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A novel strategy for nanoclay exfoliation in thermoset polyimide nanocomposite systems

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Abstract

A novel method of nanoclay exfoliation in the synthesis of nanocomposites of PMR type thermoset resins was investigated. The method involves nanoclay intercalation by lower molecular weight PMR monomer prior to dispersion in primary, higher molecular weight PMR resin and resin curing to obtain the final composites. The resultant mechanical and thermal properties were evaluated as functions of clay type, degree of clay exfoliation, and clay intercalation strategies. It was found that sonication of clay at the time of intercalation by lower molecular weight PMR resin helps to achieve higher degree of exfoliation. In addition, clays obtained from ion exchange with a 50:50 mixture of *N*-[4(4-aminobenzyl)phenyl]-5-norborene-2,3-dicarboximide (APND), and dodecylamine (C12) showed better exfoliation than Cloisite® 30B clay. The resultant nanocomposites show higher thermal stability and higher tensile modulus.

Keywords: Polymer composite materials; Nanocomposites; Polyimide

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1. Introduction

Exfoliated nanoscale layered silicate particles have shown dramatic improvements in mechanical properties of polyamide systems [1]. Numerous studies have since attempted to achieve the same degree of reinforcement in an array of thermoset and thermoplastic polymer systems using layered silicate clays [2]. Layered silicate clays have become very popular in the last two decades due to low cost, high surface area, and versatility of organic treatments available to make them compatible with a host of commercial polymer systems [3]. These clays are naturally available as tactoid structures consisting of several silicate layers stacked together in crystalline lattice [4,5]. However, optimum mechanical reinforcement and improvement in thermal properties are obtained when tactoids are fully exfoliated into individual clay platelets [1–3,6–24].

A majority of prior work on polymer nanocomposites focused on thermoplastic polymers, where clay particles were mixed with polymers during melt processing and the high shear conditions prevalent in many internal mixers and screw extruders aided exfoliation and dispersion of clay [2,14–17]. On the other hand, most thermoset systems are cured under quiescent conditions into final products. Hence, shear forces cannot be used readily for clay exfoliation and dispersion in thermosets, except in cases where clay particles are brought into suspension with low viscosity monomer with the application of shear. The magnitude of shear force in these cases is small due to low monomer viscosity. Accordingly, large clay particle agglomerates are easily broken down into smaller particle agglomerates, but exfoliation cannot occur. Consequently, an early model based on polarity-driven monomer diffusion into clay galleries was developed [3], which explained clay exfoliation during quiescent epoxy curing in a number of epoxy–clay systems [9], although a universal understanding of the mechanisms of clay exfoliation is still lacking [23–25].

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Park and Jana [23–25] took a unique approach in their work with epoxies. They intercalated clay galleries with aromatic epoxy and dispersed the mixture in a major phase aliphatic epoxy. In the process, a difference between intra- and extra-gallery crosslink density was created during curing. This resulted in much stronger elastic forces from crosslinking epoxy within the clay galleries, which effectively pushed the clay layers apart against low viscous forces originating from the crosslinking aliphatic epoxy, thus causing exfoliation. It was learned from these studies that a faster increase of intra-gallery elastic forces compared to slower increase of extra-gallery viscous forces is conducive to clay layer exfoliation. The same methodology was applied in this work in an effort to produce clay nanocomposites of PMR polyimides.

PMR-15 polyimide resin is one of the leading thermoset polymer resins for high performance aerospace applications [26]. Several studies have been conducted in an attempt to further improve the mechanical and thermal properties by incorporating layered silicate clay into the PMR-15 matrix [6–13,27,28]. Researchers at NASA Langley Research Center used high shear homogenization and ultrasonication to produce clay dispersion in a solution of similar polyimide resins, which led to exfoliation and good clay dispersion in cured specimens as a result of high shear forces [6,12]. Other researchers used various organic treatments to promote favorable interactions between clay and polymer [3,9–11,27,29–31]. It was found that chemical structure of organic surfactant affects molecular orientation within clay galleries, thus directly influencing clay spacing [27]. In addition, studies have shown that chemically reactive clay surfactants within the polymer matrix improve mechanical and thermal properties greater than nonfunctional surfactants [12,31]. Other groups of investigators explored the effect of reduced cation exchange capacity (CEC) of clay surfaces, which reduces the amount of organic surfactant [11,32]. This research showed that clay dispersion in the polymer matrix improves as clay CEC decreases, due to the difference in intra-gallery molecular orientation.

Despite such activities, to our knowledge, no recipe exists for achieving full exfoliation of clay layers in PMR-15 composites. The present work followed the methodology of Park and Jana [23–25] whereby layered silicate clay was intercalated with lower molecular weight PMR resins, such as PMR-5 or PMR-10 prior to mixing with PMR-15 resin. In the process, the intra-gallery space was populated with short chain PMR resins which upon crosslinking generated chains with higher crosslink density and offered much rapid growth of elastic forces compared to growth of viscosity of PMR-15 resin. The resultant degree of exfoliation was evaluated as function of clay treatment and the methods of dispersion of clay in PMR-resins. Only the results involving PMR-5 and PMR-15 resins are reported in this paper.

2. Experimental

2.1. Materials

Two commercial nanoclays, Cloisite® 30-B (clay 1) and Cloisite® Na$^+$, both from Southern Clay Products (Gonzales, TX), were used. Two organic amines were used for clay treatments: *N*-[4(4-aminobenzyl)phenyl]-5-norborene-2,3-dicarboximide (APND), and dodecylamine (C12), both received from Aldrich. Nadic anhydride (NA) was acquired from TCI America (Portland, OR), 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) was purchased from Chriskev (Lenexa, KS), and methylene dianiline (MDA) was obtained from Aldrich (St. Louis, MO). Methanol and *N*-methyl pyrrolidinone (NMP) were used as solvents. Properties of these materials are listed in Table 1. Molecular structures of clay modifiers and compounds used in the synthesis of PMR resins are shown in Fig. 1. The monomethyl ester (NE, Fig. 2) of NA and dimethyl esters (BTDE, Fig. 2) of BTDA were prepared separately by refluxing the anhydrides in excess methanol so as to yield a solution containing 50 wt% solids [26]. The dissolution of anhydrides indicated the formation of the acid ester. The reflux was continued for 2 h after the solid anhydride had completely dissolved. The solutions were used immediately for PMR resin synthesis following a scheme presented in Fig. 2.

2.2. Ion exchange of clay

Cloisite® Na$^+$ clay was subjected to ion exchange reactions with protonated forms of amines [3,29,30]. A 1:1 molar ratio of APND:C12 was used to obtain higher clay layer separation in treated clay, as reported in an earlier work [33]. This clay will be referred to as clay 2 in the rest of this report. The properties of composites of clay 1 and clay 2 will be compared and contrasted later.

2.3. Clay intercalation

One gram each of PMR-5 (oligomer with MW 500) and organoclay (clay 1 and clay 2) were added in methanol and stirred for approximately 18 h to promote intercalation of clay galleries by PMR-5 resins. The suspensions of PMR-5 and clay particles in methanol were stirred using magnetic bar and optionally using high shear mixer and ultrasonicating bath. In one case, the suspension was stirred for 30 min using a stir bar, followed by ultrasonication at room temperature for 30 min and continued stirring by magnetic stirrer for 18 h. In another case, the suspension was stirred only using a high shear Conn® blade mixer for 4 h at room temperature. The clay was separated from the suspension by filtration and rinsed with methanol to remove residual PMR-5. The intercalated clay was dried in a vacuum oven at 75 °C for 3 h. Clay 1 and clay 2, intercalated with PMR-5, will be referred to as clay 1A and clay 2A, respectively.

Table 1
Material properties

Materials	Molecular formula	Mol. wt. (g/mol)	Melting pt. (°C)
APND	$C_{22}H_{20}N_2O_2$	344.4	192
MDA	$CH_2(C_6H_4NH_2)_2$	198.3	92.5
C12	$CH_3(CH_2)_{11}NH_2$	185.3	28
NA	$C_9H_8O_3$	164.2	165.5
BTDA	$C_{17}H_6O_7$	322.2	226

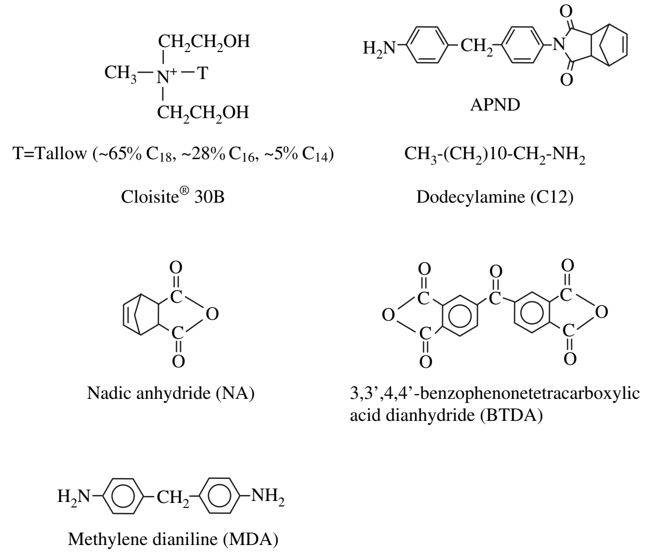

Fig. 1. Chemical structures of organic molecules used to modify clay surface and to synthesize PMR resins.

2.4. Composite synthesis

PMR-15 resin, an oligomer with molecular weight 1500, was synthesized by combining BTDE, NE, and MDA in the molar ratio of 2:2:3 in methanol, as per a standard procedure [26] (see Fig. 2) and was used as the primary resin of the composite. The clay composites were prepared by adding up to 5 wt% PMR-5-intercalated clay (clay 1A or clay 2A) to the monomer solution. A detailed procedure of the synthesis and compression molding process is presented elsewhere [33]. The composites produced will be designated by the type of clay used.

2.5. Characterization

The values of storage modulus (G') and complex viscosity (η^*) of crosslinking PMR-15 and PMR-5 resins were measured in ARES-M (TA Instruments) rheometer for curing temperatures between 50 and 330 °C at a scan rate of 5 °C/min. The oscillatory strain amplitude in a parallel plate setup was 1% and the frequency was maintained at 10 rad/s. The extent of clay layer separation and exfoliation was investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Thermal and mechanical properties were determined using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The temperatures at 5% weight loss (T_1), and the maximum rate of weight loss (T_2) were determined.

3. Results and discussion

3.1. Imbalance of molecular forces during curing

A difference in intra- vs. extra-gallery forces during crosslinking is the key to achieve exfoliation in thermoset systems, as elaborated for clay–epoxy system by Park and Jana [23–25]. Specifically, it was learned from clay–epoxy system that a faster increase of intra-gallery elastic forces compared to slower increase of extra-gallery viscous forces is conducive to clay layer exfoliation. It was achieved in this work by intercalating the clay galleries with PMR-5 resin and dispersing the PMR-5-intercalated clay in PMR-15 resin before curing. In this manner, curing of both PMR-5 and PMR-15 resins started at the same time. However, lower molecular weight PMR-5 resin yielded polymer with much higher crosslink density inside the clay galleries and produced more rapid increase of elastic forces as measured by the values of G' during curing (Fig. 3). On the other hand, the viscosity of the primary resin PMR-15 increased much more slowly due to lower crosslink density (Fig. 3). Incidentally, Fig. 3 also shows that the growth of G' for PMR-10 resin fell in between PMR-5 and PMR-15 resins, indicating that the exfoliation strategy adopted in this paper may also work with prior intercalation of clay particles by PMR-10 resin. However, we concentrated on PMR-5 resins

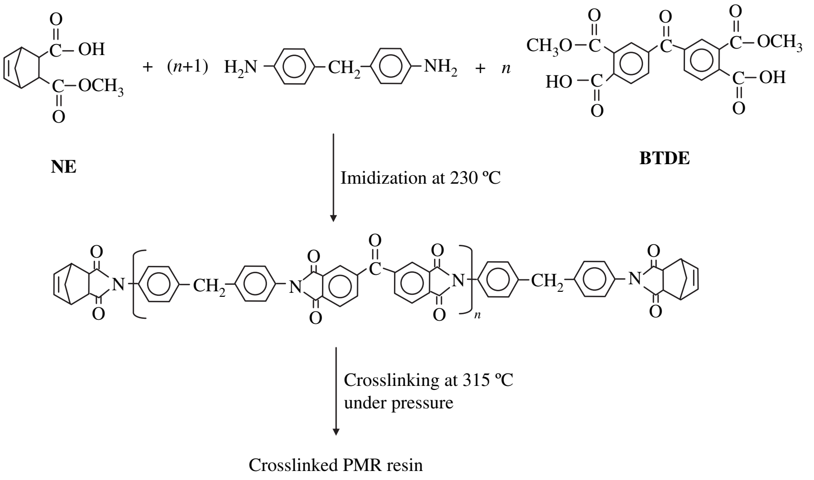

Fig. 2. Chemical reaction scheme for synthesis of crosslinked PMR-resins [26]. PMR-5, PMR-10, and PMR-15 resins are obtained, respectively, with $n = 0$, 1, and 2.

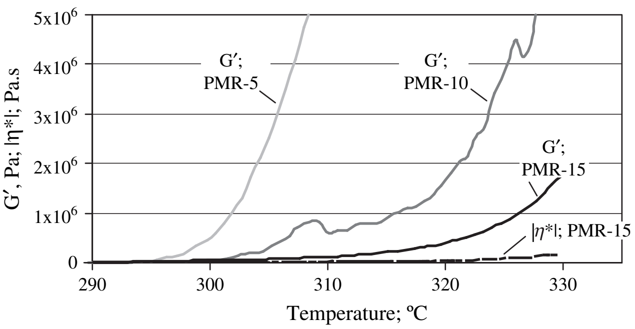

Fig. 3. Variation of G' with crosslinking of various PMR resins upon heating from 50 to 330 °C at a rate of 5 °C/min. The variation of absolute value of complex viscosity ($|\eta^*|$) of crosslinking PMR-15 is also shown.

in this work in order to capitalize on the faster rise of G' values.

It is evident from representative TEM images presented in Fig. 4 that higher degree of clay exfoliation was produced in composites of clay 1A and clay 2A compared to those of clay 1 and clay 2. Note that composites of clay 1 and clay 2 were produced by directly dispersing these clays in a solution of PMR-15 resin followed by curing. Fig. 4a and c reveal that clay particles remained mostly in tactoid forms and did not exfoliate. This is more apparent from the high magnification images. In these cases, the clay layer spacing as determined from XRD was 1.5 nm, which also corroborated the fact that clay particles remained mostly in the intercalated state in composites of clay 1 and clay 2. Representative TEM images present in Fig. 4b and d show that better exfoliation was achieved in the composites of clay 1A and clay 2A. Specifically, the adjacent clay layer separation is much greater in these cases. These results established that the methodology adopted in this work based on prior clay intercalation by PMR-5 resins can lead to higher degree of exfoliation, which may contribute positively to mechanical and thermal properties, as will be discussed later.

3.2. Effect of clay organic treatment

Recall that clay 1 is a commercial clay treated with an aliphatic quaternary ammonium ion while clay 2 contained a combination of an aromatic surfactant possessing the same norborene end group (APND) as the PMR polyimide resin

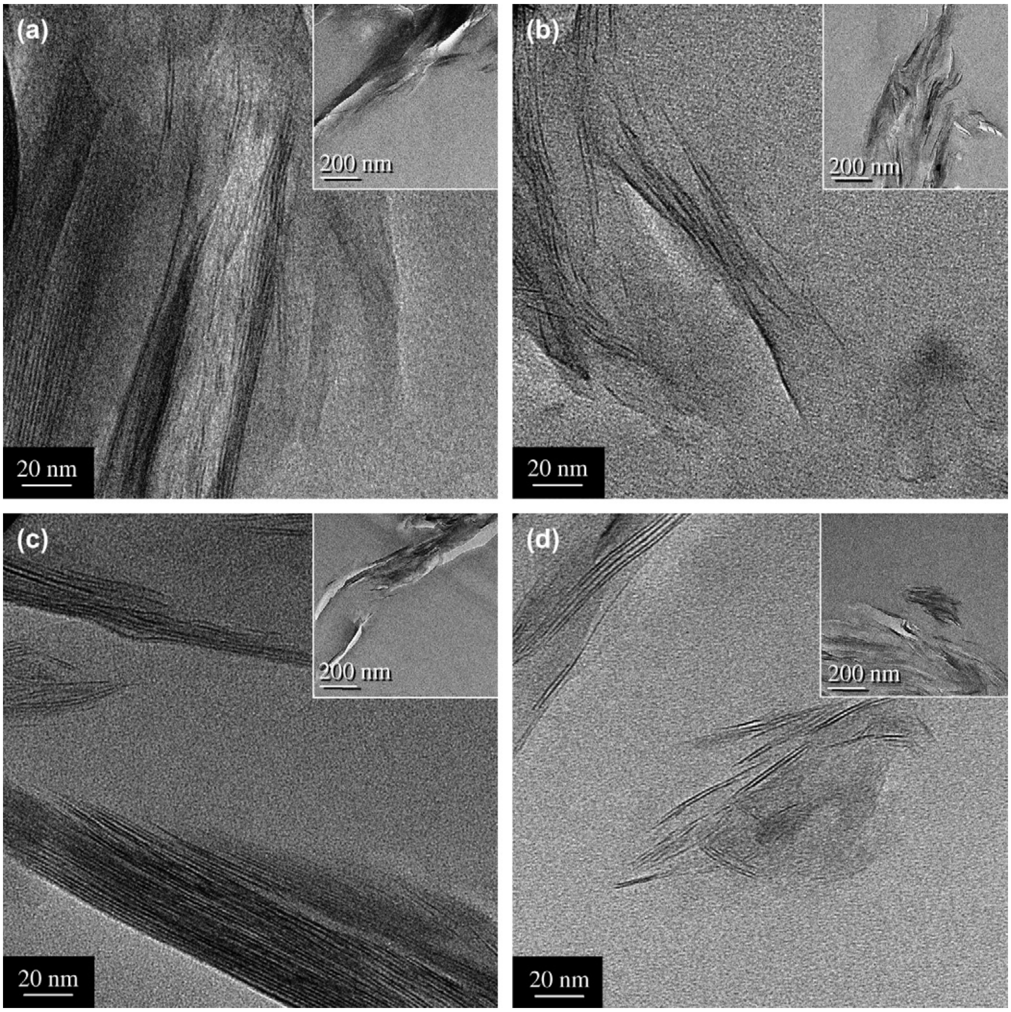

Fig. 4. TEM images of composites of (a) clay 1, (b) clay 1A, (c) clay 2, and (d) clay 2A.

and C12 aliphatic amine. Note that C12 amine was used to promote more intercalation by PMR-5 resins and hence increase the clay spacing. In the case of APND, the norborene end group can potentially participate in crosslinking reactions with the PMR resin. Such reactive clay treatments have been reported to greatly improve mechanical and thermal properties of composites [12,31].

Clay 2A was analyzed using TGA to determine the breakdown of its constituents, as depicted in Fig. 5. In view of data presented in Fig. 5, the PMR-5-intercalated clay contained the following: approximately 50 wt% silicate clay, 10 wt% C12, 10 wt% APND, 25 wt% low MW PMR intercalant, and less than 5% absorbed moisture. These values are important in calculations of clay loading and expected reinforcement, as well as offering insight as to the relation between organic treatment and thermal stability of the clay.

In this study, the performances of clay 1 and clay 2 were compared in terms of degradation temperatures T_1 and T_2 measured using TGA. The values of T_1 and T_2 are shown in Table 2. It is evident that the aromatic structure of organic treatment in clay 2 provides greater thermal stability than the aliphatic structure of organic treatment in clay 1. Note that clay 2 lost 5% weight at 365 °C, while clay 1 lost 5% weight at 280 °C. This clearly indicates that clay 2 is more suitable for use in PMR-resin nanocomposites, in light of the high curing temperature of 315 °C. It is also apparent from Table 2 that the organic treatment of clay 1 may undergo substantial degradation at high curing temperature of 315 °C, which may lead to collapse of clay galleries and act as a deterrent to clay exfoliation.

Clay layer separation as determined from the peaks in XRD of composites of clay 1A and clay 2A (Table 3) indicates that substantial thermal degradation of clay 1 occurred during resin curing at 315 °C. This resulted in a collapse of clay galleries in composites of clay 1A. On the other hand, the clay layer separation increased upon curing in the case of clay 2A (Table 3). Such increased clay layer separation, apart from higher thermal stability of clay 2 (Table 2), can be attributed to an increase in intra-gallery crosslinking density provided by the norborene end group of organic treatment in clay 2. The difference in intra-gallery crosslink density between clays 1A and 2A can be quantified using DSC to measure the energy produced during crosslinking. Fig. 6 shows that the exothermic energy produced during crosslinking of composites of clay 2A is 70% greater than that produced during crosslinking using clay 1A.

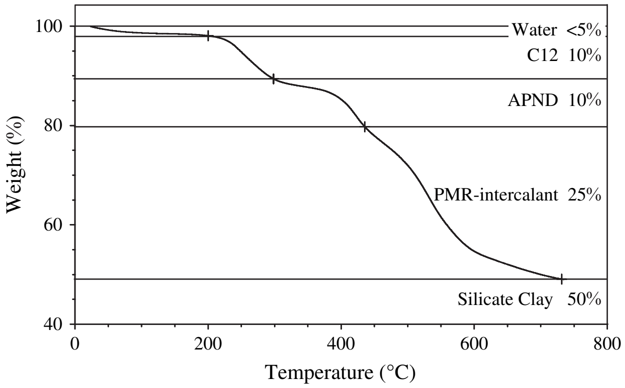

Fig. 5. Breakdown of components in clay 2A using TGA/FTIR.

Table 2
Thermal degradation temperatures of clays 1 and 2

	T_1 (°C)	T_2 (°C)
Clay1	280	400
Clay2	365	600

3.3. Effect of mixing

Park and Jana [23,25] proposed in their study on epoxy nanocomposites that clay exfoliation starts at the surface layers and continues towards the center of the tactoid until all layers are exfoliated or the crosslinking epoxy turns into gel [23]. It was shown that in the case of large tactoids, gelation may occur before all clay layers are exfoliated. In view of this, we compared three techniques for dispersion of clay in resin solution where the objective was to obtain smallest possible tactoids before resins were subjected to curing. As a baseline method, a magnetic stir bar was used to disperse clay. In addition, a high intensity mixing blade and an ultrasonicating bath were used with the expectation that better clay dispersion would be produced. Fig. 7 presents representative TEM images of clay 2A in composites produced using these three mixing methods. It is evident that the magnetic stir bar provides sufficient stirring for clay gallery intercalation by PMR-5 resin, however, the size of typical clay tactoids was large, e.g., many clay layers are seen stacked in the tactoid (Fig. 7a). Clay dispersion using high shear mixing blade, although was better than using stir bar, was not satisfactory, as large numbers of clay layers are still seen in tactoids (Fig. 7b). These blades are designed for mixing, blending, and dispersion of paints, adhesives, cements, etc. [34]; in these cases, the liquids typically are more viscous than PMR-15 monomer solution used in this work. In addition, the viscosity did not go up much due to low loading of clay in the solution. On the other hand, sonication produced best results as the number of clay layers in stacks is significantly reduced (Fig. 7c). Note that it is important to reduce the size of tactoids as much as possible before the polymer reaches its gel point and ceases the molecular motion, which in turn prevents exfoliation [23,25].

It is also interesting to monitor the separation of clay layers in each stage of composite synthesis, including clay treatment,

Table 3
Clay layer separation before and after curing for composites of clay 1A and clay 2A, at 5.0 wt% clay loading, prepared by stirring with magnetic stir bar

	d_{001} spacing (nm)	
Clay	Before curing	After curing
2A	1.5	2.2
1A	2.1	1.9

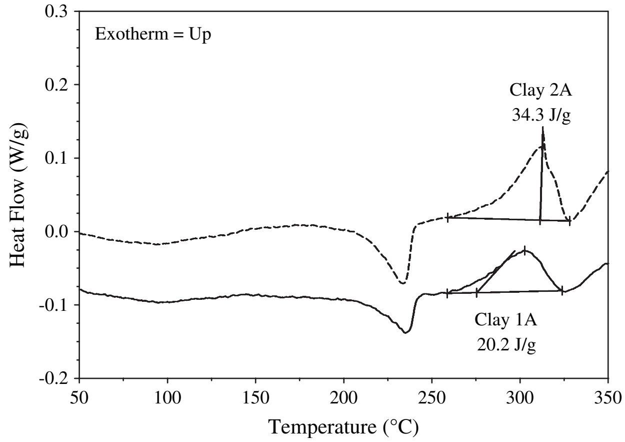

Fig. 6. DSC plot showing the difference in exothermic energy produced during crosslinking of composites of clays 1A and 2A.

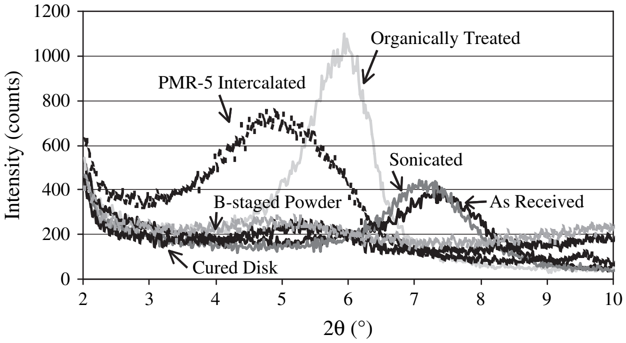

Fig. 8. XRD plots showing clay 2A spacing at each stage of processing. (Clay dispersion was prepared by stirring with stir bar and ultrasonication.)

clay intercalation by PMR-5, B-staging, and finally resin curing. The XRD results of a typical experiment are presented in Fig. 8. It is seen that spacing of clay 2A increases in each step. The clay peaks were not apparent after B-staging and curing, indicating that a majority of clay particles went through exfoliation during these steps. Other researchers have conducted similar work utilizing sonication and high shear mixing, and have shown promising results in regard to clay exfoliation and dispersion [6,11].

3.4. Clay exfoliation

Composites manufactured in this study contain mostly exfoliated clay with a small fraction of clay layers remaining in intercalated state. XRD can be used to quantify the level of intercalation in these stacks by measuring the distance between layers. The d_{001}-spacing of the clay layers can be calculated from Bragg's law, $n\lambda = 2d_{001}\sin\theta$ where n is an integer, taken to be 1, λ is the wavelength of X-ray ~ 1.54 Å, d_{001} is the spacing (Å) between planes in an atomic lattice, in this case, the layers in a clay tactoid, and θ is the angle (in radians) between the incident X-ray and the scattering planes. The well-known Scherrer formula [35] presented in Eq. (1) can be used to calculate the number of clay platelets per tactoid:

$$t = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where t is the average thickness of a clay tactoid, K is the Scherrer constant equal to 0.93 [35], and B is the width of the XRD peak at half maximum intensity. The values of t from the Scherrer formula and d_{001} from Bragg's law can be used to calculate the average number of layers remaining in stacks (N) in the composite, as given in Eq. (2):

$$N = 1 + \frac{t}{d_{001}} \tag{2}$$

A lower value of N, which may be given by small t or large d_{001}, indicates greater exfoliation of clay layers. Table 4 shows that clays 2 and 2A have fewer average clay layers per intercalated stack than clays 1 and 1A, respectively. This indicates greater exfoliation when a combination of aromatic and aliphatic clay modifiers was used compared to using aliphatic modifier alone, as in clay 1. Furthermore, composites of clays 1A and 2A have fewer average clay layers per stack than clays 1 and 2, respectively. This again supports the methodology

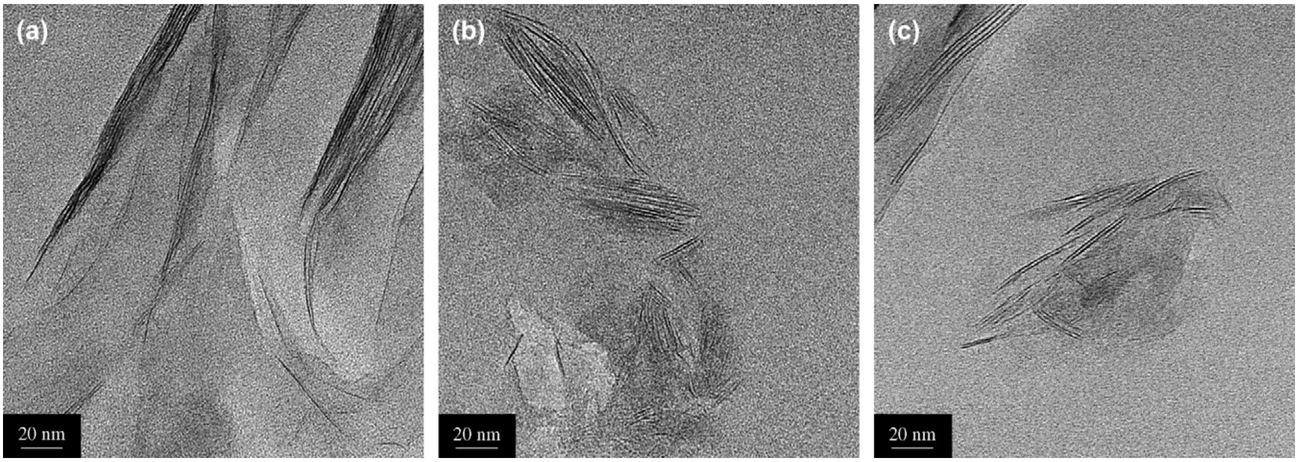

Fig. 7. TEM of composites of clay 2A by various dispersion methods: (a) stir bar, (b) high shear blade, (c) stir bar and ultrasonication.

Table 4
Values of N and TEM# representing clay delamination and dispersion in PMR-15/clay composites

Composite	N	TEM#	TEM# Std dev
1	3.47	8.9	2.0
1A	3.17	6.0	2.5
2	2.97	8.9	1.7
2A	2.55	7.9	2.4

that prior intercalation of clay by PMR-5 increases the degree of clay exfoliation in PMR-15 composites.

It is important to note that the values of N merely give an indication of the number of clay layers remaining in tactoid stacks and consequently, it does not take into account the fully exfoliated clay particles and it does not indicate if two intercalated clay particles are further apart or are very close to each other. In our case, much of the clay was exfoliated which was verified from TEM images. A method developed by Dennis et al. [36] was adopted, whereby the TEM micrographs were used to calculate the average number of clay platelets in a selected window representing 2500 nm^2 of cross-sectional area of the composite, which provides information on delamination and the quality of dispersion of clay layers. The average number of clay layers per unit area was computed from several TEM images and is referred to as the "TEM number". A higher value indicates many layers per area, indicating clay layers are closer together, suggesting a less intercalated state. Therefore, a lower TEM number indicates better exfoliation of clay layers. Using this method, composites of clays 1, 1A, 2, and 2A were compared. Table 4 shows that TEM number is less for composites of clays 1A and 2A than for clay 1 and clay 2, again supporting that prior intercalation by low molecular weight PMR increases clay exfoliation.

3.5. Thermal and mechanical properties

Improvements in thermal properties were observed in composites of clay 1A and clay 2A compared to neat resin, as shown in Table 5. Composites of clay 1A and clay 2A show an increase in T_2 by approximately 60 °C over that of the neat resin while composites of clay 1 and clay 2 showed improvement by about 30 °C. It is apparent from Table 5 that in the present system the improvement in thermo-oxidative stability (TOS) was not dependent on clay treatment. The clay particles are known to enhance TOS by creating a more tortuous path for diffusion of oxygen into the bulk of the materials [37]. Since oxidation is the primary degradation mechanism of PMR-15 [38], a reduction of oxidative degradation in the presence of clay was expected. TGA data, shown in Table 5, supports this expectation, as it is seen that the presence of clay makes no difference in values of T_2 when run under nitrogen. Table 5 also shows that the values of T_1 were not significantly different from the neat resin for any of the clay composites examined. This can be attributed to the small weight loss (less than 5%) occurring primarily at the composite surface and not affected by only 5 wt% exfoliated clay particles located primarily within the bulk of the material. Therefore, the higher degree of exfoliation observed with clay 1A and clay 2A bore no influence on T_1.

The exfoliated clay particles also slightly improved the stiffness as shown in Table 6. An increase in modulus is observed for clay composites when compared with neat PMR-15. Composites of clay 1A and clay 2A possess slightly higher stiffness at 300 °C while composites of clay 1 and clay 2 show stiffness values similar to neat PMR-15 resin.

Although the data shows improvements in TOS, the magnitude of increase in modulus is lower than expected, especially if one considers that the modulus of clay, 178 GPa [39] is much higher than that of PMR-15 (2.56 GPa). According to the Halpin Tsai equations for high aspect ratio fillers [40], the composite modulus (M_c) can be expressed as follows:

$$M_c = M_m\left(\frac{1+\zeta\eta\phi_f}{1-\eta\phi_f}\right) \tag{3}$$

$$\eta = \frac{\frac{M_f}{M_m}-1}{\frac{M_f}{M_m}+\zeta} \tag{4}$$

where M_m is polymer matrix modulus, M_f is clay filler modulus, ζ is aspect ratio of clay platelets (100 nm/1 nm), and Φ_f is vol% of clay filler (0.05%). The expected increase in modulus over that of neat resin should be about 50% at 50 °C and 70% at 300 °C. However, the highest modulus achieved in this study was 7% greater than that of neat PMR-15.

The low increase in modulus is not unusual. The Halpin Tsai equations assume full exfoliation and perfect distribution of clay platelets in the polymer matrix, as well as perfect surface interaction between the polymer and the particles [40]. Even though achieving perfect distribution is rare, several studies in the literature have reported increase in TOS as

Table 5
Thermal properties of neat PMR-15 and composites of clay 1, 1A, 2, and 2A

Composite	T_1		T_2 (air)		T_2 (N_2)	
	Average (°C)	Std dev	Average (°C)	Std dev	Average (°C)	Std dev
Neat PMR-15	469	16	672	5	574	21
Clay 1	468	12	701	25	564	5
Clay 2	474	9	697	46	576	0
Clay 1A	460	11	731	15	560	4
Clay 2A	468	1	730	14	569	12

Clay dispersion was prepared by stirring with stir bar and ultrasonication.

Table 6
Storage modulus of neat PMR-15 and composites of clay 1, 1A, 2, and 2A

Composite	G' at 50 °C		G' at 300 °C	
	Average (MPa)	Std dev	Average (MPa)	Std dev
Neat PMR-15	2559	470	1524	269
Clay 1	2679	366	1534	222
Clay 2	2562	211	1511	235
Clay 1A	2754	26	1634	24
Clay 2A	2608	278	1608	291

Clay dispersion was prepared by stirring with stir bar and ultrasonication.

well as increase in modulus by about 30% [6,8–12,29,41–43]. While these improvements are expected from clay reinforcement, other studies have shown that modulus values do not always increase significantly [32,41], and TOS is sometimes not affected at all by the inclusion of clay [13]. This implies that more work is needed to fully characterize and understand the interactions between clay and polymer in the current system, even though the present study provided better understanding on achieving clay particle exfoliation in PMR resins. Nevertheless, it must be kept in mind that PMR-resins are used in carbon fiber composite panels and the strength of such panels is derived primarily from approximately 60 wt% woven carbon fibers. In view of this, the merits of the present study can be realized in the form of increased clay exfoliation, which in turn can lead to reduced water permeability, reduced moisture diffusion, in addition to moderate improvements in thermal-oxidative stability.

4. Conclusions

This study shows that the values of G' of crosslinking PMR-5 and η^* of crosslinking PMR-15 system present conditions favorable for clay layer separation when the clay particles are intercalated with PMR-5 resin prior to dispersion in PMR-15. It was seen from experimental results that prior intercalation of clay by PMR-5 also increases thermal and mechanical properties greater than those with direct incorporation of organoclay into PMR-15 resin. Of the two organic treatments examined, a 1:1 molar mixture of APND and C12 performed better than Cloisite® 30B with regard to clay spacing and thermal properties, suggesting that aromatic reactive clay treatments are more beneficial than aliphatic modifiers for improvement of properties in PMR composites. In addition, it was seen that the method of mixing clay into the monomer solution plays a key role in achieving high degree of exfoliation. In this regard, sonication was found to be an important step in clay tactoid breakup and achieving larger degree of exfoliation.

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