Specific Interaction Governing the Melt Intercalation of Clay with Poly(styrene-co-acrylonitrile) Copolymers

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ABSTRACT: In the melt intercalation of cation-exchange clay, mixtures of montmorillonite and poly(styrene-co-acrylonitrile) (SAN) with various acrylonitrile contents were studied to examine the effect of specific interaction. When organic molecules with hydroxyl groups were used as intercalants for the clay, the amount of SAN penetrating the gallery of the layered structure of the clay and the corresponding increase in the gallery height occurred at a much higher rate because of the attractive specific interaction between acrylonitrile groups and polar groups on the clay surface. However, there was a limit to the increase in the gallery height, and the tendency for the gallery height to increase with the acrylonitrile group content disappeared when the acrylonitrile content was greater than 30 wt %, implying that excessive attractive interaction on the clay surfaces and polymer molecules glued the two adjacent silicate layers together; consequently, the increase in the gallery height could not be accomplished.

Keywords: clay; melt intercalation; poly(styrene-co-acrylonitrile); specific interaction; nanocomposite

INTRODUCTION

Some advantages to using layered silicates over conventional filler particles such as talc include their nanoscale morphology and their controllable chemical affinity. Nanoscale morphology is advantageous because nanoscale materials often exhibit physical and chemical properties that are dramatically different from those of their bulk counterparts.1–15

The synthesis of polymer–clay nanocomposite has been carried out with several methods. Typically, the intercalation of a suitable monomer promotes delamination and dispersion of the host layers. This is followed by polymerization of the monomer, which yields either linear or cross-linked polymer matrices. Often, however, the clay must be dispersed with a preliminary preswelling step of long-chain quaternary ammonium intercalation. In situ polymerizations of nylon11,12 and epoxy13–15 have resulted from these methods. Alternatively, the direct intercalation of a host silicate lattice with a melt polymer has been considered more recently and has received extensive interest because polymers can be inserted directly into the layered material without the aid of a solvent. Polymer melt intercalation offers an economically favorable and environmentally benign
alternative to traditional polymer intercalation approaches in solution. In any method, however, the complete exfoliation and homogeneous dispersions of silicate layers have been achieved in only a relatively small number of cases in the literature, including systems with a specific interaction, such as mixtures of Na–montmorillonite with nylon or epoxy. Furthermore, the factors that control the formation of such hybrids are not well understood yet because of the lack of a suitable tool capable of analyzing the internal structure on a nanometer scale. Therefore, determining what the dominant factors for clay intercalation are and what their mechanisms are is highly desirable.

In our study, for the purpose of establishing exfoliated polymer–clay nanohybrid systems with the melt intercalation method, experiments were conducted for mixtures of montmorillonite and styrenic polymers such as poly(styrene-co-acrylonitrile) (SAN), in which the factors governing the intercalation mechanism were scrutinized.

**MATERIALS**

Characteristics of the SANs and organoclay (which were organically modified montmorillonite) used in this study are listed in Tables I and II, respectively. For the removal of any impurity, polymers were dissolved in chloroform and precipitated with an excess amount of methanol. The crude precipitate, dried at 80 °C for 24 h, was ground onto a fine powder.

Organoclay, received from Southern Clays as very fine powders, were washed with deionized water several times to remove freely existing excess ionic intercalants and impurities; this was followed by centrifugation and vacuum drying at 100 °C for 24 h. The chemical structures of the organic intercalants in the organoclay used are as follows:

![Chemical structures of intercalants](image)

**EXPERIMENTAL**

Purified SAN copolymers and various organoclay were dry-mixed on a blender. When they were blended, the composition of mixing was determined to preserve the content of inorganic clay at 5 wt % in all cases. A powdery mixture in an appropriate amount was placed on a molder and heated under a pressure of 5 atm at 185 °C for various heating times. Afterward, the molder was quenched with liquid nitrogen to obtain a disk-shaped specimen 10 mm in diameter and 100 μm

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**Table I. Characteristics of the Polymers Used in This Study**

<table>
<thead>
<tr>
<th>Designation</th>
<th>AN Content (wt %)</th>
<th>T_g (°C)</th>
<th>M_w (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAN8</td>
<td>8.1</td>
<td>102</td>
<td>101,000</td>
</tr>
<tr>
<td>SAN24</td>
<td>24.2</td>
<td>109</td>
<td>140,000</td>
</tr>
<tr>
<td>SAN27</td>
<td>27.0</td>
<td>110</td>
<td>115,000</td>
</tr>
<tr>
<td>SAN33</td>
<td>32.5</td>
<td>110</td>
<td>120,000</td>
</tr>
<tr>
<td>SAN41</td>
<td>40.8</td>
<td>115</td>
<td>114,000</td>
</tr>
</tbody>
</table>

* Determined with CHN elemental analysis.
* Measured with DSC at a heating rate of 10°C/min.
* Weight-average molecular weight. Gel permeation chromatography data calibrated with a monodisperse polystyrene standard were provided by the supplier.

**Table II. Characteristics of the Organoclay**

<table>
<thead>
<tr>
<th>Designation</th>
<th>d_001 (Å)</th>
<th>Type of Intercalant</th>
<th>Intercalant Concentration (mequiv/100 g)</th>
<th>Weight Loss (%) on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>140A</td>
<td>35.3</td>
<td>A</td>
<td>140</td>
<td>47</td>
</tr>
<tr>
<td>125A</td>
<td>33.2</td>
<td>A</td>
<td>125</td>
<td>43</td>
</tr>
<tr>
<td>95A</td>
<td>24.7</td>
<td>A</td>
<td>95</td>
<td>38</td>
</tr>
<tr>
<td>125B</td>
<td>19.0</td>
<td>B</td>
<td>125</td>
<td>39</td>
</tr>
<tr>
<td>95C</td>
<td>18.6</td>
<td>C</td>
<td>95</td>
<td>32</td>
</tr>
</tbody>
</table>

* The number and character represent the CEC value of clay and the type of intercalant used to modify the clay, respectively. For example, 140A is an organoclay with a CEC at 140 mequiv/100 g containing the intercalant A.
* Calculated from the CEC value of each pristine clay and weight-loss data.
* Measured with thermogravimetric analysis.
thick for X-ray measurements and thermal analysis.

Thermal characterization was carried out with differential scanning calorimetry (DSC; Perkin-Elmer DSC7). Data were collected on a second run for unblended organoclays from −50 to 100 °C and for compression-molded mixtures from −50 to 150 °C.

The change in the gallery height of the organoclays before and after melt mixing with SAN was examined with wide-angle X-ray spectroscopy (MacScience MXP18) in the reflection mode. The X-ray generator was run at 18 kW, and the target was a Cu standard (\( \lambda = 1.5405 \) Å). Scanning was performed for \( 2\theta = 0.5–10 \) at a rate of 1 min \(^{-1}\). For correction of the scattering angle, a pure silicone standard was used. The basal spacing of the layered silicates \( (d_{001}) \) was calculated with Bragg’s law, \( \lambda = 2d\sin(\theta) \), from the position of the (001) plane peak in the X-ray diffraction (XRD) spectrum.

RESULTS AND DISCUSSION

Because pristine clay is hydrophilic, it is hard to obtain a thermodynamically homogeneous mixture of clay with hydrophobic organic polymers on the molecular level. The typical method to increase the miscibility of clay with a polymer is to block hydrophilic functional groups on the surface or attach organic molecules of long hydrocarbon tails on the surface. In this study, commercial organoclays processed by the latter method were adopted for modifying the hydrophilic nature of the clay surface. Some of the commercial organoclays used may have excess intercalant, that is, intercalant molecules that are not cationically grafted on the surfaces, which can be deintercalated and can plasticize the polymer. Plasticization dramatically affects polymer diffusion and, correspondingly, the intercalation behavior of polymer–clay mixtures. Therefore, plasticization by excess intercalant should be avoided. For that purpose, extensive purification was applied for all the organoclay, and the glass-transition temperature \( (T_g) \) was monitored to detect any possibility of plasticization for all the melt-mixed SAN–organoclays. As shown in Figure 1, there was no difference in \( T_g \) of SAN between virgin SAN and melt-mixed SAN–organoclay, and so there was no plasticization caused by excess intercalant molecules.

It has been speculated that the degree of intercalation would be determined as a function of the cation-exchange capacity (CEC) of clay (which corresponds to the concentration of intercalants grafted on the clay surface) and the molecular structures of intercalant molecules, such as the conformation geometry of a hydrocarbon tail, the cross-sectional dimension, and the functional group of the intercalant molecule. The comparison between SAN 27/140A and SAN 27/95A in Figure 2 shows that there is a large difference in the behavior of \( d_{001} \) change in terms of CEC. The mixture of SAN 27 with 140A of higher CEC resulted in no change in \( d_{001} \), whereas the mixture of SAN 27 with 95A of lower CEC showed a rapid increase in \( d_{001} \) with an increase of anneal-
ing time, implying that the diffusion of SAN 27 occurred much more effectively as CEC became lower.

Furthermore, to determine the effect of the molecular structure of the intercalant on the intercalation, we varied the number of hydrocarbon chains on the intercalant molecules. As found in the comparison of 125A (with two 18-numbered hydrocarbon chains) and 125B (with one 18-numbered hydrocarbon chain) in Table II, larger \( d_{001} \) favors the use of intercalant molecules with many hydrocarbon chains. However, Figures 3 and 4 show that, although SAN 27/125A did not show any significant change in \( d_{001} \) when the annealing time was increased, \( d_{001} \) of SAN 27/125B increased up to a magnitude comparable to that of SAN 27/125A. All the final values of \( d_{001} \) were similar, regardless of the given conditions, as found in Figures 2 and 4, suggesting that there might be a limit that cannot be overcome by simple control of the hydrophobicity or molecular structure of the intercalant and that it is very much required to introduce an additional contribution for better intercalation.

To elucidate the effectiveness of hydroxyl groups as an additional contribution, we compare melt intercalations of 95C with hydroxyl groups and 95A without them. SAN 27/95A and SAN 27/95C mixtures containing 5 wt % inorganic component were annealed at 185 °C with the heating time varied from 0.5 to 24 h. XRD spectra from these samples are shown in Figure 5, along with diffraction spectra for pure 95A and 95C. The pure 95A and 95C show first-order peaks that correspond to lamellar repeat distances of 24.6 and 18.7 Å, respectively. In all samples containing SAN 27, annealing caused the pure organoclay peak intensities to diminish and a new set of peaks corresponding to the polymer–clay intercalated structure to appear. For the SAN 27/95A composite annealed for 0.5 h, a new peak appeared at \( 2\theta = 2.6^\circ \) and, as the heating time increased, shifted to \( 2\theta = 2.4^\circ \), corresponding to \( d_{001} = 33 \) Å. For SAN 27/95C composites, a new peak was found at \( 2\theta = 2.2^\circ \), which corresponds to \( d_{001} = 35 \) Å for the sample annealed 0.5 h, and there was no further shift of the new peak with the annealing time. These results tell us that, although 95C had a narrower gallery height than 95A, the diffusion of SAN 27 into the gallery of 95C proceeded more promptly than that of 95A, and the diffused amount of SAN 27 into the gallery was much larger for 95C than 95A as well. We believe that the increase in the gallery height was due to an increase in the spacing between

**Figure 3.** XRD spectra featuring the time-dependent change of the primary peak for (a) SAN 27/125A and (b) SAN 27/125B.

**Figure 4.** Change in the gallery height as a function of heating time for SAN 27/125B and SAN 27/125A.
silicate layers through the diffusion of polymer molecules, which depended on the presence of a specific interaction. 95C had a narrower gallery of silicates than 95A due to the attractive interaction among hydroxyl groups of 95C's intercalant and polar groups on the silicate surface. For SAN 27/95C, however, another attractive interaction, hydrogen bonding between hydroxyl groups of 95C's intercalant and acrylonitrile (AN) groups of SAN, facilitates the diffusion of polymer molecules into the silicate gallery, causing the higher rate and larger degree of intercalation.

On the basis of the results of Figure 6, it is expected that an increase in the population of hydrogen bonding between polymers and intercalants bound to the silicate gallery will lead to far more effective intercalation and, finally, exfoliation of layered silicates. In Figure 7, however, it was found that when 95C was mixed with various SANs and annealed for 5 h, the gallery height of the silicate layer decreased as the AN content of SAN increased.

For clay–polymer mixtures, it was recently reported that intercalation or exfoliation could be determined by free-energy considerations through the modeling of a mixture of long-chain molecules and thin disks. According to the modeling results, an exfoliated state can only occur for a positive Flory–Huggins interaction parameter between polymers and thin disks representing silicate layers, although the polymers and clay mixture will demix. In addition, an intercalated state is expected when an interaction parameter is negative from kinetic considerations. As the polymer diffuses through the energetically favorable gallery, it maximizes contact with the
two confining silicate layers. A diffused polymer molecule glues the two adjacent surfaces together as it moves through the gallery, resulting in a kinetically trapped state. Consequently, although attractive energy between the polymer and clay is required for polymer diffusion into the gallery of silicate layers, increasing the attraction would only lead to an intercalated state, rather than an exfoliated one.

On the basis of this theoretical consideration, the results of Figure 7 can be explained as follows. AN groups of SAN in the gallery are complexed through hydrogen bonding with the hydroxyl groups on the silicate layer surface. This prevents it from retaining its coil-like conformation and gaining entropy from the polymer chain in the intergallery so that the adhesion forces between two adjacent silicate layers is not reduced. In addition, the trapped state induced by the complex formation of diffused SAN molecules and silicate layers would act as a barrier for the additional diffusion of SAN molecules required to increase the gallery height more. Increasing AN content corresponds to a higher gluing force, resulting in a decrease in the gallery height, as shown in Figure 5.

CONCLUSION

In the melt intercalation of cation-exchange clay, mixtures of montmorillonite and SAN with various AN contents were studied to examine the effect of specific interactions. When organic molecules with hydroxyl groups were used as intercalants for clay, the amount of SAN penetrating the gallery of the layered structure of the clay and the corresponding increase in the gallery height occurred at a much higher rate because of the attractive specific interaction between AN groups and polar groups on the surface of the clay. However, the tendency for the gallery height to increase with the AN group content disappeared when the AN content was greater than 30 wt %. For this result, the following is proposed. AN groups of SAN in the gallery are complexed through hydrogen bonding with the hydroxyl groups on the clay surface. This prevents it from retaining its coil-like conformation and gaining entropy from the polymer chain in the intergallery so that the adhesion forces between two adjacent silicate layers is not reduced. Consequently, although attractive energy between the polymer and clay is required for polymer diffusion into the gallery of silicate layers, increasing the attraction would only lead to an intercalated state, rather than an exfoliated one.

REFERENCES AND NOTES