

Development of SiO₂-epoxy Nanocomposites and their Thermo-mechanical Properties

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This study is focused to see reinforcing effects of SiO₂ nanoparticles on the mechanical and thermal properties of epoxy resin. For the same, SiO₂ nanoparticles up to 8 wt.% were reinforced in epoxy resin and the effect of this reinforcement was seen on fracture toughness, fracture energy and glass transition temperature. The particles were dispersed ultrasonically in epoxy resin, which gives well dispersion of nano-SiO₂ particles. A good dispersion of silica nanoparticles enhances mechanical and thermal properties up to 4 wt.% SiO₂. As a result, the value of fracture toughness increases from 1.10 to 2.90 M Pa.m^{1/2}, fracture energy increases from 2.66 to 11.50 kJ/m² and glass transition temperature increased about 9°C for the epoxy containing 4 wt.% SiO₂ nanoparticles. With further particle loading in epoxy reflected decrease in mechanical and thermal properties, which is attributed to the significant increase in clustering of the nanoparticles at higher loading concentrations.

Introduction

Epoxy resins are extensively used in the electrical circuit board laminates, structural composites, adhesives and surface coatings [1]. Higher amount of crosslinking is seen in thermosetting polymers. Epoxies show better mechanical, physical and tribological properties because of which these are used in structural applications. Epoxies have high modulus, fatigue, low creep, and also work well at elevated temperatures [2-4].

The higher cross-link density shows lesser fracture toughness, stiffness resistance to the crack initiation and its growth which in turn restricts the use of epoxy in modern applications [5]. During curing of epoxy stresses are induced in the cross-linked chain which decreases the fracture toughness, low resistance to initiation of crack and growth of void restricted due to the plastic deformation [6,7]. These can be taken as challenges by changing the composition of epoxy resins with mixing of different nano-fillers as second phase for an advanced level of composite applications [8,9]. The blending of epoxy resins with nano-fillers lead to an increase in fracture toughness, stiffness and strength [10]. These nano-fillers includes inorganic nanoparticles such as clay [11], Al₂O₃ [12], ZrO₂ [13,14] and TiO₂ [4] to the epoxy resin. With the addition of inorganic nano-fillers such as carbon nanotube [15] and SiO₂ [5], exhibits the good mechanical properties, interestingly the toughness of the epoxy increases without altering the basic properties. The morphological of the matrix changes mainly due to nano-fillers by penetrating between the dense epoxy cross-linked networks.

In the present work, an attempt has been made to produce SiO₂/epoxy nanocomposites. Ultrasonication technique was chosen by varying the concentration of

nanoparticles in epoxy resin to produce the SiO₂/epoxy nanocomposites. Dispersion by particle loading and its effect on properties such as mechanical, thermal has been studied.

Experimentation

Materials

A commercially available two-component epoxy adhesive, consisting of epoxy resin diglycidylether of bisphenol-A (Araldite AW 106) and polyaminoamide hardener (Araldite HV 953 U) has been used as base material. Silica (SiO₂) nanoparticles (~15 nm average diameter; Make: Sisco Research Laboratories Maharashtra India) with above 99.5% purity and hydrophilic in nature has been used as filler for preparation of the SiO₂/epoxy nanocomposites.

Fabrication of SiO₂/Epoxy Nanocomposites

SiO₂ nanoparticles with varying weight fraction of 2, 4, 6, and 8 wt.% were dispersed in epoxy resin. For the same SiO₂ nanoparticles were first dispersed ultrasonically in Methyl Ethyl ketone (MEK) for 10 minutes. Thereafter epoxy resin was added in to this solution. The viscosity of SiO₂/epoxy decreases with the addition of MEK. This slurry (epoxy + SiO₂ nanoparticles + MEK) was processed by ultrasonic vibration using ultrasonic mixer at a constant frequency of 30 kHz for time period of 2 hours. To reduce the temperature rise during sonication an external cooling has equipped by submerging of the beaker in cold water bath. The MEK was removed from the mixture by heating at 70°C till all the MEK has been removed. The removal of MEK was ensured by measuring the weight of mixture before and after removal of MEK. After removal of MEK, the hardener was added into the mixture with a ratio of

epoxy resin and hardener 100:80 by weight and thoroughly mixed by a glass rod for 10 minutes. The mixture of epoxy and hardener was degassed in a vacuum oven to remove any air bubble trapped during mixing. After degassing the mixture was taken in to dies and samples were cured in a hot oven air at 40°C for 16 hours. In order to obtain the uniform thickness all specimens were polished with fine grade emery paper.

Dynamic Mechanical Analysis (DMA) test

Dynamic mechanical analysis tests were performed as per ASTM D 4065-12 using samples of dimension 52 x 12 x 3 mm³ in size in three point bending mode at 1 Hz frequency. The storage modulus and damping values were calculated as a function of temperature over a range from 28 to 100°C at 2°C/min heating rate. Glass transition temperature was obtained from the peak of Tanδ curve.

Fracture toughness test

The fracture toughness (K_{1C}) and the fracture energy (G_{1C}) were identified as per ASTM standard D5045. According to the standard, tests were performed using three point bend test by making single edged notched beam (SENB) of dimensions as the length $L = 52.8$ mm, $W = 12$ mm, thickness 6 mm and with the crack length of 6mm as shown in Fig. 1. To introduce a sharp notch a hammer was tapped on a razor blade straight on the precut square notch. A computer controlled universal testing machine (Make: Tinius Olsen) was used to perform fracture test and crosshead speed was maintained at 10 mm/min at room temperature. At least three tests were performed to have confidence in results.

The fracture toughness K_{1C} was calculated using the relation (according to ASTM code):

$$K_{1C} = \left(\frac{F}{BW^{3/2}}\right) f(x) \quad (1)$$

where, F = load at the fracture point, B = thickness, W = width, a = crack length, $x = a/W$.

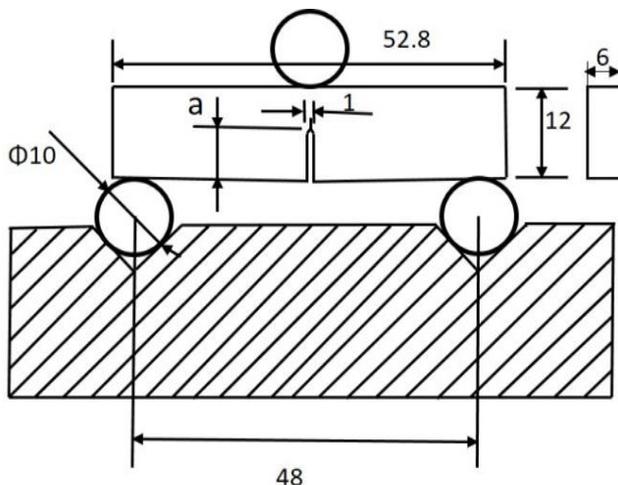


Fig. 1. Fracture test specimen as per ASTM D5045.

$$f(x) = 6\sqrt{x} \frac{[1.99-x(1-x)(2.15-3.93x+2.7x^2)]}{(1+2x)(1-x)^{3/2}} \quad (2)$$

The fracture energy G_{1C} is calculated using the relation:

$$G_{1C} = \left(\frac{U}{BW\phi}\right) \quad (3)$$

where, U = strain energy, B = thickness, W = width, ϕ = energy calibration factor which is calculated from ASTM calibration factor table.

Strain energy, U is calculated using the relation:

$$U = \left(\frac{1 \times F \times \Delta u}{2}\right) \quad (4)$$

where, F = load at fracture point, Δu = total extension from the point of indentation to fracture.

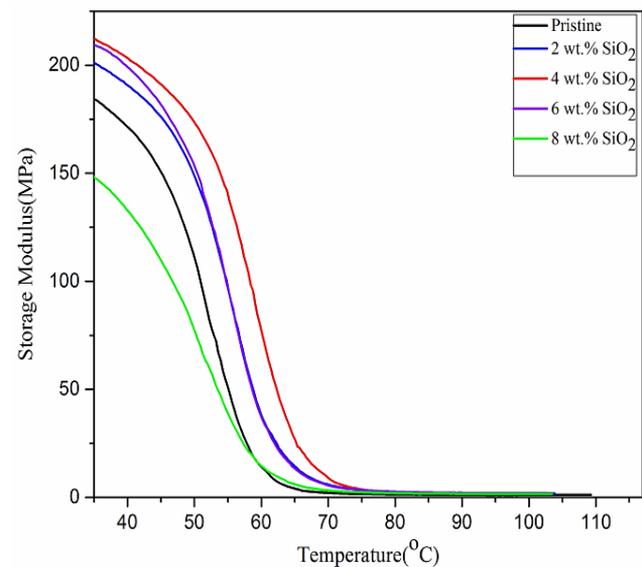


Fig. 2. Storage modulus as a function of temperature for SiO₂/epoxy nanocomposites.

Results and discussion

Dynamic Mechanical Analysis (DMA)

The results of dynamic mechanical analysis test show the variation in storage modulus as a function of temperature. The Fig. 2 shows the DMA results of pristine epoxy as well as SiO₂/epoxy nanocomposites. With the dispersion of nanoparticles in epoxy, the storage modulus increases up to 214 MPa for 4wt.% SiO₂ nanocomposites. Maximum enhancement in the storage modulus is about 14% at 32°C for 4 wt.% SiO₂/epoxy nanocomposite in the glassy. Glass transition temperature T_g was obtained from the peak of Tanδ curve for pure epoxy sample and modified epoxy with SiO₂ nanoparticles. T_g with SiO₂ dispersion of 2, 4, 6, 8 wt.% were found to be as 61.28, 68.65, 70.00, 66.95 and 63.37°C respectively as shown in Fig. 3. Increased loading fraction of nanoparticles offers hindrance in the cross-linking mechanism leading to decrease in the cross-linking density and causing reduction in glass transition temperature.

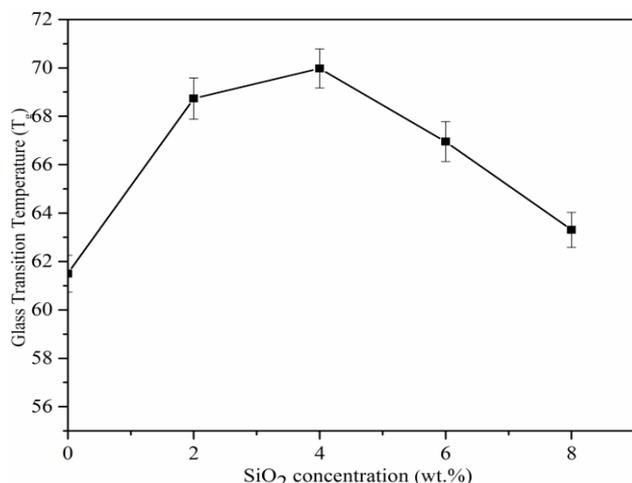


Fig. 3. Variation in glass transition temperature (T_g) of SiO₂/epoxy nanocomposites with nanoparticles loading.

Fracture properties

The calculated values of fracture toughness (K_{IC}) and fracture energy (G_{IC}) of SiO₂/epoxy composites utilizes eqs 1-4 are shown in Table 1. In case of the pristine epoxy, the calculated value of fracture toughness and fracture energy was found to be 1.10 MPa·m^{1/2} and 2.66 kJ/m² respectively. The results show improvement in fracture toughness and fracture energy by adding the SiO₂ nanoparticles in the epoxy. For all samples, the value of fracture toughness and fracture energy more than pristine epoxy. The increase in these values may be contributed to different toughening mechanisms like crack pinning, crack deflection and plastic void growth. The variation in the fracture toughness and fracture energy values with SiO₂ loading is shown in Fig. 4 and Fig. 5 respectively. The maximum value of K_{IC} and G_{IC} observed were 2.90 MPa·m^{1/2} and 11.50 kJ/m² respectively for 4 wt.% SiO₂/epoxy nanocomposite. The further decrease in the fracture and thermal characteristics may again be attributed due to non-homogeneous dispersion, significant increase in clustering of nanoparticles and settlement of the particles during curing.

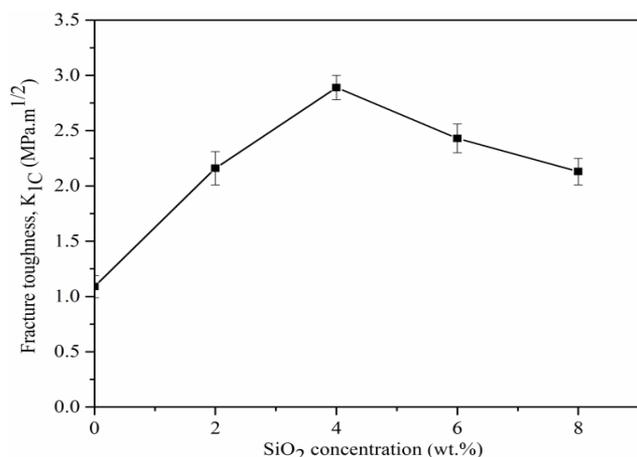


Fig. 4. The variation in fracture toughness for SiO₂/epoxy nanocomposites.

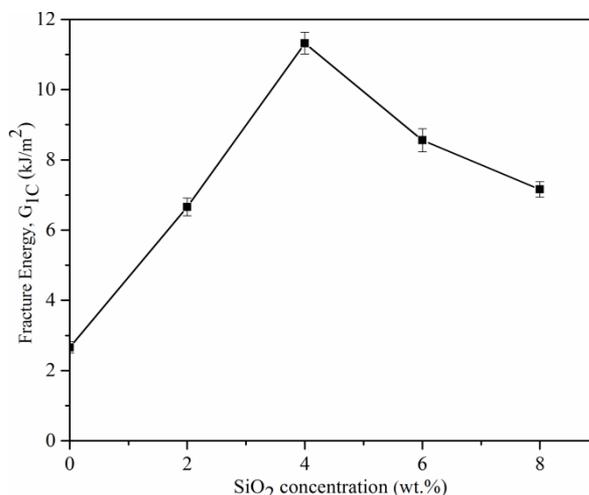


Fig. 5. The variation in fracture energy for SiO₂/epoxy nanocomposites.

Table 1. Summary of the mechanical and thermal properties of SiO₂nanoparticles reinforced epoxy composites.

Samples	Fracture Toughness (MPa·m ^{1/2})	Fracture Energy (kJ/m ²)	T _g (°C)
Pristine epoxy	1.10	2.66	61.28
2 wt.% SiO ₂	2.14	6.80	68.65
4 wt.% SiO ₂	2.90	11.50	70.00
6 wt.% SiO ₂	2.43	8.52	66.95
8 wt.% SiO ₂	2.11	7.21	63.37

Conclusions

SiO₂ nanoparticles were dispersed successfully in epoxy resin using ultrasonication. Ultrasonic vibration in presence of MEK solvent is a quite effective technique for breaking clusters of the SiO₂ nanoparticles as well as their homogeneous dispersion in the epoxy matrix without any significant deterioration of the base matrix properties. With SiO₂ dispersion, an increase of about 9°C is observed in the glass transition temperature. Also significant improvement in fracture toughness and fracture energy of SiO₂/epoxy nanocomposite is achieved with 4 wt.% nanoparticle loading in epoxy matrix. Incorporation of SiO₂ in the epoxy matrix increases the fracture toughness from 1.1 to 2.9 MPa·m^{1/2} and fracture energy from 2.66 to 11.5 kJ/m² for 4 wt.% SiO₂ nanoparticles which is attributed to the homogeneous dispersion of nanoparticles in the epoxy matrix.

Fatigue and creep testing of the epoxy nanocomposites as well as lap shear and double cantilever beam testing of the epoxy nanocomposites adhesive based joints of 7XXX series aluminium alloy substrate at elevated temperatures can be done to correlate the cohesive and adhesive properties in order to utilize the knowledge for advanced applications of epoxy nanocomposites mainly in aerospace and automobile industries.

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Keywords

Silica nanoparticles, epoxy, ultrasonic mixing, nanocomposites, mechanical and thermal properties.

References

1. Ratna, D.; Banthia, A.K.; Deb, P.C.; *J. Appl Polym Sci.*, **2001**, *80*, 1792.
2. Ellis, B.; Chemistry and technology of epoxy resins. New York, NY: Blackie Academic & Professional, **1983**.
3. Wetzel, B.; Hauptert, F.; Zhang, M.Q.; *Compos. Sci. Technol.*, **2003**, *63*, 2055.
4. Singh, S.K.; Singh, S.; Kumar, A.; Jain, A.; *Eng. Frac. Mech.*, **2017**, *184*, 241.
5. Singh, S.K.; Kumar, A.; Jain, A.; Improving tensile and flexural properties of SiO₂-epoxy polymer nanocomposite. *Materials Today: Proceedings* **2018**, *5*, 6339.
6. Chang, T. D.; Brittain, J. O.; *Polym. Eng. Sci.*, **1982**, *22*, 1228.
7. Pearson, R. A.; Yee, A. F.; *Mater. Sci.*, **1989**, *24*, 2571.
8. Zhao, Y.; Chen, Z. K.; Liu, Y.; Xiao, H.M.; Feng, Q.P.; Fu, S.Y.; *Composites, Part A*, **2013**, *66*, 178.
9. Wang, X.; Jin, J.; Song, M.; *Carbon*, **2013**, *65*, 324.
10. Gkikas, G.; Barkoula, N.; Paipetis, A.; Effect of dispersion conditions on the thermo-mechanical and toughness properties of multi walled carbon nanotubes reinforced epoxy, *Composites*, **2012**, *43*, 2697.
11. Wang, K.; Chen, L.; Wu, J.; et al. *Macromolecules* **2005**, *38*, 788.
12. Goyat, M.S.; Ray, S.; Ghosh, P.K.; *Composites Part A*, **2011**, *42*, 1421.
13. Medina, R.; Hauptert, F.; Schlarb, A.K.; *J. Mater. Sci.*, **2008**, *43*, 3245.
14. Singh, S.K.; Kumar, A.; Jain, A.; *Mat. Sc. Eng.*, **2018**, *330*, 012001.
15. Jiang, L.; *J. Adhev.*, **2010**, *86*, 273.