

Wet process and exfoliation of clay in epoxy

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Abstract—A new approach for the preparation of epoxy-clay nanocomposite (ECN) was developed based on utilization of water remains in the clay treatment as a carrier to improve clay dispersion and intercalation/exfoliation. A novel type organoclay was prepared by combining short and long chain molecule intercalants. The short chain intercalant provides the functionality ready to interact with the polymer, while the long one helps keep clay layers apart from each other. The micro- and nano-structures, physical and mechanical properties, and fire resistance of ECN were studied. The results indicated that the use of wet process and clay modification facilitates the dispersion intercalation/exfoliation of clay, the interaction between clay and epoxy, and subsequently improves ECN mechanical properties and fire resistance. The drying, grinding and screening steps in the preparation of organoclay could be eliminated, thereby reducing energy consumption. This method allows the solvent free in the preparation of ECN, which requires considerable time and cost for solvent removing. This also reduces ECN's environmental impact.

Keywords: Wet Process, Water, Dispersion, Organoclay, Nanoclay, Epoxy, Nanocomposites

INTRODUCTION

Since the Toyota researcher group's pioneering work on nanocomposites [1], extensive research on the polymer layered-silicate nanocomposites has been carried out, with most of the research focused on the preparation of the nanocomposite with clay as the nano-reinforcement for various thermoplastic and thermoset polymers [2-10]. Extensive studies of ECNs have appeared over the years [11-16]. Many attempts have been made to prepare ECN with varying degrees of success involving various preparation conditions and different chemistries of clays and matrix. However, many challenges remain. The dispersion and intercalation/exfoliation of organoclay in epoxy resin is a complex process, which takes place during the pre-mixing and curing steps. Dispersion and intercalation/exfoliation processes' parameters mainly include pre-mixing temperature, pre-mixing speed and time, power of ultrasonic tooling, and shearing forces. Therefore, different means such as mechanical shear and elevated temperature were utilized to facilitate the dispersion and intercalation/exfoliation. Both pristine and commercially treated clays tend to form stacks rather than individual platelets owing to their layer structure and the strong forces between the layers. Consequently, it is very difficult to overcome such interactions in order to disperse the clay layers individually in the epoxy matrix, especially when the two phases are incompatible. Besides modifying the clay and resin chemistries, different ways to incorporate nanoclay into epoxy have been reported in the literature, such as direct pre-

mixing, three-roll mill pre-mixing, ultrasonic pre-mixing, high-shear pre-mixing in the presence of acetone, and high-pressure pre-mixing method with assistance of acetone or other solvent etc. [5,12,13]. Our research group reported the use of homogenizer with temperature facilitates the dispersion and intercalation/exfoliation of nanoclay in epoxy system [14,15]. An acceptable level of dispersion and exfoliation has been achieved. However, achieving fine dispersion and well-exfoliated morphologies with epoxy-based nanocomposites remains a challenge. In contrast to the conventional method, a new method for the synthesis of nanocomposites was recently developed in our laboratory that combines high shear and water to improve the dispersion and intercalation/exfoliation of the organoclay in the polymer matrix and subsequently improves the mechanical and physical properties of the final materials. Water was not introduced into the final organoclay product, but rather profiting the high moisture content in the organoclay during organoclay preparation. This method eliminates the drying, grinding and screening steps during the preparation of organoclay, which consumes a large amount of energy and may damage the clay layer structure. Besides processing method, modifying clay with a combination of short and long chain molecule intercalants also contributes to dispersion and intercalation/exfoliation of the organoclay in the polymer matrix as well as the interaction between organoclay and epoxy.

EXPERIMENTAL

1. Materials

The standard diglycidyl ether of bisphenol A (DGEBA) epoxy resin EPONTM Resin 828 from Resolution Performance Products was used. The resin was cured with the polyoxypropylene diamine hardener Jeffamine[®] D-230 from Huntsman LLC at a level of 32 phr. Commercial organoclay Cloisite[®] 30B (C30B) from Southern

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^{*}This paper is dedicated to the memory of our wonderful colleague, Dr. K. C. Cole.

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Clay Products, Inc. C30B organoclay consists of montmorillonite treated with methyl tallow bis-2-hydroxyethyl quaternary ammonium intercalant. It is widely used in epoxy resins because the 2-hydroxyethyl groups provide improved chemical compatibility with the relatively polar epoxy resin. Methylammonium chloride and octadecylammonium chloride were purchased from Sigma-Aldrich. The chemicals were used for modification of clay.

2. Preparation of the PMA Organoclay (Modified Clay)

The term "organoclay" refers to organically modified clay. Although their high aspect ratio is ideal for reinforcement, the nanolayers are not easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids (as result of strong interaction by tight electrostatic forces between the layers). In addition, dispersion of the clay tactoids into individual layers is further hindered by the intrinsic incompatibility between the hydrophilic layered silicates and the more hydrophobic polymers. For these reasons the clay must be treated so it can be incorporated into a hydrophobic polymer. In this study, the PMA organoclay was prepared by treating Cloisite Na® (CEC: ~92 meq/100 g from Southern Clay Products, Inc.) with a mixture of two different chain length intercalants. The short chain intercalant provides the high functionality ready to interact with the polymer, while the long one helps keep clay layers apart from each other. The short chain was methylammonium chloride (40 molar%) and the long chain intercalant was octadecylammonium chloride (60 molar%). The methylamine hydrochloride (2.70 g) and octadecylamine hydrochloride

(18.36 g) were dissolved in 1,000 mL deionized water which was heated to 90 °C. Hundred grams of Cloisite Na clay was dispersed into 2,000 mL deionized water at 90 °C. Then, the clay suspension was added slowly into the alkylamines solution and stirred for 60 minutes at 90 °C. The PMA organoclay was washed and centrifuged until no chloride ions were detected. The resulting PMA organoclay paste was either dried or kept as is for preparation of the epoxy nanocomposites. The modification process of organoclay with long and short chain intercalants is shown in Scheme 1.

3. Preparation of the Epoxy-clay Nanocomposites

Epoxy resin and PMA organoclay were premixed together using a homogenizer at about 20,000 rpm. The desired amount of organoclay, either in dry or paste form, was added slowly into the epoxy, which was heated at 100 °C. Temperature of the mixture was then increased to 120 °C and the mixture was continuously premixed at 120 °C for 1 hour. The typical batch size for all epoxy-organoclay mixtures in the study was 200 g of epoxy resin. Premixing with dried and paste organoclay will be referred to hereafter as dried and wetted processes, respectively. Dried C30 was added slowly into the epoxy, which was heated at 100 °C. Temperature of the mixture was then ramped to 120 °C and the mixture was continuously premixed at 120 °C for 1 hour (the preparation is similar to the dried process). In all cases, the organoclays were dispersed in the epoxy resin at levels, leading to loading of 2% and 4% by weight after the addition of hardener and curing.

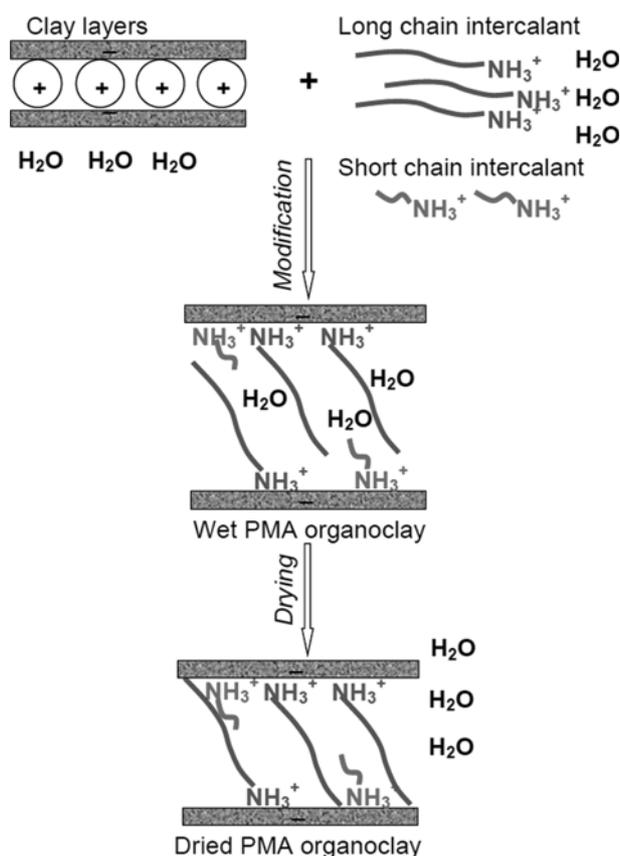
For curing, polyoxypropylene diamine hardener D-230 (32 phr) was mixed with neat epoxy resin or epoxy-organoclay mixture at room temperature for five minutes, and the mixture was then subjected to a vacuum to remove the bubbles. Samples were cured at 120 °C for two hours with subsequent post cure at 140 °C for two hours.

4. Characterizations

To evaluate the intercalation/exfoliation of the organoclay in the polymer matrix, X-ray diffraction (XRD) patterns were obtained from the surface of the samples using a Bruker Discover 8 powder X-ray diffractometer with $\text{CuK}\alpha$ radiation. A Hitachi-S4700 field emission gun scanning electron microscope (FEGSEM) was used to observe the organoclay dispersion in the epoxy matrix at the micro-level. For organoclay dispersion at the nano-level, ultrathin (50 to 80 nm) sections of nanocomposite samples were prepared with a cryo-ultramicrotome and supported on a copper 200 mesh grid for observation with a Hitachi H9000 transmission electron microscope (TEM). Thermogravimetric analysis (TGA) data was obtained on a TA-Q50 instrument using nitrogen atmosphere. The samples were heated from 30 °C to 1,000 °C at a heating rate of 20 °C·min⁻¹. Burning tests were conducted on Qualitest Limiting Oxygen Index (LOI) tester. In this study, oxygen was kept at 25% to evaluate the burning rate of different ECNs as well as epoxy system. The tensile properties of the epoxy systems with and without organoclay were determined at room temperature and relative humidity of 50% according to ASTM D638-02 on an Instron machine with crosshead speed of 5 mm/min.

RESULTS AND DISCUSSION

One way of modifying the clay surface to make it more com-



Scheme 1. The modification process of clay with long and short chain intercalants.

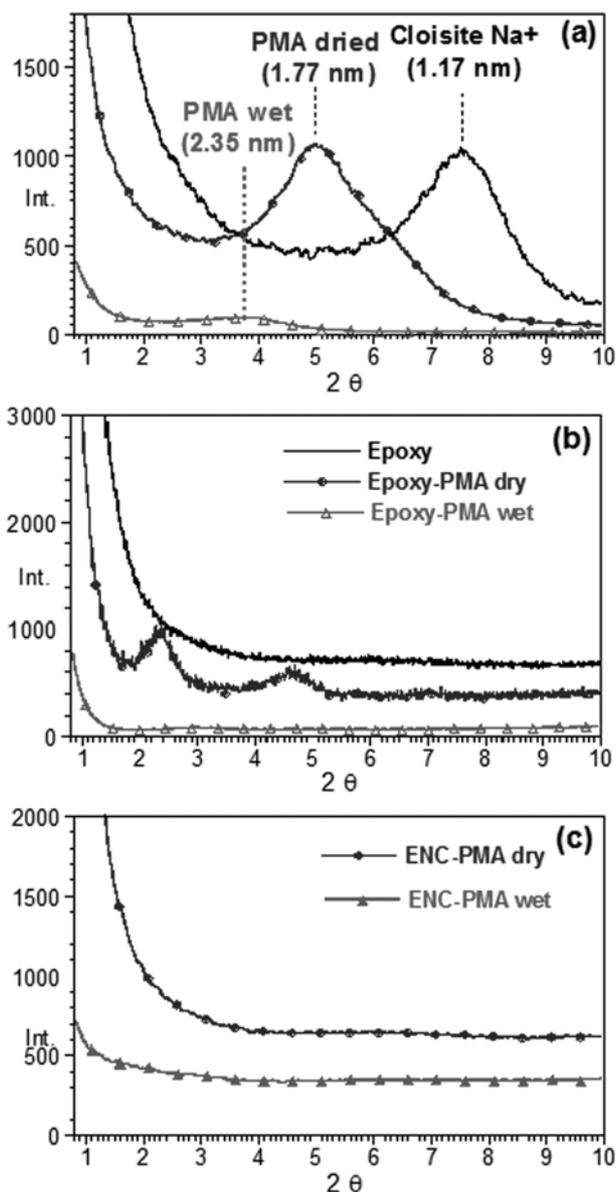


Fig. 1. X-ray diffraction curves of: (a) PMA organoclay at dry and paste stages, (b) mixture between epoxy and PMA organoclay, and (c) nanocomposites.

patible with a polymer is through ion exchanging. Since, the cations on the clay surface can be exchanged by other organic cations (so called intercalants), which are tailored to the polymer in which the clay would be become more compatible. This process renders the clay more hydrophobic and helps to open up the clay galleries (as the adding of the intercalant on the clay surface). This facilitates the penetration of polymer in the clay galleries, then subsequently intercalation/exfoliates the clay. Fig. 1(a) shows the XRD curves of the Cloisite Na and PMA organoclay in dry and wet form after preparation. Apparently, there is a peak at $d_{001}=2.35$ nm for the PMA wet (compared to original peak at $d_{001}=1.17$ nm for the Cloisite Na), but at low intensity, indicating that most of organoclay have been well expanded their clay gallery; however, it is not clear if the organoclay were well intercalated/exfoliated by intercal-

ants or the presence of water. The loss of water after drying for the dried PMA organoclay results in collapse of organoclay gallery to $d_{001}=1.77$ nm. However, this gallery for the dried PMA organoclay is larger compared to Cloisite Na, indicating dried PMA organoclay was intercalated by intercalants after treatment. The emerging data indicated that the presence of water further expanded the organoclay gallery. These PMA organoclays either in dry or paste form were premixed with epoxy resin and we further studied the dispersion and intercalation/exfoliation. Fig. 1(b) shows XRD curves of PMA organoclays in both dried and paste forms after premixing with epoxy resin. For the wet PMA organoclay after premixing with epoxy resin, there is almost no peak on the XRD curve. In contrast, two peaks appear on the XRD curve at 2-3 degree and 4-5 degree for dried PMA organoclay after premixing with epoxy, which represents for the d_{001} of around 3.8 nm and 1.9 nm, respectively. This indicates that the wet organoclay has better intercalation/exfoliation in epoxy than the dried PMA organoclay. It may be due to the loss of water during the drying of organoclay results in a smaller d-spacing (Fig. 1(a)) making the dried organoclay harder to be well intercalated/exfoliated by the epoxy resin compared to wet organoclay (Fig. 1(b)). Nevertheless, the result shows that the organoclays in both dry and wet forms were further intercalated/exfoliated after premixing with epoxy (compared the results in Figs. 1(b) and 1(a)). From that, it can be speculated that dried PMA organoclay generates intercalation and wet PMA organoclay leads to much better intercalation/exfoliation than dried PMA organoclay.

The presence of water in the organoclay results an improvement of intercalation/exfoliation of the PMA organoclay in epoxy during the premixing step. However, the dispersion intercalation/exfoliation of organoclay in epoxy nanocomposite takes place at both the pre-mixing and the curing steps. Therefore, the epoxy organoclay systems after pre-mixing were cured with Jeffamine D230 hardener and the dispersion and intercalation/exfoliation were studied. Fig. 1(c) shows the XRD diffraction curves of nanocomposites with PMA organoclays after curing. The peaks on the XRD curves disappear for both dried and wetted PMA organoclays indicating the good intercalation/exfoliation possibility for both PMA organoclay in the cured epoxy system. Although there is no peak on the XRD curves in either case, the XRD alone is not sufficient for a complete understanding of the dispersion intercalation/exfoliation of PMA organoclay in epoxy. Thus, SEM and TEM were utilized to complement the results.

The microstructures of ENCs with PMA organoclays prepared through dry and wet methods were examined by SEM and shown in Fig. 2. The bright spots on the SEM backscattered images correspond to organoclay aggregates. The microscale dispersion is good in both cases. Apparently, a portion of the organoclay remains at the micro-scale level at different size populations in both samples. However, given the resolution limitations of the SEM, one should not rule out the possibility that intercalation/exfoliation has taken place. Aggregates' size is reduced significantly with wet process as compared to the dry process. An epoxy nanocomposite system's physical and chemical properties are influenced by processing techniques, organoclay modifier and curing conditions used during the preparation of nanocomposites. Nanocomposite organoclay mor-

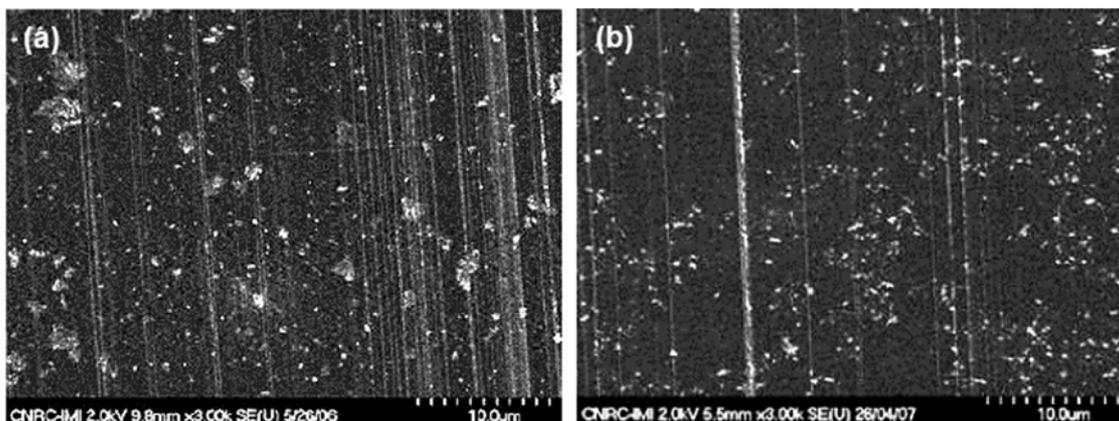


Fig. 2. SEM images of epoxy nanocomposites with 2 wt% PMA organoclay: (a) Dry process and (b) wet process.

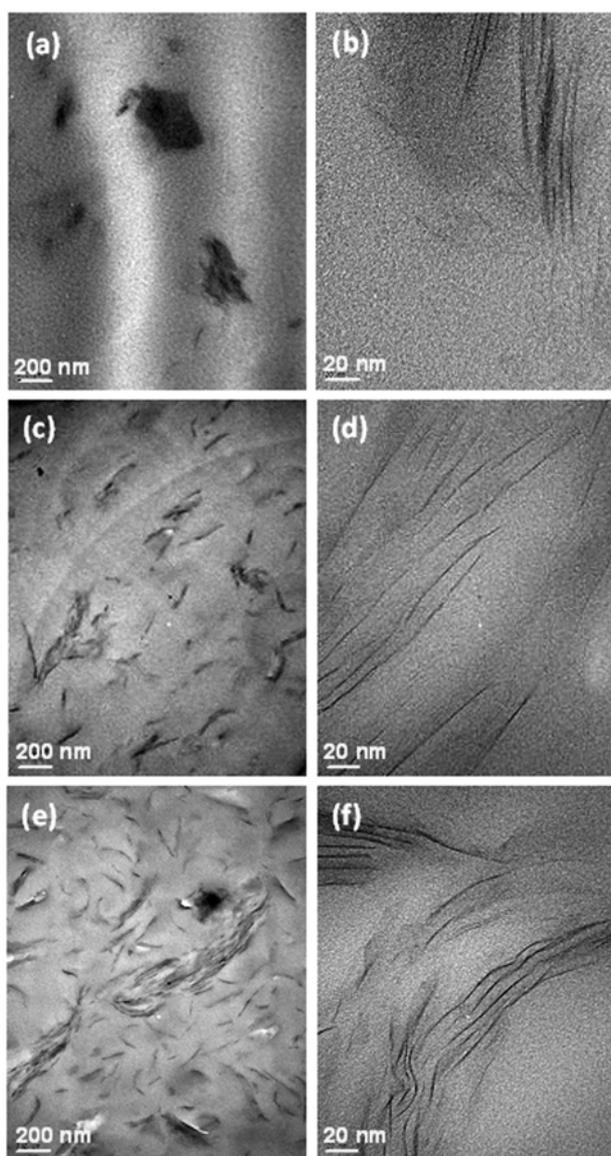
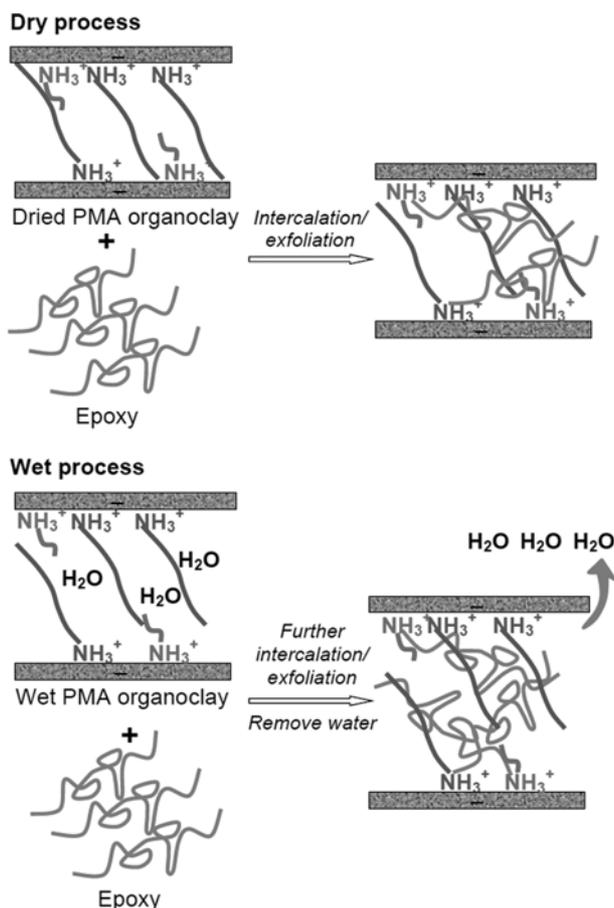


Fig. 3. TEM images of epoxy nanocomposites with 2 wt% PMA organoclay (a), (b) dry process, (c), (d) wet process, and 4% PMA (e), (f) wet process.

phology (intercalation/exfoliation) is also dependent on the above parameters.

Fig. 3 shows TEM images of nanocomposite prepared using dry and wet process at different magnifications. At low magnification (images on the left), small aggregates or organoclay stacks less than 400 nm were observed. However, the results show a much better dispersion with uniform distribution of small PMA organoclay particles in epoxy prepared using wet process than dry process. At higher magnification, it is possible to identify the individual clay layers; the dark lines indicate individual silicate nanolayers. The intergallery distance of dried PMA organoclay in cured epoxy is around 4.0–6.0 nm, quite similar to the C30B 4.03–6.69 nm which has been reported [14]. On the other hand, the intergallery distance of wet PMA organoclay in cured epoxy is much larger than of dried PMA and C30B. The intergallery distance of wet PMA organoclay in cured epoxy is around 10.0–20.0 nm depending the areas. Clay platelets were well intercalated/exfoliated by the wet process, with many regions showing single, or double clay silicate nanolayers and many nanolayers are rather randomly dispersed. This phenomenon also appears for the 4% wet PMA organoclay (Figs. 3(e) and 3(f)); however, one can see more aggregates and intergallery distance of 4 wt% wet PMA organoclay in cured epoxy is a bit smaller compared to 2 wt%.

The results from XRD, SEM and TEM combine to indicate that the water remaining in the organoclay or the wet process and the organoclay treatment contribute to the good dispersion and intercalation/exfoliation of PMA organoclay in the ECN. Although not fully exfoliated ECN structure, fine dispersion at the micro-scale, good distribution of organoclay, and good intercalation/exfoliation of organoclay in the epoxy system can be achieved. The mechanism for preparations of ENCs with PMA organoclays (during pre-mixing step) through dry and wet methods is described in Scheme 2. The modification of clay with intercalants results in a larger d -spacing as discussed above making the wet PMA organoclay easier to be well intercalated/exfoliated by the epoxy resin compared to unmodified clay. The presence of water in wet PMA organoclay results in a larger d -spacing as compared to the dried PMA organoclay. In addition, the presence of water could also decrease strong interaction between the clay layers agglomerated tactoids. This further



Scheme 2. Intercalation/exfoliation during pre-mixing step of PMA organoclay with epoxy through dry (top) and wet (bottom) methods.

assists the intercalation/exfoliation of the wet PMA organoclay as compared to dried PMA organoclay. The water was removed by heat during the premixing of wet PMA organoclay with epoxy.

The addition of organoclay to the polymers aims to improve the polymer properties and to produce nanocomposites with desired characteristics for specific applications. Clay reinforcement offers higher resistance against straining due to their higher module. When rigid filler, such as clay, is added to a soft polymer matrix, it will carry the major portion of applied load to the nanocomposite under stress conditions. Fig. 4 shows the tensile properties of EPON828-D230 (with 2 wt% PMA organoclay prepared by dry and wet method, 4 wt% PMA organoclay prepared by wet process and 2 wt% C30B prepared by dried process). The presence of organoclay results in an improvement in modulus of the epoxy for all cases and tensile modulus increases with increase of organoclay loading in nanocomposite. Since clay has a much higher modulus than the epoxy matrix, it is easy to understand why the modulus of the ENC can be improved by adding organoclay and with organoclay loading.

Fig. 4 also shows the improvement of the epoxy nanocomposite strength at 2 wt% of organoclay. This illustrates the organoclay plays a role as reinforcement for epoxy. A better strength of ENC was achieved when prepared with PMA organoclay compared to C30B organoclay. This may be due to good interface between PMA

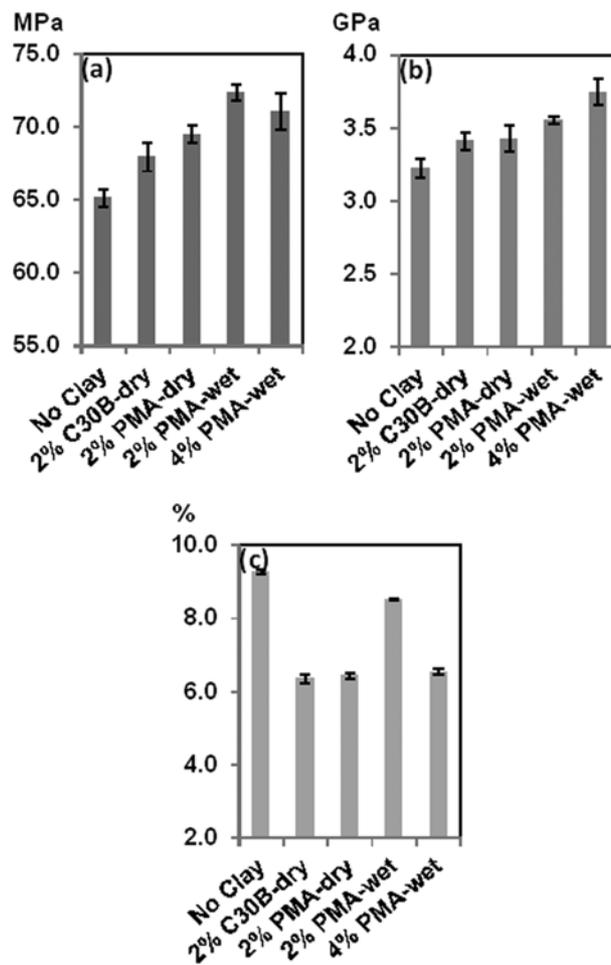


Fig. 4. Tensile properties of epoxy and its nanocomposites with PMA organoclay (a) strength, (b) modulus, and (c) strain.

organoclay and epoxy matrix. It means PMA organoclay prepared using the combination of short and long chain molecule intercalants is suitable for reinforcing the epoxy resin. The result also shows the improvement of the epoxy nanocomposite strength is even more pronounced under wet process as compared to dry process. Clays have received much attention as reinforcing materials for polymers because of their potentially high aspect ratio and unique intercalation/exfoliation characteristics. However, the strength of the materials depends not only on the quality of the interface between clay and matrix and the dispersion and intercalation/exfoliation of the clay in the matrix, but also on the presence of material defects (voids, holes, etc.), and the structure of the materials. It can be assumed that finer and more uniform dispersion of the clay in the matrix can increase the clay surface area, better interacting with the matrix and reducing the possibility of stress concentration in large aggregates that will initiate failure under stress. Better dispersion intercalation/exfoliation of PMA organoclay and better interfacial interactions between organoclay and matrix when prepared using wet process as compared to dried process results in the improved strength of the epoxy nanocomposite. Adding 4 wt% PMA organoclay did not further improve the tensile strength for epoxy nanocomposite as 2 wt%. This may be because the intercalation/exfoliation

state of 4 wt% is poorer than the 2 wt% as observed in the Fig. 3. The tensile strain at failure for ENCs is shown in Fig. 4(c). In general, the epoxy nanocomposites are stiffer and more brittle compared to the epoxy. This happens for all the ECNs prepared by different processes and for organoclay loading (wetted process). The improvement in tensile strength at 2 wt% of PMA organoclay, especially with wet process illustrated in this study, should be considered a positive outcome. The result shows the advantage of processing and organoclay modification in the formation and performance of nanocomposites. Thereby, further discussion will focus on the PMA and its nanocomposites prepared by wet process.

It has been reported that polymer/organoclay nanocomposites are thermally more stable than pure polymers [17-19]. TGA data of EPON828-D230 and its nanocomposites are shown in Fig. 5 and Table 1, where it can be seen that the clay has positive effect on the thermal property of epoxy. Clays are inorganic materials that are almost stable in the temperature ranges that organic polymers are degraded into volatile compounds. Therefore, in TGA experiments, clay content in epoxy nanocomposites remains as a residue after heating program stability of epoxy. The incorporation of clay fillers into the polymer matrices results in an improvement of their thermal stability due to the superior insulation and the mass transport barrier properties of clay layers against the volatile compounds

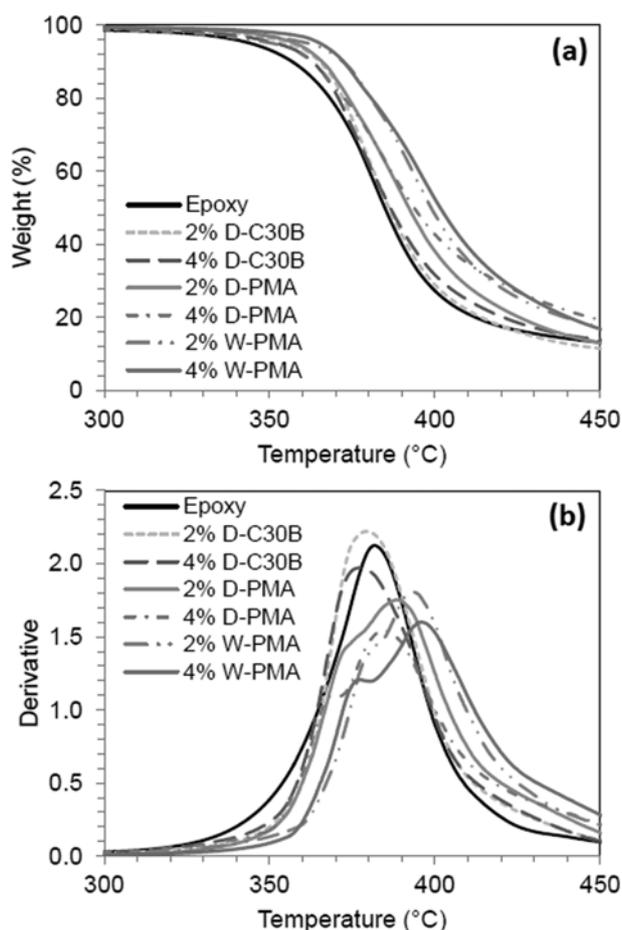


Fig. 5. TGA results of epoxy and epoxy nanocomposites with C30B and PMA organoclays.

Table 1. Summary of TGA results for of epoxy and epoxy nanocomposites with C30B and PMA organoclays

Sample	T_{onset} (°C)	T_{10} (°C)	T_{30} (°C)	T_{50} (°C)
Epoxy	352	357	375	385
2% D-C30B	363	365	376	386
4% D-C30B	362	363	376	393
2% D-PMA	363	366	381	392
4% D-PMA	364	368	381	394
2% W-PMA	367	372	387	399
4% W-PMA	368	372	389	402

T_x is the temperature of x percent of weight loss

generated during the polymer decomposition under thermal conditions [20]. In addition, clays assist in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite [21].

The presence of organoclay C30B slightly influences the TGA results of the epoxy system, while the PMA organoclay has strong influence on the TGA of the epoxy system. Note that not all reported results in the literature on thermoset/clay nanocomposites demonstrate enhanced thermal properties. Slight changes of the structure may produce contradictory results on thermal stability [6,22]. The EPON828-D230 system with PMA organoclay is more thermally stable than the EPON828-D230 system with C30B; its T_{onset} temperature is higher. The maximum temperature and the temperature corresponding to any given weight loss is also higher for PMA organoclay compared to C30B epoxy nanocomposites. This can be attributed to the better dispersion of PMA into epoxy system compared to C30B, and also to the chemistry of the intercalants of PMA organoclay, which is speculated to have better interaction with the epoxy compared to C30B organoclay at both 2 wt% and 4 wt%, offering subsequent the thermal stability improvement of ECN. Although the wet process further improved the intercalation/exfoliation of the organoclay, the result from XRD, SEM and TEM indicated not fully exfoliated structure was obtained in this study. Therefore, this may explain why the thermal stability result is not significant improvement compared to some reports in the literature for exfoliated epoxy composites [23]. However, not all results in the literature on thermoset/clay nanocomposites demonstrated enhancement of thermal properties. Slight changes of the structure may produce contradictory results on thermal stability. A similar observation to the literature, the thermal stability of the polymer nanocomposites was reported to be strongly affected by the amount of organoclay, its exfoliation in the polymer matrix, the thermal stability of the organoclay intercalant, and the type of polymer matrix as well as the interaction between polymer and organoclay [24-26].

Burning tests were conducted on Qualitest LOI tester at 25% of oxygen to evaluate the burning rate of different ECNs as well as epoxy system, and the results are shown in Fig. 6. The addition of organoclay improves the flame resistance of the epoxy system, perhaps explained by the diffusion of oxygen into the sample and decreased transportation of the burning gas product out of the sample with the presence of clay. After burning, more char remains in

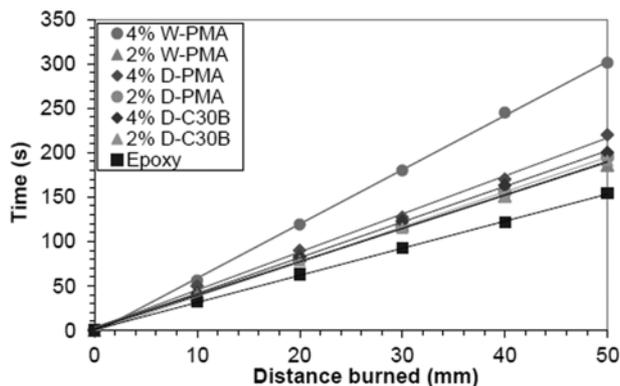


Fig. 6. Burning rate for epoxy and epoxy nanocomposites with C30B and PMA organoclays at 25% oxygen.

the nanocomposites for all studied ENCs. The results illustrate that ENCs prepared by dry process with C30B and dry PMA organoclay did not show significant difference in their flame resistance. The wet process results are slightly better compared to the dry process on the flame resistance for ECN. This may be due to better interface between organoclay and epoxy matrix as well better intercalation/exfoliation of wet PMA organoclay than dry PMA organoclay. It was reported that one of nanocomposites flame retardant mechanisms is a consequence of high performance carbonaceous-silicate char building up on the surface during burning, insulating the underlying materials and slowing down the mass loss decom-

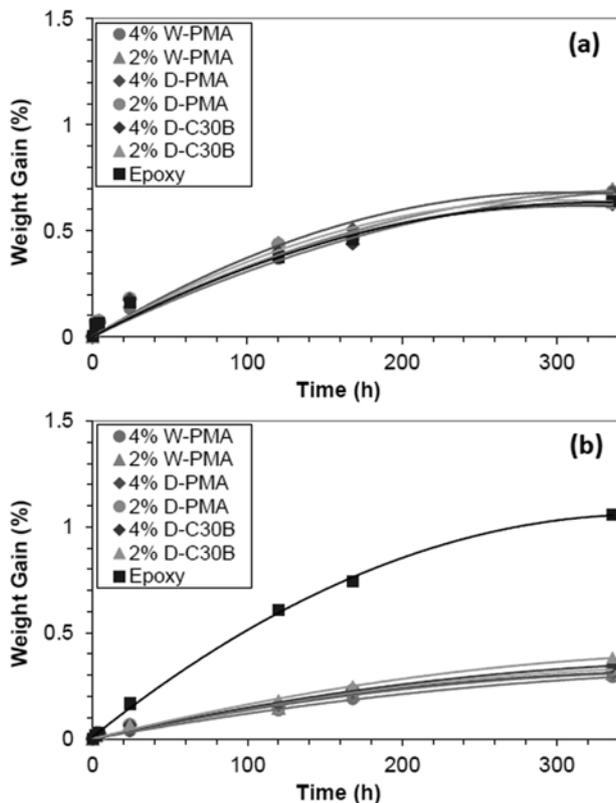


Fig. 7. Water (a) and toluene (b) absorption for epoxy and epoxy nanocomposites with C30B and PMA organoclays.

position.

Nanoclays frequently exhibit unexpected properties including reduced gas permeability, improved solvent resistance, and superior mechanical and enhance flame retardant properties [27,28]. Fig. 7 shows water and toluene absorptions of epoxy and its nanocomposite with C30B and PMA organoclay. According to Becker et al. [17], the equilibrium water uptake of ECN was reduced compared to the neat epoxy system. Water uptake may be due to the capability of the water molecules to penetrate through the epoxy network. Water diffusion occurs in epoxy resin due to the nature of the polymer, which shows strong interaction with water. In epoxy matrices, water molecules couple strongly with hydrophilic functional groups (such as hydroxyl or amine in epoxy resin). In general, added organoclay in epoxy matrix may reduce the water uptake since it results in the reduction of the tortuosity path. However, the results in this study show organoclay has only a slight effect on the water absorption of epoxy (Fig. 7(a)).

The result also demonstrates that the presence of C30B and PMA organoclays (both dry and wet processes) increases the solvent resistance (Fig. 7(b)). Solvent uptake after being subjected to toluene absorption for 350 hours immersion in epoxy is about 1.0%, while only about 0.30% for the ECNs. Clay layers in the polymer matrix can act as an effective barrier to the penetrants. The enhanced barrier properties of polymer nanocomposites are due to the labyrinth or tortuous path the penetrants must take [29]. The presence of PMA organoclay slightly better compared to C30B on reducing the penetration of toluene into the ECN.

CONCLUSIONS

A novel type of PMA organoclay was prepared by treating clay with a combination of short and long chain molecule intercalants. The short chain intercalant provides a functionality ready to interact with the polymer, while the long one helps keep clay layers apart from each other. In addition, a wet process was developed of epoxy nanocomposites preparation. The results demonstrated that a better strength of ENC was achieved using PMA organoclay in epoxy as compared to C30B organoclay. Furthermore, the wet process combination with the PMA organoclay results in a high level of micro-dispersion and exfoliation epoxy nanocomposites when compared to the dry process. The utilization of remaining water in the clay modification eliminates the energy required for drying the organoclay. The method also eliminates the need for solvents in ECN preparation, while providing good dispersion and interaction/exfoliation of organoclay. The final morphology, physical, chemical and barrier properties of the nanocomposites were influenced by processing method and selection of organoclay modifier. Despite this, improvements in mechanical performance were still modest, likely as performance nears the theoretical limit for un-oriented clay platelets in epoxy resin. Thermal stability and barrier properties were significantly improved by the incorporation of clay particles into epoxy systems. Nanocomposites made by a wet process with the PMA organoclay show to be more effective than C30B in increasing the thermal decomposition temperature and flammability resistance. The presence of organoclay has only a slight effect on the epoxy's water absorption, but it substantially decreases tolu-

ene absorption.

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TABLE OF NOMENCLATURE

C30B	: Organoclay Cloisite® 30B
DGEBA	: Diglycidyl Ether of Bisphenol A
ECN	: Epoxy-Clay Nanocomposite
FEGSEM	: Field Emission Gun Scanning Electron Microscope
LOI	: Limiting Oxygen Index
PMA	: Organoclay was prepared by treating Cloisite Na® with a mixture of methylammonium chloride and octadecylammonium Chloride
TEM	: Transmission Electron Microscope
TGA	: Thermogravimetric Analysis
XRD	: X-ray diffraction

REFERENCES

1. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).
2. E. P. Giannelis, *Adv. Mater.*, **8**, 29 (1996).
3. P. C. LeBaron, Z. Wang and T. J. Pinnavaia, *J. Appl. Clay Sci.*, **15**, 11 (1999).
4. R. A. Vaia, K. D. Jandt, E. J. Krammer and E. P. Giannelis, *Chem. Mater.*, **8**, 2628 (1996).
5. I. J. Chin, T. Thurn-Albrecht, H. C. Kim, T. P. Russell and J. Wang, *Polymer*, **42**, 5947 (2001).
6. J. W. Gilman, *Appl. Clay Sci.*, **15**, 31 (1999).
7. J. L. Jyi and M. D. Isaac, *Compos. Sci. Technol.*, **63**, 1607 (2003).
8. L. R. Xu, B. Vikram, H. Z. Wei, J. Li and C. M. Lukehart, *J. Compos. Mater.*, **38**, 1563 (2004).
9. J. W. Gilman and A. B. Morgan, *J. Appl. Polym. Sci.*, **87**, 1329 (2003).
10. S. Lin and J. P. Chang, *J. Vac. Sci. Technol.*, **22**, 88 (2004).
11. M. S. Wang and T. J. Pinnavaia, *Chem. Mater.*, **6**, 4, 468 (1994).
12. J. M. Brown, D. Curliss and R. A. Vaia, *Chem. Mater.*, **12**, 3376 (2000).
13. X. Kornmann, R. Thomann, R. Mülhaupt, J. Finter and L. A. Berglund, *Polym. Eng. Sci.*, **42**, 9, 1815 (2002).
14. T.-D. Ngo, M.-T. Ton-That, S. V. Hoa and K. C. Cole, *Compos. Sci. Technol.*, **69**, 1831 (2009).
15. T.-D. Ngo, M.-T. Ton-That, S. V. Hoa and K. C. Cole, *Polym. Eng. Sci.*, **49**, 666 (2009).
16. A. Yasmin, J. L. Abot and I. M. Daniel, *Scripta Materialia*, **49**, 81 (2003).
17. O. Becker, R. J. Varley and G. P. Simon, *Eur. Polym. J.*, **40**, 187 (2004).
18. M. Zanetti, P. Bracco and L. Costa, *Polym. Degrad. Stab.*, **85**, 657 (2004).
19. S. Wang, Y. Hu, L. Song, Z. Wang, Z. Chen and W. Fan, *Polym. Degrad. Stab.*, **77**, 423 (2002).
20. J. Zhu, F. M. Uhl, A. B. Morgan and C. A. Wilkie, *Chem. Mater.*, **13**, 4649 (2001).
21. S. S. Ray and M. Okamoto, *Prog. Polym. Sci.*, **28**, 1539 (2003).
22. J. W. Gilman, T. Kashiwagi, A. B. Morgan, R. H. Harris Jr, L. Brasel, M. Vanlandingham and C. L. Jackson, *Flammability of Polymer Clay Nanocomposite Consortium: Year One Annual Report*, US Department of Commerce, National Institute of Standards and Technology, Report NISTIR#6531, Gaithersburg, MD, USA (2000).
23. H.-B. Hsueh and Ch.-Y. Chen, *Polymer*, **44**, 5275 (2003).
24. E. Manias, A. A. Touny, L. Wu, B. Lu, K. Strawhecker, J. W. Gilman and T. C. Chung, *Proceedings of the ACS Division of Polymeric Materials: Science and Engineering (PMSE)*, **82**, 282 (2000).
25. J. Zhu, F. M. Uhl, A. B. Morgan and C. A. Wilkie, *Chem. Mater.*, **13**, 4649 (2001).
26. R. A. Vaia, G. Price, P. N. Ruth, H. T. Nguyen and J. Lichtenhan, *Appl. Clay Sci.*, **15**, 67 (1999).
27. A. R. Horrocks and D. Price, *Fire retardant materials*, CRC Press, Cambridge (2001).
28. Y. Zhou, F. Pervin, M. A. Biswas, V. K. Rangari and S. Jeelani, *Mater. Lett.*, **60**, 869 (2006).
29. K. Yano, A. Usuki, A. Okada, T. Kurauchi and O. Kamigaito, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 2493 (1993).