ABSTRACT

A brief review of the research literature that deals with the exfoliation of montmorillonite clay exchanged with \( \omega \)-amino acid and long-chain alkylamines is presented. From this review data, clay-matrix adhesion, in addition to clay-platelet dispersion, are considered critical-path parameters for the development of structural nanocomposites. In an attempt to identify a suitable functionalized clay surface, we assess the feasibility of using \( \omega \)-hydroxylamines as a potential candidate to fulfill these two requirements. In this research, readily available short-chain \( \omega \)-hydroxylamines amines and alkylamines of comparable chain length are ion exchanged with the Na\(^+\) ions on the clay surface. X-Ray Diffraction data revealed that the basal spacing of the two classes of ammonium salts are very similar, suggesting that \( \omega \)-hydroxylamines of suitable chain length may provide a route for enhancing the adhesion between the clay platelets and the epoxy amine matrix, while promoting dispersion during the epoxy-amine chemical reaction.

INTRODUCTION

In 1989, the Toyota research group [1-3], by dispersing functionalized montmorillonite clay in nylon, developed polymer-clay hybrid (PCH) nanocomposites, a new material class. The nylon-clay hybrid (NCH) nanocomposite exhibited, with a 5-wt. % clay loading, marked improvements in heat deflection temperature (HDT), tensile strength, and tensile modulus with minimal reduction in the impact strength and virtually no increase in the specific gravity of the composite relative to the base resin. In this polymer-based
"molecular composite", moisture absorption, the thermal expansion coefficient, and flammability of the composite part were reduced, while maintaining the transparency of the nylon resin. The “molecular composite” nomenclature and the latter property arise because the 10 Å silicate layers are approximately the size of molecules and the wavelength of visible-light. In addition, nanoclays are inexpensive relative to traditional reinforcing materials, thermally inert, and environmentally friendly. With these potential property enhancements, the automotive and aerospace industries view PCH nanocomposites as the structural materials of the 21st century.

In a cover story, Plastics Technology observed through nanocomposite technology the potential to improve the physical properties of low-modulus polymers, such as polyolefins, to levels competitive with costlier engineering polymers. Potential applications include molded car parts (e.g., body panels and under-hood components), electrical/electronic parts, power-tool housings, lawn mowers, aircraft interiors, and appliance components. Property improvements (e.g., fracture toughness, fatigue resistance) in conventional fibrous composites are also being pursued.

Although the flame-retardant property of PCH nanocomposites appears universal, consistent improvements in mechanical properties - the key drivers controlling these materials’ use in structural applications - has been more elusive. Indeed, the initial automotive timing belt covers developed from NCH nanocomposites were discontinued. This disuse, which may be related to the nanocomposite’s long-term creep behavior, underscores the need for continued fundamental research relating chemical structure, polymeric properties, and matrix-clay interactions to short- and long-term nanocomposite mechanical properties.

In this paper we focus on developing strategies for the dispersion of clay platelets in amine cured epoxy resins. Epoxy resins cured with aromatic diamines are generally used in structural composites, because of their dimensional and environmental stability, high Tg, and good fiber-matrix adhesion. However, the brittle resin limits energy absorption in the composite and restricts their use in structural applications where controlled ductile failure is important. Performance improvements in this resin class by clay reinforcement would represent a major technical achievement for high-temperature advanced structural materials. To understand the strategies we are developing in pursuit of this goal, it is worthwhile to present a brief review of the relevant literature that we think indicates the key challenges that must be overcome. From our review of the literature there are some property enhancements that may be unique to the molecular structure of nylon and hence, will not be achievable in an epoxy-amine resin system.

**BRIEF LITERATURE REVIEW**

**Nylon Based Nanoclay Composites**

These nanocomposites are composed of montmorillonite clay exchanged with 12-aminolauric acid to yield functionalized clay known as 12-montmorillonite. The clay was then intercalated with ε-caprolactam at (2 to 70) wt. % of clay. The ε-
caprolactam was polymerized in situ (reactor route) by accelerating the nylon-6 polymerization reaction with a small amount of 6-aminocaproic acid to yield a NCH nanocomposite, where the nylon is really a copolymer of nylon-6 and a small amount of nylon-12.

At 5-wt. % clay loading, several designed related properties increased the in situ NCH nanocomposites relative to the pristine nylon-6 polymer. In particular, the tensile strength, tensile modulus, flexural strength, flexural modulus, and heat deflection temperature (HDT) increased. The Izod and Charpy impact strengths in the nanocomposite decreased by approximately 13 % and 4 %, respectively (see Table 1). Although most of the properties are self explanatory, the HDT is not generally quoted for metallic materials and is important in polymer design because the polymeric glass transition temperature (Tg) is often accessible with moderate temperature changes. The HDT is a measure of the upper use temperature of a material and generally follows its Tg or melt temperature (Tm).

Using storage and loss modulus data at Tg, Kojima et al. [4] suggest that the increases in mechanical properties are due to contributions from constrained matrix regions. In a 1995 review of polymer-clay hybrids, Okada et al. [5] observed that a substantial amount of the nylon molecules are ion-bonded to the clay at the amine end and covalently bonded to the polymer network through the carboxylic acid group. As a result, the clay acts as a nanoscale cross-linker in the nylon polymer and hence, restricts the motion of the nylon polymer chains in the network (see Table 1). This contrasts most of the current research in which non-functionalized alkylammonium salts are deposited on the clay surface. These non-functionalized clays do not bond with the host matrix.

Since the HDT is loosely related to Tg, the mechanism responsible for its dramatic increase can only be understood by examining the temperature dependent response of the NCH nanocomposite relative to the pristine polymer. In Figure 1, the dynamic mechanical storage modulus (E') and tan δ responses of a 2-wt. % NCH nanocomposite (curve 1), a nylon-6 polymer (curve 2), and a 30-wt. % surface-modified short glass-fiber nylon-6 (SMSGF/N6) composite (curve 3) are plotted versus increasing temperature [6]. The tan δ responses of the three systems are similar, with the only notable difference occurring in the magnitude of the αr-absorption region. This region has been associated with the Tg of nylon-6, and the constancy of the peak maxima between these specimens indicates that the glass transition temperature of the nylon-6 was not significantly altered by the addition of the montmorillonite clay or the SMSGFs.

However, the reduction in the relaxation strength of the αr-absorption in the NCH nanocomposite and SFSGF/N6 composite does imply a restriction of thermal molecular motion in the nylon-6 amorphous regions. This restricted mobility translates into a significant reduction in the mobility of the polymer chains above Tg and hence, plateau modulus increases in the two composites relative to nylon-6. These increases coupled with the fact that the semi-crystalline nylon polymer has a stiffness of ~0.2 GPa, between Tg and the melting point of the crystalline region are responsible for the observed increases in HDT.
TABLE 1. MECHANICAL PROPERTIES OF NCH, L-NCH AND NYLON 6

<table>
<thead>
<tr>
<th>Properties</th>
<th>In situ – NCH*</th>
<th>Nylon-6*</th>
<th>Nylon-6**</th>
<th>MI-NCH**</th>
<th>L-NCH***</th>
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</thead>
<tbody>
<tr>
<td>Montmorillonite Content, wt. %</td>
<td>4.7</td>
<td>N/A</td>
<td>N/A</td>
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<td>Molecular weight</td>
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<td>13,000</td>
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<tr>
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<tr>
<td>Crystallinity</td>
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<td>23 °C</td>
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<td>89.3</td>
<td>93.5</td>
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<td>Izod Impact Strength, J/m²</td>
<td>18.1</td>
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<td>Charpy Impact Strength, KJ/m²</td>
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<td>6.21</td>
<td></td>
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<td>HDT (1.82 MPa), °C</td>
<td>152</td>
<td>65</td>
<td>62</td>
<td>112</td>
<td>164</td>
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</tbody>
</table>


** Liu, Qi, Zhu (Journal of Applied Polymer Science, 1999), MI-NCH - montmorillonite clay intercalated with octadecyl quaternary ammonium salt and melt intercalated with nylon 6.


Of the two composites, the NCH nanocomposite has the best fatigue resistance. These authors [6] concluded that uniform clay dispersion and small clay-platelet size, coupled with the strong interaction between the nylon and clay reduced the chance of crack formation resulting in improved fatigue strength.

In apparent contrast to the in situ NCH nanocomposite results, Liu et al. [7] observed an increase in HDT for melt-intercalated NCH (MI-NCH) nanocomposite when the montmorillonite clay was exchanged with a non-bonding organic ammonium cation (compounding route – see Table 1). Although the increase is half that observed in the in situ NCH nanocomposite, this data suggests that clay exfoliation also restricts polymer chain mobility in the host matrix. However, when the clay is melt-intercalated at approximately 18-wt. % the HDT only increases to

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130 °C, whereas the HDT is 152 °C in the 5-wt. clay % loaded in situ NCH nanocomposite. From this observation, strong interactions between the clay and matrix are needed in addition to exfoliation to obtain the HDT increase observed in the in situ NCH nanocomposite.

As a final comment related to clay-matrix interactions in nylon polymers, Kojima et al. [8] demonstrated how the HDT is affected by the presence of nylon-12 copolymer at the clay-matrix interface of the in situ NCH nanocomposite. By exchanging and intercalating the montmorillonite clay with ε-caprolactam only instead of 12-aminolaauric acid and ε-caprolactam, these researchers obtained the first nylon-6 clay hybrid (L-NCH) nanocomposite. The L-NCH nanocomposite HDT increased by an additional 12 °C, relative to the NCH nanocomposite (see Table 1).

Polyolefin Based Nanoclay Composites

Polypropylene (PP) is one of the most widely used polyolefin polymers. Polypropylene-clay hybrid (PPCH) nanocomposite research by Usuki et al. [9] showed no clay-platelet exfoliation when montmorillonite clay is exchanged with the distearyldimethylammonium cation (DSDM-MT) and melt intercalated with polypropylene. However, when a polyolefin oligomer with telechelic OH groups (PO-OH) is co-exchanged with DSDM before melt intercalation with polypropylene, partial exfoliation is obtained. These researchers inferred that PO-OH interacted with the clay by hydrogen bonding to the clay surface polar hydroxyl groups.

Figure 1. Storage modulus (E') and tan δ responses of NCH, Nylon-6, and SMSGF/N6 versus temperature. [6] Reprinted with permission

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In subsequent research, Kawasumi et al. [10,11] co-exchanged montmorillonite clay with stearylamine and maleic anhydride modified PP (PP-MA) oligomers. Almost complete exfoliation and dispersion of the clay was achieved with this approach. Consistent with the nylon results, minimal change in the PPCH nanocomposite Tg was observed relative to PP. At approximately 10 °C above the PP-Tg (13 °C), the PPCH storage modulus increased by 51 % relative to PP. However, the PPCH nanocomposite tensile strength, (30 to 35) MPa, did not increase relative to PP, 33 MPa. In addition, a dramatic decrease in the strain-to-failure of the PPCH nanocomposites, (6 to 9) %, compared to PP, > 150 %, was observed. Since PP is nonpolar, the PP-MA only facilitates clay-platelet dispersion. Hence, the clay-matrix interface is weak and may serve as sites for crack initiation in the host matrix [6].

The interfacial adhesion between dissimilar materials is a property that is important in composites [12,13], adhesive joints [14], polymer blends [15], and many other disciplines. Since clay nanocomposites are often thought of as molecular composites, it is worthwhile reinforcing the importance of this concept by quoting directly from a widely used text on polymer blends.

"For phase-separated systems, the interfacial adhesion between the respective phases governs the ultimate mechanical properties. For polymeric constituents having limited affinity for each other, the interface represents a flaw yielding ultimate properties significantly lower than that expected from constituent values.”

from Polymer-Polymer Miscibility by Olabisi, Robeson, and Shaw

Epoxy Based Nanoclay Composites

Among thermoset systems, epoxy is one of the most widely used materials for structural applications in aerospace and automotive. Previous research on amine-cured ECR nanocomposites by Pinnavaia et al. [16,17] and Giannelis et al. [18] have shown ECR nanocomposite exfoliation to depend on the following parameters:

1. Alkyl-ammonium ion type
   a. primary, secondary, or tertiary
   b. affects intra-gallery polymerization rates and clay-matrix dispersion
2. Length of the alkyl chain
   a. impacts swelling of clay by DGEBA monomer
   b. controls intra-gallery diffusion
3. Curing agent type
   a. aromatic diamines, aliphatic diamines, anhydrides, and homopolymerization curing agents
   b. affects resin glass transition temperature (Tg)
4. Curing conditions
   a. affects intra- and extra-gallery polymerization rates and resin Tg
(5) Charge density of the clay
   a. impacts swelling of clay by DGEBA monomer

Optimizing the above parameters, exfoliated ECH nanocomposites of montmorillonite clay and amine-cured epoxy resins (e.g., DGEBA/m-PDA and DGEBA/poly(ether amine)) are formed. For the DGEBA/m-PDA ECH nanocomposite, the Drzal curing regime, which is designed to increase the strain-to-failure of the brittle DGEBA/m-PDA epoxy with minimal impact to the Tg, was used. The resulting DGEBA/m-PDA ECH nanocomposite exhibited a modest improvement in modulus relative to the pristine polymer [(1.49 ± 0.03) GPa vs. (1.10 ± 0.03) GPa]. The tensile strength [(92 ± 5) MPa vs. (90 ± 3) MPa], Tg, and strain-to-failure of the nanocomposite were not enhanced. The Tg and strain-to-failure of the DGEBA/m-PDA epoxy are 142 °C and (5 to 8) %, respectively.

However, when amine-cured ECH nanocomposite are prepared with the DGEBA/poly(ether amine) matrix a pronounced improvement in modulus and tensile strength with no deleterious affect on the strain-to-failure of the epoxy resin network (40 to 60) % results. Consistent with the low Tg of this material (= 45 °C), the fracture toughness of this resin is higher than the DGEBA/m-PDA resin. These results suggest that strategies to modify or account for the intrinsic toughness of the resin are needed if clay reinforcement is to be successful in brittle epoxy networks. Indeed, this problem has thwarted, for years, the use of conventional rubber toughening technology in brittle epoxies.

It Figure 1 of this paper, it is shown that clay reinforcement increased the HDT in the NCH nanocomposite by reducing the mobility of the nylon-6 chains in the rubbery plateau region without a significant increase in the nylon Tg. The rubbery plateau modulus of the NCH nanocomposite increased from ≈ 0.2 GPa at 152 °C to ≈ 0.6 GPa, while the Tg remained at 77 °C. Also, the modulus drop at Tg in the nylon resin is less than 1 decade (2 GPa to 0.3 GPa). Messersmith and Giannelis [18] synthesized DGEBA/benzyldimethylamine (BDMA) ECH nanocomposite whose base resin Tg is ≈ 120 °C. Although the Tg of the epoxy resin is = 40 °C higher than nylon, the modulus drop in the epoxy resin from below to above Tg is approximately 2 decades (1.6 GPa to 0.01 GPa) (see Figure 2 - diamond symbols).

Clay reinforced DGEBA/BDMA (see Figure 2 – circle symbols) shows a 450 % increase in the resin stiffness in the rubbery plateau region (i.e., 0.05 GPa). Although this stiffness is = 250 % higher than a brittle amine-cured epoxy resin with Tg of 220 °C, the DGEBA/BDMA ECH nanocomposite stiffness is an order of magnitude softer than the NCH nanocomposite at 127 °C. Since significant increases in the Tg have not been demonstrated using clay reinforcement, the primary role of clay reinforcement in ECH nanocomposites will be to enhance the fracture toughness of typically brittle epoxy resins. Hence, the Tg of the base resin must exceed the HDT requirement for the structural application. ECH strategies must therefore be developed to enhance the intrinsic base resin toughness without significantly reducing the Tg.
Figure 2. Storage modulus ($E'$) and tan δ responses of DGEBA/BDMA epoxy resin and clay reinforced DGEBA/BDMA. [18] Reprinted with permission

Recently, Vaia et al., [19] investigated the ability of secondary functional groups on the alkylammonium cations to promote intra-gallary polymerization and clay exfoliation. These researchers, found clay exfoliation facilitated in DGEBA/poly(ether amine) epoxy resins by the hydroxyl groups on the bis(2-hydroxy-ethyl)methyl tallow ammonium cation. Interestingly, a similar strategy employed by Messersmith and Giannelis [18] using the brittle DGEBA/m-PDA epoxy resulted in clay-platelet re-aggregation and a cloudy ECH nanocomposite.

PMR-15/Layered Silicate Nanocomposites

Cotton and Wilkinson [20] have stated that ammonium salts volatilize with dissociation around 300 °C. Recent research by Dean [21] has shown, using DSC measurements, that the ion-bond that is formed between the clay platelets and the alkyl-ammonium ions that are typically used to exfoliate the clay platelets is thermally unstable at approximately 220 °C. Since the MI-NCH nanocomposites were processed in this temperature range, this observation may provide an alternative explanation for the property increase observed with the “non-bonding” clay surface.

TECHNICAL STRATEGIES

There are many unresolved issues in PCH research related to the synthesis of polymer-clay hybrids, choice of intercalating agent, processing, morphology control, and engineering property optimization. In the NIST research program, the effect of clay dispersion and clay-matrix adhesion on the structural and non-structural properties of a thermoplastic (PP) and a thermoset (DGEBA/m-PDA) polymer-clay hybrid nanocomposites are being investigated. For the DGEBA/m-PDA ECH nanocomposite compatibility between the clay surface and the matrix
during the curing reaction must be maintained while promoting clay-matrix interactions that enhance nanocomposite performance. From an engineering design perspective, developing strategies to enhance the host matrix HDT while maintaining or increasing the host matrix ductility will be particularly challenging, since increasing one of these properties tends to reduce the other.

It is possible that hydroxyl-hydroxyl interactions between the clay surface and the epoxide-amine reaction products may stabilize the dispersion of the clay until the matrix is completely cured. However, the addition of polar groups might also impede the intercalation of the clay platelets by the DGEBA molecule. One approach may be to exchange the sodium ions in the clay with ω-hydroxyl amines of suitable chain length that promotes intercalation by the DGEBA molecule and interaction with the epoxide-amine reaction products. Since the ω-hydroxyl amines contain two polar groups, it is necessary to determine if ω-hydroxyl amines will undergo the exchange reaction in a manner similar to alkyl-amines. To investigate this aspect of the research program we will use readily available short chain ω-hydroxylamines to monitor the exchange process.

EXPERIMENTAL

Establishing the Controls

X-Ray Diffraction was performed on clay samples of Cloisites® 10A, 20A, 25A, 30B, and Na⁺. These numbered specimens contain tallow based long-chain alkylammonium ions that are adsorbed on the clay surface.

Three solutions of NaCl with varying concentrations were prepared. The concentrations were 0.1N, 0.01N, and 0.001N. A 0.159M sample of silver nitrate was prepared to test for the presence of chloride in the clay sample. The Na⁺ Cloisite was mixed with water and filtered. The filtrate was collected, and a chloride test was performed.

Preparation of Ion Exchanged Clays

Hexylamine and 5-Amino-1-pentanol. A 0.1 M hexylamine solution was prepared by mixing 13.2 ml of 99 % hexylamine with an equimolar amount of HCl (4 ml) into a 250 ml flask partially filled with water. This solution was then diluted to volume. The solution was then transferred to a 500 ml flask and then diluted with 250 ml of ethyl alcohol. A 0.1 M 5-amino-1-pentanol solution was similarly prepared by using 10.3 g of solid 5-amino-1-pentanol.

Approximately 2g of sodium Cloisite were added to the solution containing the hexylamine, HCl, and ethanol. 2g of clay were also added to the second solution containing the HCl, ethanol, and 5-amino-1-pentanol. Both mixtures were stirred,
and placed in an oven at 75°C for 24 h. The samples were then removed from the oven and filtered. Once the solid was separated from the filtrate, the filtrate was placed in a refrigerator for later observation. The collected solids were filtered again and rinsed with distilled water several times. A vacuum-suction-filtration mechanism was allowed to run on both samples for 24 h. Both samples were allowed to dry on the filter paper.

**Ethanolamine and Propylamine.** Using the above procedure ion exchanged clays with ethanolamine and propylamine were prepared by using 8.2 ml of propylamine and 6.4 ml of ethanolamine.

**X-Ray Diffraction Analysis**

Once the clay samples had dried, they were removed from the filter paper and weighed to determine the amount of montmorillonite that was recovered. A portion of each sample was acquired and ground using a mortar and pestle. Samples of each ion exchanged montmorillonite were then prepared for X-Ray Diffraction. The standard Cloisite specimens were also analyzed by X-Ray Diffraction.

**RESULTS AND DISCUSSION**

The plots of the ion exchanged montmorillonite clays relative to the Na⁺ Cloisite clay are shown in Figure 3, Figure 4, and Figure 5.

![Figure 3. X-Ray Diffraction pattern of Na⁺ Cloisite and Hexylammonium Cloisite (duplicate scans).](image)

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Figure 4. X-Ray Diffraction pattern of Na⁺ Cloisite and 5-Amino-1-pentanol Cloisite (duplicate scans).

Figure 5. X-Ray Diffraction pattern of Na⁺ Cloisite, Propylammonium Cloisite, and Ethanolammonium Cloisite.

In each figure there is a dramatic change in the X-Ray Diffraction spectrum of the ion-exchanged clay relative to Na⁺ Cloisite. The similarity between Figure 3 and Figure 4 and the similarity in the two X-Ray Diffraction patterns in Figure 5 indicate that ω-hydroxylamines and alkylamines absorb onto the clay surface in a similar manner. In all cases there is a small but definite shift of the basal spacing peak to a higher value relative to the Na⁺ Cloisite basal spacing. This shift reflects a decrease in the interspacing between the ion exchanged galleries relative to Na⁺ Cloisite.

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Calculations of the basal spacing of the ion-exchanged and the Cloisite montmorillonites are given in Table 2. The basal spacings for the propylammonium and ethanolammonium exchanged clays are smaller than the butylammonium exchanged clay (13.5 \( \Lambda \)) reported by Pinnavaia et al. [17]. Comparison with the \( \omega \)-amino acid exchanged clays researched by Usuki et al. [22], indicates that the basal spacing of the two clays are comparable to an \( \omega \)-amino acid of general formula \((\text{NH}_2-\text{(CH}_2)_n-\text{COOH})\) with \(n\) between 3 and 4.

The basal spacing of the hexylammonium clay and 5-amino-l-pentanol ammonium clay are also slightly smaller than the butylammonium exchanged clay basal spacing published by Pinnavaia et al. However, comparing these two exchanged clays to the data by Usuki et al. indicates that the basal spacing of these two clays are comparable to an \( \omega \)-amino acid of general formula \((\text{NH}_2-\text{(CH}_2)_n-\text{COOH})\) with \(n\) between 6 and 8.

<table>
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<tr>
<th>Montmorillonite Clay Type</th>
<th>Basal Spacing</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Basal Spacing</td>
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<td>Ethanolamine</td>
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<td>5-Amino-l-Pentanol</td>
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<td>Cloisite 30 B</td>
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</table>

From the work of Pinnavaia et al. it appears that the clays synthesized in this research exist in the monolayer orientation in the dry state. As expected, it was difficult to swell these short-chain exchanged clays with unreacted DGEBA. Research is currently underway to synthesize longer chain \( \omega \)-hydroxyalkamines.

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