

A Comparison of Various Methods for the Preparation of Polystyrene and Poly(methyl methacrylate) Clay Nanocomposites

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Received February 26, 2002. Revised Manuscript Received July 8, 2002

Polymer–clay nanocomposites of styrene and methyl methacrylate have been prepared by bulk, solution, suspension, and emulsion polymerization as well as by melt blending. Two different organic modifications of montmorillonite have been used: one contains a styryl monomer on the ammonium ion while the other has no double bond. The organic modification as well as the mode of preparation determines if the material will be exfoliated or intercalated. Exfoliation is more likely to occur if the ammonium ion contains a double bond which can participate in the polymerization reaction, but the mere presence of this double bond is not sufficient to always produce an exfoliated system. Solution polymerization always produced intercalated systems. Neither thermogravimetric analysis nor the tensile modulus can be used to evaluate the type of nanocomposite that has been formed.

Introduction

The study of polymer clay nanocomposites is one of the most active research fields in polymer and materials science. Much attention has been directed toward the preparation of polystyrene, PS, and poly(methyl methacrylate), PMMA, clay nanocomposites. The preparation of PS–clay nanocomposites has been reported through bulk, solution and emulsion polymerization and by melt blending.^{1–12} The preparation of PMMA nanocomposites has utilized bulk and emulsion polymerization and melt blending.^{13–17} For the PS systems, both intercalated and exfoliated nanocomposites have been obtained, depending upon the particular organic treatment which has been applied. The normal characterization of the struc-

ture of a nanocomposite requires X-ray diffraction (XRD) measurements to show changes in the *d* spacing of the clay and transmission electron microscopy (TEM) to image the individual clay layers and thus show the exact nature of the clay–polymer interaction.

In addition to these techniques, many others have been used to evaluate the utility of the nanocomposites. The advantage in mechanical properties is well-known.¹⁸ Thermogravimetric analysis (TGA) has been used and the onset temperature of thermal degradation is increased compared to that of virgin polymer in some systems,^{4,5,12} but there is no change in others.¹⁹ Dynamic mechanical analysis (DMA) shows either an increase or no change in the storage modulus and the glass transition temperature, T_g .^{2,7}

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In the previous work, PS and PMMA nanocomposites have been prepared by one preparative techniques and characterized in different ways; there have been no attempts to compare the various preparative methods to determine the effect that the mode of preparation has on the resulting nanocomposite. This work is a systematic investigation of the preparation of these nanocomposites by bulk, solution, suspension, and emulsion polymerization and melt blending and the characterization of these to determine what, if any, effects there are on the nanocomposite structure for each mode of preparation.

Experimental Section

Materials. Monomeric styrene and methyl methacrylate, initiators benzoyl peroxide (BPO) (97%) and azobis(isobuty-

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ronitrile) (AIBN) (98%), and chemically pure acetone, methanol, toluene, and potassium hydroxide (KOH) were acquired from the Aldrich Chemical Co., Inc. The monomer was purified by removing the inhibitor using an inhibitor removal column, also acquired from Aldrich. Poly(vinyl alcohol), PVOH, 88% hydrolyzed, was obtained from Acros Organics; its average molecular weight is 22 000. Sodium dodecyl sulfate, SDS, and hydrochloride acid were from Curtin Matheson Scientific, Inc., while potassium persulfate, $K_2S_2O_8$, and aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, were acquired from Fisher Scientific Co. The organic clay 10A was a gift from Southern Clay Co., while organic clay VB16 is synthesized in this laboratory⁴ through the reaction of styryldimethylhexadecylammonium chloride with the sodium clay. Commercial polystyrene is a product of Aldrich Chemical Co., Inc. with a melt index (200 °C/5 kg, ASTM D 1238) of 8.5 g/10 min, average molecular weight M_w ca. 230 000, and M_n ca. 140 000. All materials were used as received, except monomeric styrene and methyl methacrylate. Distilled water was used throughout.

Synthesis of Clays. The organically modified clay was obtained by treatment of sodium montmorillonite with the appropriate ammonium salt, as previously described.⁴

Synthesis of Polymer—Clay Nanocomposites. Bulk Polymerization.^{4,5,12,17} In a 200 mL beaker were placed 3.0 g of organically modified clay, 1.0 g of azobis(isobutyronitrile) (AIBN) as radical initiator, and 100 g of styrene monomer. This mixture was treated as follows: first, it was stirred at room temperature under flowing N_2 gas until it became homogeneous; second, the homogeneous system was heated to 80 °C for a few minutes to obtain a prepolymer which was then cooled; third, polymerization was carried out at 60 °C for 24 h and at 80 °C for another 24 h under a nitrogen atmosphere; finally, it was dried under vacuum for 6 h at 100 °C to obtain the nanocomposite.

Solution Polymerization. In a 100 mL round-bottom flask were placed 0.10 g of BPO, 0.30 g of organic clay, 10 g of styrene and 40 mL of toluene; the mixture was stirred for 1 h at room temperature and then heated to 80 °C and maintained at this temperature for 24 h. At the conclusion of the reaction, the solution was cooled, and then the solvent was removed on a rotary evaporator and the solid material was dried in a vacuum oven for 6 h at 100 °C to obtain the nanocomposite.

Suspension Polymerization. In a 250 mL three-neck flask were placed 100 mL of H_2O and 0.10 g of poly(vinyl alcohol), PVOH, and the mixture stirred for 1 h at 95 °C. Then the temperature was decreased to 85 °C. In a separate flask was placed monomer and the initiator (0.1 g of BPO dissolved in 20 g of monomer); this was cooled to 0 °C, and then 0.6 g organically modified clay was added with magnetic stirring to obtain a homogeneously dispersed system. The clay–polymer–initiator mixture was transferred to an addition funnel and added dropwise to the water–PVOH system. After the addition was complete, the contents were stirred at 85 °C for 5 h and then at 95 °C for an additional 3 h. The flask was allowed to cool for 1 h with stirring, and then the contents were poured into another vessel and allowed to sit for 24 h. The polymer was repeatedly washed with water, and then the suspension was filtered and washed again with water and methanol. The polymer was air-dried and then dried in a vacuum oven for 15–20 h at 80–100 °C.

Emulsion Polymerization. In a 250 mL three-neck round-bottom flask were placed 0.04 g of potassium hydroxide, KOH, and 0.12 g of sodium dodecyl sulfate, SDS, dissolved in 80 mL of H_2O , and the flask and its contents were heated to 50 °C. A 20 g portion of monomer and 0.60 g of organic clay were mixed in another flask and treated at 0 °C for 2 h in an ultrasonic bath. A 0.10 g portion of potassium persulfate, $K_2S_2O_8$, was dissolved in 5–10 mL of distilled water. Then both the monomer/clay mixture and initiator solution were added dropwise to the flask over 5 min, and polymerization was performed at 50 °C for 4 h. After cooling, 10 mL of a 2.5% aqueous solution of aluminum sulfate, Al_2SO_4 , was added to the polymerized emulsion, followed by addition of 10 mL of dilute hydrochloride acid with stirring. Finally, acetone was used to completely break the emulsion. The polymer was then

washed several times with methanol and distilled water, and it was dried in a vacuum oven at 80 °C overnight.

Melt Blending. A 50 g sample of of commercial polystyrene was mixed in a container with 1.5 g of organic clay, either VB16 clay or 10A clay, and the mixture was melt-blended on Brabender Plasti-Cord at 200 °C at high rotor speed for 30 min.

All the materials were compression molded at 170–180 °C to 20 mm × 15 mm × 1 mm plaques for XRD measurements.

Determination of Molecular Weight By Viscosity. The molecular weight of the PS and PMMA samples were obtained from viscosity data. The nanocomposites were extracted, using a Soxhlet extractor, to obtain the polymer free of the clay and the viscosity measurements were performed. The results are an average of three determinations, and the Mark–Houwink constants were obtained from published data.²⁰

Instrumentation. X-ray diffraction (XRD) patterns were obtained by using a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu $K\alpha$ generator ($\lambda = 1.5404 \text{ \AA}$). Generator tension is 50 kV, and generator current is 20 mA. Bright field transmission electron microscopy (TEM) images of the composites were obtained at 60 kV with a Zeiss 10c electron microscope. The samples were ultramicrotomed with a diamond knife on a Riechert-Jung Ultra-Cut E microtome at room temperature to give ~70 nm thick sections. The sections were transferred from the knife-edge to 600 hexagonal mesh Cu grids. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging is required. Thermogravimetric analysis (TGA) was performed on an Omnitherm 1000 unit under a 30 mL/min flowing nitrogen atmosphere at a scan rate of 10 °C/min from 20 to 600 °C; temperatures are reproducible to ± 3 °C, and the fraction of nonvolatile material is reproducible to $\pm 3\%$. Dynamic mechanical properties of the compression-molded samples were measured by a dynamic mechanical thermal analysis system (TA Instruments thermal analysis–DMA multifrequency–tension), in the cantilever mode. The frequency used was 1 Hz, and heating was carried out under an inert nitrogen atmosphere at a rate of 5 °C/min. Mechanical properties were measured using a SINTECH 10 (Systems Integration Technology, Inc.) computerized system for material testing at a crosshead speed of 0.05 in/min; the reported values are the average of five determinations. The samples for mechanical testing were prepared by injection molding using an Atlas model CS 183MMX mini max molder

Results and Discussion

This work focused on two organically modified clays, one of which is labeled as VB16, where the ammonium salt contains one long chain, two methyl groups, and a styryl unit, while the other is labeled 10A, where the ammonium cation contains a long chain, two methyl groups, and a benzyl group. The structures of the ammonium salts used to prepare the clays are shown in Figure 1. In previous work, it has been shown that the first of these, VB16, gives an exfoliated material upon bulk polymerization with styrene and a mixed intercalated/exfoliated material upon bulk polymerization with methyl methacrylate. The second organically modified clay, 10A, gives only intercalated material upon bulk polymerization with both styrene and methyl methacrylate. These clays were chosen to see if the same type of nanocomposite would be obtained when other means were used to form the nanocomposites. A working hypothesis is that the preparation of an exfoliated nanocomposite is more likely when a double bond that

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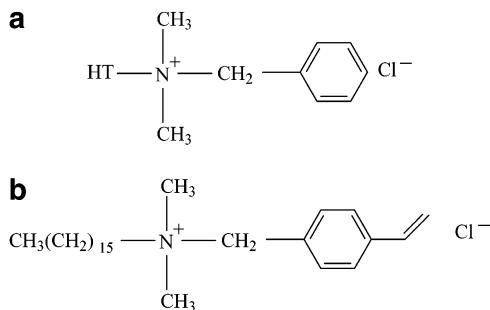


Figure 1. (a) Chemical structure of organic clay 10A, in which HT is hydrogenated tallow with ~65% C18, ~30% C16, and ~5% C14. (b) Chemical structure of organic clay VB16.

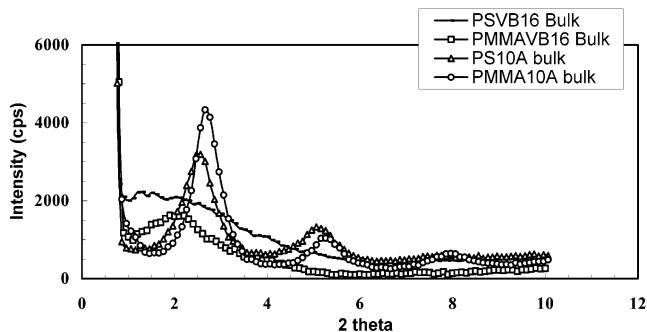


Figure 2. Comparison of the XRD patterns for PS and PMMA nanocomposites prepared by bulk polymerization.

may be involved in the polymerization reaction is present in the cation of the clay.

X-ray Diffraction. X-ray diffraction (XRD) was used to characterize the layered structure of polymer–clay nanocomposites, since changes in 2θ indicate changes in the gallery height of the clay. Figure 2 shows the XRD results for bulk polymerization of both PS and PMMA with VB16 and 10A. A strong peak near 2.5° (d spacing = 3.5 nm) is evident for both polymers with the 10A clay (d spacing in the clay is 1.9 nm). These data suggest an intercalated structure, in agreement with results that have been previously reported for similar clays with these polymers.^{4,17} For the VB16 clays, the XRD data suggest an exfoliated structure for PS; this structure has been previously reported by TEM for this mode of preparation.⁴ There is a peak in the PMMA–VB16 system which corresponds to a d spacing of 4.3 nm; previous work in this system has shown similar results, and the TEM suggests the presence of a mixed intercalated–exfoliated structure.¹⁷ If a large peak is seen in the XRD, one can anticipate an intercalated structure. The presence of a small, probably diffuse, peak suggests a mixed intercalated–exfoliated structure.

Figure 3 shows the XRD results from suspension polymerization; no peak is observed for PMMA–VB16, but a peak is observed for PS–VB16, PS–10A, and PMMA–10A at about $2\theta = 2.5^\circ$. This suggests that an intercalated nanocomposite is formed for all, except PMMA–VB16, by suspension polymerization. The polymerization reaction is similar to a mini-bulk polymerization, so most of the samples will form an intercalated structure. For MMA polymerization in this system, because the MMA monomer has higher solubility in water than styrene monomer, it is suggested that two phases exist. One phase is colloidal, formed with PVOH, and the polymerization inside this colloid is like tradi-

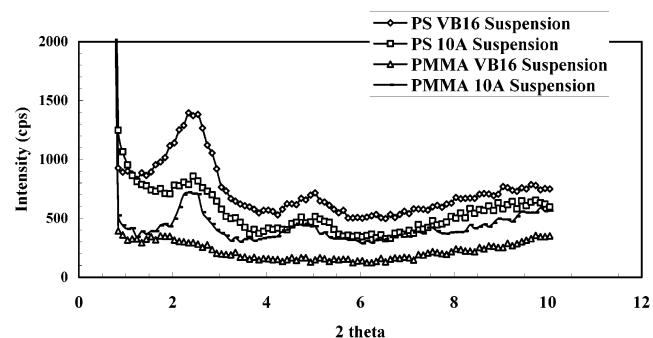


Figure 3. Comparison of the XRD patterns for PS and PMMA nanocomposites prepared by suspension polymerization.

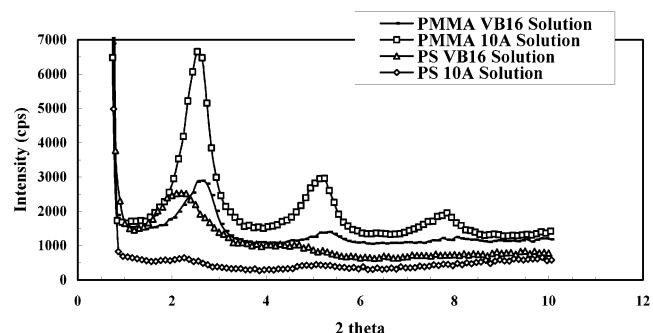


Figure 4. Comparison of the XRD patterns for PS and PMMA nanocomposites prepared by solution polymerization.

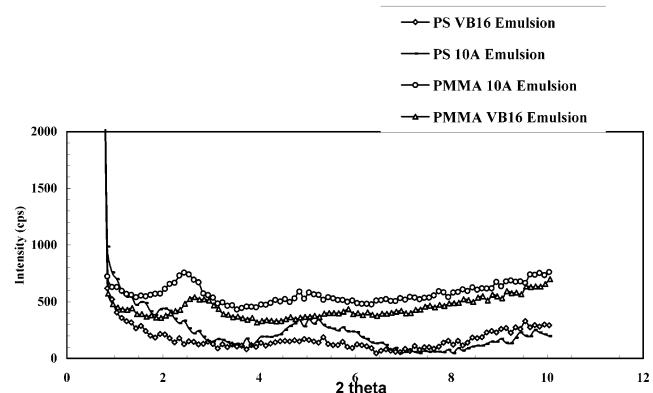


Figure 5. Comparison of the XRD patterns for PS and PMMA nanocomposites prepared by emulsion polymerization.

tional suspension polymerization. The other phase is well-dispersed MMA monomer in water with clay, forming an emulsion. The well-dispersed clay layers will be easily penetrated by MMA and PMMA molecules, yielding an exfoliated material.

The solution polymerization XRD results are shown in Figure 4. All the samples show a peak, indicating the formation of intercalated structures. For both PMMA–VB16 and PMMA–10A samples, the d spacing increase is less than in the PS–VB16 and PS–10A nanocomposites. It is not surprising that toluene will interact more favorably with PS than with PMMA and facilitate insertion of monomer/polymer into the clay layers.

The results from emulsion polymerization are shown in Figure 5. PS–10A shows a sloping line with a broad peak at about 2θ around 2 (d spacing 4.4 nm), which may indicate a partially exfoliated structure, while no peak is observed for PS–VB16. Both PMMA materials show XRD peaks and are likely to be intercalated.

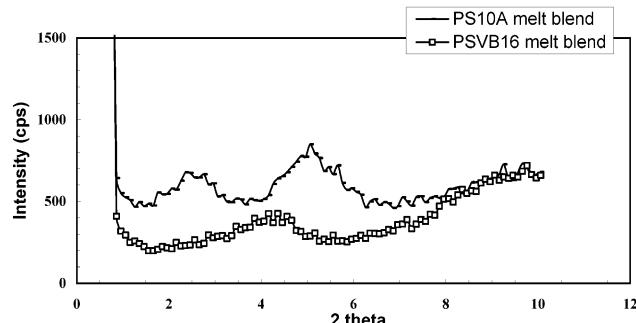


Figure 6. Comparison of the XRD patterns for PS nanocomposites prepared by melt blending.

Melt blending yields an intercalated structure for PS–10A (Figure 6). The d spacing of melt-blended PS–VB16 decreases from the 2.9 nm value of the VB16 clay to 2.1 nm in the nanocomposite. This may indicate the loss of the organic modifier of the clay, which is known to begin at about 200 °C.⁴

The XRD results noted above give useful information on the state of the nanocomposites but do not provide a complete picture of the state of the nanocomposites, for this information actual images of the material, such as can be obtained by TEM, are required. It is well-known that XRD information alone is not sufficient to characterize a nanocomposite. For instance, Morgan et al., have shown that the d spacing of a *n*-dodecylamine ammonium salt treated montmorillonite–poly(ether imide) nanocomposite does not change when compared to the virgin clay, suggesting an immiscible material. TEM, on the other hand, shows the presence of exfoliated material; this is best described as an exfoliated–immiscible system.²¹

Transmission Electron Microscopy. TEM images have been obtained for the PS–VB16 emulsion and the PMMA–VB16 suspension products. The XRD data for both of these suggests the formation of exfoliated nanocomposites. Figure 7 shows the TEM images for the styrene polymer; one can see a fair degree of delamination in this material, so it is reasonable to describe this material as exfoliated, perhaps with a small amount of intercalation. Figure 8 presents the TEM images of the PMMA material; these images show a mixed intercalated–exfoliated structure. It must be noted that TEM images of the PS and the PMMA material prepared by bulk polymerization have been previously reported.^{4,17} The PS material is completely exfoliated while the PMMA is a mixed intercalated–exfoliated structure. The XRD results provided the first clues as to the nature of these nanocomposites and the TEM images have confirmed these observations and enable one to assert the nature of those materials which have not been examined by TEM.

Molecular Weight of Solvent Extractable Polymer–Clay Nanocomposites. The molecular weights of the polymers which have been prepared have been determined after removal of all of the clay; the results are shown in Table 1. For the virgin polymers, the highest molecular weight was observed for emulsion polymerization, followed by suspension, bulk, and solution polymerization of styrene, which gives the lowest

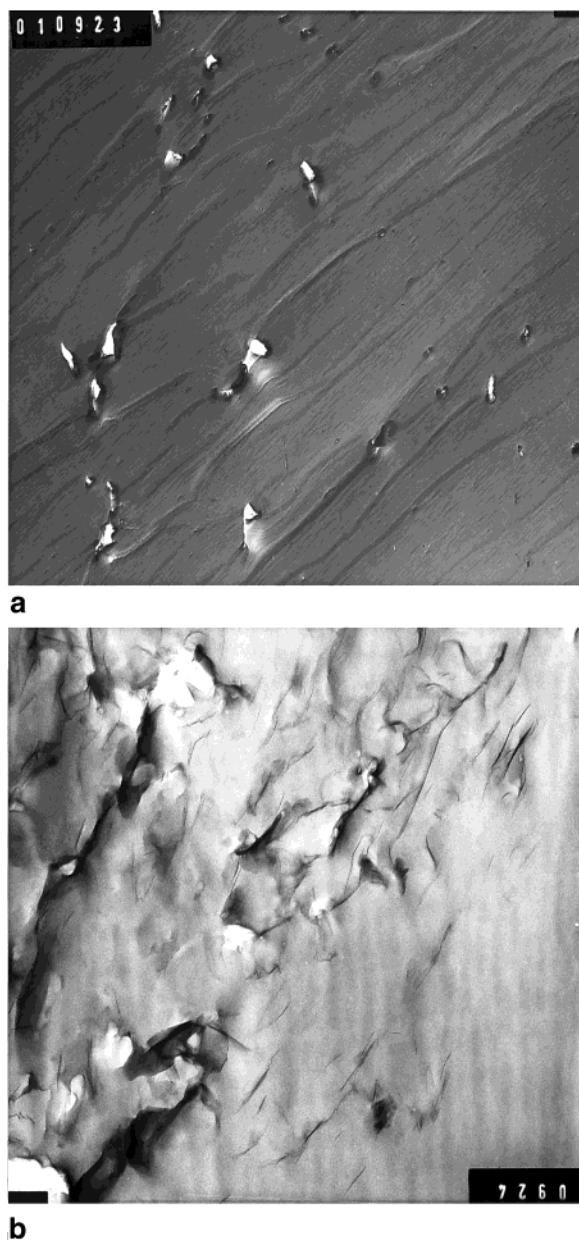


Figure 7. (a) TEM image of PS/VB16 emulsion-polymerized nanocomposite at low magnification. (b) TEM image of PS–VB16 suspension-polymerized nanocomposite at high magnification.

molecular weight. For PMMA, the molecular weights are higher and solution polymerization gives a higher value than that observed by bulk polymerization. In the presence of the clay, the molecular weights are invariably lower, and the results are roughly comparable regardless of the particular organically modified clay which is used. The one exception to this statement is for suspension polymerization where the presence of the clay has no effect on molecular weight. The largest decrease in molecular weight is seen in emulsion polymerization, the molecular weight of an emulsion-polymerized material is 60–90% lower in the presence of clay than in its absence. The clay can act as an additional micelle, thus polymerization occurs in more micelles and the molecular weight must decrease. There is a big difference between the behavior of PS and PMMA in solution polymerization. For PMMA, the molecular weights are lower in the presence of the clay

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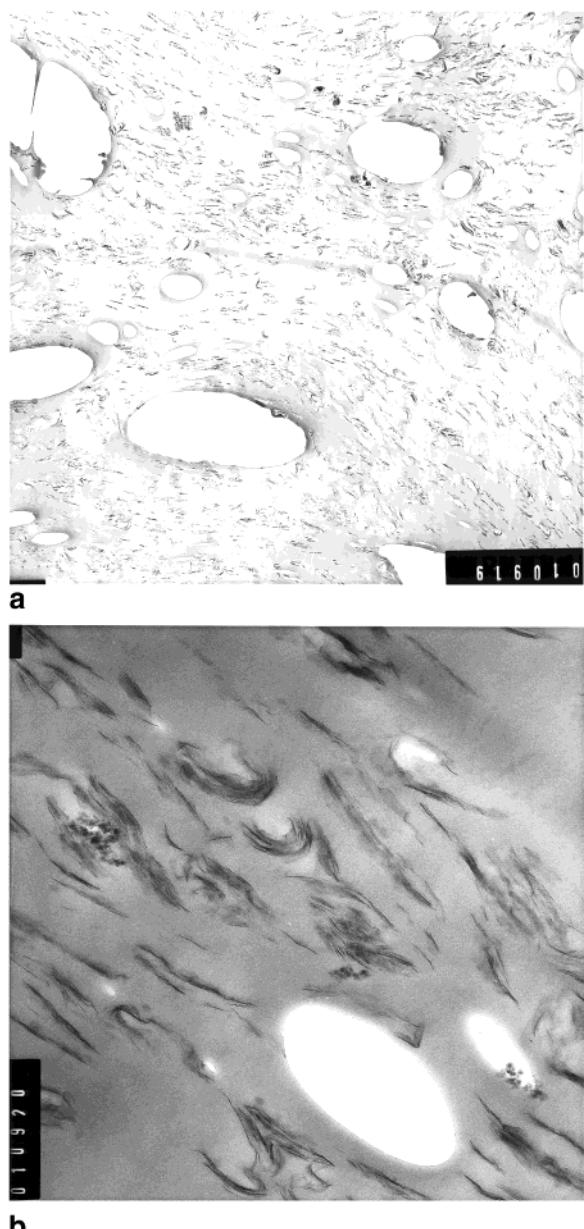


Figure 8. (a) TEM image of PMMA–VB16 suspension-polymerized nanocomposite at low magnification. (b) TEM image of the PMMA–VB16 suspension-polymerized nanocomposite at high magnification.

Table 1. Molecular Weight ($\times 10^{-4}$) from Viscosity Measurements

	bulk	solution	suspension	emulsion
PS	7.5	1.6	14.3	147.4
PS–VB16	11.7	5.1	8.4	35.0
PS–10A	8.5	4.3	12.2	34.3
PMMA	7.3	19.4	49.4	221.0
PMMA–VB16	13.4	3.9	50.5	31.5
PMMA–10A	7.4	3.8	50.1	85.1

but they are higher for PS in the presence of clay. A possible explanation is that both ammonium salts on the clays contain aromatic rings, these rings would be expected to better interact with styrene than with methacrylate, and this may enhance propagation of the polymerization.

Thermogravimetric Analysis (TGA). Table 2 provides TGA data for the polymer and nanocomposites. The data includes the temperature at which 10% mass

is lost, indicative of the onset temperature of the degradation, the temperature at which 50% mass is lost, a measure of the course of the degradation, and the fraction which is not volatile at 600 °C, labeled as char. One thing that is immediately clear from examining these data is the lack of consistency. For PS nanocomposites, compared to PS prepared by the same technique, the onset temperature of the degradation increases for bulk polymerization, decreases for solution polymerization, is slightly increased for suspension polymerization, and does not change for emulsion polymerization. If one includes the changes that occur in the temperature at which 50% mass loss occurs, the temperature for either 10% or 50% or both increases for all but solution polymerization. As expected, there is an amount of nonvolatile residue still present at 600 °C, which may be attributed to the clay residues. For PMMA systems, there is an increase for bulk, solution and emulsion, but no change for suspension polymerization. For PMMA, there is an increased temperature of the degradation at some stage for all but the suspension polymerization. In previous studies of PS nanocomposites, the formation of a nanocomposite always leads to an increase in the onset temperature of the degradation and this calls into question the exact state of the PS solution-polymerized material. For PMMA, one must question suspension polymerization. These data are directly available for the PMMA–VB16 suspension from the TEM image reported earlier and a mixed intercalated–exfoliated material is produced. In some cases the formation of a nanocomposite may yield some change in TGA properties, as previously reported for polystyrene systems from this laboratory,^{4,5,12} while in other cases, there is no change in TGA behavior.¹⁹ TGA behavior is not an indicator of nanocomposite formation nor of the type of nanocomposite which has been formed.

Mechanical Properties. The mechanical properties, percent elongation, tensile modulus, and Young's modulus, of the nanocomposites have been assayed, and the results are shown in Tables 3 and 4; we have been unable to obtain these data for the solution-polymerized materials because the samples are too brittle.

It must be emphasized that the values reported in this work are obtained for the polymers and nanocomposites without any processing aids or other additives. Elongation at break has not been extensively studied, but there is normally a decrease upon nanocomposite formation. This has been observed in these studies for all modes of preparation and for both ammonium cations.

For PMMA, the tensile strength is, in general, higher for the nanocomposites than for the virgin polymer and Young's modulus is usually higher. Young's modulus is higher for the VB16 nanocomposites, which are more likely to be exfoliated, than for the intercalated 10A nanocomposites. For PS there is some variability in both tensile strength and in Young's modulus. Young's modulus is lower for the exfoliated nanocomposites than for the virgin polymer and the intercalated nanocomposite. This may be related to the decrease in molecular weight observed for the nanocomposites. Previous literature¹⁸ suggests that Young's modulus is higher for exfoliated nanocomposites than for the virgin polymer

Table 2. TGA Results for PS and PMMA and Their Nanocomposites

	bulk			solution			suspension			emulsion		
	10%	50%	char	10%	50%	char	10%	50%	char	10%	50%	char
PS	351	404	0	374	423	0	409	433	2	393	423	0
PS-VB16	408	444	6	351	412	5	419	441	6	390	454	10
PS-10A	396	435	4	348	407	7	424	449	4	393	448	10
PMMA	236	350	1	260	343	3	276	334	5	258	308	8
PMMA-VB16	269	371	6	233	357	8	272	334	8	301	348	8
PMMA-10A	244	300	5	256	349	16	274	341	12	278	325	8

Table 3. Mechanical Properties of PMMA-Clay Nanocomposites

sample ID	tensile strength (MPa)	Young's modulus (GPa)	elongation (%)
PMMA bulk	12.2	0.92	3.8
PMMA-VB16 bulk	9.8	1.06	1.2
PMMA suspension	19.8	1.77	2.7
PMMA-VB16 suspension	22.8	1.81	1.4
PMMA-10A suspension	23.1	1.13	0.6
PMMA emulsion	19.7	0.93	1.9
PMMA-VB16 emulsion	23.9	1.40	1.5
PMMA-10A emulsion	20.7	0.94	1.3

Table 4. Mechanical Properties of PS-Clay Nanocomposites

sample ID	tensile strength (MPa)	Young's modulus (GPa)	elongation (%)
PS bulk	5.9	0.74	1.1
PS-VB16 bulk	8.1	1.14	0.8
PS-10A bulk	3.5	1.00	0.4
PS suspension	6.9	1.30	2.9
PS-VB16 suspension	7.3	0.90	1.5
PS-10A suspension	9.4	1.44	0.7
PS emulsion	11.2	1.08	7.2
PS-VB16 emulsion	12.5	1.05	1.6
PS-10A emulsion	8.1	0.95	0.8

and intercalated nanocomposites. This is especially true for polyamide-6 and polypropylene. Noh and Lee⁷ have reported both stress and strain for polystyrene nanocomposites prepared by emulsion polymerization, using the sodium clay. They observe that the stress at maximum load is decreased for the nanocomposite relative to the virgin polymer, however Young's modulus increases. For PMMA, Lee and Jang¹⁶ show that both the stress at maximum load and Young's modulus increase for the nanocomposites relative to the virgin polymer. It has been suggested that the modulus increases as the amount of exfoliation increases.¹⁸ These results call into question the idea that the strength depends on the extent of exfoliation and, indeed, the entire question of the variation of mechanical properties of nanocomposites. It is certainly not true from these results that exfoliated systems have a higher tensile strength than other systems.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) is used to measure the response of a material to a cyclic deformation; three main parameters may be obtained, the storage modulus (E'), corresponding to the elastic response to the deformation, the loss modulus (E''), the plastic response to the deformation, and their ratio, $\tan \delta$, useful to obtain information on transitions involving mobility, such as the glass transition temperature. There has not been a great deal

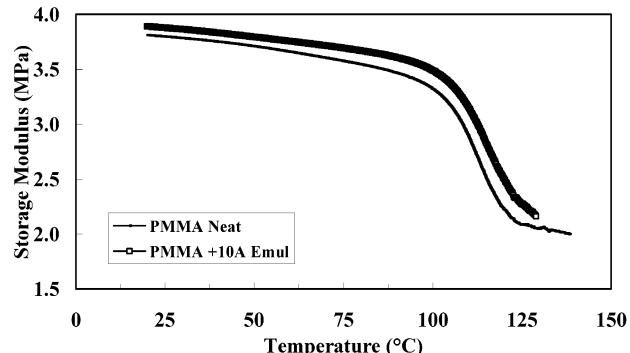


Figure 9. Storage modulus of PMMA-clay nanocomposites via emulsion polymerization.

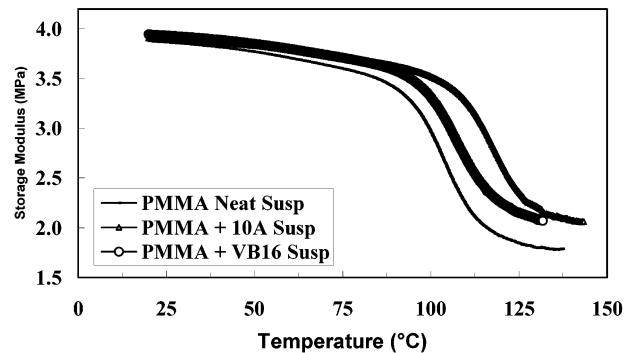


Figure 10. Storage modulus of PMMA-clay nanocomposites via suspension polymerization.

of DMA work in nanocomposites. Noh and Lee have shown that the storage modulus does not change significantly for an emulsion-polymerized polystyrene nanocomposite.⁷ The variations in the storage modulus as a function of temperature obtained in this study are shown in Figures 9 and 10 for PMMA nanocomposites. It is clear that the storage modulus is higher for the nanocomposites than for the virgin material, unlike what was seen by Noh and Lee. Until more data are available on these polymers, it would be rash to attempt to draw conclusions.

Conclusions

When the organic treatment that has been applied to a clay incorporates a polymerizable double bond, the possibility to obtain an exfoliated nanocomposite are increased. However the particular preparative technique that is used has a large effect on the type of material that may be obtained. Solution polymerization of both methyl methacrylate and styrene, in the presence of a clay containing a double bond or one without such a double bond, yields only intercalated systems. Emulsion, suspension and bulk polymerization can yield either exfoliated or intercalated nanocomposites, de-

pending upon the particular organic treatment that has been used.

Neither the onset temperature of thermal degradation nor mechanical properties can accurately predict the formation or the nature of PS and PMMA nanocomposites.

Acknowledgment. This work was performed under the sponsorship of the U.S. Department of Commerce,

National Institute of Standards and Technology, Grant 70NANB6D0119. We thank Peggy Miller, University of Texas Health Center in San Antonio, TX, and Ryan Dennis, Southern Clay Products, for obtaining the transmission electron micrographs. The assistance of Paul Adair and Hugh Yang at Brady USA in obtaining the mechanical properties is gratefully acknowledged.

CM011656+