An optimum organic treatment of nanoclay for PMR-15 nanocomposites

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Abstract

The present study examined ion exchange of layered silicate clay by ammonium ions and investigated thermal dissociation of ammonium ions and the presence of nadic endgroups in ammonium ions on the potential of clay exfoliation in nanocomposites of PMR-15 (an oligomer with molecular weight 1500). A novel method of organoclay exfoliation was used. It involved organoclay intercalation by lower molecular weight PMR-5 oligomer, dispersion of PMR-5/clay mixture in higher molecular weight PMR-15 resin, and curing of the resultant mixtures at approximately 315 °C. The PMR-5 resin residing inside the clay galleries underwent crosslinking during curing and produced higher elastic forces to facilitate clay platelets exfoliation against a slower rising viscous force in the matrix PMR-15 resin. It was found that the ammonium ions with nadic endgroups participated in intra-gallery PMR-5 resin crosslinking reactions and promoted better exfoliation compared to non-reactive ammonium ions. Improvements in thermal and mechanical properties were also observed.
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Keywords: Nanocomposites; Layered silicate clay; Organic treatment

1. Introduction

PMR-15 thermoset polyimide has been a leading aerospace resin for over 30 years, due to its thermal stability and superior mechanical properties [1,2] in addition to its ease of processing [3]. This resin is commonly used in conjunction with multi-layer carbon fabric or fiberglass to make large panels that must withstand high thermal and physical stresses. High thermo-oxidative stability [4,5] and strong mechanical properties of PMR-15 resin make it suitable for many high performance applications [6–8]. Despite meeting some of the desirable properties, continued improvements of mechanical and thermal properties are often sought [9], especially to capitalize on some of the useful attributes offered by nanoparticles. The resultant PMR-15 nanocomposites can potentially offer higher strength-to-weight ratio. It is conceivable that weight reduction is always a priority in aerospace applications [1]. Another potential benefit of PMR-15 nanocomposites is the reduction of oxygen permeability, especially in light of oxidation being the primary mode of PMR-15 degradation [5,10,11]. A third consideration is the need for continuous development of materials technology whereby the envelope of current technology is expanded to obtain higher performance materials. In view of these, the development of methods for improvement of thermal stability and stiffness and reduction of oxygen permeability in PMR-15 composites is considered significant advancement in aerospace materials technology.

A spate of research over the past two decades established the benefits of nanoscale layered silicate clay as reinforcement of polymer systems [12–33]. A key to such success lies with the availability of proper organic surfactants for treatment of clay [34–36] and fundamental understanding of clay exfoliation process in several thermoset [15,36–42] and thermoplastic polymer systems [25,26,43–46]. Many studies have shown that only small loadings of fully exfoliated clay are necessary to attain significant improvements in properties, with potential

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savings in weight of the materials compared to those filled with glass fibers [47−49].

In our previous work, a novel method was described for incorporation of organoclay into PMR-15 resin so as to achieve increased clay exfoliation [50]. Note that clay exfoliation in thermoset polymer systems, such as PMR resins, suffers from some inherent difficulties associated with the absence of imposed flow during crosslinking reactions. In epoxy-clay systems, a disparity between the intra- and extra-gallery polymerization rates was used to interpret full clay exfoliation [36−38]. Park and Jana [40,42] explained that the disparity between the intra- and extra-gallery polymerization rates is not necessary for clay exfoliation in epoxy systems. Instead, these authors established that the storage modulus of crosslinking epoxy inside the clay galleries should increase more rapidly than the viscosity of the extra-gallery epoxy to produce clay exfoliation. Our previous work [50] highlighted a method whereby organoclay galleries were first intercalated by a lower molecular weight PMR oligomer before incorporation of such treated clay into higher molecular weight PMR matrix resin. During the crosslinking step, the lower molecular weight PMR resin inside the clay galleries gave rise to higher crosslink density, which in turn resulted in higher elastic force within the clay galleries compared to a slowly increasing viscosity of the higher molecular weight PMR matrix resin surrounding the clay tactoids. This scenario is schematically presented in Fig. 1. The imbalance of molecular forces during crosslinking as depicted in Fig. 1 results in an exfoliated clay structure, whereby the distance between the neighboring clay particles is at least 6 nm [40,50].

The present work sought an optimum organic treatment for nanoclay which is compatible with PMR resin system especially to withstand a curing temperature of approximately 315 °C and simultaneously aid clay exfoliation. Note that conventional aliphatic quaternary ammonium ions experience substantial thermal degradation at temperatures around 200 °C [51−54] and hence cannot withstand temperatures greater than 300 °C customarily used in PMR-15 polyimide resin curing [3]. It was found in our earlier work that Cloisite® 30B clay loses 5% weight at 280 °C due to decomposition of aliphatic side chains of the quaternary ammonium ions. It was anticipated that an organic ammonium ion with aromatic side groups should be more thermally stable at PMR-15 curing temperature of 315 °C. In addition, it was anticipated that an organic ammonium ion with nadic endgroup may potentially participate in crosslinking with the intra-gallery PMR-5 resin and help tether clay particles with the PMR resin. Several studies have already shown that reactive clay treatments are more beneficial in property improvement than non-reactive surfactants [8,25,27,55]. For example, Ahmed and Jones [55] demonstrated that the interfacial adhesion between the matrix resin and the particulate reinforcement is very important for polymer composites, and an organic ammonium ion that reacts chemically with the surrounding polymer improves interfacial adhesion. Pattanayak and Jana [25] synthesized polyurethane nanocomposites using reactive organoclay and reported large increases in tensile modulus and strength with inclusion of 1%, 3%, and 5% organoclay
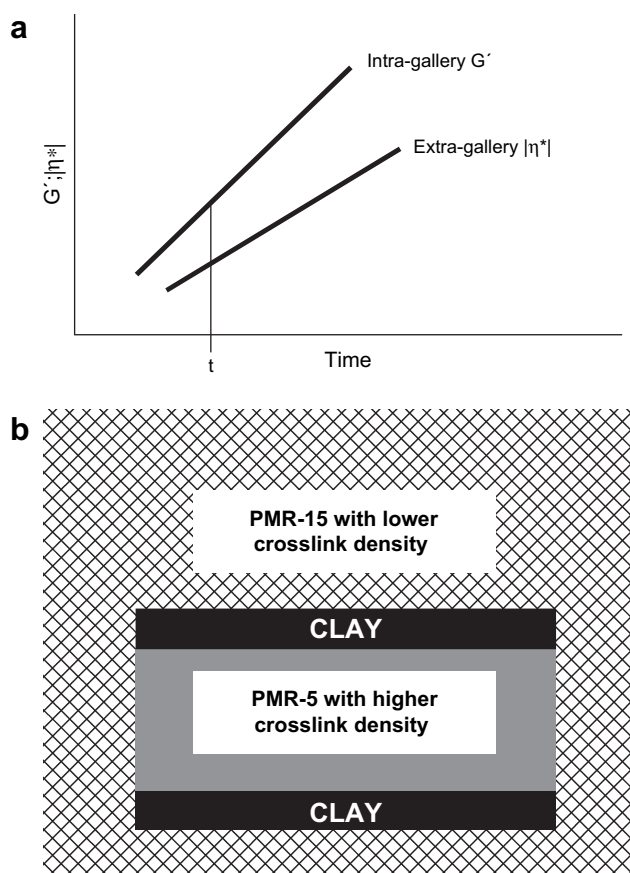

Fig. 1. (a) The relationship between viscosity ($|\eta^*|$) and modulus (G') of intra-gallery and extra-gallery PMR resin with crosslinking time. (b) Schematic showing higher crosslink density inside clay galleries than in the matrix polymer.

by weight. Tyan et al. [24] showed that polyimide composites derived from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride and reinforced by 1−7% by weight of clay treated with hydrochloride salt of 4,4′-oxydianiline improved mechanical properties significantly over those of neat polyimide. This was due to strong tethering between the clay and the polymer, which originated from the chemical reactions between the clay treatment and the polyimide resin.

The present study examined four clay treatments for potential use in conjunction with the PMR-15 system. First, one commercially available montmorillonite clay was treated separately with an aliphatic quaternary ammonium ion, a simple aliphatic primary ammonium ion, and two primary ammonium ions based on aromatic amines, one of which possessed the same reactive nadic endgroup as the PMR-5 and PMR-15 oligomers. The nadic endgroups have the potential to participate in crosslinking with the surrounding PMR resin. The clay particles thus obtained were subjected to the same thermal cycles as in PMR-15 imidization and crosslinking steps. In addition, composites manufactured using treated clays were analyzed to obtain information on thermal stability, energy produced during crosslinking of intra-gallery resin, and overall increase of clay layer separation during composite manufacturing.

2. Experimental

2.1. Materials

Two commercial nanoclay specimens, Cloisite® 30B (clay 1) and Cloisite® Na⁺, were obtained from Southern Clay Products (Gonzales, TX). The organic amines used for clay treatments were N-[4(4-aminobenzyl)phenyl]-5-norbornene-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. Selected properties of these materials are listed in Table 1. Fig. 2 presents chemical structures of quaternary ammonium ion treatment in clay 1 and the amines used in ion exchange of Cloisite® Na⁺. The molecular structures of compounds used in the synthesis of PMR resins are shown in Fig. 3. The monomethyl ester (NE) of NA and dimethyl esters

Table 1
Selected properties of organic compounds

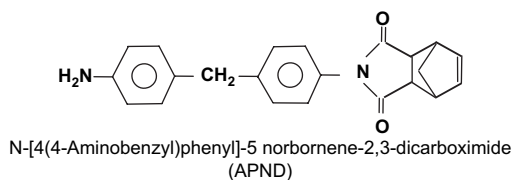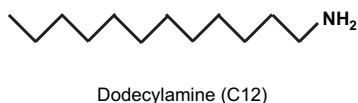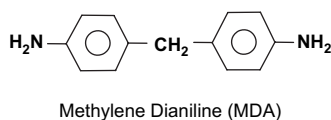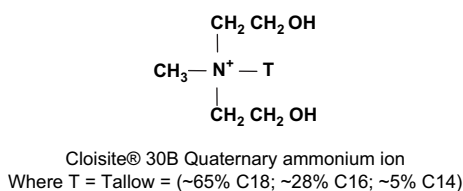| Materials	Molecular formula	Molecular weight (g/mol)	Melting point (°C)
APND	$C_{22}H_{20}N_2O_2$	344.4	192
MDA	$CH_2(C_6H_4NH_2)_2$	198.3	92.5
C12	$CH_3(CH_2)_{11}NH_2$	185.3	28
NA	$C_9H_8O_3$	164.2	165.5
BTDA	$C_{17}H_6O_7$	322.2	226

Fig. 2. Chemical structures of organic surfactant in Cloisite® 30B and the primary amines used in the study for clay treatment.
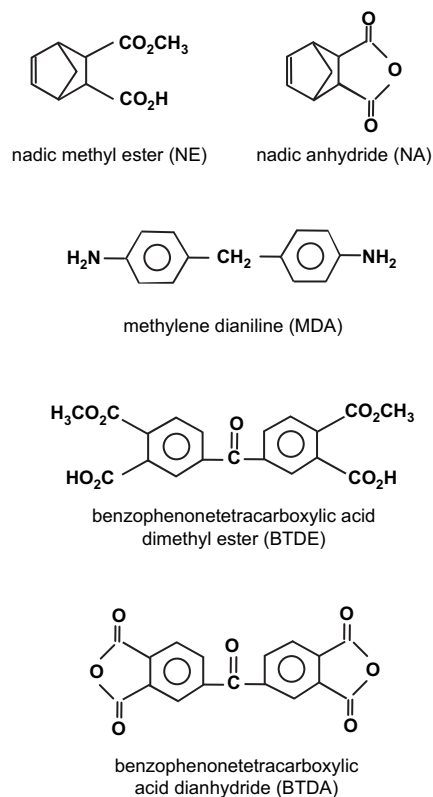

Fig. 3. Chemicals used in the synthesis of PMR resin.

(BTDE) of BTDA were prepared separately by refluxing the anhydrides in excess methanol so as to yield a solution containing 50 wt% solids [3]. 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 shown in Fig. 4.

2.2. Ion exchange of clay

Cloisite® Na⁺ was ion exchanged separately with aqueous solutions of the hydrochloride salts of APND, MDA, and C12 amines using a procedure published elsewhere [34,35]. In addition, amine mixtures in combinations of APND/C12 and MDA/C12 were used to treat Cloisite® Na⁺ clay. Unless otherwise stated, APND and C12 or MDA and C12 were mixed in 50:50 ratio by weight. These clays are referred to as clay 2, clay 3, etc. as listed in Table 2. It was found earlier that combinations of MDA/C12 amines help obtain greater clay layer separation in treated clay [8].

2.3. Clay intercalation by PMR-5 resin

One gram each of PMR-5 (an oligomer with molecular weight 500; structure shown in Fig. 4) and organoclay were mixed in methanol. The mixture was stirred for 30 min at room temperature using a magnetic stir bar, followed by ultrasonication at room temperature for 30 min, and continued stirring by magnetic stir bar for 18 h. The clay was then separated
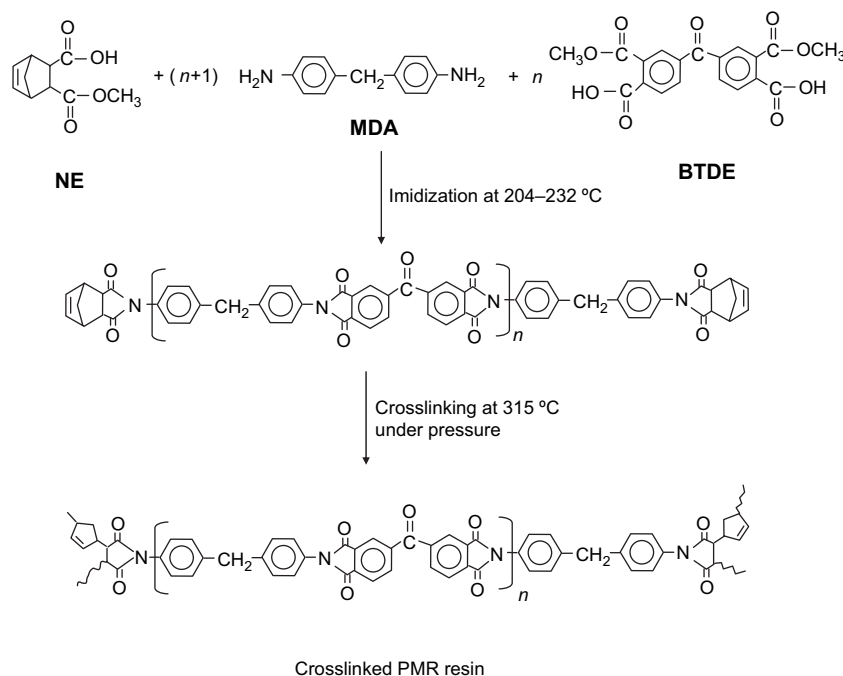
Fig. 4. Chemical reaction scheme for synthesis of crosslinked PMR resins [3]. PMR-5, PMR-10, and PMR-15 resins are obtained, respectively, with $n = 0$, 1, and 2.

Table 2
Designation of organoclays

Amine and amine mixtures	Name
APND	Clay 2
Dodecylamine	Clay 3
Methylene dianiline	Clay 4
APND/C12	Clay 5
MDA/C12	Clay 6

Cloisite® 30B is designated as clay 1.

from the suspension by filtration and rinsed with methanol to remove the residual PMR-5 resin. The intercalated clay was dried in a vacuum oven at 75 °C for 3 h.

2.4. Composite synthesis

The composites of PMR-15 (oligomer with molecular weight 1500, structure shown in Fig. 4) were synthesized by combining NE, MDA, and BTDE in the molar ratio of 2:2.087:3.087 in methanol, as per a standard procedure described elsewhere [3] and adding 5 wt% organoclay intercalated by PMR-5 resin. The mixture was stirred with heating, thus boiling off most of the methanol before imidization (called B-staging) was conducted in a circulating air oven at 204–232 °C for 3 h to form the imidized oligomer containing a desired loading of intercalated clay. This PMR-15 oligomer/clay mixture was ground into powder and cured in a compression mold at 315 °C, 16.2 MPa, for 2 h, to obtain 1-inch-diameter circular composite disks. The polymer underwent crosslinking reactions at this time. The disks were then post-cured in a circulating air oven for 16 h at 315 °C to ensure complete crosslinking.

2.5. Thermal treatment of organically treated clay

The organoclays (see Table 2) were subjected to heating in an oven following the same thermal cycle as experienced by PMR-15 oligomer during curing. To distinguish clays at various stages of thermal treatment we designate the clays before heating as "X" clays in this paper. Specimens of each organoclay before and after intercalation by PMR-5 oligomer were subjected to heating cycle. Two samples of each organoclay were placed in a circulating air oven with temperature ramp between 204–232 °C for 3 h to simulate the PMR-15 B-staging procedure. Clays obtained immediately after this thermal treatment step are referred to as "Y" clays. One sample of "Y" clay was then kept in the oven at 315 °C for 2 h to simulate the thermal cycle of PMR curing reactions. These clays are referred to as "Z" clays. A summary of heat treatment methods is shown in Table 3.

2.6. Characterization

The X-, Y-, and Z-type thermally treated organoclays were analyzed by thermogravimetric analysis (TGA) method. The temperatures at 5% weight loss (T_1) and at maximum rate of weight loss (T_2) were determined after subjecting the clay

Table 3
Designation of organically treated clays as function of heat treatments

Designation	Temperature (°C)	Time (h)	Simulated stage of composite processing
X	–	–	(a) Clay after ion exchange, (b) clay after PMR-5 intercalation
Y	204–232	3	PMR-15 B-staging
Z	315	2	PMR-15 curing

specimens to heating in air at a scanning rate of 10 °C/min from 20 °C to 750 °C. Differential scanning calorimetry (DSC) was used to monitor crosslinking of PMR-5 oligomer in PMR-5 intercalated clays. The thermal energy produced by crosslinking reactions was determined from DSC traces. DSC traces were obtained by heating clay specimens under nitrogen environment at 1.4 MPa from room temperature to 450 °C at 5 °C/min. A higher pressure was used to simulate PMR curing conditions. The extent of clay layer separation in "X", "Y", or "Z" clays was investigated by wide angle X-ray diffraction (XRD) method. The extent of clay layer separation and exfoliation in PMR composites was investigated by XRD and transmission electron microscopy (TEM). Approximately 70 nm thick specimens were microtomed from cured PMR-15 nanocomposites and used to generate TEM image using Philips CM 200 transmission electron microscope at an acceleration voltage of 200 kV. Thermal properties of composites were determined by TGA. A TA instrument dynamic mechanical analyzer (DMA) was used to measure storage modulus (G'), loss modulus (G''), tangent delta (tan δ), and glass transition temperature (T_g) of the nanocomposites. For this purpose, cantilever specimens of size $17.4 \times 5.0 \times 1.7$ mm were subjected to dynamic oscillation of 10 μm amplitude with a frequency of 1 Hz and the thermal scan was carried out at a rate of 2.5 °C/min.

3. Results and discussion

3.1. Thermo-oxidative stability of organoclay

The material property of most significant interest in this work is the thermo-oxidative stability (TOS) of nanoclay and the composites. However, we first discuss the thermal stability of organoclays as determined by TGA, in the form of values of T_1 and T_2 (Table 4). We were specifically interested in monitoring thermal degradation of clay at each stage of PMR-15 composite preparation. Recall that X-, Y-, and Z-clay represent, respectively, the organoclay with no heat treatment, heat treatment simulating the thermal conditions of PMR-15 B-staging step, and heat treatment reproducing the temperatures experienced during PMR curing. In view of this, the data on thermal stability of X-, Y-, and Z-clay are presented in Table 4. Note that the state of clays in the composites will be assessed later in terms of the values of T_1 and T_2 of the composite materials.

Table 4
Values of T_1 (°C) and T_2 (°C) of organoclays as a function of clay treatment at various stages of thermal treatment

Clay	T_1; X-clay	T_2; X-clay	T_1; Y-clay	T_2; Y-clay	T_1; Z-clay	T_2; Z-clay
1	276	400	342	365	497	601
2	260	564	300	576	420	566
3	276	329	359	602	508	608
4	386	716	563	720	581	719
5	365	623	390	609	461	608
6	378	651	468	621	530	612

The values of T_1 of clays 1, 2, and 3 as prepared (X-clay) fell well below the curing temperature (approximately 315 °C) of PMR-15 resin, indicating that these clays are not suitable for PMR-15 composite preparation. The data on X-clays also show that clays 4, 5, and 6 are more thermally stable than other organically treated clays; the presence of aromatic amines, MDA and APND, in these clays provided greater thermal stability. In the cases of Y- and Z-clay, the values of T_1 shifted to much higher temperatures compared to X-clays, although the same trend is seen, i.e., the presence of aromatic amines provided greater thermal stability. A higher value of T_1 for Y- and Z-clay is not surprising as the clays lost most small molecules during thermal cycle of the B-staging and curing steps, respectively. It is seen from Table 4 that Y-clays containing aromatic amines – clays 4, 5, and 6 – can withstand the high curing temperature (∼315 °C) of PMR-15 without much loss of mass. In view of higher thermal stability of clay 5, it is surprising to see that clay 2, i.e., clay treated with APND alone, shows poor thermal stability. This can be attributed to degradation of the nadic endcap, which undergoes a reverse Diels–Alder (RDA) reaction at these temperatures and ambient pressure [56]. In this case, the RDA reaction of the nadic endcaps in APND was favored as the pressure was atmospheric during thermal treatment. Note that high pressure is used during PMR-15 curing in order to keep the RDA reaction under control and to drive the reversible crosslinking reaction in the desired direction. For this purpose, a 16.2 MPa pressure is used routinely for curing of PMR-15 nanocomposites. On the other hand, clay 5, i.e., clay containing 50:50 weight ratio of APND and C12, contained much less nadic endgroups and consequently showed higher TOS than clay 2, even at ambient pressure.

3.2. Intra-gallery PMR-5 crosslinking

Next we investigated whether PMR-5 resin intercalated into clay galleries did indeed undergo crosslinking reactions during B-staging or when exposed to PMR-15 curing temperature of 315 °C. Note that these crosslinking reactions are exothermic. In view of this, DSC was used to determine the extent of exothermic heat released during crosslinking of intra-gallery PMR-5 molecules. The heat release data were also used to determine whether APND molecules present in clays 2 and 5 participated in crosslinking reactions themselves or with the molecules of PMR-5 oligomer inside the clay galleries. Note that both APND and PMR-5 oligomer molecules contain nadic endgroups. As expected, DSC traces for all organoclay intercalated with PMR-5 show exothermic peak at ∼315 °C corresponding to crosslinking of PMR-5 oligomer molecules inside the clay galleries (Fig. 5). The integration of these peaks gives a quantitative measurement of the energy released during crosslinking reaction, as presented in Table 5.

It is found that APND-treated clays (clays 2 and 5) released significantly greater energy than MDA-treated clays, as presented in Table 5. Note that clay 5, intercalated with PMR-5, released 27 J/g during crosslinking, while clay 6 intercalated with PMR-5 released less heat, 20 J/g. It is believed
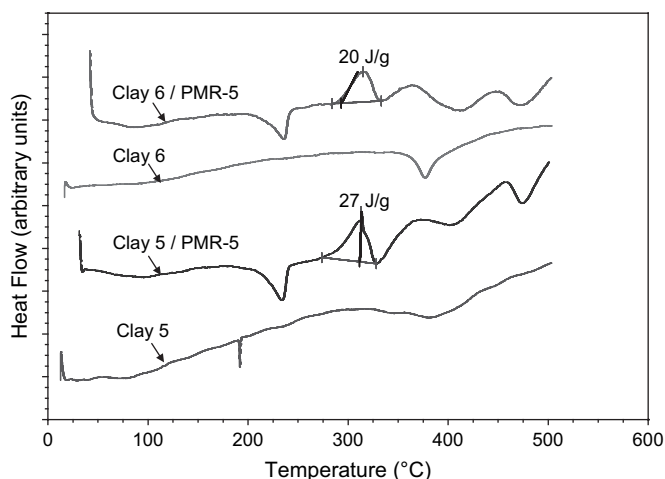
Fig. 5. DSC traces of clays 5 and 6 and their counterparts after intercalation with PMR-5 resin designated, respectively, as clay 5/PMR-5 and clay 6/PMR-5.

that the nadic endgroup of APND, a constituent in clay 5, participated in crosslinking and resulted in greater energy release during the crosslinking step. The long aliphatic chains of C12 and the large quaternary ammonium ion in Cloisite® 30B clay helped expand gallery height (see later) in clays 1 and 3, respectively, such that large amounts of PMR-5 oligomer may have intercalated inside the clay galleries. This, in turn, resulted in a high degree of intra-gallery crosslinking, and consequently, a high level of energy released for clays 1 and 3. On the other hand, MDA-treated clay intercalated with PMR-5 oligomer released much smaller exothermic heat (Table 5). This can be interpreted as follows. Clays treated with MDA (clays 4 and 6) did not show much increase of gallery height (see later) and hence did not allow much PMR-5 resin to intercalate inside the clay galleries. In addition, unlike APND molecules, MDA molecules could not participate in crosslinking reactions with PMR-5 oligomer.

The amount of energy released during intra-gallery crosslinking and as function of organic treatment of clay bears another significance. A higher energy released during crosslinking reaction also indicates a higher intra-gallery crosslink density. A higher crosslink density, in turn, may mean greater elastic force available for exfoliation of clay layers. In view of this, clays 1, 2, 3, and 5 all have the potential to aid exfoliation of clay layers in the composites. The participation of APND molecules in crosslinking with PMR-5 oligomers may also potentially offer the scope for tethering between the polymer chains and the clay particles, especially in clays 2 and 5.

Let us now turn our attention to DSC data of Y-clays, i.e., clays obtained after subjecting to B-staging temperatures of 232 °C for 3 h. Interestingly, no exothermic peaks were seen in DSC traces of Y-clays. This suggests that the intra-gallery PMR-5 crosslinking took place during the B-stage reaction, although the temperature of B-staging (232 °C) was much lower than the peak PMR-5 curing temperature of 315 °C as seen in Fig. 5. A reflection into exothermic peaks seen in Fig. 5 reveals that PMR-5 oligomer curing was complete in approximately 12 min between the onset at ∼260 °C and end at ∼320 °C. However, Y-clays were subjected to a temperature of 232 °C for 3 h. It is understood that the rate of PMR-5 oligomer crosslinking was much slower at 232 °C, but a long reaction time of 3 h helped in completing the reactions.

3.3. d_{001}-Spacing of organoclays and modulus of composites

Note that an increase of d_{001}-spacing of the clay layers during B-staging may later lead to fully exfoliated clay morphology in the composites. In this study, the d_{001}-spacing between clay layers was obtained from XRD diagrams. It is seen that clay treated with aliphatic amines (clays 1 and 3), or a combination of aliphatic and aromatic amines (clays 5 and 6), produced much higher d_{001}-spacing as shown in Table 6. However, clay 1 starts degradation at 220 °C [51,54] and loses 5 wt% at 276 °C (Table 4), which are much lower than the temperature used for PMR-15 curing at 315 °C [3,50]. In view of this, clay 1 was discounted from further consideration in this study. It is also seen from Table 6 that combinations of aromatic and aliphatic amines help expand clay gallery more than either the aromatic or the aliphatic amines.

A second observation is that X-clays treated with a combination of aromatic and aliphatic amines (clays 5 and 6) show higher d_{001}-spacing than those treated with only aromatic amines (clays 2 and 4), indicating that the presence of C12 in the galleries promoted non-parallel orientation of the aromatic ammonium ions inside the clay galleries. This trend was also true for Y- and Z-clay. It is also noticed that the d_{001}-spacing of Z-clays corresponding to clays 3, 5, and 6, i.e., those treated with aliphatic ammonium ions C12, decreased substantially compared to Y-clays. This can be attributed to clay gallery collapse in Z-clays after heating at 315 °C owing to thermal degradation of C12 chains. This is more apparent in the case of clay 6 where the d-spacing of Z-clay is in the same neighborhood of X-clay. An increase of d_{001}-spacing

Table 5
Exothermic energy released in J/g of organoclay during intra-gallery PMR-5 crosslinking in intercalated organoclays

Clay treatment	Energy released (J/g)
Clay 1	18
Clay 2	31
Clay 3	25
Clay 4	13
Clay 5	27
Clay 6	20

Table 6
d_{001}-Spacing of PMR-5-intercalated clay after each stage of thermal treatment

Clay treatment	X-clay (nm)	Y-clay (nm)	Z-clay (nm)
Clay 1	2.25	2.95	2.50
Clay 2	1.51	1.51	1.47
Clay 3	2.06	2.49	2.06
Clay 4	1.46	1.48	1.40
Clay 5	1.97	2.54	2.21
Clay 6	2.14	2.56	2.19

for almost all X-clays during B-staging can be attributed to intra-gallery crosslinking of PMR-5 oligomer molecules.

We can now evaluate an outstanding issue of the correspondence between the energy released during heating of clay and the d_{001}-spacing. The energy released was the highest for clay 2 among all organically treated clay particles (Table 5). One might argue that clay 2 would show the strongest potential to exfoliate among all clay specimens used in this study. However, it is apparent from the data presented in Table 6 that d_{001}-spacing in clay 2 was smaller than clay 5. In addition, the d_{001}-spacing of clay 5 increased during B-staging, while that of clay 2 remained the same. This can be attributed to poor thermal stability of clay 2 as discussed in Section 3.1. In this case, the nadic endcaps underwent reverse Diels–Alder (RDA) reaction and participated in crosslinking reactions among the adjacent APND molecules in the clay galleries, which in turn released large exothermic heat. It is also surmised from a low value of d_{001}-spacing of clay 2 (Table 6) that not much PMR-5 oligomer intercalated into the galleries of clay 2.

It is also important to consider that XRD only measures the spacing between parallel clay layers in a stacked, tactoid configuration. In view of this, TEM images were taken to visually examine the extent of clay exfoliation and to determine the size of intercalated tactoids in PMR-15 composites of clays 5 and 6. Fig. 6 presents typical TEM images where intercalated clay galleries are revealed. Although some areas in Fig. 6 show greater clay gallery height (~2 nm) for clay 5 than clay 6 (~1.5 nm), examination of several TEM images at low magnifications (2 × 2 mm window) indicates that the difference in gallery height between these two materials is not discernible. In similar fashion, the level of clay layer exfoliation as revealed by d_{001}-spacing greater than 6 nm in some areas of the composites, is similar in composites of clays 5 and 6.

Now recall that the nadic endgroups of APND molecules in clay 5 participated in crosslinking reactions with PMR-5

Table 7
Average storage modulus (MPa) of PMR-15 composites using clay treated with 1:1 aromatic:aliphatic modifiers

Composite	G' at 50 °C (MPa)	G' at 300 °C (MPa)
Neat PMR-15	2559 ± 470	1524 ± 269
15/AC/5	2737 ± 530	1662 ± 272
15/MC/5	2530 ± 393	1606 ± 396

oligomer as revealed from excess exothermic energy data in Table 5. This additional degree of crosslinking may result in an improvement in mechanical properties. In order to test this, the storage modulus of composites of clays 5 and 6 were measured in DMA, and the data is compiled in Table 7. In this case, the values of G' were recorded at 50 °C and at 300 °C, to give a measure of the stiffness in both the glassy state and at temperature close to the glass transition of PMR-15 (~340 °C). Although the trend seen from the average values of G' presented in Table 7 indicates that the composites of clay 5 provide higher average values of G' than those of clay 6 and neat PMR-15, it can be inferred in view of the large standard deviation that these composites provided modulus at least similar to that of unfilled PMR-15.

Another factor in determining the most appropriate clay treatment is toxicity. It is well known that MDA is a mutagen and a suspected carcinogen [57–60]. Thus, its handling during sample preparation may pose health problems. This concern, however, does not exist with APND.

In view of the data discussed above, it can be inferred that clays treated with aromatic surfactants, or combinations of aromatic and aliphatic surfactants, are more thermally stable. Of the two aromatic treatments examined, APND-treated clays produced greater thermal energy during crosslinking than MDA-treated clays, and resulted in higher average values of storage modulus. These clays are also much less toxic, indicating that APND is a more appropriate clay treatment than MDA for the PMR system. Furthermore, it was seen earlier that the combination of APND and C12 produces greater increase in
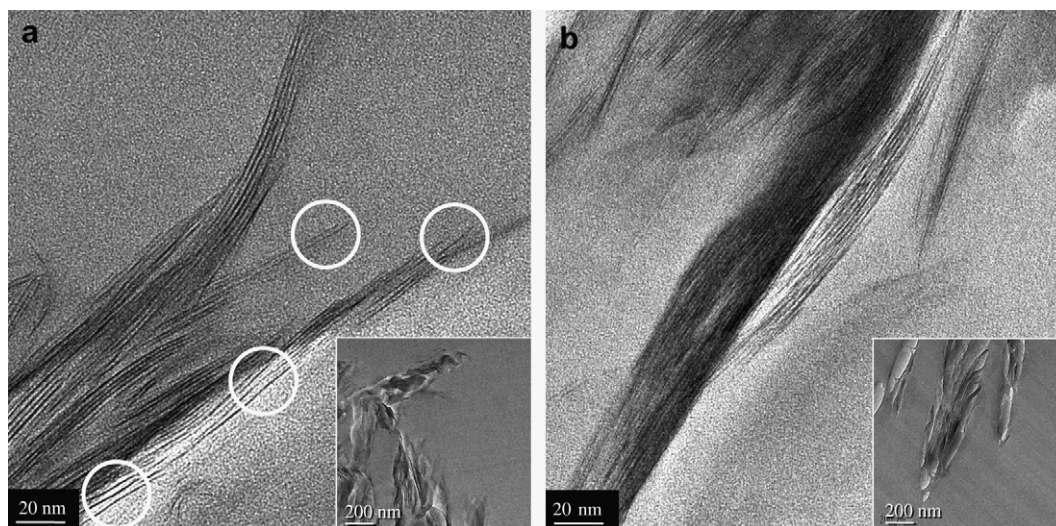

Fig. 6. Typical TEM images of PMR-15 composites of (a) clay 5 and (b) clay 6 at 5 wt% loading. Typical areas of clay layer separation by larger than 6 nm are shown enclosed in white circles.

Table 8
Effect of ratio of APND and C12 amines on clay spacing and properties of PMR-15 nanocomposites containing 5 wt% of clay

APND (wt%)	C12 (wt%)	d_{001}-Spacing of treated clay (nm)	d_{001}-Spacing of clay in composite (nm)	T_1 (°C)	T_2 (°C)	% Weight loss after aging	G' at 50 °C (MPa)	G' at 300 °C (MPa)
100	0	1.51	1.55	470	746	14	2209 ± 784	1411 ± 407
75	25	1.56	1.61	485	770	8.4	1907 ± 545	1049 ± 242
50	50	1.87	1.64	469	703	7.5	2543 ± 370	1527 ± 159
25	75	2.36	1.83	480	865	7.1	2531 ± 697	1433 ± 356
0	100	1.76	1.68	483	749	8.6	2607 ± 408	1577 ± 231

The values of T_1 and T_2 were determined for composites.

d_{001}-spacing than APND alone. From these observations, it can be concluded that a combination of APND and C12 amines works best as clay treatment for PMR-15 composites.

3.4. Optimum composition of aromatic–aliphatic amines

The benefits of combining aromatic and aliphatic surfactants to treat clay for PMR-15 composites were also reported by other authors [8]. It was shown that clay treated with 1:1 molar mixture of MDA and C12 resulted in an improvement in thermo-oxidative stability of PMR-15 nanocomposites. In light of toxicity issues with MDA, we further explored mixtures of APND and C12 as clay modifiers [57–60]. Specifically, we investigated the effect of various weight ratios of these amines on resultant clay d_{001}-spacing, level of clay exfoliation within PMR-15 composites, composite modulus, and T_1 and T_2 values. These are presented in Table 8. Note that PMR-15 composites were prepared in the same manner as discussed earlier with 5 wt% organoclay.

It is seen from Table 8 that APND and C12 amines mixed in 1:3 ratio by weight produced the largest d_{001}-spacing as measured by XRD. This significant increase in gallery height allowed a large amount of PMR-5 to intercalate into the clay galleries. The same was translated into PMR-15 composites – the clay treated with 1:3 ratio by weight of APND and C12 produced the largest d_{001}-spacing in cured composites. The value of T_1 was found to be the same for all of the composites. This is most likely due to the fact that the chemical nature of the amines in these cases were the same and the small weight loss measured by T_1, i.e., at 5% weight loss, occurred mostly from the materials at the surface of the specimens. Since the majority of clay was located within the bulk of the composite specimen, the clay did not have significant impact on T_1. However, the values of T_2 show a dependence on the ratio of APND to C12. Again, it is seen that clays treated with 1:3 ratio by weight of APND and C12 had the largest T_2 value. Samples of these composites were also examined by oven aging for 500 h at 315 °C, giving a better representation of TOS. Again, it is seen that composites of this clay resulted in the least amount of weight loss.

It is also seen from Table 8 that the clay treated with 1:3 ratio by weight of APND and C12 produced the second highest composite modulus of all mass ratios examined, while a 50:50 ratio of APND/C12 produced a slightly higher modulus. This trend was observed at both 50 °C (glassy modulus) and 300 °C (near T_g). The improvements in modulus observed

in comparison to neat PMR-15 are only slight. However, it is conceivable that up to 60% by weight of carbon fibers present in carbon fiber panels made using this nanocomposite resin will govern the mechanical properties. Therefore, a modulus value similar to that of neat PMR-15 is acceptable as significant improvements in other properties, such as TOS were obtained.

4. Conclusions

The study showed that an optimum organic treatment of layered silicate clay for use in PMR-15 nanocomposites should contain combinations of aromatic and aliphatic amines, the former to provide thermal stability and the later to promote intercalation of nanoclay by PMR-5 oligomer. Of the two aromatic amines examined, APND performed better in terms of higher TOS and larger clay gallery spacing. It was found that a 1:3 ratio by weight of APND and C12 amines results in a clay with required high thermal stability, increased cross-link density, maximum clay exfoliation, and improved thermal properties in PMR-15 composites. Results indicate that the nadic endgroup of APND participates in crosslinking with the nadic endgroup of PMR-5 resin. The study also showed that intra-gallery PMR-5 crosslinking reactions occurred during the PMR B-staging step, which aided clay layer separation.

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