

Review Article

The Effect of Nanoparticles Percentage on Mechanical Behavior of Silica-Epoxy Nanocomposites

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Silica-epoxy nanocomposites are very common among nanocomposites, which makes them very important. Several researchers have studied the effect of nanoparticle's size, shape, and loading on mechanical behavior of silica-epoxy nanocomposites. This paper reviews the most important research done on the effect of nanoparticle loading on mechanical properties of silica-epoxy nanocomposites. While the main focus is the tensile behavior of nanocomposite, the compressive behavior and flexural behavior were also reviewed. Finally, some of the published experimental data were combined in the graphs, using dimensionless parameters. Later, the best fitted curves were used to derive some empirical formulas for mechanical properties of silica-epoxy nanocomposites as functions of weight or volume fraction of nanoparticles.

1. Introduction

Nanotechnology, technologies at nanoscale, is a new science that involves enhancing and engineering the material properties and technologies at the nanoscale. In comparison with the microtechnology, nanotechnology leads to extremely different phenomena and performances. The nanocomposite products contain reinforcing or fillers in nanoscale (less than 100 nm). Most of the mechanical properties can be improved using nanoscale fillers [1]. Researchers have studied the current and future prospective products within the nanoscience [2]. They predicted that nanomaterial would open new dimensions in the industrial applications. In order to produce polymer nanocomposites with desirable properties, there are various kinds of nanoparticles that can be added to a polymer matrix [2].

The nanostructured materials may be classified according to their dimensionality, morphology, composition, and uniformity/agglomeration states [3]. Based on dimensionality, nanostructured materials are classified into 1D (i.e., thin films or surface coatings), 2D (i.e., fixed long nanostructures, thick membranes with nanopores, and free long aspect ratio nanowires), and 3D (i.e., fixed small nanostructures,

membranes with nanopores, and free small aspect ratio nanoparticles) [3]. Additional examples of 2D fillers include smectic clays or phyllosilicates [4], layered silicic acids [5], kanemite ($\text{Na}_2\text{HSi}_2\text{O}_5$), makatite [$\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$], octosilicate ($\text{Na}_2\text{Si}_8\text{O}_{17} \cdot n\text{H}_2\text{O}$), kenyaite ($\text{Na}_2\text{Si}_2\text{O}_{41} \cdot n\text{H}_2\text{O}$) [6], and layered double hydroxides (LDH) [7]. The polymers that are used for making polymer nanocomposites are thermoplastics, thermosets, and elastomers.

Nanofillers may be classified into three categories based on their sizes, morphologies, and shapes [8]. In the first category, there are fibers that have a diameter of less than 100 nm and the aspect ratio from 100 to 10^6 . Some examples of this type are nanoscale graphite fibers, carbon nanotubes, and hexagonal boron/nitrogen nanotubes [9]. In the second category, the three-dimensional nanofillers are comparatively equiaxed, and their size of the largest dimension is less than 100 nm [8]. Some examples are silica nanoparticles, titania nanoparticles (TiO_2), aluminum oxide nanoparticles (Al_2O_3), cerium oxide nanoparticle (CeO_2), and zinc oxide nanoparticle (ZnO) [4]. In the third category, there are plate-like nanofillers, which are layered materials, with a thickness of about 1 nm and an aspect ratio of at least 25 in two

dimensions [8]. Most common nanoparticles of this type are layered silicates (i.e., mica) [10].

Nanofillers that are categorized by their morphology may be classified into high aspect ratio and low aspect ratio nanostructures. Moreover, in case of composition, they can be grouped into single material and composite nanostructures (i.e., coated nanostructures and encapsulated nanostructures) [3]. Dispersed or agglomerated are other classifications based on uniformity and agglomeration state of nanofillers [3].

The factors that play a major role in the properties of nanocomposites are nanoparticle-matrix interaction and particle-particle interaction [11]. The attraction forces between particles, due to the van der Waals and electrostatic forces, affect the particle-particle interaction and deteriorate the composite's performances [11, 12]. The repulsion and attraction forces can be controlled by particle weight fraction (wt.%), particle volume fraction (vol.%), particle surface modification, and particle size [13–20]. The improved mechanical properties can be achieved through improved interface between the particle and matrix [11]. Increase in particle loading due to increase in weight fraction or volume fraction leads to uniform and continuous interface that may create a strong polymer network improving the mechanical properties [18]. The quality of interface and the strength of the adhesion at the interface determine load transfer between the matrix and the nanofillers [21]. Extensive research has been conducted on several polymer nanocomposites in order to understand the effect of weight fraction and volume fraction (vol.%) on mechanical properties of polymer nanocomposite [13–20]. In the majority of these studies, epoxy and nanosilica were used, as the polymer matrix and nanoparticle, respectively, which shows the popularity of epoxy-silica nanocomposites. In this paper, the previous research on the effect of nanoparticle size and weight fraction on mechanical properties of epoxy-silica nanocomposites is reviewed.

2. Preprocessing of Nanocomposites

As it was explained in the previous section, the factors that play a main role in the performances and properties of nanocomposites are particle-particle interactions and particle-matrix interactions [11]. The particle-particle interaction deteriorates the composite's performances, whereas the filler-matrix interaction produces a composite with improved performances. The attraction and repulsion between the particles, due to van der Waals and electrostatic forces, affect the particle-particle interaction in a composite [12]. The reduction in the repulsive forces between the particles can be achieved by decreasing the particle size in the nanoscale. The adverse impact of the particle-particle interaction can attribute to particle aggregation and, consequentially, the performance of the nanocomposite may deteriorate [23].

Some chemical modification methods, such as in situ processing method, allow controlling “morphology” and “polymer-nanofiller interface” in polymer nanocomposites.

The interfacial area between the nanofillers and the polymer controls the properties of a polymer nanocomposite. The chemical properties of this region affect the polymer chain mobility, degree of curing, and the crystallinity. The interfacial size can range from 2 nm up to 50 nm [24]; the higher the size of this region, the higher the effect of nanofillers on the polymers. There are some processing methods to control the dispersion of nanofillers and size of the interfacial zone [24]. Nanoparticles show high rate of agglomeration. Some preprocessing methods are adapted in order to reduce the surface energy and to disperse the nanofillers into the matrix by engineering the interfacial region and particle-particle interaction [25].

2.1. Agglomeration. As nanoparticles have high surface area to volume fraction and high surface energy, it is difficult to disperse them uniformly in a polymer matrix. Moreover, as they are hydrophilic, they are not compatible with the hydrophobic polymer matrices. Some preprocessing methods are suggested to reduce the surface energy and to disperse nanofillers into the matrix by engineering the interfacial region [25]. The use of coupling agents (e.g. silane for silica) [26–29] and grafting polymers [30–33] are conventional methods for treating the nanoparticles.

In case of grafting, the grafted polymers that are adhered to the nanoparticles are not miscible to the matrix and reactive compatibilization is suggested to resolve this issue [25]. Two polymers would form a compatible mixture when they have functional groups capable of generating covalent, ionic, donor-acceptor, or hydrogen bonds between them [25]. For reactive compatibilization, the reactive polymers are added that are miscible in the first blend component, while these added polymers are reactive to the functional groups of the second component [34]. Research has demonstrated that reactive compatibilization is the best method for blend compatibilization [25, 35].

2.2. Surface Modification. The interface between the particle and the matrix can be modified using chemical [25, 36] or physical methods [26, 33]. After the desired modification is achieved, the surface bonds, which are a mixture of secondary bonds and chemical bonds, will be at optimum level [23].

Chemical modification can be done either by modifying agents or by grafting polymers [25]. Silane coupling agents are the most common modifiers for silica nanoparticles. They have both organ functional and hydrolysable ends. The general structure of the coupling agents can be represented as RSiX_3 , where the X represents the hydrolysable groups, which could be chloro, methoxy, or ethoxy groups [29]. The organ group, R, can have a variety of functionalities, which can be selected according to the particular requirements of the polymer matrix. An example of coupling agents is silanization, which can be used to modify the colloidal silica to prevent particle aggregation [36].

Inorganic nanoparticles can be modified by adsorption of a surfactant or macromolecule on the particle surface to prevent particle aggregation [25, 33]. Controlling the interfacial interactions is not limited to single layer coatings.

Multicomponent organic and inorganic coatings can be applied using core-shell technique, where multiple layers of coatings are applied to obtain different functionalities [24]. Then, the coated nanoparticles can be easily added to the matrix to form polymer nanocomposite [24].

3. Theory of Nanoparticle's Weight Fraction Effect

In this section the effect of weight fraction on the Young's modulus of elasticity, compressive and tensile strengths, and fracture toughness is described.

3.1. Effect on Young's Modulus. Einstein [37, 38] proposed a linear model to explain the relationship between the volume fraction of rigid spherical particles and Young's modulus of composite. This model assumed perfect adhesion between the filler and matrix and no interaction between the particles, which led to the following equation:

$$\frac{E_c}{E_m} = 1 + 2.5V_f, \quad (1)$$

where E_c is Young's modulus of nanocomposite, E_m is Young's modulus of matrix, and V_f is volume fraction of the filler. The above equation is valid only for low particle loading and does not consider the interparticle interaction [21]. Guth [39] proposed the following model that includes particle interaction effect at high particle loading after modifying Einstein's model:

$$\frac{E_c}{E_m} = 1 + 2.5V_f + 14.1V_f^2. \quad (2)$$

The above two models are valid only for nanocomposites with spherical particles [21]. Mooney [40] modified Einstein's model and proposed the following model for Young's modulus of composites with nonspherical particle at high particle loading:

$$\frac{E_c}{E_m} = e^{(2.5V_f + 0.407(p-1)^{1.508} + V_f)/(1-sV_f)}, \quad (3)$$

where s is the crowding factor of nanoparticle that is related to interparticle interactions and p is the aspect ratio of particles [40].

For silica-epoxy nanocomposites, the Kerner model [41] showed the closest agreement with the experimental data [42]. The equation for Young's modulus in Kerner model is

$$\frac{E_c}{E_m} = \frac{1 + ABV_f}{1 - B\psi V_f}, \quad (4a)$$

where A and B are constants and ψ is the maximum packing fraction of filler in the matrix. A and B are defined as follows:

$$A = K_e - 1, \quad (4b)$$

$$B = \frac{E_f/E_m - 1}{E_f/E_m - A}, \quad (4c)$$

where K_e is Einstein's coefficient and E_f is Young's modulus of filler [41].

3.2. Effect on Compressive or Tensile Strength. The ultimate strength of polymer nanocomposite depends on the interaction between the matrix and the fillers [21]. A number of models have been developed to investigate the strength of adhesion between the filler and matrix [43–48]. One of the models that considers poor adhesion of particle with the matrix proposes the following model to define a relationship between ultimate tensile stress (σ_c) and volume fraction (V_f) of nanocomposites [43, 44]:

$$\sigma_c = \sigma_m (1 - aV_f^b), \quad (5)$$

where σ_c is the ultimate tensile stress of the nanocomposite, σ_m is ultimate tensile stress of the matrix, and a and b are constants that depend on the shape and arrangement of the nanoparticles. a and b are equal to 1.21 and 2/3 when there is no adhesion between the nanofillers and the matrix [45]. Other investigators proposed the following model, which considers the particle/matrix friction and residual pressure [46]:

$$\sigma_c = 0.83pfV_f + \sigma_m k(1 - V_f) + H\sigma_a(1 - V_f), \quad (6)$$

where f is friction coefficient, k is relative change of stress due to inclusion of filler, σ_a is adhesion stress, H is a constant, and p is pressure. They considered that stress was transferred completely from the matrix to the fillers.

Another study proposed the following model for very strongly bonded fillers and matrices [47, 48]:

$$\sigma_c = \left(\frac{1 - V_f}{1 + 2.5V_f} \sigma_m \right) e^{B_e V_f}, \quad (7)$$

where B_e is an empirical constant that depends on the surface area of particle, particle density, and interfacial bonding energy between filler and matrix.

3.3. Effect on Fracture Toughness. The fracture energy of composite (G_c) depends on the effective load bearing area [49, 50]. Most of the models proposed for predicting fracture toughness are either inaccurate or difficult to use because of their complexities and narrow composition ranges [51–56]. However, some researchers [57] proposed the following simple model that considered the fracture resistance of matrix, its change with composition of composite, change in effective matrix cross section, and interaction:

$$G_c = \frac{G_m}{E/E_o} \frac{1 - V_f}{1 - 2.5V_f} e^{B_f V_f}, \quad (8)$$

where G_c is fracture toughness of composite, G_m is fracture toughness of polymer matrix without reinforcement, E/E_o is related to resistance of matrix against plastic deformation, and B_f is proportionality constant that depends on size of the interphase and strength of interaction between filler and matrix.

4. Effect of Nanoparticle Size and Fraction on Mechanical Properties

4.1. Tensile Behavior. In an effort to study the effect of weight fraction of silica nanoparticles on the tensile behavior of epoxy, Liu et al. measured Young's modulus and yield stress at different weight fractions [13]. The results revealed that both Young's modulus and yield stress of epoxy/silica nanocomposite have increased gradually with increasing the weight fraction of silica particles. Some researchers studied the effect of different weight fractions of silica on tensile behavior of epoxy resin [18, 58]. In these studies, pure resin and epoxy/silica nanocomposites were used to measure the tensile properties. The values of Young's modulus and yield stress of silica-epoxy nanocomposites at 20% weight fraction were found to be 1.22 and 1.28 times the corresponding values of the epoxy. The improvement of Young's modulus of nanocomposite at 20% weight fraction of silica nanoparticle was 1.4 times that of the pure epoxy [58]. However, they found that the tensile stress remains constant as weight fraction increases from zero to 10%.

In contrast to the stiffening effect of silica nanoparticles on the epoxy, Young's modulus and yield stress of rubber-epoxy nanocomposite decrease linearly with increasing weight fraction of nanofillers [13]. In case of rubber/epoxy system, the nanoparticles act as stress concentrators leading to the plastic deformation of the matrix [59]. In case of silica/epoxy nanocomposite, the rigid silica nanoparticles increase stiffness of the matrix system.

Mahrholz et al. [18] reported an increase in tensile stress and Young's modulus of nanocomposites with the increase of weight fraction of silica nanofillers. They also found a critical value of 15% for weight fraction at which the maximum elongation was observed. Chasiotis [19] found that in comparison with Young's modulus of epoxy resin (3.09 GPa), Young's modulus of epoxy-silica nanocomposite (with 12 nm particle) increased monotonically with the increasing weight fraction of up to 15%. Uddin and Sun [16] showed that the mean values of longitudinal and transverse tensile stress of epoxy-silica nanocomposites increase to 11% and 32%, respectively, compared with the epoxy. The silica nanoparticles showed little effect on Young's modulus of the nanocomposite [16].

Ahmad et al. [14] used mineral silica particles of different shapes instead of conventional fumed silica to make epoxy-silica nanocomposites. They used silica particles at different volume fractions and concluded that higher volume fraction of silica nanoparticles produces higher stress and Young's modulus of the nanocomposites. Moreover, the highest improvement was reported with elongated silica nanoparticles compared with the angular and cubical silica.

Zamanian et al. [60] observed more improvement in Young's modulus of nanocomposites at higher weight fractions of nanoparticles. The improvement was higher when smaller nanoparticles were used. Islam [61] studied the effect of variable particle sizes on the tensile behavior of epoxy/silica nanocomposite having a fixed weight fraction of 5%. As expected, they observed improvement in the tensile stress, 0.2% offset yield stress, and Young's modulus after adding the silica nanoparticle to the pure epoxy. It was also

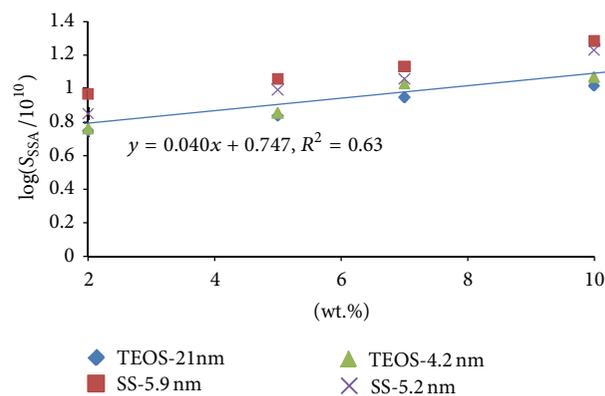


FIGURE 1: The effect of weight fraction of mesoporous silica nanoparticles on the dimensionless tensile strength of rubbery epoxy mesocomposite [17]. (TEOS and SS indicate tetraethyl orthosilicate and sodium silicate. The number after the precursor indicates pore size of the mesoporous silica nanoparticles).

observed that by adding 5% silica nanoparticles of 20 nm, the ultimate and yield stress increased by 20% and 50%, respectively, over the epoxy.

Some researchers studied the effect of microparticle and nanoparticle size silica on the mechanical properties of epoxy polymers [42]. They found that, due to existence of microparticles, inclusion of nanoparticles did not show any significant effect on Young's modulus. However, the maximum improvement for Young's modulus and yield stress was seen at higher volume fraction of nanoparticles [42].

Tsai et al. [62] investigated the effect of particle weight fraction on two different kinds of polymer matrices. They used two types of curing agents for making ductile and brittle epoxy-silica nanocomposites. It was reported that, in case of ductile epoxy/silica nanocomposites, both Young's modulus and stress were increased with increasing weight fractions of nanoparticle. However, for the brittle one, only Young's modulus showed the similar trend, while stress increased up to an optimum level at weight fraction of 20%.

Sun et al. [15] investigated the effect of particle modification and various weight fractions of silica fume on the yield stress of PVC/silica nanocomposite. Tests were made on four samples: pure PVC, untreated fumed silica/PVC nanocomposite, dimethyl dichlorosilane treated silica (DDS)/PVC nanocomposite, and γ -methacryloxypropyl trimethoxy silane treated silica (KHS)/PVC nanocomposite. They concluded that the tensile strength of a polymer nanocomposite is influenced by both particle weight fraction and particle modification.

In another experiment, the tensile stress, Young's modulus, and strain-at-break of rubbery epoxy/silica nanocomposites were measured using four different types of mesoporous silica [17]. They found that the tensile stress and Young's modulus of epoxy/mesoporous silica nanocomposite increase linearly with the increasing weight fraction of nanoparticles (see Figures 1 and 2). It was found that nanocomposites with mesoporous silica having higher pore size show higher improvement than those having smaller pore size.

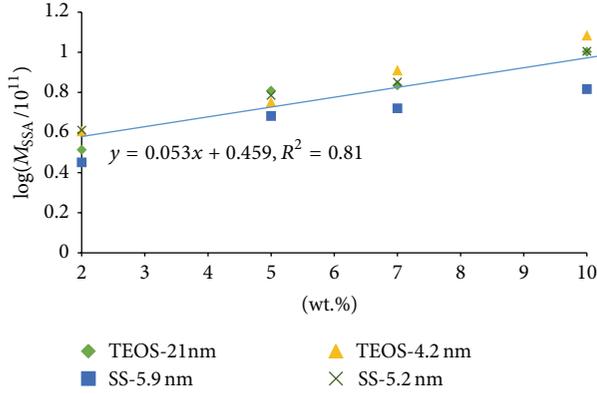


FIGURE 2: The effect of weight fraction of mesoporous silica nanoparticles on the dimensionless Young's modulus of rubbery epoxy mesocomposite [17]. (TEOS and SS indicate tetraethyl orthosilicate and sodium silicate. The number after the precursor indicates pore size of the mesoporous nanoparticles).

To compare the available experimental data, the following expressions were used to transform Young's modulus and tensile stress into dimensionless variables for mesoporous silica nanocomposites:

$$\begin{aligned} M_{SSA} &= \left(E \frac{SSA}{g} \right), \\ S_{SSA} &= \left(\sigma \frac{SSA}{g} \right), \end{aligned} \quad (9)$$

where M_{SSA} is dimensionless Young's modulus, S_{SSA} is dimensionless stress, E is Young's modulus of nanocomposite, σ is tensile stress of nanocomposite, SSA is specific surface area, and g is gravitational acceleration.

Shokrieh et al. [63] found that Young's modulus of clay/epoxy nanocomposite improves about 12.5% at 4% weight fraction of nanofiller. They found that ultimate tensile stress decreases for nanocomposites with higher weight fraction of nanoclay. This phenomenon was attributed to the aggregation of nanoclay at higher weight fraction of nanoparticles. Jurkowski and Olkhov [64] reported that tensile stress and Young's modulus of poly- ϵ -caprolactam/montmorillonite polymer nanocomposite improved about 41% and 73% compared to the pure polymer after adding 4.2% weight fraction of nanoparticle. In other studies, the effects of organoclay on modulus of elasticity [65], fracture toughness [66], and tensile stress [67] of epoxy resins were investigated. These studies showed an increase in the modulus of elasticity and toughness with increasing of weight fraction.

In epoxy/clay nanocomposites, the tensile stress reduces with an increase in particle loading [67, 68]. Some researchers attributed this phenomenon to the formation of voids within the nanocomposite, which acts as a stress concentrator [67]. However, others claimed that the stress concentration is due to the formation of agglomerates at higher particle loading [68].

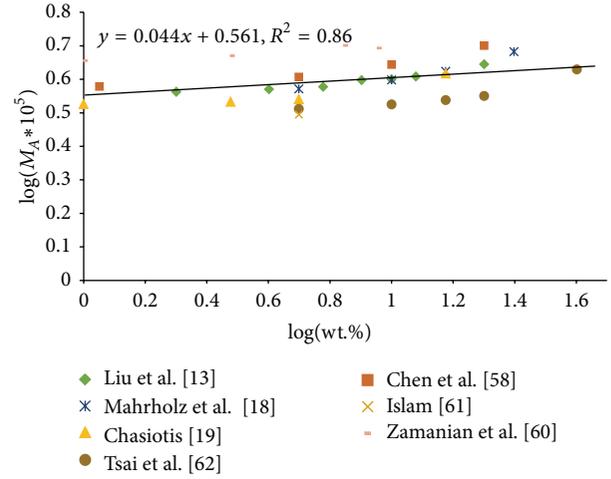


FIGURE 3: The effect of weight fraction of nanosilica on the dimensionless Young's modulus in epoxy/silica nanocomposites.

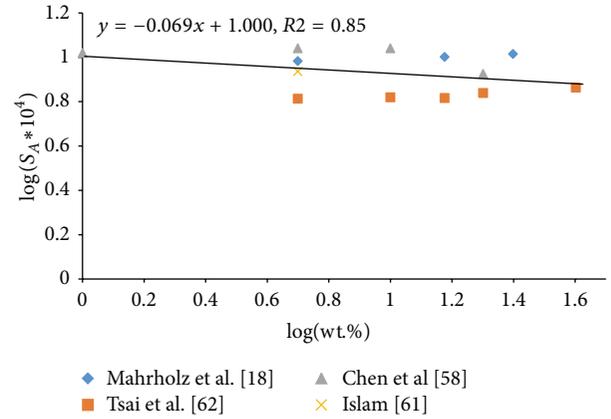


FIGURE 4: The effect of weight fraction of nanoparticles on the dimensionless tensile strength in epoxy/silica nanocomposites.

To compare the test results obtained from different articles, the following expressions were used to transform Young's modulus and stress into dimensionless variables,

$$\begin{aligned} M_A &= \left(\frac{EA}{W} \right), \\ S_A &= \left(\sigma \frac{A}{W} \right), \end{aligned} \quad (10)$$

where M_A is dimensionless Young's modulus, S_A is dimensionless stress, E is Young's modulus, σ is tensile stress, A is the average surface area of nanoparticle, and W is average weight of nanoparticles. Figures 3 and 4 show dimensionless Young's modulus and dimensionless tensile stress, respectively, versus weight fraction reported by several researchers.

4.2. Compressive Behavior. Uddin and Sun [16] used standard DGBEA epoxy and sol-gel technique to prepare epoxy/silica nanocomposite having nanofillers at 15% weight fraction. It was reported that silica/epoxy nanocomposite has higher

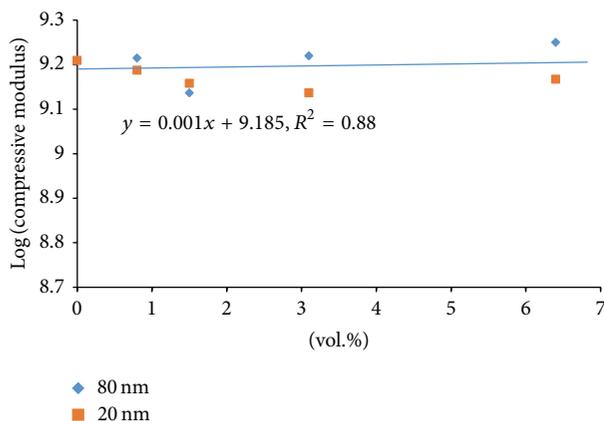


FIGURE 5: The effect of volume fraction of nanosilica on the compressive modulus of hybrid epoxy-silica-rubber nanocomposites (HESRN) [22].

compressive stress and elastic modulus than the pure epoxy [16]. They reported that the nanocomposite showed an improvement of 40% in elastic modulus [16]. It was also seen that the compression stress for the epoxy and the silica/epoxy nanocomposite at 10% elongation were about 92 MPa and 108 MPa, respectively. It means a significant improvement was achieved after adding the nanoparticles [16].

Regardless of the fact that compressive stress of composites with higher volume fraction of glass fiber is higher, it was observed that silica nanoparticle reinforced glass-epoxy nanocomposite shows higher off-axis compressive stress than the pure glass/epoxy composites [15, 16]. Liang and Pearson [22] used different volume fractions of nanosilica of two different sizes (20 nm and 80 nm) with carboxyl terminated butadiene acrylonitrile (CTBN) to make epoxy/rubber composite. It was reported that the compressive modulus and compressive yield stress of this hybrid nanocomposite increased linearly up to a volume fraction of 7% and then decreased beyond that (see Figures 5 and 6).

As reported by Kinloch et al. [69], the compressive modulus and compressive yield stress increased monotonically with increasing volume fraction of nanosilica. Liang and Pearson [22] claimed that such unexpected results are due to aggregation of the nanosilica.

Shokrieh et al. [63] used modified clay with epoxy resin instead of silica nanoparticles to study the effect of weight fraction of nanoclay on the compressive behavior. They reported that the compressive stress increased up to 3% weight fraction and then decreased beyond that. However, the compressive stress of nanoclay-epoxy nanocomposite improved after adding nanoclay at any weight fraction.

Akbari and Bagheri [59] investigated the effect of variable weight fraction of organophilic montmorillonite on the compressive stress of epoxy polymer. Unexpectedly, the compressive stress decreased linearly with increasing weight fractions of nanofiller. They concluded that this is due to the release of free radicals during the homopolymerization between nanoclay and epoxy, which lead to weak interactions

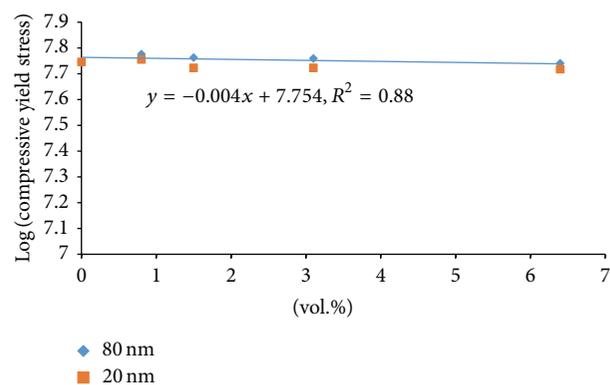


FIGURE 6: The effect of volume fraction of nanosilica on the compressive yield stress of hybrid epoxy-silica-rubber nanocomposites (HESRN) [22].

between nanoclay and epoxy. It was also claimed that this could be due to the high temperature that was used to decrease the viscosity that reduced the time for the curing agent molecule to get diffused into the nanoclay.

4.3. Flexural Properties. Ahmad et al. [14] tested the flexural behavior of silica-epoxy nanocomposites at different volume fractions of nanofillers having three different shapes. The flexural modulus of silica/epoxy showed higher improvement with cubical and angular nanoparticles. They also reported that flexural modulus of silica/epoxy composite with all three different shapes of nanoparticle increases with the increase in volume fractions of nanofillers.

The flexural stress of both brittle and ductile matrix epoxy-silica nanocomposite improved linearly with an increase in particle loading. The same results were seen in case of fracture toughness for both types of nanocomposites. Tensile stress of ductile matrix nanocomposite was also improved linearly with increase in the particle loading. However, for brittle matrix nanocomposites, the improvement in tensile stress compared to the pure epoxy was seen only at 5%, 10%, and 15% weight fractions [62]. The same results were seen in case of fracture toughness for both types of nanocomposites. However, in case of fracture toughness, ductile epoxy-silica nanocomposite showed higher fracture toughness than the brittle one at any nanoparticle loading [62].

Mahrholz et al. [18] reported that flexural stress increases linearly with an increase in weight fraction of nanofiller up to 25%. The flexural modulus and tensile stress of epoxy-silica nanocomposite having 25% weight fraction of nanoparticle improved by 29.8% and 8.9%, respectively, compared with the pure epoxy.

Chasiotis [19] studied fracture behavior of epoxy-fumed silica nanocomposites having different weight fractions of nanoparticles. Significant improvements in fracture toughness of nanocomposites were seen at small weight fractions (up to 1%) of nanoparticles. However, the improvement

TABLE 1: Suggested expressions to estimate mechanical behavior of silica-epoxy nanocomposites at different fractions of nanoparticles.

Nanocomposite	Suggested equation	Nanoparticle dimension	Ranges of applications	
			wt% or vol%	Remark
Silica-epoxy	$E = 3.639 \times 10^{-5} \frac{W}{A} \text{wt}^{0.04}$ [in GPa]	8–50 nm	1–40 (wt%)	Sol-gel processing
Rubbery silica epoxy mesocomposite	$E = \frac{g}{SSA} 288 \times 10^{0.053 \text{ wt}}$ [in GPa]	10–100 nm	2–10 (wt%)	Nanoparticle's pore size: 4–21 nm
Silica-epoxy	$\sigma = \frac{W}{A} \text{wt}^{-0.069}$ [in kPa]	8–50 nm	1–40 (wt%)	Sol-gel processing
Rubbery silica epoxy mesocomposite	$\sigma = \frac{g}{SSA} 55.8 \times 10^{0.04 \text{ wt}}$ [in GPa]	10–100 nm	2–10 (wt%)	Nanoparticle's pore size: 4–21 nm
Epoxy-silica-rubber	$\sigma_{\text{cy}} = 56.8 \times 10^{-0.004 \text{ vol}}$ [in MPa]	20 nm, 80 nm	0–6.4 (vol%)	CTBN processing
Epoxy-silica-rubber	$E_c = 1.53 \times 10^{0.001 \text{ vol}}$ [in GPa]	20 nm, 80 nm	0–6.4 (vol%)	CTBN processing

Where E is Young's modulus, σ is tensile stress, SSA is specific surface area in m^2/kg , g is gravitational acceleration in m/s^2 , A is the average surface area of nanoparticle in m^2 , W is average weight of nanoparticles in N , wt% and vol% are weight and volume fractions [$0 \leq \text{wt} \leq 100$, $0 \leq \text{vol} \leq 100$], σ_{cy} is the compressive yield stress, and E_c is the compressive modulus.

was not significant at higher weight fractions of nanoparticles. Significant improvement in the fracture toughness of nanocomposites at smaller weight fractions and small increase at higher weight fractures were also reported [62]. Moreover, at higher weight fractions and high aspect ratio of nanoparticles, the nanocomposite toughness remains constant [22, 69, 70].

Individual and synergistic effect of rubber and silica nanofillers on the fracture toughness of epoxy was studied by Liu et al. [13]. This work reveals that fracture toughness of silica-epoxy, rubber-epoxy, and rubber-silica-epoxy nanocomposites increases monotonically with the increase in weight fraction of nanofillers. The improvement was higher in case of rubber-epoxy nanocomposite compared with the silica-epoxy nanocomposite. Synergistic effect of both rubber and silica nanoparticles is present in Young's modulus of rubber-silica-epoxy nanocomposite. However, these two types of particles showed no significant effect on fracture toughness.

Total fracture energy of nanocomposite depends on energy dissipation mechanisms such as void expansion, matrix shear deformation [21], crack deflection [21], twisting, and bridging [71–73]. Energy dissipation requires debonding in hard particles [21, 74], and cavitation in soft particles [75].

Some researchers studied the effect of particle aggregation on nanocomposites and compared it with microcomposites [76, 77]. It was shown that nanocomposites have higher chance of getting particle agglomeration, due to having higher aspect ratio and smaller particle size. Such agglomeration reduces the mechanical properties [76, 77] while an efficient dispersion of nanoparticles improves the mechanical properties of nanocomposites [16]. In some cases, the polymer nanocomposites show higher fracture toughness than

the polymer when the particle agglomeration acts as stress concentrator [78, 79]. Chasiotis [19] showed that fracture toughness reaches a steady state at higher particle loading. However, after reaching to an optimum level, any increase in particle loading leads to void formation, which induces crack formation, and reduces the mechanical properties of nanocomposites [78].

5. Suggested Empirical Formula

Based on linear curve fittings shown in Figures 1 to 6, some empirical expressions were derived for estimating the mechanical behavior of silica-epoxy nanocomposites at different weight/volume fractions. Table 1 shows the suggested empirical equations and their range of applications.

6. Summary and Conclusions

In this paper, the recent research papers on the effect of weight fraction of nanoparticles on mechanical behavior of silica-epoxy nanocomposites were reviewed. The standard linear curve fitting technique was used to find some empirical formulas for estimating the mechanical behavior of nanocomposites at different weight fractions. The following conclusions are made.

- (1) Young's modulus, tensile stress, and yield stress of most of the nanocomposites with rigid nanoparticles (i.e., silica) increase linearly with the increasing particle loading. The opposite results are seen for the nanocomposites with soft nanoparticles such as rubber.

- (2) The tensile and compressive strengths and Young's modulus increase with increasing particle loading. A few exceptions are also seen that are due to the agglomeration of nanoparticles at higher particle loading and formation of microvoids.
- (3) The flexural strength and flexural modulus usually increase with increasing particle loading.
- (4) The fracture toughness increases with increasing of particle loading and ultimately it reaches a steady state.

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