Chem. Mater. **1998,** *10,* 3769−3771

Nanolayer Reinforcement of Elastomeric Polyurethane

Zhen Wang and Thomas J. Pinnavaia*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

Received June 23, 1998
Revised Manuscript Received September 25, 1998

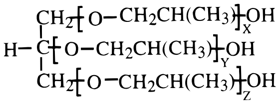
Layered materials are potentially well-suited for the design of hybrid composites, because their lamellar elements have high in-plane strength, stiffness, and a high aspect ratio.[1] Virtually all families of lamellar solids share these attributes, but the smectite clays (e.g., montmorillonite) and related layered silicates are the materials of choice for polymer nanocomposite design for two principal reasons. First, they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale. Second, they occur ubiquitously in nature and can be obtained in mineralogically pure form at low cost.

The unparalleled ability of smectite clays to boost the mechanical properties of an engineered plastic was first demonstrated in a stunning example by Toyota researchers.[2−4] By replacing the hydrophilic Na^+ and Ca^{2+} exchange cations of the native clay with a more hydrophobic onium ion, they were able to polymerize ϵ-caprolactam in the interlayer gallery region of the clay to form a nylon−clay hybrid. At a loading of only 4.2 wt % clay the modulus doubled, the strength increased more than 50%, and the heat distortion temperature increased 80 °C compared to the pristine polymer.

Considerable effort has been invested in extending the nanolayer reinforcement concept to polymer systems other than nylon-6.[5−12] Thermoset epoxy systems, in particular, have been studied in considerable detail.[8,9,13,14] In fact, the intercalation chemistry of epoxy−clay nanocomposites has been developed to the point where we can expect to apply this knowledge to other thermoset polymer systems and derive maximum benefit from nanolayer dispersal and reinforcement. In the present work, we report the first examples of elastomeric polyurethane−clay nanocomposites with greatly improved performance properties compared to the pristine polymer.

To disperse montmorillonite nanolayers in a polyurethane matrix, it was necessary to first replace the hydrophilic inorganic exchange cations of the native mineral with the more organophillic alkylammonium ions $C_{12}H_{25}NH_3^+$ and $C_{18}H_{37}NH_3^+$, henceforth abbreviated C12A and C18A, respectively. The ion exchange reaction was accomplished using previously described methods[13] and purified SWy-2 (Wyoming) montmorillonite with a unit cell formula of $Na_{0.86}[Mg_{0.86}Al_{3.14}](Si_{8.00})O_{20}(OH)_4$. The clay was purchased from the University of Missouri−Columbia, Source Clay Mineral Repository, Columbia, MO. In addition, commercially available alkylammonium-exchanged montmorillonites from Nanocor, Inc. (Arlington, IL) were used to form polyurethane nanocomposites. These latter clays, designated C12A-CWC and C18A-CWC, have unit cell formulas of $Z^+_{1.08}[Mg_{0.54}Al_{3.38}](Si_{7.64}\ Al_{0.36})O_{20}(OH)_4$, where Z^+ is the exchange cation.

Conventional polyurethane composites are usually formulated by premixing the inorganic component with the alcohol precursor and then curing the mixture with the diisocyanate.[15] Our approach to forming polyurethane nanocomposites, therefore, focused on the solvation of the organoclay by polyols. Interestingly, we found that montmorillonites exchanged with long chain onium ions (carbon number ⩾ 12) are easily solvated by several polyols that are commonly used in polyurethane chemistry as chain extenders or cross-linkers. These included ethylene glycol, poly(ethylene glycol), poly(propylene glycol), and three Voranol glycerol propoxylates (Dow Chemical Co.) with the general formula:



$$\begin{array}{l} \quad\ \ CH_2\!\left[O-CH_2CH(CH_3)\right]_X OH \\ \quad\ \ | \\ H-C\left[O-CH_2CH(CH_3)\right]_Y OH \\ \quad\ \ | \\ \quad\ \ CH_2\!\left[O-CH_2CH(CH_3)\right]_Z OH \end{array}$$

Figure 1 illustrates the XRD patterns for the solvated phases of C18A-CWC montmorillonite at 50 °C. This solvation reaction occurs at room temperature, but solvation is facilitated at an elevated temperature. The mixture of organoclay and polyol is easily pourable when the loading of organoclay is below 20 wt %. Varying the molecular weight ranges from 62 to 2000 for the diols and from 700 to 3000 for the triols has little effect on the solvated clay galleries. Instead, the gallery height is determined primarily by the chain length of the onium ion. Table 1 compares the basal spacings of C12A-CWC and C18A-CWC montmorillonite solvation. All of the observed basal spacings agree well with the calculated basal spacing (d_{calc}) for clay layers (9.6 Å) separated by gallery onium ions oriented with the alkyl chains perpendicular to the clay basal surface, but there is no direct evidence for an all-trans vertical orientation. Initially, the onium ion chains in the unsolvated gal-

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10.1021/cm980448n CCC: $15.00

Table 1. Basal Spacings (Å) of Alkylammonium-Exchanged Montmorillonite Solvated by Polyols

					glycerol propoxylates (Voranol)			
organoclay[a]	air-dried	glycol (62)[b]	PEG300 (300)[b]	PPG2000 (2000)[b]	V230-238 (700)[b]	V230-112 (1500)[b]	V230-056 (3000)[b]	d_{calc}[c]
C12A-CWC	22.2	33.9	32.0	33.1	32.3	32.9	32.9	31.0
C18A-CWC	23.0	36.7	36.6	37.8	37.4	37.1	38.0	38.7

[a] C12A and C18A denote $C_{12}H_{25}NH_3^+$ and $C_{18}H_{37}NH_3^+$ exchange cations, respectively, and CWC is an industrially purified montmorillonite supplied by Nanocor, Inc. [b] Molecular weight of the polyol. [c] Calculated basal spacing for a vertical orientation of the gallery onium ions.

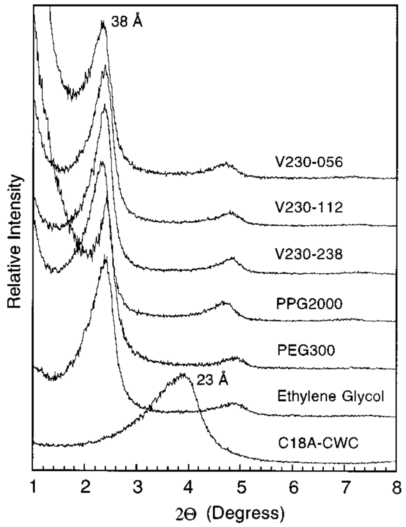

Figure 1. X-ray diffraction patterns (Cu Kα) for C18A-CWC montmorillonite in an air-dried state (bottom) and solvated by various polyols at 50 °C. The molecular weight for each polyol is given in Table 1. Samples were prepared as thin films on glass slides. The patterns were recorded on a Rigaku Rotaflex 200B diffractometer.

leries are oriented parallel to the layers, as judged by the basal spacings of 22.2 and 23.0 Å, but the onium ions reorient from this position to optimize solvation by the polyol. Also, similar basal spacings were observed for C18A-SWy montmorillonite with a lower layer charge density than C18A-CWC montmorillonite. We conclude, therefore, that the extent of gallery expansion is mainly determined by the chain length of the gallery onium ions and is independent of the functionality or molecular weight of the polyols and the charge density of the clay.

Representative polyurethane nanocomposites were formed by adding a Rubinate methylene diphenyl diisocyanate prepolymer with MW 1050 and a functionality of 2.0, designated R9272, to a mixture of organoclay and V230-238. Gallery expansion as a function of time was investigated by XRD. The organoclay was preintercalated with glycerol propoxylate V230-238 by stirring with a magnetic stirrer at 50 °C for 12 h in a sealed container. The polyol was degassed under vacuum at 100 °C for 6 h before use. Methylene diphenyl diisocyanate prepolymer (R9272) was added and stirred at 70 °C for an additional 15 min before degassing at 95 °C in a vacuum oven. The mixtures remained pourable at concentrations of organoclay up to 10 wt %. The bubble-free mixture was poured into a stainless steel mold for curing at 95 °C for 10 h under an N_2 atmosphere. The alkylammonium exchange ions of the organoclay were considered to be active reagents for coupling to isocyanate and were counted as contributors to the stoichiometry for polymerization by reducing the amount of V230-238 in proportion to the cation exchange capacity of the clay. No catalyst was used for composite formation.

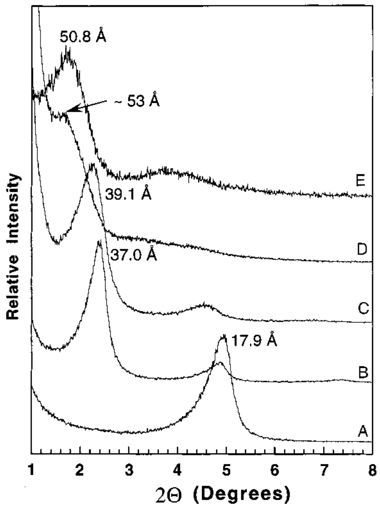

Figure 2. X-ray diffraction patterns of C18A-SWy montmorillonite: (A) unsolvated clay and (B) solvated by polyol V230-238. The remaining curves are for mixtures of organoclay (10 wt %), polyol, and Rubinate diisocyanate R9272 after curing at (C) 95 °C for 10 min, (D) 95 °C for 25 min, and (E) 95 °C for 10 h. Sample A was a packed powder, samples B–D were films smeared on glass slides, and sample E was a self-supported block of cured nanocomposite.

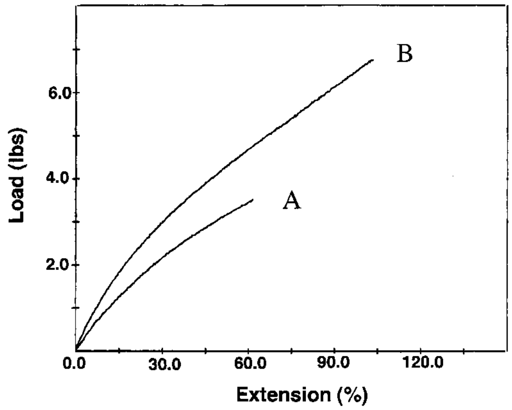

Figure 3. Stress–strain curves for (A) a pristine polyurethane elastomer and (B) a polyurethane–clay nanocomposite prepared from C18A-SWy montmorillonite (5 wt %). The load cell had a capacity of 20 lbs and the strain rate was 1.0 in./min.

As shown in Figure 2C for C18A-SWy, the expansion of the organoclay increased with increasing curing time at 95 °C. Gallery expansion beyond the initial value for polyol solvation was evidenced by the appearance of a broad diffraction peak at low angle (Figure 2D), signifying that intragallery polymerization contributes to the dispersal of the nanolayers. At equilibrium, the basal spacing (Figure 2E) is less than the spacing

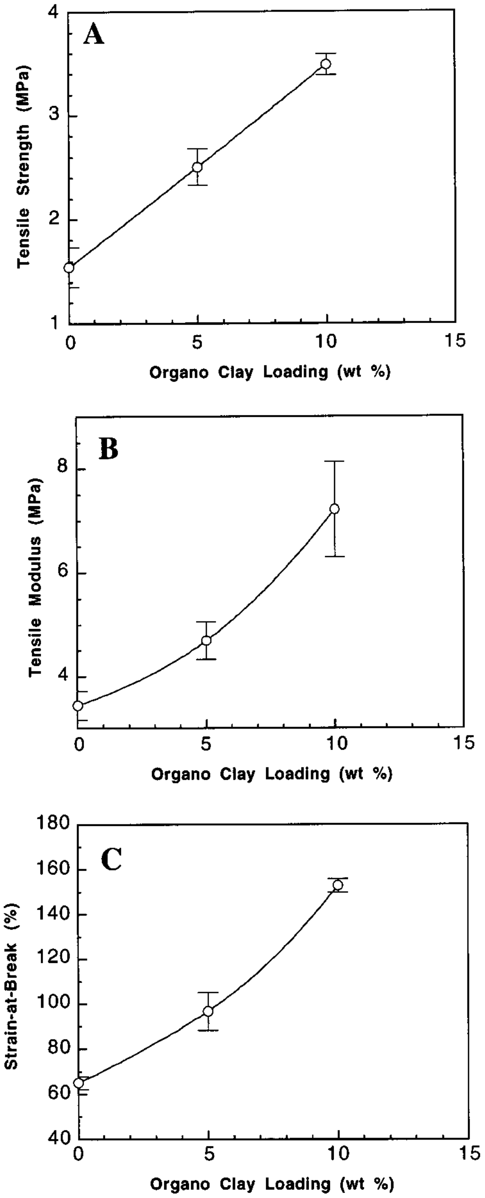

Figure 4. Tensile properties vs organoclay loadings for polyurethane–clay nanocomposites prepared from C18A-SWy montmorillonite, polyol V230-238, and diisocyanate R9272: (A) tensile strength, (B) tensile modulus, and (C) strain-at-break. All samples were cured at 95 °C for 10 h.

expected for a lipidlike bilayer orientation of onium ions, indicating that a layered silicate intercalate is formed in the final cured nanocomposite. C18A-CWC exhibited equivalent behavior in forming an intercalated nanocomposite. The presence of Bragg reflections indicates that the nanolayers are largely stacked in crystallographical order in the polymer matrix, but the distance between the nanolayers and the dispersion of the intercalated tactoids within the polymer matrix are in the range where matrix reinforcement may be expected.

Inorganic fillers are commonly used in polyurethane chemistry to reduce formulation cost and to increase stiffness. But the improvements in modulus for conventional polyurethane composites are compromised by a sacrifice of elastomeric properties.[15,17] The nanocompsoites reported here exhibit an improvement in elasticity, as well as in modulus. Typical stress–strain curves for the pristine polyurethane elastomer and the nanocomposite prepared from C18A-SWy are shown in Figure 3. Curves of tensile strength, tensile modulus, and strain-at-break vs organoclay loading are plotted in Figure 4. Clearly, the clay nanolayers, even when aggregated in the form of intercalated tactoids, strengthen, stiffen, and toughen the matrix. At a loading of only 10 wt % organoclay the strength, modulus, and strain-at-break all are increased by more than 100%. These tensile properties all increase with increasing loading of silicate nanolayers. It is very unusual to improve modulus while at the same time significantly improving the strength and toughness. The enhancement in strength and modulus is directly attributable to the reinforcement provided by the dispersed silicate nanolayers. The improved elasticity may be attributed in part to the plasticizing effect of gallery onium ions, which contribute to dangling chain formation in the matrix, as well as to conformational effects on the polymer at the clay–matrix interface. Analogous nanocomposites prepared from C18A-CWC montmorillonite showed performance properties very similar to those formed from C18A-SWy. Consequently, the benefits of nanolayer reinforcement are not highly dependent on the magnitude of the clay layer charge.

Another significant property of our polyurethane–clay nanocomposites is their high optical transparency. As observed previously for the related epoxy–clay nanocomposites and other systems, we expect the dispersal of silicate nanolayers to substantially reduce the permeability of the polymer[5–7] and to improve solvent resistance.[10] The transparent properties of the composites, together with the anticipated barrier film properties of these materials, should make them especially attractive for high-performance packaging materials, protective films, and high-barrier sealants.

Acknowledgment. The partial support of this research by the Michigan State University Center for Fundamental Materials Research and Nanocor, Inc. is gratefully acknowledged.

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