Effect of Post Curing Temperature on Viscoelastic and Flexural Properties of Epoxy/Alumina Polymer Nanocomposites

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Abstract

In the present work, effect of post curing temperature on viscoelastic and flexural properties of epoxy/alumina polymer nanocomposite was evaluated in order to optimize the post curing temperature. Polymer nanocomposites (PNC) containing of 0.5, 1 and 1.5 wt.% of rod shape alumina nanoparticles were prepared by in-situ polymerization technique. Good dispersion of nanoparticles in epoxy matrix was observed through transmission electron micrographs of nanocomposites. The curing reaction of the epoxy and nanocomposites was analyzed through Differential Scanning Calorimetry (DSC) for temperature varying from 25°C to 200°C. Temperatures 80°C, 100°C, 120°C and 150°C were selected for post curing on the basis of DSC thermographs. Dynamic mechanical analysis (DMA) tests were performed to determine the viscoelastic properties and three point bend flexural tests were conducted to evaluate the flexural properties of PNC. The results indicated that the post curing at a temperature below the glass transition temperature of epoxy enhanced the viscoelastic and flexural properties of PNC’s and post curing temperature above the glass transition temperature of epoxy had a detrimental effect on the properties for both neat epoxy as well as nanocomposites. As the post curing temperature was increased the glass transition temperature increases for both the neat epoxy and nanocomposites, however the increment in glass transition temperature of PNC was more in comparison to that of neat epoxy. Flexural modulus and strength of epoxy and PNC decreased with the increase in post cure temperature.

Keywords: viscoelastic properties; flexural properties; polymer nanocomposites; post curing temperature; dynamic scanning calorimeter;

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1. Introduction

The post curing temperature of polymer plays an important role in enhancing the viscoelastic and mechanical properties of composites. A small fraction of reinforcement of nano rigid particles in the polymer matrix enhances the viscoelastic and mechanical properties. Montazeri et al.[1] reported that prolonging the post curing time reduces the enhancement of mechanical and viscoelastic properties of neat epoxy as well as CNT reinforced composite. Villoria et al.[2] reported increment in mechanical properties with the increase in cure time. Young’s modulus of the composites was not affected by curing process, however young's modulus of neat epoxy decreased with the increase in curing time. The properties of polymer nanocomposites depend on the dispersion of nanoparticle and interaction between nanoparticles and polymer matrix. Omarani et al. [3] reported that from DSC thermograph of cured epoxy and its composites that the curing peak is attained at lower temperature and heat flow decreases with the increasing amount of alumina nano particles. It was further reported that there was 42% and 69% increment in storage modulus and flexural modulus respectively at 2 phr and decreases on further increase in nano particle concentration due to agglomeration.

The effect of alternate heating rate during cure is a important factor for structure-property relationships be time Jahan et al.[4] reported that varying heating rates during cure (3°C/min and 10°C/min) affects the glass transition temperature of the nanocomposites. The nanocomposites cured at 3°C/min exhibit an increase in glass transition temperature in comparison 10°C/min curing. Montazeri and Montazeri [5] reported that 0.5 wt.% MWNT/ epoxy resin showed the highest improvement in viscoelastic properties, as compared to neat and other nanocomposites. There was 46% improvement in storage modulus in 0.5 wt.% MWCNT/epoxy at room temperature. Again Montazeri et al.[6] reported that there was 11% increment in storage modulus for 0.5 wt.%. But higher percentage of nanotubes content shows a decline in the modulus at room temperature. The decline in elastic modulus is attributed to appearance of large agglomerations. Baskaran et al.[7] reported that agglomeration of particles was found at higher filler loading(>5 wt.%) and this reduces the viscoelastic and mechanical properties. An increment of 51% was reported for storage modulus at 5 wt.% of nano alumina. Reduction in storage modulus for higher wt.% (7 and 9) was observed. There was increment of 14% and 11% in tensile strength and flexural strength respectively up to 5 wt.% and further addition of nano alumina decreases the values however, the value of tensile strength and flexural strength of composite at 7 and 9 wt.% was higher in comparison to that of neat epoxy. Naous et al.[8] reported that 15% increment in storage modulus, and 9% increment young’s modulus with the incorporation of AL2O3 nanoparticles in to the epoxy. Rodgers et al.[9] reported that Optimal loading of the SiC nanoparticles is seen to be around 1wt.% for the best combination of thermal and mechanical properties of the nanocomposites. Nano particle loading beyond this point (1 wt. %) seems to degrade properties and it becomes severe around 2 wt.% loading. In general, the viscoelastic and flexural properties found to depend on the degree of dispersion of nanoparticles.

In the present work, effect of post curing temperature on viscoelastic and flexural properties of epoxy/alumina polymer nanocomposite was evaluated in order to optimize the post curing temperature. Polymer nanocomposites (PNC) containing of 0.5, 1 and 1.5 wt.% of rod shape alumina nanoparticles having diameter in the range of 10 nm and a length less than 50 nm were prepared by in-situ polymerization technique. The curing reaction of the epoxy and nanocomposites was analyzed through differential scanning calorimetry (DSC) for temperature varying from 25°C to 200°C. Temperatures 80°C, 100°C, 120°C and 150°C were selected for post curing on the basis of DSC thermographs of curing process of epoxy.

2. Experimental

2.1. Material system.

Epoxy (Bisphenol-A) synthesized by resin Araldite LY556® (density 1.17 gm/cc at 25°C) and hardener, LY951® (density 0.98 gm/cc at 25°C) supplied by Vantico Performance Polymers Pvt. Ltd., India, was used as matrix material in this study.
Alumina nano rods having diameter in the range of 10 nm and length less than 50 nm, density 4.0 gm/cc supplied by Sigma Aldrich, India. Transmission electron microscope images of alumina nanorods are shown in Fig.1a-c.

Fig.1. TEM images of composites showing distribution of alumina nano rods in the epoxy for composites (a) 0.5% (b) 1% (c) 1.5%

2.2. Composite preparation

Nanocomposites were prepared by in-situ polymerization technique. Nanoparticles were heated at 150°C for 4 hours to remove moisture. The required amounts of dried nanoparticles were then mixed with acetone and the mixture was sonicated for an hour at 50 Hz frequency and 230W power rating. Then required amount of epoxy was mixed with the sonicated mixture. This mixture was again sonicated for an hour. The mixture was heated to remove the acetone. After removing the acetone, the mixture was kept in vacuum for half an hour to remove any entrapped gases. Hardener in the ratio of 1:10 by weight of resin was gently mixed. This mixture was poured in vertical acrylic mold and was allowed to cure at room temperature for 24 hours. After curing at room temperature, the composite sheet was taken out of the mould and post cured at 100 °C for 4 hours. Nanocomposites having 0.5, 1 and 1.5 wt % of alumina nano rods were synthesized.

2.3. Characterization

Dispersion of alumina nanorods in the epoxy matrix was examined by transmission electron microscopy (TEM). Specimen preparation for TEM was done by cutting slices of specimen of less than 100 nm thickness from the composite disk using a diamond Knife on Ultracut ultra microtome and TEM was carried out on JEOL JEM–2100 HRTEM, having an accelerating voltage of 200kv. Differential Scanning Calorimetry (DSC) measurements were performed with a TG/DTA 6200 SII Exster Calorimetry using nitrogen atmosphere. The temperature range was varied from 25°C to 200°C to analyze the uncured sample at a heating rate 10°C/min. Upward peaks were considered exothermic for all the DSC thermographs. Cure initiation, total heat of reaction and peak temperature were calculated from the heat flow curve.

2.4. Mechanical characterization

Dynamic mechanical analysis tests were performed on Dynamic Mechanical Spectrometer (SII nanotechnology Inc.) Japan. Dimensions of DMA test specimen were 50×10×2.7 mm³. Tests were carried out at a frequency of 1 Hz and at a heating rate of 2 °C/min. The temperature range was varied from 28°C to 200°C. Tests were performed in accordance with the ASTM standard D 4065-12 and storage and loss modulus were recorded. Glass transition temperature was obtained from the peak of tanδ curve[10].
Flexural test of samples was carried out as per ASTM standard D790 [11] on universal testing machine (Tinius Olsen machine) with a 250 N load cell. The length, width and thickness of the flexural test specimen were 54.8, 12.7 and 2.7 mm respectively. At least five tests were conducted to determine the average modulus, strength and failure strain of the composite at cross head speed of 1.077 mm/mm/min for each type of nano composites.

3. Results and discussion

It can observed from the TEM images of composites having 0.5 and 1 wt.% of alumina nanorods are dispersed uniformly in the matrix without any agglomeration. Some agglomerations can be observed for composites having 1.5 wt. % of nano rods.

3.1. Differential scanning calorimeter

The curing reaction of Epoxy/alumina nano composites was investigated by means of DSC thermographs. DSC thermographs shown in Fig.2 indicates that the temperature of curing peak reduced with the increase in the wt.% of alumina nanorods due to the catalytic effect of nanorods on curing of epoxy. Heat of reaction was found to be maximum for PNC having 1wt.% of alumina nanorods. DSC for temperature varied from 25°C to 200°C. Temperatures 80°C, 100°C, 120°C and 150°C were selected for post curing on the basis of DSC thermographs. The value of reaction enthalpy is found to be 254, 231, 188 and 230 J/mg for the neat epoxy, 0.5%, 1% and 1.5% wt.% of alumina nanorods respectively. The glass transition temperature of the uncured compositions having neat epoxy, 0.5%, 1% and 1.5% of alumina nanorods is 102.2°C, 100.91°C, 99.98°C and 99.70°C respectively.
3.2. Viscoelastic properties

![Graphs showing storage modulus as a function of temperature for epoxy and nanocomposites having different wt.% of alumina nanorods for different curing temperature: (a) 80°C, (b) 100°C, (c) 120°C, (d) 150°C.](image)

Variation in the storage modulus of epoxy and nanocomposites cured at various temperatures as a function of temperature is shown in Fig. 3a-d. In general, storage modulus of nanocomposites increases with the increase in the wt.% of alumina nanorods in the glassy region whereas there is no significant effect of wt.% of nanorods in the rubbery region. For post curing temperature of 80°C and 100°C of nanocomposites samples, storage modulus of nanocomposite having 1.5 wt.% of nanorods was in the range that of neat epoxy, that is the maximum increase in storage modulus observed at for composites having 1 wt.% of nanorods. The decrease in the storage modulus of nanocomposites at higher wt.% of nanorods may be attributed to the aggregation of the nanorods which can be seen in Fig.1c. Storage modulus of epoxy and nanocomposites at the room temperature decreased as an effect of increase in the post curing temperature from 80°C and 100°C. The rate of decrease in the storage modulus with the increase in post curing temperature was slowest for composites having 1.5 wt.% of alumina nanorods. In case of post curing temperature of 120°C and 150°C (above glass transition temperature of epoxy) maximum increment was observed for nanocomposites having 1.5 wt.% of alumina nanorods.
Fig. 4. Tan delta of epoxy and composites with different wt.% and post curing temperature.

Fig. 5. Glass transition temperature of epoxy and composites with different wt.% and post curing temperature.
The loss factors (tan δ) values for the nanocomposites were obtained from the ratio of loss modulus by corresponding storage modulus of the composites as shown in Fig.4a-d. loss factor of epoxy and nanocomposites decreased with the increase in the post curing temperature. The peak of tan δ curves becomes flatter with the increase in post curing temperature. At higher post curing temperature (above and in the range of glass transition temperature of epoxy) the cross linking of the polymer chains gets broken causing a both decrease the storage modulus and loss modulus of the nanocomposites however the rate of reduction in the loss modulus of nanocomposites is more in comparison to that of rate of reduction in the storage modulus. Thus, loss factor of nanocomposites decreases with the increase in the post curing temperature. The peak of tan δ curves for nanocomposites shifts towards higher temperature with the increase in the post curing temperature i.e. is the glass transition temperature increases with the increase in the post curing temperature as shown in Fig.5.

3.3. Flexural properties

Fig.6. Stress strain curve as a function of wt.% of alumina nanorods
The flexural stress strain curves for the nanocomposites are shown in Fig.6 a-d. It is clear from the Fig.7a that the flexural modulus of the nanocomposites increases with the increase in the wt.% of alumina nanorods up to 1 wt.% and modulus decreases on further addition of nanorods however the modulus of nanocomposite at 1.5 wt.% is higher in comparison to that of neat epoxy. The nanorods restrict the motion of polymer chains causing the increment in the flexural modulus. At higher wt.% of alumina nanorods, modulus decreases due to agglomeration of nanorods. The increment in the flexural modulus of nanocomposites as a result of increase in the wt.% of nanorods reduces with the increase in the post curing temperature. Similar trend was observed for the flexural strength Fig.7b of nanocomposites. The increment provides by the reinforcement of alumina nanorods is diminished by the effect of damage in the cross linking of polymer chain due to post curing at higher temperature.

4. Conclusions

Effect of post curing temperature on viscoelastic and flexural properties of epoxy/alumina polymer nano composite was evaluated in order to optimize the post curing temperature. Temperatures 80°C, 100°C, 120°C and 150°C were selected for post curing on the basis of DSC thermographs. The results indicated that the post curing at a temperature below the glass transition temperature i.e. 80°C of epoxy enhanced the viscoelastic and flexural properties of PNC’s and post curing temperature above the glass transition temperature of epoxy i.e. at 120°C and a50°C had a detrimental effect on the properties for both neat epoxy as well as of nano composites. As the post curing temperature was increased the glass transition temperature increases for both the neat epoxy and nanocomposites, however the increment in glass transition temperature of PNC was more in comparison to that of neat epoxy.

References


