Maleated polystyrene improves the barrier properties of nanocomposites

Musa Kamal and Jorge Uribe-Calderon

Polystyrene nanocomposites incorporating phosphonium-modified montmorillonite and a variety of polar compatibilizers have useful mechanical properties.

Montmorillonite (MMT) clay nanocomposites incorporating polar polymers—e.g., polyamides, poly(vinyl acetate)—have been prepared successfully, as the polar groups enhance the affinity and adhesion between the clay and polymer. However, the preparation of nanocomposites using nonpolar polymers—e.g., polyolefins and polystyrene (PS), which represent the largest segment of the plastics industry—is more difficult. It has been suggested that the incorporation of polar groups into nonpolar polymers, by blending or reaction, could enhance polymer/clay compatibility as well as yield better dispersion and polymer intercalation into the clay.\(^1,2\)

Thus, we prepared PS/clay nanocomposites with a variety of compatibilizers (PS resins with various polar functional groups) and determined their properties. Melt preparation of PS/clay nanocomposites requires high processing temperatures that may cause degradation of the ammonium surfactants conventionally used to modify the clay. We have shown that some phosphonium surfactants provide improved thermal stability in clays and nanocomposites.\(^3,4\)

Initially, we used thermogravimetric analysis and surface energy measurements to compare the thermal stability and surface characteristics of four phosphonium-modified MMT clays and commercial ammonium-modified clays. On the basis of this study and evaluation of the corresponding nanocomposites, we selected tributyl tetradeyl phosphonium chloride as the most suitable surfactant. Subsequently, we prepared blends of PS with the functionalized polar PS polymers shown in Table 1.

The organoclay was added to a solution of the polar compatibilizer in benzene. The mixture was dried and ground. Compounding with polystyrene PS1220 (NOVA Chemical) took place in a twin screw extruder equipped with special accessories to increase the residence time and improve the clay dispersion. The extrusion conditions were 200rpm and 220°C. After extrusion, we molded the resulting material, in ribbon form, into 140 × 140mm plates or thin films by compression molding. All nanocomposites contained 2wt% MMT and 5wt% compatibilizer.

We took samples for x-ray, mechanical, and barrier testing from the resulting plates. Flexural mechanical properties were determined for the resulting nanocomposites at room temperature following the American standard test method (ASTM) D 790–98. In addition, we determined the oxygen permeability of thin films of PS nanocomposites following ASTM D 3985–95. Samples were ultramicrotomed with a diamond knife at room temperature for analysis by transmission electron microscopy (TEM).

Figure 1 compares the x-ray diffractograms for nanocomposites prepared using the various compatibilizers. The position of the peak indicates the magnitude of the interlayer spacing (d-spacing) of the clay in the nanocomposite. The occurrence of the peak at lower angles signifies larger spacing, and thus a higher degree of intercalation. The Dylark 332 maleated PS—styrene maleic anhydride (SMA)—clearly produces the highest degree of intercalation. Similar evidence of intercalation in the SMA nanocomposite is apparent in the TEM images shown in Figure 2. Nanocomposites containing the other

<table>
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<tr>
<td>PS1220</td>
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<td>–</td>
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<td>Block-12% MA</td>
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Figure 1. Effects of compatibilizers on the basal spacing in clay/polymer nanocomposites. PS: Polystyrene. Ph1: MMT-tributyl tetradecyl phosphonium. \(2\theta\): \(2 \times \) the angle of diffraction. A.U.: Arbitrary units.

Figure 2. TEM pictures of PS/clay nanocomposites. The nanocomposite made with Dylark 332 exhibits a high degree of intercalation, while the one made with acrylate-13 shows much less.

Figure 3. Effect of different compatibilizers on the flexural modulus of nanocomposites. Except for Dylark, the compatibilizers are denoted by their functional group and molecular weight from Table 1.

Figure 4. Effect of the type of compatibilizer on the oxygen permeability of nanocomposites.

This study shows that the use of compatibilizers and thermally stable surfactants improves the mechanical and barrier properties of nanocomposites. Dylark SMA yields the best intercalation level as well as improvements in dispersion and nanocomposite properties. Further work is needed to study the effects of compatibilizer molecular weight and concentration of polar groups (e.g., maleic anhydride, OH, COOH). Similar work on other nonpolar polymers (e.g., polyolefins) also would be useful. The surface and interfacial energy characteristics of the various components could provide a basis for the selection of compatibilizers.

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References


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