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Processing of clay/epoxy nanocomposites by shear mixing

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Abstract

A three-roll mill was used to disperse/exfoliate the clay nanoparticles in an epoxy matrix. The compounding process was carried out with varying clay contents (1–10 wt.%). The technique was found highly efficient and environmentally friendly in achieving high levels of exfoliation and dispersion within a short period of time.

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1. Introduction

It has been proven in recent years that polymer based nanocomposites reinforced with a small amount of nanosize clay particles (<5 vol.%) significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix [1–11]. Furthermore, these improvements are achieved through conventional processing techniques and without affecting substantially the density of the matrix. These composites are now being considered for a wide range of applications including packaging, coating, electronic, automotive and aerospace industries. It is generally believed that the improvement of properties of clay nanocomposites is directly related to the complete exfoliation of silicate layers in the polymer matrix. However, a processing technique that produces complete exfoliation is still a technical challenge. This may be due to the high viscosity of the resin and the strong

tendency of clay nanoparticles to agglomerate [3]. It is also reported that the degree of exfoliation depends on the structure of the clay, curing temperature and curing agent [4]. The commonly used techniques for processing clay-epoxy nanocomposites are: direct mixing and solution mixing [4–7]. However, these techniques produce intercalated or intercalated/exfoliated composites rather than fully exfoliated composites. Vaia et al. [8] have suggested that the degree of exfoliation can be improved through the aid of conventional shear devices such as extruders, mixers, ultrasonicators, etc. In the present study, a three-roll mill was used as a means of applying external shearing forces to disperse and exfoliate the silicate clay layers in the epoxy matrix. The structure–property relationship for clay nanocomposites is also discussed here.

2. Experimental

2.1. Materials

The matrix used in the present study was a three-component epoxy resin system from

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Vantico, where epoxy resin DGEBA (GY6010), anhydride hardener (Aradur 917) and accelerator (DY070) were mixed in proportions of 100:90:1 (in phr), respectively. The reinforcing clay nanoparticle was Cloisite® 30 B, commercially available from Southern Clay Products, Inc., USA. It is a natural montmorillonite (MMT) organically modified with a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium. Table 1 shows the physical properties of Cloisite® 30 B [12].

2.2. Fabrication

In this study, a three-roll mill (Ross Bench Top Model 52M 2.5" × 5") was used to disperse and exfoliate the clay nanoparticles in the epoxy matrix. First, the epoxy resin (DGEBA) was placed between the feed and the center rolls. Once the rolls started moving, the clay particles were spread gradually on the resin to get direct and maximum contact with the rolls. The dispersion was achieved by the shear forces generated between the adjacent rolls. Compounding was carried out at room temperature for 3 h, with a rotation speed of 500 rpm and a feed rate of 120 g/h. It was observed that the solution became viscous and opaque as the silicate layers dispersed and expanded with time. However, when the dispersion was completed, it produced a clear and transparent solution. The final product from the mill was then collected and mixed with the hardener at 60 °C for 1 h on a hot plate. After adding accelerator and mixing for a few minutes, the solution was left overnight for degassing. After degassing, the solution was cast in an aluminum mold following ASTM standard D638-99 and cured in an oven at 148 °C for 1 h. Nanocomposites were prepared with clay contents from 1 to 10 wt.%.

Table 1
Properties of clay particles

Physical properties	Cloisite® 30 B
Color	Off white
Density, g/cc	1.98
d-spacing (d_{001}), Å	18.5
Aspect ratio	200–1000
Surface area, m ² /g	750
Mean particle size, μ	6

2.3. Characterization

Small angle X-ray scattering (SAXS) was performed on both clay and cured samples to evaluate the degree of exfoliation and the d-spacing between clay platelets. SAXS was carried out on a Bruker AXS solid-state detector with Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) and operating at 30 kV and 13 mA. The 2D-diffraction pattern for each sample was collected for 1.5 h. To clarify the nanoscale structure, a JEOL TEM operating at an accelerating voltage of 100 kV was also used. The ultrathin TEM samples with a thickness of 60 nm were cut using a microtome at room temperature. The tensile samples were tested on an Instron 8500 servohydraulic machine at a crosshead rate of 0.127 mm/min. The fracture surfaces of tensile specimens were examined using a Hitachi S4500 FE SEM. The fracture surfaces were examined at 3 kV accelerating voltage and were gold coated prior to SEM investigation to avoid charging.

3. Results and discussion

3.1. Density measurements

Fig. 1 shows the effect of clay content on the density of clay nanocomposites. The density of pure epoxy is 1.2 g/cc and is found to increase only 3% with an addition of 10 wt.% of clay. Therefore, the effect of clay content on the density is not significant.

3.2. Morphology

The SAXS patterns of all cured nanocomposites containing varying clay contents are shown in Fig. 2. The diffraction pattern for pure Cloisite® 30 B is also shown in the same figure. Cloisite® 30 B shows a characteristic diffraction peak corresponding to the (001) plane at 18 Å (1.8 nm). However, none of the nanocomposites shows any peak. In general, the absence of diffraction peaks can be attributed to two possible reasons: (a) exfoliated structure or (b) disordered intercalated structure with an average d-spacing higher than 7 nm. This can be further confirmed by TEM

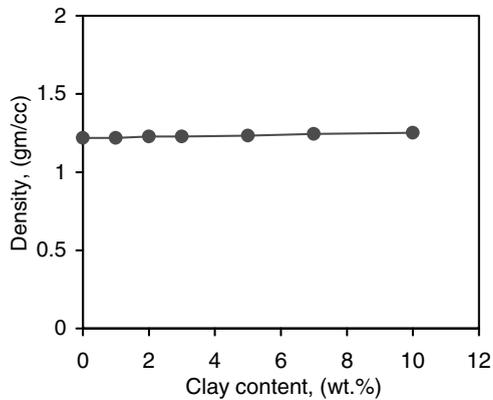


Fig. 1. Density versus clay content for clay nanocomposites.

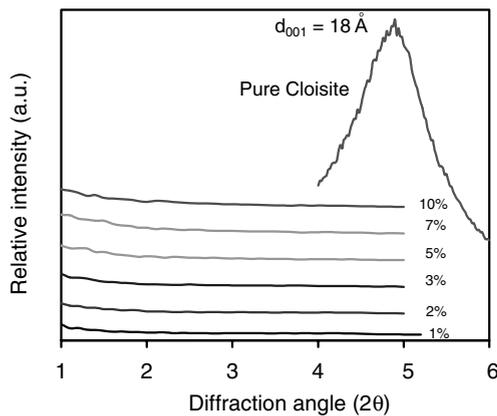


Fig. 2. SAXS patterns of nanocomposites with varying clay contents.

observation as shown in Fig. 3. All three nanocomposites containing 1, 5 and 10 wt.% of clay, respectively, show homogenous dispersion of nanoparticles throughout the cross-section. The TEM images also show disordered intercalates rather than complete exfoliation for any clay content. As shear mixing progresses, the solution becomes more and more viscous with the dispersion of clay particles. At higher clay contents, the viscosity increases even further and it can be assumed that the extra shear force generated by high viscosity will increase the basal spacing of clay platelets in the epoxy resin [11]. It is, therefore, suggested that the shear mixing provides good dispersion of clay nanoparticles including interca-

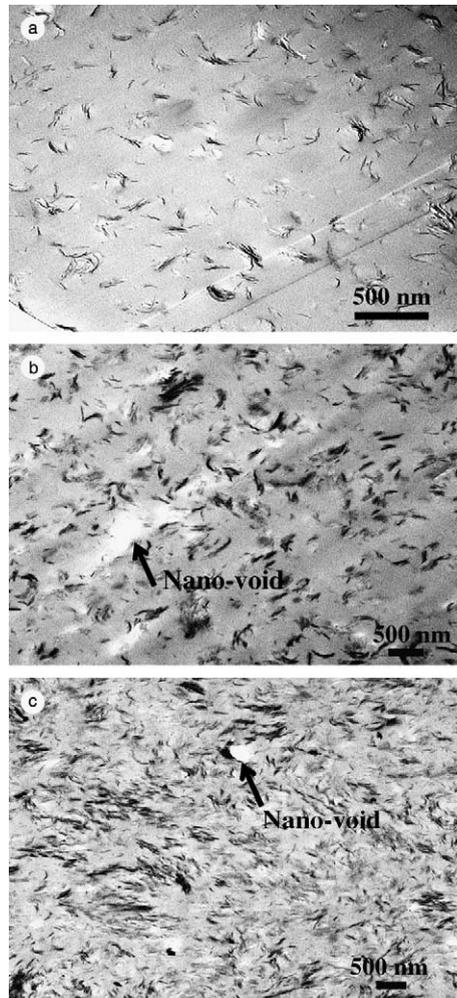


Fig. 3. TEM images of clay nanocomposites at low magnification: (a) 1 wt.%, (b) 5 wt.% and (c) 10 wt.%.

lation and exfoliation for the shear force and residence time applied in this study. However, it is of interest to mention that the nanocomposites reinforced with Nanomer I.28E (Nanocor, Inc.) prepared under identical conditions showed only ordered intercalates with an average basal spacing of 3.5 nm regardless of clay content [13]. Therefore, it can be suggested that the degree of intercalation or exfoliation depends on the type of clay and its surface modification. It is also important to mention that the processing of nanocomposites by shear mixing produces a foamy and viscous solution and makes degassing quite difficult. This, in

turn, may leave some nanovoids inside the silicate clay layers as shown in Fig. 3.

Fig. 4 shows the TEM images of clay nanocomposites with stacks of disordered intercalates at high magnification. The dark lines are the intersections of silicate layers of 1 nm thickness. In Fig. 4a, the average distance between clay platelets and the average length of the platelets for a 5 wt.% clay nanocomposite are ~ 8 and 120 nm, respectively. Similarly, in Fig. 4b, the average distance between clay platelets and the average length of the platelets for a 10 wt.% clay nanocomposite are ~ 5 and 90 nm, respectively. Therefore, a smaller d-spacing is observed in the latter case. In general, the smaller d-spacing at higher clay contents is attributed to the increased intercalation/exfoliation sites with increased clay content that might impede the higher basal spacing or exfoliation of individual silicate layers [9]. Furthermore, it can be seen from Fig. 4b that the maximum number of platelets in a certain direction is around 16. However, the X-ray diffraction from these planes does not produce any pronounced peak although the platelets are about

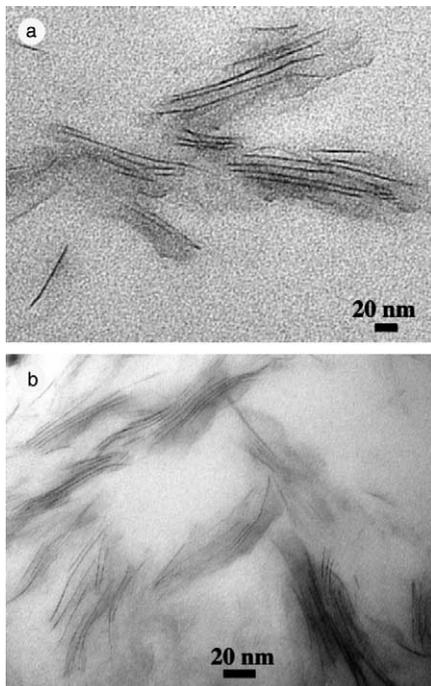


Fig. 4. TEM images of clay nanocomposites at high magnification: (a) 5 wt.% and (b) 10 wt.%.

5 nm apart. This could be attributed to either the misalignment or waviness of the clay platelets as seen in Fig. 4b. However, this behavior is in contrast to that observed in nanocomposites reinforced with Nanomer I.28E, where a number of perfectly parallel platelets (or ordered intercalates) were observed in a certain direction [13]. Therefore, the absence of peaks observed in the present study can be attributed to: (1) higher basal spacing, (2) limited number of platelets in a certain direction and (3) random orientation of platelets.

It is also observed that the processing of nanocomposite by shear mixing reduces the initial aspect ratio of clay platelets from 200–1000 to 90–120. This can be attributed to the milling process, which breaks the clay platelet during mixing. However, the resultant nanocomposites still exhibit significant improvement of mechanical properties as discussed later on.

3.3. Mechanical behavior

The stress–strain behavior of all nanocomposites under uniaxial tension is shown in Fig. 5. As the clay content increases, the strain to failure decreases. Fig. 6a shows the variation of elastic modulus with clay content. It is observed that the modulus of the nanocomposites increases continuously with increasing clay content. An improvement of about 25% is observed with an addition of 1 wt.% of clay, whereas a maximum of 80% improvement is observed with an addition of 10 wt.%

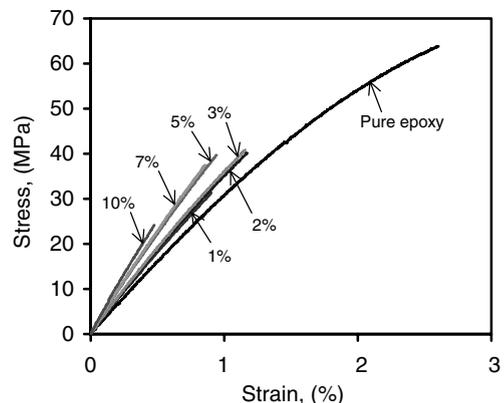


Fig. 5. Stress–strain behavior of clay nanocomposites.

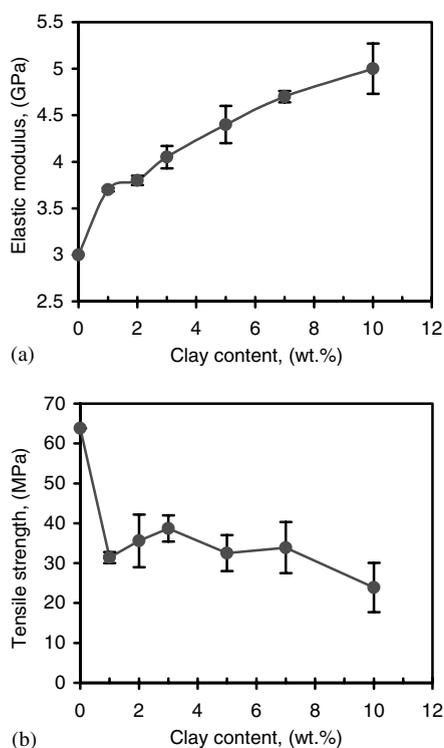


Fig. 6. Effect of clay content on the mechanical properties of nanocomposites: (a) elastic modulus and (b) tensile strength.

of clay. From Fig. 6a, it is also observed that although the rate of improvement at the beginning is dramatic, it decreases continuously as the clay content increases. The improvement in elastic modulus can be attributed to the exfoliation and good dispersion of nanosize clay particles that restricts the mobility of polymer chains under loading as well as to the good interfacial adhesion between the particles and the epoxy matrix [3]. The orientation of clay platelets and polymer chains with respect to the loading direction can also contribute to the reinforcement effects [10]. However, the decreasing rate of elastic modulus improvement with higher clay content can be attributed to the presence of unexfoliated aggregates [10].

Fig. 6b shows the variation in tensile strength with clay content. Unlike the elastic modulus, nanocomposites of any clay content show a lower tensile strength than that of pure epoxy. This is similar to the results reported by Zerda et al. [5] but

in contrast to the tensile strength values of nanocomposites reported elsewhere [3,10,11]. In the present study, the failure of all nanocomposites at strengths lower than that of the pure epoxy can be assumed to be process related. As mentioned before, the compounding of nanoclay in an epoxy matrix with a three-roll mill produces a highly viscous and foamy material, and the higher the clay content the higher the viscosity. Furthermore, the ammonium ion used to treat Cloisite® 30 B can readily participate in the curing reaction and favor the delamination of the clay platelets [12]. As a result, the mixture becomes highly viscous with time and hinders the complete degassing before casting. It is also observed that for nanocomposites containing 5 or higher wt.% of clay, the degassing problem becomes critical. The presence of nanovoids in 5 and 10 wt.% clay nanocomposites (Fig. 3) confirms this. The other source of voids could be trapped air during pouring of the highly viscous material onto the mold. Finally, the failure of all specimens at a strength range of 25–40 MPa indicates crack initiation from similar types of defects. Therefore, it can be assumed that under tensile loading, cracks can initiate from these tiny voids and cause specimen failure at relatively low strains similar to that observed in a previous study [13].

In a further effort to improve the tensile strength, nanocomposites were prepared under identical conditions, but were degassed for a longer time and cured in an open mold so that all trapped air could escape. Fig. 7 shows the effect of degassing on the tensile strength of 3 wt.% clay nanocomposites. After processing with the new technique, the nanocomposite shows the same elastic modulus but about 45% higher tensile strength (58 MPa). This confirms that a higher strength can be achieved with a better degassing technique although the resulting strength is still lower than that of the pure epoxy (63 MPa). Furthermore, the same elastic modulus before and after degassing (Fig. 7) confirms the reproducibility of results obtained by mill mixing.

Fig. 8 shows the fracture surface of 7 wt.% clay nanocomposite. The bright spots correspond to the clay aggregates finely dispersed in the material. This observation confirms the inevitable aggregation of clay layers in this type of nanocomposites.

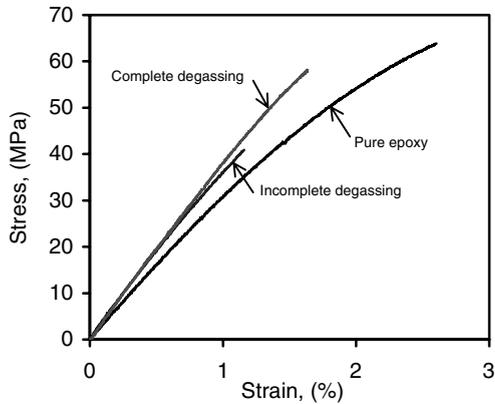


Fig. 7. Effect of degassing on the tensile strength of 3 wt.% clay nanocomposites.

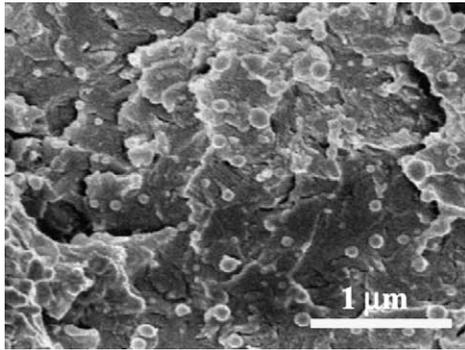


Fig. 8. SEM fractograph of 7 wt.% clay nanocomposite, showing clay aggregation on the fracture surface.

The presence of such clay aggregates in the microstructure of nanocomposites is also reported by Kornmann et al. [7] and Yasmin et al. [13]. These loose clusters or unexfoliated nanoparticles in the matrix may act as additional crack initiation sites by splitting up easily under applied load [5].

4. Conclusions

The compounding of clay nanocomposites with a three-roll mill is found to be highly appealing. It produces good dispersion of clay particles within a short period of time and also disordered intercalates with an average basal spacing higher than 5 nm regardless of clay content. Furthermore, it is environmentally friendly since no solvent is required.

The elastic modulus of the nanocomposites is found to increase with increasing concentration of clay and a maximum of 80% improvement is observed for an addition of 10 wt.% of clay. However, the decreasing rate of elastic modulus improvement with higher clay content can be attributed to the inevitable aggregation of clay particles. The apparent lower or no improvement in tensile strength of the nanocomposites over pure epoxy can be attributed to the clustering of nanoparticles and/or to the occasional occurrence of nano- to micro-size voids in the microstructure. The observed higher tensile strength with better degassing also confirms the importance of degassing in reducing the number of nano- to micro-size voids.

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References

- [1] Wang Z, Pinnavaia TJ. *Chem Mater* 1998;10:3769.
- [2] Vaia RA, Ishii H, Giannelis EP. *Chem Mater* 1993;5:1694.
- [3] Wei CL, Zhang MQ, Rong MZ, Friedrich K. *Comp Sci Tech* 2002;62:1327.
- [4] Jiankun L, Yucai K, Zongneng Q, Xiao-Su Y. *J Polym Sci: Part B* 2000;39:115.
- [5] Zerda AS, Lesser AJ. *J Polym Sci: Part B* 2001;39:1137.
- [6] LeBaron PC, Wang Z, Pinnavaia TJ. *J App Clay Sci* 1999;15:11.
- [7] Kornmann X, Lindberg H, Berglund LA. *Polymer* 2001;42:1303.
- [8] Vaia RA, Jandt KD, Kramer EJ, Giannelis EP. *Chem Mater* 1996;8:2628.
- [9] Nam PH, Maiti P, Okamoto M, Kotaka T, Hasegawa N, Usuki A. *Polymer* 2001;42:9633.
- [10] Liu X, Wu Q. *Polymer* 2001;42:10013.
- [11] Fornes TD, Yoon PJ, Keskkula H, Paul DR. *Polymer* 2001;42:9929.
- [12] Southern Clay Products, Inc., Technical data.
- [13] Yasmin A, Abot JL, Daniel IM. *Mat Res Soc Symp Proc* 2003;740:1.37.