EFFECT OF SHEARING ON DISPERSION, INTERCALATION/EXFOLIATION OF CLAY IN EPOXY

Tri-Dung Ngo*, Van-Suong Hoa*, Minh-Tan Ton-That*
* Department of Mechanical & Industrial Engineering, Concordia University, Montreal, Quebec, Canada, H3G 1M8, ** National Research Council Canada, Industrial Materials Institute, Boucherville, Quebec, Canada, J4B 6Y4

Keywords: *nanoclay, epoxy, nanocomposites, mixing, shear, dispersion and mechanical properties.*

Abstract

Nanocomposites from Shell EPON828 and Jeffamine D230 (D230) were prepared by different mixing methods which can generate different shear forces such as mechanical stirrer, microfluidizer and homogenizer. An organoclay Cloisite 30B (montmorillonite treated with a quaternary ammonium intercalant) was used. The quality of dispersion and intercalation/exfoliation was analyzed by XRD, FEGSEM and TEM. The tensile and compressive properties of the epoxy and epoxy nanocomposites (ENC) were also determined.The result indicates that well dispersed and well intercalated/exfoliated ENC is achieved with a non solvent assistance method. It is also found that with finer and more uniform dispersion of the clay in ENC achieved by this solvent free method the tensile strength is improved.

1 Introduction

Processing parameters have important influence on the dispersion of clay in polymer. This in turn has effect on physical and mechanical properties of nanocomposites. Dispersion process parameters mainly include mixing temperature and time, speed and time of stirring, power of ultrasonic tooling, shearing forces etc. Direct mixing of organoclay and epoxy with mechanical stirring and sonication is widely used to disperse nanoclay in epoxy [1, 2, 3, 4, 5]. However it is not enough for well dispersion of clay in epoxy. Yasmin et al. [6] used a three-roll mill to disperse the clay nanoparticles in an epoxy matrix and improved distributions of nanoclay particles in epoxy. Chen and Tolle [7] achieved the fully exfoliated layer silicate epoxies by high-shear mixing in the presence of acetone. Liu et al. [8, 9, 10] used a high pressure mixing method with assistance of acetone solvent to improve the dispersion of clay in epoxy and obtained strong improvement on fracture toughness of epoxy nanocomposites. However, a lot of solvent were used as well as time was required for removing the solvent. There is still work to be done to develop nanocomposites with fine dispersions and exfoliated morphologies. Achieving such morphologies with epoxy-based nanocomposites is a challenge, since high shear is always required but epoxy has low viscosity. In this paper, exploration of a different way to generate the shear in order to improve the quality of dispersion and intercalation/exfoliation of clay in epoxy is discussed.

2 Experimental

Epoxy and clay were mixed together by different devices. The first one was a room temperature without mechanical shear process (Rm), in which the clay and epoxy were stirred at room temperature by hand at 100 rpm for a few minutes then kept at room temperature for 1 hour. The second one was a high temperature without shear process (Tm), in which the clay and epoxy were stirred at 120°C by hand at 100 rpm for a few minutes then kept in an oven at 120°C for 1 hour. The third method was a high temperature with low speed process (TM), in which the clay and epoxy were stirred at 120°C for 1 hour by a mechanical stirrer at 1000 rpm. The fourth one was a room temperature and high speed process (RS), in which the clay and epoxy were stirred at room temperature by a homogenizer at high speed of 24000 rpm for 1 h. The fifth method was a high temperature and high speed process (TS), in which the clay and epoxy were stirred at 120°C by a homogenizer at high speed of 24000 rpm for 1 h. The sixth one was a high pressure process (HP), in which organoclay was first dispersed in acetone (about 8% of organoclay in acetone) to form a suspension with

TRI-DUNG NGO*, Van-Suong Hoa*, Minh-Tan Ton-That**

microfluidizer (15000 psi ≈ 103.42 MPa), and then the suspension was added into the epoxy resins as used by Liu et al. [8, 9, 10]. The desired amount of paste of organoclay and acetone was added to epoxy resin and then the mixture was stirred by hand at room temperature. When the epoxy was visibly dispersed, the mixture was mechanically stirred at 1000 rpm in a fume hood at room temperature for 30 minutes, followed by slow heating to 80°C for 1 hour. Finally, the mixture was degassed under vacuum at 95°C for 30 minutes. For curing, the required amount of hardener was mixed with epoxy or epoxy-clay mixtures at room temperature for 5 min then subjected to vacuum. Samples were cured either at room temperature for 2 days or at 120°C for 2 hours, with subsequent post cure at 140°C for 2 hours in both cases.

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 CuKα radiation. A Hitachi-S4700 FEGSEM was used to observe the dispersion of clay in the epoxy matrix at the micro-level. For clay dispersion at the nano-level, ultra-thin (50 to 80 nm) sections of nanocomposite samples were prepared with a cryoultramicrotome and supported on a copper 200 mesh grid for observation with a Hitachi H9000 TEM. The tensile and compression properties of the epoxy system with and without clay were determined at room temperature and 50% relative humidity according to ASTM D638-2002 and ASTM D695-2002 on an Instron 5500R machine, with crosshead speeds of 5 mm/min and 1.3 mm/min, respectively.

3 Results

X-ray diffraction curves of the epoxy and its nanocomposites based on C30B and made by different stirring methods are illustrated in Figures 1 and 2. In all nanocomposite samples the clay layer separation (degree of intercalation) is considerably higher than in the original C30B. Clays have been well further intercalated by the epoxy matrix for both curing at room and high temperatures.
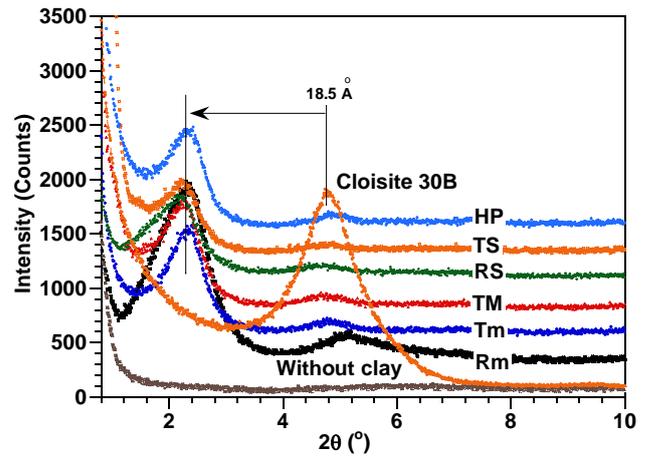
Fig. 2. X-ray diffraction curves of EPON828-D230 system, C30B and their nanocomposites at 2 wt% C30B made by different methods and cured at RT
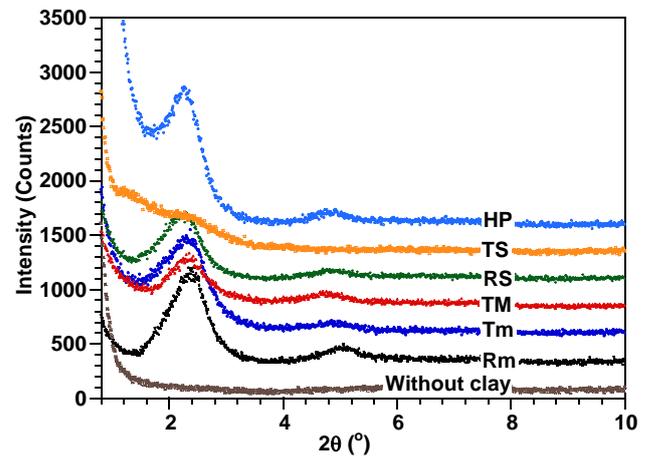
Fig. 2. X-ray diffraction curves of EPON828-D230 system, C30B and their nanocomposites at 2 wt% C30B made by different methods and cured at 120°C for 2 h

When samples were cured at room temperature (RT), there is no significant difference between the positions of the peak on the XRD curves. However, the intensity (area under the peak) changed depending on stirring methods. At the same loading level of 2 wt% C30B, the ENC made by high temperature method (Tm) shows better intercalation than the ENC made by room temperature method (Rm). The intensity of the XRD peak for stirring with Tm is lower than for stirring with Rm. This means that stirring at high temperature leads to better delamination of clay than stirring at room temperature. On comparing between high speed at high temperature (TS) and high speed at room temperature (RS), the same phenomenon occurred for two ENCs prepared by these stirring methods.

High speed at high temperature stirring (TS) also shows better intercalation/exfoliation than mechanical stirring (1000 rpm) at high temperature (TM) and just high temperature (Tm). This indicates the effect of shear on the level of intercalation/exfoliation of clay in epoxy nanocomposites.

Curing at high temperature (120°C) provides better intercalation/exfoliation as compared to curing at room temperature. With the same stirring method, the intensity of the XRD peak is lower for curing at 120°C than for 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 [4, 11]. A similar effect can be seen here on the intercalation/exfoliation of clay in epoxy matrix when temperature and speed were introduced at the stirring step. The intensity of the peak for ENC became smaller when the temperature and speed were introduced in the stirring step. The orders of intercalation/exfoliation are now TS > RS, TM > Tm > Rm, TS > TM > Tm and RS > Rm. Note that there is little difference in intensity of the peak between Tm and TM. It can also be seen that there are two peaks in all the XRD curves for ENCs prepared by the Rm, Tm, TM, RS, HP and TS methods. For ENC which was prepared by Rm, Tm, TM and RS, the two peaks were at around 2.3^o and 4.8^o. However, the peaks shifted to lower angles for the TS method. They are located at 1.3^o and 2.2^o, corresponding to *d*-spacings of 66.9 Å and 40.3 Å, respectively. The TS method shows better intercalation/exfoliation as compared to HP, RS, TM, Tm and Rm methods. The intensity of XRD peaks of ENC made by HP method is lower than for the RS method. In addition the XRD peak is more asymmetric for the ENC made by HP method compared to the RS method. It is believed that the HP method gives better intercalation/exfoliation than RS although the *d*-spacing is a little lower for HP than RS method. In general, it can be noted here that the level of intercalation and exfoliation of clay in epoxy nanccomposites is in the following order: TS > HP > RS > TM > Tm > Rm. The explanation for the better intercalation/exfoliation at this step with ENC prepared with the high speed and temperature stirring methods is that the high speed and temperature helped to break down the clay aggregates to smaller sizes and improve dispersion

of clay in the epoxy resin (more homogenous dispersion) during the stirring step. Because of this it can have an indirect effect on the intercalation/exfoliation of clay in epoxy matrix at the curing step. Epoxy and hardener have more chance to diffuse into the clay galleries (for the smaller aggregates and uniform distribution than the large aggregates and not uniform distribution) and further expand the distance between clay platelets especially with high temperature curing when the mobility of the molecules increases.

The microstructures of ENC based on C30B and made by different stirring methods are illustrated by SEM and presented in Figure 3. The bright spots on the backscattered images correspond to clay aggregates. Apparently, a portion of the clay remains at the micro-scale level with different size populations depending on the stirring conditions. However, due to the limitation of the SEM, one should not rule out the possibility that some exfoliation does take place. The size of aggregates is reduced significantly with high speed (Figure 3b) as compared to mechanical stirring (Figure 3a). The size of aggregates became much smaller when both high speed and temperature were introduced at the stirring step (Figure 3c). The result also confirms that the micro dispersion of ENC made by different stirring methods follows the order TS > HP > RS > TM > Tm > Rm. The average size of clay aggregates greatly decreased to below 1.0 µm and uniform distribution in epoxy system is obtained with TS method. This is much smaller size compared to direct mixing method with mechanical stirrer (around 3.0 µm and many large aggregates in ENC). During mixing, shear forces broke down clay aggregates to smaller sizes. This has indirect effect on intercalation/exfoliation of clay in epoxy at curing step especially at high temperature.

Figure 4 shows the TEM photo of nanocomposite prepared by the TS technique (120°C and 24000 rpm in 1 hour) at different magnifications. It can be seen in Figure 4a that clays have been well dispersed in the epoxy matrix. The size of small aggregates or clay stacks is less than 0.5µ. When the clays are focused at high magnification (Figure 4b), the dark lines indicate the silicate nanolayers. Although the clay particles were not completely exfoliated into individual platelets, there are many regions of nanocomposites which contain single, double and triple clay silicate nanolayers. So far, the results from XRD, SEM and

TEM combine to indicate that with high speed and temperature assistance, one can obtain a fine dispersion at the micro-scale, good distribution of clay, and good intercalation/exfoliation of clay in the epoxy system.
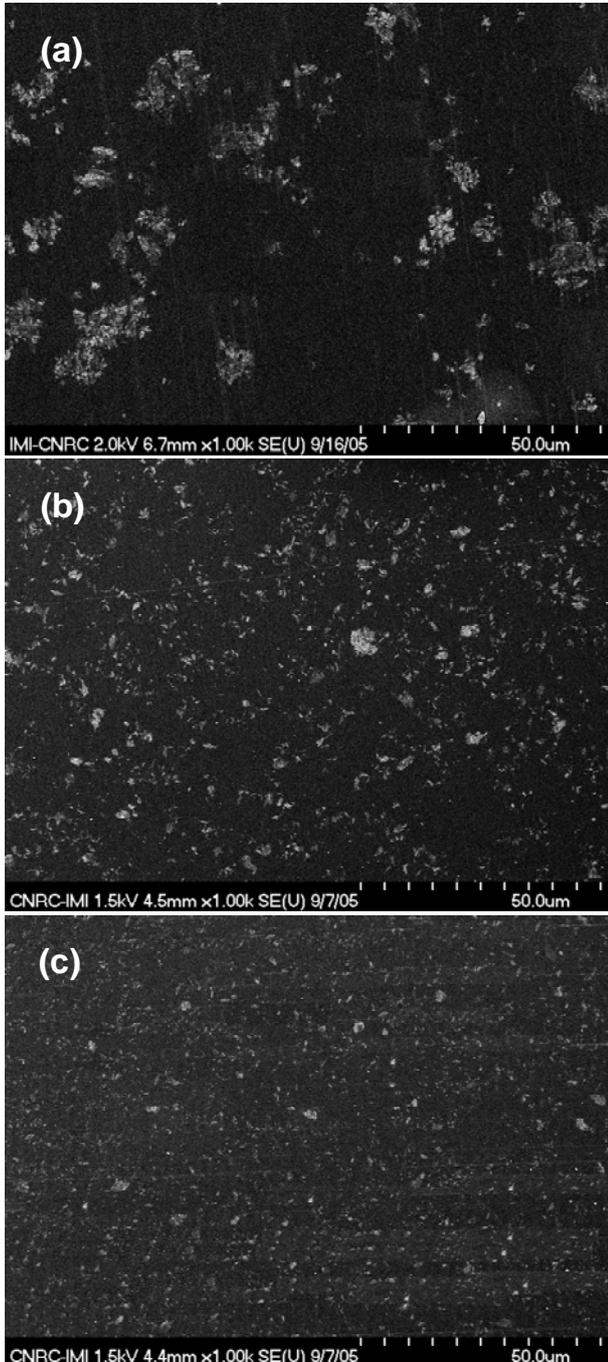
Fig. 3. SEM micrographs of ENC based on EPON828 and D230 with 2 wt% C30B made by different stirring methods: (a) TM, (b) RS, and (c) TS
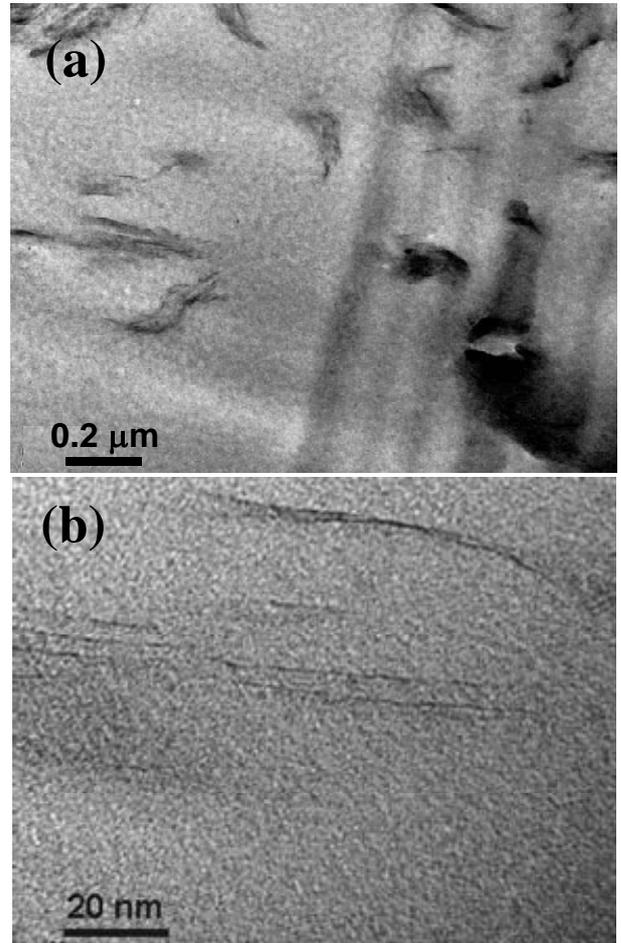
Fig. 4. TEM photo of 2 wt% Cloisite 30B preapared by TS method

The tensile properties of EPON828-D230 with 2 wt% C30B prepared with different stirring methods are shown in Figure 5. The presence of clay results in improvement in modulus for all cases of stirring (Figure 5a). A similar effect was reported by other researchers that addition of clay (from 5wt% and above) increases modulus [2, 4]. However, this study demonstrates that even with a small amount of clay of 2wt% the modulus can also significantly be improved. Since clay has a much higher modulus than the epoxy matrix, it is easy to understand, based on the rule of mixtures, why the modulus of the ENCs can be improved by adding nanoclay. In addition, the modulus of the nanocomposites can follow the order $E_{TS} > E_{HP} > E_{RS} > E_{TM} > E_{Tm} > E_{Rm} > E_{Epoxy}$. The level of increase in the modulus of ENCs prepared with TS, HP, RS, TM, Tm, and Rm stirring methods compared to epoxy is 10.4%, 10.2%, 9.5%, 8.3%, 7.2%, and 5.6% respectively.
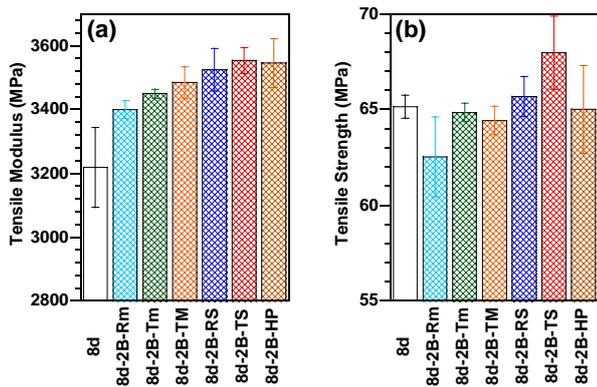
Fig. 5 Tensile properties for EPON828 resin and its nanocomposites made by different stirring methods (a) tensile modulus, (b) tensile strength

From the XRD and FEGSEM results in Figures 2 and 3, the dependence of dispersion of clay in ENCs on stirring conditions also follows the order of TS > HP > RS > TM > Tm > Rm. Relating to the clay dispersion and the modulus of ENCs, it seems that the better is the dispersion of the nanoclay in ENCs, the higher is the modulus of ENCs. It can be seen clearly that the modulus of ENCs prepared with Tm stirring method is slightly higher than Rm stirring method ($E_{Tm} > E_{Rm}$) and the modulus of ENC prepared with TS stirring method is slightly higher than RS stirring method ($E_{TS} > E_{RS}$). From there, one can see that the stirring temperature has a positive effect not only on the dispersion, intercalation/exfoliation of clay in ENCs but also on the mechanical performance of ENC. Stirring speed also shows its effect on the modulus of ENC. At the same stirring temperature of 120°C, the modulus of ENC prepared with high speed stirring method (TS) is higher than that of ENC prepared with low speed stirring method (TM) and without stirring (Tm) ($E_{TS} > E_{TM} > E_{Tm}$). This is similar for stirring at room temperature; the modulus of ENC prepared with RS stirring method is higher than that of ENC prepared with Rm stirring method ($E_{RS} > E_{Rm}$). Both stirring temperature and speed show a positive effect on modulus of ENCs, however, stirring speed appears to have a greater effect.

Unlike the modulus, the strength of the materials depends not only on the dispersion of the clay in the matrix but also on the presence of material defects (voids, holes, etc.), the quality of the interface between clay and matrix, and the structure of the materials. Thus the strength does not follow the same trends as the modulus. The tensile strength of the ENCs is almost the same as that of the epoxy matrix if standard deviation is considered (Figure 5b). It is well documented in the literature that improvement in tensile strength was reported only for rubbery epoxy systems while for glassy epoxy systems great reduction in tensile strength was often obtained [2, 3, 5, 12, 13, 14]. For example, a record loss of 39.5% in tensile strength for glassy ENC was provided by Zilg et al [14]. The reason why nanoclays can only improve the strength of rubbery systems but not glassy systems is still unclear up to now. In the following study this matter will be better addressed with different explanations. Therefore, no loss in tensile strength as found in this study should be considered as a positive message, although it would be more gratifying to obtain a gain. If only the average is considered, the general trend of the tensile strength of the ENCs alone in Figure 5b is somewhat similar to the trend of the tensile modulus (except for the sample prepared by HP) in Figure 5a, which means that the strength has a tendency of increasing with the improvement in dispersion. It can be interpreted that finer and more uniform dispersion can increase the clay surface area for interacting with the matrix and reduce the possibility of stress concentration in the large aggregates that will initiate the failure under stress. Thus the tensile strength is improved. Among them, the sample prepared with TS provides the greatest strength while the poor stirring approach Rm contributes the poorest strength. The exception for HP may be related to the fact that the solvent used in this process was not removed completely from the system.

Tensile properties of epoxy nanocomposites according to the various clay concentrations prepared with high speed at high temperature (TS) and at high temperature without mechanical stirring (Tm) are shown in Figure 6. The modulus increases almost linearly with the clay loading. The modulus shows a similar trend for both stirring with and without high speed at high temperature (Figure 6a). Again, the result shows the better advantage of high speed mixing on the formation of nanocomposites and this advantage becomes greater as the clay loading increases. At the same clay loading, the modulus of the epoxy nanocomposite prepared by high speed is higher than that of the one made without mechanical stirring. For example at a clay loading level of 6 wt%, the modulus of the epoxy nanocomposite prepared by the TS method increases 29.3 % with respect to epoxy, compared to 21.3 % for the one without mechanical stirring.

The strength of epoxy nanocomposite is also affected by high speed stirring. The strength of samples with high speed stirring appears higher than the strength of samples without mechanical stirring especially at high clay concentrations (Figure 6b). Again it confirms that better dispersion gave better strength. As discussed earlier, the findings in this study are quite superior to data reported in the literature for glassy ENCs, which show only a loss in tensile strength. The increase in tensile strength seems to reach a plateau at 4 wt% clay loading. The tensile strength goes up 12% with 4 wt% of organoclay Cloisite 30B.
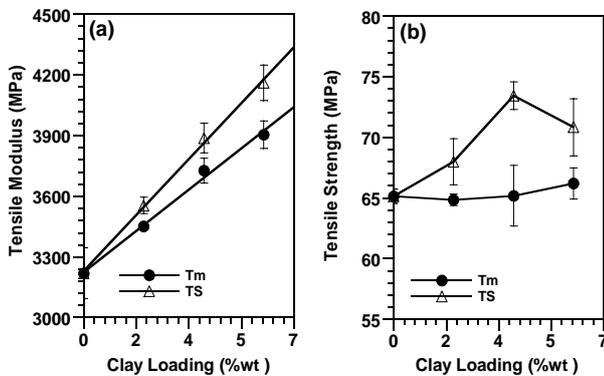
Fig. 6. Tensile properties for EPON828 resin and its nanocomposites at different clay concentrations made by Tm and TS methods (a) tensile modulus, (b) tensile strength

Figure 7 shows the compressive properties for epoxy and its nanocomposites which were prepared by different stirring methods. Stirring method again shows an effect on compressive properties of nanocomposites. The presence of clay results in improvement in modulus for all cases of stirring (Figure 7a). In general, the compressive modulus of the nanocomposites also follows the order $E_{TS} > E_{HP} > E_{RS} > E_{TM} > E_{Tm} > E_{Rm} > E_{Epoxy}$. The level of increase in the compressive modulus of ENCs prepared with TS, HP, RS, TM, Tm, and Rm stirring methods compared to epoxy is 10.1%, 8.8%, 5.7%, 3.4%, 2.8%, and 2.4% respectively, which is similar to the increase in tensile modulus. Again, it confirms that the better is the dispersion of the nanoclays in ENCs, the higher is the modulus of the nanocomposites. It also confirmed a slightly better advantage of the Tm over Rm stirring method (if only the average is considered), the TS over the TM and RS stirring methods, and the best advantage of the TS stirring method among all of them. Compressive strength is reduced for ENC prepared

with the Rm stirring method compared to neat epoxy (Figure 7b) as the result of its poor dispersion with large clay aggregates. Compressive strength increases for ENCs prepared with Tm, TM, RS, TS and HP stirring methods compared to neat epoxy and it follows the order of TS > HP > RS > TM > Tm > Epoxy. The explanation for that should be similar to that for tensile strength as discussed earlier. The improvement in compressive strength is more significant than in tensile strength because compressive strength is less sensitive to the defects of the testing sample.
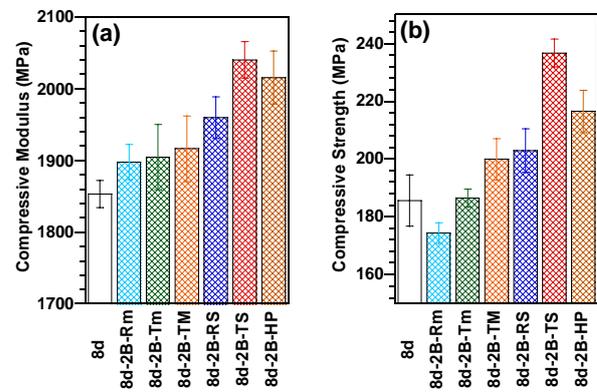
Fig. 7. Compressive properties for EPON828-D230 resin and its nanocomposites made by different stirring methods (a) compressive modulus, (b) compressive strength.
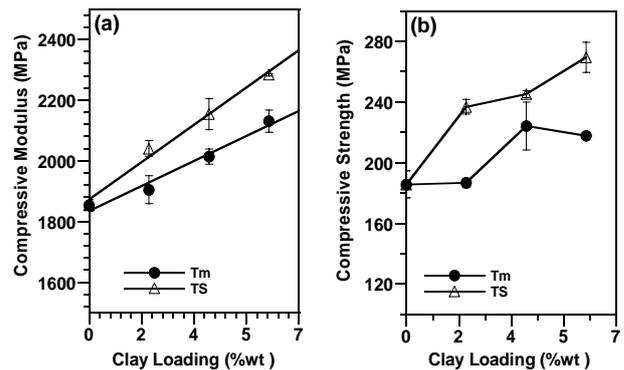
Fig. 8. Compressive properties for EPON828-D230 resin and its nanocomposites at different clay concentrations made by Tm and TS methods: (a) compressive modulus, (b) compressive strength

Comparing the compressive properties of nanocomposites at different clay loadings for stirring with high speed at high temperature (TS) and without mechanical stirring at high temperature (Tm), the modulus shows a similar trend for both

cases. The compressive modulus and strength show an improvement with clay loading (Figure 8).

4 Conclusions

Well dispersed and well intercalated/exfoliated ENC is achieved with a non-solvent-assistance method. With this method, shear force can be generated and can be applied on the clay particle during mixing step. Small tactoids are dispersed and formed high surface area in epoxy matrix with high shear. Thus, this dispersed nanoclay particle has important effect on mechanical properties of nanocomposites. The advantages of this method are simple, fast and easy to carry out. This method also eliminates the use of solvent for dispersing clay in epoxy. Due to free solvent, it can save a lot of time and cost as well as it is friendly with the environment.

5 Acknowledgements

References

[1] Wang M. S. and Pinnavaia T. J. ''Clay-Polymer Nanocomposites Formed from Acidic Derivatives of Montmorillonite and an Epoxy Resin''. *Chem. Mater.*, Vol. 6, No. 4, pp 468 - 474, 1994.

[2] Lan T. and Pinnavaia T. J. "Clay-Reinforced Epoxy Nanocomposites". *Chem. Mater.*, Vol. 6, No. 12, pp 2216 - 2219, 1994.

[3] Kornmann X., Lindberg H. and Berglund L. A. "Synthesis of epoxy–clay nanocomposites: influence of the nature of the clay on structure". *Polymer*, Vol. l. 42, No. 4, pp 1303-1310, 2001.

[4] Kornmann X., Lindberg H. and Berglund L. A. "Synthesis of epoxy–clay nanocomposites. Influence of the nature of the curing agent on structure". *Polymer*, Vol. 42, No. 10, pp 4493-4499, 2001.

[5] Massam J. and Pinnavaia T. J. "Clay nanolayer reinforcement of glassy epoxy polymer". *Mater. Res. Soc. Symp. Proc*. Spring Meeting, San Francisco, CA (US), Vol. 520, pp 223-232, 1998.

[6] Yasmin A., Abot J. L. and Daniel I. M. "Processing of clay/epoxy nanocomposites by shear mixing". *Scripta Materialia*, Vol. 49, No. 1, pp 81-86, 2003.

[7] Chen C. and Tolle T. B. "Fully exfoliated layered silicate epoxy nanocomposites" *J. Polym Sci Part B: Polym. Phys.*, Vol. 42, No. 21, pp 3981-3986, 2004.

[8] Liu W. P., Hoa S. V. and Pugh M. "Morphology and performance of epoxy nanocomposites modified with organoclay and rubber". *Polym. Eng. Sci.*, Vol. 44, No. 6, pp 1178-1186, 2004.

[9] Liu W. P., Hoa S. V. and Pugh M. "Organoclay-modified high performance epoxy nanocomposites". *Compos. Sci. Technol.*, Vol. 65, pp 307-316 (2004).

[10] Liu W. P., Hoa S. V. and Pugh M. "Fracture toughness and water uptake of high- performance epoxy/nanoclay nanocomposites". *Compos. Sci. Technol.*, Vol. 65, 2364-2373 (2005).

[11] Ngo T.-D., Ton-That M.-T., Hoa S. V. and Cole K. C. "Curing kinetics and mechanical properties of epoxy nanocomposites based on different organoclays". in press, Polymer Engineering and Science, Vol. 47, No. 5 (2007).

[12] Utracki L. A. "*Clay-containing polymeric nanocomposites*", Rapra Technology (2004).

[13] Lan T., Kaviratna P. D. and Pinnavaia T. J. "Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites". *Chem. Mater.*, Vol. 7, No. 11, 2144-2150 (1995).

[14] Zilg C., Thomann R., Finter J. and Mülhaupt R. "The influence of silicate modification and compatibilizers on mechanical properties and morphology of anhydride-cured epoxy nanocomposites". *Macromol. Mater. Eng.*, 280/281, 41-46 (2000).