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Interfacial Effects on the Reinforcement Properties of Polymer−Organoclay Nanocomposites

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The inclusion of metal oxide particles in organic polymer matrixes via sol−gel processes is an effective approach to enhancing the tensile properties of the matrix.[1,2] Inorganic materials that can be broken down into their nanoscale building blocks, such as smectite clays, can be superior alternatives to the sol−gel process for the preparation of nanostructured hybrid organic−inorganic composites.[3] Intercalated polymer−clay nanocomposites have been synthesized by direct polymer intercalation[4,5] and in situ intercalative polymerization of monomers in the clay galleries.[6,7] Owing to the spatial confinement of the polymer between the dense clay layers, intercalated polymer−clay nanocomposites exhibited impressive conductivity[4] and barrier properties.[5]

The exfoliation of smectite clays in a polymer matrix provides 10 Å thick silicate layers with high in-plane bond strength and aspect ratios comparable to those found for fiber-reinforced polymer composites. For instance, clay exfoliation in a nylon-6 matrix was shown by Toyota researchers[8−10] to greatly improve the mechanical, thermal and rheological properties of the matrix, making possible new high-temperature applications of this polymer. However, it is relatively difficult to achieve complete exfoliation of smectite clays into a continuous polymer matrix, because of the strong electrostatic attraction between the silicate layers and the intergallery cations.

Ion exchange of the Na^+ or Ca^{2+} gallery cations in the pristine mineral by organic cations, particularly alkylammonium ions, allows modification of the gallery surfaces for intercalation of polymer precursors.[11] To achieve full exfoliation of the clay, the alkylammonium cations normally typically contained chains longer than eight carbon atoms. Our earlier attempts to exfoliate shorter alkylammonium-exchanged clays in epoxy matrixes afforded only partially exfoliated nanocomposites with poor reinforcement properties, suggesting that the chain length of the onium ion at the interface may play an important role in the exfoliation process. The interactions occurring at the polymer−organoclay interface, however, are very complex. The polymer may bind (adsorb) directly to the chemically inert Kagomè network of siloxane oxygen atoms on the basal surfaces of the silicate layers. In addition, the alkylammonium chains may "dissolve" to different degrees into the polymer matrix. These two types of interfacial interactions, designated types A and B, respectively, are schematically illustrated in Figure 1. Binding of the hydroxylated edges of the silicate layer with the polymer matrix (type C) represents yet another interfacial interaction.

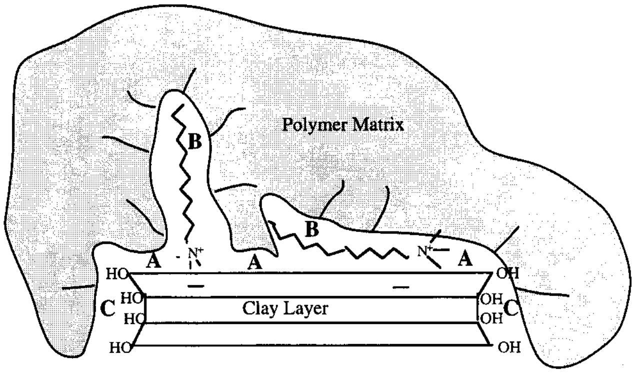

Figure 1. Schematical illustration of the types of interfacial interactions occurring in polymer−organoclay nanocomposites include direct binding (adsorption) of the polymer to the basal siloxane oxygens (type A), "dissolving" of the onium ion chains into the polymer matrix (type B), and polymer binding to hydroxylated edge sites (type C).

Probing the relative importance of types A and B interfacial interactions in organoclay nanocomposites has been relatively difficult, in part because of the eight-carbon-atom threshold for nanolayer exfoliation. As demonstrated in the present work, however, we can now achieve exfoliated clay nanocomposite formation with onium ion chain lengths as short as three carbon atoms. Thus, by greatly reducing the size of the onium ion for type B interaction while retaining oxide surface available for type A interactions, we are able to vary the relative contribution of these two binding interactions in an effort to evaluate these relative contributions to the reinforcement mechanism.

The exfoliation of clay nanolayers containing short chain alkylammonium ions ($n \le 8$) in a thermoset epoxy matrix was achieved by first subjecting the initial clay to ion exchange to replace almost all of the inorganic exchange cations on the basal surfaces with onium ions. To compare the extent of organo cation exchange on clay nanolayer exfoliation, we compared the properties of montmorillonite (Wyoming Swy2, CEC = 92 mequiv/100 g) subjected to a single-ion-exchange reaction to those prepared by triple-ion-exchange reactions. Each exchange reaction was carried out in aqueous solution at 70−75 °C for 24 h at 10:1 onium ion:clay molar ratios. For convenience, the products were denoted *n*A-mont-1× and *n*A-mont-3×, where *n* designates the carbon number of the ammonium exchange ion and 1× and 3× indicates the number of exchange cycles used to prepare the clay.

The air-dried clays with a particle size smaller than 50 μm were used to prepare epoxy-clay composites

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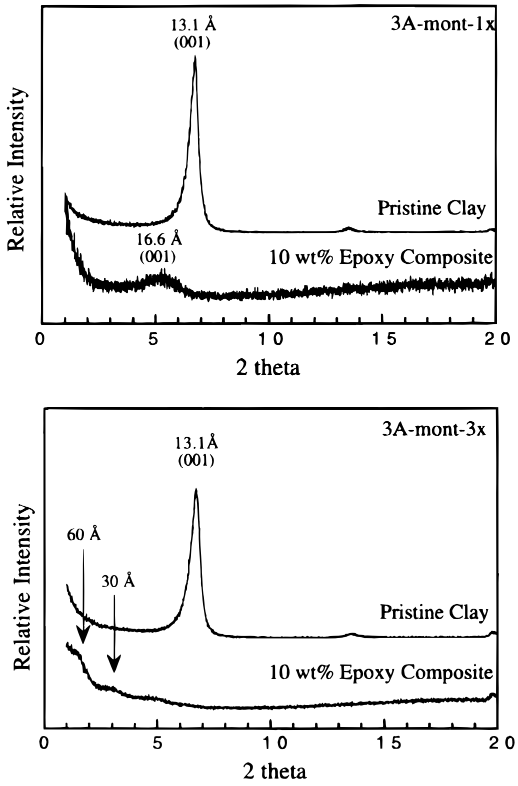
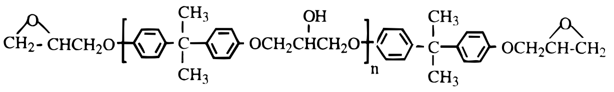


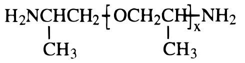
Figure 2. XRD patterns of 3A-mont-1× and 3A-mont clays as pristine intercalates and as reinforcing agents dispersed in the 10 wt% level in Epon 828/Jeffamine D2000 epoxy composites. The composites were molded and cured at 125 °C for 6 h.

derived from the diglycidyl ether of bisphenol A (Epon-828, Shell Chemical Co.):



n = 0 (88%); n = 1 (10%); n = 2 (2%).

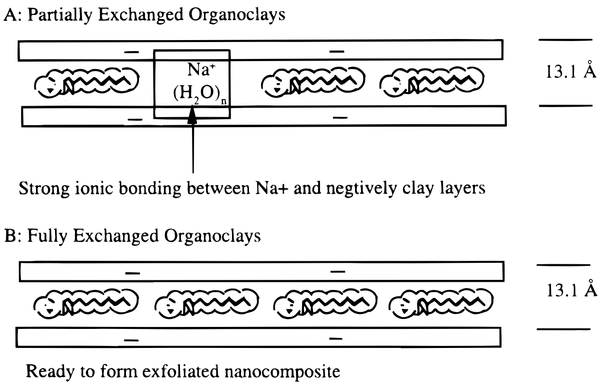
A stoichiometric quantity of the polyetheramine Jeffamine D2000 (Huntsman Chemical Co.) was used as the curing agent to form a matrix with a subambient glass transition temperature:



$$H_2N\underset{CH_3}{CH}CH_2\left[OCH_2\underset{CH_3}{CH}\right]_x NH_2$$

where $x = 33.1$ and the molecular weight is 2000. To promote clay nanolayer exfoliation and ensure optimum network cross-linking, the newly developed hot-mold-casting[12] method was used to cure the composites at 125 °C for 6 h. Figure 2 shows the XRD patterns for the 3A-mont-1× and 3A-mont-3× as well as for the nanocomposites containing 10 wt % of the corresponding clays. Although 3A-mont-1× and 3A-mont-3× have essentially the same d_{001}, they perform very differently in nanocomposite formation. 3A-mont-1× is an intercalated nanocomposite with a more-or-less regular clay basal spacing (~16.6 Å) equivalent to a gallery height only ~3.5 Å larger than the pristine onium ion clay. In contrast, the composite containing 3A-mont-3× is an exfoliated clay nanocomposite, with most of the layers separated by an average spacing of ~60 Å. Analogous differences in nanocomposite formation were obtained for 4A- and 8A-mont prepared by one and three onium ion-exchange reactions. This demonstrates that different exchange reaction conditions provide clays that perform differently for nanocomposite formation.

Scheme 1



To elucidate the physical differences between products 3A-mont-1× and -3×, we carried out TGA and elemental analyses. The analogous 8A-mont-1× and -3× reaction products were included for comparison purposes. As shown by the results in Table 1, the products prepared by one and three ion-exchange reactions differ significantly in onium ion and Na^+ content. For 3A-mont-1×, the 317 ppm Na^+ content accounts for less than 2% of the total cation exchange capacity. Yet, this relatively low level of gallery Na^+ ions is sufficient to limit polymer intercalation to simple monolayer formation of polymer between the gallery onium ions. Although 3A-mont-3× exhibits the same basal spacing as 3A-mont-1×, the former organo clay contains no detectable Na^+ and readily forms an exfoliated nanocomposite. Qualitatively analogous differences are found for 8A-mont-1× and 8A-mont-3×.

The types of the epoxy composites formed from nA-mont-1× and -3× clays with $n = 3-8$ are of three types, namely, conventional composites in which the clay remains phase segregated with no polymer intercalated between the layers ($d_{001} = 13.1$ Å), intercalated nanocomposites wherein the clay is intercalated by a polymer monolayer ($d_{001} \sim 16.6$ Å), and exfoliated nanocomposites wherein the layers are completely separated by several nanometers of polymer. Table 2 summarizes the types of composites formed under hot molding and conventional curing conditions. The nearly fully onium ion-exchanged *n*A-mont-3× clays facilitate nanocomposite formation, whereas the incompletely exchanged *n*A-mont-1× derivatives containing as little as 2 mol % Na^+ on the exchange sites impede exfoliated nanocomposite formation. As illustrated in Scheme 1, we propose that the Na^+ centers in alkylammonium-exchanged clays with chain lengths $n < 8$ act as pinning points preventing gallery expansion by the polymer precursors. This pinning behavior by Na^+ seems to operate only when the onium ions co-occupying the gallery surfaces adopt a lateral monolayer orientation, as shown in Scheme 1. As the alkyl chain length is increased ($n > 8$), the onium ions abandon the lateral monolayer orientation and begin to adopt lateral bilayer and paraffin-like gallery structures. Under these latter conditions the presence of small concentrations of Na^+

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Table 1. Exchange Ion Content of Organoclays Obtained from TGA and Carbon Analysis

	TGA^a		carbon analysis			calcd^d
organoclays	H_2O (wt %)	onium (wt %)	Na^+ (ppm)	carbon (wt %)	onium (wt %)	onium (wt %)
3A-mont-1×	6.9	5.0	317	3.27	5.45	5.52
3A-mont-3×	5.8	5.9	0	3.83	6.3	5.52
8A-mont-1×	1.0	11.5	75	8.84	11.97	11.6
8A-mont-3×	0.9	12.7	33	10.11	13.67	11.6

[a] H_2O content was determined from room temperature to 120 °C and the onium content was determined from 200 to 400 °C. [b] Calculation based on CEC value of 92 mequiv/100 g.

Table 2. Conventional (C), Intercalated (I), and Exfoliated (E) Nanocomposites Formed from *n*A-Mont-1× and -3× Oniun Ion Clays Prepared by Different Exchange Reaction Conditions^a

$CH_3(CH_2)_n$-$1NH_3^+$ exchange cation	room temp molding and sequential curing at 75 °C, 3 h and 125 °C, 3 h		125 °C molding and curing at 125 °C, 6 h	
n	1×	3×	1×	3×
3	C	I	I	E
4	C	E	I	E
6	C + E	E	E	E
8	I + E	E	E	E

[a] Conventional composites exhibit no polymer intercalation, d_{001} ~ 13.1 Å. Intercalated nanocomposites have d_{001} = 16−18 Å. Exfoliated nanocomposites have $d_{001} \geq 60$ Å.

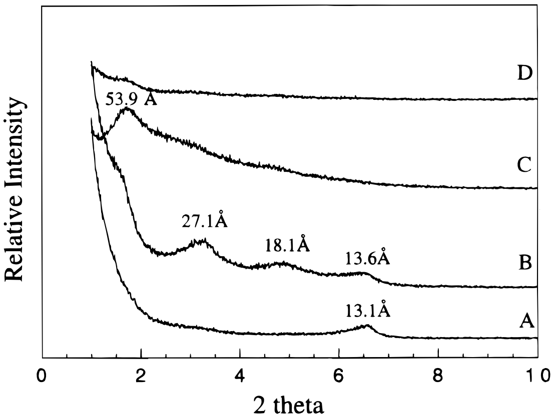

Figure 3. X-ray diffraction patterns of 3A-mont-3× clay in stoichiometric mixtures of Epon-828 resin and polyetheramine D2000 after reaction under the following conditions: (A) 25 °C, mixing; (B) 75 °C, 10 min; (C) 75 °C, 3 h and 125 °C, 1 h; (D) 75 °C, 3 h and 125 °C, 3 h. The clay loading was 10 wt %.

ions in the galleries has little effect on the gallery polarity, pinning behavior is lost, and the polymer precursors readily penetrate the gallery region of the clay.

Our earlier studies of the mechanism of organoclay exfoliation[11] showed that for long-chain onium ion clays ($n > 8$), the amount of polymer precursor that can be loaded into the gallery region of an onium ion clay depends in part on solvation interactions with the gallery onium ions in a vertical bilayer orientation. Preloading of the galleries prior to matrix polymerization plays an important role in determining whether intercalated or exfoliated composites will be formed. Gallery preloading also is important in forming exfoliated nanocomposites from short-chain onium ion clays interlayered with $n < 8$. Figure 3 displays the changes in the XRD patterns for a 4A-mont-3x clay in the process of forming an exfoliated nanocomposite. The clay basal spacing is greatly increased from 13.1 to ~54 Å after solvation by the reaction mixture at 75 °C for only 10 min. FTIR spectra of the reaction mixture heated at 75 °C for up to 3 h contained a 916 cm^{-1} band characteristic of the epoxy ring stretching frequency, indicating the presence of uncured resin. Additional heating caused complete gallery polymerization and nanolayer exfoliation, resulting in a nearly amorphous XRD pattern.

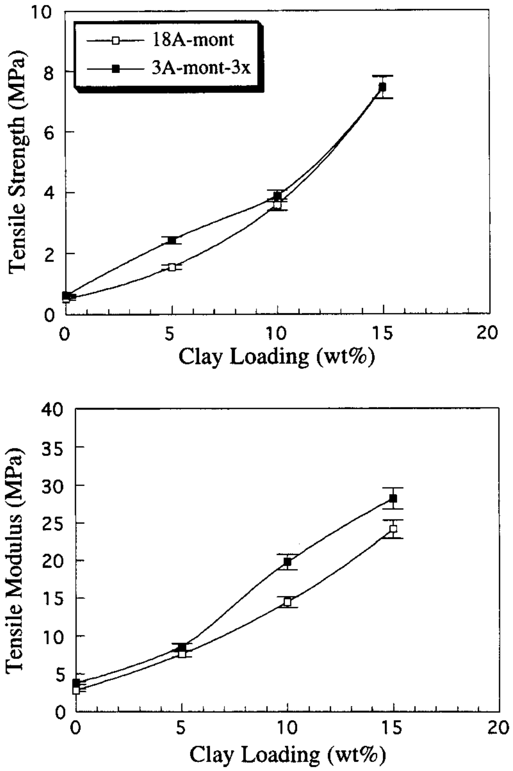

Figure 4. Comparison of the of tensile strengths and moduli for epoxy−clay nanocomposites formed from 3A-mont-3× and 18A-mont-1× clays.

The tensile properties of nanocomposites formed from short chain (3A-mont-3×) and long-chain (18A-mont-1×) onium ion clays were measured to determine the effect of interfacial properties on reinforcement. Figure 4 compares the tensile strengths and moduli as a function of clay loading. XRD and IR results indicated that in both systems the clay nanolayers are fully exfoliated and the matrix is fully cured. It is noteworthy that the two nanocomposite systems behave similarly with the tensile strength and modulus increasing with clay loading. Also, the composites formed from 3A-mont-3x have slightly higher strength and stiffness than the 18A-mont-1× composites. These results strongly suggest that among the three types of interfacial interactions defined in Figure 1, type A binding interactions of the polymer to the siloxane basal surfaces are the most important. However, due to the relative high water content of the 3A-mont samples, the mechanical benefit provided by these compositions may be limited. Substantial contributions from type B van der Waals interactions between the polymer and the alkyl chains of the onium ions are precluded, because the tensile properties do not improve with increasing chain length. Future studies will be needed to evaluate the role of type C edge interactions.

In summary, the results of this work suggest that exfoliated forms of smectite clays would be good reinforcement agents for epoxy matrixes even in the absence of onium-exchange cations on the gallery surfaces. However, inorganic exchange forms of smectite clays are not able to form epoxide nanocomposites for both thermodynamic and kinetic reasons. Onium ions are needed to modify the surface polarity, thereby allowing thermodynamically favorable preloading of the galleries with polymer precursors. Also, as demonstrated in our earlier work,[11] the acidity of the onium ions is needed in order to catalyzing the intragallery polymerization. Comparable intra- and extragallery polymerization rates are essential for achieving uniform clay nanolayer exfoliation in a monolithic polymer matrix. If the intragallery polymerization is too slow, only intercalated nanocomposites will be formed with tensile properties that are inferior to exfoliated nanocomposites.

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