Polymer−Clay Nanocomposites from Directly Micellized Polymer/Toluene in Water and Their Characterization by WAXD and Solid-State NMR Spectroscopy

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Polymer−clay nanocomposites (PCNs) consist of layered silicates such as montmorillonite (MMT) that contain intercalated polymer or have exfoliated in the organic polymer matrix. Because of strong synergistic effects between the organic polymer and silicate layers, some PCNs containing a few weight percent of clay exhibit unprecedented mechanical and thermal properties and, therefore, have recently received much interest in academic and industrial studies.[1−4]

Several strategies have been considered to prepare PCNs, including the four main processes of exfoliation−adsorption, in situ intercalative polymerization, melt intercalation, and template synthesis.[2] The easiest method is exfoliation−adsorption, because it requires only mixing of unmodified neat clay and hydrophilic polymer directly in a common solvent. Exfoliation here means that layered silicates are dispersed in adequate polar solvents, such as water, as a result of the weak attractive forces between the silicate layers. The soluble polymer can then adsorb onto the delaminated silicate layers, and the layers reassemble after the solvent has been evaporated. This process is mainly applied to synthesize PCNs with water-soluble polymers, such as poly(vinyl alcohol),[5,6] poly(ethylene oxide),[7,8] and poly(acrylic acid).[9] However, exfoliation−adsorption is not applicable to hydrophobic polymers, such as poly(styrene) (PS) or poly(methyl methacrylate) (PMMA). No known solvent is capable of dispersing hydrophilic unmodified clay and dissolving hydrophobic polymers simultaneously. Moreover, the hydrophilic characteristics of the unmodified silicate layer surfaces prevent the adsorption of hydrophobic polymers. Therefore, organo-modification of clay with small-molecule surfactants, such as long alkyl chains with onium salts,[2] has been needed for preparing PCN-containing hydrophobic polymers.

Although melt intercalation and exfoliation−adsorption by emulsion polymerization or radical polymerization[10−12] using organo-modified clay have been reported to yield PS (or PMMA)−clay intercalated nanocomposites, these methods have only produced silicate basal spacings of less than 3 nm, and it has been difficult to control the overall polymer architecture through either regular emulsion or radical polymerization. In this communication, we introduce a novel approach, based on exfoliation−adsorption, to prepare PS−clay and PMMA−clay intercalated nanocomposites by using unmodified clay and directly surfactant-micellized polymer/toluene in one pot. To synthesize a PS(50k)−MMT sample, for example, 1.0 g of PS (M_w = 50 000) and 0.05 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 3.0 g of toluene. The emulsion was made by adding 8.0 g of water and sonicating for 10 min. The micelle stabilized by CTAB is composed of PS and toluene. This emulsion was mixed with an aqueous solution of dispersed clay, which was prepared by stirring 0.05 g of MMT in 8.0 g of water. The mixture was then continuously sonicated by cyclic sonic pulses of 20 s on and 40 s off for 3 h in an ice bath. Through sonication, the mixture could be kept stably dispersed without precipitation. The micelles could then adsorb onto the silicate surfaces via strong interactions between the positive charges of the cationic surfactants and the negative charges of the silicate surface. Water and toluene were evaporated on a flat disk at 50 °C in a fume hood. The raw product was subsequently dissolved in toluene and dried again at 50 °C to give a homogeneous film. Finally, the resulting film was dried at 80 °C under vacuum for 48 h. The major advantages of this method are that (1) original clay instead of organo-modified clay can be used and (2) the desired polymer is used directly so that the chemical structure of the polymer can be easily varied.

Direct evidence of the intercalation of polymer into the silicate galleries is provided by the shift of the (001) WAXD peak of PCN, compared to neat clay, to a smaller 2Θ angle, corresponding to an increase in the layer period. Figure 1a shows the WAXD patterns of PCNs made from Na^+-montmorillonite (MMT) with PS or PMMA. The interlayer spacing of the (001) plane ($d_{(001)}$) of neat MMT is 1.17 nm. For PS(50k)−MMT, $d_{(001)}$ increases to 4.44 nm, and the width of the (001) peak is smaller than that of neat MMT. This indicates that the degree of coherent layer stacking has increased in PS(50k)−MMT. As mentioned above, the molecular weight or chemical structure of the polymer can be easily controlled simply by changing the starting polymer. PS(280k)−MMT was prepared from PS of high MW (280 000) and MMT under the same experimental conditions. The WAXD pattern of PS(280k)−MMT exhibits a peak at $2\Theta = 2.24°$ ($d_{(001)} = 3.93$ nm) with a slightly larger width, as compared to that of PS(50k)−MMT. Thus, the stacking of silicate layers in the high-MW polymer is more disordered. This approach can be

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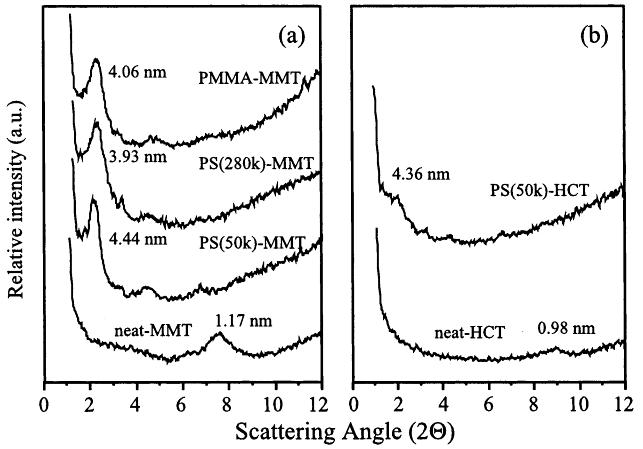

Figure 1. WAXD diffractograms of (a) PCNs made from MMT and (b) a PCN made from HCT clays.

applied to other toluene-soluble hydrophobic polymers, such as PMMA (here $M_w = 75\,000$). The WAXD pattern of PMMA−MMT (top of Figure 1a) shows a peak with a width and $d_{(001)}$ (4.06 nm) similar to those of PS(280k)−MMT. Using the 4.44-nm interlayer spacing obtained from XRD and assuming two 0.25-nm-thick surface layers of surfactant as in standard organically modified clay,[13] the increase in d spacing due to swelling by PS is 2.8 nm. Thus, the intercalated PS takes 2.8 nm/1.17 nm = 2.4 times the original clay volume. Given the 4.7% weight and 2.4% volume fraction of pure clay in the sample, a fraction of ca. 6 wt % of PS is found to be intercalated.

We have recently shown[14] that polymer intercalation can be assessed in terms of ^{1}H and ^{29}Si solid-state NMR spectroscopy applied to PCNs containing smectite clays low in paramagnetic ions. For example, hectorite clay (HCT) has the same crystal structure as MMT, but it contains much less Fe^{3+} than MMT. The plate thicknesses for the two clays are both ca. 1 nm, but the diameters are ca. 250 and 50 nm for MMT and HCT, respectively.[2] The PCN sample for the NMR study, PS(50k)−HCT, was prepared from PS (MW = 50k) and HCT. Its WAXD pattern (Figure 1b) shows a very small (001) peak of large width centered at $2\Theta = 2.02°$ ($d_{(001)} = 4.36$ nm). This weak intercalated basal reflection indicates more disorder in PS(50k)−HCT, compared to PS(50k)−MMT. The difference in stacking order might be due to the larger aspect ratio of MMT silicate plates compared to those of HCT, which results in different rearrangements of silicate layers during the evaporation and recasting process.

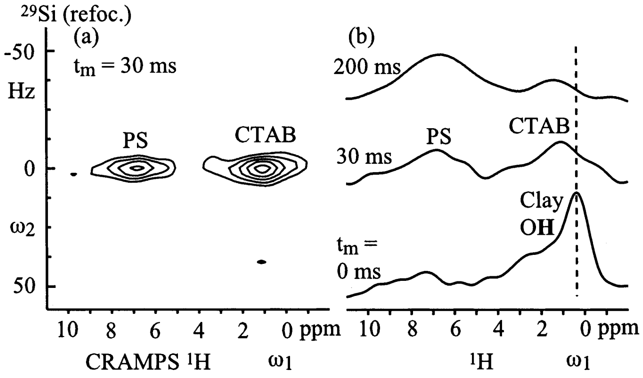

Figure 2. (a) 2D ^{1}H−^{29}Si HECTOR NMR spectrum with 30 ms of ^{1}H spin diffusion before CP for PS(50k)−HCT at $\nu_r = 5$ kHz. Frequency-switched Lee−Goldburg (FSLG) homonuclear decoupling is applied during t_1 evolution, so the proton spectrum obtained in the ω_1 dimension will reflect the chemical shifts of organic matter whose magnetization diffuses to the clay OH protons that cross polarize the ^{29}Si nuclei. This spectrum is rotated by 90° from the conventional representation, to display the proton dimension more conveniently. (b) Cross sections along ω_1 taken at the center of the ^{29}Si peak in ω_2, obtained from 2D spectra for three spin-diffusion times.

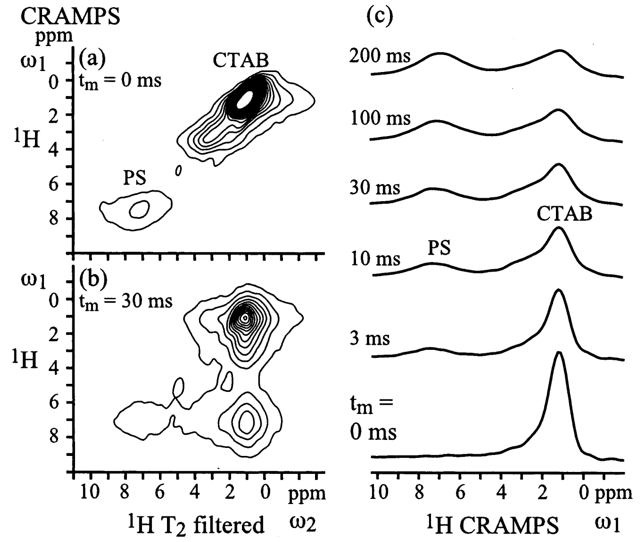

Figure 3. 2D ^{1}H−^{1}H correlation with ^{1}H evolution under combined rotation and multiple-pulse spectroscopy (CRAMPS), followed by a mixing time for spin diffusion and T_2-filtered detection, at $\nu_r = 5.5$ kHz. An echo time of two rotor periods (360 μs) was used for T_2-filtered detection. (a), (b) 2D spectra with mixing times of 0 and 30 ms, respectively. (c) Cross sections along ω_1 taken at the CTAB peak in ω_2 for a series of spin-diffusion times.

The samples prepared in this study have a clay content of only 4.7 wt %; therefore, systematic ^{29}Si NMR studies require sensitivity enhancement. We have recently shown that ^{29}Si NMR sensitivity in clays can be increased 5-fold by refocusing the ^{29}Si magnetization during detection.[14] Figure 2a shows a two-dimensional ^{1}H−^{29}Si HETCOR spectrum obtained with a mixing time of 30 ms for ^{1}H spin diffusion from the organic segments to the OH protons in the clay. The correlation peaks observed in the spectrum represent the protons near the silicate surface. Figure 2b shows cross sections through the centers of the ^{29}Si signals obtained from a series of such 2D spectra. The ^{1}H peak at 0.4 ppm in the spectrum of $t_m = 0$ ms has been assigned to the Si−OH protons within the silicate layers.[14] After 30 ms of spin diffusion, the intensity of the clay OH peak has been reduced, and a peak at 1.2 ppm has grown in, indicating magnetization transfer between the Si−OH protons and the surfactant (CTAB). At the same time, the presence of an aromatic PS peak indicates that polymer segments are also near the silicate surface. Given a spin-diffusion coefficient of ca. 0.5 nm^2/ms, within 30 ms, the ^{1}H magnetization will have equilibrated throughout the ca. 4-nm-wide galleries of intercalated PS and CTAB. The observed peak area ratio is

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consistent with the 45:55 aromatic/aliphatic proton ratio calculated from the 2.8-nm-thick layer of intercalated PS, with its 5:3 aromatic/aliphatic proton ratio and the two 0.25-nm layers of the aliphatic surfactant, which have a proton density twice as high as that of PS. At longer times, the polystyrene signal increases even further (see the top spectrum in Figure 2b). This indicates that the ∼50-nm-diameter stacks of intercalated clay are dispersed in the polystyrene matrix. Upon diffusing into the matrix for 200 ms, the ^{1}H magnetization will polarize a PS layer of ca. 20 nm around the clay stack, which has a volume larger than that of the stack itself.

Figure 3 shows results of a ^{1}H−^{1}H correlation experiment with homonuclear-decoupled evolution followed by spin diffusion and ^{1}H T_2-filtered detection.[14] It confirms the ^{1}H−^{29}Si HETCOR NMR results, but with the higher sensitivity of ^{1}H detection. At $t_m = 0$, only the CTAB molecules near the silicate surface are observed (Figure 3a), since the signal of the mobile CTAB segments has been selected by the ^{1}H T_2-filter. Figure 3a also shows a small peak of mobile aromatic rings of PS; a similar signal is observed in the T_2-filtered ^{1}H spectrum of pure PS. The proton spectrum of the segments close to the silicate surface can be acquired by taking the cross section at the CTAB peak position. Figure 3c shows that the intensity of the PS peak continues to increase with the spin-diffusion time, confirming that the stacks of PS-intercalated, surfactant-covered clay are dispersed in the PS matrix.

In conclusion, we have demonstrated an easy method for preparing PCN-containing hydrophobic polymer using the original clay, the polymer itself, and a surfactant in one pot. WAXD has shown that the polymer intercalation of the clay is similar observed in PCNs prepared from organo-modified clay, but the polymer layer is thicker in our system ($d_{(001)} \approx 4$ nm). Two-dimensional ^{1}H−^{29}Si and ^{1}H−^{1}H correlation solid-state NMR experiments with spin diffusion have confirmed the intercalation of clay in the surfactant-covered silicate and also indicate that the intercalated clay stacks are dispersed in the polymer matrix.

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