

Spontaneous Formation of an Exfoliated Polystyrene–Clay Nanocomposite Using a Star-Shaped Polymer

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There has been intense interest in polymer–clay nanocomposites recently because such materials have been demonstrated to possess significantly improved physical properties over the unmodified polymer.^{1,2} For example, incorporation of a few percent of clay in many cases increases the modulus, strength, gas barrier properties, and heat distortion temperature, compared to the unmodified polymers. The presence of clay is also reported to impart fire-retardant properties.³

The most common morphology for miscible polymer–clay dispersions is known as *intercalation*. In this case, the host polymer penetrates between the clay platelets, separating them only slightly but maintaining the parallel, regular structure. The physical properties of intercalated polymer–clay nanocomposites often show some measurable improvements. A less common but much more desirable situation is known as *exfoliation*. In this case, the clay platelets become thoroughly separated by the host polymer so that their original crystallographic register is lost. Fully exfoliated polymer–clay nanocomposites lead to superior physical properties but are notoriously difficult to attain, particularly for nonpolar polymer hosts.

Ordinary polystyrene has been shown previously to produce intercalated nanocomposites when melt-blended with clay.⁴ Exfoliated polystyrene–clay nanocomposites have been produced by in situ polymerization using polar comonomers³ or surface-bound initiators,⁵ methods that may be economically impractical. Until the present work, the preparation of exfoliated polystyrene–clay nanocomposites by direct compounding has remained an unattained goal.

Our work in this field was instigated by the theoretical paper of Singh and Balazs,⁶ who used self-consistent field theory to predict that star-shaped polymers might form thermodynamically stable exfoliated clay nanocomposites. Coincidentally, we had been engaged in research dealing with the synthesis of such star polymers.⁷ Therefore, we set out to test the predictions of Singh and Balazs and possibly realize the expected physical property improvements of the resulting nanocomposite.

A star-shaped polystyrene with five arms (**PS5**) was prepared by atom-transfer radical polymerization from a pentafunctional initiator, similar to procedures described previously.⁷ **PS5** was found indeed to contain five arms, within experimental error, throughout most of its molar mass distribution, as assayed by multidetector size exclusion chromatography (SEC).⁷ A control sample (**PS1**) of linear polystyrene was prepared similarly but using a monofunctional initiator. Both of the polystyrene samples were treated with tributyl tin hydride to reduce the chloride end groups to hydrogen⁸ before mixing with clay. This post-polymerization reaction was done to ensure the stability of the polymers at elevated temperatures but may not be necessary.

Samples of the polystyrene and clay⁹ (10–15% w/w clay polymer) were briefly hand mixed above T_g and then held *unstirred* at 220 °C for various periods of time and analyzed by X-ray

Table 1. Polystyrene Characterization Information

sample	arms	\bar{M}_n^a	\bar{M}_w^a	PDI ^b	T_g (°C)
PS1	1	38 300	57 600	1.50	100
PS5	5	37 100	46 400	1.25	98

^a Absolute molar mass determined by SEC. ^b Polydispersity \bar{M}_w/\bar{M}_n .

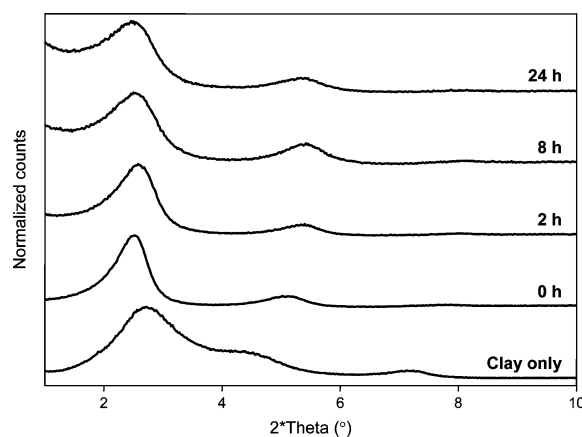


Figure 1. X-ray diffraction of a linear polystyrene (**PS1**) mixture with Cloisite 15A clay annealed for various periods of time at 220 °C.

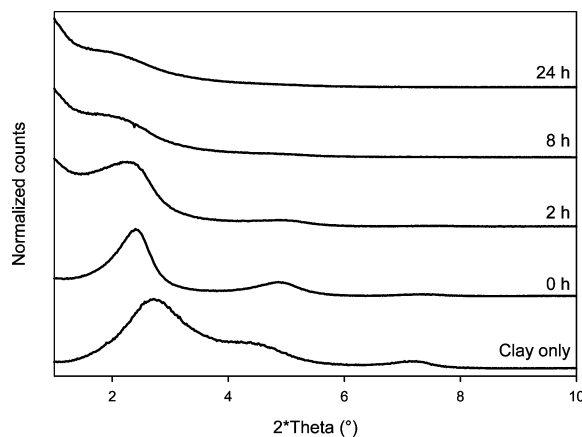


Figure 2. X-ray diffraction of a mixture of five-arm polystyrene (**PS5**) with Cloisite 15A clay annealed for various periods of time at 220 °C.

diffraction. Figure 1 shows the results for the linear polymer, **PS1** with Cloisite 15A. The 2θ position of the (001) basal plane diffraction peaks, compared to that of the original clay, changes slightly to lower 2θ (large d spacing) on initial compounding to produce a pattern consistent with intercalation. Continued heating produced no further changes. Similar results were obtained for **PS1** with Cloisite 10A (i.e., intercalation).

With **PS5**, the situation was completely different (Figure 2). Again, the original clay diffraction pattern changed immediately to one consistent with intercalation. Remarkably, on continued

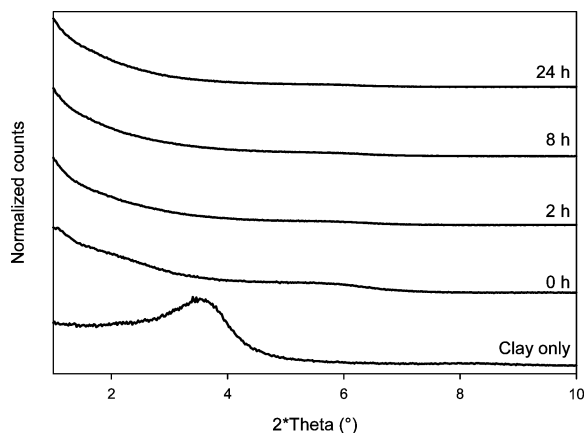


Figure 3. X-ray diffraction of a five-arm polystyrene (PSS) mixture with Cloisite 10A clay annealed for various periods of time at 220 °C.

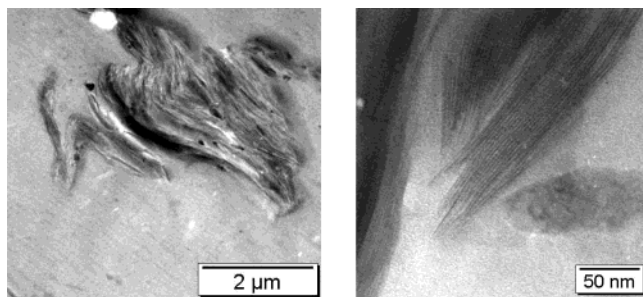


Figure 4. Transmission electron microscopy of a mixture of linear polystyrene (PS1) and Cloisite 15A clay after annealing at 220 °C for 24 h.

heating, the peaks broadened and nearly disappeared after a few hours. The featureless, diffuse diffraction pattern obtained is indicative of an exfoliated morphology.

The nature of the surfactant on the organoclay was found to have significant influence on the apparent rate of exfoliation. For example, when Cloisite 10A was annealed with PSS, exfoliation occurred considerably faster and was completed in less than 2 h (Figure 3). The surfactant in Cloisite 10A contains benzyl groups, which one might expect to possess more favorable interactions with the polystyrene chains than the exclusively alkyl groups present in Cloisite 15A. This observation is in agreement with the work of Singh and Balazs,⁶ who based their predictions on Flory–Huggins χ interaction parameters between the polymer and the surfactant.

The morphologies of the nanocomposites were further examined by transmission electron microscopy (TEM). For the annealed mixture of linear polymer (PS1) and clay, numerous agglomerated particles (“tactoids”) were evident (Figure 4). At increased magnification, the tightly associated, parallel plates of the intercalated nanocomposite can be seen. In contrast, for the annealed star polymer (PSS) nanocomposites, no tactoids were detected (Figure 5). In the higher magnification image, widely separated, uncorrelated platelets are clearly visible, confirming exfoliation. The star polymer–clay nanocomposite could subsequently be blended with commodity polystyrene, and the exfoliated morphology was preserved.

It is significant that no shear, only annealing, was required to achieve exfoliation, suggesting that the *observed morphology* is

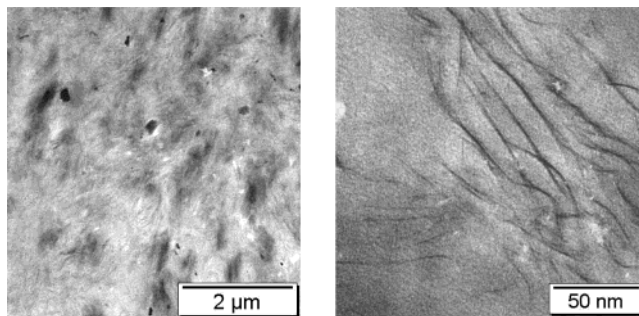


Figure 5. Transmission electron microscopy of a mixture of five-arm star polystyrene (PSS) and Cloisite 15A clay after annealing at 220 °C for 8 h.

thermodynamically stable for star polystyrene and driven by the architecture of the star structure. These results substantiate the theory of Singh and Balazs⁶ and indicate a general method for forming clay nanocomposites in commodity polymers by simple melt compounding. Presumably, the relatively compact size of the star polymer combined with the multiple points of interaction with the surfactant-covered surface of the clay promotes separation of the clay plates. We are currently exploring the scope and limitations of this discovery in hopes of optimizing the process and extending the technology to other polymers. In addition, we are assessing the physical properties of the exfoliated nanocomposites. If the expected improvements are realized, this finding may represent a significant advance in the field of polymer nanocomposites.

Acknowledgment. We thank C. Bauer, J. Hammerschmidt, D. Majumdar, D. Massa, J. Pochan, and Y.-Q. Rao for enlightening discussions concerning polymer–clay nanocomposites; R. Meyer for TEM measurements; and T. Mourey, K. Le, and T. Bryan for SEC measurements, all members of Eastman Kodak Company R&D Laboratories.

Supporting Information Available: Description of the synthesis of PS1 and PS5, molar mass, and arm number measurements by SEC, and X-ray diffraction of PS1–Cloisite 10A clay. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Coessens, V.; Matyjaszewski, K. *Makromol. Chem., Rapid Commun.* **1999**, *20*, 66–70.
- (9) Cloisite 15A, obtained from Southern Clay Products, Inc., 1212 Church St., Gonzales, TX 78629, is a natural montmorillonite clay pretreated with a quaternary ammonium salt, $\text{NMe}_2\text{R}_2\text{Cl}$, in which R is hydrogenated tallow (~65% C_{18} ; ~30% C_{16} ; ~5% C_{14}). Cloisite 10A is a similar material, except the quaternary ammonium salt is $\text{NMe}(\text{CH}_2\text{Ph})\text{RCl}$.

JA048211H