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Effect of temperature, duration and speed of pre-mixing on the dispersion of clay/epoxy nanocomposites

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ABSTRACT

The effect of temperature, duration and speed of pre-mixing on the dispersion of organoclay in epoxy was studied. The technique of high-speed mixing process was used. Epoxy and Cloisite 30B were pre-mixed at different temperatures, different speeds and for different durations of time. The quality of dispersion and intercalation/exfoliation of organoclay in epoxy after pre-mixing (before adding hardener) was analyzed by means of X-ray diffraction (XRD) and viscosity measurement. The dispersion and intercalation/exfoliation of organoclay in the epoxy nanocomposites (ENCs) after curing were characterized by XRD, field emission gun scanning electron microscopy (FEGSEM) and TEM. The results illustrate that the clay particles were broken down to smaller and smaller sizes with increase of pre-mixing temperature and especially with increase in pre-mixing speed. These parameters do not significantly affect the intercalation/exfoliation of organoclay in epoxy at the pre-mixing step, but they have indirect effect on intercalation/exfoliation at the curing step.

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1. Introduction

Polymer-layered-silicate nanocomposites are becoming a very promising new class of materials. The intercalated or exfoliated forms of nanolayer silicates in many polymer systems have improved stiffness, strength, fracture toughness, fire resistance, barrier properties, and dimensional stability of the material [1–6]. The reinforcing ability of nanoclay is due to its high modulus, high strength and high aspect ratio. The greater is the exfoliation of the nanoclays in the polymer matrix, the greater is the reinforcing effect [2]. However, dispersion of organoclays in epoxy is a complex process, which takes place during the pre-mixing step and the curing step after mixing with hardener.

In general, there are several different possible levels of dispersion of organoclays in epoxy nanocomposites. They are depicted in Fig. 1 and can be classified as follows:

- The left side of Fig. 1a shows a typical clay aggregate. There are three multiple-stacks in this aggregate. Each multi-stack contains several stacks and each stack has many clay layers. When the clay aggregates are immersed in a solution such as that of an

epoxy resin, the resin molecules tend to diffuse into the space between the clay stacks.

- If there is significant break-up of the aggregate due to motions such as shearing, or collision against hard obstacles, the configuration of the clay structure is represented on the right side of Fig. 1b. Diffusion of the resin molecules always takes place.
- Fig. 1c shows the continuation of the breaking up of the clay aggregates after further diffusion.
- If the configurations in Fig. 1b and c are subjected to further breaking up by either shearing or collision against obstacles, the size of the stacks is reduced further to consist of a smaller number of layers per stack, as shown in Fig. 1d.
- Fig. 1e shows that the diffusion of the resin molecules may peel off individual layers or stack of layers.

The above shows that the mechanisms for breaking down the clay aggregates can be categorized in the following way:

1. By using mechanical forces such as shear or impact. Vaia et al. [7] suggested that the degree of exfoliation could be improved through the aid of conventional shear devices. They assumed that the individual plates peel apart through a combination of shear and diffusion of polymer chains in the organoclay gallery. Liu et al. [8–10] used a high-pressure mixing method with assistance of acetone solvent to improve the dispersion of clay in epoxy and observed significant improvement in fracture toughness of epoxy nanocomposites. Within this, higher shear was also applied on the clay particles.

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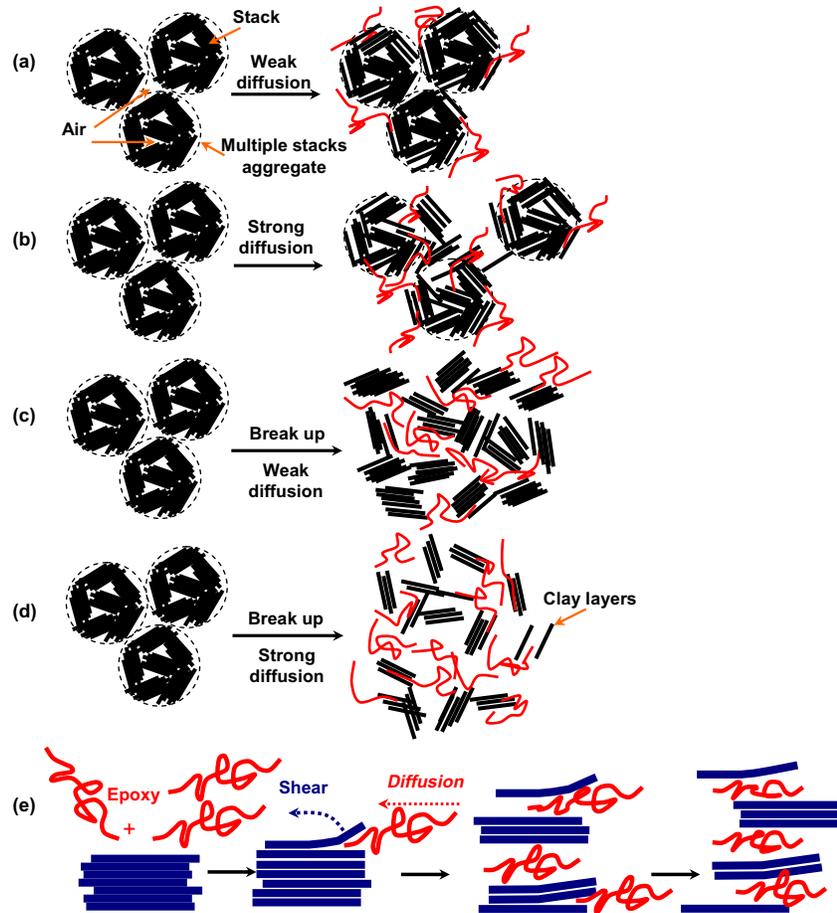


Fig. 1. Schematic graph for dispersion of clay.

2. By diffusion of the small molecules into the spaces between the clay sheets. The diffusion depends on the space between the clay sheets, the mobility of the resin molecules (which in turn depends on the viscosity of the liquid and its temperature), and on the thermodynamic forces holding the clay sheets together.

Researchers at Concordia have developed a technique (called high-pressure mixing technique) for the good dispersion of clays in epoxy, in which a microfluidizer controlled at 15,000 psi (103 MPa) was used [8–10]. However this technique utilizes solvent. To overcome the cumbersome aspect of solvent, another technique was used (called the high-speed mixing technique) [11]. Excellent results have been obtained. Fig. 2 shows the improvement in fracture toughness of two epoxy–clay material systems using this technique [11]. The strain energy release rate is increased from 100 J/m^2 to 1300 J/m^2 for one epoxy resin system. In the “high-speed mixing” process, the clay and epoxy were stirred with a homogenizer, equipped with a cylindrical rotor–stator mixing head of diameter 20 mm. Temperature and speed were controlled. In order to understand the effect of different parameters on the dispersion and thus the properties of the epoxy/clay nanocomposite materials made by this high-speed mixing technique, a systematic study of the effect of pre-mixing parameters was undertaken. These parameters are the effect of temperature, speed and duration of pre-mixing (note that pre-mixing means mixing of the clay in the epoxy without hardener, and mixing means the mixing of the hardener into the epoxy–clay system).

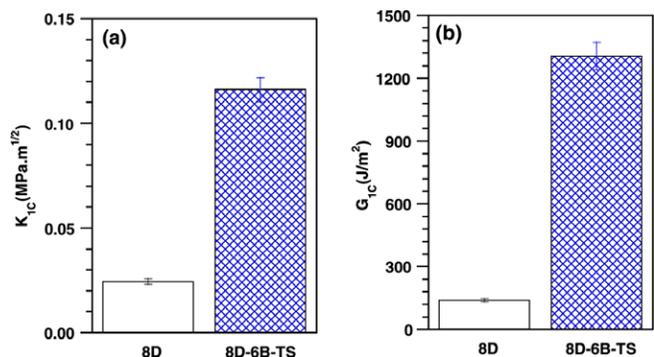


Fig. 2. Improvement of fracture toughness (K_{1c} and G_{1c}) for Epon 828-D2000 resin and its clay nanocomposite by pre-mixing at high-speed and high-temperature [11].

2. Experiments

The resin selected for this study was EPON™ 828, from Resolution Performance Products LLC (Houston, TX, USA). The hardener was amine-terminated polyoxypropylene Jeffamine® D-230, from Huntsman Corp. An organoclay recommended for use with amine-cured epoxy systems was used, namely Cloisite® 30B (montmorillonite treated with methyl tallow bis-(2-hydroxyethyl) quaternary ammonium) from Southern Clay Products Inc. (Gonzales, TX, USA). The amount of clay is 2 wt.%. Henceforth the hardener and clay are designated in shortened form as D230 and C30B,

Table 1
Parameters examined for the experiments.

| Experiment name | Temperature (°C) | Speed (rpm) | Duration (min) |
|-----------------------|------------------|-------------------------------|--------------------------|
| Effect of temperature | RT, 60, 120, 180 | 0, 24,000 | 60 |
| Effect of speed | RT, 120 | 0, 1000, 9500, 17,500, 24,000 | 60 |
| Effect of duration | RT, 120, 180 | 24,000 | 2, 4, 10, 20, 30, 45, 60 |

RT means room temperature.

respectively. The clay and epoxy were pre-mixed at different conditions as shown in Table 1. The suspensions of clay and epoxy were prepared by the high-speed mixing technique, in which clay and epoxy were stirred with a homogenizer, as mentioned above. These consist of four levels of temperature, five speeds and six durations of pre-mixing. Viscosity measurement at room temperature for epoxy–clay suspensions after pre-mixing was performed on a Brookfield CAP2000+ viscometer for the epoxy and the epoxy–organoclay suspensions using cone and plate geometry at room temperature. To evaluate the intercalation/exfoliation of the nanoclay in the polymer matrix, X-ray diffraction (XRD) patterns were obtained from the surface of the samples with a Bruker Discover 8 powder X-ray diffractometer with Cu K α radiation. A Hitachi-S4700 FEGSEM was used to observe the dispersion of clay in the epoxy matrix at the micro-level. Samples were cured either at room temperature for 2 days or at 120 °C for 2 h, with subsequent post cure at 140 °C for 2 h in both cases. To determine the T_g and to confirm the absence of any residual curing, the cured samples were heated in a Perkin–Elmer Pyris 1 DSC instrument using nitrogen atmosphere from 30 °C to 150 °C at 20 °C min⁻¹, then cooled to 30 °C at 20 °C min⁻¹ to minimize the enthalpy relaxation in the second heating scan, which involved reheating to 150 °C at 20 °C min⁻¹.

3. Results

3.1. Effect of pre-mixing temperature

3.1.1. Characteristics of liquid suspension of epoxy nanocomposites

The d -spacings of organoclay C30B alone and C30B in liquid epoxy resin after pre-mixing at different temperatures were examined by X-ray diffraction. The results are shown in Fig. 3 and Table 2. C30B has one peak at 4.8° and this is related to the d -spacing of 1.85 nm. It appears that in epoxy–clay mixtures, there are two distinct peaks at around 2.3–2.4° and 4.7–4.8°. This may be interpreted that they have two different extents of clay intercalation. According to Bragg's law, the harmonic peak (reflection peak) of the first one (around 2.3–2.4°) should be around the same location

Table 2
Effect of pre-mixing temperature and speed on d_{001} .

| Temperature (°C) | d_{001} (nm) | |
|------------------|---------------------|--------------------------|
| | Pre-mixing at 0 rpm | Pre-mixing at 24,000 rpm |
| RT | 3.72 | 3.80 |
| 60 | 3.72 | 3.80 |
| 120 | 3.74 | 3.81 |
| 180 | 3.76 | 3.81 |

at 4.6–4.8°. However, the coincidence is that this second peak is also located right at the position of the C30B peak (Fig. 3). Therefore it is not clear if the second peak may represent the harmonic of the first one or the remaining C30B (that has not been further intercalated by epoxy resin) or both. Because of this, it is difficult to say whether there is only one clay intercalation level in the mixtures of epoxy–clay (at the position of the first peak on XRD curves) or there are two different clay intercalation levels. It appears in the XRD curves that the first peak shifts to lower angle for all epoxy–clay mixtures compared to the peak of the starting clay C30B. A shift of the peak to lower angle proves that intercalation has taken place at pre-mixing step. The clay layer separation (degree of intercalation around 3.72–3.81 nm) is considerably higher than in the original C30B (1.85 nm). XRD curves for the epoxy–clay mixtures prepared at different temperatures and speeds show very similar trends and clays have been well further intercalated by the epoxy resins at the pre-mixing step.

It can also be seen that even hand mixing (designated as 0 rpm) can also produce intercalation. This means liquid epoxy resin can easily diffuse into the clay galleries and further intercalate the clay even without the presence of mechanical stirring. It also can be seen that there is a small increase in the d -spacing for epoxy–clay mixture which was prepared at high temperature (180 °C, 120 °C, and 60 °C) compared to the mixture which was prepared at room temperature. Also the intercalation of clay in epoxy is slightly increased for pre-mixing at 24,000 rpm as compared to hand mixing.

The viscosities of the epoxy–clay suspensions were measured with a Brookfield CAP2000+ viscometer, using cone and plate geometry (samples were cooled down to RT before the measurement was done). Fig. 4 shows the viscosity–shear rate curves at 25 °C of epoxy EPON 828 and its mixtures with organoclay C30B after being pre-mixed at different temperatures for 0 rpm and 24,000 rpm. There is only a slight decrease in the viscosity of EPON 828 with the shear rate; thus this epoxy resin can be considered as a Newtonian fluid more or less. With the presence of clay, the viscosity of the epoxy–clay suspension is higher than that of pure epoxy. However, the viscosity of epoxy–clay also decreases with the shear rate. The effect of pre-mixing temperature on the viscosity of epoxy–clay mixture at shear rates of 167 s⁻¹ and 667 s⁻¹ are

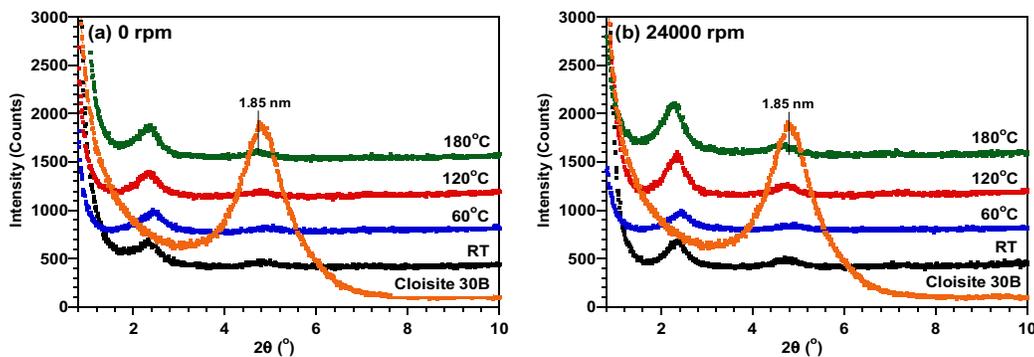


Fig. 3. X-ray diffraction curves of C30B and its EPON828–C30B mixtures after being pre-mixed at different temperatures for (a) 0 rpm (by hand) and (b) 24,000 rpm.

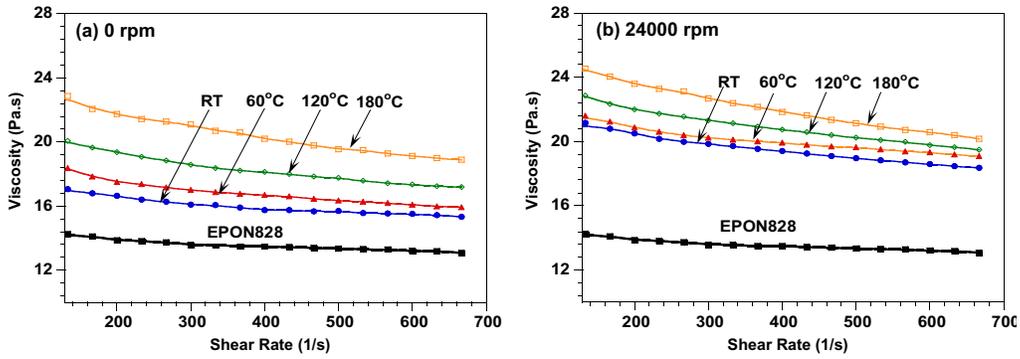


Fig. 4. Viscosity–shear rate curves of EPON828–C30B mixtures after being pre-mixed at different temperatures for two speeds: (a) 0 rpm and (b) 24,000 rpm.

shown in Fig. 5. Pre-mixing at high temperature for both 0 rpm and 24,000 rpm showed higher viscosity compared to pre-mixing at room temperature. This is due to finer dispersion of the clay when pre-mixing is done at higher temperature (due to lower thermodynamic forces holding the clay sheets together and due to higher mobility of the resin molecules).

3.1.2. Characteristics of cured epoxy nanocomposites

The pre-mixed samples were cured at room temperature and at 120 °C. X-ray diffraction curves of the epoxy nanocomposites pre-mixed at room temperature and 120 °C are shown in Fig. 6. The summary of the first peak positions (d_{001}) on the XRD curves is shown in Table 3. It is observed that with the same curing temperature, pre-mixing at higher temperature shows somewhat better intercalation than pre-mixing at room temperature. In addition, it is also noticed that higher curing temperature leads to better clay

intercalation as observed by the reduction of the intensity or the asymmetry of the XRD peak. This behavior can be explained by the high mobility of the molecules at higher temperature. In the case of pre-mixing, higher mobility of the epoxy molecules allows

Table 3

Summary of XRD results of epoxy nanocomposites with 2 wt.% C30B pre-mixed at different temperatures then cured at room temperature and 120 °C.

| Pre-mixing temperature (°C) | d_{001} (nm) | |
|-----------------------------|---------------------|------------------|
| | Pre-mixing at 0 rpm | |
| | Curing at RT | Curing at 120 °C |
| RT | 3.73 | 3.76 |
| 60 | 3.72 | 3.81 |
| 120 | 3.83 | 3.84 |
| 180 | 3.92 | 3.93 |

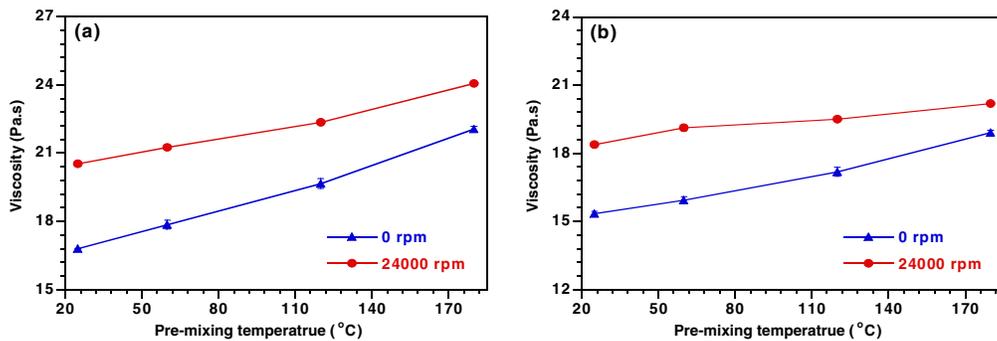


Fig. 5. Effect of pre-mixing temperature on viscosity of EPON828–C30B after being pre-mixed at 0 rpm and 24,000 rpm for 60 min at shear rate (a) 167 s⁻¹ and (b) 667 s⁻¹.

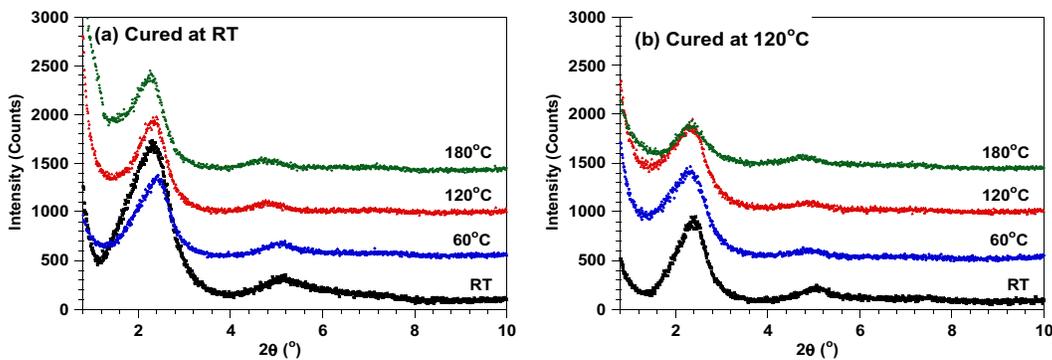


Fig. 6. X-ray diffraction curves of samples pre-mixed at different temperatures and cured at (a) room temperature and (b) 120 °C.

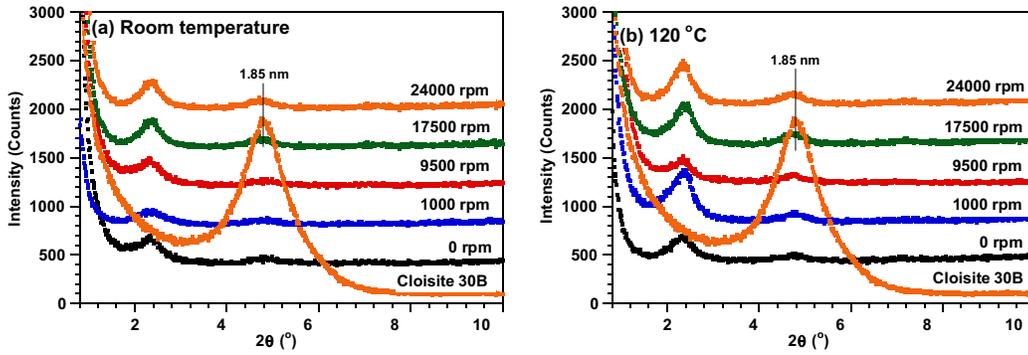


Fig. 7. X-ray diffraction curves of C30B and its EPON828–C30B mixtures after being pre-mixed at different speeds: (a) room temperature and (b) 120 °C.

Table 4

The effect of pre-mixing speed on d_{001} of EPON828–C30B mixtures.

| Speed (rpm) | d_{001} (nm) | |
|-------------|------------------|----------------------|
| | Pre-mixing at RT | Pre-mixing at 120 °C |
| 0 | 3.72 | 3.74 |
| 1000 | 3.73 | 3.76 |
| 9500 | 3.78 | 3.80 |
| 17,500 | 3.79 | 3.80 |
| 24,000 | 3.80 | 3.81 |

them to better penetrate into the space between the clay sheets and help to disperse the clay sheets. In the case of curing at higher temperature, higher mobility of the curing agent molecules allow them to penetrate into the spaces between the clay sheets and react with the epoxy molecules already in there. This also helps to disperse the clay sheets [12]. This indicates that pre-mixing and curing temperatures play a very important role in clay intercalation.

3.2. Effect of pre-mixing speed

3.2.1. Liquid suspension

The effect of pre-mixing speed on the intercalation/exfoliation of clay in epoxy was examined by XRD. The results are shown in Fig. 7 and Table 4. There is only a slight increase in d -spacing for epoxy–clay mixture with increase of the pre-mixing speed. It is also noted here that for pre-mixing at 120 °C, the d -spacing is almost stable for pre-mixing speeds above 10,000 rpm. The result also confirms that there is a slight increase in d -spacing for epoxy–clay mixture which was pre-mixed at high temperature (120 °C) compared to the epoxy–clay mixture which was pre-mixed at room temperature.

Fig. 8 shows the viscosity–shear rate curves at 25 °C of epoxy EPON 828 and its mixtures with organoclay C30B after being pre-mixed at different speeds of 0 rpm, 1000 rpm, and 24,000 rpm for two different temperatures (room temperature and 120 °C). In general, pre-mixing at higher speed for both room temperature and 120 °C resulted in a higher viscosity suspension compared to that at low speed. The effect of pre-mixing speed on the viscosity of epoxy–clay mixtures at shear rates of 167 s⁻¹ and 667 s⁻¹ is shown in Fig. 9. As discussed above, the increase in the viscosity of the suspension may be due to the reduction of size of particles and higher aspect ratio of clay particles after being pre-mixed at high speed compared to hand mixing.

3.2.2. Characteristics of cured samples

X-ray diffraction curves of the epoxy nanocomposites based on Cloisite 30B that were pre-mixed at different speeds and cured are shown in Fig. 10. The summary of the first peak positions (d_{001}) on the XRD curves of the epoxy–clay mixtures is shown in Table 5. The results indicate that the higher is the pre-mixing speed, the better is the intercalation/exfoliation for curing at both room temperature and 120 °C. Although pre-mixing speed does not show a strong effect on the intercalation/exfoliation of clay at the pre-mixing step, it has a significant effect on the intercalation/exfoliation of the clay at the curing step. The higher is the speed of pre-mixing the better is the intercalation/exfoliation of clay after cure. Again, the results confirm that the high curing temperature also leads to a better clay intercalation/exfoliation.

3.3. Effect of pre-mixing duration

3.3.1. Liquid suspension

The results for liquid epoxy–clay after pre-mixing experiments at high speed (24,000 rpm) at room temperature, 120 °C, and

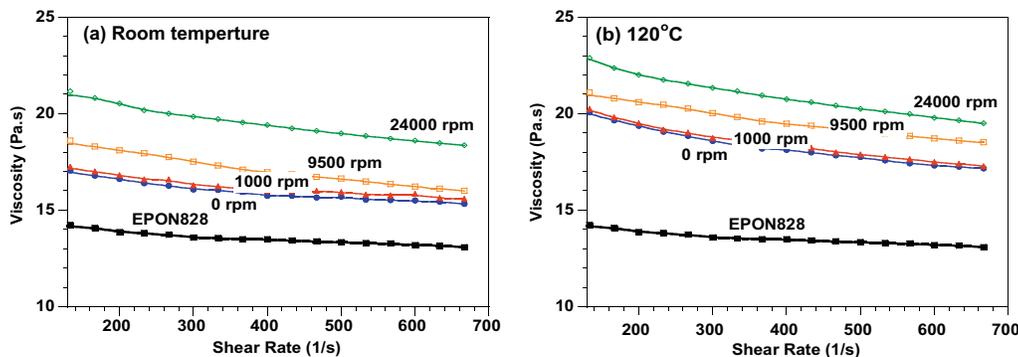


Fig. 8. Viscosity–shear rate curves of EPON828–C30B mixtures after being pre-mixed at different speeds for (a) room temperature and (b) 120 °C.

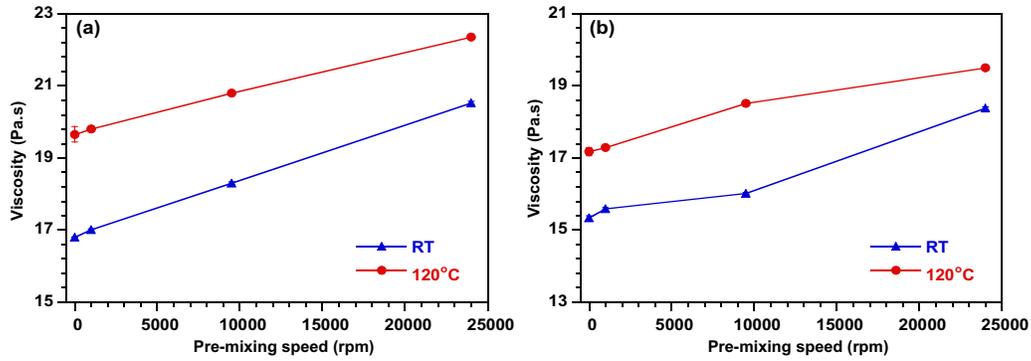


Fig. 9. The effect of pre-mixing speed on viscosity of EPON828–C30B after being pre-mixed at room temperature and 120 °C for 60 min at shear rate (a) 167 s⁻¹ and (b) 667 s⁻¹.

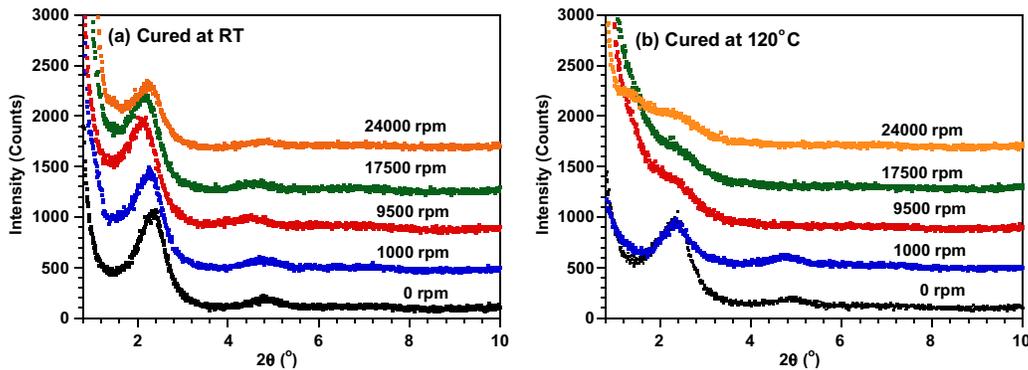


Fig. 10. X-ray diffraction curves of nanocomposites at 2 wt.% C30B pre-mixed at different speeds and cured at (a) room temperature and (b) at 120 °C.

Table 5

Summary of XRD results of epoxy nanocomposites with 2 wt.% C30B pre-mixed at different speeds then cured at room temperature and 120 °C.

| Pre-mixing speed (rpm) | <i>d</i> ₀₀₁ (nm) | |
|------------------------|------------------------------|------------------|
| | Pre-mixing at 120 °C | Curing at 120 °C |
| 0 | 3.83 | 3.84 |
| 1000 | 3.86 | 3.86 |
| 9500 | 3.97 | 3.95 |
| 17,500 | 3.95 | 3.95 |
| 24,000 | 4.01 | 4.03–6.69 |

180 °C for different pre-mixing durations are shown in Fig. 11. The summary of the first peak positions (*d*₀₀₁) on the XRD curves of the

epoxy–clay mixtures is shown in Table 6. The results show that there is only a very small effect of pre-mixing duration and pre-mixing temperature on the XRD peak positions. Therefore one can conclude that pre-mixing temperature and duration do not significantly affect the intercalation/exfoliation of clay in epoxy resin at this step of fabrication (for pre-mixing speed of 24,000 rpm). The results also indicated that full exfoliation can not be achieved at the pre-mixing step based on the presence of the peaks on the XRD curves. Even though the pre-mixing duration and pre-mixing temperature do not show a strong influence on intercalation/exfoliation of clay in epoxy resin at this step, this does not mean that they do not have an effect on the quality of micro-dispersion of clay in epoxy in the curing step.

The viscosities of the epoxy–clay suspensions with C30B after being pre-mixed at room temperature and at 120 °C for different

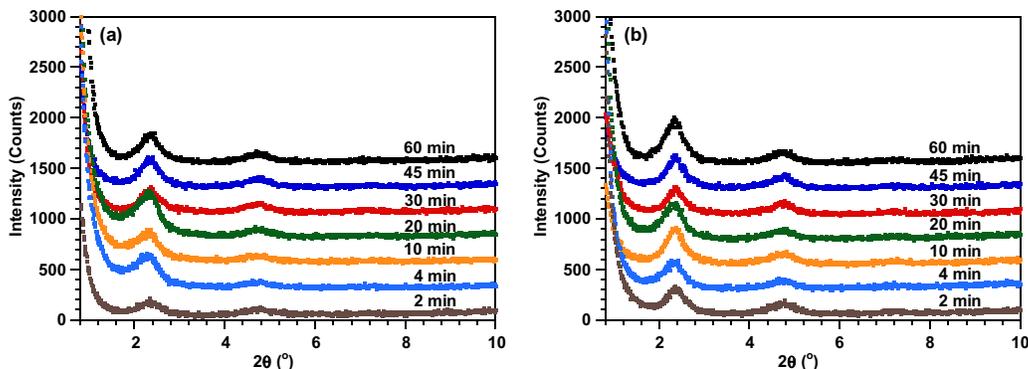


Fig. 11. X-ray diffraction curves of EPON828, C30B and EPON828–C30B mixtures after being pre-mixed at (a) room temperature, (b) 120 °C, and (c) 180 °C for different durations (24,000 rpm).

Table 6The effect of pre-mixing duration and temperature on d_{001} .

| Pre-mixing duration (min) | d_{001} (nm) | | |
|---------------------------|------------------|----------------------|----------------------|
| | Pre-mixing at RT | Pre-mixing at 120 °C | Pre-mixing at 180 °C |
| 2 | 3.74 | 3.74 | 3.76 |
| 4 | 3.76 | 3.76 | 3.77 |
| 10 | 3.78 | 3.79 | 3.77 |
| 20 | 3.79 | 3.79 | 3.79 |
| 30 | 3.79 | 3.79 | 3.80 |
| 45 | 3.80 | 3.79 | 3.80 |
| 60 | 3.80 | 3.81 | 3.80 |

pre-mixing durations were also examined at room temperature (suspensions were cooled down before measurement was done). Fig. 12 shows the viscosity of the EPON828–C30B mixtures. The results indicate that the viscosity of the suspension increases with pre-mixing duration. The increase in viscosity of the epoxy–clay suspension may be related to the level of micro-dispersion of the clay in the epoxy [13]. The clay particles (agglomerates) were broken down into smaller, higher-aspect-ratio particles with longer duration of pre-mixing and this results in an increase in the viscosity. In addition, for the same pre-mixing duration, the viscosity of epoxy–clay suspension prepared at 120 °C is always higher than the viscosity of suspension prepared at room temperature. This indicates better dispersion of clay in epoxy prepared at 120 °C compared to room temperature.

3.3.2. Cured samples

In order to study the effect of pre-mixing conditions on the intercalation/exfoliation of the cured epoxy nanocomposites

(ENCs), the samples were cured at room temperature and at 120 °C and subjected to XRD analysis. The XRD curves for these samples are shown in Figs. 13–15. A summary of the first peak positions (d_{001}) of the mixtures and their T_g is given in Table 7. There are two peaks at around 3.90 nm and 1.85 nm on each XRD curve for all ENCs cured at room temperature independent of pre-mixing time and temperature (Figs. 13a, 14a and 15a). It is not clear whether the peak corresponding to 1.85 nm arises from undispersed C30B (it matches the peak shown by neat C30B powder) or whether it is a harmonic of the first peak or both. However, the longer is the duration of pre-mixing, the lower is the intensity of the XRD peaks. A reduction in the peak intensity indicates that the amount of intercalated clay has decreased, or in other words, the dispersion has been improved by breakdown of clusters or even exfoliation. The improvement of dispersion and intercalation/exfoliation by duration of pre-mixing can be understood by better diffusion of epoxy and hardener into the clay galleries. With longer duration of pre-mixing, smaller aggregates can be achieved. Because of this, epoxy and hardener have more chance to penetrate to further expand the clay galleries at the curing step. When ENCs were cured at 120 °C after being pre-mixed at room temperature, the two peaks on the XRD curves still remain at 3.90 nm and 1.85 nm (Fig. 13b) for pre-mixing durations up to 1 h. However, only one peak at 3.90 nm can be seen clearly for the ENCs which were pre-mixed for 10–30 min at 120 °C (Fig. 14b). The second peak at 1.85 nm has almost disappeared. In addition, the two peaks appear again but at 6.70 nm and 3.90 nm for those samples pre-mixed at longer durations of 45–60 min. For samples pre-mixed at 180 °C, there are two peaks on the XRD curves at 6.70 nm and 3.90 nm (Fig. 15b) for all cases of pre-mixing duration. This could be interpreted as indicative of two different extents of clay interca-

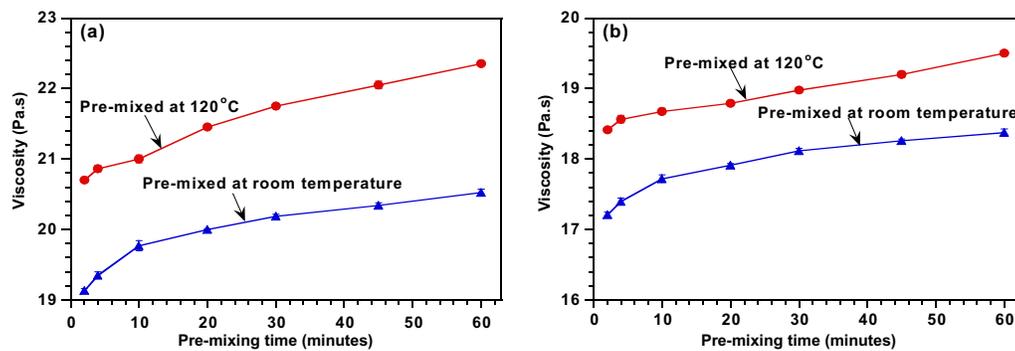


Fig. 12. Viscosity of EPON828–C30B mixtures after being pre-mixed for different durations at room temperature and 120 °C at shear rate (a) 167 s^{-1} and (b) 667 s^{-1} .

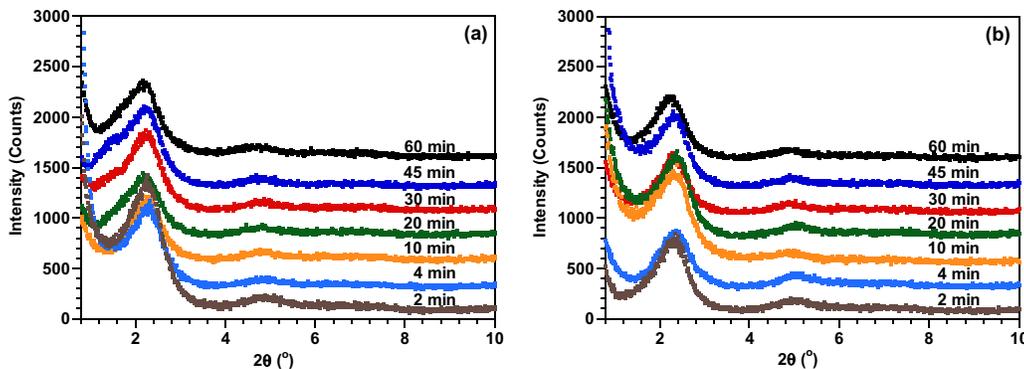


Fig. 13. X-ray diffraction curves of nanocomposite pre-mixed at room temperature for different durations and cured at (a) room temperature and (b) 120 °C.

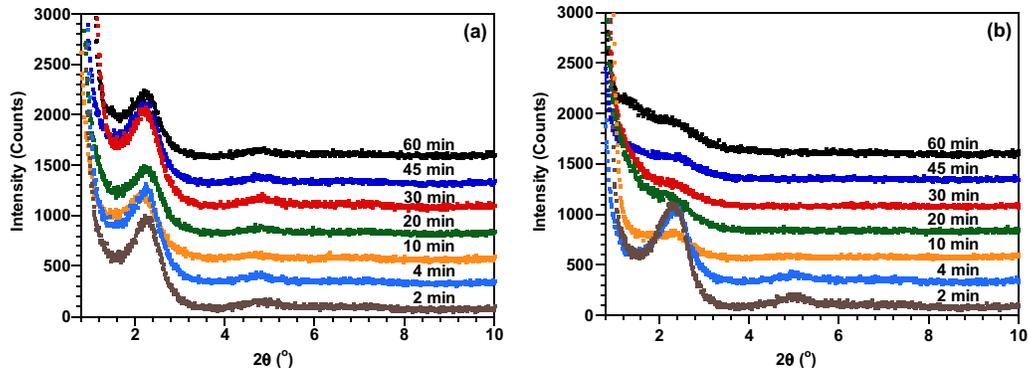


Fig. 14. X-ray diffraction curves of nanocomposite pre-mixed at 120 °C for different durations and cured at (a) room temperature and (b) 120 °C.

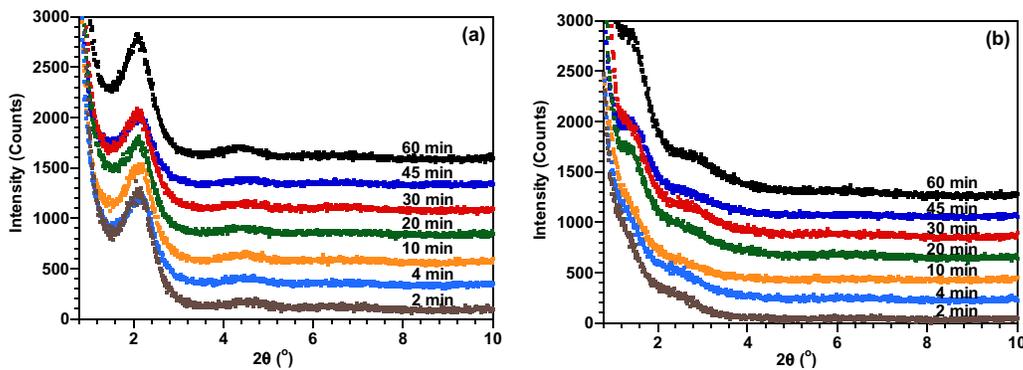


Fig. 15. X-ray diffraction curves of nanocomposite pre-mixed at 180 °C for different durations and cured at (a) room temperature and (b) 120 °C.

Table 7

Summary of XRD, and T_g results of epoxy nanocomposites pre-mixed at different durations then cured at room temperature or 120 °C.

| Duration of pre-mixing (min) | d_{001} (nm) | | T_g (°C) |
|------------------------------|----------------|------------------|----------------|
| | Curing at RT | Curing at 120 °C | |
| <i>Pre-mixing at RT</i> | | | |
| 2 | 3.79 | 3.80 | 86.8 ± 1.5 |
| 4 | 3.80 | 3.81 | – |
| 10 | 3.85 | 3.85 | – |
| 20 | 3.86 | 3.85 | – |
| 30 | 3.90 | 3.88 | – |
| 45 | 3.93 | 3.94 | – |
| 60 | 3.91 | 3.95 | 87.1 ± 1.2 |
| <i>Pre-mixing at 120 °C</i> | | | |
| 2 | 3.81 | 3.81 | 86.5 ± 2.0 |
| 4 | 3.81 | 3.81 | – |
| 10 | 3.87 | 3.88 | – |
| 20 | 3.86 | 3.88 | – |
| 30 | 3.88 | 3.92 | – |
| 45 | 3.94 | 4.02–6.67 | – |
| 60 | 3.95 | 4.03–6.69 | 86.9 ± 1.4 |
| <i>Pre-mixing at 180 °C</i> | | | |
| 2 | 4.18 | 6.43 | 87.0 ± 1.9 |
| 4 | 4.18 | 6.49 | – |
| 10 | 4.21 | 6.49 | – |
| 20 | 4.23 | 6.52 | – |
| 30 | 4.20 | 6.55 | – |
| 45 | 4.21 | 6.56 | – |
| 60 | 4.26 | 6.62 | 87.3 ± 1.6 |

Note: T_g was for samples after cured at 120 °C.

T_g of the cured epoxy sample without clay is 86.8 ± 1.3 °C.

T_g of the epoxy samples without clay after pre-mixed at 24,000 rpm for 1 h at 120 °C and at 180 °C is 86.9 ± 2.1 and 86.5 ± 1.5 °C, respectively.

lation. In this case, the first peak at 6.70 nm would represent newly intercalated clay that just appeared, while the second peak at 3.90 nm would represent a lower degree of clay intercalation (like the first peak in the previous cases). Note that curing at 120 °C results in better intercalation/exfoliation than curing at room temperature. This can be explained by the fact when the temperature increases, the mobility of epoxy and hardener molecules increase and because of this, they can diffuse more easily into the clay galleries and further intercalate or exfoliate the clay [2,12]. The best nanocomposite preparation conditions are pre-mixing at 180 °C and curing at 120 °C. Generally speaking, the duration of pre-mixing does not contribute to the exfoliation of clay in epoxy. However, it has an influence on the dispersion of organoclay in epoxy resin at the micro level, and thus facilitates the diffusion of epoxy and hardener at the curing step. The results also show that the presence of C30B and mixing conditions does not influence the T_g of epoxy.

The effect of pre-mixing temperature, speed and duration on the dispersion of C30B in epoxy matrix was also observed by FEG-SEM. FEGSEM photos of the epoxy nanocomposites based on EPON828–D230 with 2 wt.% of C30B for different pre-mixing durations are shown in Fig. 16. The bright spots on the back-scattered images correspond to clay aggregates. Apparently, a portion of the clay remains at the micro-scale level with different size populations of clay aggregates depending on the pre-mixing conditions. The clay particles are slightly more uniformly and finely dispersed in epoxy that was prepared at high-temperature compared to room temperature. In the absence of high-speed pre-mixing, Fig. 16b (120 °C) shows a greater density of small particles and a lower density of large particles than Fig. 16a (RT). The increase in the distribution and reduction of the size of the clay aggregates indicates

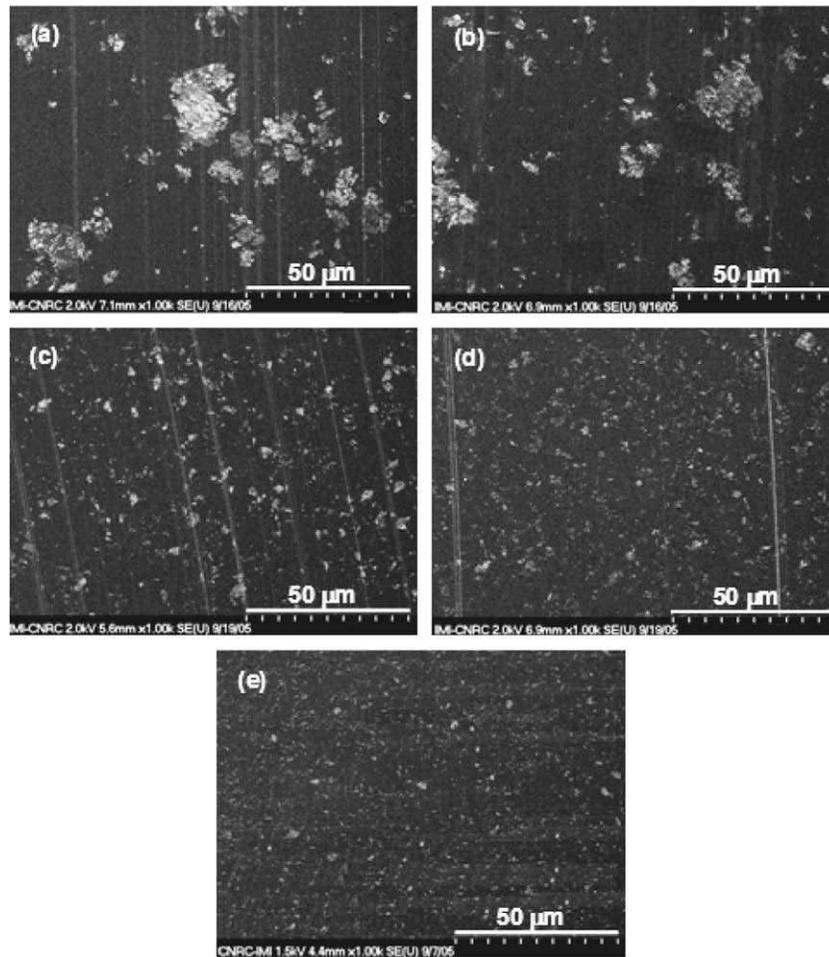


Fig. 16. SEM photos of nanocomposites: pre-mixed at room temperature with 0 rpm. (a) Pre-mixed at 120 °C for: (b) 0 min with 0 rpm, (c) 2 min with 24,000 rpm, (d) 10 min with 24,000 rpm, and (e) 60 min with 24,000 rpm.

that high-temperature pre-mixing has a positive effect on the general dispersion of the clay in the materials, demonstrating that the thermodynamics of the system plays an important role in the clay dispersion. Fig. 16b–e indicates that clay aggregates have been broken down to smaller sizes with increase in the pre-mixing duration. It proves that the size of aggregates is smaller with longer pre-mixing duration and this can help to improve the level of intercalation and exfoliation of epoxy nanocomposites during the curing step. The TEM photos of the epoxy nanocomposites for two different pre-mixing durations are shown in Fig. 17. Again, this confirms that the pre-mixing duration and pre-mixing speed have an effect on the size reduction of clay aggregates. Similar results were also obtained with other clay loadings of 4 wt.% and 6 wt.% [11].

The efficiency of the high speed pre-mixing method is illustrated by comparison with results obtained using other mixing methods. Comparison is based on XRD curves and on micrographs obtained from FEGSEM and TEM. Dispersion using high speed pre-mixing produces clay aggregates with average size of around 0.4 μm and maximum size of 2 μm, and with intergallery distance of 4.03–6.69 nm. Dispersion using a direct pre-mixing method with mechanical stirrer produces clay aggregates of average size around 6 μm and many large aggregates of greater than 25 μm [2,6,8]. Direct pre-mixing carried out by the authors (pre-mixing at below 1000 rpm) produces aggregates with average size around 3–5 μm and many large aggregates more than 23 μm. From TEM pictures, high-speed pre-mixing at 24,000 rpm breaks the clay

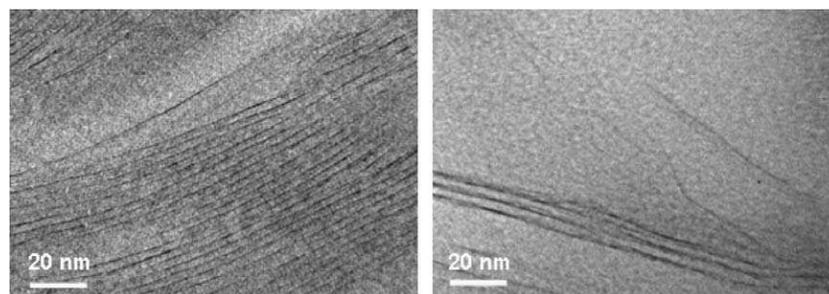


Fig. 17. TEM photos of nanocomposites: Pre-mixed at 120 °C for: (a) 0 min with 0 rpm and (b) 60 min with 24,000 rpm.

aggregates down to smaller particles consisting of about four clay platelets. High pressure pre-mixing method with solvent assistance produces aggregates of around six clay platelets [9]. Luo and Daniel [14] mixed Cloisite 30B clays in epoxy with the assistance of acetone solvent and sonication. They reported that the *d*-spacing of Cloisite 30B increased from 1.85 nm to 3.4–3.8 nm, and the TEM shows stacks of more than ten clay platelets.

4. Discussion

The use of high-speed mixing may cause breaking up of the clay sheets (which reduce their aspect ratio). It may also cause high temperature rise in the sample. These may give rise to degradation. However measurement of T_g (Table 7) shows that T_{gs} are not affected by high-speed mixing. Tensile strengths of the samples also do not seem to be affected [11].

5. Conclusions

The effects of temperature, speed, and time at the pre-mixing step on the dispersion and intercalation/exfoliation of clay in epoxy resin have been studied. Pre-mixing temperature, speed and time do not significantly affect the intercalation of organoclay at the pre-mixing step. However they have a positive effect on the dispersion of nanoclay into smaller aggregates. In addition, speed is more powerful than temperature in terms of clay dispersion. Fine dispersion and distribution was achieved with pre-mixing at 120 °C and 24,000 rpm.

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