

Effect of nanoparticles dispersion on viscoelastic properties of epoxy–zirconia polymer nanocomposites

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Abstract. In the present work zirconia-nanoparticles were dispersed in epoxy matrix to form epoxy-zirconia polymer nanocomposites using ultrasonication and viscoelastic properties of nanocomposites were investigated. For the same spherical zirconia-nanoparticles (45 nm) were dispersed in weight fraction of 2, 4, 6 and 8 % to reinforce the epoxy. DMA results show the significant enhancement in viscoelastic properties with the dispersion of zirconia nanoparticles in the epoxy matrix. The value of storage modulus and glass transition temperature increases from 179 MPa (pristine) to 225 MPa (6 wt.% ZrO₂) and 61 °C (pristine) to 70 °C (6 wt.% ZrO₂) respectively with the dispersion of zirconia nanoparticles in the epoxy.

1. Introduction

Many of the modern and advanced technological systems require polymers with enhanced properties which conventional polymer does not possess. Therefore, there is a requirement to enhance their characteristic and to enhance the various mechanical, thermal, viscoelastic and optical properties of polymer; a secondary phase is usually introduced into the polymer matrix to form composite with enhanced properties [1]. In most of the composite systems, fillers are selected as the reinforced hard phase. Among these composite systems, polymers have occupied an integral place in structural design of various products owing to its high resistance to environmental degradation and high strength to weight ratio [2]. Polymer-matrix composites are very popular among the various industrial applications such as electrical, automotive, semiconductor, and aerospace. This is because of the reason that the composite materials show a significant improvement in the properties such as chemical, electrical, mechanical, and coefficient of thermal expansion as compared to their original phase. In corporation of filler particles in the polymer matrix in nanometre range renders improvement in its mechanical and thermal properties [3]. Extremely cross linked structure and easiness of processing of thermosetting polymers due to their liquid form at room temperature when uncured has rendered it preferentially more suitable for structural applications in comparison to its thermoplastic counterparts [4, 5]. In spite of its vast advantages, the main drawback is its inherent brittleness. To overcome this problem many researchers and industries has opted for the incorporation of various filler particles as a solution to solve these structural problems [6]. This has led to the extensive use of traditional toughening agents such as rubber and other thermoplastic particles. In spite of their extensive use and high expectations, they fail to exhibit better properties because they reduces other properties such as strength, elastic modulus, glass transition temperature in the structure related industrial applications. The research progress in this field has led to the knowledge of the fact that the incorporation of inorganic filler material that ranges from 5 to 100 µm in epoxy matrix shows comparatively high thermal impedance properties with poor fracture toughness values. The poor fracture toughness values results due to high stress concentration zones at the vicinity of these micron sized filler particles [7]. Therefore, the use of nanofillers is preferred. An addition of small amount of nano-fillers in epoxy matrix leads to a considerable enhancement of thermo mechanical properties of the base epoxy. Dispersion affects properties like toughness, stiffness, storage modulus and glass transition temperature. Zirconia shows good chemical resistance, excellent wear resistance and high hardness properties and



also exhibits low thermal conductivity, high modulus, good strength and good fracture toughness [8]. These favourable qualities of zirconia have gained considerable attention in the anti-corrosion coatings and wear resistant materials. In the present work, zirconia nanoparticles were dispersed to synthesize epoxy-zirconia nanocomposites using ultrasonification (for homogenous dispersion of zirconia in epoxy). The outcome of zirconia dispersion on the viscoelastic properties of epoxy-zirconia nanocomposites has been studied.

2. Experimental

2.1 Materials

A two constituent epoxy adhesive (Araldite AW-106) composed of polyaminoamide hardener (Araldite HV 953 U) and epoxy resin diglycidylether of bisphenol-A procured from Huntsman company is used as a base material. Zirconium dioxide nanoparticles (45 nm, purity 99.5 %) having density of 5680 kg/m³ procured from Sisco Research Laboratories Maharashtra India, is used as the filler material for synthesizing epoxy-zirconia nanocomposites.

2.2 Preparation of epoxy-zirconia nanocomposites

At the start, zirconia nanoparticles were dispersed in the epoxy resin of varying weight fractions of 2, 4, 6 and 8 wt.% and stirred for 10 minutes using glass rod. Then, dilution of epoxy resin-zirconia mixture was done with the help of Methyl Ether Ketone (MEK) bought from Merck Company. Add one part of MEK to one part of mixture by weight to decrease the viscosity. This process was followed by ultrasonic mixing (UM) for two hours. To remove MEK, mixture was heated up to 70 °C till all the MEK was removed. The removal of MEK was ensured by measuring the weight of mixture before and after removal of MEK. After complete removal of MEK, the hardener with a ratio of 100:80 (epoxy resin:hardener) by weight was added into the mixture. The mixture was then completely mixed with the help of a glass rod for 15 minutes. Then the mixture of hardener and epoxy was kept in vacuum oven at 40 °C for about 15 minutes at a vacuum of 760 mm of Hg to completely remove air bubbles developed during the mixing operation. The mixture after degassing was poured into the die to prepare specimens for investigation of viscoelastic properties. The specimens were lastly cured in hot air oven at a temperature of 40 °C for about 16 hours.

2.3 Specimen testing

ASTM standard D 4065-12 was used to perform dynamic mechanical analysis (DMA) tests on Dynamic Mechanical Spectrometer (SII Nanotechnology Inc., Japan). The DMA test specimen's span length, breadth and thickness were 56 mm, 12 mm and 3 mm respectively. Heating rate was maintained at 2 °C/min and was frequency maintained at 1 Hz for conducting the DMA tests. Temperature was increased from 28 to 100 °C during the entire test run. Storage modulus and loss modulus were observed and recorded. To calculate Tan δ , the ratio of loss modulus and storage modulus was determined. The maximum peak of tan δ curve gives an indication of the glass transition temperature (T_g) of epoxy-zirconia nanocomposite.

3. Results and Discussion

Fig. 1(a) shows that how the storage modulus varies with temperature for the pure epoxy and epoxy-zirconia nanocomposite. The value of storage modulus increases from 179 MPa (pristine) to 225 MPa with increase in 6 wt.% of the zirconia nanoparticles in the epoxy matrix. Maximum enhancement in the storage modulus of zirconia dispersed epoxy nanocomposites was found at 6 wt.% dispersion. Further dispersion of nanoparticles (i.e. 8 wt.%) results in a decrease in the storage modulus as shown in Fig. 1(b). However, at 8 wt.% filler dispersion the storage modulus remains higher than that of pristine epoxy system. The decrease in storage modulus reflects the increase in flexibility of the system at higher dispersion (8 wt.%) concentration. The decrease of storage modulus at higher weight fractions of zirconia nanoparticles may be attributed to bigger lumps (agglomerates) which results in less energy dissipation in nanocomposites under viscoelastic deformation [9]. Stress concentration sites are formed because of increase in density of agglomerates of the dispersed zirconia nanoparticles that lead to premature localized failure. This causes easier movement of chains and molecular motion, leading to a decrease in storage modulus [10].

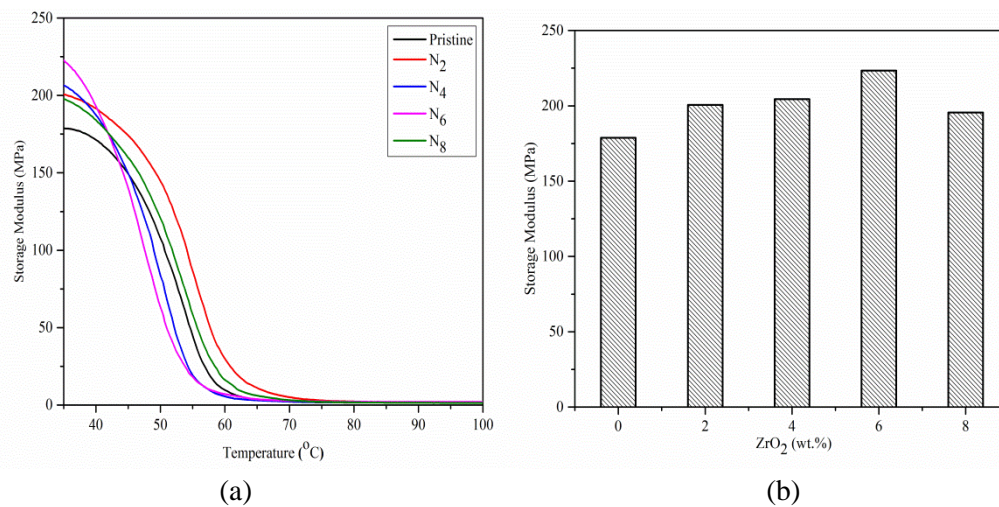


Fig.1. Variation of Storage modulus for epoxy and epoxy-zirconia nanocomposites as a function of temperature for varying wt.% of zirconia nanoparticles.

Glassy region is strongly affected by the concentration of zirconia nanoparticle in comparison to the rubbery region. Maximum improvement of 25 % in storage modulus at 35°C for zirconia (6 wt.%) nanoparticles dispersed epoxy matrix was observed as compared to pristine epoxy in the glassy regions. The homogeneous and cluster free dispersion of zirconia nanoparticles in epoxy resin matrix causes dissipation of energy due to opposition offered by the surrounding matrix to the viscoelastic deformation. The rubbery region is identified with only a slight change in elastic properties because of relatively higher amplitude of molecular vibration in rubbery region [11]. The loss modulus is an indicative of the conversion of molecular vibrational energy into heat. The satisfactorily dispersed particles would help in dissipating energy in the presence of viscoelastic deformation of the neighbouring resin blend matrix. In case of pristine epoxy, the value of loss modulus is observed to be 21MPa and the same increases to 28 MPa with dispersion of 6 wt.% of Zirconia nanoparticles. The modulus decreases further with the dispersion of higher concentration of zirconia nanoparticles (i.e. at 8wt.%) as depicted in Fig.2.

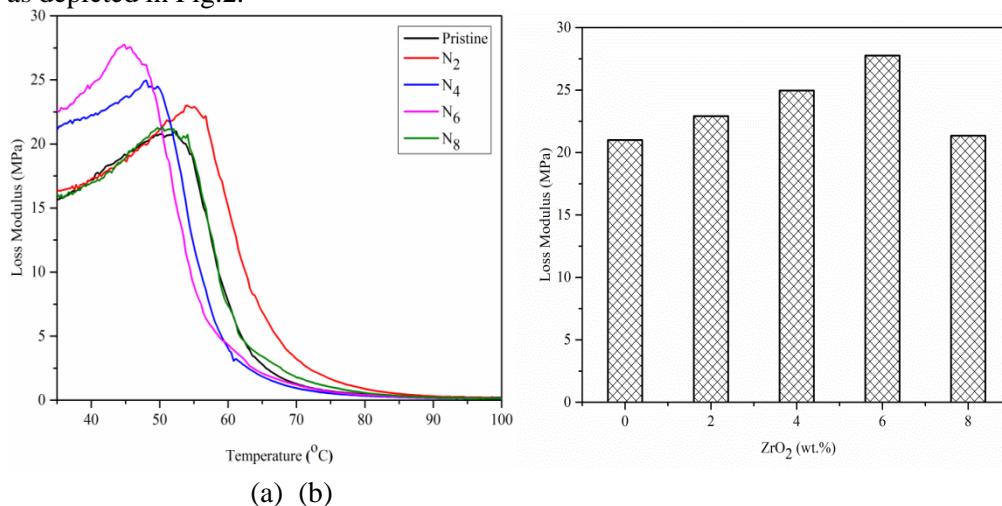


Fig.2. Variation of loss modulus for epoxy and epoxy-zirconia nanocomposites as a function of temperature for varying wt.% of zirconia nanoparticles.

Damping factor ($\tan\delta$) of epoxy-zirconia nanocomposites is defined as the ratio of energy dissipated (loss modulus) to the corresponding energy stored (storage modulus) [12]. Variation in damping factor ($\tan\delta$) of the nanocomposites with varying temperature has been shown in Fig.3. The homogeneous

dispersion and nano-cluster size of zirconia nanoparticles in the epoxy matrix have been found to be effective in dissipating energy as heat under viscoelastic deformation [13]. The temperature range for which $\tan\delta > 0.3$ is considered as a standard to assess the damping property of materials [14]. For zirconia dispersed nanocomposites, $\tan\delta$ peak shows a wider trend than that of pristine epoxy making the zirconia nanocomposites more suitable for the damping application for broader range of temperature. Glass transition temperature was calculated from the peak of curve of $\tan\delta$ for pristine epoxy system and modified epoxy with zirconia nanoparticle at 2, 4, 6 and 8 wt.%. Variation in glass transition temperature of the epoxy-zirconia nanocomposites with varying wt.% has been shown in Fig.4. In case of the pristine epoxy the value of glass transition temperature is 61°C and increases to 70°C up to 6 wt.% of zirconia nanoparticles. Increased loading fraction of nanoparticles offers resistance in the cross-linking mechanism leading to decrease in the cross-linking density and causing decrease in glass transition temperature.

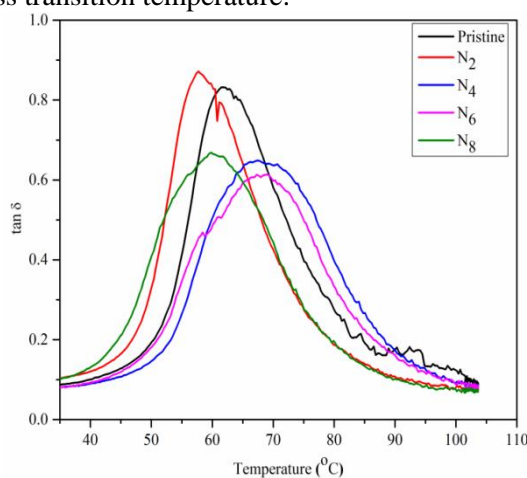


Fig.3. $\tan\delta$ vs. temperature curve of pure and epoxy-zirconia Nanocomposites

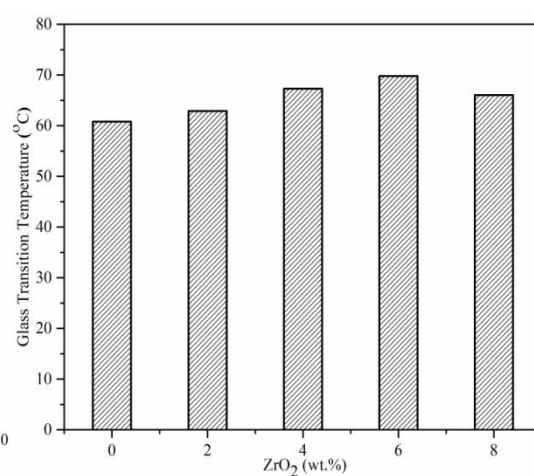


Fig.4. Glass transition temperature of pure and epoxy-zirconia nanocomposites with different wt.% of zirconia nanoparticles.

4. Conclusions

The Ultrasonic mixing has been found to be very effective means for achieving cluster free homogeneous dispersion of zirconia dispersed epoxy nanocomposites without significant worsening of the base matrix properties. The glass transition temperature (T_g) exhibited an enhancement of about 9°C. Significant enhancement in the storage modulus and loss modulus of nanocomposites has been achieved with nanoparticles dispersion. Maximum improvement of 25 % in storage modulus at 35°C for zirconia (6 wt.%) nanoparticles dispersed epoxy matrix was observed as compared to pristine epoxy in the glassy regions, which has become possible due to the homogeneous dispersion of zirconia nanoparticles in the epoxy resin matrix. However, it was found that the glass transition temperature (T_g) and viscoelastic properties of epoxy-zirconia nanocomposites depreciated for higher dispersion fractions (above 6 wt.%) due to significant upsurge in agglomeration of zirconia nanoparticles.

5. References

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