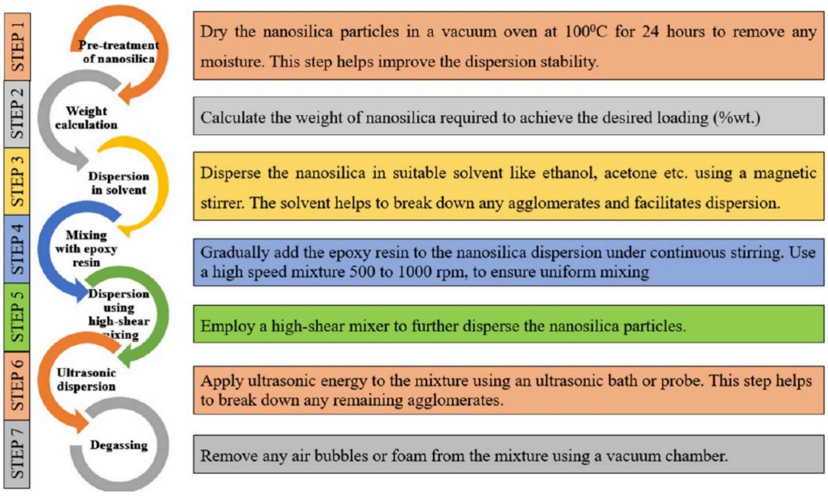
Dynamic Light Scattering (DLS):

This technique measures the particle size and size distribution in a liquid medium before curing. When the narrow dispersion curves are achieved, it indicates good dispersion.

Laser Diffraction:

Table 8. Nanosilica Toughened Epoxies

Sr. No.	Composite Materials	Nanosilica Content (% wt.)	Mechanical Properties Improved	Key Observation	Ref
1.	Silica, epoxy	1% to 5%	Elastic modulus	Absence of particle aggregation Reinforcing effect is observed as E is increased 15% ↑ in E, E = 2.3 GPa	165
2.	Wax microcapsules, silica, epoxy	-	Tribological properties – specific wear rate, COF	10-fold ↓ in COF, COF = 0.1 at 23%wt. silica and 10%wt. wax microcapsules 3-fold ↓ in specific wear rate, Ws = 4.39×10^{-7} mm^3/Nm Thin and continuous films of fillers were developed at the ball of the tribometer which improves tribological properties	149
3.	Fumed Silica, epoxy	0.3%, 1%, 3%	Elastic modulus, Ultimate strength	Functionalization of silica is done for better dispersion into epoxy resin At 1%wt., 11% ↑ in ultimate strength is observed. Value = 85.74 MPa Till 1%wt., slight ↑ in modulus of elasticity is observed. Value = 3633 MPa, after that %wt., property degrades	166
4.	Silica	0% to 25%	Elastic modulus, Strength, toughness	All the properties improves until 5%wt. of silica, then these properties deteriorates	



Dry the nanosilica particles in a vacuum oven at 100⁰C for 24 hours to remove any moisture. This step helps improve the dispersion stability.

Calculate the weight of nanosilica required to achieve the desired loading (%wt.)

Disperse the nanosilica in suitable solvent like ethanol, acetone etc. using a magnetic stirrer. The solvent helps to break down any agglomerates and facilitates dispersion.

Gradually add the epoxy resin to the nanosilica dispersion under continuous stirring. Use a high speed mixture 500 to 1000 rpm, to ensure uniform mixing

Employ a high-shear mixer to further disperse the nanosilica particles.

Apply ultrasonic energy to the mixture using an ultrasonic bath or probe. This step helps to break down any remaining agglomerates.

Remove any air bubbles or foam from the mixture using a vacuum chamber.

Figure 12. Method of dispersion of nanosilica into epoxy resin.

This technique is useful for analyzing particle size across a wide range. This technique monitors the reduction in large particle aggregates after dispersion.

6.1.3. Rheological Testing. Rheological behavior correlates with the nanosilica dispersion quality and the flow behavior, which is very important in applications like casting and molding where a smooth flow of nanosilica reinforced epoxy resins is required.

Viscosity measurement:

The viscosity of nanosilica containing epoxy resin is high as compared to the neat epoxy resins. But the uniformly dispersed nanosilica increases the viscosity in a more consistent manner as compared to agglomerated nanosilica. Shear thinning behavior highlighting decreasing viscosity with shear rate indicates good dispersion.

Oscillatory rheology:

It is performed to obtain the properties like storage modulus and loss modulus, which evaluate particle matrix interactions.

6.1.4. Mechanical Property Testing. Mechanical properties provide indirect insights into the dispersion quality. The increase in ultimate tensile strength and flexural strength is observed when well-dispersed nanosilica particles reinforce the epoxy resin systems. Higher impact properties suggest that there is a uniform particle distribution and good energy absorption properties.

6.1.5. Thermal Property Testing. Dispersion of nanosilica influences the thermal properties of nanocomposites. Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) are the testing techniques which are performed to evaluate the properties like glass transition temperature etc. Improved thermal conductivity indicates uniform dispersion, as the agglomerated particles hinder the heat transfer.

6.1.6. Electrical Property Testing. Many grades of epoxy resin have applications as composite materials in electrical components. Uniformly distributed nanosilica enhances the dielectric properties. Variations in measurements indicate uneven dispersion or clustering.

6.1.7. Dispersion State Quantification. This technique evaluates the uniform distribution of nanosilica into a matrix medium like an epoxy matrix. The below methods are used for dispersion state quantification:

UV Spectroscopy:

This technique measures light absorbance or transmittance in a dispersion to detect particle agglomeration.

Zeta Potential:

This technique evaluates particle stability in a suspension. Higher values of zeta potential indicate the better dispersion of nanosilica into the matrix materials.

6.1.8. Morphological and Structural Characterization. These techniques focus on examining the physical structure, distribution, and interaction of nanosilica into epoxy resin.

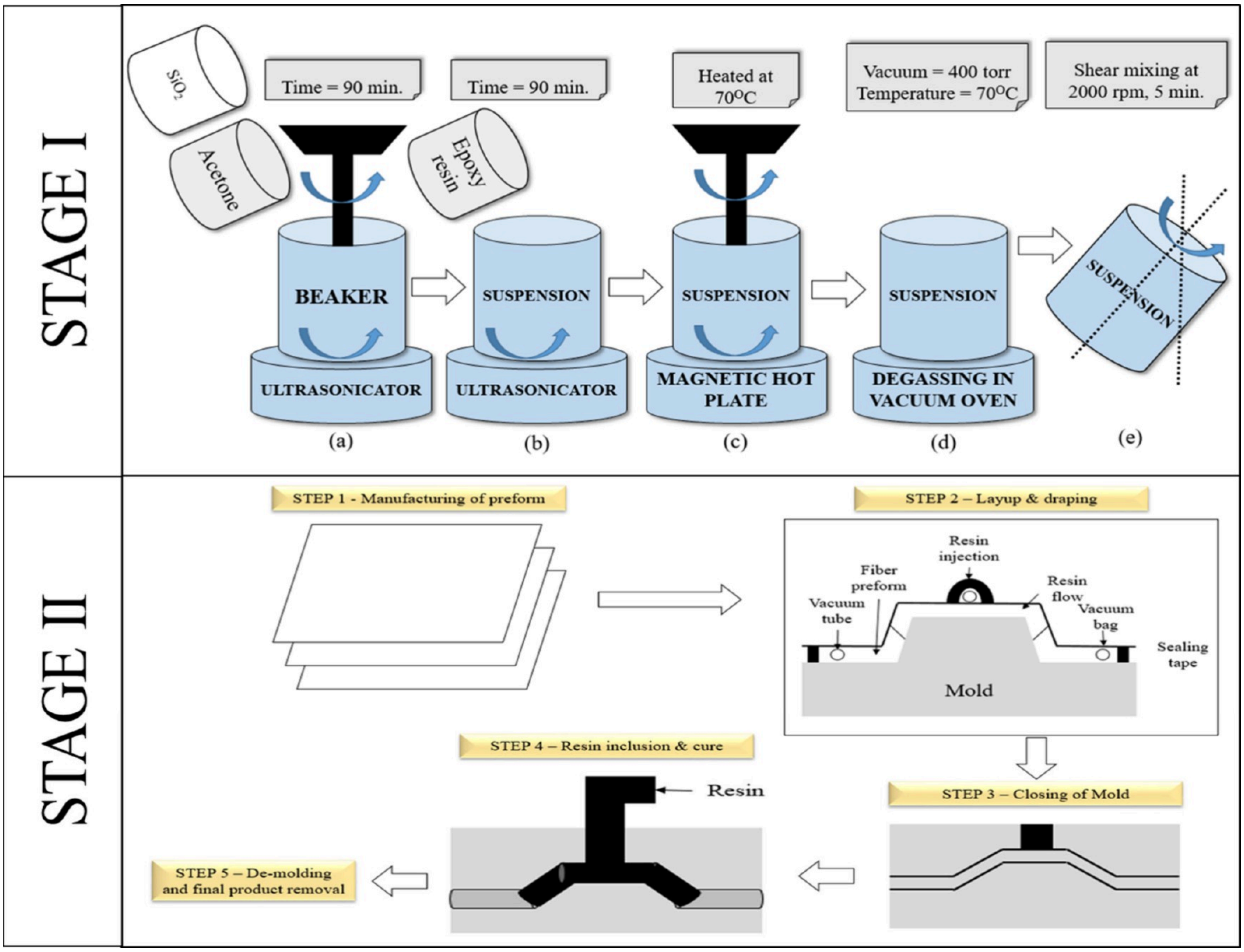


Figure 13. STAGE I-Steps for incorporating nanosilica into epoxy resin. STAGE II- Preparation of epoxy-silica nanocomposite.

These help in analyzing the dispersion quality and nanosilica interaction at different scales from bulk morphology to nanoscale features.

6.1.9. X-ray Diffraction (XRD). This technique analyzes changes in crystallinity due to dispersion of nanosilica. Peak intensities and broadening of the curve indicate the interaction between nanosilica and epoxy resins.

6.1.10. Fourier Transform Infrared Spectroscopy (FTIR). This technique identifies chemical networks between nanosilica and epoxy resin.

7. PREPARATION TECHNIQUES FOR NANOSILICA TOUGHENED EPOXY COMPOSITES

Epoxy diglycidyl ether of bisphenol A (DGEBA) is a thermosetting polymer that serves as the basis for the carbon fiber-reinforced plastic matrix in aerospace composites. In this study, matrix material was fabricated from this polymer. Commercially available epoxy resin 2000-B and hardener 2120-B were provided by Fiber Glast-USA. There is great potential for the use of silica nanoparticles in industry due to their abundance and low cost. Fumed silica nanoparticles were thus added to our system as the nano modifier. Sigma-Aldrich was contacted for the supply of S5130 fumed silica particles. The nanospheres can be found in clusters, and their average diameter is 7 nm. Epoxy resin has a high viscosity, making it challenging to create a nanocomposite system with silica nanoparticles, because of their large surface area. If particles are not prevented from accumulating, then direct mechanical mixing could lead to a huge problem. Thus, acetone, a low viscosity solvent, was combined with the silica nanoparticles, and the resulting solution was sonicated for about 90 min, Figure 13a. Another 90 minutes of sonication was applied to the mixture following the addition of the resin, as shown in Figure 13b. Following that, in order to evaporate the solvent, the suspension was heated to 700 °C while being continuously stirred on a magnetic hot plate. Figure 13 illustrates this method. The suspension was vacuum-dried at 700 °C and 400 Torr for 12 h to remove any trace of solvent, as shown in Figure 13d. Shear mixing at around 2000 rpm for about 5 min with a manufacturer-recommended volume of hardener Model ARE250, Figure 13e, is then performed on the nano modified resin. The final mixture of epoxy-silica nanocomposites is poured into molds, and after it cures, compact tension specimens are extracted. For the purpose of maintaining consistent sample thickness, the specimens' surfaces are polished and ground. The procedure is replicated with different proportions of silica injection.

This result pertains to nanoparticles containing 5% SiO_2; comparable dispersion was also noted at 2.5% and 7.5% SiO_2 wt %. There were no indications of larger agglomerations of

Table 9. Property of Epoxy-Based Composites Enhanced by Nanosilica

Sr. No.	Composite	Filler Material	Method of Fabrication	Properties Analyzed	Standards Used	Key Findings	Ref
1.	Carbon − kevlar − epoxy hybrid composite	Nanosilica	VARIM	Flexural properties	ASTM D790	Optimum concentration of nanosilica is 0.5% wt. Optimum stacking sequence is 5 carbon and 4 kevlar fiber layer Highest flexural strength = 480 MPa Highest flexural modulus = 30 GPa	169
2.	Glass fiber epoxy composite	Nanosilica & multilayer graphene	Hand lay-up	Flexural strength Glass transition temp	ASTM D7264	Optimum concentration of nanosilica and graphene as 2% and 0.1% wt. respectively. Flexural strength increases Decrease in Tg	170
3.	Glass fiber epoxy composite	Nanosilica & nanoclay	Hand lay-up	Flexural strength Glass transition temp	ASTM D7264	Optimum concentration of nanosilica and nanoclay as 1% and 2% wt. respectively. Flexural strength increases by 10.81% = 350 MPa Flexural modulus increases = 19 GPa Decrease in Tg = 91.18 °C	171

SiO_2 infill in the SEM images. Since it decreases the surface area of contact between the nano filler and the matrix, filler aggregation is typically viewed as a defect in nanocomposites. Nonetheless, the interspersion of “nanoparticle-rich” and “resin-rich” locations in SEM reveals microscale stochasticity in the distribution. By comparing the silica/epoxy nanocomposite to pure epoxy, the latter displays a more homogeneous field of material stiffness due to the former’s stochastic dispersion.[167,168] By modification of fracture tip fields, this material heterogeneity considerably adds to toughening. Figure 13 STAGE II shows the representation of preparation of GFRP composite by the vacuum assisted resin infusion molding technique.

7.1. Role of Nanosilica in Enhancing Mechanical and Thermal Properties in Epoxy Composites.

Nanosilica is capable of enhancing the thermal properties because of its high surface area to volume ratio, which makes it capable of interacting more, leading to increased heat transfer capabilities. As proven, nanosilica is capable of dispersing uniformly into the epoxy matrix, which facilitates better heat conduction throughout the material. In addition to improving thermal properties, nanosilica also enhances the mechanical properties. It acts as a reinforcing agent when incorporated into polymer matrices. Due to its high surface area, ease of stress distribution occurs, leading to enhanced strength and stiffness. Good dispersion and better interaction result in improved bonding between the nanoparticles and matrix material, which in turn enhances tensile strength and modulus. Nanosilica fills the gaps and voids, which reduces the porosity of the material. This results in a compact structure, improving the material’s resistance to crack propagation and growth, effectively increasing fracture toughness of the material. Table 9 describes the importance of using nanosilica on the properties of different composite materials.

8. TESTING OF EPOXY COMPOSITES

To develop the composite materials demands full characterization to analyze the anisotropic and heterogeneous material in depth prior to their applications in various areas. Figure 14 gives details about the mechanical and physical tests involved in composite materials. The tensile test is used to measure the force required to break the composite specimen. It is a destructive method of testing which is used to calculate properties like tensile strength, yield strength, tensile modulus and ductility of the composite material. It also measures the strain of the specimen until it elongates and breaks. Alignment during testing of composite materials is very important, as these are anisotropic materials, which means that they have different properties in different directions depending on the direction of applied load. Flexural test of the composite is done to measure the force required to bend the sample under three point and four point bending conditions. It is applicable for rigid, flexible, resin, and FRP materials. The test sample is kept on the support span, and load is applied at the center at a specified rate. According to different standards, a test stops when a sample breaks, or until 5% deflection. Impact testing of composite material is done to determine its behavior toward sudden load. In this testing, a specimen includes either V, U, or a keyhole notch. In a Charpy impact test, the notch faces the striker and is placed horizontally, while in an Izod impact test, the specimen is made to stand vertically erect. Compressive testing involves the introduction of compressive loads while preventing the bucking of the sample. This testing gives a

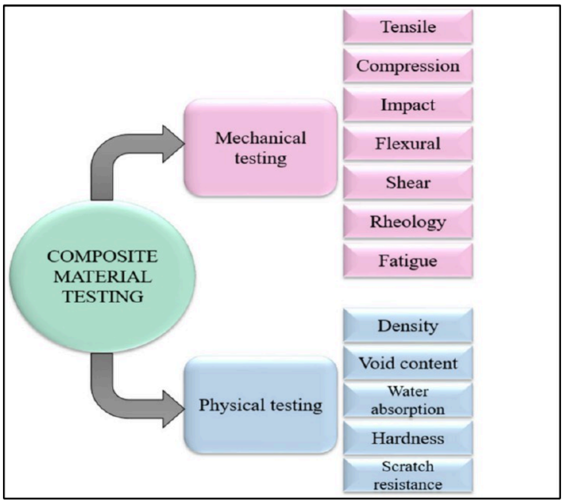


Figure 14. Testing of composite materials.

stress−strain diagram which provides the properties of the composite. Compression after the impact test is done with the help of a drop tower which gives an impact, before the conduction of the compression test. An ILSS test gives an idea about the quality of the laminate made. The shear strength of the matrix material between the laminate layers is measured by this test. A cryogenic test is carried out to measure all the mechanical properties in extremely low temperatures especially for applications related to space and aeronautic structures. It is carried out in a cryostat where absolute zero temperature is maintained by using liquid helium. Fatigue testing is done by the cyclic loads, to measure the number of cycles the composite material is capable of sustaining. Fatigue life is affected by many parameters including cyclic stresses, residual stresses, material properties, internal defects, etc. Table 10 gives an idea of the test required to characterize the nanocomposite, along with the properties measured and standards followed.

8.1. Enhancement of Mechanical Properties by Incorporating Nanosilica into Epoxy Composites.

The highest concentrations of silicon nanoparticles in epoxy resins are currently found in fiber-reinforced composites. As a result, there are now many researchers focusing on this area, and numerous patent applications are pending. Even the tightest woven textiles can benefit from the injection or infusion of silica nanoparticles because of their tiny size in relation to the diameters of the fibers. Louis et al.[172] found no filtration of amine-cured DGEBA containing silica nanoparticles during the infusion phase of their RTM study. The quantities of nanosilica did not exhibit any fluctuations, even when transported over considerable distances, in the presence of a twill weave aramid textile. Zhang et al.[172] examined the impact of silica nanoparticles on the interfacial characteristics of an anhydride-cured DGEBA epoxy resin reinforced with carbon fiber bundles in an attempt to replicate a unidirectional laminate. When incorporated at a 10% weight percentage, nanoparticles raised the ILSS by 13%. The results of the nanoparticles showed that the matrix was strengthened by the dispersion of deformation energy and the decrease in stress concentration at the fibers. There was an obstruction to the fracture formation process between the epoxy resin matrix and the carbon fiber. Figure 15 compares the fracture mechanism and stress distribution in neat epoxy and a nanosilica-epoxy matrix both reinforced with carbon fibers. It can be observed that the interfacial layer plays a critical role in transferring stress between the fibers and the matrix. Without reinforcing agents, the epoxy matrix is prone to brittle failure, with cracks propagating through it with minimal resistance. Stress concentration at the crack tips causes crack growth, while silica nanoparticles help in distributing stress more evenly across the matrix, reducing the stress concentration at the fiber matrix interface. Microcracks around the silica particles absorb additional energy, further enhancing the toughness of the matrix. Table 11 gives a comparison between neat and reinforced matrices. As per the graph in Figure 16, at a lower concentration of nanosilica, the strength remains relatively

Table 10. Characterization of Composites

Sr. No.	Test	Standards	Properties Measured
1.	Tensile test	ISO 527-4, ISO 527-5, ASTM D 638, ASTM D 3039, ASTM C 297	Ultimate tensile strength, Yield strength Ultimate force, Ductility
2.	Flexural test	ISO 14, 125, ISO 178, ASTM D 790, ASTM D 6272	Flexural stress at yield, Flexural strain at yield, Flexural stress at break, Flexural strain at break, Flexural stress at 3.5% (ISO) Flexural stress at 5% (ASTM) Flexural modulus
3.	Impact test		Impact energy Impact strength
4.	Compression test	ASTM D 695, ASTM D 3410, ISO 14, 126	Compressive strength Yield strength Elastic limit, proportional limit
5.	Compression after Impact	ASTM D 7136, ASTM D 7137	Compressive residual strength after impact
6.	Bending test		Bending strength, deflection
7.	Interlaminar shear strength test	DIN EN 2563	Shear stress, shear strain, shear modulus
8.	Cryogenic test		All mechanical properties in liquid helium
10.	Fatigues test		Fatigue strength, Fatigue life
11.	Water absorption test	ASTM D 570	Amount of water absorbed under specified conditions
12.	Density	ASTM D 792-75, ASTM D 792−91, ASTM D 1895	Mass, volume
13.	Void content	ASTM D 2734	Theoretical and experimental density
14.	Rockwell hardness	ASTM D 785, ISO 2039	Indentation hardness
15.	Scratch test		Abrasive resistance

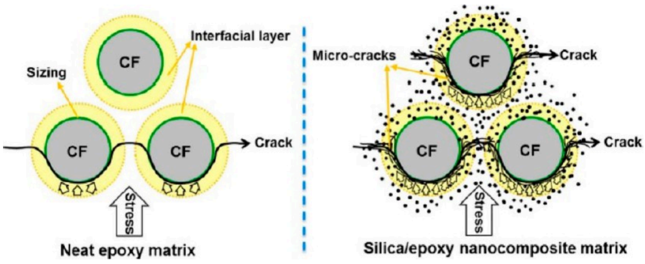


Figure 15. Schematic representation of stress transport and energy dissipation in the fiber reinforced composite interphase layer for both an unmodified and a nanomodified epoxy matrix. Reprinted in part with permission from ref 172. Copyright [ELSEVIER].

Table 11. Comparison between Neat and Nanosilica Reinforced Matrices, Both Toughened with Fibers

Aspect	Neat Epoxy Matrix	Nanosilica-Epoxy Matrix
Stress Distribution	Concentrated at fiber-matrix interface	Evenly distributed, reducing local stress
Crack Propagation	Direct and rapid	Slowed by crack deflection and microcracks
Fracture Toughness	Lower	Higher due to silica reinforcement
Energy Absorption	Minimal	Increased through microcrack formation and deflection

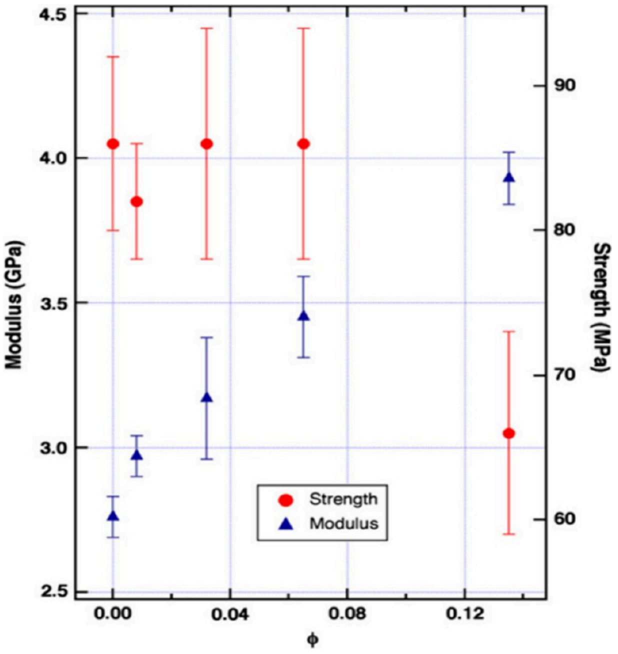


Figure 16. Variation of modulus and strength with volume fraction of nanosilica. Reprinted in part with permission from ref 62. Copyright [2008]. [ELSEVIER].

stable with a slight increase. However, beyond 0.12 concentration, a noticeable reduction in strength is observed, which is likely due to filler agglomeration or poor interfacial bonding. This strength decline may also be attributed to stress concentration points caused by particle clustering. In contrast, the modulus shows a distinct upward trend demonstrating the material's increased stiffness. The modulus reaches its peak value, indicating effective stress transfer between the filler and the matrix.

Through a vacuum-assisted resin infusion setup, various laminates were produced utilizing 450 multiaxial glass fiber fabric and DGEBA that has been cured with anhydride. Two varieties of core−shell rubber polybutadiene core and poly-Siloxane core were incorporated into epoxy resin to alter its properties, along with silica nanoparticles. The crack toughness exhibited an upward trend as the concentration of the nanosilica increased. In comparison to traditional elastomeric core−shell tougheners with a micrometer-scale particle size, the differences are marginal. Prior research has documented comparable results. While it does not substantially enhance the toughness of the laminate, the incorporation of nanosilica into the material does yield substantial improvements in various attributes such as fatigue performance when subjected to cyclic loading. Figure 17 shows that the material exhibits the combination of brittle matrix cracking and interfacial debonding. The fiber pull out in Figure 17(b) suggests energy dissipation, but the fracture surfaces indicate a primarily brittle fracture mode. Good fiber-matrix-nanosilica adhesion is indicated by matrix material clinging to the fibers. The layered structure in Figure 17(a) suggested a laminate design with weaknesses in interlaminar bonding leading to delamination. High stress or cyclic loading leading to matrix cracking and delamination is a potential cause of failure. Figure 17(c) shows the composite with 5 wt % nanosilica, where voids are clearly visible on the fracture surface. The toughness is increased, confirmed by debonding and void growth.

Figure 17(a) shows a low-magnification overview of fracture morphology, (b) shows a higher magnification revealing intergranular and transgranular features, and (c) shows a close-up image of the crack-path indicating fracture mechanisms. It shows that the strength slightly lowers and then rises to the same level as of neat epoxy composites, indicating strong material properties. It also indicates that there is a property drop at higher volumes of nanosilica, which indicates that there is a change in the microstructure, like porosity, phase change,

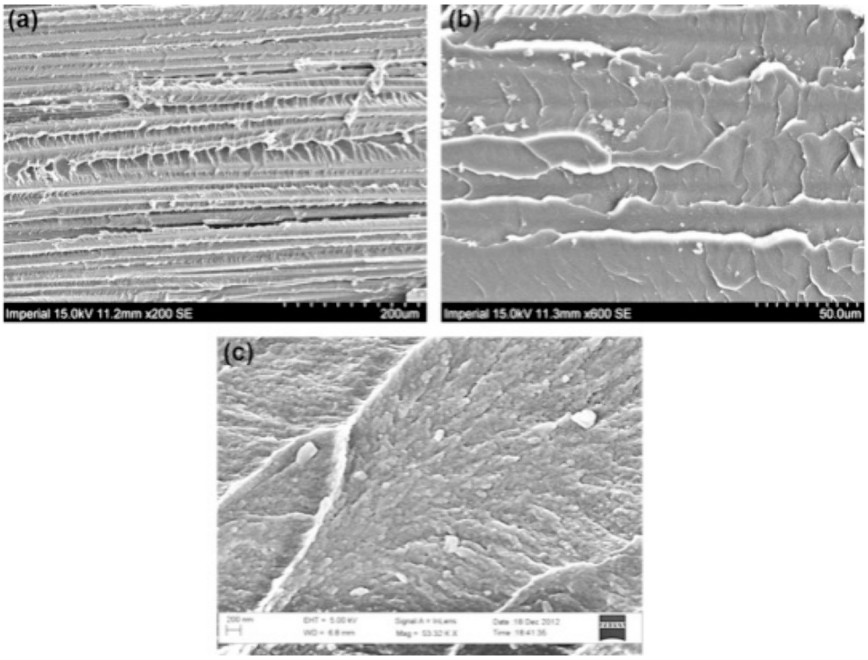


Figure 17. SEM images of fractured surfaces of nanosilica glass fiber composite as shown in parts a−c. Reprinted in part with permission from refs 173. Copyright [ELSEVIER].

etc., which might cause degradation in both the properties. The optimum weight of nanosilica should be taken to avail maximum enhancement in properties, which will grant better performance characteristics of the material.

8.2. Enhancement of Impact Properties after Incorporating Nanosilica into Epoxy Composites. When the impact properties of the hybrid carbon/aramid fiber composite reinforced with clay and nanosilica were being investigated, it was found that there was an increase in the impact energy and strength of the composite until 10% and 3% of weight, respectively.[174] Table 12 gives the test results of the impact testing of epoxy-based composites.

8.3. Enhancement in Fracture and Fatigue Properties on Incorporating Nanosilica into Epoxy Composites. Silica nanoparticles are rigid and spherical shaped and possess large surface area and high Young's modulus, so these are very suitable candidates to enhance toughness and other mechanical properties of thermosetting polymer-based composites.[94] The rate of energy release from silica-epoxy system specimens subjected to statically determined compact tension tests was ascertained. The nanocomposite exhibited a substantial enhancement in the static fracture performance as the proportion of silica added to the input increased. As can be seen in Figure 18a, failure of specimens' fracture surfaces was analyzed with a profilometer, and the surface characteristics profile was subjected to a power spectral density analysis. Figure 18d shows that the presence of nanocomposite samples with microscopic properties on the order of several micrometers was observed, whereas these properties were not detectable in the pure epoxy. As the fracture surface has become more abrasive, this is evidence of fissure deflection.[178] In addition, fractography analysis uncovers indications of particle debonding and cavity growth, Figure 18e, both of which hinder the advancement of fractures.[179][180]. The epoxy material experiences a uniform distribution of rigidity as a result of random dispersion of impurities. Toughening is observed, because a mesoscale toughening mechanism is made possible by this heterogeneity. The study examines the impact of carbon fiber content on the fracture toughness of carbon fiber and silica carbide ceramic matrix composites and their corresponding microstructural changes. The results show that the fracture toughness increases with carbon fiber addition and decreases with further fiber addition. A sample gains a maximum fracture toughness of 3.40 MPam$^{1/2}$ and attains the increment of 33.33% as compared to the composite without carbon fibers.[181] A study is conducted which demonstrates a multiscale synergistic toughening method using hydroxyl-functionalized block polyimide filming as interleaves to improve the inter laminar fracture toughness of carbon fiber/epoxy composites. The method increases mode I interlaminar toughness by 126% and mode II interlaminar toughness by 206%. This new method offers a new way to enhance CF/EP composites' mechanical strength.[182] Carbon fiber epoxy laminates with 10 and 20 wt % were investigated for transverse tensile properties, interlaminar shear strength, and mode I mode II interlaminar fracture toughness. Transverse tensile properties and mode I interlaminar fracture toughness increased when the nanosilica content is increased. However, the interlaminar shear strength and mode II interlaminar fracture toughness decreased with nanosilica concentration. Due to two conflicting causes, the zipper like pattern formed by matrix Microcracks aligned 45° ahead of the

Table 12. Impact Test for Composites

Sr. No.	Material	Test Specification	Specimen Size	Impact Property	Key Findings	Ref
1.	Epoxy and silica nanoparticles	U-notch = 2 mm deep and 2 mm diameter Support span = 70 mm Weight of hammer = 6 kg Length of hammer arm = 0.6 Hammer speed = 1.10 m/s	15 × 15 × 90 mm^3	Impact energy = 0.4 J	Load at specimen break, displacement at specimen break and impact-absorbed energy increased by decreasing particle size.	175
2.	Glass fiber epoxy composite with MWCNT	ISO 179 Impact hammer = 5 J energy capacity	15 × 5 × 90 mm^3	20% ↑ in impact strength = 189.3 kJ/m2 17% ↑ CAI stress = 165 MPa 21% ↑ CAI modulus = 172.8	By adding 0.2% by wt. MWCNT, toughness of the composite increased, because of coating of CNT on fibers results in superior interfacial bonding.	176
3.	Glass fiber and epoxy	Drop weight impact tester, 20 kg Impact velocity = 6.28 m/s	100 × 100 × 2 mm^3 ASTM 3029	Saturation impact energy = 53 J	For this material, within specified loading conditions and impact speed range, the mechanical properties of glass fiber epoxy matrix are unaffected by strain rate	177

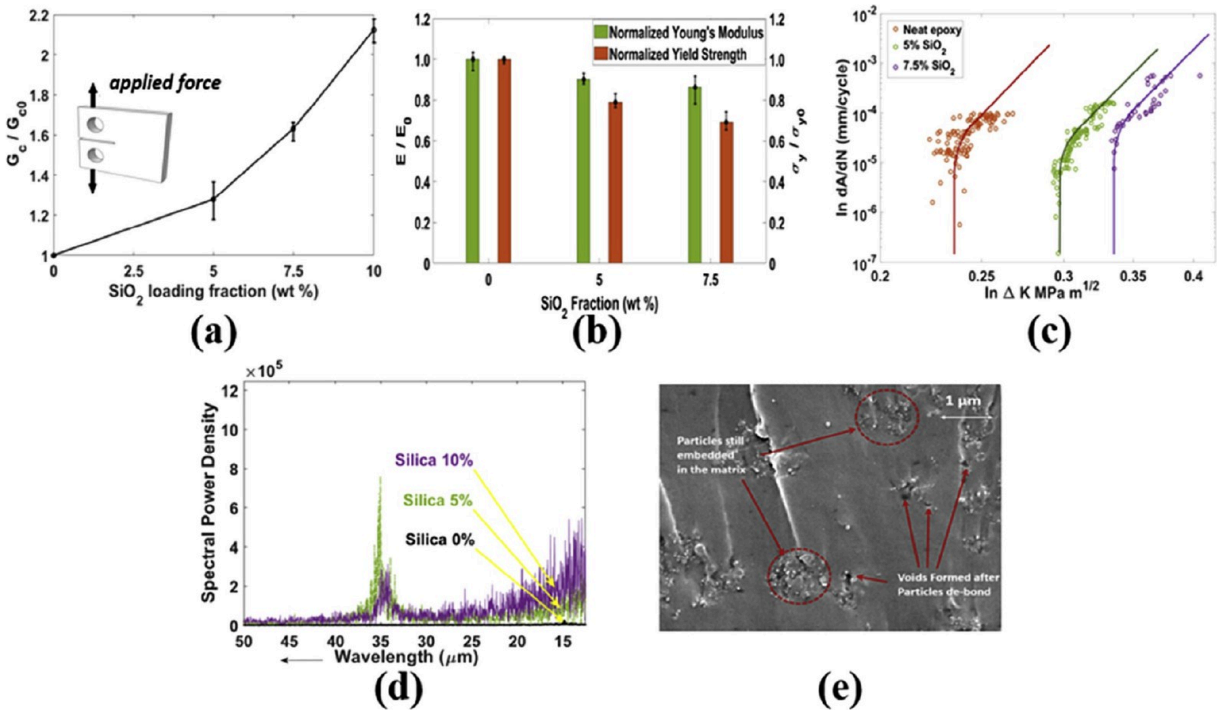


Figure 18. Fracture and fatigue in epoxy-silica nanocomposite. (a) GIC enhancement of silica-epoxy nanocomposites (inset: CT specimen static test schematic). (b) An analysis of the yield strength and elastic moduli of epoxy-silica nanocomposites. In order to facilitate comprehension, the values are normalized using the mean values of the yield strength (98.47 MPa) and modulus (2.76 GPa) of pure epoxy. (c) Fatigue performance enhancement in nanocomposites composed of epoxy and silica. Analysis of the nanocomposites' surface profiles reveals the existence of microscopic characteristics that are not present in pure epoxy. (e) SEM of the fracture surface of the nanocomposite reveals void formation and stochastic nanofiller dispersion. Reprinted in part with permission from ref 184. Copyright [ELSEVIER]. This is mistakenly put above, it wasnt there in the original draft. Please put this caption below figures.

Table 13. Fracture Test Result of Composite

Sr. No.	Material	Fillers	Test	Standard and Dimension of Specimen	Configuration	Crosshead Speed	Improvement in Property	Ref
1.	Kevlar/epoxy composites	CNT	Mode I fracture toughness test	ASTM D5528−13 125 × 20 × 4 mm^3	Double cantilever beam	5 mm/min	Mode I fracture toughness = 60%; 275 J/m^2	195
2.			Mode II fracture toughness test	ASTM D7905 100 × 20 × 4 mm^3	End notched flexure, 3 point bending	5 mm/min	Mode II fracture toughness = 13%; 800 J/m^2	

Table 14. Fatigue Test Results for Composite Material

Sr. No.	Material	Filler	Stress Level	R-Ratio	Frequency (Hz)	Number of Cycles to Failure	Ref
1.	Carbon fiber epoxy-based composite	Graphene NP	680 MPa	0.1	5	20 times more = 105	196

crack tip and matrix shear failure diminish the mode II interlaminar fracture toughness value.[183]

Specimens of plain epoxy and epoxy nanocomposite were statically loaded to measure their modulus and yield strength in accordance with ASTM D790 (Figure 18b. Pure epoxy was found to have an average elastic modulus of 2.76 GPa. Moduli of 2.45 and 2.36 GPa were found for epoxy reinforced with nanosilica at loading fractions of 5% and 7.5%, respectively. Therefore, the silica-modified epoxy exhibits moduli that are exceptionally similar to those of the unmodified epoxy. Nonetheless, it was found that the yield strength of the nanocomposite significantly dropped as the injection fraction rose. The calculated mean yield strength of epoxy was 98.47 MPa; however, it decreased to 77.86 and 68.24 MPa, respectively, upon adding 5% and 7.5% nanosilica loading fraction. Our previous studies predicted that nanoparticles would induce nanoscale plasticity via toughening mechanisms such as debonding and cavity formation. Thus, it is reasonable to expect this type of behavior. The compression test specimens underwent cyclic loading to assess the nanocomposite's fatigue performance following the determination of its static performance. Every sample was measured using a load ratio (R) of less than 0.1 and at a frequency of roughly 3 Hz. All of the steps in the testing process, from collecting data to analyzing the results, were performed in accordance with the requirements of ASTM E647. Fracture propagation graphs obtained show that fatigue performance increases with increasing loading fraction of SiO_2, Figure 18c. The $\sigma_{max}/\sigma_{failure}$ value, which represents the onset of continuous crack propagation, is proportional to the loading fraction. This fracture growth rate curve has a constant slope, as Figure 18c illustrates, independent of the silica loading fraction. This finding is consistent with the toughness result shown in Figure 18a and provides additional evidence that the early stages of the crack effectively delay the onset of stable fracture growth due to the emergence of localized interactions between SiO_2

nanoparticles and the crack. The antifracture characteristics of nanoparticles would postpone the emergence of unstable crack formation, prolonging the fatigue lifetime. Table 13 and Table 14 give the fracture and fatigue test results of the composite.

Taylor et al.[141] conducted a comprehensive study on anhydride-cured DGEBF modified with 10% nanosilica solution and 9% rubber toughener CTBN by employing a VARI process, and 45-degree biaxial textile, glass fiber-reinforced laminates were manufactured. When nanosilica was added to the control material alone, the GIC increased from 1.09 to 1.31 kJ/m^2, while the addition of CTBN alone increased the value to 1.83 kJ/m^2. The GIC value of the hybrid resin system with both modifications was 1.65 kJ/m^2. The threshold fracture energy was significantly enhanced as a result of synergy between the two modifications. In order to assess laminates produced via the VARTM method and a ±45 biaxial glass fiber fabric, Tate et al.[109] conducted a low-velocity impact study. A solution of amine-cured DGEBA was mixed with silica nanoparticles containing 8.1% CTBN. The enhanced capacity of the hybrid system to dissipate impact energy is probably the cause of the decrease in compressive strength that occurs after impact. The mitigation of backside delamination is an exceedingly critical characteristic in ballistic applications, where resistance to penetration takes precedence over damage minimization. The behavior of carbon fiber-reinforced laminates was similar.[185] In an independent study,[186] Tate et al. investigated a conventional wind energy generator rotor blade system. The VARTM method was used to infuse an amine-cured DGEBA into a 45O multi axial glass fiber fabric. The addition of silica nanoparticles increased the tensile, flexural, and ILSS strengths by 6% as well as the tensile and flexural modulus. The most notable development, shown in Figure 19, is the enhanced fatigue performance of the laminates. The test specimen for silica nanoparticle modeled UD laminates was constructed from 12 K carbon fiber bundles. They noted an improvement in bulk resin modulus and strength. This improved the laminates' transverse tensile strength. Carbon fiber reinforced UD laminates were produced using a VARTM process by Tang et al.[187] from amine cured DGEBA. Increases of 17% in GIC and 8% in interlaminar shear strength ILSS were seen after 2% nanosilica was added to the laminate. Adding 3% more polydopamine raised both the GIC and ILSS. Every week for 3 weeks, the test specimen was submerged in salt water. Both GIC and ILSS were reduced after being exposed to salt spray, but the modified laminates performed much better than the control had they been constructed with the same materials to begin with. Mahrholz et al.[188] looked into how different process parameters affected the surface quality of CFRCs. The RTM method was used to create laminates from UD carbon fiber textile woven in a satin weave. The amine-cured DGEBA was modified by the addition of silicon nanoparticles. Lessening of volume shrinkage during precuring at lower temperatures is mirrored by an improved laminate surface. The modulus and strength of bulk resins were nearly linearly improved by adding nanosilica. It was discovered that the thermal expansion coefficient decreased as the quantity of SiO$_2$ increased, both below and above the glass transition temperature (Tg). There was a 75% decrease in the total volume. Class A surfaces were achieved in laminates through the incorporation of nanoparticles and an optimized curing cycle. Sprenger et al.[189] examined the properties of a VARTM-fabricated CFRC comprised of an amine-cured DGEBA and a 45-degree biaxial textile. After adding 10% weight nanosilica and 10% CTBN to the system, there was no discernible change in modulus, but GIC increased by 250% in comparison to the unmodified control. Compressive strength was lower and the delaminated area larger after impact compared to the control position. This shows that the hybrid epoxy resin used in the laminate is very effective at dissipating the impact energy. Abliz et al.[190] used a carbon fiber fabric that was only partially unidirectional, and the DGEBA they used was cured with anhydride. Epoxy resins' fluidity was altered with the help of boehmite nanoparticles and silica nanoparticles. They can show how the dispersion and particle size distribution of nanoparticles become more significant as the fiber's volume fraction increases.[191] An amine-cured DGEBA was developed by Landowski et al.[191] and VARI integrated into a plain-weave carbon fiber fabric. Their evaluation of various attributes revealed an intriguing discovery: an epoxy resin that was infused with 8% silica nanoparticles exhibited a 27% reduction in the damage area. The aforementioned results seem to be in opposition to the prior conclusions reached by other scholars. Nevertheless, such an incident merely serves to underscore the critical significance of reinforcement textiles when examining the impact. Through the manipulation of fiber orientation in the direction of impact, the engineer can alter the design to attain distinctly different mechanical behaviors. Kinloch and colleagues examined the mechanical and fracture characteristics of a DGEBA combined with an aliphatic epoxy and cured with anhydride in ref 152. The laminates that were examined were produced utilizing a biaxial 45 in. carbon fiber fabric and the VARI technology. In order to modify the epoxy resin, silica nanoparticles and Type III core−shell particles were utilized. At temperatures of −20 °C and −80 °C, the fracture resistance was assessed. At room temperature and −80 °C, the bulk GIC of the unaltered control was 0.17 and 0.15 kJ/m^2, respectively. There was a difference between the fiber-reinforced composite's GIC values of 0.87 kJ/m^2 at −80 °C and 1.25 kJ/m^2 at room temperature. Fracture toughness was enhanced by 15% and 5% in bulk and composite, respectively, with the addition of 8% nanosilica by weight percent. Similarly, the inclusion of an 8% core−shell elastomer increased fracture toughness by 4440 and 35%, respectively. Again, the best performance was shown by the hybrid resin system consisting

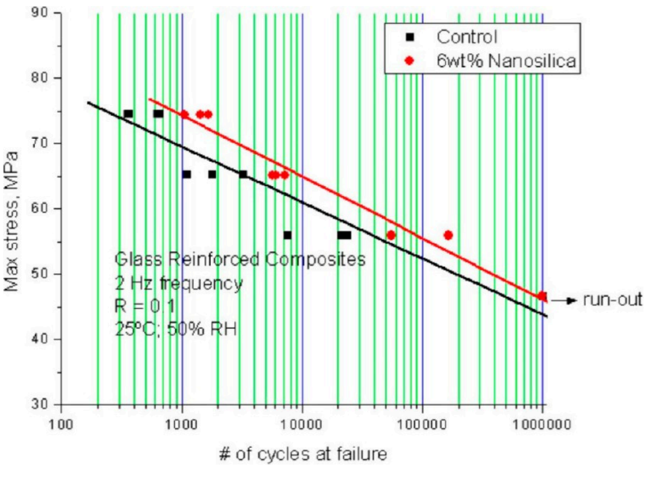


Figure 19. Curves of stress versus number of cycles until failure (S−N) for epoxy GFRC containing and lacking 6 wt % SiO$_2$. Reprinted in part with permission from ref 185. Copyright [2018], [SAGE].

of 8% SiO_2 and 8% core−shell, with GIC gains of 1.22 kJ/m^2 in bulk and 1.76 kJ/m^2 in composite or 600% and 40%, respectively. The composite control laminate experienced a 30% reduction in GIC at −80 °C, whereas the laminate manufactured by using the hybrid resin system only exhibited a 23% decrease in value. The primary mechanisms of toughening involved the growth of plastic voids surrounding cavitated core−shell elastomer particles and the localized plastic shear-band yielding caused by the nanoparticles. Carolan et al.[192] used a modeling approach to fracture mechanisms to predict fracture energies. The experimental and theoretical energies were found to be very close to one another at both temperatures. The measured and calculated energies at both temperatures tested agreed very closely. Tsai et al.[118] examined the toughness characteristics of carbon fiber-reinforced composites using carbon fibers sized with silica nanoparticles. This was achieved using an entirely new method. The fibers are protected during processing and weaving because of sizing, a thin coating that is typically applied during fiber manufacturing when the composite is curing, to improve the adhesion between the matrix and fiber. DGEBA that was treated with anhydride was used as the matrix. The laminates exhibited a 33% increase in GIC as determined by fragility tests, notwithstanding the fact that there was less than 1 wt % of nanosilica localized on the fiber and introduced through the sizing process. This highlights the significance of the fiber matrix interphase, which offers an elegant and reasonably priced way to extend the life of laminates, in contrast to the suggested stress distribution mechanisms. Despite a marginal reduction in the fatigue life, the observed advantage was not substantial. Fiber-reinforced composites employ a wide variety of silica nanoparticles.[189] Nanosilica has been found to be compatible with all current composite manufacturing processes and can significantly improve laminates' mechanical and other important properties. Furthermore, they emphasized the necessity of a fine dispersion of nanosilica in the epoxy resin in order to achieve the intended improvements. Regardless of the weave or composition of the reinforcing fibers, another analysis revealed a relationship between the fracture energy of the bulk epoxy resin matrix and that of the laminate.[193] The percentage increase in GIC is explained by the addition of an elastomeric toughener and silica nanoparticles to the bulk epoxy resin. This improvement surpasses the corresponding laminate's GIC by 0.18 transfer factors. This information can be used by engineers to create a better matrix resin: substituting a nanomodified resin with a GIC 170% higher than the previous resin for the epoxy resin results in a 30% increase in the laminate's fracture toughness. Glass and carbon fiber-reinforced laminates made from these systems are compared to their GIC in Figure 20. An elastomeric toughener and silica nanoparticles were added to the bulk resin systems. The data suggest that these resin systems are widely used in the composites industry. There will be a total of 12 polymer 2020 courses assessed. Twenty-one of twenty-seven low-cost approaches to making laminates last longer. However, significant gains were not observed in the fatigue resistance. In a review, Zhang et al.[26] compared the developments in carbon fiber and glass. As consumer demand for ecofriendly goods and renewable materials rises, natural fibers are being utilized more frequently as reinforcement in composite materials. After studying a DGEBA matrix system that had been cured with anhydride, Kinloch et al.[194] added silica nanoparticles and a reactive liquid rubber CTBN. The VARI technique was used to create laminates composed of plain-woven regenerated cellulose fiber fabric and UD flax fiber fabric. In this case, typical glass fiber textile-reinforced laminates were used as a benchmark. Since natural fibers absorb moisture when stored, resulting in laminates, predrying is essential only before the infusion procedure. The hybrid epoxy resin that included CTBN and nanosilica performed better than the others, despite both modifications increasing the laminate toughness. The modulus-dependent GIC values of composites made of hybrid epoxy resin Si10R9 supplemented with 10% nanosilica and 9% CTBN by weight, as well as unmodified epoxy resin Si0R0, are shown in Figure 20. Take note of the different GIC scales along the *y*-axis.

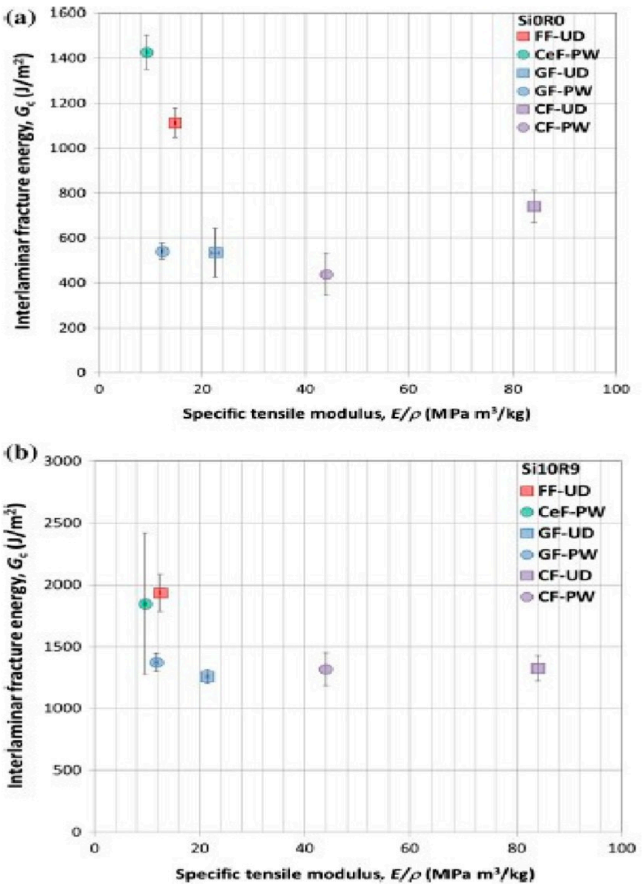


Figure 20. Fracture energy against modulus for different laminates with unmodified epoxy resin and epoxy resin treated with (a) 10% nanosilica and (b) 9% CTBN. Reprinted in part with permission from ref 173. Copyright [2015], [ELSEVIER].

9. ADVANCES IN EPOXY COMPOSITES

Since the past decade, there has been a huge amount of research in the field of smart materials, which perform better and react to the environmental conditions in a better way. Similarly, researchers have created smart behavior in epoxy-based composites also. A novel smart composite was created using Poly Urea (PU) shelled micro-Phase Change Material (PCM) which was incorporated into an epoxy matrix; it has been concluded that this smart material was evenly distributed into the matrix, and the heat storing ability and thermal stability have increased along with good thermal cycling reliability. There was an increase in Tg, but the storage modulus was compromised.[197] When carbon nanotubes are incorporated into epoxy resins, an intelligent material is created, which is used in structural health monitoring applications with high sensitivity.[198] Another smart material named as Shape Memory Alloy (SMA) wires is implemented as a layer in epoxy/carbon composites by vacuum infusion and the hand lay-up technique. It behaves smartly under controlled thermal loading, by bending specifically because of prestrained SMA wires.[199] Figure 21 gives a brief overview of the smart materials' behavior and applications.

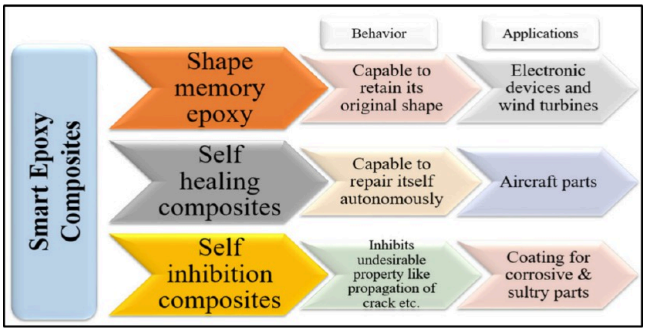


Figure 21. Smart composites overview.[199]

For nanosilica reinforced and reactive liquid rubber toughened epoxy-based composites to qualify as smart materials, they must exhibit specific characteristics that will enable them to respond dynamically to environment stimuli. These requirements include self-sensing of damage detection and structural health monitoring of composites. These composites should be capable of detecting cracks, stresses, or damage using embedded nanoparticles or piezoresistive sensors. Integration of electrically conductive networks within the composites allows real-time monitoring of structural integrity. Techniques like dielectric sensing, strain sensitive nanofillers, or fiber gratings can be used to make them smart materials. Another major skill of a smart composite is its self-healing capability. It should be able to autonomously repair microcracks and prevent failure. This may be achieved by incorporation of microcapsules filled with liquid healing agents, phase separating rubbers, or shape memory polymers. It also has the ability to change shape and recover to its original form whenever exposed to temperature, light, or electric or magnetic fields. For these composites to be truly smart materials, they must go beyond mechanical enhancement and respond intelligently to environmental conditions. This can be achieved through functional nanofillers, self-healing mechanisms, shape-memory properties, and real-time sensing abilities.

10. FUTURE OPPORTUNITIES AND CHALLENGES

The use of nanocomposites has been very crucial in the aerospace industry's revolutionary accomplishments. Improved fatigue strength, toughness, and lightweight components are outcomes of using nanocomposite material advancements. The development and processing of nanocomposite components indulges many production techniques, and the innovative techniques are regularly studied and updated for better improvement by researchers across the globe. The choice of technique significantly impacts the quality of the nanocomposite, considering challenges during the followed procedure and the complexities of the machine. It is suggested that researchers investigate the effect of different tougheners for specific polymers used for composite production. Also, there is scope to check the compatibility of a specific toughener along with the nanoparticles in an epoxy-based composite. Additionally, it is suggested to explore the thermal, mechanical, and tribological properties of toughened epoxies of different types, which will eventually give a clear idea of the area of application. In this study, un to 10% by weight nanosilica loadings were analyzed. This restricted range has two drawbacks: it did not give a thorough grasp of the ideal loading level and it does not investigate the implications of greater loadings. Absence of Long-Term Durability evaluation of toughened nanosilica composite is there. It appears that the primary emphasis is on the nanocomposite's immediate mechanical and thermal properties. Long-term robustness and resistance to the environment, which are essential for automotive and aerospace applications, are not covered, though. Important factors like the stability of the composite over time, exposure to hostile conditions, and the effects of aging are the fields that are unexplored. There is a limited examination of composite manufacturing. The majority of the study's focus is on the composites' testing and characterization; it does not, however, explore the practicalities of producing these nanosilica-reinforced composites on a wider scale. The discussion of the production process's scalability or manufacturing difficulties is needed to be studied by future researchers. Many studies have been done on the mechanical characteristics, such as fracture toughness and tensile modulus, but little attention has been paid to other crucial attributes such as impact resistance, electrical conductivity, and agent resistance. For practical uses, a deeper examination of the material's characteristics is required. The complexity of real-world applications is to be analyzed; while the research mentions the materials' potential for use in the automobile and aerospace industries, it does not address the intricate standards, regulations, and requirements unique to these sectors. Making the switch from a laboratory environment to real-world applications can be quite difficult. Understanding the exclusion zone is unexplored in this study. The study notes that there is an exclusion zone surrounding silica particles, but it does not go into great length to explain what it means or how it might be used. To gain a deeper understanding of this phenomenon, more research is required. The environmental impact of these types of nanocomposites is not addressed. The study does not address the effects of nanosilica-reinforced composites on the environment, including problems with material disposal or the effects of the synthesis processes on the environment. These nanocomposites may come into contact with other materials in practical applications, which may have an impact on their characteristics and performance. Other material interactions are not taken into account. Whether employing nanosilica-reinforced composites for automotive or aerospace applications is cost-effective and commercially viable is not covered in this study. In many industries, the acceptance of new materials is heavily influenced by economic factors. To properly evaluate the potential of nanosilica-reinforced composites for aerospace and automotive applications and enable their practical deployment, it will be necessary to address these restrictions and carry out additional research to close these gaps.

The main challenge regarding nanosilica as a toughening agent for epoxy composites in aerospace applications is dispersion and agglomeration of nanosilica into epoxy. Achieving uniform dispersion of nanosilica into an epoxy matrix is difficult due to high surface area, leading to high agglomeration. Poor dispersion leads to stress concentration points, which reduce the performance characteristics of composites. Effective functionalization of strategies is required to enhance compatibility with the epoxy matrix. Determining the optimal content of nanosilica is challenging, as excessive loading increases viscosity and reduces processability. It is challenging to enhance toughness without compromising other mechanical properties. Increased viscosity due to nanosilica incorporation can make fabrication methods like VARTM etc. more challenging. For this, there is a need for modified curing strategies to accommodate nanosilica without compromising epoxy cross-linking. When nanosilica enhances toughness, its impact on thermal stability and electrical conductivity for aerospace applications needs careful consideration. The interfacial bonding between nanosilica, fibers, and epoxy resin is challenging and plays an important role in mechanical performance, ensuring that nanosilica does not interrupt fiber-matrix adhesion which leads to weak interfaces. The high costs of nanosilica synthesis and surface modification may limit large-scale adoption, ensuring that processing methods are scalable and compatible with aerospace industry standards.

11. CONCLUSION

This paper presents an inclusive review on the use of nanosilica as a reinforcing agent to the epoxy-based composite, with a motive to improve the mechanical properties like strength, modulus, toughness, fracture properties, etc. It can be concluded that nanosilica is capable of proving its worth in enhancing the properties because of its high surface area and smooth nonporous surface. This is because high surface area provides better interaction with the matrix material. Due to this, better stress transfer is achieved, resulting in improvement of the mechanical performance of the epoxy system. During the study, silica loading into the epoxy matrix was also analyzed. The conclusion drawn is that, until 5% wt of nanosilica, there is increment in properties but, beyond that weight, either there is no significant improvement or there is deterioration in properties. This is because of the fact that, at higher loadings, these particles tend to agglomerate due to strong van der Waal forces, which leads to stress concentration points, further giving birth to cracks, and eventually there is reduction in mechanical properties. At higher loadings, there is poor dispersion and higher viscosity, which makes processing very difficult. The procedure to incorporate nanosilica into epoxy resin is discussed in this review paper and suggested to be used for researchers working in the same field. Toughening agents like the reactive liquid rubbers CTBN, ETBN, etc., following the heterogeneous toughening method, have proved their worth in significantly increasing mechanical properties without sacrificing other properties. So, this paper highlights the transformative potential of these materials in shaping the future of aerospace engineering and emphasizes the importance of ongoing research and innovation in this field.

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■ ABBREVIATIONS

PMC, polymer matrix composite; MMC, metal matrix composite; CMC, ceramic matrix composite; VARIM, vacuum assisted resin infused molding; MWCNT, multiwalled carbon nano tube; Tg, glass transition temperature; TP, thermoplastics; GIC, interlaminar fracture toughness; KIC, maximum fracture toughness; ILSS, interlaminar shear strength increment decrement; abrCTBN, carboxyl terminated butadiene nitrile; ETBN, epoxy terminated butadiene nitrile; abrHTBN, hydroxyl terminated butadiene nitrile; MTBN, mercaptan terminated butadiene nitrile; PTBN, phenol terminated butadiene nitrile; PU, polyurethane; PES, polyethersulphone; PSO, polysiloxane; MEK, methyl ethyl ketone; DGEBA, diglycidyl ether of bisphenol A; TGAP, triglycidyl *p*-aminophenol

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