

Effect of ZnO nanoparticles on the thermal and mechanical properties of epoxy-based nanocomposite

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Abstract Effect of ZnO nanoparticles particles on the mechanical properties and the curing behavior of an epoxy nanocomposite were studied. Nanocomposites were prepared using different loadings of pre-dispersed ZnO nanoparticles having an average size of 40 nm. The surface topography and morphology of the nanocomposites were studied using atomic force microscope (AFM). The mechanical properties of nanocomposites were studied using analytical techniques including dynamic mechanical thermal analysis and micro-Vickers hardness. Effects of ZnO nanoparticles on the curing behavior of these nanocomposites were investigated utilizing isothermal and non-isothermal differential scanning calorimeter techniques. In addition, chemical compositions of coatings containing different ZnO nanoparticles contents were studied using a Fourier transform inferred. It was found that, ZnO nanoparticles can effectively influence the mechanical properties of epoxy coating. In addition, lower curing degrees, and therefore crosslinking density of epoxy coating including higher ZnO nanoparticles were obtained. This effect was completely different at low and high loadings of the particles.

Keywords Nanocomposite · ZnO nanoparticles · DMTA · FTIR

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Introduction

During the last decade, attempts have done to improve the properties of the organic coatings. Corrosion resistance, mechanical properties, appearance, and resistance against ultraviolet (UV) have been the most important of these. Different organic/inorganic pigments are able to improve these properties. However, they may cause some unwilling problems like poor adhesion, and reducing coating flexibility, impact, abrasion, and transparency. Nanotechnology has been utilized to decrease these problems in recent years. It has been found that, nano-sized particles, owing small size and high surface area, can produce less negative defects on the optical and mechanical properties of organic coatings. Also, the required content of these are used less than micro-sized pigments. Also, due to the higher specific area of these particles, the required content of these are used less than micro-sized pigments [1–8]. Based on which property of the coating is required to be improved, different types of these nanoparticles have been produced. SiO₂ nanoparticle, TiO₂ nanoparticle, and Al₂O₃ nanoparticle are the most important pigments among these. ZnO nanoparticles, due to the excellent properties which could produce, are also one of these materials which have been interested in the recent years. Optical, chemical, and biological properties of coating are the most important of these properties. This nanoparticle could also improve coating photo degradation resistance by blocking and absorbing the UV radiation [2, 4]. Improving this characteristic of an epoxy coating which has low UV resistance is very important. In addition, ZnO nanoparticles are a non-toxic material producing environmentally friendly coatings [2, 4]. Although, it has been found that [7] the anticorrosion resistance of coating including this nanoparticle can be superiorly improved.

It has been reported that, the curing behavior of organic coatings can be affected. As a result of this, cross-linking density and therefore many other properties of coating can be changed [8–19]. This effect completely depends on the surface modification (particles surface functionality, being active or not) and the chemical composition of the coating. An improved curing behavior of organic coating has been demonstrated, in the presence of ZnO nanoparticles, by Dhoke et al. [1–3].

Different observation has been reported by Shi et al. [4]. Based on their findings, ZnO nanoparticles can negatively influence the cross-linking density and curing of an alkyd resin. They showed that, the increased viscosity of coating, in the presence of nanoparticles, is responsible for such an observation. This study aims to investigate the effect of ZnO nanoparticles particles on the mechanical properties and the curing behavior of an epoxy nanocomposite.

Experimental

Sample preparation

Epoxy nanocomposites were prepared using ZnO nanoparticles. To this end, nanoparticle, at different mass ratios, were added to epoxy resin of Araldite G27 7071X75 (based on bisphenol-A in a xylene solution having solid content, epoxy value and density of 74–76%, 0.14–0.16 Eq/100 g and 1.08 g cm^{-3} respectively). Pre-stabilized ZnO nanoparticle (BYK-3842) with average size of 40 nm was used as dispersed in an aromatic free alcohol, with a concentration of 40%. Mass ratios (%) of 2, 3.5, 5, and 6.5% of ZnO particles were added to epoxy resin having solid content of 50%. The mixture (resin and nanoparticles) then followed by mixing at shear rate and mixing time of 2000 rpm and 20 min, respectively. The resultant formulations were then mixed (at 2000 rpm for 5 min) with the stoichiometric mass ratio (70/30) of polyamine curing agent (having 75–80% solid content). Leveling agent (BYK-306) and defoamer (Efka-2025) were added to the nanocomposites to improve film application property of the coating.

Free films were prepared using glass sheets. To this end, they were carefully cleaned and degreased using acetone solvent. Samples then were kept in an oven at 313 K to be dried. A steel-type applicator (having 3 cm in width and 5 cm in length) was utilized to apply nanocomposites over these cleaned glass sheets. Films with wet thickness of 90 μm were applied over the sheets. Samples then were kept in an oven at 393 K for 30 min. Finally, glass sheets were kept in water at 313 K for 60 min. The free films obtained in this method had thickness of 45 μm .

Samples characterization

Tritec 2000 type dynamic mechanical thermal analysis (DMTA) and Leica VMHTMOT (micro-Vickers having Berkovich tip type and indentation load of 19.6 N) instruments were used to investigate nanocomposites mechanical properties at different mass loadings (%) of ZnO nanoparticles free films. DMTA was performed at the frequency, temperature, and heating rate of 1 Hz, 243–433 K, and 278 K min^{-1} , respectively. Effects of nanoparticles on the curing behavior of epoxy nanocomposites were studied using a METTLER TOLEDO DSC calorimeter, in isothermal and non-isothermal conditions. The differential scanning calorimetry (DSC) analysis was performed on liquid epoxy coatings. In addition, the chemical composition of each nanocomposite was investigated using an Equinox-55 FTIR spectrometer (Fourier transform infrared). The dynamic mechanical thermal analysis (DMTA) and atomic force microscopy (AFM) techniques were used to study the effect of nanoparticles loadings on the morphology and topography of the nanocomposites.

Result and discussion

Microstructure analysis

The AFM images of epoxy-ZnO-based nanocomposites containing different nanoparticles loading values are presented in Fig. 1. The surface roughnesses of coatings calculated from AFM data are shown in Table 1. S_a , S_z , and S_q are defined by the Eqs. 1, 2, and 3, respectively, where the S_a and S_q show the mean values of the surface roughness factor and the standard deviation, respectively.

$$S_a = \int_a \int_a / Z(x, y) / dx dy \quad (1)$$

$$S_q = \sqrt{\int_a \int_a (Z(x, y))^2 dx dy} \quad (2)$$

$$S_z = \frac{\sum_1^5 / \text{peak heights} / + \sum_1^5 / \text{valley depths} /}{5} \quad (3)$$

From the 3D AFM data shown in Fig. 1a2–a3, one can notice that the surface roughness parameters (S_a , S_z , and S_q) of nanocomposites significantly increase for nanoparticle content of 2 and 3.5%. However, using further nanoparticles (5 and 6.5%) did not cause greater roughnesses. The increased roughness can be attributed to the presence of nanoparticles at coating surface. On the other hand, decreased roughness may be explained by the

Fig. 1 3D topographic AFM images (a1–a5) and phase micrographs (b1–b5) of epoxy-ZnO-based nanocomposites containing different ZnO nanoparticle loadings

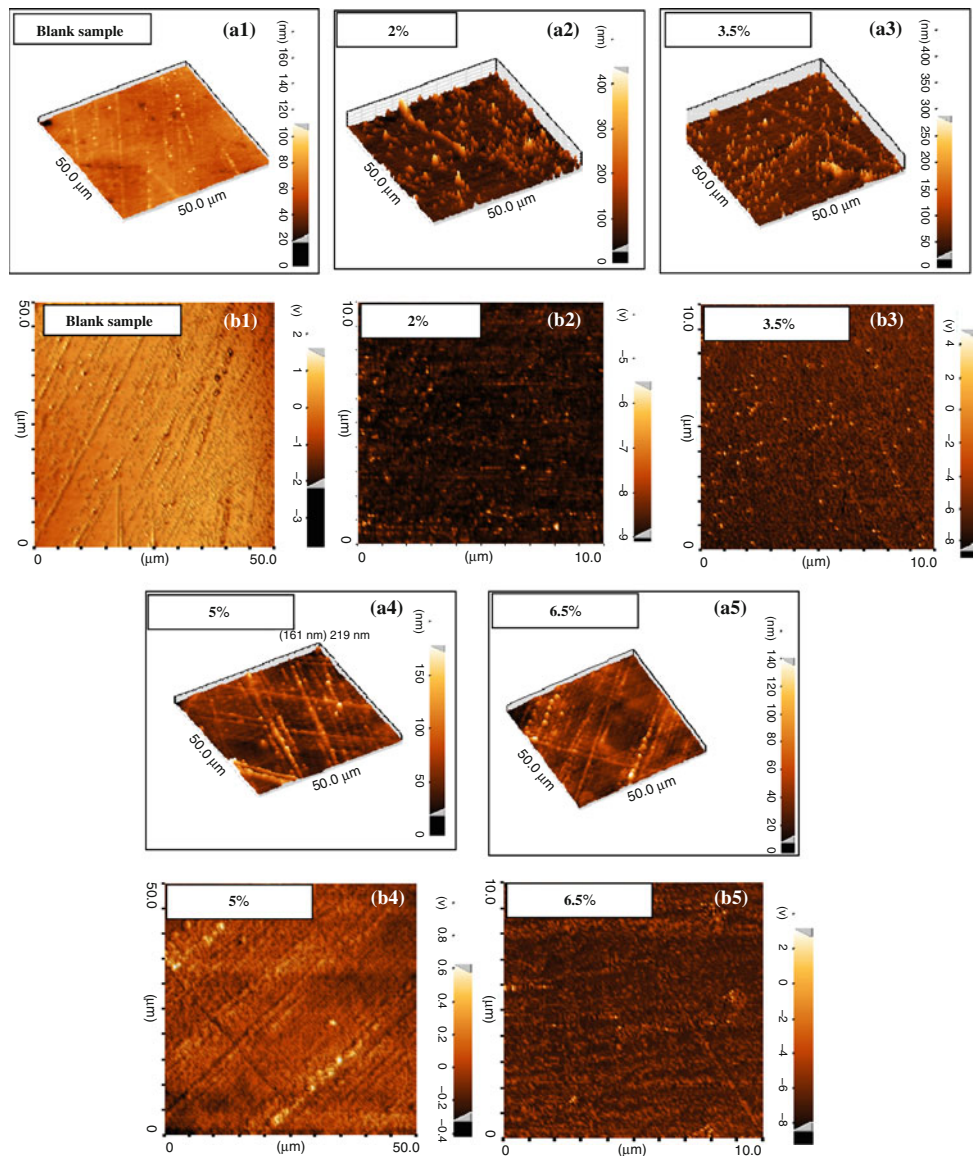


Table 1 Micro-hardness and roughness parameters of different nanocomposites (obtained from the AFM images shown in Fig. 1)

Sample	Roughness parameters/nm			Micro-hardness/HV
	S_z	S_a	S_q	
Blank sample	116	5.27	7.39	22.0
2%	487	27.9	45.7	19.50
3.5%	383	17.4	30.5	15.20
5%	179	15	20.4	16.90
6.5%	149	11.1	15.30	15.80

lower surface concentration of nanoparticles at higher loadings. One may possible for such an observation is the greater tendency which nanoparticles have to be in the bulk of coating (rather than its surface) [17]. Nanoparticles agglomeration (occurring at high loadings of particles) may

be responsible for such an observation. The physical entanglement among resin chains and particles agglomerates can cause a lower particles migration to surface. Extra information can be obtained from the 2D AFM phase images presented in Fig. 1b1–b5. Using this method, different phases presented on the coatings surfaces can be distinguished. Results can show one phase for blank coating and two phases on the nanocomposites. These two different phases can be clearly separated by the dark and light dots on coatings surfaces shown in Fig. 1b1–b5. These dark and light dots are, respectively, referred to the low and high elastic parts of coatings which can be attributed to the polymeric matrix and nanoparticles. A homogenous distribution of these light dots can be observed for the nanocomposites including 2 and 3.5% ZnO nanoparticles. This can clearly illustrate the better dispersion of particles in the case of coatings included 2

Fig. 2 Variation of the tan delta versus temperature for the epoxy-nanocomposites with different ZnO nanoparticle loadings

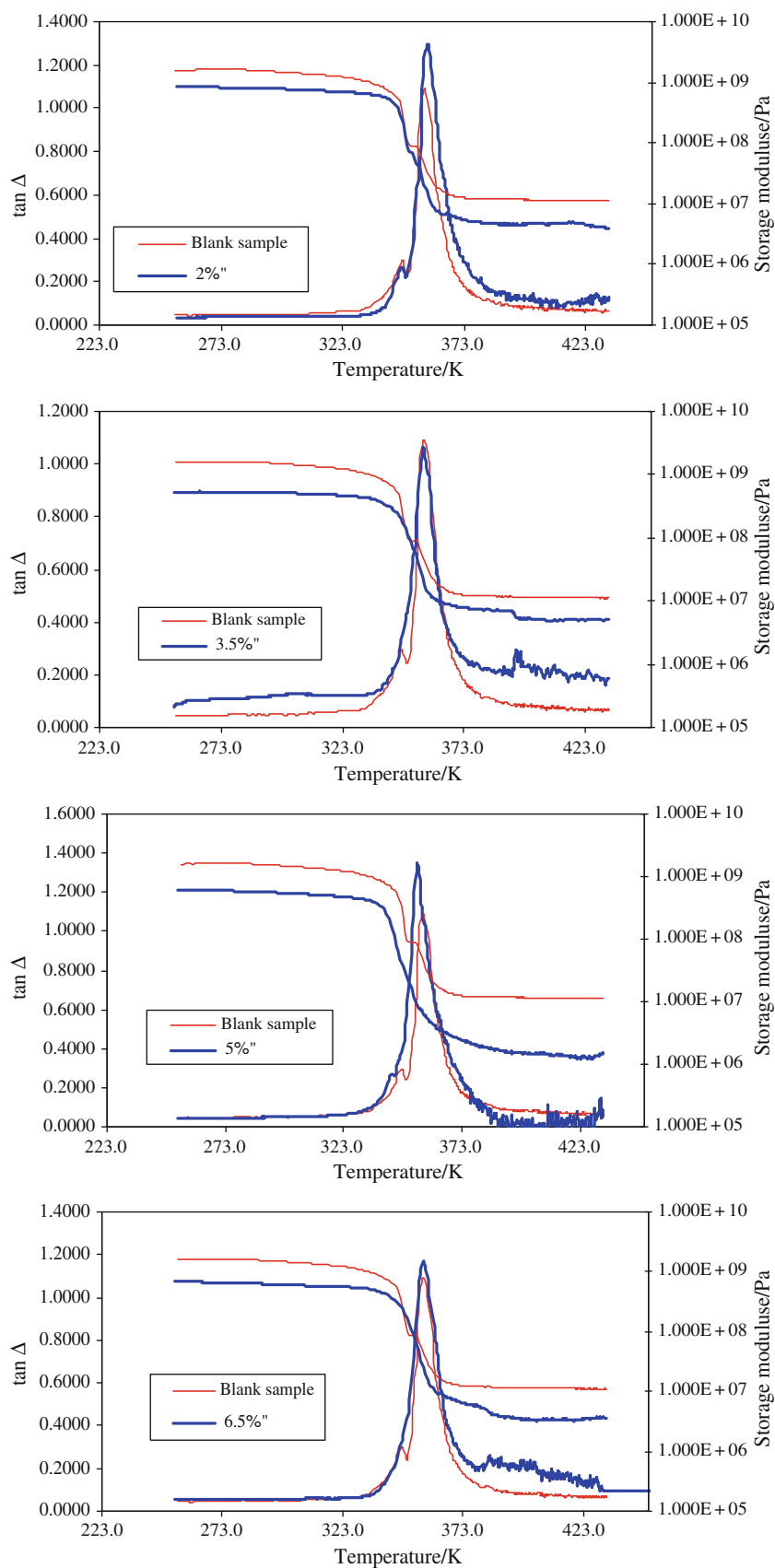
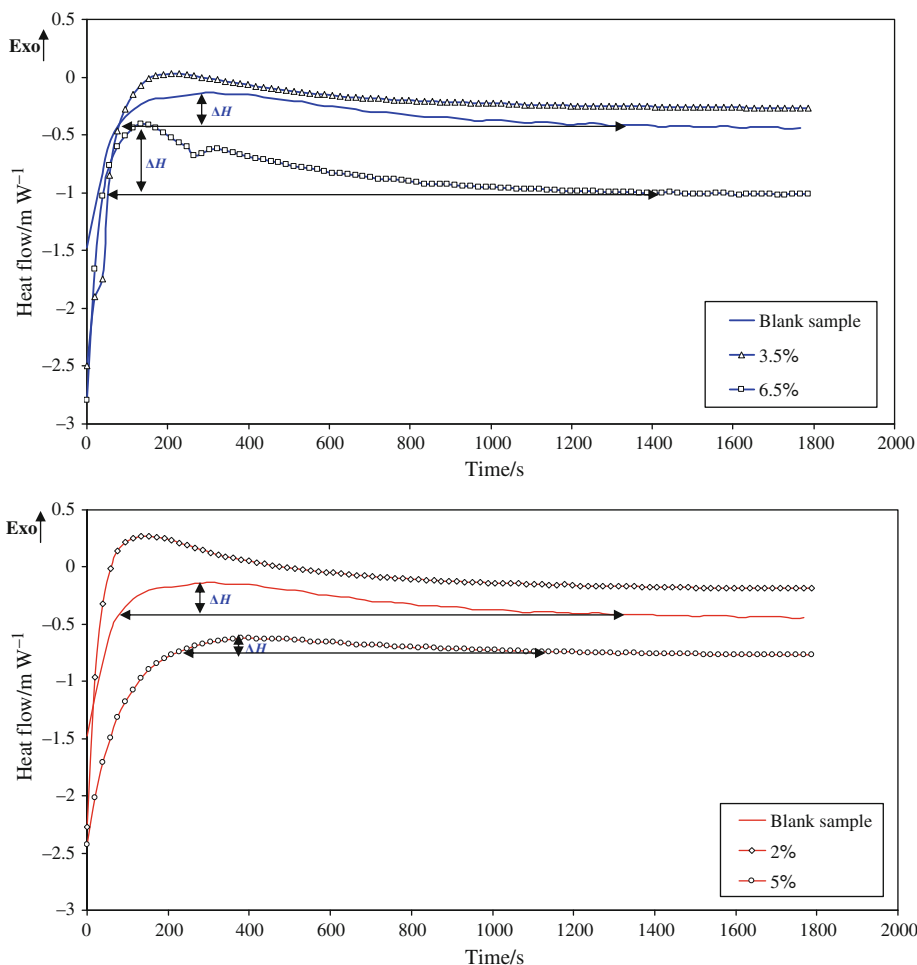


Table 2 Variation of heat flow (obtained from isothermal DSC curve shown in Fig. 3) and different parameters obtained from the DMTA curves (shown in Fig. 2)

Sample	T_g /K	v_e /mol cm ⁻³	Loss peak width/K	Loss peak height	Heat flow/m W ⁻¹
Blank sample	356.9	0.0011	282.80	1.080	185.53
2%	358.2	0.0005	285.10	1.290	178.42
3.5%	356.5	0.0005	284.80	1.060	131.38
5%	353.5	0.0001	285.10	1.330	72.23
6.5%	356.9	0.0003	284.50	1.060	115.0

Fig. 3 Isothermal DSC curves of epoxy-ZnO nanocomposites, at 293 K



and 3.5%. However, this cannot be observed at the greater nanoparticles loadings (5 and 6.5%).

Mechanical properties of epoxy/ZnO nanocomposite coatings

Variations of loss peak (tan delta) and storage modulus of different samples against the temperature are shown in Fig. 2. The values of parameters including T_g (glass transition temperature), cross-linking density (v_e), and loss peak characteristics were calculated from these curves and

are shown in Table 2. The T_g was obtained from the temperature which the value of tan delta was maximum. In addition, cross-linking density was calculated at the minimum temperature of plateau rubbery zone using Eq. 4 [20]:

$$v_e = \frac{E}{3RT} \tag{4}$$

where E and T are the minimum storage modulus and temperature at plateau rubbery zone, respectively. In addition, R in this equation is the ideal gas constant.

There is the increased T_g peak width and height in the case of the nanocomposite having 2% nano-ZnO particle

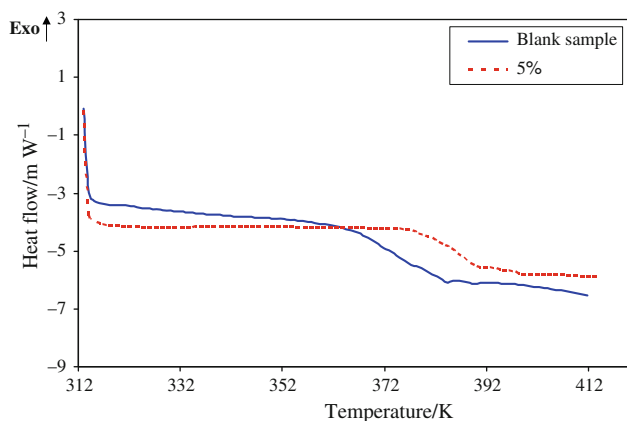


Fig. 4 Non-isothermal DSC curves of epoxy-nanocomposites recorded at heating rate of 276 K/min

was observed while the cross-linking was decreased. This may indicate that the effect of the mineral nano-ZnO particles on improving the mechanical properties of the nanocomposite is more important than the decreasing of the cross-linking. The higher and wider loss peak may elucidate the homogenous distribution of the nanoparticles together with a greater damping behavior of epoxy coating including 2% ZnO nanoparticles. Differently from sample included 2% nanoparticles, decreased T_g s were observed at greater nanoparticles loadings. In addition, the cross-linking densities of these samples were significantly decreased. These decreased (T_g and cross-linking density) was more pronounced at 5% of ZnO nanoparticles. Two main reasons can be mentioned for such observations. First, spherical nanoparticles, due to the weak interaction which they produce with epoxy coating matrix, can cause lower storage modulus in the rubbery plateau zone. This effect (which has named ball bearing effect) can cause lower ν_e of coating [17, 21]. However, this decreased ν_e does not show the decreased chemical crosslinks among resin chains.

Secondly, it has been reported that, nanoparticles may influence the curing behavior of coating in both positive and/or negative direction [2, 4, 13, 14]. Isothermal DSC technique was utilized to reveal such phenomenon. The DSC results show the effect of nanoparticles on the reaction between polymer chains and crosslinker, which will be discussed later.

The micro-Vickers hardness of blank epoxy and epoxy-nanocomposites are shown in Table 1.

In a micro-Vickers, opposite of DMTA analysis (which can investigate both surface and bulk properties), the mechanical properties of coating surface can be obtained. A decreased micro-hardness of nanocomposites including 2% nanoparticles was observed. This decrease was more severe at 3.5%. Although, the lowest T_g and cross-linking density of nanocomposite was observed at 5% nanoparticle content, the lowest micro-hardness was not observed at the same content. This difference may be resulted from the differences between two testing methods. As it is shown in Fig. 1 and previously discussed, at a loading greater than 3.5%, the nanoparticles tend to disperse in the bulk of nanocomposite instead being at the surface.

Differential scanning calorimetric study

The results of the isothermal and non-isothermal DSC analyses on the nanocomposite samples are shown in Figs. 3 and 4, respectively. The corresponding calculated heat flow values are presented in Table 2.

These results clearly illustrate the decrease of the curing enthalpy of epoxy coating by the increasing nanoparticles loading up to 5%. This can be attributed to the affected curing of epoxy in the presence of ZnO nanoparticles. Decreased enthalpy can be resulted from the lower reaction of the epoxy and curing agent functional groups due to the steric hindrance of these nanoparticles. It has been previously demonstrated that, increased viscosity of coating (alkyd), in the presence of nanoparticles (ZnO), can be responsible for the lower curing and therefore cross-linking density of coating [4]. This increased viscosity can be resulted from the physical network which nanoparticles produce with polymer matrix. This may reduce the reaction among resin and the crosslinker functional groups.

A higher enthalpy value for the nanocomposite having 6.5% ZnO nanoparticles, compared the one having only 5%, may be due to the nanoparticles agglomeration. The lower steric hindrance of aggregated particles against

Fig. 5 Chemical structure of **a** epoxy resin based on bisphenol A, and **b** amino curing agent used for the nanocomposite preparation

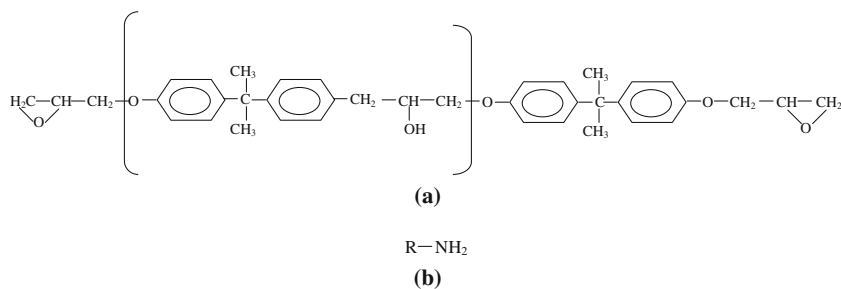
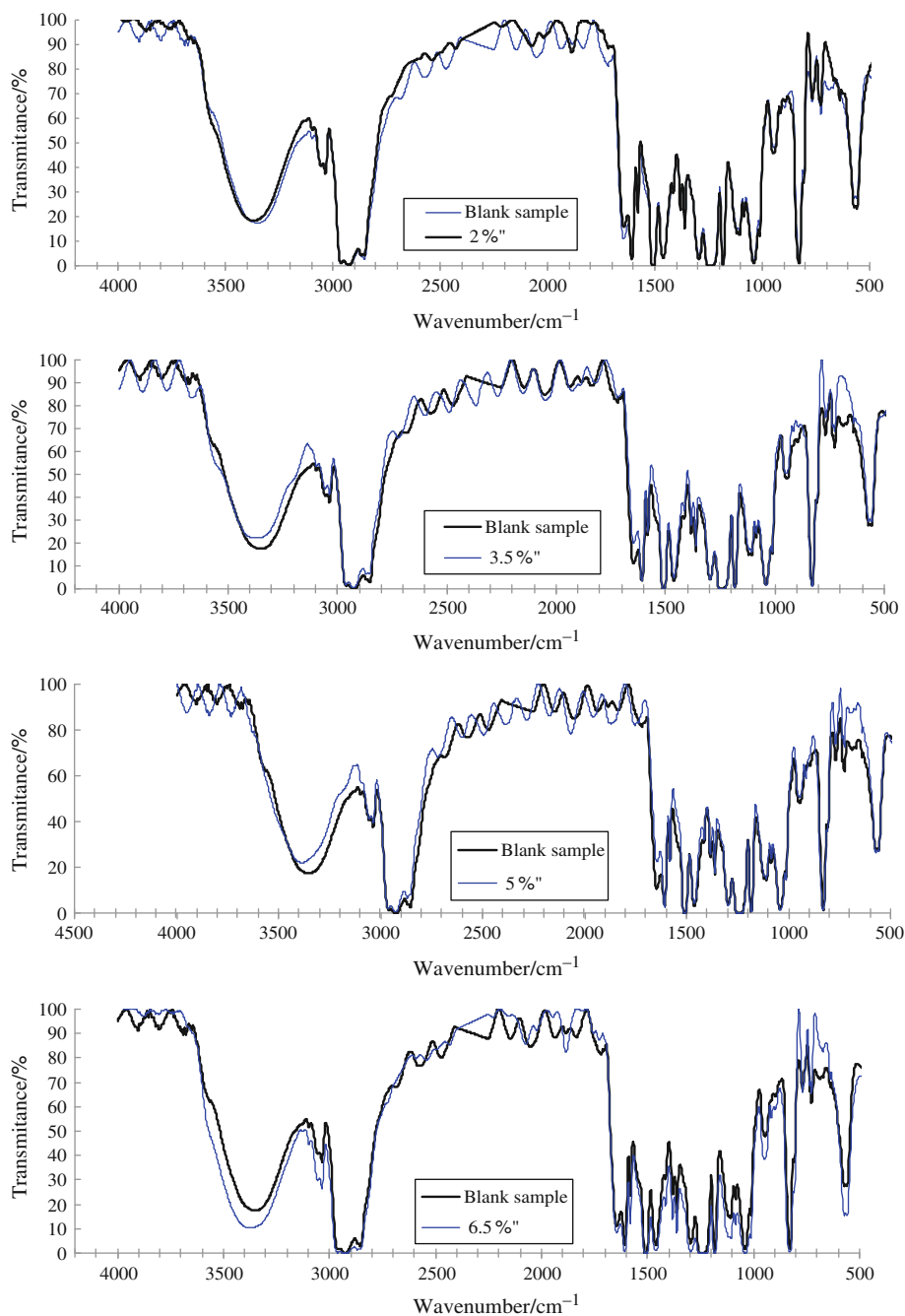


Fig. 6 FTIR spectra of the nanocomposite coating samples



curing process can be responsible for the greater cross-linking density for this sample (6.5%).

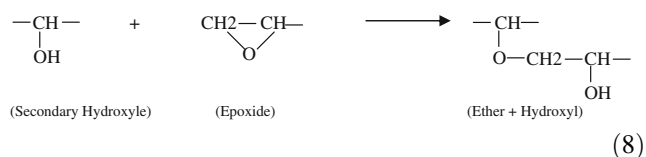
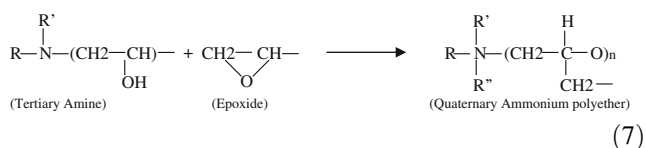
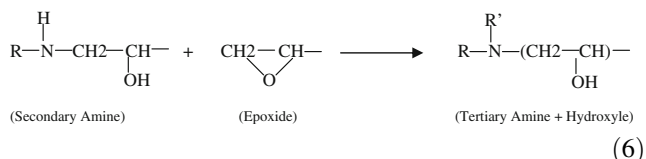
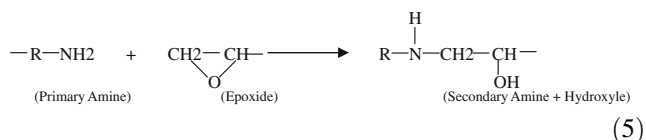
The non-isothermal DSC was performed to a blank epoxy and a nanocomposite containing 5% nanoparticle at the temperature range of 323–413 K (Fig. 4). Epoxy resin curing is an exothermic phenomenon and xylene solvent evaporation is an endothermic phenomenon. As a result of this, the endothermic and exothermic heat flow can influence each other. Therefore, studying the effect of nanoparticles on the curing of epoxy resin is not completely applicable. It is expected to see exothermic behavior in the diagram.

However, the endothermic phenomenon is observed. This could be due to the greater influence of solvent evaporation than epoxy curing in the system. The lower endothermic heat flow for the blank specimen, the better curing in the system would be.

FTIR analysis of the epoxy/ZnO nanocomposite coatings

Chemical compositions of nanocomposites, including different contents of ZnO particles, were studied by a FTIR technique to reveal how these particles affect the coating

curing behavior. The general illustrations of the chemical structures of epoxy resin and polyamine curing agent are shown in Fig. 5. In addition, the possible reactions among these two resins functional groups are also represented by Eqs. 5–8 [22].



According to the chemical reactions described by Eqs. 5–8, during the curing process, a decrease in the IR bands intensity until the disappearance of ---NH vibrations is expectable. During the curing process, the primary amine become to secondary (Eq. 5) and the secondary one become to tertiary (Eq. 5). Tertiary amine, due to its catalytic effect, can cause epoxide group self-polymerization and polyether bonds formation. Hydroxyl group formation can result in a ring opening of the oxiran groups. Another possible reaction, according to Eq. 8, is the homo-polymerization of epoxy and hydroxyl groups. However, the negligible reaction between these two groups (epoxy and hydroxyl groups) can cause increase in the vibration intensity of hydroxyl group during the curing process. Regarding the above explanations, the most variable vibration peaks of epoxy coating during the curing are epoxide group at 3056 cm^{-1} ($\nu_{\text{C-H}}$) and 915 cm^{-1} ($\nu_{\text{C-O}}$), NH_2 vibration absorption at $3340\text{--}3200 \text{ cm}^{-1}$, C-OH at $3400\text{--}3500 \text{ cm}^{-1}$ and ---CN group vibration at 1109 cm^{-1} . The results obtained from the FTIR analysis are shown in Fig. 6.

The transmittance intensities of 63 (at 0%), 62 (at 2%), 60 (at 3.5%), 58 (at 5%) and 55 (at 6.5%) were obtained at 915 cm^{-1} ($\nu_{\text{C-O}}$). These intensities were 39 (at 0%), 40 (at 2%), 44 (at 3.5%), 43 (at 5%), and 35 (at 6.5%) at

3056 cm^{-1} ($\nu_{\text{C-H}}$). These can show an increased vibration intensities of epoxide groups at 915 cm^{-1} ($\nu_{\text{C-O}}$) and a decreased at 3056 cm^{-1} ($\nu_{\text{C-H}}$) of coating including ZnO nanoparticles. It was found that, using greater contents of ZnO nanoparticles can cause greater increase in the vibration bond absorption at 915 cm^{-1} ($\nu_{\text{C-O}}$) and decrease at 3056 cm^{-1} ($\nu_{\text{C-H}}$). The transmittance intensities of 13 (at 0%), 14 (at 2%), 16 (at 3.5%), 17 (at 5%), and 10 (at 6.5%) were obtained at 1109 cm^{-1} . These can illustrate the greater absorption intensity of ---CN vibration of blank sample compared with the nanocomposite (at 1109 cm^{-1}). This may demonstrate the lower curing of the epoxy and polyamine curing agent in the presence of the nanoparticles. The transmittance intensities of 17 (0%), 19 (2%), 22 (3.5%), 22 (5%), and 15 (6.5%) were obtained at 3336 cm^{-1} . These can reveal that, using higher contents of ZnO nanoparticles, up to 5%, can cause lower intensity of ---OH vibration at 3336 cm^{-1} . Different results were observed at further nanoparticles loading (6.5% ZnO nanoparticles).

Based on the above explanations, lower reaction of amine (related to the curing agent) and epoxide (related to the epoxy resin) groups can be obtained when they were included nanoparticles. This observation is completely in agreement with the results shown in Fig. 2 and Table 2.

Conclusions

ZnO-epoxy nanocomposites including ZnO nanoparticles, at different contents, were prepared. The surface morphology and curing behavior of the resultant nanocomposites were studied.

It was found that at lower loadings of nanoparticles cause an increase in the surface roughness of the nanocomposite. However, lower surface roughnesses, due to the nanoparticles tendency for being in the bulk of the coating can be obtained at higher contents. Results revealed that ZnO nanoparticles can significantly affect the curing behavior of epoxy coating. It was found that, the steric hindrance which these nanoparticles produce can be responsible for the decreased reaction of epoxy and crosslinker. The cross-linking density, T_g and micro-hardness of epoxy-nanocomposites were significantly reduced at the loading which the curing was not complete.

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