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COPOLYMERS AND BLENDS OF METHYL ACRYLATE AND ACRYLIC ISOBUTYL POSS NANOMATERIALS

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Introduction

Polymeric hybrid materials have attracted great interest recently due to their performance relative to their non-hybrid counterparts.[1] Interest in these hybrid polymers has increased significantly due to the enhanced thermal properties and reinforcing properties these materials possess.[2] As hybrid materials are copolymers based on inorganic and organic comonomers, they display enhanced properties by bridging the range of properties between two dissimilar types of materials.[3] These hybrid materials generally contain an inorganic phase, which may serve as a cross linker, bound (often covalently) with an organic phase. Based on the relative amounts of the inorganic and the organic components, the properties of the resulting hybrid polymer are intermediate between those of the inorganic polymer and the organic polymer.[3]

Polyhedral Oligomeric Silsesquioxanes (POSS) macromers usually have an inorganic, silica-like core surrounded by eight organic groups, of which seven are inert groups that generally aid in solubilization, and one is a reactive functional group.[3] These POSS macromers are "cage-like" materials generally and can be represented by $(RSiO_{1.5})_8$.[3] Polymerization, at the single reactive site, can be done using various polymerization techniques, that result in a polymer containing the nanosized inorganic POSS clusters, pendant to the organic polymer backbone.[3] POSS macromers, with acrylate or methacrylate functional groups as the reactive groups, have been copolymerized with various acrylic comonomers like methyl methacrylate (MMA) and butyl acrylate (BA). The properties of the resulting copolymers have been studied and reported.[2,4]

This work consists of two parts. The first part involves synthesis of copolymers of methyl acrylate (MA) and acrylo isobutyl POSS (IB-POSS), with increasing levels of POSS loading in the copolymer matrix; the second part involves the physical blending of the IB-POSS macromers into a poly(methyl acrylate) (PMA) matrix, and comparing the thermal properties of the copolymers with those of the blends. This POSS has an "acrylo" (-CH=CH$_2$) functional group, on one corner of the cage, as the reactive polymerizable functional group, while the isobutyl groups, as solubilizing groups, are on the other seven corners of the cage.

Experimental

Copolymer Synthesis. Methyl acrylate (MA) (Lancaster Synthesis Inc, 99%), was washed with 10% NaOH solution twice to remove the inhibitor, and then washed with distilled water three times, to remove the NaOH. The MA was then distilled from calcium hydride under reduced pressure. Acryloisobutyl POSS (IB-POSS) was obtained from Hybrid Plastics and was used as received. The copolymers with different POSS loadings were synthesized by atom transfer radical polymerization (ATRP).[2] The POSS content in the copolymer was varied by changing the POSS loading in the feed.

Characterization. The weight % of IB-POSS in the copolymer was determined using thermogravimetric analysis (TGA) (TA Instruments, New Castle, DE). Refractive index increments with concentration (dn/dc) of the copolymers, in tetrahydrofuran (THF), were measured with an Optilab DSP differential refractometer (Wyatt Technology, Santa Barbara, CA), from solutions of the concentration range of 0.1 to 3 mg/mL. Molecular masses of the copolymers were measured using gel permeation chromatography (GPC) in tetrahydrofuran (THF), using the Optilab DSP differential refractometer and a DAWN EOS light scattering detector (Wyatt Technology) at 690 nm. The glass transition temperatures (T$_g$s) were measured with a TA instruments model 2920 MDSC (New Castle, DE). Two heating scans and one cooling scan were taken from -40 to 175 ^{0}C, at a rate of 10 ^{0}C/min, with a modulation amplitude of $\pm$ 1 ^{0}C and a period of 60. The mass of the samples used for the DSC experiments was 7 to 15 mg.

Results and Discussion

The characterization results and the copolymer names are listed in Table 1. The thermal studies of the copolymers and blends were done using DSC and TGA. Figure 1 shows the DSC results for the copolymers with different POSS loadings. The T$_g$s of the bulk PMA and the PMA-co-POSS copolymers were estimated as the maximum in the derivative DSC curves.[5] The presence of a POSS moiety modifies the thermal properties and permits tailoring the polymer-softening temperature by changing the percentage of POSS in a copolymer formulation.[3] We observed this phenomenon from the DSC results of the copolymers shown in Figure 1. The values of T$_g$ for the bulk PMA and the PMA-co-POSS copolymers are listed in Table 2.
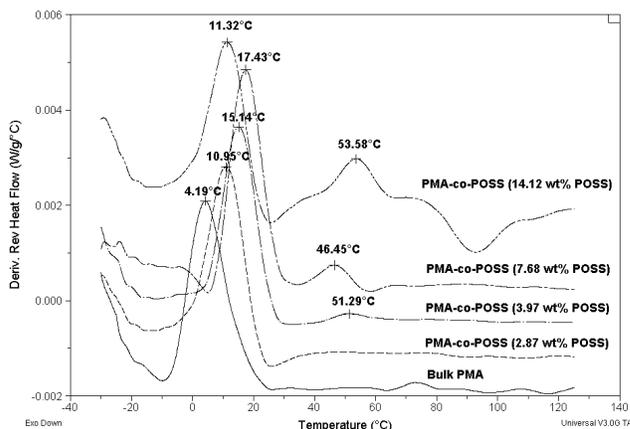

Figure 1. DSC curves for comparison of bulk PMA with PMA-co-POSS copolymers with increasing POSS loading.

Table 1. Characterization data for the PMA-co-POSS copolymers.

PMA-co-POSS copolymer name	Weight% POSS[a]	dn/dc (mL/g)	M_w (g/mol)	Polydispersity
C 21	2.87 %	0.077 ± 0.003	52,310	1.10 ± 0.04
C 26	3.97 %	0.106 ± 0.009	59,110	1.02 ± 0.03
C 27	7.68 %	0.274 ±0.004	10,210	1.04 ± 0.03
C 28	14.12 %	0.285 ±0.012	14,510	1.10 ± 0.03

[a] by TGA

Table 2. Glass transition temperatures of the PMA-co-POSS copolymers and bulk PMA.

Copolymer Sample	Peaks in derivative DSC curves corresponding to T$_g$ (^{0}C)
Bulk PMA	4.19
C 21	10.95
C 26	15.14 , 51.29
C 27	17.43 , 46.45
C 28	11.32 , 53.58

For bulk PMA, we obtained a single peak corresponding to the T$_g$ of PMA. We observed that as the POSS content increased in the copolymer, the T$_g$ also increased (relative to the bulk PMA), to values shown in Table 2. However, for the relatively higher POSS loadings (C 26, C 27 and C 28 copolymers), two distinct transitions were observed, as seen in Table 2 and Figure 1, which means that there is more than one T$_g$. This probably indicates that, though the POSS moieties are homogeneously incorporated into the copolymer backbone by polymerization, the POSS content is low, relative to the PMA content in the matrix, and POSS-rich fractions and PMA-rich fractions seem to exist in the copolymer matrix. The lower T$_g$ among the two

T_gs is probably due to the PMA-rich part of the copolymer, and the higher T_g is due to the POSS-rich part. Nevertheless, the lower T_g is still higher than that for the bulk PMA, indicating that the incorporation of POSS has restricted the mobility of the polymer chains. For the copolymers, it was also observed that, as the POSS content increased in the copolymer, there was an increase in the dn/dc of the copolymer in a THF solution. Studies of reactivity ratios of POSS macromers with other acrylic comonomers have been reported.[6,7] The resulting copolymers have been reported to be alternating or random copolymers.[6,7]

We compared the thermal results of the PMA-co-POSS copolymers with those of the PMA/POSS blends, formed by physically mixing the POSS macromers with a solution of bulk PMA (M_w = 28,670 g/mol) in acetone, and evaporating the acetone by drying the blends in a vacuum oven. The blends were made so that, the weight %s of POSS in the PMA/POSS blends were similar to those obtained by TGA for the copolymers (Table 1). The DSC results for the PMA/POSS blends are shown in Figure 2.
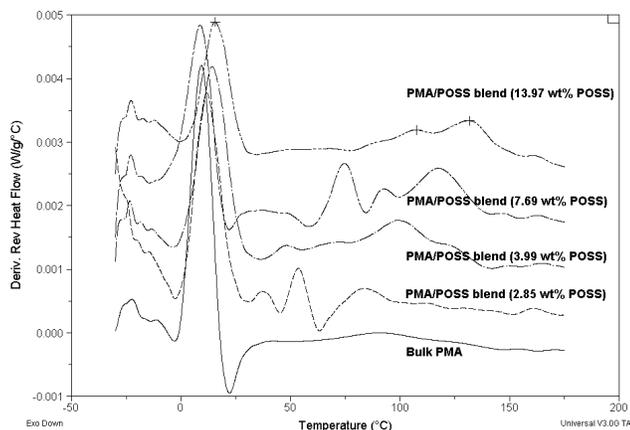

Figure 2. DSC curves for comparison of bulk PMA with PMA/POSS blends with increasing POSS content.

Figure 2 shows the DSC peaks for the PMA/POSS blends. We observed that there were three or more peaks for each blend, as seen in Table 3, indicating that the POSS moieties are not homogeneously dispersed in the blends. This is probably due to the fact that the POSS macromers are not incorporated into the backbone of the polymer chains, and so the mobility of the polymer chains in the blends is not as restricted as it is in the copolymers. Nevertheless, we observed peaks at higher temperatures in the DSC results for the blends, because POSS moieties were present in the blend in a localized manner, which created POSS-rich and POSS-poor regions in the blend. The POSS-rich regions exhibited highly restricted polymer motion, in comparison with the POSS-poor regions of the blend. We also observed that since, in the blend, the POSS was not incorporated into the backbone of the polymer chain, the POSS did not bring about as much of an increase in the T_g of the bulk PMA as it did when it was copolymerized with PMA, indicating that, when the POSS was in the blend, there was only localized reinforcement due to POSS.

Table 3. Compositions and T_gs of PMA/POSS blends.

Sample	Weight % POSS in Blends	Peaks in derivative DSC curves
Bulk PMA	-	9.22
B 21 blend	2.85 %	11.88 , 37.36 , 53.65 , 83.27
B 26 blend	3.99 %	14.25 , 48.32 , 99.56
B 27 blend	7.69 %	8.55 , 74.32 , 92.71 , 117.46
B 28 blend	13.97 %	15.62, 107.56, 131.60

Conclusions

Acrylic isobutyl POSS macromers were copolymerized with methyl acrylate by ATRP, and copolymers with narrow molecular-weight distributions and various POSS contents were obtained. The copolymers exhibited a higher T_g than the bulk PMA, because of effective reinforcement of the copolymer matrix by the incorporation of POSS in the backbone. At relatively higher POSS loadings, two distinct transitions were observed. The first one was a still higher transition than that for the bulk PMA, because of the presence of POSS in the backbone; and the second one was that for the POSS-rich fraction of the copolymer matrix.

The copolymers were compared with blends containing similar amounts of POSS (as in the copolymers), but mixed physically. It was observed that the T_gs of the blends were not as homogeneous as those for the copolymers. The DSC results of the blends displayed high heterogeneity in the distribution of POSS in the blend. The POSS brought about localized non-uniform reinforcement to the PMA, since it was not incorporated into the backbone of the polymer.

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