Nanostructure and Properties of Polysiloxane-Layered Silicate Nanocomposites

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ABSTRACT: The relationship between nanostructure and properties in polysiloxane layered silicate nanocomposites is presented. Solvent uptake (swelling) in dispersed nanocomposites was dramatically decreased as compared to conventional composites, though intercalated nanocomposites and immiscible hybrids exhibited more conventional behavior. The swelling behavior is correlated to the amount of bound polymer (bound rubber) in the nanocomposites. Thermal analysis of the bound polymer chains showed an increase and broadening of the glass-transition temperature and loss of the crystallization transition. Both modulus and solvent uptake could be related to the amount of bound polymer formed in the system. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 1595–1604, 2000

Keywords: nanocomposites; elastomers; swelling; bound polymer

INTRODUCTION

Recent interest in composites with nanoscale or molecular dimensions has grown as researchers strive to extend the utility of these materials.1–8 Polymer matrix nanocomposites in particular have been studied extensively as workers discover improvements in physical properties both through optimizing molecular interactions between reinforcer and matrix and through reduction in size of the reinforcing agent. For example, poly(vinyl acetate) nanocomposites reinforced with in situ sol-gel derived silica demonstrate remarkably higher tensile properties above the glass-transition temperature ($T_g$) when compared to samples reinforced with conventional fumed silica.4 The enhancements were attributed to extensive hydrogen bonding between the polymer and the in situ derived silica samples, which was not observed in samples reinforced with fumed silica. Mark and coworkers have also noted significant enhancements in ultimate strength and rupture energy in poly(dimethyl siloxane) (PDMS) reinforced with nanosize, in situ sol-gel derived silica when compared to PDMS composites filled with fumed silica.1–3

Of particular interest are layer inorganic materials which can act as nanofillers. Conducting polymers have been combined with layered inorganics to form anisotropically conducting nanocomposites as potential battery materials.9–12 Polymer layered silicate nanocomposites also exhibit dramatic property enhancements in permeability, modulus, thermal stability, and flame retardancy.13–18 These enhancements have been attributed to the large aspect ratios provided by layered materials with thicknesses on the order of a nanometer and widths and lengths on the order of 100–1000 nm.

Elastomeric nanocomposites represent an interesting subgroup.17–22 There is a rich history of elastomers filled with traditional fillers such as carbon black, fumed silica, or minerals.23 The polymer/reinforcer interface has been found to play an overwhelmingly crucial role in determin-
ing reinforcement levels and concomitant property enhancements. The level of reinforcement depends on the interaction between the inorganic and polymer and the surface area available for interaction, and is typically reflected in properties such as modulus, swelling, abrasion resistance, and strength. Models have been developed to predict interfacial strength from swelling behavior.

In previous work, poly(dimethylsiloxane) (PDMS) nanocomposites reinforced with organically modified layered silicates were synthesized and their thermal stability investigated. In this paper, we present the mechanical properties and solvent uptake of these novel materials and discuss them in terms of their nanostructure.

**EXPERIMENTAL**

**Nanocomposite Synthesis**

α,ω-silanol terminated PDMS ($M_w = 19,000$, $M_w/M_n = 1.5$ from United Chemical Technologies) was used as received, and was combined neat with the proper amount of dimethylditallow-exchanged montmorillonite (Southern Clay Products) by sonicating the mixture for 2 min with an ultrasound probe (Sonics and Materials Vibra-Cell). The dimethylditallow montmorillonite is a commercial product, which was synthesized by ion-exchanging Na⁺-montmorillonite with a cation exchange capacity of 0.9 meq/g with dimethyl ditallow ammonium bromide containing 70, 25, 4, and 1 mol% of C₁₈, C₁₆, C₁₄, and C₁₂ carbon chains, respectively. The concentration of the organosilicate in the nanocomposites ranged from 0.5–10 wt%.

Table I lists the relative amounts of reactants per gram of nanocomposite. Volumes were carefully measured using a Fisher Microtip Pipette. When larger samples were required, the amounts were multiplied appropriately. In some preparations 1–10 µL of deionized water or absolute ethanol per gram of silicate were also added to aid dispersion. Tetraethylorthosilicate (TEOS, Aldrich) was used as a crosslinking additive, and tin (II) ethylhexanoate (Gelest) served as a catalyst. For every gram of polymer, 30 µL of TEOS and 5 µL of tin ethylhexanoate were used. Samples were crosslinked at room temperature under vacuum to remove both gases generated during crosslinking and air pockets introduced into the mixture during sonication. Products were allowed to cure for a minimum of 12 h. A copolymer of poly(dimethylsiloxane) with poly(diphenylsiloxane) ($M_w = 25,000$, $M_w/M_n = 1.5$, PDPS–14–18 mol%, United Chemicals) was used as an alternate polymer matrix. Sodium montmorillonite (CEC = 0.9 meq/g, Southern Clay Products) was substituted for the organically modified montmorillonite in some mixtures with PDMS.

**Characterization**

X-ray diffraction patterns were obtained on a Scintag X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å).

Thermal transitions were probed using a Seiko 5200 differential scanning calorimeter (DSC) cooled with liquid nitrogen in an atmosphere of flowing nitrogen. Samples were scanned at a rate of 10 °C/min in a nitrogen atmosphere over a temperature range of −150 °C to room temperature. Samples were initially cooled to −90 °C at a rate of 10 °C/min and left to equilibrate for 5 min to allow for crystallization. After cooling to −150 °C, the samples were allowed an additional 5 min for equilibration. A PerkinElmer System 7e dynamic mechanical analyzer (DMA) equipped with a liquid nitrogen dewar in a helium atmosphere was used to characterize mechanical behavior. The modulus of crosslinked samples was mea-

<table>
<thead>
<tr>
<th>Mass Polymer (g)</th>
<th>Mass Silicate (g)</th>
<th>Weight % Silicate</th>
<th>Volume Fraction Silicate (φ)</th>
<th>Water (µL)</th>
<th>TEOS (µL)</th>
<th>Tin(II) Ethylhexanoate (µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>0.005</td>
<td>0.5</td>
<td>0.0019</td>
<td>1</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>0.995</td>
<td>0.01</td>
<td>1</td>
<td>0.0037</td>
<td>1</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>0.97</td>
<td>0.03</td>
<td>3</td>
<td>0.011</td>
<td>3</td>
<td>29</td>
<td>5</td>
</tr>
<tr>
<td>0.95</td>
<td>0.05</td>
<td>5</td>
<td>0.022</td>
<td>5</td>
<td>28</td>
<td>5</td>
</tr>
<tr>
<td>0.93</td>
<td>0.07</td>
<td>7</td>
<td>0.028</td>
<td>7</td>
<td>28</td>
<td>5</td>
</tr>
<tr>
<td>0.9</td>
<td>0.10</td>
<td>10</td>
<td>0.040</td>
<td>10</td>
<td>27</td>
<td>5</td>
</tr>
</tbody>
</table>
measured as a function of temperature while increasing the temperature at a rate of 15 °C/min. The instrument was operated in the tensile mode at a constant frequency of 1 Hz and at a strain of 0.7%.

Solvent uptake was measured on crosslinked samples using previously published techniques.26 A sample was weighed and then immersed in toluene. After three days, the swollen sample was rapidly blotted and reweighed, minimizing evaporation of the toluene. The sample was reimmersed in toluene. Reweighing continued for successive days and the final weight of the swollen sample was recorded when three weighings agreed with each other, indicating the establishment of an equilibrium.

The amount of bound polymer was determined thermogravimetrically using established procedures.27 Uncrosslinked samples were put in an excess of toluene, a good solvent for PDMS (10–20 × the sample weight), and stirred rapidly at temperatures between 30 and 40 °C to remove the unbound PDMS chains. The toluene was exchanged daily for 5 days. The remaining gel was put in a vacuum oven at 100 °C overnight to remove excess toluene. TGA analysis of the gel was performed from room temperature to 800 °C in a nitrogen atmosphere, degrading the polymer chains and alkyl ammonium chains but leaving the silicate layers intact. A PerkinElmer TGA 7 was used for the thermogravimetric analysis. The amount of bound polymer was calculated from the TGA data after correcting for the mass of the alkyl ammonium cations in the organosilicate.

RESULTS AND DISCUSSION

Synthesis and Structure Determination

Siloxane nanocomposites are prepared by suspending the organosilicate in a free-flowing siloxane at room temperature and sonicating. Previously, we showed that the nanostructure of PDMS-silicate hybrids is determined by the type of organic cation in the silicate.17 The degree of silicate dispersion is usually obtained using X-ray diffraction (XRD) measurements. Intense reflections in the range 2θ = 3–9° indicate a well-ordered intercalated hybrid with alternating polymer–silicate layers. In contrast, dispersed or exfoliated hybrids exhibit no distinct features in this 2θ range due to the lack of layer registry. Organically modified silicates containing dimethylditallow cations lead to dispersed or exfoliated nanocomposites, as suggested by the lack of distinct reflections in the XRD pattern shown in Figure 1. The original (001) peak of the layered silicate before mixing with PDMS is shown for comparison with a d-spacing of 25Å. The lack of layer registry and order evidenced by the lack of X-ray diffraction pattern in the hybrid is suggestive of layer delamination and the formation of dispersed nanocomposites. Hybrids prepared from a PDMS-poly(diphenyl siloxane) random copolymer containing 14–18 mol % diphenylsiloxane and a dimethylditallow-exchanged layered silicate show a distinct (001) peak at 39Å, suggesting that the copolymer chains have intercalated into the layers increasing the d-spacing but have not caused layer delamination as in the PDMS case. (Hybrids that maintain the layer registry of the silicate particles are termed intercalated.) In contrast, no intercalation or dispersion takes place when pristine (sodium-exchanged) montmorillonite is combined with either PDMS or the PDMS-PDPS copolymer leading to immiscible hybrids. Recent experimental and theoretical work has shown that the interactions between the polymer matrix and the silicate can be tailored to produce a range of microstructures, from immiscible to dispersed.28 This and the work cited above underscore the importance of tailoring the polymer–silicate interactions in order to optimize silicate delamination and dispersion.

Solvent Uptake and Determination of Bound Rubber

Equilibrium swelling data in toluene for different siloxane nanocomposites as a function of silicate loading are shown in Figure 2. $V_{ro}/V_{rf}$, where the subscripts o and f refer to the unfilled network and nanocomposite respectively, is the relative solvent uptake calculated using

$$V_r = \frac{\text{volume of unswollen polymer matrix}}{\text{volume of swollen polymer matrix}} = \left[1 + \left(\frac{m_s - m}{m}\right)\left(\frac{\rho_{PDMS}}{\rho_{Toluene}}\right)\right]^{-1}$$

$m_s$ and $m$ are the weight of the swollen and unswollen samples, respectively, and $\rho_{Toluene}$ and $\rho_{network}$ are the corresponding densities. As normal in elastomer literature, the swelling values are plotted as a function of $\phi(1 - \phi)$, where $\phi$ is the volume fraction of silicate in the hybrid to correct for the inability of the inorganic material
to swell. For the small volume fractions used in this study, this correction is minimal. The dispersed nanocomposites exhibit greatly reduced solvent uptake when compared to intercalated or immiscible hybrids. In the dispersed hybrids, the solvent uptake initially decreases dramatically, then begins to level off as silicate loadings approach 2%. Similar plateaus in solvent uptake have been previously noted in other nanocomposites.20,21 In contrast to the dispersed nanocomposites, the intercalated and immiscible systems decrease quasilinearly over the same loading range. This behavior mimics that of conventional elastomeric composites such as styrene (butadiene) rubber (SBR) filled with carbon black, where the solvent uptake expressed as $V_{ro}/V_{rf}$ is a linear function of $\phi/(1 - \phi)$ (Fig. 2). In that case the slope corresponds to the interfacial strength.25

In conventional elastomeric composites the reduction in solvent uptake with increasing filler content has been correlated to the formation of bound rubber, viz., polymer chains at the interface, which are affected by the filler. The formation of bound rubber has been attributed to either physisorption, or in extreme cases, chemisorption of the polymer on the filler surface.25

Table II quantifies the bound rubber formed in the uncrosslinked dispersed hybrid with varying silicate loading, from TGA analysis of the gel (bound polymer and silicate) remaining after extraction of an uncrosslinked nanocomposite with toluene, a good solvent for PDMS. The initial dramatic increase with final plateau mirrors the swelling behavior for this system, suggesting an inverse relation between solvent uptake and bound rubber formation in the nanocomposite. Interestingly, beyond an initial plateau, the amount of bound rubber per silicate layer decreases with increased silicate content (Table II and Fig. 3). We suggest this decrease arises from possible overlap of bound polymer regions as the amount of silicate content increases.

Conventional composites with carbon black display roughly 30–40% bound rubber at filler concentrations of 20–30% (vol).24 In dispersed nanocomposites comparable amounts of bound polymer can be achieved at roughly one twentieth of the inorganic loading. We attribute the large amount of bound rubber to the large surface area

![Figure 1. X-ray diffraction patterns of intercalated and disordered or exfoliated nanocomposites. The layered silicate is a dimethyliditallow ammonium-exchanged montmorillonite shown also for comparison. The intercalated nanocomposite contains 10 wt % silicate and a copolymer of poly(dimethylsiloxane) with poly(diphenylsiloxane) [PDPS-14-18% (mol), remainder PDMS]. The disordered nanocomposites contains 10% (wt) silicate and poly(dimethylsiloxane).](image.png)
available in the layered silicate system (750 m$^2$/g for montmorillonite$^{29}$) as compared to that of conventional fillers, such as unaggregated carbon black (13–100 m$^2$/g$^{24}$). This large surface area of the silicates can only be exploited in the dispersed or exfoliated nanocomposites.

We note that the measurement of bound rubber has been performed on an uncrosslinked system. Since the swelling behavior practically mirrors the amount of bound polymer in the nanocomposite we suggest that the swelling behavior arises from the nanostructure rather than from increased crosslinks in the network. Other fillers, notably carbon black, have been shown to increase the activity of crosslinking additives in the network-forming system and result in increased crosslink density.$^{30}$ As enhanced moduli and decreased solvent uptake can also be due to increased crosslink density, it is important to differentiate between the two causes when attempting to understand the behavior of a system.

### Thermal Transitions

Differential scanning calorimetry (DSC) was used to probe the crystalline and glass transitions in the nanocomposites (Table III). Below room temperature, the pure siloxane exhibits a glass transition ($T_g = -125$ °C), a “cold” crystallization ($T_c = -84$ °C), and two melting transitions ($T_{m1} = -47$, $T_{m2} = -35$ °C), in good agreement with literature data for PDMS.$^{31}$ The dual melting

Table II. Bound Polymer in PDMS Disordered Nanocomposites

<table>
<thead>
<tr>
<th>Bound Rubber Fraction</th>
<th>Bound Rubber Fraction per Layer$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>(1 $\times$ 10$^6$ nm$^3$/layer)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.002</td>
<td>0.08</td>
</tr>
<tr>
<td>0.004</td>
<td>0.16</td>
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<td>0.01</td>
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<td>0.57</td>
</tr>
<tr>
<td>0.05</td>
<td>0.60</td>
</tr>
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</table>

$^a$Calculated using an estimated volume per silicate layer of 1.0 $\times$ 10$^{-21}$ m$^3$ and assuming a homogeneous composite.
transitions are thought to reflect differences in crystallite size or perfection due to defects from chain ends. The nanocomposites display slightly higher $T_g$ and broader transitions than the pure PDMS. PDMS filled with in situ generated SiO$_2$ and TiO$_2$ also show slight increases in glass-transition temperature as previously noted. In contrast, the crystallization process is affected more in the nanocomposites. The cold crystallization temperature remains fairly constant but the enthalpy of crystallization is dramatically decreased (Table III). In addition, the melting transitions remain virtually unchanged but the heat of fusion decreased. PDMS filled with fumed silica exhibit lower enthalpies and higher $T_m$, as measured using calorimetry. Crosslinked networks containing in situ generated PDMS exhibit no cold crystallization transition. It has been suggested that fillers accelerate the rate of crystallization due to either orientation of the adsorbed layer (bound polymer) or lower activation energy of nucleation due to the silica particles. Decreases in the enthalpy of fusion have been shown to only qualitatively relate to the

Table III. Thermal Transitions in PDMS Disordered Nanocomposites by DSC

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$T_g$ (°C)</th>
<th>$T_x$ (°C)</th>
<th>$\Delta H_v$ (mJ·mg$^{-1}$)</th>
<th>$T_{m1}$ (°C)</th>
<th>$\Delta H_{m1}$ (mJ·mg$^{-1}$)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_{m2}$ (mJ·mg$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>-124.7</td>
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<td>-2.5</td>
<td>-47.3</td>
<td>6.0</td>
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<td>11.7</td>
</tr>
<tr>
<td>0.011</td>
<td>-123.2</td>
<td>-84.4</td>
<td>-1.7</td>
<td>-47.4</td>
<td>5.5</td>
<td>-35.3</td>
<td>11.5</td>
</tr>
<tr>
<td>0.028</td>
<td>-123.0</td>
<td>-84.6</td>
<td>-1.8</td>
<td>-47.6</td>
<td>5.3</td>
<td>-35.6</td>
<td>11.6</td>
</tr>
<tr>
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<td>-84.5</td>
<td>-1.6</td>
<td>-47.7</td>
<td>5.2</td>
<td>-35.7</td>
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</tr>
<tr>
<td>0.011</td>
<td>-114.3</td>
<td>—</td>
<td>—</td>
<td>-48.1</td>
<td>2.9</td>
<td>-35.6</td>
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</tr>
<tr>
<td>0.028</td>
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<td>—</td>
<td>—</td>
<td>-48.2</td>
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<td>-48.3</td>
<td>3.2</td>
<td>-36.1</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 3. Bound rubber fraction (triangles) and volume of bound polymer per silicate layer (circles) in PDMS nanocomposites as a function of silicate loading.
amount of bound polymer, so a more detailed analysis is not presented here.\textsuperscript{35}

To further characterize the nature of the bound polymer calorimetry data were also obtained from hybrids were the noninteracting polymer (non-bound polymer) has been removed (Table III). These samples exhibit a very broad glass-transition temperature, at temperatures generally higher than the pure PDMS. In the sample with the highest concentration of silicate (0.04) the transition was too broad to measure. Additionally, no enthalpy of crystallization is observed for the cold crystallization transition and the melting temperatures are slightly lowered, with decreased enthalpies of fusion. The bound polymer formed in fumed silica/PDMS composites similarly exhibit neither a glass transition nor a crystallization temperature.\textsuperscript{36} With a maximum bound polymer fraction of 0.27, these fumed silica composites have enthalpies of fusion, which decrease by roughly one third as compared to pure PDMS. The decrease in enthalpy of fusion is larger for the layered silicate nanocomposite as compared to the fumed silica containing hybrids qualitatively reflecting the greater amounts of bound polymer formed with layered silicate reinforcement.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was used to measure viscoelastic properties as a function of temperature in both unfilled and PDMS nanocomposites (Table IV). The thermal transitions were calculated from plots of tan $\delta$. Figure 4 compares the unfilled PDMS network and a dispersed nanocomposite containing 4% silicate. The unreinforced sample displays two transitions, one at $-110 \, ^\circ\text{C}$, corresponding to the $\alpha$ or glass transition, and one at $-73 \, ^\circ\text{C}$, corresponding to the crystalline transitions. These temperatures corre-

![Figure 4](image)

**Figure 4.** DMA data for a crosslinked PDMS disordered nanocomposite containing 4% silicate (dashed line) and a reference PDMS sample (solid line).
late well with those previously observed in pure PDMS samples using DMA.\(^{37}\) In contrast, the nanocomposites exhibit a less well-defined transition at \(-107\) to \(-100\) °C. The crystalline transitions have also been extremely broadened, such that separating the \(\alpha\) transition from the crystalline transition is extremely difficult and no temperature assignments were attempted. Siloxane systems filled with fumed silica also exhibit extensively broad tan \(\delta\) peaks. Additionally, samples at loadings at or in excess of 20 wt % fumed silica exhibit a broad second thermal transition 40–50 °C above the glass transition, which extends for roughly 75 °C.\(^{38}\) This thermal transition has been attributed to the polymer closely interacting with the silica filler, what we have termed the bound polymer. The siloxane polymer used in the fumed silica study was a copolymer of PDMS with 7 mol % methylphenyl siloxane to inhibit crystallization of the PDMS and allow observation of the peak arising from the bound polymer. Other workers have studied pure PDMS filled with fumed silica (14–31 vol %) or sodium chloride (48 vol %), reporting that fumed silica filled samples exhibit broadened thermal transitions while the sodium chloride filler did not broaden or shift the transitions.\(^{37}\) The difference between the two systems was attributed to polymer-fumed silica interactions, which are absent in sodium chloride. We note that the level of reinforcement necessary to observe broadened transitions in either of the previous studies is well above that in layered silicate nanocomposites, a reflection of the high amounts of bound polymer formed at low concentrations of layered silicate.

Figure 4 shows the DMA pattern for PDMS and a dispersed PDMS nanocomposite containing 4% silicate. Samples were observed from 2150 °C to approximately 225 °C, to enable the analyzer parameters to be optimized for the three decade loss in modulus. As no thermal transitions are observed between room temperature and 100 °C, tan \(\delta\) data for this region is omitted for clarity. Below the glass transition, roughly a 40–50% increase in modulus is observed in the nanocomposite as compared to the unfilled polymer. From room temperature to 100 °C, storage moduli were temperature independent, as expected for crosslinked elastomers. The nanocomposites displayed moduli higher than the unreinforced PDMS, with the maximally reinforced system exhibiting a modulus roughly three times that of the polymer (Table IV).

Figure 5 compares the amount of bound polymer to the relative modulus as a function of silicate in the nanocomposites. Modulus increases seen in other filled polymer systems have been
attributed to entanglements, temporary restrictions, which prevent the easy movement of the polymer chains past one another, between the free and the bound polymer. For example, poly(ethylene) composites filled with silica do not exhibit any reinforcement, as measured using tear strength, until the bound polymer chains are long enough to allow for entanglements. Additionally, a mean-field-like tube model has been developed to describe polymer-filler junctions in carbon black filled poly(butadiene) and SBR where modulus increases are concluded to emanate from entanglements between the bound polymer and the free polymer. Thus, we suggest that the modulus enhancements observed herein also arise from interactions between the bound and the free polymer in the matrix.

CONCLUSIONS

The mechanical properties and swelling behavior of PDMS nanocomposites is discussed in terms of their nanostructure. Solvent uptake (swelling) in dispersed nanocomposites was dramatically decreased as compared to conventional composites, though intercalated nanocomposites and immiscible hybrids exhibited more conventional behavior. The swelling behavior is correlated to the amount of bound polymer (bound rubber) in the nanocomposites. Thermal analysis of the bound polymer chains showed an increase and broadening of the glass-transition temperature and loss of the crystallization transition. Both modulus and solvent uptake could be related to the amount of bound polymer formed in the system, indicative of the large influence of bound polymer in these nanocomposite systems as compared to more conventional composites.

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REFERENCES AND NOTES