Synthesis and Characterization of PMMA Nanocomposites by Suspension and Emulsion Polymerization

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ABSTRACT: PMMA-layered silicate nanocomposites were prepared by in-situ suspension polymerization and emulsion polymerization. For the suspension polymerization, the silicate layers were dispersed individually in water, and we speculate that they are adsorbed on the surface of monomer droplets. For the emulsion polymerization, the nanocomposite was obtained by adding an aqueous dispersion of layered silicate into the polymer emulsion. Wide-angle X-ray diffraction (WAXD) and atom force microscopy (AFM) were used to characterize the structures of the nanocomposites. Analysis of samples from emulsion and suspension polymerization was consistent with an exfoliated structure; after melt pressing, WAXD analysis indicated that both intercalated and exfoliated structures were observed. The exfoliated structure was preserved when organic modifiers that produced tethered polymer chains were used. Compared to a PMMA macrocomposite, the nanocomposites prepared by these methods display glass transition temperatures that are up to 15 °C higher and thermal degradation temperatures that are up to 60 °C higher.

Introduction

Nanocomposites[1−3] often exhibit physical and chemical properties that are dramatically different from conventional microcomposites.[3−5] Research is often focusing on layered smectite clays as the reinforcing part of the matrix.[6−21] These polymer-layered silicate nanocomposites can exhibit increased modulus,[6−8] decreased thermal expansion coefficients,[7] reduced gas permeability,[7,9] increased solvent resistance,[10] and enhanced ionic conductivity[11] when compared to the polymers alone. A key discovery in the field was a nylon 6-clay hybrid.[2,6,12] By replacing the hydrophilic Na^+ and Ca^+ cations of native montmorillonite with a more hydrophobic onium ion, researchers at Toyota initiated the polymerization of ϵ-caprolactam in the interlayer gallery of montmorillonite. For a nanocomposite containing 4.2 wt % montmorillonite, the modulus doubled, the strength increased more than 50%, and the heat distortion temperature increased 80 °C. Several other organic−inorganic nanocomposites have been reported.[7,9,13,21] In earlier work from these laboratories, we reported the formation of bisphenol A polycarbonate nanocomposites by performing an in-situ ring-opening polymerization of carbonate cyclic oligomers in the presence of organically modified silicates (OLS).[22]

In general, two idealized polymer-layered silicate structures are possible: *intercalated* and *exfoliated*. The greatest property enhancements are observed for exfoliated nanocomposites. These consist of individual nanometer-thick silicate layers suspended in a polymer matrix resulting from extensive polymer penetration and delamination of the silicate crystallites. In contrast, polymer penetration resulting in finite expansion of the silicate crystallites produces intercalated hybrids consisting of well-ordered multilayers with alternating polymer/silicate layers and a repeat distance of a few nanometers. In reality, many systems fall short of the idealized exfoliated morphology. More commonly, *partially exfoliated* nanocomposites, containing small stacks of 2−4 layers uniformly dispersed in the polymer medium, are obtained. Often, the layer correlation is not detectable by conventional WAXD, and observation relies on transmission electron microscopy (TEM).[23] Nevertheless, these systems may still exhibit substantial physical property enhancements.

Poly(methyl methacrylate) (PMMA) is an important member in the family of polyacrylic and methacrylic esters. PMMA has several desirable properties, including exceptional optical clarity, good weatherability, high strength, and excellent dimensional stability. PMMA nanocomposites offer the potential for reduced gas permeability, improved physical performance, and increased heat resistance, without a sacrifice in optical clarity. We observed that the optical clarity of polycarbonate was not diminished significantly in silicate nanocomposites.[22] The literature contains several reports on the interaction of PMMA and layered silicates. Early work focused on the effect of the layered silicate on MMA polymerization behavior rather than the structure and properties of the final hybrid.[26,27] Biasci and co-workers[19] obtained intercalated PMMA/clay hybrid structures by two methods: (1) polymerization of MMA with montmorillonite modified by 2-(*N*-methyl-*N*,*N*-diethylammonium iodide)ethyl acrylate and (2) direct interaction of MMA copolymers (which contained pendent ammonium groups) with an OLS. Chen and co-workers[24] and Okamoto and co-workers[27] prepared partially exfoliated PMMA nanocomposites by the bulk polymerization of MMA in the presence of an OLS. Dietsche and co-workers[28] prepared an amidinium-functionalized PMMA (M_n = 3200 g/mol) and used this material as an organic modifier for fluorohectorite. Effective exfoliation was observed using this oligomeric modifier in the bulk polymerization of MMA and MMA/comonomer mixtures. This result is consistent with the view that tethered polymer chains promote exfoliation. We are aware of two reports that describe the preparation of PMMA/clay hybrids by emulsion polymerization of MMA.[20,29] In both reports, the layered silicate was present during polymerization. Lee and Jang[20] observed only intercalated structures. Recent work by Bandyopadhyay, Giannelis, and Hsieh[29] demonstrated formation of an exfoliated PMMA nanocomposite which displayed a 6 °C increase in T_g and 50 °C increase in the decomposition temperature.

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In this paper, we report the synthesis of PMMA-layered silicate nanocomposites by suspension polymerization and emulsion polymerization. To the best of our knowledge, there are no reports of nanocomposite formation by suspension polymerization. Although there have been previous reports of PMMA/clay nanocomposite formation via emulsion polymerization, our experimental method is substantially different.

Experimental Section

Materials. The layered silicates (Gelwhite GP and Laponite XLS) used in this study were supplied by Southern Clay Products. Methyl methacrylate (MMA) was purchased from Aldrich and was distilled from CaH_2. Other inorganic and organic materials were commercially available and used as received.

Preparation of PMMA Macrocomposite. The desired amount of PMMA powder and unmodified montmorillonite were mechanically mixed and heated to 180 °C under pressure.

Suspension Polymerization with Alkyl Chain Modified Layered Silicate. 1 g of layered silicate was added to 100 mL of argon-purged distilled water. The dispersion was heated to 60 °C with mechanical stirring overnight. 20 wt % (based on silicate) of *n*-decyltrimethylammonium chloride (**1**) in 10 mL of H_2O was added dropwise followed by a mixture of 20 mL of MMA monomer and 0.094 g (0.3 mol %, 0.5 wt %, based on MMA) of AIBN initiator. The suspension got more turbid after the addition of organic modifier but did not precipitate. The polymerization was carried out at 80 °C overnight with vigorous stirring. After cooling, 100 mL of methanol was added, and the precipitate was filtered, washed with methanol and water, and then dried in vacuo at 60 °C.

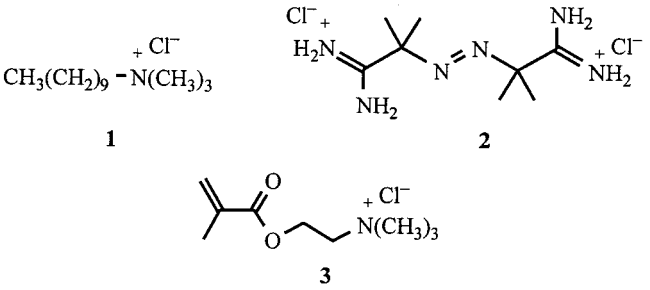
Suspension Polymerization with Initiator (2) Modified Silicate. 1 g of layered silicate was added to 90 mL of argon-purged distilled water. The dispersion was heated to 60 °C with mechanical stirring for overnight. 0.47 g (0.9 mol %, 2.5 wt % based on MMA) of 2,2′-azobis(isobutylamidine hydrochloride) (AIBA) (**2**) in 10 mL of distilled water was added dropwise; after 0.5 h, 20 mL of MMA monomer was added to the dispersion. The polymerization was carried out at 80 °C overnight with vigorous stirring. After cooling, 100 mL of methanol was added, and the precipitate was filtered, washed with methanol and water, and then dried in vacuo at 60 °C.

Suspension Polymerization with Comonomer (3) Modified Silicate. 1 g of layered silicate was added to 90 mL of argon-purged distilled water. The dispersion was heated to 60 °C with mechanical stirring for overnight. 0.3 g (30 wt % based on silicate) of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (**3**) (75 wt % solution in water) diluted in 10 mL of H_2O was added dropwise. A mixture of 0.094 g (0.3 mol %, 0.5 wt %, based on MMA) of AIBN and 20 mL of MMA monomer was added to the dispersion. The polymerization was carried out at 80 °C overnight with vigorous stirring. After cooling, 100 mL of methanol was added, and the precipitate was filtered, washed with methanol and water, and then dried in vacuo at 60 °C.

PMMA-Layered Silicate Nanocomposite by Emulsion Polymerization. A mixture of 20 mL of MMA and 100 mL of distilled water was bubbled with argon for 1 h. The surfactant (0.1 g of *n*-decyltrimethylammonium chloride (**1**) or 0.15 g of [2-(methacryloyloxy)ethyl] trimethylammonium chloride (**3**)) and 0.094 g (0.18 mol %, 0.5 wt % based on MMA) of AIBA initiator were added. The polymerization was carried out at 80 °C for 12 h with stirring. After the temperature was decreased to 23 °C, a suspension of layered silicate in distilled water was added dropwise into the emulsion. The resulting polymer composite was collected by centrifugation, the product was washed with distilled water and dried in vacuo at 60 °C overnight.

Characterization and Methods. Melt pressing was performed using a hydraulic press; samples were treated at 180 °C for 10 min. Wide-angle X-ray diffraction (WAXD) analysis was performed on Rigaku diffractometer equipped with a rotating-anode generator system using Cu Kα radiation. The slit width was 0.15 mm. The operating current was 150 mA, and the voltage was 50 kV; the scanning rate was 1°/min. 2D WAXS experiments were conducted on Rigaku 18 kW rotating-anode generator equipped with an image plate as the detector, and the detector was calibrated using silicon powders with 2θ being 28.4° under Cu Kα radiation. The air scattering was subtracted. Thermogravimetric analysis (TGA) was performed on a Hi-Res TGA 2950 thermogravimetric analyzer (TA instruments) over the temperature range 23−800 °C at a rate of 20 °C/min. Differential scanning calorimetry was performed on a DSC 2910 differential scanning calorimeter (DuPont Instruments) from −80 to 150 °C at a heating (and cooling) rate of 10 °C/min. Atomic force microscopy (AFM) was performed in tapping mode using an Autoprobe M5 (Park Scientific Instruments) under ambient conditions with a commercial Ultralever silicon probe and a V-shape cantilever. The soft tapping and on resonance technique was used in AFM. Molecular weight analysis was performed by gel permeation chromatography (GPC) with a Waters 510 pump, two PLgel (Polymer Laboratories) mixed D columns (5 u), and a Waters 410 differential refractometer. Molecular weights were calibrated by comparison to narrow MWD PMMA samples using eight standards covering the molecular weight range of 2900−74 500 g/mol (Polymer Laboratories). Data analysis was performed with the E-Z Chrom software package.

Scheme 1. Structure of Onium Ions Used as Modifiers for the Layered Silicate



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Results

PMMA-Layered Silicate Nanocomposites via Suspension Polymerization. Suspension polymerization is a commonly used method for free radical polymerization of vinyl monomers. Here, we have used organically modified silicates (OLS) as suspension stabilizers.[29] The use of inorganic materials like silicates in suspension polymerization is well-known. We used three different modifiers (Scheme 1) for the layered silicate (either montmorillonite or laponite): *n*-decyltrimethylammonium chloride (**1**), 2,2′-azobis(isobutylamidine hydrochloride) (**2**), and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (**3**). The typical polymerization procedure first involves the dispersion of the layered silicate in water followed by addition of the organic modifier. Subsequently, a mixture of MMA and AIBN initiator was added to the aqueous phase with vigorous stirring. A typical volume ratio of water:MMA was 5:1. The final products were analyzed by GPC, WAXD, TGA, DSC, and AFM. For comparison, we also prepared a conventional macrocomposite of PMMA and silicate by physical mixing of the two materials followed by heat treatment under pressure.

For a 5% PMMA nanocomposite prepared with the silicate modified by **1**, the WAXD (Figure 1) shows the significant difference between the structure of the sample before and after melt pressing. In contrast, PMMA samples prepared from the OLS made with either the azo-modifier **2** or the polymerizable modifier **3** exhibited no feature peak in WAXD before and after melt pressing (Figure 2).

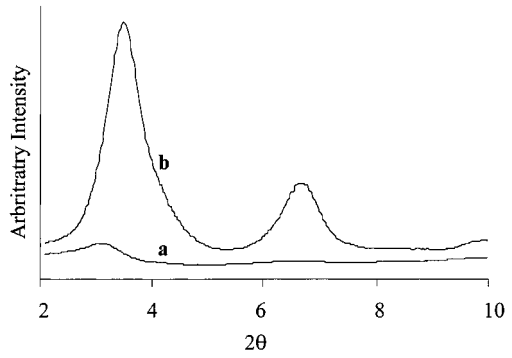

Figure 1. WAXD analysis of PMMA nanocomposite prepared by suspension polymerization with 5 wt % montmorillonite/**1**: (a) before melt pressing, (b) after melt pressing.

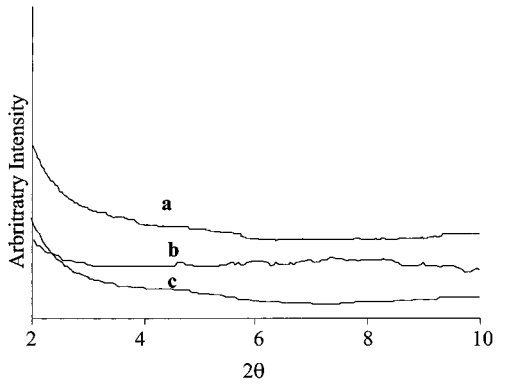

Figure 2. WAXD analysis of PMMA nanocomposites prepared by suspension polymerization: (a) nanocomposite with 5 wt % montmorillonite/**2** (before melt pressing); (b) nanocomposite with 5 wt % montmorillonite/**2** (after melt pressing); (c) nanocomposite with 5 wt % montmorillonite/**3** (after melt pressing).

Table 1. Properties of PMMA Nanocomposites

OLS[a,b]	method	T_g, °C	T, °C for 20 wt % loss	$M_w \times 10^3$, g/mol
montmorillonite[c]	melt intercalation	100	279	330
montmorillonite/**1**	suspension	100	294	264
montmorillonite/**2**	suspension	114	329	367
montmorillonite/**3**	suspension	105	301	475
laponite/**3**	suspension	106	303	482
montmorillonite + **1**	emulsion	111	314	587
montmorillonite + **3**	emulsion	115	341	565
laponite + **3**	emulsion	106	303	565

[a] OLS = organically modified layered silicate; for the suspension polymerization, the OLS was prepared prior to polymerization; for the emulsion polymerization, the organic modifier was used as a surfactant and the silicate was added in a postpolymerization process. [b] 5 wt % OLS. [c] Unmodified montmorillonite.

DSC analysis of the PMMA macrocomposite revealed a T_g at 100 °C while DSC analysis of the PMMA nanocomposites indicated elevated glass transition temperatures (T_g); see Table 1. Figure 3 shows the TGA results for the PMMA macrocomposite and several suspension nanocomposites. The onset of thermal decomposition for the nanocomposites shifted to higher temperatures. To augment our WAXD analysis of the nanocomposite structure, we studied several samples using AFM. The phase images of intercalated (nanocomposite prepared using montmorillonite/**1**) and exfoliated (nanocomposite prepared using montmorillonite/**2**) structures are shown in Figure 4.

PMMA-Layered Silicate Nanocomposites by Emulsion Polymerization. The experimental procedure for PMMA nanocomposite formation by emulsion polymerization differs significantly from the suspension process. A conventional emulsion polymerization was conducted using a 5:1 (v/v) ratio of water:MMA and a water-soluble azo initiator (**2**). Two different surfactants were used: *n*-decyltrimethylammonium chloride (**1**) or [2-(methacryloyloxy)ethyl]trimethylammonium chloride (**3**). Following polymerization, an aqueous dispersion of layered silicate was added dropwise to the emulsion. The resulting product was collected by centrifugation and analyzed. Table 1 contains molecular weight values for some of the samples prepared in this study; the observed values are comparable to the commercial sample of PMMA used to prepare the macrocomposite.

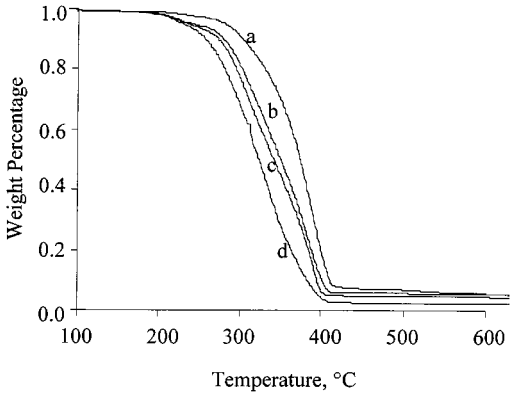

Figure 3. TGA traces of PMMA nanocomposites prepared by suspension polymerization: (a) nanocomposite with 5 wt % montmorillonite/**2**; (b) nanocomposite with 5 wt % montmorillonite/**3**; (c) PMMA macrocomposite; (d) nanocomposite with 5 wt % montmorillonite/**1**.

Like the PMMA nanocomposites prepared by suspension polymerization, the WAXD of nanocomposites from emulsion polymerization was featureless before melt pressing. But a strong peak was shown in the WAXD of the emulsion nanocomposite prepared using **1** as the surfactant after melt pressing (Figure 5); however, no significant change was observed in WAXD analysis of the emulsion nanocomposite when surfactant **2** was used. The TGA analysis of these nanocomposites is shown in Figure 6. The onset of thermal decomposition for the nanocomposites shifted to higher temperatures in Figure 6; a summary of TGA and DSC data is given in Table 1.

Discussion

For the suspension polymerization, the layered silicate was dispersed into the water first and organically modified by the addition of an alkylammonium salt (**1**−**3**). After addition of monomer and initiator, we speculate that delaminated OLS was adsorbed to the monomer droplets. Figure 1 shows the WAXD of PMMA nanocomposites prepared by a suspension polymerization with a conventional OLS (montmorillonite/**1**). A weak, broad peak was observed in the WAXD before melt pressing. We suspect that this weak signal may be caused by nonadsorbed silicate layers which may have aggregated and re-formed a multilayered structure with intercalated PMMA chains. Multilayered silicate absorbed on the surface is also a possibility. After melt pressing at 180 °C (which is above flowing temperature of PMMA), the position of the basal reflection did not change significantly (d = 2.85 nm to d = 2.62 nm), but the intensity increased and a secondary reflection (d002) appeared. This could be caused by the orientation of the

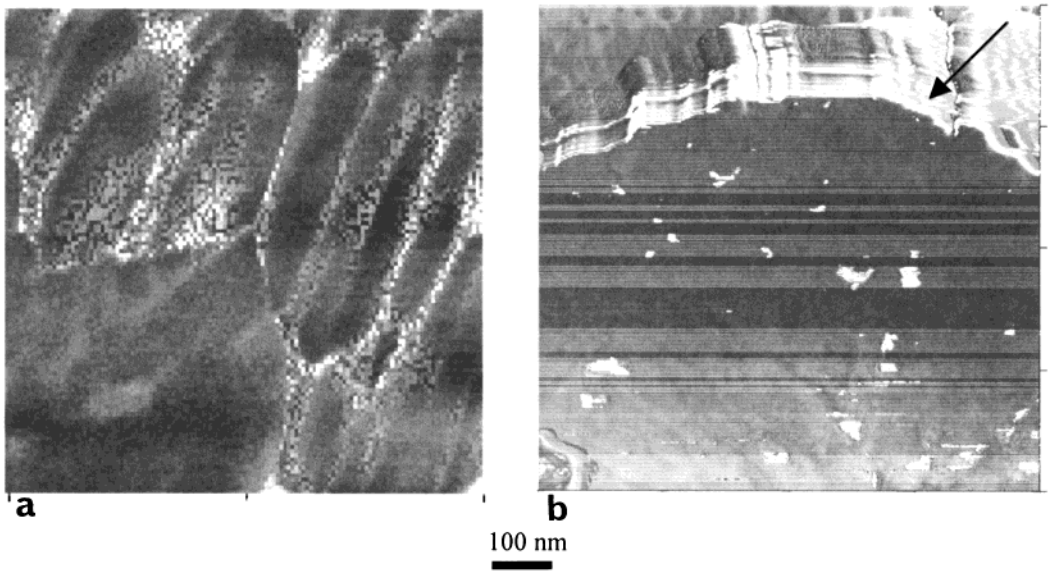

Figure 4. AFM phase images of PMMA/clay hybrids prepared by suspension polymerization: (a) exfoliated nanocomposite prepared using montmorillonite/**2**; (b) intercalated nanocomposite prepared using montmorillonite/**1**.

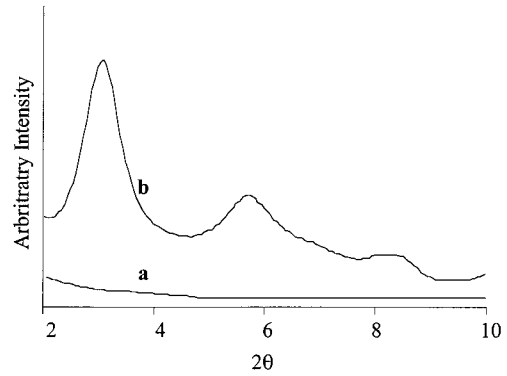

Figure 5. WAXD analysis of PMMA nanocomposites prepared by emulsion polymerization: (a) nanocomposite with 5 wt % montmorillonite + **3**; (b) nanocomposite with 5 wt % montmorillonite + **1**.

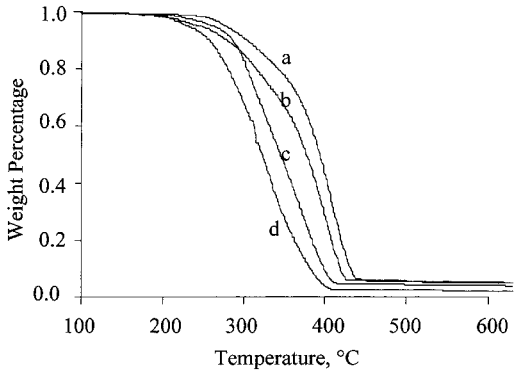

Figure 6. TGA traces of PMMA nanocomposites prepared by emulsion polymerization: (a) nanocomposite with 5 wt % montmorillonite + **2**; (b) nanocomposite with 5 wt % montmorillonite + **1**; (c) nanocomposite with 5 wt % laponite + **2**; (d) PMMA macrocomposite.

silicate layers parallel to the pellet surface after the melt pressing. The 2D-WAXD on the cross section of the sample confirmed this explanation (Figure 7). Silicate layers that have aggregated and re-formed a multilayered structure might also contribute to the change in the WAXD peak.

For an OLS modified by with an initiator cation (**2**) or comonomer cation (**3**), WAXD analysis indicated that

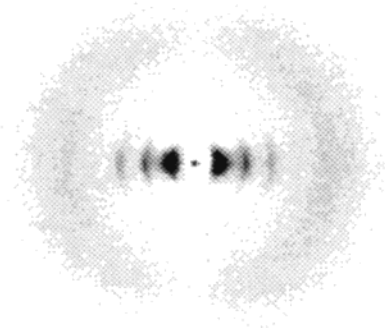

Figure 7. 2D WAXD analysis on the cross section of PMMA nanocomposite prepared by suspension polymerization with 5 wt % montmorillonite/**1** after melt pressing.

the exfoliated structure was preserved after melt pressing (Figures 2 and 4). For nanocomposites prepared using an OLS modified with **2** or **3**, the PMMA chains will become tethered to the surface. Tethering of polymer chains to a layered silicate is a key concept for many exfoliated structures that are thermodynamically stable. Theoretical work by Balazs and co-workers[30] has shown that tethered polymer chains change the phase diagram for nanocomposites. In addition, there are several experimental studies[2,6,12,16] that confirm the importance of tethered polymer chains to the preservation of an exfoliated structure including the early work on nylon-6 by researchers at Toyota[2,6,12] and the recent PMMA nanocomposite work reported by Dietsche and coworkers.[28] Polymer chains that are tethered to the silicate layers hinder the aggregation of the silicate layers and help preserve the exfoliated structure. For matrix polymers that possess a high melt viscosity or that are cross-linked, the exfoliated structure may also be preserved due to kinetics.

AFM was used to augment WAXD analysis of nanocomposite structures. Figure 4b shows the phase image of the nanocomposite prepared using montmorillionite/**1**, after the sample had been subjected to melt pressing. This image clearly reveals a multilayered structure, consistent with an intercalated hybrid structure and in accord with the WAXD analysis. For the nanocomposite prepared using montmorillionite/**2**, the AFM phase

image, after the sample was subjected to melt pressing, is shown in Figure 4a. The image reveals individual silicate sheets which confirms the exfoliated structure that was indicated by WAXD analysis. The AFM image of the exfoliated structure shown in Figure 4a is similar in appearance to a recently published transmission electron micrograph of an exfoliated polystyrene nanocomposite.[31]

From the TGA study, both intercalated and exfoliated PMMA nanocomposites showed higher decomposition temperatures when compared to a macrocomposite (Table 1). The nanocomposite with OLS prepared from montmorillonite/**2** showed a 50 °C increase in decomposition temperature for 20% weight loss; the intercalated nanocomposites exhibited a 15 °C increase for the same weight loss. An increase in T_g of 5−14 °C was observed for the exfoliated PMMA nanocomposite prepared using **2** or **3** as silicate modifiers. A negligible increase in T_g was observed for both the PMMA macrocomposites and the intercalated nanocomposite prepared using **1** as an organic modifier. The origin of these effects on T_g and decomposition is not clear and remains a subject of investigation in our laboratories. The increase in the decomposition temperature may be associated with barrier properties, although slower heating rates did not affect our results significantly.

Clays are known to be free-radical scavengers and traps.[33] The clay minerals inhibit the free-radical reactions by absorption of the propagating or initiating radicals to the Lewis acid surface. The radicals then either undergo bimolecular termination or form carbocations by electron transfer to the Lewis acid site. Minerals containing higher amounts of aluminosilicates are more effective inhibitors. From previous studies[33] polymerization of MMA with the presence of clay (kaolin) increased the molecular weight from 887K (without clay) to 944K (kaolin) and 912K (polyphosphated kaolin). Montmorillonite was less effective than kaolin. Since this small MW change on polymer will not affect the properties of the composites significantly, we did not study how the clay affects the polymerization in detail.

For the emulsion polymerization, the first step is exactly the same as conventional emulsion polymerization. The silicate (which is not organically modified) is added in a postpolymerization step. Because the latex particles have cationic surface charges and the silicate layers have anionic charges, electrostatic forces promote an interaction between the silicate and polymer particles. The practical advantages of this method are obvious: the silicate can be used without modification, and it is simple to vary the silicate loading. Another advantage of this method is that the silicate is combined with the polymer at room temperature, which reduces the problem of polymer degradation during a melt intercalation process. The organic modifiers used for the suspension process are used as surfactants in the emulsion process.

If the nonfunctional cationic surfactant **1** is used in the emulsion polymerization, WAXD indicated that the exfoliated structure was not preserved after melt processing (Figure 5). However, if the polymerizable surfactant **3** is used in the emulsion polymerization, exfoliated PMMA nanocomposites can be prepared that remain stable during melt processing; this nanocomposite displayed a 15 °C increase in T_g and a 62 °C increase in the temperature for 20% weight loss. Bandyopadhyan and co-workers[29] observed a 6 °C increase in T_g and a 50 °C increase in decomposition temperature for a PMMA nanocomposite prepared by an emulsion process when the silicate was present during the polymerization.

This work has demonstrated simple polymerization methods for the formation of thermodynamically stable, exfoliated PMMA nanocomposites. One of our interests in PMMA as a matrix was the potential to improve properties without a sacrifice in optical properties. Montmorillonite has the disadvantage of adding color to the sample. To overcome this problem, we prepared nanocomposites with the synthetic clay, laponite. One difference between montmorillonite and laponite is the average size, which is 1000 nm for montmorillonite and 25 nm for laponite.[32] Because of the very small size of the laponite layers, it only displays an extremely weak and broad peak on WAXD. The structures of the laponite nanocomposites are difficult to characterize by WAXD. Laponite PMMA nanocomposites retained good optical properties as deduced by visual observation, but the improvements in decomposition temperature and in T_g were not as high as the montmorillonite nanocomposites; see Table 1.

Conclusion

PMMA nanocomposites were prepared by in-situ suspension polymerization and emulsion polymerization. WAXD analysis indicated that exfoliated structures can be obtained by both methods. The exfoliated structure remained stable during melt processing for samples prepared using organic modifiers **2** and **3**. Organic modifiers **2** and **3** produced tethered polymer chains, which we believe is an important concept for the synthesis of thermodynamically stable, exfoliated nanocomposites. For the emulsion polymerization, unmodified silicate is added in a postpolymerization step, which has several practical advantages. TGA and DSC analyses showed significant improvements in the thermal properties of the PMMA nanocomposites. For the exfoliated PMMA nanocomposites, 5−15 °C increases in T_g and up to 60 °C increases in decomposition temperatures were observed.

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