EFFECT OF SONICATION AND HIGH SHEAR MIXING PARAMETERS ON NANOCLAY DISPERSION IN EPOXY

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Abstract

In this study we have investigated the effects of mixing parameters on the extent and structural morphology of the nanoclay dispersion and distribution in the epoxy matrix. Two mixing methods namely, sonication mixing and high shear mixing were used to disperse organically modified Nanomer I.30E nanoclay within Diglycidyl ether of Bisphenol A (DGEBA) epoxy resin. Mixing by sonication was performed for periods ranging from 5 to 60 minutes, whereas high shear mixing (HSM) was performed at mixing speeds ranging from 500 to 8000 rpm and mixing durations of 15 to 90 minutes. Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) techniques were employed to examine the effects of sonication time and HSM speed and time on the extent of dispersion and structural morphology of the nanocomposite. The results show that under the same optimal curing conditions, the mixing parameters play a significant role in determining the degree and structural morphology of clay dispersion in the epoxy matrix. Increasing sonication time enhanced the clay dispersion and the highest d-spacing was observed for nanocomposite sonicated for 30 minutes. The optimum structural morphologies resulted from HSM at 6000 rpm for 60 minutes. Both techniques predominantly produced intercalated morphologies and the d-spacing of nanocomposites fabricated by HSM is higher than that of sample prepared by sonication which indicated that HSM is more effective than sonication in nanoclay dispersion.

1 Introduction

Thermoset polymers have been widely used for engineering components, adhesives and matrix for fiber-reinforced composites due to their good mechanical properties compared to those of thermoplastic polymers. Epoxy resins are one of the most applied thermoset polymers that exhibit an attractive combination of stiffness, strength, high heat distortion temperature, creep resistance, thermal and environmental stability [1]. The addition of organically modified montmorillonite (MMT) clay to reinforced epoxy matrix have attracted significant attention because the dispersion of nano thin layered structure of nanoclay in polymer matrix offer new and greatly improved properties over pristine polymers. The unique layered structure of a collection of 1 nm thin, high strength and high aspect ratio (up to 1000) clay sheets, enable nanoclay to improve polymer matrix properties at very low clay loadings. A number of clay fillers and different mixing techniques have been used to synthesize epoxy-clay nanocomposites [2-5]. The most common techniques that are used to synthesize epoxy-clay nanocomposites are the ultrasonication mixing and shear mixing. Improvements in tensile strength, modulus, fracture strength, glass transition temperature and reduction in moisture absorption of polymers have been reported for a variety of nanocomposite systems [3-7].

The enhancement in epoxy properties due to clay addition depends on a number of parameters including the type of polymer and clay [2,8], curing conditions [6], clay concentration [9] and the techniques that are used to disperse the clay into polymer matrix [3,10,11]. Contradictory results have been reported about the effect of clay addition on the mechanical and physical properties of polymers. In fact the epoxy-clay nanocomposites properties are highly dependent on the resultant morphology. Based on the material types and the dispersion techniques two nanoclay structural morphologies i.e. intercalated or exfoliated morphologies have been reported. The degree of clay dispersion is believed to be the key factor responsible for the change in the properties of nanocomposites, exfoliated structures are reported to possess better properties than the intercalated ones [3,7]. Exfoliated morphology of the polymer-clay nanocomposites yields the maximum improvement in properties because maximum reinforcement is achieved. In this paper, the synthesis of epoxy-clay nanocomposites by sonication and high shear mixing is presented along with the analysis of manufacturing parameters on the morphology and structure of the resulting nanocomposite.

2 Materials and testing methods

2.1 Materials

The epoxy used in this study is the diglycidyl ether of bisphenol A (DGEBA), supplied by JANA, KSA, with an average weight per epoxide, 186 g/eq, viscosity at 25°C, 11 Pa.s, and density, 1.16 g/cm^3. The curing agent used is isophoronediamine (IPDA), product of HUNTSMAN. The average viscosity and density at 25°C of this hardener are 15 mPa.s and 0.92 g/cm^3, respectively. Octadecyl ammonium ion modified montmorillonite clay, Nanomer I.30 E, from Nanocor, is used as the filler material.

2.2 Synthesis of nanocomposites

The preparation of nanocomposites started with manually mixing of the nanoclay into the epoxy for 5 min to ensure good distribution of the clay particles in the epoxy. This initial mixing is important to properly distribute the clay powder into the epoxy monomers. After that high shear mixer (Model L4RT, Silverson, UK) was used to disperse the clay into epoxy matrix. Different HSM speeds and times were explored (500 to 8000 rpm and 15 to 90 minutes, respectively) to determine the optimum HSM parameters. During HSM the mixture temperature was maintained between 35-45°C by using a cold water bath. The epoxy/clay mixture was then fully degassed at 65°C for 10 hours after that stoichiometric amount of the hardener was added to the mixture (24 g of hardener for each 100 of epoxy) and gently mixed together for 5 min to ensure proper mixing of the hardener-epoxy. Finally, the mixture was poured into aluminum molds and pre-cured at 100°C for one hour followed by post-curing at 170°C for another hour. These optimum curing conditions were determined in an earlier work by the proponents [12]. The procedure followed during the fabrication of nanocomposites by sonication is similar to that used to synthesize nanocomposites employing HSM except that instead of HSM, the nanoclay was dispersed using Sonic vc-33 high intensity ultrasonicator. Four nanocomposites were fabricated using the sonication periods of 5, 10, 30 and 60 minutes.

2.3 Characterization of nanocomposites

The structure of the synthesized nanocomposites was investigated using high resolution scanning electron microscope (HRSEM) and X-Ray Difraction (XRD). The XRD scans were conducted using Bruker D8 Advance equipped with Cu radiation at 40 kV and 30 mA. All scans were run from 2 to 60 degrees using a step of 0.02^{o}. TSM-6460 SEM was used to inspect the clay distribution; the surfaces of specimens were coated with gold using JEOL Fine Coat Ion Sputter JFC-1100 sputtering equipment. Differential scanning calorimeter (DSC-822^{e}) was used to determine the glass transition temperature (T_g), which is used as an indicator of the degree of curing and crosslinking.

3 Results and discussion

3.1 Effect of HSM speed and time on nanoclay dispersion

Samples of nanocomposites were fabricated with high shear mixing speeds of 500, 1000, 2000, 4000, 6000 and 8000 rpm to determine the effect of mixing speed on the degree of clay dispersion. In this part of the study, the mixing time was kept constant at 30 minutes. At low mixing speeds of 500 and 1000 rpm, the generated shear forces and vortices were found to be insufficient to properly blend the mixture and hence these samples were excluded from further analysis. As shown in the SEM micrographs of Figure 1, increasing HSM speed improved clay dispersion and the size of agglomerated clay cluster decreased from about 45 μm at 2000 rpm to less than 20 μm at 6000 rpm; no further reduction in the average cluster size was observed for the sample mixed at 8000 rpm. The improvement is brought about by the induced shear force which is known to depend mainly on the mixing speed.

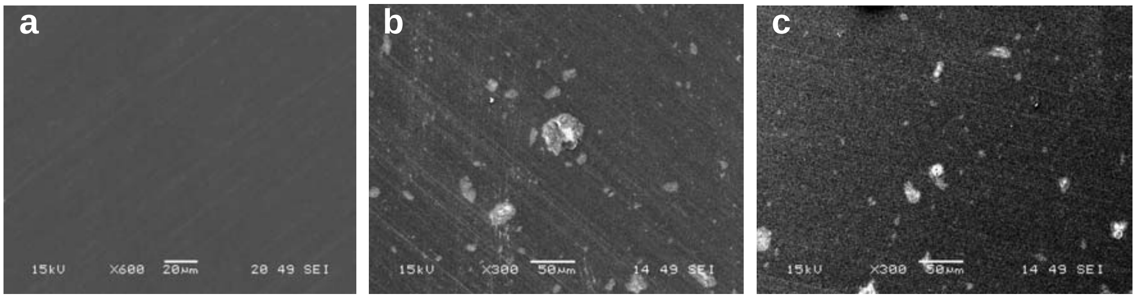
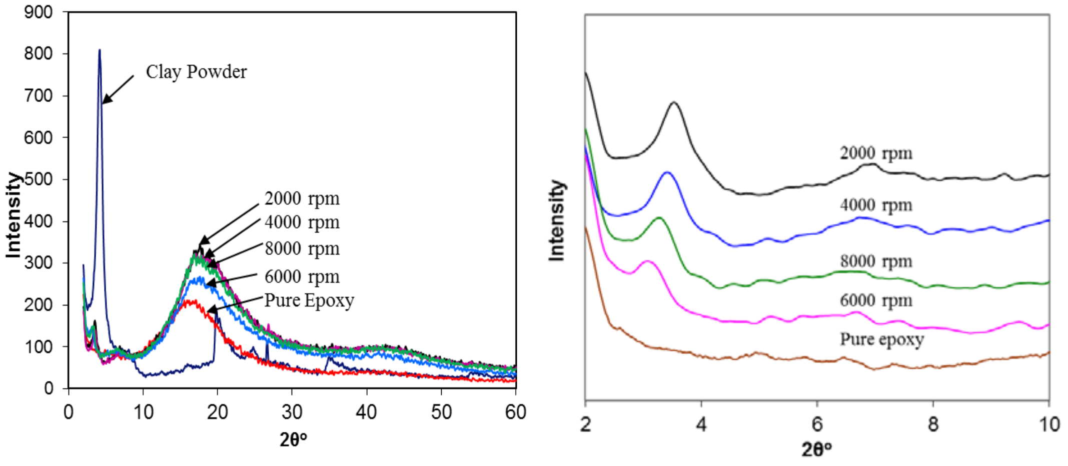


Figure 1. SEM micrographs of (a) pure epoxy and nanocomposites mixed for 30 min with different mixing speeds: (b) 2000 rpm and (c) 6000 rpm.

To determine the effect of mixing speed on d-spacing of the clay layer, XRD was used and the X-ray diffraction spectra of pure epoxy, clay powder and nanocomposites are shown in Figure 2(a). As illustrated in the figure the diffraction angle (2θ) for the clay powder was 4.0^{o} resulting in a d-spacing of 2.2 nm which agreed with the results reported for pristine I.30E clay in other studies [11, 13]. To have a better estimation of the diffraction angles for prepared nanocomposites, the data was re-plotted in Figure 2(b) with 2θ varying between 2 and 10^{o}. The intensities of the peaks for the nanocomposites are lower than that of the clay powder, and their angular positions are less than that of the clay powder indicating higher d-spacing. This increase in d-spacing can be attributed to the polymer diffusion between the clay layers causing finite increase in the intergallery spacing.

The variations of d-spacings and peaks relative intensities with HSM speed are illustrated in Figure 3. As can be seen in the figure, the d-spacings increased with increasing mixing speed indicating that more chains of epoxy molecules have diffused into the intergallery between the clay layers. The peaks relative intensity decreased with increasing mixing speed indicating less orderly clay layers were present in each clay tactoids, which means that the sizes of clay tactoids and clay particles which remain in orderly stack after mixing are smaller. As shown in Figure 3, the maximum d-spacing and minimum peaks intensity were for the nanocomposite prepared at an HSM speed of 6000 rpm. The reduction in the d-spacing and increase in the peaks intensity for 8000 rpm can be related to the decrease in the viscosity of epoxy/clay mixture that results from the observed increase in temperature and bubbles generated during mixing. This reduction in the viscosity leads to a decrease in the shear force during high shear mixing of epoxy and clay. The above findings lead to the conclusion that for the present nanocomposite, the optimum clay dispersion was achieved at an HSM speed of 6000 rpm.



(a) **(b)**

Figure 2. (a) X-ray diffraction spectra for clay powder, pure epoxy, and nanocomposites mixed for 30 min with indicated mixing speed over full spectrum and (b) pure epoxy, and nanocomposites in the range of 2θ = 2 to 10°.

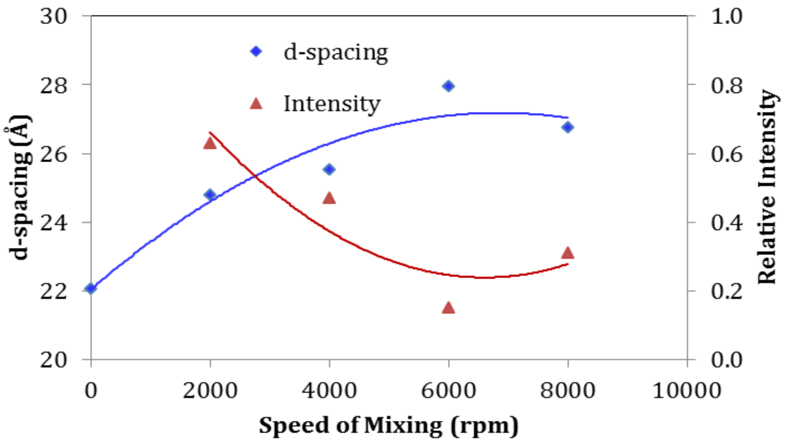


Figure 3. Variations of d-spacings and peak relative intensities at the diffraction angles with mixing speeds.

After determining the optimum HSM speed at the mixing time of 30 minutes, samples of nanocomposites have been prepared using the optimum HSM speed of 6000 rpm with mixing times of 15, 30, 45, 60 and 90 minutes. The objective of this part of the study was to find out the optimum HSM time. The SEM results (Fig. 4) showed that the degree of mixing was enhanced with increasing HSM time; longer mixing time resulted in breaking of the agglomerated clay clusters. The size of the largest clay cluster decreased from about 50 µm for the sample mixed for 15 min to less than 15 µm for the samples mixed for 60 min as illustrated in Figure 4(a) and (b). Beyond 60 min the improvement in the degree of dispersion was negligible. A closer SEM look at the nanocomposite prepared at 6000 rpm for 60 minutes reveals that the majority of the clay aggregates have sizes less than 5 µm as shown in Figure 4(c). Using a mechanical stirrer Qi et al. [13] showed that the size maximum clay clusters was about 60 µm, while Liu et al. [3] found that using high pressure mixing (HPM) the size of clay cluster was about 2 µm. It is worth mentioning that HSM process is simpler than HPM.

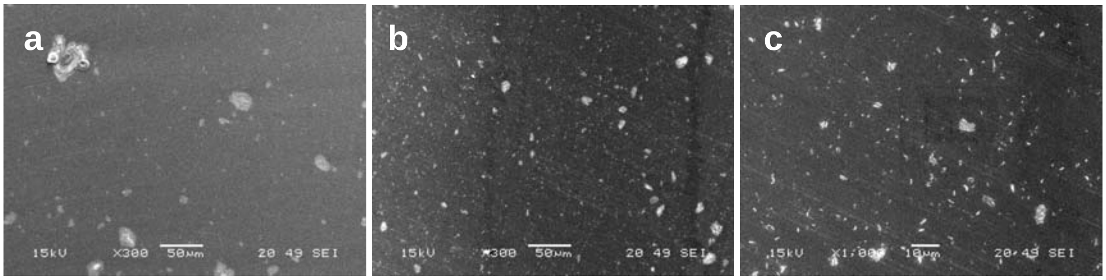
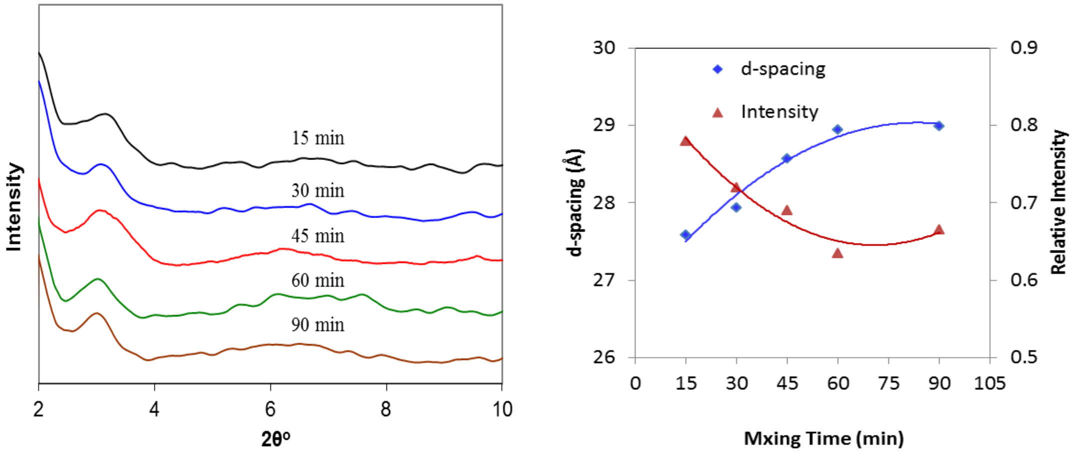


Figure 4. SEM micrographs for nanocomposites prepared at 6000 rpm with different mixing time (a) 15 min at X300, (b) 60 min at X300 and (c) 60 min at X1000.

The x-ray diffraction spectra curves for nanocomposite samples that have been prepared at different HSM times are shown in Figure 5(a). The variation of d-spacing and relative intensity at the diffraction angles with mixing time are illustrated in Figure 5(b). These results show that there is improvement in d-spacing with increasing the mixing time. The d-spacing increases from 2.2 nm for the clay powder to 2.9 nm for the sample mixed for 60 minutes. The enhancement in the d-spacing when the mixing time increased beyond 60 min is negligible. Similarly, the relative intensities at the diffraction angles reduced with increasing the mixing time indicating an improvement in the degree of clay dispersion. The above findings lead to the conclusion that the optimum clay dispersion at 6000 rpm is achieved with mixing time of 60 minutes. Using high speed mixing Ngo et al. [6] found that the d-spacing increased from 1.85 nm for clay to 3.8 nm for epoxy-clay nanocomposite prepared with C30B nanoclay.

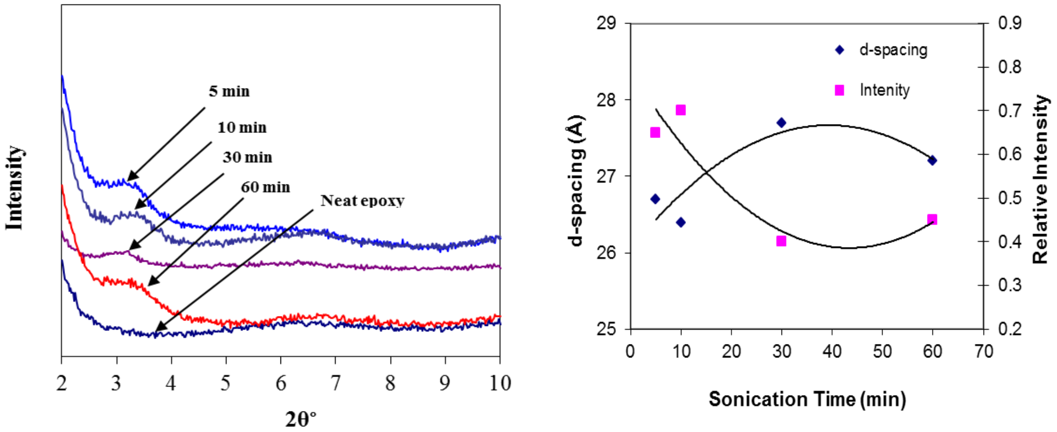


(a) **(b)**

Figure 5. (a) X-ray diffraction spectra curves for nanocomposites prepared at 6000 rpm using different mixing times and (b) variation of d-spacing and relative intensity at the diffraction angles with mixing time.

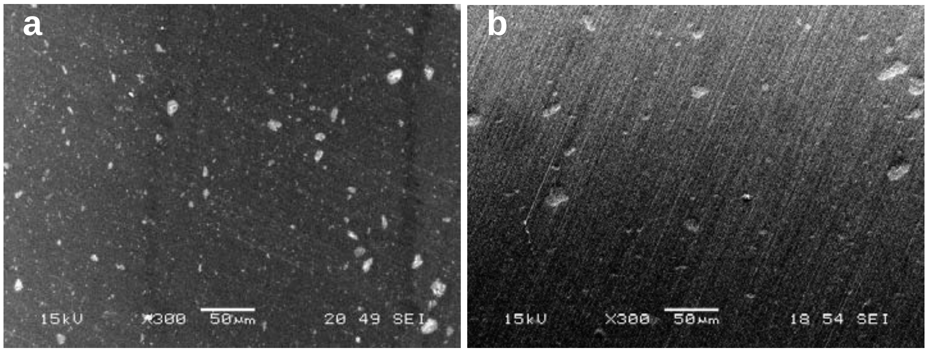
3.1 Effect of sonication time on nanoclay dispersion

To study the effect of sonication time on clay dispersion samples were fabricated using different sonication time (5, 10, 30 and 60 min) [14]. The XRD results shown in Figure 6(a) illustrate that, the d-spacing improved with increasing the sonication time and the sample sonicated for 30 min has the highest value of d-spacing (2.77 nm) and lowest value of relative intensity as shown in Figure 6(b). The SEM analysis reveals that the clay cluster reduced with raising sonication time up to 30 min and the enhancement in clay dispersion is negligible after that. Therefore 30 min of sonication time was considered to be the optimum sonication time. As indicated from XRD results, the d-spacing for the nanocomposite fabricated by HSM is higher than that for the sample prepared by sonication (2.9 nm compared to 2.77 nm). Also the size of the largest agglomerated clay clusters for nanocomposite fabricated using HSM was smaller than that for samples prepared by sonication as shown from Figure 7. This result provides clear evidence that HSM is more effective than sonication for clay dispersion in epoxy. Similar conclusions were drawn by Liu et al. [3] when comparing HPM with sonication.



(a) **(b)**

Figure 6. (a) X-ray diffraction spectra curves for nanocomposites prepared using different sonication time and (b) variation of d-spacing and relative intensity at the diffraction angles with mixing time.



(a) **(b)**

Figure 7. SEM images for nanocomposites prepared by (a) HSM at 6000 rpm for 60 min and (b) Sonication for 30 min (X300).

3.3 Effect of mixing parameters on glass transition temperature

To investigate the effect of mixing speed and mixing time on the crosslinking density, glass transition temperatures (T_g) were determined for all prepared nanocomposites using differential scanning calorimeter (DSC). The results show that T_g for the nanocomposites was slightly lower than that of neat epoxy; 148^{o}C as compared to 152^{o}C for epoxy. The DSC analysis revealed that the effect of mixing technique on the glass transition temperature and hence on the degree of crosslinking was negligible. All the nanocomposites that have been fabricated using high shear and sonication have almost the same T_g. This result agreed well with that reported by Ngo et al. [6], where T_g was found to be insensitive to change in high speed mixing and time.

4. Conclusions

High shear mixing and sonication techniques were used to synthesize nanoclay/epoxy composites. The effects of HSM speed and time and sonication durations on the material morphology were studied. Following are the conclusions:

- The mixing parameters play a significant role in determining the degree of clay dispersion in the epoxy matrix.
- The optimum structural morphologies resulted from HSM at 6000 rpm for 60 minutes.
- T_g was found to be insensitive to change in mixing speed and time.
- Increasing sonication time enhanced the clay dispersion and the highest d-spacing was observed for nanocomposite sonicated for 30 minutes.
- Both techniques predominantly produced intercalated morphologies and the d-spacing of nanocomposites fabricated by HSM is higher than that of sample prepared by sonication.

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