NOTE

Small Angle X-Ray Scattering Investigations of Zeolite-Penetrated Poly(ethyl acrylate) Composites

INTRODUCTION

Introduction of fillers is an important and effective technique to reinforce polymeric materials, especially elastomers. In order to gain a better understanding of how such fillers provide reinforcement, there have been considerable attempts to study the interactions between fillers and their host elastomeric matrices.¹⁻⁴ Since there are both physical and chemical aspects to such interactions, the mechanism of reinforcement is obviously very complicated and current understanding of it is far from complete.

Of considerable help in this regard is small-angle scattering, since it has had widespread applications in studying morphologies, particle sizes, size distributions, characteristics of the particle surfaces, and degrees of aggregation and inhomogeneity.^{5,6} In fact, there have now been a number of small-angle scattering studies of the interactions between filler particles and host polymer matrices.⁷⁻¹⁰

The use of zeolites as reinforcing fillers¹¹⁻¹³ is particularly interesting for at least two reasons. First, the materials are crystalline and their structures are known, thanks to strong interests in their structures by inorganic structural chemists and by workers in the area of catalysis. Zeolites also generally have cavities, some with sizes that would permit interpenetration by polymer chains. Thus, zeolites can serve as excellent candidates for the study of interactions between filler particles and the polymer matrices they reinforce. This article presents the results of small-angle X-ray scattering (SAXS) investigations of the structure of poly(ethyl acrylate) composites prepared in such a way that some of the polymer chains interpenetrate zeolite fillers introduced to reinforce this elastomeric polymer.

EXPERIMENTAL

Preparation of Zeolite/Poly(ethyl acrylate) Hybrid Composites

Ethyl acrylate monomer (reagent grade, 99%) was obtained from the Aldrich Company. It was mixed with 10% aqueous NaOH to remove inhibitor, washed with distilled water, dried over anhydrous Na₂SO₄, and finally distilled at 50°C under dry nitrogen gas at low pressure. A free radical initiator, benzoyl peroxide (BPO) (97% pure), was dissolved in carbon tetrachloride, precipitated, washed with cool methanol, and then dried at room temperature under a vacuum of 4 mm Hg. The zeolite chosen, zeolite 13X with pore size 10 Å, was obtained from Aldrich. It was dried in an oven under vacuum, above 250°C, for more than 8 h before use.

The zeolite/poly(ethyl acrylate) hybrids were prepared as follows: 1 wt % BPO was dissolved in distilled ethyl acrylate monomer under nitrogen gas at room temperature, with moderate stirring. A convenient volume of the solution was poured into a clean glass bottle containing a weighed amount of the dry zeolite powder. The bottle was then filled with nitrogen gas, sealed tightly, and then kept in the dark at 40°C for 3 days. The hybrid composites prepared by the resulting polymerization process were then kept in an oven at 150°C for 3 days. They were then further dried at 80°C under vacuum, for 2 days. It is anticipated that some of the cavities were filled with ethyl acrylate monomer, which became part of polymer chains passing through a series of these cavities.

To extract the zeolite/poly(ethyl acrylate) hybrids, weighed samples were placed into ethyl acetate at room temperature overnight without any stirring. The samples thus extracted were filtered, washed with fresh solvent, and then dried in an oven under vacuum overnight at 50° C. Samples were reweighed and the weight loss calculated.

Small-Angle X-Ray Scattering

Scattering experiments were conducted on the 10-m pinhole camera at Oak Ridge National Laboratory. Data were corrected to absolute intensities by measurements of sample thickness and through comparisons with secondary standards. Because the samples studied were powders, the thickness measurement has an accuracy of only about $\pm 30\%$. Notwithstanding, the scattering data from different samples can be qualitatively compared and interpreted, although some degree of error must be taken into account in more quantitative comparisons.

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Figure 1. Scattering profiles for pure zeolite powder and pure poly(ethyl acrylate), in which Q is the scattering vector (in reciprocal angstroms).

RESULTS AND DISCUSSION

The scattering data of the samples thus prepared are shown in Figures 1 and 2, as double logarithmic plots. Figure 1 shows the scattering profiles for pure zeolite and pure poly(ethyl acrylate). Those for the zeolite/poly(ethyl acrylate) hybrid composites, unextracted and extracted, are shown in Figure 2. One can see from these two figures that the scattered intensities from pure poly(ethyl acrylate) are very low, while those from the zeolite are quite high. Over a wide range of scattering vector Q, the scattering profiles of the composites are similar to that of zeolite, in spite of the fact that the scattering profiles of the pure zeolite and pure poly(ethyl acrylate) differ greatly. This is not unexpected, since the scattering cross section of the zeolite is much larger than that of poly(ethyl acrvlate), and therefore it dominates in the overall scattering profile of the composite material.

One interesting observation is the occurrence of an excess scattering intensity in the composites, as illustrated in Figure 3. According to Porod's Law, the scattered intensity I(Q) in the relevant range of scattering vector can be written

$$I(Q) \propto \frac{(\rho_s - \rho_p)^2 \cdot S}{Q^4 \cdot V} \tag{1}$$

where ρ_s is the scattering density of the solid region, ρ_p the scattering density of the pores, S the surface area, and V the volume seen by the incident beam. This indicates that the scattered intensity-scattering vector plots on a double-logarithmic scale should be straight lines. It can be seen from Figure 1 that the scattered intensity from the pure zeolite powder does obey Porod's Law over a rather wide Q range, with no deviation at all. But as can



Figure 2. Scattering profiles for the unextracted and extracted zeolite/poly(ethyl acrylate) composites.

be seen from the data for the composite in Figure 3, Porod's Law is obeyed only in the lower Q range. At higher values of Q, an intensity well in excess of that of the zeolite is clearly in evidence. This can be associated with interactions between the poly(ethyl acrylate) matrix and the zeolite particle surfaces.

The most important result obtained from these scattering data is the occurrence of two scattering peaks, around Q = 0.443 and 0.220 Å⁻¹, respectively. This may be interpreted by¹⁴

$$I(Q) = \frac{k}{V} \left| \int_{v} \rho(r) e^{iQr} dr \right|^{2}$$
(2)



Figure 3. Excess scattering intensities for the composites, as estimated from Porod's Law.

where r is the position vector, $\rho(r)$ the scattering density, and k an arbitrary constant. The measured scattered intensity I(Q) is the Fourier transformation of the scattering density $\rho(r)$, i.e., each scattering peak should correspond to a certain size scale in the sample according to Bragg's Law. As illustrated in Figures 1 and 2, pure poly(ethyl acrylate) does not show any peak in the region of Q = 0.443and 0.220 Å⁻¹, while pure zeolite gives a peak around Q= 0.443 Å⁻¹. It is inferred that the scattering peak around Q = 0.443 Å⁻¹ corresponds to a size scale for the zeolite powder, and the scattering peak around 0.220 Å⁻¹ in the composite, on the other hand, suggests the existence of another size scale resulting from the interactions between the poly(ethyl acrylate) and zeolite.

The interaction between the poly(ethyl acrylate) and zeolite can be interpreted as a relatively regular arrangement of filled and unfilled cavities in the zeolite. Although this type of cavity filling is only a conjecture at this point, it is useful to construct a model, illustrated in Figure 4, to test the assumption. The figure shows an idealized regular pore distribution in a zeolite, with unfilled circles representing unfilled pores and filled circles representing filled ones. From the Bragg condition, the distance d between two points that scatter in a given scattering pattern can be expressed by $d = 2\pi/Q$. The distances d in Figure 4 were thus determined to be $d_1 = 2\pi/Q_1 = 2\pi/0.443 = 14.3$ Å, and $d_2 = 2\pi/Q_2 = 2\pi/0.220 = 28.6$ Å. As was assumed, the value $d_1 = 14.3$ Å corresponds to the distance between two neighboring pores in the zeolite. Also, zeolite X is known to have a cage structure.¹⁵⁻¹⁷ Considering the facts that the pore size of zeolite 13X is around 10 Å and that there exists a wall thickness between neighboring pores, this assumption is quite reasonable. The period doubling $d_2/d_1 = 2$ indicates that different pairs of pores exist to produce the scattering peak at Q = 0.220 Å⁻¹ and the value $d_2 = 28.6$ Å suggests that a pair of pores is generally separated by another unfilled pore.

Relevant to this preliminary suggestion is the observation that the period doubling disappears after a composite has been extracted, as illustrated in Figure 2. This suggests that the trapping of ethyl acrylate monomers and/ or poly(ethyl acrylate) chains in zeolite pores does contribute to this period doubling. It is shown that the extraction process does not completely remove the poly(ethyl acrylate) chains trapped in zeolite cavities,¹⁸ but the period doubling no longer shows up because the partial removal of the filled cavities has suppressed its corresponding scattering pattern.

The intensity difference between the two scattering peaks at Q = 0.443 and 0.220 Å⁻¹ can be explained as follows: Porod's Law shows that the scattered intensity is directly proportional to the square of the scattering density difference between the solid parts of a zeolite and its pore regions, namely, $(\rho_s - \rho_p)^2$ (which is termed the contrast factor). In the case where a pore does not contain any monomer or polymer repeat unit, $\rho_p = 0$. When some pores are filled with either species, $0 < \rho'_p < \rho_s$, and $\rho_s^2 > (\rho_s - \rho'_p)^2$ and I(Q) > I'(Q). Of course, it is also possible



Figure 4. A tentative pore distribution model for (a) pure zeolite, and (b) zeolite/poly(ethyl acrylate) composites. Open circles represent empty pores, while filled circles represent pores containing either ethyl acrylate monomer and/or poly(ethyl acrylate) repeat units.

that the difference in the number of filled and unfilled pores is another factor causing differences between the intensities of the scattering peaks.

Additional scattering studies of these novel composites could clarify some of these specific issues, and some more general ones about reinforcement of elastomers as well.

CONCLUSIONS

Zeolite/poly(ethyl acrylate) hybrid composites were synthesized by blending zeolite with ethyl acrylate monomer, which was subsequently polymerized in a free radical process. These conditions should result in the absorption of some of the monomer into the zeolite cavities, and its remaining there as repeat units in the resulting elastomer. The structures of these materials were studied with small angle X-ray scattering. One scattering peak was observed for the pure zeolite powder, and another at a different scattering vector (Q) position was observed for the composites. The Q values of these two scattering peaks were in a ratio of 2:1 and it was conjectured that this was due to the period doubling of the scattering peak of the zeolite. A tentative model for the distributions of filled and unfilled pores was proposed to account for the origin of the period doubling, and the distances between pores which correspond to these two scattering peaks were estimated.

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