

# Studies of Organoclays with Functionalized Pillaring Agents

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**ABSTRACT:** A series of clay pillaring agents with amino, olefin, and epoxy groups were synthesized. These pillaring agents were used to modify montmorillonite clay by ion-exchange reactions. TGA studies showed that organoclays with imidazolium pillaring agents have a higher thermal stability than those with ammonium groups. The *d*-spacings of organoclays were not affected by the pillaring agent functional groups and were sensitive to the size of pillaring agents. The dynamic-mechanical properties of

the resulting clay/epoxy composites determined by DMA were similar. The addition of these clays to this epoxy resin enhanced the  $T_g$  value of the resulting composites and greatly enhanced the storage moduli versus the pure epoxy resin by 1.6–1.8 times at 135°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2430–2441, 2011

**Key words:** clay; surface modification; nanocomposites; thermosets; thermal properties

## INTRODUCTION

Montmorillonite (MMT) clay is a layered material with exchangeable cations incorporated between alumina silicate clay platelets.<sup>1,2</sup> MMT clay can be incorporated into thermoplastic<sup>3–6</sup> and thermoset polymer matrices<sup>7–22</sup> to improve the materials' mechanical<sup>22,23</sup> and other properties.<sup>7–9,14–16,23,24</sup> It is important to modify clay using specific and suitable pillaring agents for each type of polymer matrix and application. Ion-exchange of Na<sup>+</sup> MMT clay (MMT-Na<sup>+</sup>) with organic cations is the most widely used modification method.<sup>1,2</sup> This process can expand interplatelet distances and the hydrophobic/hydrophilic balance in the clay galleries between platelets, thereby assisting intercalation of polymers and exfoliation of the layered clay structure. The properties of modified organoclays can be tailored by changing the organic cation modifiers' (pillaring agents) structures.<sup>7,25–27</sup>

Initially, ammonium ions<sup>8–10,24,25</sup> were the most widely used organic cations for pillaring clays because these modifiers were readily available or easily prepared. The modified clay *d*-spacings depend on the size of organic cations, but there is no strict linear relationship between the organic cation size and the clay *d*-spacing.<sup>7,25–27</sup> Varying degrees of organoclay

exfoliation during composite preparation can be achieved with long chain ammonium cation modification.<sup>3,11,28,29</sup>

Unfortunately, ammonium cations have only moderate thermal stability, limiting the use of high processing temperatures.<sup>30–32</sup> Ammonium cations decompose below ~ 200°C most often by Hoffman degradation.<sup>30,31</sup> This decreases the time available for intercalation and exfoliation at higher temperatures. The *d*-spacings can collapse to give smaller gaps when pillaring agents decompose, further inhibiting polymer movement into galleries.<sup>30</sup> Consequently, more thermally stable modifiers have been developed. Alkyl phosphonium<sup>33,34</sup> and imidazolium<sup>7,26,27</sup> cation-pillaring agents have higher decomposition temperatures that are above most polymer processing temperatures. They can also be intercalated readily into clay galleries by ion exchange.

Pillaring agents containing other functional groups can also be synthesized.<sup>7,12,13,34</sup> Proper design could allow them to undergo polymer to pillaring agent reactions. Functionalized pillaring agents might react either with monomers, matrix thermoplastic polymers, or growing thermosets during curing. The formation of covalent bonds to the pillaring agents in these reactions would connect the organic matrix polymer to alumina silicate clay platelets through the pillaring agent's ionic bonding.

In this research, the synthesis of new epoxy-, amino-, and olefin-functionalized clay pillaring agents was performed. Imidazolium compounds were used as pillaring agents to enhance the organoclays' thermal stability. Subsequently, higher

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processing temperatures can be used. The organoclays were studied by TGA and X-ray diffraction (XRD). The properties of clay/epoxy composites were investigated by DMA.

## EXPERIMENTAL

### Materials

The MMT clay, Na-Cloisite, was provided by Southern Clay Products. Na-Cloisite has a  $d_{001} = 11.7 \text{ \AA}$  and cation exchange capacity = 92.6 meq/100 g. The amine-terminated polypropylene glycols (PPGs) D-230 (MW = 230) and D-2000 (MW = 2000) were provided by Huntsman Company. Epon 862 (provided by Hexion Specialty Chemicals Company) is a bisphenol F epoxy resin (166–177 g/mol of epoxy groups). EpiCure-W (provided by Shell Chemicals Company) is an aromatic amine curing agent with 43–46 g/mol of active hydrogen (e.g., per N–H). Each amine group is flanked by two ortho substituents, which lead to slower reaction rates with epoxy functions. Other chemicals were purchased from Sigma-Aldrich Company.

### NMR, TGA, XRD, and DMA analysis

NMR analysis was conducted on a Bruker AVANCE III 300 MHz instrument, using  $\text{CDCl}_3$  as the solvent. TGA was performed under nitrogen on a Perkin-Elmer Thermogravimetric Analyzer (TGA 7) or a SetSys EVO 2000 instrument (manufactured by Setaram Instrumentation Technologies) to evaluate the thermal stability of the organoclays and to calculate the pillaring agent content in organoclays. The temperature range from 50 to 800°C was scanned at a heating rate of 10°C/min. X-ray diffraction (XRD) analysis was conducted on a Bruker AXS D8 or a Rigaku Ultima III X-ray diffractometer at room temperature. The X-ray wavelength was 1.54 Å, and the scattering angle,  $2\theta$ , was examined between 0° and 11° with 0.1° step lengths.

DMA testing was conducted on a TA DMA Q800 instrument, using a single cantilever clamp in the three-point bending mode with an oscillation frequency of 1.0 MHz and amplitude of 15  $\mu\text{m}$ . The testing temperature was raised from room temperature to 250°C at a 2.00°C/min ramp rate. The samples are rectangular with a nominal 35 mm  $\times$  12.5 mm  $\times$  3 mm dimension.

### Organoclay synthesis

MMT clay, Na-Cloisite, was used to synthesize organoclays. Table I illustrates the chemical structure of all the pillaring agents synthesized, the amount of pillaring agent exchanged into organoclays prepared

in this effort, and the resulting  $d$ -spacings. Four new pillaring agents and their organoclays were synthesized. They are shown as structures 1–4 in Table I. Na-Cloisite was subjected to ion-exchange with these four pillaring agents to generate these new organoclays shown in Table I.

### Synthesis of Clay 1<sup>25,27</sup>

*Synthesis of Clay 1a.* The amine-terminated PPG D-230 was used to synthesize clays 1 and 2. D-230 is a mixture of short chain, amine-terminated PPGs with an average molecular weight of 230. The structure of protonated D-230 is shown in Table I.

Pillaring agent 1 is synthesized by monoprotection with HCl. D-230 (4.0 g, 17.4 mmol) was dissolved in 80.0 g  $\text{H}_2\text{O}/\text{EtOH}$  (1/1 v/v) in a 400-mL beaker. The solution was magnetically stirred for 10 min. Then 1.72 g hydrochloric acid (37 wt %,  $d = 1.19 \text{ g/mL}$ , containing 17.4 mmol HCl) was added to the D-230 solution. Stirring was continued for an additional 30 min. Then dry Na-Cloisite powder (11.3 g, containing 10.5 mmol of exchangeable  $\text{Na}^+$ ) was added to this solution. Thus, a pillaring agent 1/ $\text{Na}^+$  ratio of 1.66 was present. This mixture was stirred for another 5 h to permit ion exchange. Then, the suspension was filtered and washed with 25 mL  $\text{H}_2\text{O}/\text{EtOH}$  (1/1 v/v) three times. The filter cake was dried at 100°C for 12 h. Then, it was ground to a powder (Clay 1a) with a mortar and pestle. Pillar 1, 36 meq/100 g clay, was intercalated into the Na-Cloisite. About 39% of the  $\text{Na}^+$  in Na-Cloisite was replaced by pillar 1.

*Synthesis of Clays 1b–1e.* Clays were also synthesized with higher pillar/ $\text{Na}^+$  ratios, longer cation exchange times, and larger pillar agent. Clay 1b and Clay 1c were synthesized with a molar ratio of pillar 1/ $\text{Na}^+ = 5/1$  and 10/1, respectively, using the same preparation process as for Clay 1a. Clay 1d was prepared by repeating the ion exchange step five times with a molar ratio of pillar 1/ $\text{Na}^+ = 5/1$  in each successive exchange step. Clay 1e was synthesized with a larger amine-terminated PPG, monoprotected D-2000, using the same preparation process as for Clay 1a with a molar ratio of pillar/ $\text{Na}^+ = 5/1$  and one-time exchange.

### Synthesis of Clay 2

The synthesis of pillar 2 was performed by diprotecting D-230, using the same procedure as was utilized in the synthesis of pillar 1. D-230 (4.0 g, 17.4 mmol) was dissolved in 80.0 g  $\text{H}_2\text{O}/\text{EtOH}$  (1/1 v/v) in a 400-mL beaker. The solution was magnetically stirred for 10 min. Next, 3.44 g hydrochloric acid (37 wt %,  $d = 1.19 \text{ g/mL}$ , containing 34.8 mmol HCl) was added to the D-230 solution. Stirring was continued for an additional 30 min. Then, Na-Cloisite

TABLE I  
Synthesized Pillaring Agents and Organoclays

| Name                 | Structure of pillaring agents  | Pillaring agent content <sup>a</sup> (meq/100 g clay) | 2θ   | d <sub>001</sub> (Å) |
|----------------------|--|---|------|----------------------|
| Clay 1a <sup>b</sup> | $\text{H}_2\text{NCH}_2\text{CH}_2\text{O}-\left[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}\right]_{2.6}-\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ <p style="text-align: center;">pillar 1</p>                      | 36.0  | 6.47 | 13.7                 |
| Clay 2               | $\text{Cl}^- \text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{O}-\left[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}\right]_{2.6}-\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ <p style="text-align: center;">pillar 2</p> | 29.4  | 6.27 | 14.1                 |
| Clay 3a              | $\text{Br}^- \text{Me}-\text{N}^+\text{C}_2\text{H}_4\text{N}^+(\text{CH}_2)_9\text{CH}=\text{CH}_2$ <p style="text-align: center;">pillar 3</p>   | 39.3  | 6.21 | 14.2                 |
| Clay 3b              | Same as Clay 3   | 106.1   | 5.31 | 16.6                 |
| Clay 3c              | Same as Clay 3   | 84.9  | 5.56 | 15.9                 |
| Clay 4               | $\text{Br}^- \text{Me}-\text{N}^+\text{C}_2\text{H}_4\text{N}^+(\text{CH}_2)_9\text{CH}(\text{OCH}_2)\text{CH}_2$ <p style="text-align: center;">pillar 4</p>  | 36.0  | 6.18 | 14.3                 |
| Na-Cloisite          | No organic pillaring agents  | 92.6  | 7.80 | 11.3                 |

<sup>a</sup> The numbers were determined by TGA measurement assuming that the total weight losses of organoclays included the complete loss of all N, C, H, and O from the pillaring agents and the bound water.

<sup>b</sup> Clays 1b–1d were made with far higher pillar 1 to Na<sup>+</sup> ratio during exchange. These results are summarized in Table IV. In these clays, the amounts of pillar exchanged were greater (44.6–52.4 meq/100 g), but the *d*-spacing remained the same as that of 1a (13.6–13.7 Å).

(11.3 g, containing 10.5 mmol of exchangeable Na<sup>+</sup>) was added to this solution (2/Na<sup>+</sup> mole ratio = 1.66). This mixture was stirred for another 5 h to permit ion exchange. The suspension was then filtered and washed with 25 mL H<sub>2</sub>O/EtOH (1/1 v/v) three times. The filter cake was dried at 100°C for 12 h. Next, it was ground to a powder (Clay 2) with a mortar and pestle. Pillar 2, 29.4 meq/100 g clay, was intercalated into the Na-Cloisite, replacing 31.7% of the Na<sup>+</sup> in this clay.

#### Synthesis of Clays 3a–3c

The pillaring agent 3 was synthesized by the reaction of 11-bromo-1-undecene with 1-methylimidazole and then used in preparing Clays 3a–3c.

*Synthesis of pillaring agent 3.*<sup>35</sup> 11-Bromo-1-undecene (2.0 g, 8.58 mmol) and 1-methylimidazole (0.589 g, 7.17 mmol) were added into a 50-mL two-necked flask. Then 25-mL CHCl<sub>3</sub> was added. The flask was equipped with a condenser and a thermometer. The temperature was raised to 50°C, and the solution was magnetically stirred at 50°C for about 15 h. The solvent was then removed by rotary evaporation, and a viscous liquid was left in the flask. The liquid was washed five times with 15-mL cyclohexane/ethyl acetate (1 : 1 v/v). Then, the residual solvent was further evaporated with a rotary evaporator, leaving the ionic liquid 3 (1.49 g, 66%). The <sup>1</sup>H and <sup>13</sup>C-NMR spectra of pillar 3 are shown in Figures 1 and 2, respectively, and summarized below.

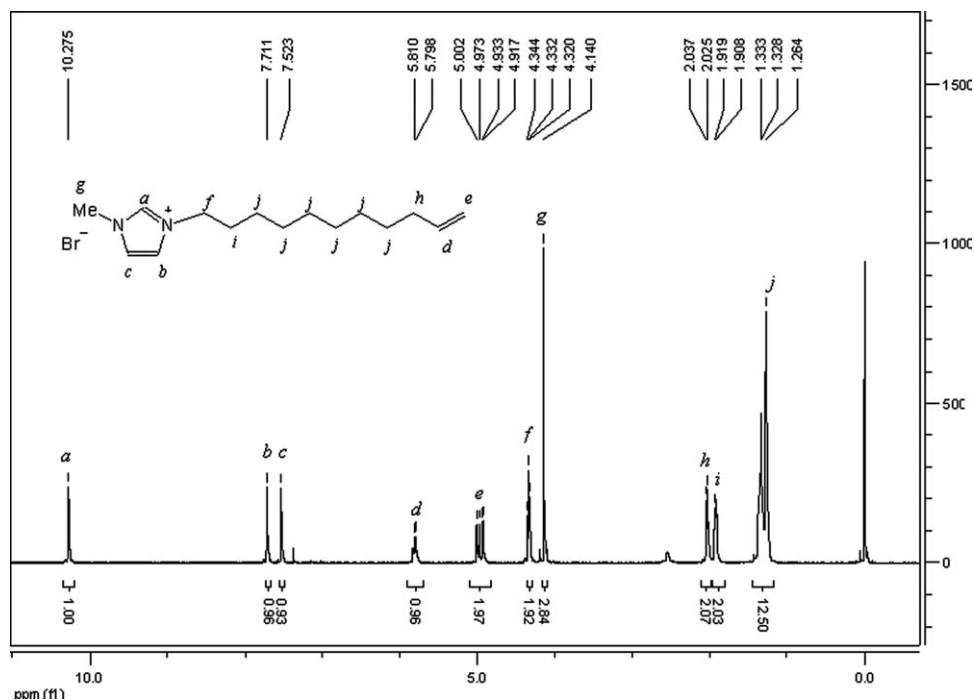


Figure 1 <sup>1</sup>H-NMR spectrum of pillar 3 (in CDCl<sub>3</sub>).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_H$ /ppm: 10.3 (s, 1H), 7.7 (s, 1H), 7.5 (s, 1H), 5.8 (m, 1H), 5.0 (d,  $J = 17.1$  Hz, 1H), 4.9 (d,  $J = 10.1$  Hz, 1H), 4.3 (t,  $J = 7.4$  Hz, 2H), 4.1 (s, 3H), 2.0 (quad,  $J = 14$  Hz, 2H), 1.9 (t,  $J = 6.7$  Hz, 2H), and 1.2–1.4 (m, 12H).

<sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_C$ /ppm: 138.8, 136.9, 123.6, 121.8, 113.9, 49.9, 36.5, 33.5, 30.1, 29.0, 29.0, 28.7, 28.7, 28.6, and 26.0.

*Synthesis of Clay 3a by ion exchange.*<sup>25,27</sup> Na-Cloisite (3.4 g, 3.15 mmol exchangeable Na<sup>+</sup>) was added to 600 mL H<sub>2</sub>O/EtOH (1/1 v/v) in a 1000-mL beaker. The suspension was sonicated for 20 min. Then, pillaring agent 3 (1.49 g, 4.73 mmol) was dissolved in 50 mL hot water (~50°C) and added to the Na-Cloisite suspension (3/Na<sup>+</sup> mole ratio = 1.50). The suspension was magnetically stirred at 50°C for

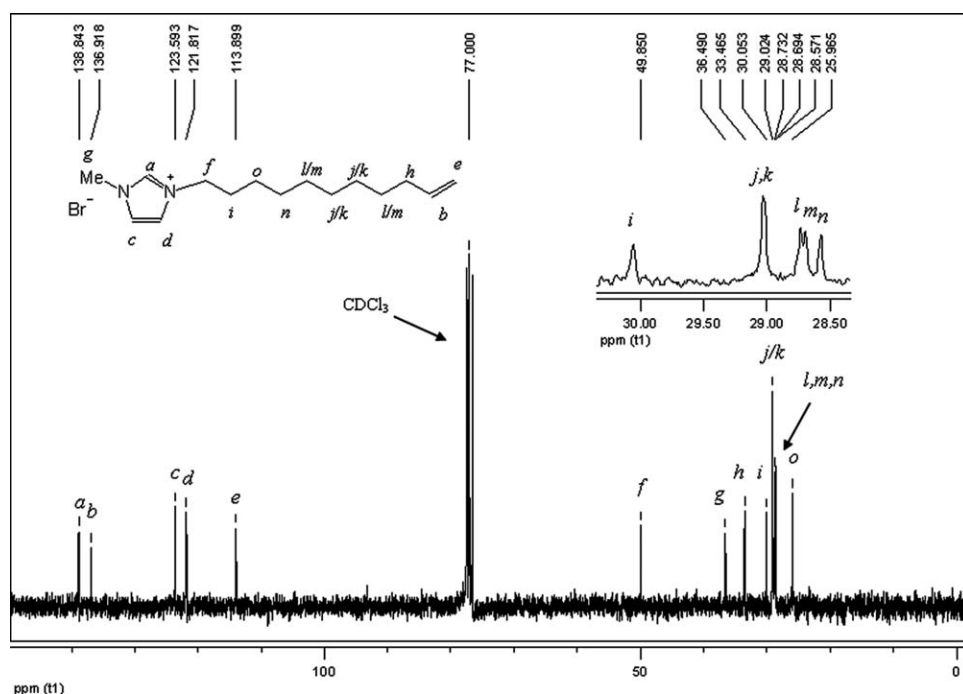
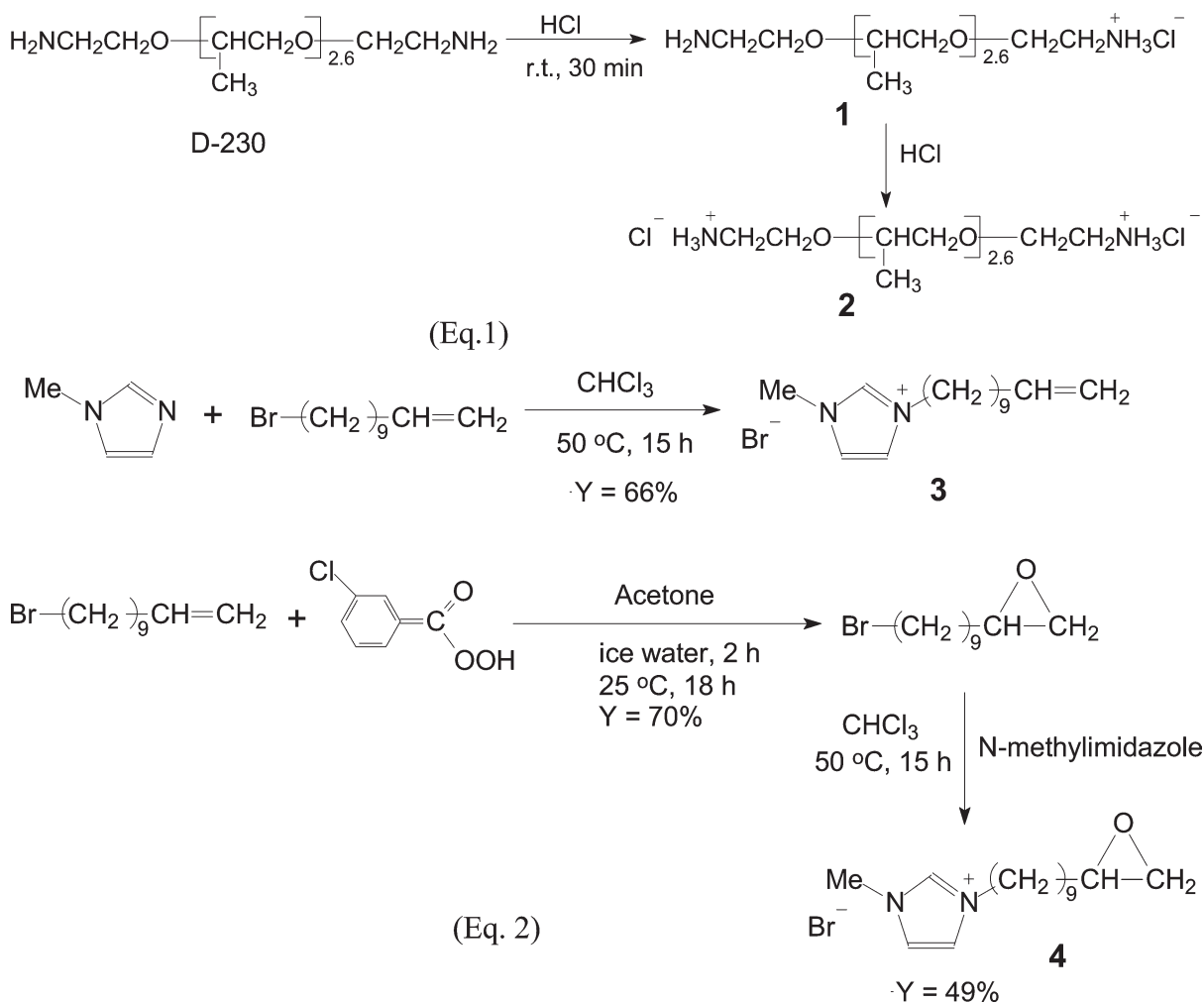


Figure 2 <sup>13</sup>C-NMR spectrum of pillar 3 (in CDCl<sub>3</sub>).



**Scheme 1** Synthesis of pillaring agents 1, 2, 3 and 4.

about 24 h. Then the suspension was filtered, and the filter cake was washed three times with 20 mL of EtOH. The filter cake was then dried (<5 mm Hg) at 80°C for 24 h. Then it was ground to a powder with a mortar and pestle to give 3.68 g organoclay (Clay 3a). Pillar 3 (39.3 meq/100 g clay) was intercalated into the Na-Cloisite, replacing 42.4% of the Na<sup>+</sup>.

*Synthesis of Clays 3b and 3c by ion-exchange.* The procedure to synthesize Clays 3b and 3c was similar to the synthesis of Clay 3a, but a higher pillaring agent 3/Na<sup>+</sup> ratio was used.

Na-Cloisite (1.15 g, 1.06 mmol exchangeable Na<sup>+</sup>) was added to 300 mL H<sub>2</sub>O/EtOH (1/1 v/v) in a 500-mL beaker. The suspension was sonicated at 75°C for 20 min. Then pillaring agent 3 (1.02 g, 3.24 mmol) was dissolved in hot water (50 mL) and added to the Na-Cloisite suspension (3/Na<sup>+</sup> mole ratio = 3.06). The suspension was heated to 75°C and sonicated at this temperature for 6 h. Then the suspension was filtered. This filter cake was not washed with EtOH and resulted in Clay 3b. The filter cake was then dried for 24 h at 40°C (<5 mm

Hg). Then it was ground to a powder with a mortar and pestle to give 1.21 g of organoclay (Clay 3b). An aliquote of Clay 3b (~ 0.6 g) was removed and washed with hot-distilled water three times. Again the suspension was filtered. The filter cake was dried for 24 h at 40°C (<5 mm Hg) to give Clay 3c, which was ground to a powder with a mortar and pestle. The amounts of pillar 3 were found to be 106.1 meq/100 g in Clay 3b and 84.9 meq/100 g clay in 3c after intercalation into the Na-Cloisite. The difference between Clays 3b and 3c shows that subsequent washing with EtOH removes some of the pillaring agent 3.

#### Synthesis of Clay 4

The pillaring agent 4 was synthesized as illustrated in Scheme 1 and isolated to prepare Clay 4.

*Synthesis of pillaring agent 4.* Pillaring agent 4 was synthesized by epoxidation of 11-bromo-1-undecene followed by nucleophilic displacement of bromide from the resulting 11-bromo-1,2-epoxyundecane by 1-methylimidazole.

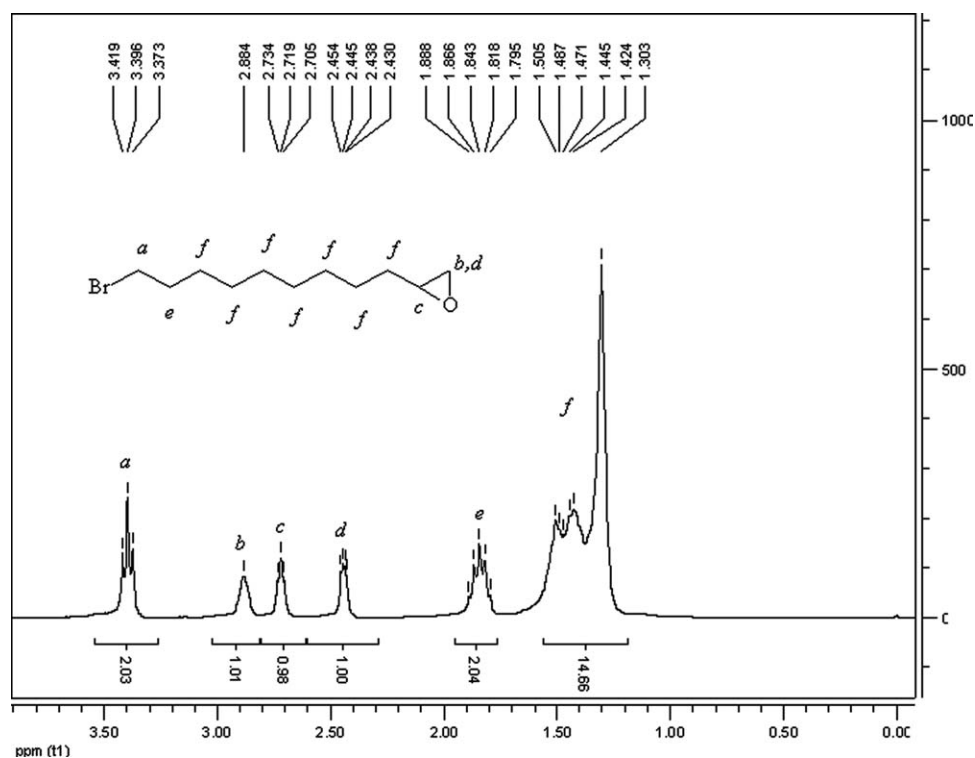


Figure 3  $^1\text{H}$ -NMR spectrum of 11-bromo-1,2-epoxyundecane (in  $\text{CDCl}_3$ ).

Step 1:<sup>36,37</sup> A 11-bromo-1-undecene (4.0 g, 17.15 mmol) solution in acetone (30 mL) in a 100-mL flask was cooled with an ice/water bath. *m*-Chloroperoxybenzoic acid ( $\leq 77\%$ , 5.80 g, and  $\leq 25.88$  mmol), dissolved in acetone (20 mL), was added dropwise to this magnetically stirred 11-bromo-1-undecene solution. After the addition was completed, the temperature was raised slowly to room temperature and held for 22 h. Acetone was removed by rotary evaporation. A white solid was left in the flask, to which  $\text{CH}_2\text{Cl}_2$  (20 mL) was added. The resulting suspension was filtered to remove most of the *m*-chlorobenzoic acid. The filtrate was concentrated and purified by column chromatography over silica gel using petroleum ether/ethylacetate (20 : 1, v/v) as the eluent. This product was further purified by washing its  $\text{CH}_2\text{Cl}_2$  solution (20 mL) with saturated aqueous  $\text{Na}_2\text{CO}_3$  solution ( $3 \times 20$  mL) to remove traces of *m*-chlorobenzoic acid. The extracted  $\text{CH}_2\text{Cl}_2$  solution was dried over 5 g of anhydrous  $\text{Na}_2\text{SO}_4$  for 24 h. Then,  $\text{Na}_2\text{SO}_4$  was removed by filtration, and  $\text{CH}_2\text{Cl}_2$  was removed by rotary evaporation. Liquid 11-bromo-1,2-epoxyundecane was collected (3.0 g, 70%). Its  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra are tabulated below and shown in Figures 3 and 4, respectively.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ /ppm: 3.4 (t,  $J = 6.8$  Hz, 2H), 2.9 (s, 1H), 2.7 (t,  $J = 4.4$  Hz, 1H), 2.4 (quad,  $J = 2.5$  Hz, 1H), 1.8 (quintet,  $J = 6.7$  Hz, 2H), and 1.3–1.5 (m, 14H).

$^{13}\text{C}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ /ppm: 52.0, 46.7, 33.6, 32.6, 32.2, 29.2, 29.1, 29.1, 28.5, 27.9, and 25.7.

Step 2:<sup>35</sup> 11-Bromo-1,2-epoxyundecane (2.0 g, 8.03 mmol) and 1-methylimidazole (0.66 g, 8.04 mmol) were added into a 100-mL two-necked flask equipped with a condenser and a thermometer. Then  $\text{CHCl}_3$  (30 mL) was added. The temperature was raised to  $50^\circ\text{C}$ , and the solution was magnetically stirred for about 24 h. Then the solvent was removed by rotary evaporation. A viscous ionic liquid left in the flask was washed with cyclohexane/ethyl acetate (1 : 1 v/v)  $4 \times 25$  mL, followed by washing with ethyl acetate ( $2 \times 15$  mL). The residual solvent was removed by rotary evaporation. Pillaring agent 4 (white solid, 1.31 g, 49%) was left in the flask. Its  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra with resonance assignments are shown in Figures 5 and 6, respectively, and the data are tabulated below.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ /ppm: 10.2 (s, 1H), 7.7 (s, 1H), 7.6 (s, 1H), 4.3 (s, 2H), 4.1 (s, 3H), 2.9 (s, 1H), 2.8 (s, 1H), 2.5 (s, 1H), 1.9 (s, 1H), and 1.3 (Br, 14H).

$^{13}\text{C}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ /ppm: 136.7, 123.5, 121.8, 52.0, 49.7, 46.7, 36.3, 32.0, 29.9, 28.9, 28.9, 28.8, 28.5, 25.8, and 25.5.

*Synthesis of Clay 4 by ion-exchange reaction.*<sup>25,27</sup> Na-Cloisite (2.44 g, 2.26 mmol exchangeable  $\text{Na}^+$ ) was added to 300 mL  $\text{H}_2\text{O}$ /acetone (1/1 v/v) in a

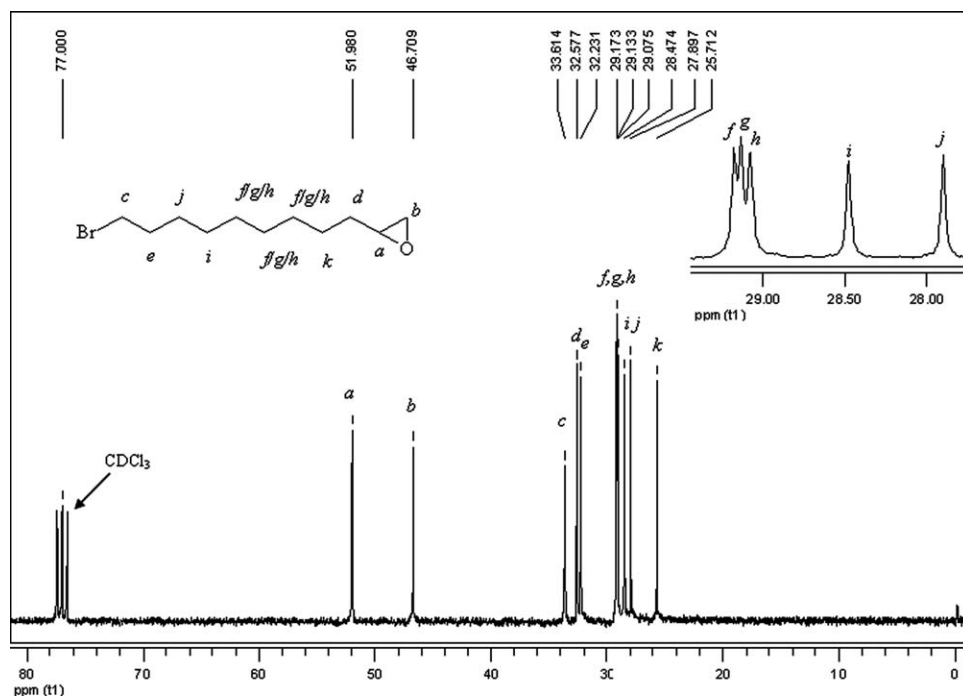


Figure 4  $^{13}\text{C}$ -NMR spectrum of 11-bromo-1,2-epoxyundecane (in  $\text{CDCl}_3$ ).

500-mL beaker. The suspension was sonicated for 20 min. Then, pillaring agent 4 (1.12 g, 3.38 mmol) was dissolved in 50 mL  $\text{H}_2\text{O}$ /acetone (1/1 v/v) and added to the Na-Cloisite suspension (4/ $\text{Na}^+$  mole ratio = 1.50). The stirred suspension

was heated to  $55^\circ\text{C}$  for about 24 h. Then the suspension was filtered, and the filter cake was washed with 20 mL  $\text{H}_2\text{O}$ /acetone (1/1 v/v), followed by washing twice with acetone (15 mL). The filter cake was then dried for 24 h at

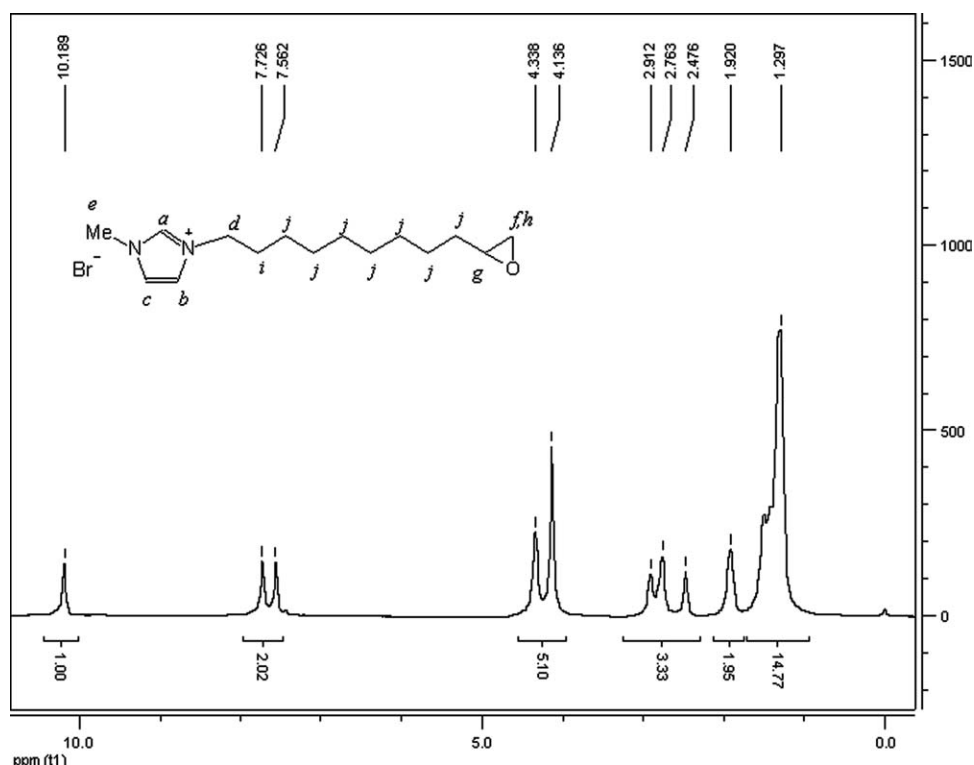


Figure 5  $^1\text{H}$ -NMR spectrum of pillar 4 (in  $\text{CDCl}_3$ ).

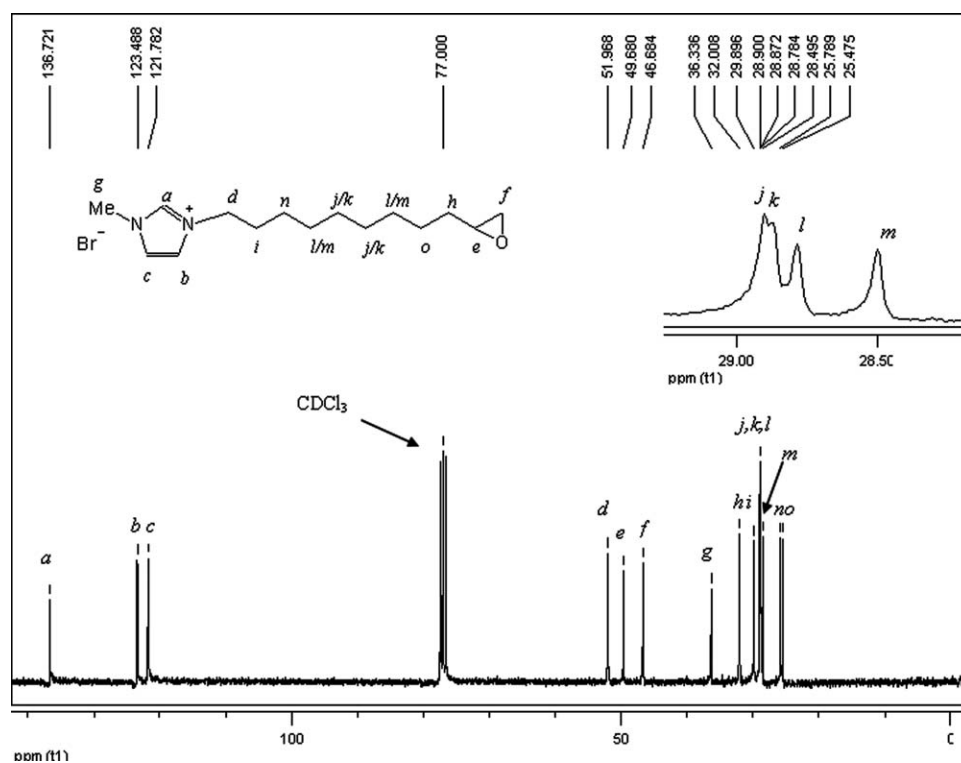


Figure 6  $^{13}\text{C}$ -NMR spectrum of pillar 4 (in  $\text{CDCl}_3$ ).

80°C (<5 mm Hg) and ground to a powder (Clay 4, 2.27 g).

*Fabrication of clay/epoxy composites.*<sup>25,27</sup> The liquid matrix resin, Epon 862, and curing agent EpiCure-W were blended with Na-Cloisite or organoclays 1–4 in a ratio of (100/26.4/1.0 wt/wt/wt). Clay and Epon 862 were first premixed by sonication at room temperature for 5 min and then vigorously mixed in a high-shear mixer at 4000 rpm for 15 min and followed by further sonication at room temperature for 15 min. Then EpiCure-W was added to the clay/resin suspension. This suspension was sonicated at room temperature for another 5 min and then degassed for 10 min at 60°C (<5 mm Hg). The composites were cured at 120°C for 2 h followed by 2 h at 175°C.

## RESULTS AND DISCUSSION

Pillaring agents 1 and 2 are the mono- and diprotated version of diamine D-230 shown in eq. (1). Pillaring agents 3 and 4 were synthesized as shown in Scheme 1 and described in the Experimental section. D-230 and pillars 1 and 2 have methyl branches and either three or four oxygens along their chain structure, which will retard chain alignment after exchange into the clay galleries. The terminal amine of 1 is available after exchange to react with epoxy monomers diffusing into the galleries, thereby per-

mitting this pillar to chemically bond to any infused epoxy resin or to epoxy resin surrounding the clay platelets if platelets have exfoliated. The *N*-methylimidazolium pillar 3 was prepared from 11-bromo-1-undecene by nucleophilic displacement with 1-methylimidazole. 11-Bromo-undecene epoxidation with *m*-chloroperbenzoic acid followed by nucleophilic substitution by *N*-methylimidazole generated pillar 4 (Scheme 1).

The pillaring agent content was calculated from TGA weight loss studies, and *d*-spacings were determined from XRD analyses. These results are summarized in Tables I, II, and IV, respectively.

### TGA analysis of organoclays

The organoclays exhibited weight loss in two temperature regions (Fig. 7). The first weight loss region occurred at 240–300°C. This includes loss of any physically absorbed pillaring agents along with losses due to decomposition of the exchanged pillaring agents.<sup>31</sup> Decomposition occurs by Hoffman-type eliminations to generate volatile terminal olefin functions, which escape as gases [eqs. (3) and (4)] or further thermally decompose into smaller fragments. The reaction in eq. (4) has a higher activation barrier than eq. (3). This accounts for the higher thermal stability of imidazolium pillars.

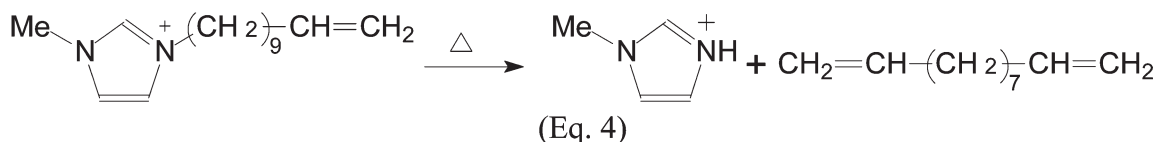
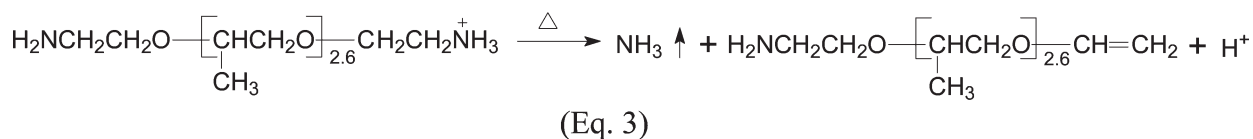


TABLE II  
TGA (Under N<sub>2</sub>) Analysis of Clays

| Clay sample          | Temperature (°C)<br>First Peak | Weight loss (wt %)<br>First Period | Temperature (°C)<br>Second Peak | Weight loss (wt %)<br>Second Period | Total weight<br>loss <sup>a</sup> (wt %) | Pillaring agent<br>content<br>(meq/100 g clay) |
|----------------------|--------------------------------|------------------------------------|---------------------------------|-------------------------------------|--|--|
| Na-Cloisite          |                                |                                    | 630                             | 3.5                                 | 3.5                                      | –  |
| Clay 1a              | 244                            | 4.1                                | 593                             | 7.7                                 | 11.8                                     | 36.0   |
| Clay 2               | 239                            | 3.4                                | 596                             | 6.9                                 | 10.3                                     | 29.4   |
| Clay 3a              | 296                            | 3.7                                | 617                             | 9.1                                 | 12.8                                     | 39.3   |
| Clay 3b <sup>b</sup> | 267                            | 11.0                               | 425                             | 17.5                                | 28.5                                     | 106.1  |
| Clay 3c <sup>b</sup> | 283                            | –                                  | 425                             | 23.5                                | 23.5                                     | 84.9   |
| Clay 4               | 284                            | 4.7                                | 603                             | 7.9                                 | 12.6                                     | 36.0   |

<sup>a</sup> The weight loss of Na-Cloisite at 800°C is 3.54 wt %. This amount has been subtracted from the organoclay weight loss to obtain the real values of weight loss due to the loss of pillaring agent (e.g., Clay 1a really lost 11.8–3.5 = 8.3 wt % by loss of pillar 1).

<sup>b</sup> Data were obtained by Dr. Mitra Yoonessi at the Wright Patterson Air Force Laboratories.



The second weight loss region occurred at 400–600°C. This is due to the decomposition of the remnants of the pillaring agents and the dehydroxylation of some structural hydroxyl groups in the clay.<sup>27</sup> The Na-Cloisite also exhibits some weight loss due to dehydroxylation at ~ 600°C. This Na-Cloisite weight loss was subtracted from the values of the organoclay total weight losses when determin-

ing each clay's pillaring agent content from the total weight loss obtained by TGA. This method of determining the pillaring agent content assumes that the total weight losses of organoclays included the complete loss of all N, C, H, and O from the pillaring agents and the bound water. The weight loss, temperature of the maximum rate of weight

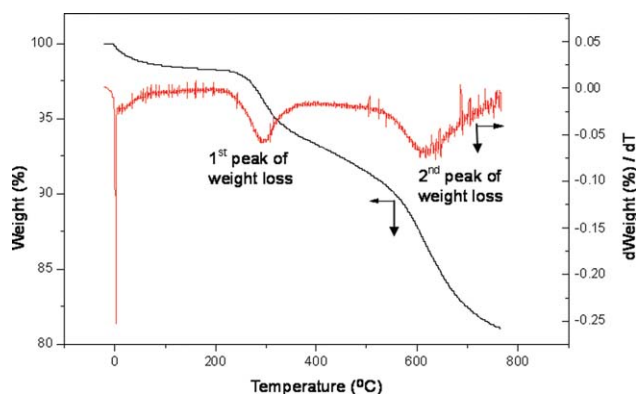


Figure 7 TGA (under N<sub>2</sub>) of Clay 3a pillared by 39.3 meq of pillar 3 per 100 g of MMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

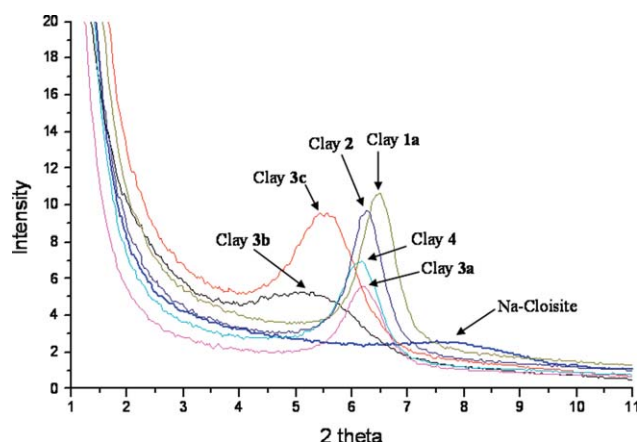
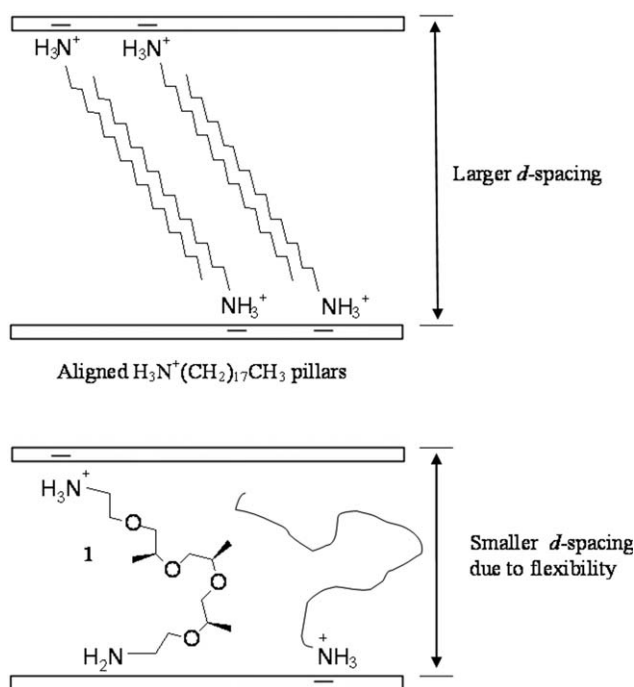


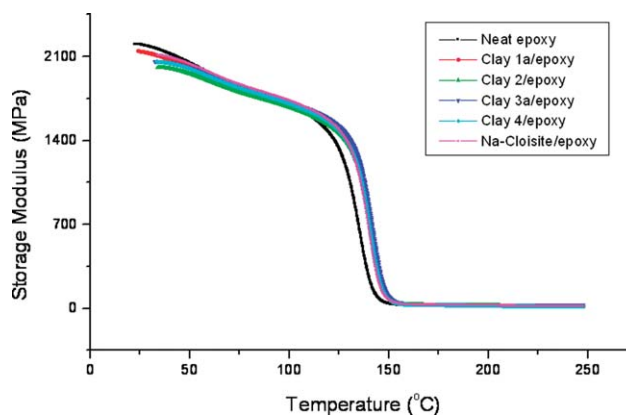
Figure 8 XRD plots of the organoclays versus Na-Cloisite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 9** Clays intercalated with  $\text{H}_3\text{N}^+(\text{CH}_2)_{17}\text{CH}_3$  and pillar 1.

loss, and calculated pillaring agent contents are illustrated in Table II. The pillar contents of Clays **1a–1e** are shown in Table IV.

Pillar **2** has two ammonium cation sites per molecule, while each pillar **1** has only one. Each intercalated molecule of **2** might replace two chloride ions. This might account for Clay **2** having a lower pillaring agent content than Clay **1a** (Table II). The pillar content of Clay **2** could only be half that of Clay **1a**, if all the ammonium cations are exchanged with  $\text{Na}^+$  and no physically adsorbed pillaring agent existed at the clay surfaces. Not all  $\text{Na}^+$  in Clay **1a** or **2** were exchanged, and the pillar content of Clay **2** is much larger than one half of that of Clay **1a**. The incorporation level of the imidazolium ion pillar **3** was high but dropped sharply on EtOH washing. Clay **3b** (not washed) and Clay **3c** (washed with hot water) have much higher pillaring agent loadings than Clay **3a** (washed with EtOH) (see Table II). Two factors could contribute to this difference:



**Figure 10** Storage moduli of clay/epoxy composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

(1) Higher pillaring agent/ $\text{Na-Cloisite}$  ratios were used in preparations of Clays **3b** and **3c**. This may lead to a higher ion-exchange efficacy. (2) The exchanged clay was washed with ethanol during Clay **3a** preparation. The solubility of pillar **3** in ethanol may be greater than in water.

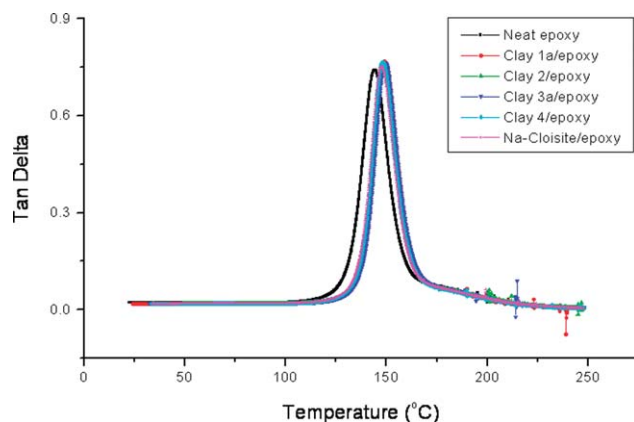
### XRD analysis of organoclays

The clay  $d$ -spacings were calculated with Bragg's equation,  $d = \lambda/2 \sin \theta$ , and the  $2\theta$  peak values and calculated  $d$ -spacings are summarized in Table I. The diffraction intensities versus  $2\theta$  angle are shown in Figure 8 for each type of clay.

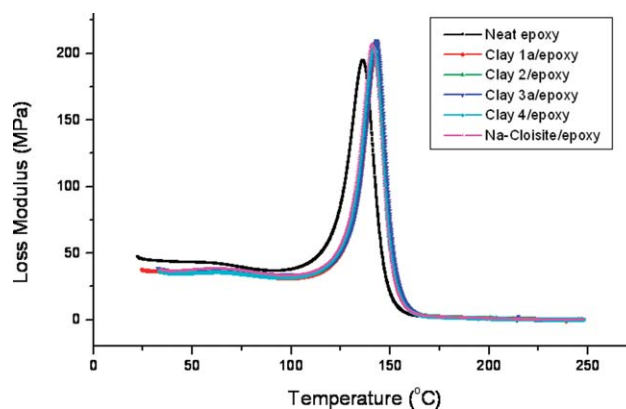
The  $d$ -spacings of Clays **1–4** are similar, falling between 13.7 and 14.3 Å, as shown in Table I. Clays **3b** and **3c** showed larger  $d$ -spacings than Clay **3a**, probably due to their higher pillaring agent contents (Table II). Pillaring agent **1** is highly flexible. Its chain disorder will prevent the higher alignment of adjacent pillars achieved by  $\text{H}_3\text{N}^+(\text{CH}_2)_{17}\text{CH}_3$  (Fig. 9).<sup>25</sup> This would likely be more serious at lower levels of ion exchange into the clay. Epoxy-functionalized Clay **4** has a similar pillar content (36 meq/100 g clay), and  $d$ -spacing (14.3 Å) as olefin-functionalized Clay **3a** (39.3 meq/100 g clay, 14.2 Å, see Table I). The epoxy functional groups had little effect on the  $d$ -spacing of the modified clay.

**TABLE III**  
Storage Moduli ( $E'$ ) and  $T_g$  Values (Tan  $\delta$  Peak Temperature) of Clay/Epoxy Composites

| Material                                  | $T_g$ (°C) | $E'$ (MPa) at |       |       |
|---|------------|---------------|-------|-------|
|   |            | 35°C          | 125°C | 135°C |
| Neat epoxy                                | 144        | 2157          | 1337  | 695   |
| Clay <b>1a</b> /epoxy composite (1.0 phr) | 149        | 2103          | 1477  | 1180  |
| Clay <b>2</b> /epoxy composite (1.0 phr)  | 149        | 2009          | 1460  | 1162  |
| Clay <b>3a</b> /epoxy composite (1.0 phr) | 149        | 2057          | 1520  | 1248  |
| Clay <b>4</b> /epoxy composite (1.0 phr)  | 148        | 2054          | 1478  | 1149  |
| Na-Cloisite/epoxy composite (1.0 phr)     | 148        | 2110          | 1493  | 1131  |



**Figure 11** Tan  $\delta$  plots of clay/epoxy composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 12** Loss moduli of clay/epoxy composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### DMA analysis of organoclay/epoxy composites

The storage moduli, tan  $\delta$ , and loss moduli of clay/epoxy composites by DMA are depicted in Figures 10–12. The dynamic-mechanical properties of all the organoclay composites are similar to each other. The storage moduli of all the clay containing composites were higher than that of the neat epoxy sample. The composite-containing Clay **3a** with olefin functionalized pillar exhibited the highest storage modulus values at temperatures from 125 to 150°C (Fig. 10). The differences among the variously pillared clays, however, are small. The epoxy function on the pillar can react during curing with matrix epoxy resin, which has intercalated into the galleries before or while curing. However, this did not enhance the storage moduli versus the olefin pillar in Clay **3a**. The *d*-spacings of Clays **1–4** are also similar (Table I). This suggests that the properties of the clay/epoxy composites depend more strongly on the degree of intercalation/exfoliation which

occurred, rather than the type of pillaring agent incorporated.

Table III lists the  $T_g$  values of these clay/epoxy composites determined by their tan  $\delta$  values from DMA measurements. The addition of the organoclays (1.0 phr) to the epoxy resin improves the  $T_g$  by 3–5°C, but only 1–2°C above that of the 1 phr Na-Cloisite/epoxy composite. The changes in dynamic-mechanical properties were modest at 35°C (Table III). The effects of organoclay addition were most likely muted by the small *d*-spacings, which retard resin intercalation into the galleries and make exfoliation more difficult. However, as the temperature increases to 125°C, the clay nanocomposite properties begin to surpass these of the pure resin. At 135°C, this difference becomes very pronounced. The clay/epoxy nanocomposite storage moduli (1131–1248 MPa) are 1.6–1.8 times greater than that of neat epoxy resin (695 MPa).

**TABLE IV**  
TGA (Under N<sub>2</sub>) and XRD Analysis of Clays **1a–1e**

| Clay sample    | Pillaring agent       | Pillar/Na <sup>+</sup> ratio | Cation exchange times | Temperature of weight loss (°C)First Peak | Total weight loss <sup>a,b</sup> (wt %) | Pillaring agent content (meq/100 g clay) | $d_{001}$ (Å) |
|----------------|-----------------------|------------------------------|-----------------------|---|---|--|---------------|
| Na-Cloisite    | –                     | –                            | –                     | –   | 3.5                                     | –  | 11.3          |
| Clay <b>1a</b> | Monoprotonated D-230  | 1.7/1                        | 1                     | 257                                       | 13.8 <sup>b</sup>                       | 44.6                                     | 13.7          |
| Clay <b>1b</b> | Monoprotonated D-230  | 5/1                          | 1                     | 259                                       | 14.8                                    | 49.0                                     | 13.6          |
| Clay <b>1c</b> | Monoprotonated D-230  | 10/1                         | 1                     | 258                                       | 15.2                                    | 50.7                                     | 13.7          |
| Clay <b>1d</b> | Monoprotonated D-230  | 5/1                          | 5                     | 261                                       | 15.6                                    | 52.4                                     | 13.6          |
| Clay <b>1e</b> | Monoprotonated D-2000 | 5/1                          | 1                     | 247                                       | 36.6                                    | 16.5                                     | 18.2          |

<sup>a</sup> The weight loss of Na-Cloisite at 800°C is 3.5 wt %. This amount has been subtracted from the organoclay weight loss to obtain the values of weight loss due to the loss of pillaring agent (e.g., Clay **1a** really lost 13.8–3.5 = 10.3 wt % by loss of pillaring **1**).

<sup>b</sup> This was obtained using a TGA instrument (SetSys EVO 2000, manufactured by Setaram Instrumentation Technologies). This was a different instrument than that used for Clay **1a** in Table 2.

### Analysis of organoclay prepared under different conditions

Clays **1b–1d** were also synthesized at higher pillar/ $\text{Na}^+$  ratios and longer exchange times. Clay **1e** used the high-molecular weight pillar D-2000. Their TGA and XRD results are listed in Table IV. The exchanged pillaring agent content slightly increased from 44.6 meq/100 g clay in **1a** to 50.7 meq/100 g clay when the pillaring agent/ $\text{Na}^+$  ratio increased from 1.7/1 to 10/1 (Clays **1a** to **1c** in Table IV). When the cation exchange was repeated five times, the pillaring agent content slightly increased from 49.0 to 52.4 meq/100 g clay (Clays **1b** and **1d** in Table IV). However, these increases in pillaring agent content caused no change in the clay *d*-spacings. In contrast, when the size of the pillaring agent increased from monoprotonated D230 (polyether diamine with an average of 2.5 ether units per molecule) to monoprotonated D-2000 (polyether diamine with an average of 33 ether units per molecule), the *d*-spacing increased from 13.6 to 18.2 Å (Clays **1b** vs. **1e** in Table IV). Only 16.5 meq/100 g clay was present in Clay **1e** for monoprotonated D-2000 pillar. Clay *d*-spacing was sensitive to the pillaring agent size. D-230 pillaring agent **1**, with an average 2.5 ether units per molecule, increases the *d*-spacing by about 0.9 Å per ether unit versus the *d*-spacing from Na-Cloisite. The *d*-spacing increases by about 0.2 Å per ether unit for the much larger monoprotonated D-2000 pillar. It is obvious that the flexible molecular chains of D-230 and D-2000 folded, coiled, or spread out in the clay intragallery spaces.<sup>25</sup>

### CONCLUSIONS

The organoclays were prepared containing pillaring agents that were functionalized with amino, olefin, and epoxy groups. Clay *d*-spacings increased modestly when  $\text{Na}^+$ -MMT clay was intercalated with these pillaring agents. The clay *d*-spacings are sensitive to the size of pillaring agents, increasing more with the large flexible D-2000 pillar. Imidazolium ion-based pillars are more thermally stable. The addition of clay (1.0 phr) to epoxy resin improves  $T_g$  by 3–5°C. The storage and loss moduli for the organoclay/epoxy composites were similar to each other at 30°C, but at 135°C, the storage moduli were 1.6–1.8 times greater than the neat epoxy resin for ~ 1 wt % (1 phr) organoclay loadings. The *d*-spacings of the organoclays did not increase substantially versus that of Na-Cloisite composite. This limited resin intercalation and clay exfoliation. Hence, these nanoclay dispersions did not give larger property improvements. SEM/TEM studies of the clay nanodispersions (tactoid thickness distributions and statistical analysis of tactoid spacings) were not carried out, because large changes in composite properties were not observed.

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