

Homostructured Mixed Inorganic–Organic Ion Clays: A New Approach to Epoxy Polymer–Exfoliated Clay Nanocomposites with a Reduced Organic Modifier Content

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A new approach to the preparation of epoxy–clay nanocomposites is reported based on the intercalation and exfoliation of homostructured mixed inorganic/organic cation exchanged forms of a commercially available montmorillonite (PGW) and a synthetic fluorohectorite (FH) clay. In these mixed-ion homostructures both the organic onium ions and the inorganic exchange ions co-occupy the gallery surfaces of the clay, thereby dramatically reducing the amount of organic modifier needed to access the galleries for nanocomposite formation. The homostructures were prepared by ion exchanging the inorganic H^+ and Li^+ forms of the smectite clays with diprotonated primary α,ω -diamines of the type $H_2NCH(CH_3)CH_2[OCH_2-CH(CH_3)]_xNH_2$ (denoted Jeffamine D2000 with $x = 33.1$). Varying the ratio of inorganic cations to onium ions afforded homostructured mixed-ion intercalates with basal spacings ranging from ~ 17 Å (25% onium ion exchange) to ~ 46 Å (65% onium ion exchange), indicating the Jeffamine D2000 modifier adopted extended chain to folded chain configurations depending on loading. Thermoset glassy epoxy–clay nanocomposites were prepared using EPON 826 resin and Jeffamine D-230 ($x = 2.6$) as a curing agent. Depending on the fraction of onium ions in the mixed-ion homostructures and on the method of nanocomposite preparation, intercalated and exfoliated clay nanolayers were achieved. The intercalated α,ω -diamine played the dual role of organic modifier of the clay and the curing agent in the thermoset epoxy matrix. Whereas the use of fully exchanged Jeffamine D2000 organoclays compromised the T_g of the matrix, mixed inorganic–organic ion clay homostructures made it possible to limit the plasticizing effect of the long-chain organic modifier and to preserve the glass transition temperature ($T_g \sim 78$ –85 °C) while improving the storage modulus. Mixed inorganic–organic ion homostructured clays should also provide a useful approach to forming nanocomposites with other engineering polymers, while reducing the need for an organic clay surface modifier.

Introduction

The materials applications of engineering thermoplastic and thermoset polymers can be substantially expanded through the formation of nanocomposites in which smectite clay nanolayers act as the reinforcing agents. The rich intercalation and ion-exchange chemistry of smectite clays enables them to be chemically modified through the introduction of organic cations or polymerization catalysts on the basal surfaces. The resulting intercalates exhibit improved mechanical properties (modulus, strength, heat distortion temperature, thermal expansion coefficient), barrier properties, thermal stability, resistance to solvent swelling, flammability resistance, and ablation performance compared to unmodified polymers and conventional composites. These improvements are primarily a consequence of the unique interfacial effects that result from the dispersion of the silicate nanolayers in the polymer matrix^{1–7} and

the high-in-plane strength and the high aspect ratio of the lamellar nanoparticles.⁸ Additionally, even though clays can be synthesized, they occur ubiquitously in nature and can be purified at relatively low cost.

Following the pioneering work of Toyota researchers in the early 90s demonstrating the first practical application of a nylon–montmorillonite clay nanocomposite in the automobile industry,^{9–11} numerous studies reported the preparation of exfoliated clay nanocomposites of polyimide, epoxy, acrylonitrile rubber, poly-

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propylene, polystyrene, polyether, and polysiloxane matrixes^{12–22} and many other polymer systems. The application of this new technology, however, has been impeded in large part by the high materials cost and processing time needed to exfoliate the clay nanoparticles in the polymer matrix. As illustrated by numerous studies of epoxy–clay nanocomposites formed from smectite clays^{12,17–19,23–29} and layered silicic acids,³⁰ alkylammonium ions and related onium ions are the most commonly used compatibilizing agents and polymerization catalysts for the formation of clay–polymer nanocomposites. Reducing the need for organic modifiers in the synthesis of polymer–clay nanocomposites would greatly expand the practical applications of these materials.

One approach to reducing the concentration of organic cations on a clay surface is to substitute a fraction of the organic cation exchange sites with inorganic cations within the same galleries.³¹ Such mixed exchange ion clays may be described as being “homostructured” because each gallery in the stacked tactoids would be equivalent in composition and intercalation properties. Also, homostructured mixed-ion clays are distinguishable from their “heterostructured” analogues in which the organic and inorganic exchange cations are segregated into separate galleries with very different intercalation properties.³² Whether a smectite clay will form a mixed-ion homostructure or a mixed-ion heterostructure will depend on the nature of the inorganic and organic exchange ions, the charge density on the clay layers, and the method used to form the mixed-ion composition. In general, organic and inorganic cations have very different solvation properties, thermodynamically favoring the segregation of the ions to be segregated into separate galleries. However, it is also possible to form thermodynamically unstable mixed ion homostructures by bringing the ion-exchange reaction under

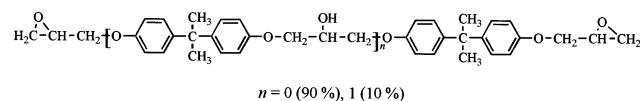
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kinetic control and trapping the two different exchange ions in the same galleries.

In the present work we report the preparation and properties of mixed inorganic–organic cation-exchange forms of montmorillonite and fluorohectorite clays for the nanolayer reinforcement of a thermoset glassy epoxy polymer. Substantial improvements in mechanical properties were observed for mixed-ion clay homostructures with onium ion-to-proton ratios in the range from 25:75 to 65:35. A long-chain diprotonated α,ω -diamine cation that facilitates pre-polymer intercalation and functions as a cross-linking agent was selected as the clay surface modifier.

Experimental Section

Materials. The epoxide resin used for the formation of the pristine glassy epoxy polymer and the epoxy–clay nanocomposites was a diglycidyl ether of bisphenol A (DGEBA), more specifically, Shell EPON 826 with an epoxy equivalent weight of ~ 182 :



The curing agent was a polyoxypropylene diamine of the type $\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2[\text{OCH}_2\text{CH}(\text{CH}_3)]_x\text{NH}_2$ ($x = 2.6$), which was provided by Huntsman Chemicals under the trade name Jeffamine D230. Jeffamine D2000 (MW ~ 2000 , $x = 33.1$) was used for the synthesis of homoionic clays, as well as homostructured mixed-ion clays, as is described below. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of Homoionic and Mixed-Ion Inorganic/Organic Clays. An industrially purified Na^+ –montmorillonite clay (PGW, Nanocor Inc.) with a cation-exchange capacity CEC = 120 mequiv/100 g was used to produce the H^+ and Li^+ forms of montmorillonite clay by ion exchange with dilute aqueous HCl (for H^+ –clays) or LiCl (for Li^+ –clays). A synthetic Li^+ –fluorohectorite clay (FH, Corning Inc.) with a CEC similar to that of the PGW montmorillonite also was used as a parent clay in this study.

The homoionic organic clays and the mixed-ion inorganic/organic clays were prepared by ion exchange of the inorganic clay with the desired amount of diprotonated diamine Jeffamine D2000. Typically, an aqueous inorganic clay suspension was blended for 1–2 min with a solution of the Jeffamine in aqueous HCl, using a small excess of H^+ to ensure the formation of the diprotonated form. The blended mixture was further stirred for 48 h at ambient temperature. For the preparation of the homoionic organic clays, the amount of D2000 used was in small excess of the stoichiometric ion exchange of the inorganic clay. In the case of the mixed-ion clays, the mole ratio of onium ions to inorganic cations in the reaction mixture was adjusted to achieve the desired degree of onium ion binding to the exchange sites. The ion-exchanged clays were separated by centrifugation and washed 3–4 times with deionized water (until free of Cl^-) and once with ethanol, prior to air drying at room temperature. The dried products were ground and sieved to a particle size <270 mesh (53 μm). The percent ion exchange of the inorganic cations with onium ions and the basal spacing of all the homoionic and mixed-ion clays produced are shown in Table 1.

Preparation of Epoxy–Clay Nanocomposites. The pristine glassy epoxy polymer was formed by mixing the epoxy monomer (EPON 826) with the curing agent (Jeffamine D230) at 50 °C for ~ 30 min, outgassing of the liquid mixture at room temperature, and curing in RTV silicone rubber molds at 75 °C for 3 h and, subsequently, at 125 °C for an additional 3 h under nitrogen.

**Table 1. Basal Spacings of Homoionic and Mixed-Ion
Homostructures of Montmorillonite (PGW) and
Fluorohectorite (FH)**

| clay sample designation | parent inorganic clay | organic modifier ^a | | basal spacings d_{001} (Å) |
|-----------------------------|-----------------------|-------------------------------|----------------------|------------------------------|
| | | onium ion (%) | diprotonated diamine | |
| H-PGW | Na-PGW | 0 | none | 13.4 |
| Li-PGW | Na-PGW | 0 | none | 12.4 |
| Li-FH | Li-FH | 0 | none | 12.3 |
| H/D2000 ₂₅ -PGW | H-PGW | 25 | D2000 | 16.9 |
| H/D2000 ₃₅ -PGW | H-PGW | 35 | D2000 | 17.8 |
| Li/D2000 ₃₅ -PGW | Li-PGW | 35 | D2000 | 17.6 |
| H/D2000 ₅₀ -PGW | H-PGW | 50 | D2000 | 43.7 |
| Li/D2000 ₆₅ -FH | Li-FH | 65 | D2000 | 45.3 |
| D2000-PGW | Na-PGW | saturated | D2000 | 45.5 |
| D2000-FH | Li-FH | saturated | D2000 | 46.0 |

^a The mixed-ion clays were formed by ion exchange of the parent inorganic clay with the diprotonated Jeffamine D2000 onium ion (Huntsman Chemical).

For the preparation of the epoxy-clay nanocomposites the clay was added to the epoxy EPON 826-Jeffamine D230 mixture at 50 °C under stirring for 30 min, followed by outgassing and curing at 75 and 125 °C (procedure *P-1*) in a manner analogous to pristine polymer formation. Alternatively, the epoxy EPON 826 was initially mixed with the clay at 50 °C and then the curing agent D230 was added (procedure *P-2*). Premixing of the clay with the epoxy monomer also was done in the presence of low-boiling-point solvents, e.g., acetone, ethanol (EtOH), and isopropyl alcohol (IPA). The epoxy-clay-solvent mixture was stirred at 25 °C for 30 min. The solvent was evaporated over a 1-h period at 25 °C, 30 min at 50 °C, and 1 h at 75 °C under vacuum. The amount of solvent used was 25 wt % of the epoxy weight. For the composites prepared from homoionic organoclays and homostructured mixed-ion clays, the moles of onium ions present in the clays were counted as contributing to the curing process, supplementary to the amine groups of Jeffamine D230, which was the main curing agent for the formation of the glassy epoxy polymers. The amount of onium ions due to the organic modifier of the clays was always <4% of the total amine groups necessary for complete cross-linking of the epoxy monomers. The clay loading of the nanocomposites prepared was 6 wt % on a silicate basis.

Characterization and Testing of Clays and Nano-composites. X-ray diffraction (XRD) patterns were obtained on a Rigaku rotaflex 200B diffractometer equipped with Cu K α X-ray radiation and a curved crystal graphite monochromator, operating at 45 kV and 100 mA. The diffraction patterns were collected between 1° and 12° 2 θ at a scanning rate of 1°/min. Samples of the liquid (gel-like) epoxy–clay mixtures or of the uncured epoxy–curing agent–clay mixtures were prepared by applying a thin film on filter paper mounted on a glass slide. Cured composite samples were prepared by mounting a rectangular flat specimen onto an aluminum holder.

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-100CX II microscope with a CeB₆ filament and an accelerating voltage of 120 kV, a beam diameter of $\sim 5 \mu\text{m}$, and an objective aperture of 20 μm . The TEM samples were prepared by supporting thin sections (80–100 nm) of the nanocomposite samples onto 300-mesh nickel grids.

Dynamic mechanical analysis tests were performed on a DMA 2980 dynamic mechanic analyzer (TA instruments) in the three-point bending mode at a frequency of 1 Hz and amplitude of 20 μm , from 25 to 140 $^{\circ}\text{C}$ at a heating rate of 4 $^{\circ}\text{C}/\text{min}$. The pristine epoxy polymer and the nanocomposite specimens were rectangular bars with dimensions 60 \times 13 \times 3 mm.

Thermogravimetric analyses (TGA) were performed using a Cahn TG System 121 Analyzer. The powdered clays, the pristine epoxy polymer, and the nanocomposite samples tested

were heated to 800 °C at a heating rate of 5 °C/min under N₂ flow.

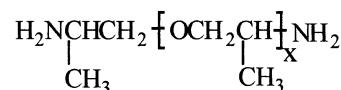
The composition of the inorganic and the organic clays was determined by energy-dispersive spectroscopy (EDS), CHN, and TGA analysis.

Results and Discussion

Homostructured Mixed-Ion Clay Intercalates.

The basal spacing of a homoionic organoclay depends on the chain length of the alkylammonium ion and the charge density of the layered silicate. Both factors control the packing and configuration of the onium-ion modifier in the constrained gallery and, consequently, the height of the gallery.^{3,33,34} Organoclays are normally formed through an ion-exchange reaction of an inorganic parent clay with the desired onium ion. The partial replacement of the inorganic cations by onium ions normally results in the segregation of the two types of cations into separate galleries, affording either an interstratified intercalate or a mixture of organic and inorganic clay phases. However, using smectite clays of the appropriate layer charge density, it is possible to prepare homostructured mixed-ion clays, wherein both the organic and inorganic cations are more or less uniformly distributed in every gallery.³¹ Because homostructured mixed-ion clays exhibit uniform basal spacing and intercalation properties, they are potential candidates for the preparation of polymer-exfoliated clay nanocomposites.

In the present study we synthesized homostructured mixed-ion smectite clays with comparatively low onium-ion contents and examined their properties as reinforcing agents in thermoset epoxy-clay nanocomposites. The use of a relatively long-chain α,ω primary diamine of the type allowed us to synthesize clay homostructures



with relatively high basal spacing, particularly when $x = 33.1$, as in the commercially available diamine Jeffamine D2000.

Figure 1 provides representative XRD powder patterns for mixed-ion PGW montmorillonites interlayered by protons and diprotonated Jeffamine cations at the 35% and 50% onium-ion equivalent level (denoted H/D2000₃₅– and H/D2000₅₀–PGW, respectively), along with the pattern for a homostructured fluorohectorite interlayered by 35% Li⁺ and 65% Jeffamine D2000 onium-ion equivalents (denoted Li/D2000₆₅–FH). Included for comparison are representative patterns for a homoionic organo fluorohectorite intercalated exclusively by diprotonated Jeffamine D2000 (denoted D2000–FH) and a homoionic inorganic montmorillonite (denoted H–PGW). There is no indication of an inorganic-rich phase (*d* spacing \sim 12–14 Å) in any of the mixed-ion clays. Also, the mixed-ion Li/D2000₆₅–FH and H/D2000₅₀–PGW homostructures exhibit a basal spacing (44–45 Å) very near the spacing for a homoionic organoclay interlayered completely by Jeffamine D2000

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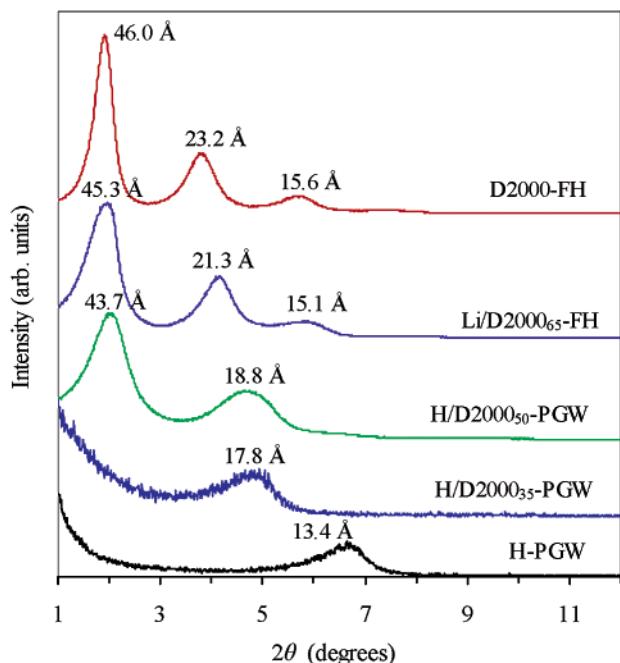


Figure 1. X-ray diffraction patterns of homoionic and mixed-ion homostructured montmorillonite (PGW) and fluorohectorite (FH) clays prepared by ion exchange of the Na^+ , Li^+ , or H^+ exchange form of the parent clay with diprotonated Jeffamine D2000 onium ions.

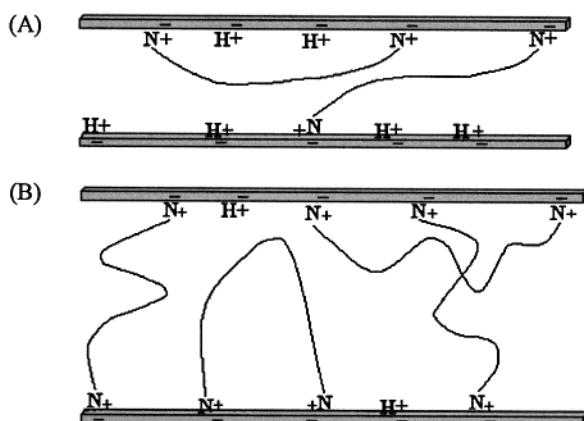


Figure 2. Schematic representation of the orientations of the diprotonated Jeffamine D2000 onium ions intercalated in the galleries of a mixed-proton–onium-ion homostructured PGW montmorillonite clay: (A) the diamine adopts an extended chain configuration at relatively lower onium-ion loadings, e.g., for onium-ions to protons ratio lower than 35% (d spacing $\sim 17\text{--}18\text{ \AA}$); (B) the diamine adopts a folded chain configuration at relatively high onium-ion loadings, e.g., for onium-ions to protons ratio higher than 50% (d spacing $\sim 44\text{--}46\text{ \AA}$).

onium ions, indicating that the onium ion adopts a folded conformation in all three clays. However, for the $\text{H/D}2000_{35}\text{-PGW}$ homostructure, the spacing is only $\sim 17\text{ \AA}$, suggesting that the onium ion at this composition adopts a more extended-chain conformation in the galleries. The structures of the mixed-proton–onium-ion homostructured Jeffamine-intercalated PGW clays are schematically represented in Figure 2. Table 1 summarizes the compositions and basal spacing for homoionic and mixed-ion homostructures of montmorillonite and fluorohectorite used in this study.

It is noteworthy that the same basal spacing is observed for the homostructured intercalates interlay-

ered by 50%, 65%, and 100% D2000 onium ions. These onium ions have ~ 33 isopropoxy segments separating the protonated amino groups. Clearly, the chain is coiled to the same extent in each of the three compositions, giving rise to the same basal spacing, but the lateral distance between the coiled chains increases with decreasing onium-ion loading.

Epoxy–Homostructured Mixed-Ion Clay Nanocomposites. The exfoliation of clay nanolayers in a polymer matrix requires polarity matching between the clay surface and the polymer precursors to allow optimal access to the gallery. In addition, the intragallery polymerization rate should be comparable to that of the bulk polymer matrix to allow expansion of the galleries with an increasing degree of cure. The modification of clay basal surfaces by acidic primary onium ions provides an appropriate hydrophobic environment for the catalytic epoxy-ring opening by diamine curing agents. When the acidic onium-ion modifier contains a flexible chain as in the diprotonated form of the α,ω -diamine Jeffamine D2000, the ion serves as a curing agent for a 3D epoxy network formation, as well as an acid catalyst, thus eliminating the undesirable plasticizing effect that can result from the dangling chains of conventional monoamine modifiers.^{12,30,35} Moreover, clay nanolayer exfoliation can be achieved without requiring that the diprotonated diamine modifier occupy all of the exchange sites of the clay.

The processing conditions used to cure a thermoset polymer–clay nanocomposite can significantly affect the degree of clay nanolayer exfoliation in a nanocomposite. For instance, the pre-intercalation of the epoxy monomers prior to the addition of the curing agent usually results in a higher degree of clay nanolayer exfoliation. The importance of preswelling the clay galleries prior to curing was more pronounced for the glassy epoxy polymers of this study than for previously reported rubbery epoxy systems that utilize larger, more flexible curing agents.^{27,30} Also, heating the epoxy–mixed-ion–clay mixture at 50 °C lowers the viscosity and facilitates the diffusion of the epoxy monomers into the galleries. Under these latter conditions, however, care must be taken to keep the solvation temperature below the point where gelation of the resin will occur.

Figure 3 provides the XRD patterns for a homostructured mixed-ion fluorohectorite $\text{Li/D}2000_{65}\text{-FH}$ fluorohectorite at different stages of solvation and cure with epoxy monomer EPON 826 and curing agent Jeffamine D230. Pre-intercalating the clay with the epoxy monomer at 50 °C resulted in the swelling of the nanolayers to a basal spacing of $\sim 60\text{ \AA}$ (Figure 3A). The subsequent addition of the diamine curing agent induced rapid intragallery polymerization and the exfoliation of the nanolayers (Figure 3B). Upon completion of the curing process at higher temperatures, the nanolayers remained highly separated, resulting in the absence of Bragg peaks in the small-angle region of the XRD pattern (Figure 3C). The retention of the clay structure in the exfoliated state was verified by the presence of an in-plane 060 reflection. The presence of this latter reflection verifies that the unit cell of a single-clay sheet is propagated along the in-plane b direction, even

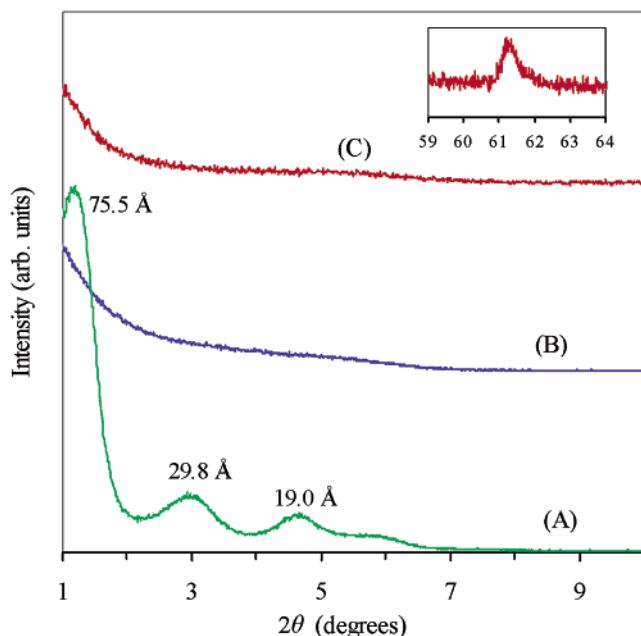


Figure 3. X-ray diffraction patterns of homostructured mixed-ion fluorohectorite Li/D2000₆₅-FH at different stages of solvation and cure with epoxy monomer EPON 826 and curing agent Jeffamine D230: (A) after intercalation of EPON 826 at 50 °C for 12 h, (B) after addition of Jeffamine D230 to the mixture of step A and outgassing at 25 °C, (C) after curing the mixture of step B at 75 °C, 3 h and 125 °C, 3 h. The inset shows the in-plane 060 clay reflection in the cured nanocomposite. The clay loading was 6 wt % on a silicate basis.

though the sheet is not stacked. The exfoliation of the clay nanolayers in the mixed-ion homostructure parallels the exfoliation behavior of a fully exchanged, homoionic D2000-FH organic clay.³⁵ However, for the homostructured mixed-ion clay, only 65% of the exchange sites are occupied by onium ions, resulting in a significant savings in the amount of modifier needed to achieve exfoliation.

An alternative approach to improving the degree of exfoliation in a clay–prepolymer reaction mixture is to use a low-boiling-point polar solvent, such as acetone,²⁷ ethanol (EtOH), and isopropyl alcohol (IPA), to assist in the preswelling and loading of the galleries with prepolymer. These solvents were used in the present work to form glassy epoxy–clay nanocomposites containing the homostructured mixed-ion montmorillonite clay H/D2000₅₀-PGW, wherein the fraction of organic modifier was reduced further to a ratio of onium ion to proton equivalents of 50:50. Figure 4 shows the XRD patterns for the nanocomposites formed from this mixed-ion homostructure in the three different solvent systems. Included for comparison are the composites formed by the direct solvation of the mixed-ion homostructure by an EPON 826 epoxy resin–Jeffamine D230 curing agent mixture and by the neat epoxy monomer prior to the addition of the curing agent. The beneficial effect of using EtOH and IPA to assist in the presolvation of the clay galleries is clearly evident from these diffraction patterns. A broad peak with *d* spacing ~18.5 Å is clearly resolved in the samples prepared through the use of acetone, as well as for the composites prepared through the use of no solvent, indicating the presence of un-exfoliated clay in these nanocomposites. This diffraction line was eliminated for the samples

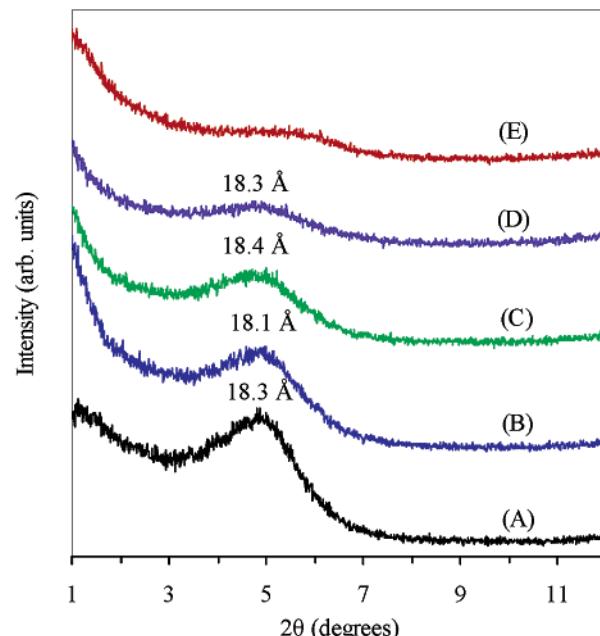


Figure 4. X-ray diffraction patterns of cured composites formed from homostructured H/D2000₅₀-PGW montmorillonite clay by solvating the homostructure in (A) the pre-polymer mixture, (B) neat EPON 826, (C) EPON 826 in acetone, (D) EPON 826 in ethanol, and (E) EPON 826 in 2-propanol. The amount of solvent used was 25 wt % of the epoxy resin. The clay loading of the final nanocomposite was 6 wt % on a silicate basis.

where EtOH and IPA were used as the swelling solvents. These differences can be attributed to the greater swelling ability of EtOH and IPA in facilitating the transport of the prepolymer resin into the clay galleries. Efforts to prepare glassy epoxy nanocomposites using mixed-ion clays with still lower onium ion-to-proton ratios (e.g., 35:65 and 25:75) afforded primarily intercalated nanocomposites with or without the use of solvents, as evidenced by the presence of a broad, low intensity *d*₀₀₁ peak with a *d* spacing of ~17–18 Å. Also, a purely inorganic proton-exchanged montmorillonite H-PGW (*d*₀₀₁ ~ 13.7 Å) failed to imbibe polymer precursors, resulting in the formation of conventional, non-intercalated epoxy–clay composite. Thus, highly exfoliated nanocomposites were possible for mixed-ion Li/D2000₆₅-FH fluorohectorite and H/D2000₅₀-PGW montmorillonite clays, but progressively less clay layer exfoliation was realized for onium-ion to inorganic-ion ratios below these values.

TEM images of the nanocomposite samples prepared from the mixed-ion Li/D2000₆₅-FH fluorohectorite and H/D2000₅₀-PGW montmorillonite clays are shown in Figure 5. The clay loading in both samples were 6 wt % (silicate basis). The Li/D2000₆₅-FH nanocomposite was comprised mainly of face–face groupings of highly exfoliated clay layers separated by 5–20 nm of polymer. Individual, shorter layers could also be found on the edges of the primary dispersed particles and most frequently in domains with a relatively low number of layers. Similar images of exfoliated clay nanolayers were observed for a glassy EPON 826–Jeffamine D230 epoxy made from a homoionic D2000-FH organic fluorohectorite clay. A more disordered exfoliated clay phase (i.e., fewer face–face orientations of nanolayers) was found for the H/D2000₅₀-PGW nanocomposite, in which most

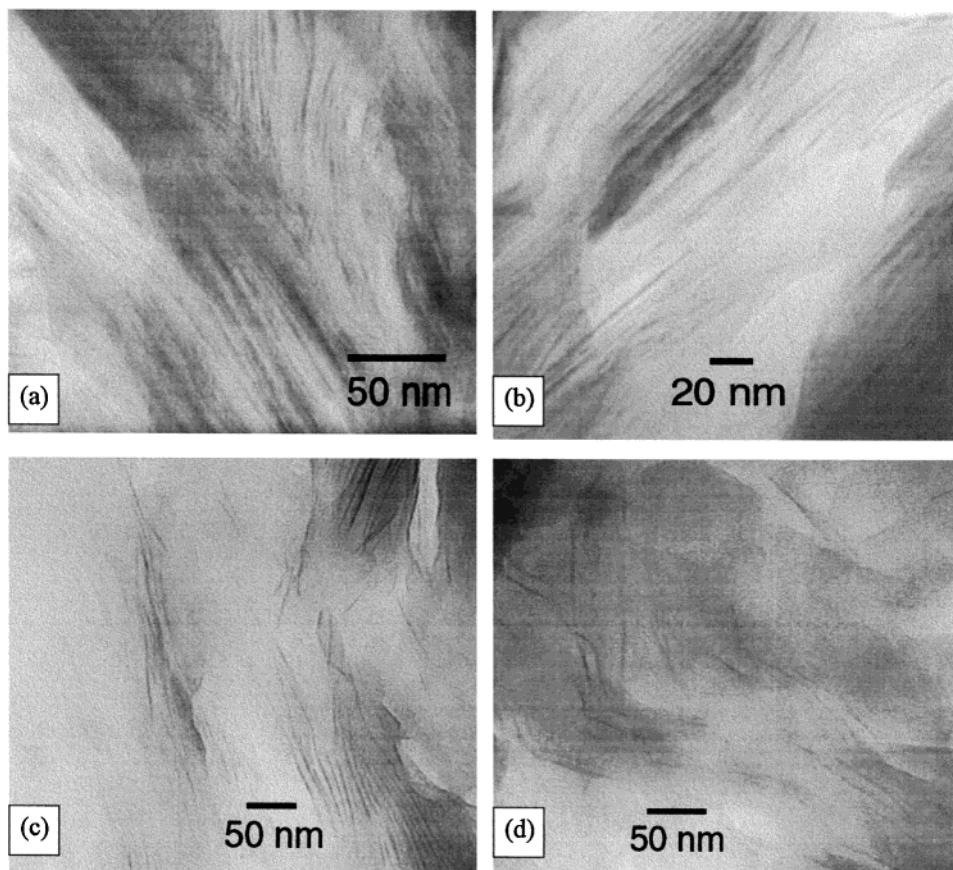


Figure 5. TEM images of thin sections of glassy epoxy nanocomposites prepared from mixed-ion clay homostructures: (a,b) Li/D2000₆₅–FH fluorohectorite and (c,d) H/D2000₅₀–PGW montmorillonite. The nanostructure shown in (c) and (d) was formed by pre-solvating the clay with EPON 826 in 2-propanol. The clay loading was 6 wt % on a silicate basis.

of the nanolayers were separated by more than 10 nm of polymer. The difference in the degree of face–face nanolayer orientation between the two types of smectite clays was also observed in the homoionic organic forms of these clays. We attribute these differences in nanolayer orientation to the significantly higher aspect ratio of the fluorohectorite (~2000) compared to that of the montmorillonite clay (~200).

Nanocomposite Properties. Dynamic mechanical analysis (DMA) tests were used to determine the reinforcement properties provided by the mixed-ion clay homostructures. The DMA technique provides two different moduli, an elastic or storage modulus (E) which is related to the ability of the material to return or store energy when an oscillatory force is applied to the specimen and an imaginary (loss) modulus (E') which relates to its ability to lose energy. The ratio E'/E is called tan delta ($\tan \delta$), which typically reaches a maximum at the glass transition (T_g) of the polymer. The DMA tests of this study were carried out using a three-point bending (flexural) mode. The curves in parts a and b of Figure 6 show the dependence of the storage modulus and the $\tan \delta$, respectively, on temperature for representative nanocomposite samples prepared from homostructured mixed-ion clays, as well as the corresponding homoionic organic clays, at clay loadings of 6 wt % (silicate basis). The data in Table 2 summarize the storage modulus values for the pristine polymer at 40 °C (glassy region, below T_g) and at 110 °C (rubbery region, above T_g), along with the T_g values obtained from the maximum in $\tan \delta$.

The storage modulus and the T_g values for the conventional, non-exfoliated composite formed from the inorganic H–PGW montmorillonite clay were similar to those of the pristine epoxy polymer. The effective clay loading for this specimen was lower than 6 wt % on a silicate basis because much of the initially added clay settled at the bottom of the composite specimen. Furthermore, the dispersion of the clay primary particles was not homogeneous and the clay concentration was gradually increased from the top to the bottom of the sample. However, an interesting finding was that no damage by oxidation or thermal decomposition was observed for this composite sample due to the presence of protons on the surface of clay layers. The nanocomposite sample formed from homoionic D2000–PGW montmorillonite showed a ~25% increase in storage modulus in both the glassy and rubbery region, while 35% and 65% increases, respectively, were found for the nanocomposite made from the D2000–FH organic clay, indicating better reinforcing properties for the high-aspect ratio fluorohectorite nanolayers in comparison to that of the smaller montmorillonite nanolayers. However, a small decrease in the T_g value was observed with the homoionic organic clays, which could be minimized by optimizing the fabrication procedure, for example, by pre-intercalating the epoxy monomers in the clay prior to adding the curing agent (compare samples D2000–PGW and D2000–PGW, P-2 in Table 2). In addition, when the nanocomposites formed from the organic D2000-exchanged clays were compared to the pristine polymer in which a similar amount of

Table 2. Dynamic Mechanical Analysis and Thermal Analysis Data for Pristine Epoxy Polymers and Epoxy–Clay Nanocomposites^a

| clay additive | storage modulus (<i>E</i>) | | | thermal stability ^b (°C) |
|------------------------------------------------|---------------------------------|--------------------|------------------------------|-------------------------------------------|
| | at 40 °C (GPa) | at 110 °C (MPa) | <i>T_g</i> (°C) | |
| none: pristine epoxy-A | 2.9 | 18.4 | 82.6 | 373 |
| none: pristine epoxy-B ^c | 3.0 | 20.1 | 75.5 | 361 |
| H–PGW | 2.9 | 22.1 | 82.8 | 354 |
| Li–PGW | 2.7 | 19.9 | 82.3 | 356 |
| Li–FH | 3.1 | 25.2 | 85.2 | 351 |
| H/D2000 ₂₅ –PGW | 3.7 | 26.0 | 80.2 | 342 |
| H/D2000 ₃₅ –PGW | 3.8 | 26.8 | 79.0 | 339 |
| H/D2000 ₃₅ – <i>P2</i> ^d | 3.6 | 38.3 | 85.1 | 342 |
| Li/D2000 ₃₅ –PGW | 3.5 | 24.1 | 81.7 | 342 |
| H/D2000 ₅₀ –PGW | 3.3 | 22.7 | 78.0 | 339 |
| H/D2000 ₅₀ –PGW– <i>P2</i> | 3.2 | 28.0 | 82.6 | 341 |
| H/D2000 ₅₀ –PGW– <i>P2</i> /acetone | 3.6 | 35.2 | 83.1 | 339 |
| H/D2000 ₅₀ –PGW– <i>P2</i> /EtOH | 3.4 | 32.4 | 83.1 | 330 |
| H/D2000 ₅₀ –PGW– <i>P2</i> /IPA | 3.6 | 31.6 | 80.4 | 347 |
| Li/D2000 ₆₅ –FH | 4.0 | 27.6 | 78.0 | 328 |
| D2000–PGW | 3.8 | 21.5 | 69.8 | 336 |
| D2000–PGW– <i>P2</i> | 3.6 | 24.0 | 75.1 | 339 |
| D2000–FH | 3.9 | 30.5 | 73.7 | 323 |

^a The clay loading for each nanocomposite sample was 6 wt % on a silicate basis. ^b Temperature at which the weight loss in TGA was 1.5%. ^c For this pristine polymer 4 mol % of the D230 Jeffamine curing agent was replaced by Jeffamine D2000. ^d *P2* identifies the nanocomposites prepared by premixing the epoxy monomer with the clay additive with or without the use of solvent (acetone, EtOH, IPA); the remaining samples in the table were prepared by the direct addition of the clay to the epoxy–curing agent mixture (procedure *P1*).

D2000 was used as the curing agent (\sim 4 mol % of the total curing agent), the above decrease in T_g was eliminated. Therefore, the slight decrease in T_g for the nanocomposite can be attributed to the 4 mol % Jeffamine D2000 originating from the clay organic modifier. Although the mole fraction of Jeffamine D2000 incorporated into the cured epoxy matrix is small (4 mol %), there are approximately 13 times more propylene oxide units in D2000 than in D230. Thus, about one-third of the propylene oxide segments in the curing agent is in the form of flexible long chains, which contribute to the decrease in T_g .

Interestingly, similar or even higher increases in storage modulus without any significant changes in T_g could be achieved with the mixed-ion clays, even for the intercalated nanocomposite sample prepared from a mixed-ion clay with an onium-ions to protons ratio of 25:75 (Figure 6 and Table 2). More specifically, the nanocomposite sample formed from the H/D2000₂₅–PGW clay showed a 30% and 40% increase of storage modulus in the glassy and rubbery region, respectively, the sample prepared from H/D2000₅₀–PGW with the use of isopropyl alcohol as a mixing solvent showed 25% and 70% increases, and the sample formed from Li/D2000₆₅–FH showed 40% and 50% increases. The T_g for all these samples ranged from \sim 78–85 °C compared to 83 °C of the pristine glassy epoxy polymer. These increases in storage modulus are in the same range found for nanocomposites made from homoionic organic clays.^{17,27,29} Yet up to 75% of the clay ion-exchange sites in the mixed-ion homostructures are occupied by inorganic cations, resulting in a substantial savings in the amount of organic modifier needed to achieve nanocomposite formation.

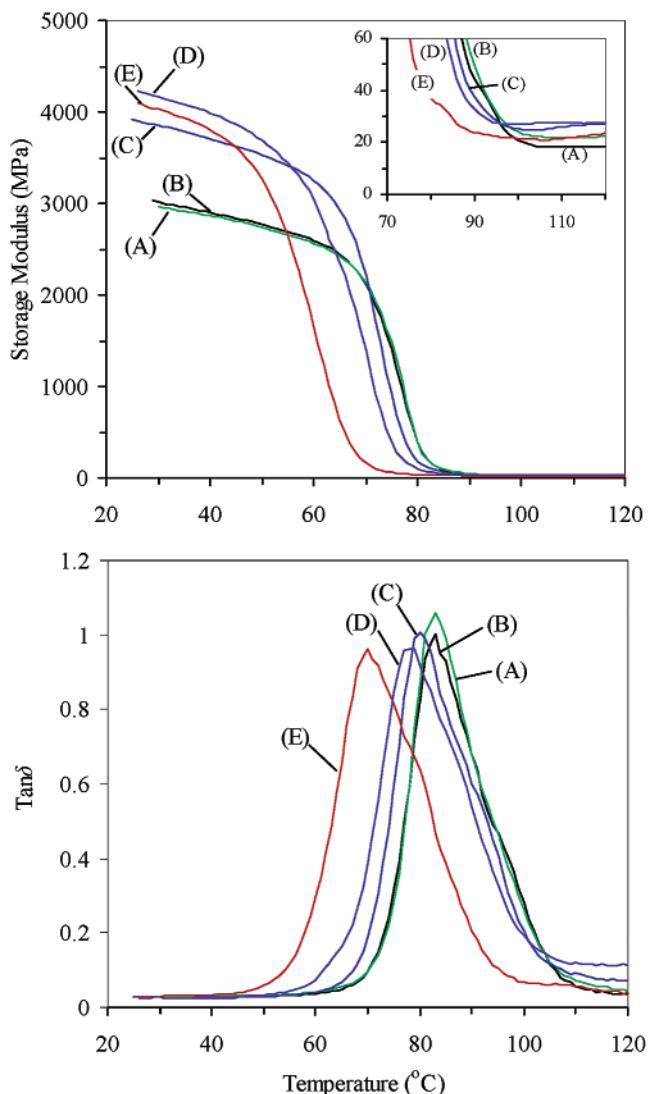


Figure 6. Dynamic mechanical analysis measurements: (a) Storage modulus vs temperature and (b) $\tan \delta$ vs temperature for (A) pristine-A epoxy polymer and for the nanocomposite samples prepared from (B) H–PGW montmorillonite, (C) H/D2000₂₅–PGW montmorillonite, (D) Li/D2000₆₅–FH fluorohectorite, and (E) D2000–PGW montmorillonite. The clay loading of the nanocomposite samples was 6.0 wt % on a silicate basis.

Thermogravimetric analyses of the mixed-ion clays showed that when protons are present on the gallery surfaces, decomposition of the Jeffamine D2000 modifier occurred at a lower temperature in comparison to that of a homoionic organoclays or to a mixed-ion clay in which the inorganic cation was Li^+ instead of H^+ . Presumably, the decomposition reaction involved the Hoffman degradation of the onium ion to an olefin and an amine. However, the deleterious effect of protons was not observed for the cured glassy epoxy–clay nanocomposite samples, as can be seen from the TGA curves in Figure 7 and the data in Table 2. The thermal stability of the nanocomposite formed from the H^+ /D2000 mixed-ion clays was as good as that of the pristine polymer. In addition, the high thermal stability of the nanocomposites prepared from both the homoionic and the mixed-ion diamine-modified clays suggested that the surface onium ions of the diamine were incorporated

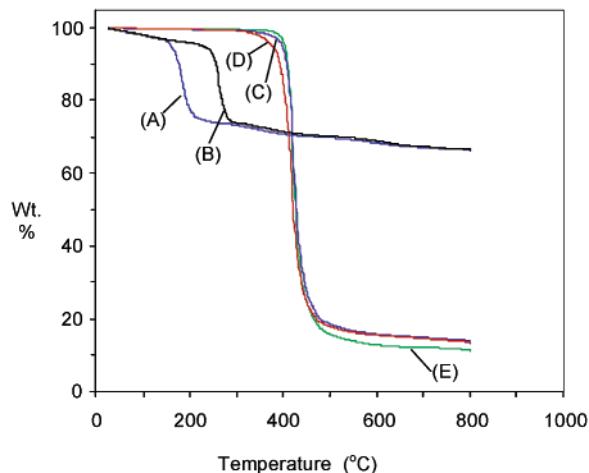


Figure 7. TGA curves for intercalated mixed-ion clay homostructures: (A) H/D2000₃₅–PGW montmorillonite and (B) Li/D2000₃₅–PGW montmorillonite in comparison to TGA curves for nanocomposites made from EPON 826–Jeffamine D230 and reinforced with (C) H/D2000₂₅–PGW montmorillonite and (D) D2000–PGW montmorillonite. Curve (E) is for the pristine epoxy polymer. The clay loading of each of the nanocomposite samples was 6 wt % on a silicate basis.

into the polymer network, resulting in nanocomposites with improved interfacial and physical properties.

Conclusions

Using a glassy epoxy polymer matrix system as an example, we have demonstrated that the amount of

organic modifier needed to transform a smectite clay into a derivative suitable for nanocomposite formation can be dramatically reduced by converting the clay into a mixed-ion homostructure in which inorganic and organic cations mixtures co-occupy the gallery regions between nanolayers. Up to 75% of the ion-exchange sites of a naturally occurring montmorillonite or synthetic fluorohectorite can be replaced with low-cost inorganic cations (e.g., H⁺ and Li⁺) without sacrificing the reinforcement benefits that would be provided by the same clays in fully exchanged organo-cation form. Owing to the high degree of nanolayer orientation in these samples, epoxy nanocomposites prepared from mixed-ion clay homostructures may find applications as high barrier thin films or coatings. In addition, we anticipate that mixed inorganic–organic ion homostructured clays will also be useful for nanocomposite formation in other engineering polymer systems, including thermoplastic as well as thermoset polymers.

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