

The Effect of Incorporation of POSS Units on Polymer Blend Compatibility

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Received 21 August 2008; accepted 28 July 2009

DOI 10.1002/app.31225

Published online 15 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this work, the compatibility of poly(methyl methacrylate) (PMMA) and polystyrene (PS) polymers with their polyhedral oligomeric silsesquioxane (POSS) copolymers combined by solution blending is investigated, to determine the effect of incorporation of the POSS unit on polymer compatibility. The morphology of these tethered POSS copolymer/polymer blends was studied by electron microscopy, thermal analysis, and density. Although the basic PS/PMMA blend was clearly immiscible, it was also found that the incorporation of POSS into the PS chain led to incompatibility when the POSS-co-PS copolymer was blended with PS homopolymer. However, conversely, in the case where the POSS moiety was included as part of a copolymer with PMMA, the copolymer was miscible with the PMMA homo-

polymer. The presence of isobutyl units on the corners of POSS cage is clearly sufficient to encourage miscibility with PMMA. Interestingly, blends of the two different POSS copolymers led to an immiscible structure, despite having the common POSS units, the interactions between the POSS moieties clearly not being sufficient to drive compatibility. The POSS copolymers have also been used as interfacial agents in immiscible PS and PMMA blend, and it has been found that the appearance of the interface bonding is improved, although the phase morphology is only slightly changed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1153–1159, 2010

Key words: blends; compatibility; morphology; POSS; nanostructure

INTRODUCTION

A new class of nanofiller, polyhedral oligomeric silsesquioxanes (POSS) are hybrid materials containing polyhedral silicon–oxygen nanostructured skeletons or cages. POSS chemistry is very versatile and allows attachment of different kinds of functional or nonfunctional organic groups to the apex of the cages for further reaction.^{1–3} The interaction between such organic ligands and the matrix controls the initial solubility of the POSS in the medium, and thus the degree of dispersion of POSS and property modification.^{4–6} It has been shown in the literature that the chemical nature of the inert organic ligand plays a major role in the control of the morphologies generated in the hybrid materials, including the possibility to have amorphous or crystalline POSS aggregates. The incorporation of POSS cages into polymeric materials may result in dramatic improvements in polymer properties, including in the upper use temperature, oxidative resistance, and surface

hardening, leading to improved mechanical properties and a reduction in flammability.^{7–10}

Rafailovich and coworkers¹¹ have found that random copolymers functionalized with POSS groups can be very efficient at compatibilizing immiscible polymer blends. This compatibilization was proposed to be due to increases in site functionality provided by the POSS molecule, without the entropic penalty associated with functionalities grafted directly onto the polymer chains.¹² Compatibilization occurred if the POSS was grafted onto the backbone of one of the polymers and had the following consequences: reduced domain size, increased interfacial width, and greatly improved fracture toughness between immiscible polymers.^{11,13,14}

In this study, we focused on the effect of inter-chain interaction on the compatibility when POSS is a pendant moiety attached to the polymer main chain. The aim is to see what the effect of incorporation of POSS units into a copolymer has on miscibility, both with the corresponding homopolymers and between two different POSS copolymers. The materials chosen are poly(methyl methacrylate) (PMMA) and polystyrene (PS) homopolymers and copolymers, and a range of techniques were used to assess compatibility. The ultimate intention of this work is the possible use of such POSS copolymers as interfacial agents in immiscible blends to refine dispersed

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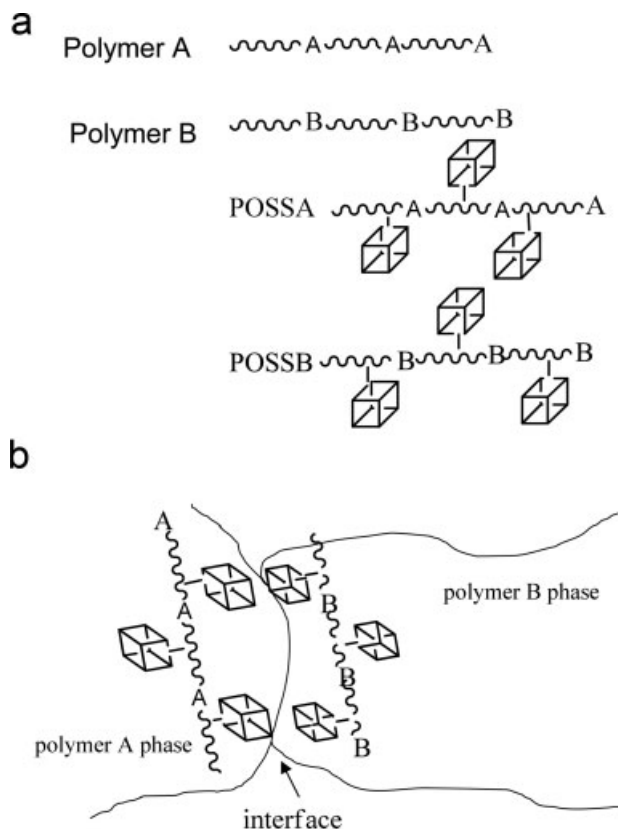


Figure 1 (a) Skeleton of POSS grafted in the polymer and (b) proposed eventual possible use of POSS copolymers as interfacial agents.

phase size and improve interfacial adhesion. For example, the intention would be to exploit POSScoPOSS interactions by incorporating a POSS copolymer of polymer A into homopolymer A and a POSS copolymer of polymer B into homopolymer B, with the idea that the copolymers would reside at the interface embedded in their respective homopolymers (A and B) and both refine the morphology and increase interfacial strength due to the interaction of POSS cages across the boundary (Fig. 1). In this work, we investigate the morphology, structure, and properties of various POSS copolymer nanocomposites using SEM techniques, density, and DSC.

EXPERIMENTAL

Materials

Poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-(methyl methacrylate)] (POSScoPMMA) (M_w 276,000) and poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-styrene] (POSScoPS) (M_w 12,800) (shown in Fig. 2) were purchased from Hybrid Plastics, POSS content is 45 wt %. Poly(methyl methacrylate (PMMA) (M_w 120,000) was purchased from Sigma Aldrich. Dicarboxy-terminated polystyrene (M_w 150,000) was supplied by Scientific Polymer Products. All materials were dried before using in vacuum oven overnight at 50°C.

Solution blending

The composition of the blends both as one component and interfacial agent is shown in Table I, where POSS copolymers at different loadings were prepared by solution blending. Each blend was produced by dissolving POSS copolymer and polymers in THF (3 wt %) using a magnetic stirrer at room temperature for 20 h till homogeneous. This well-mixed solution was cast into a Petri dish, and the solvent allowed to evaporate over a period of 48 h in fume hood at room temperature. The films were then placed in a vacuum oven at 60°C for 24 h and 106°C for 48 h to remove residual solvent.

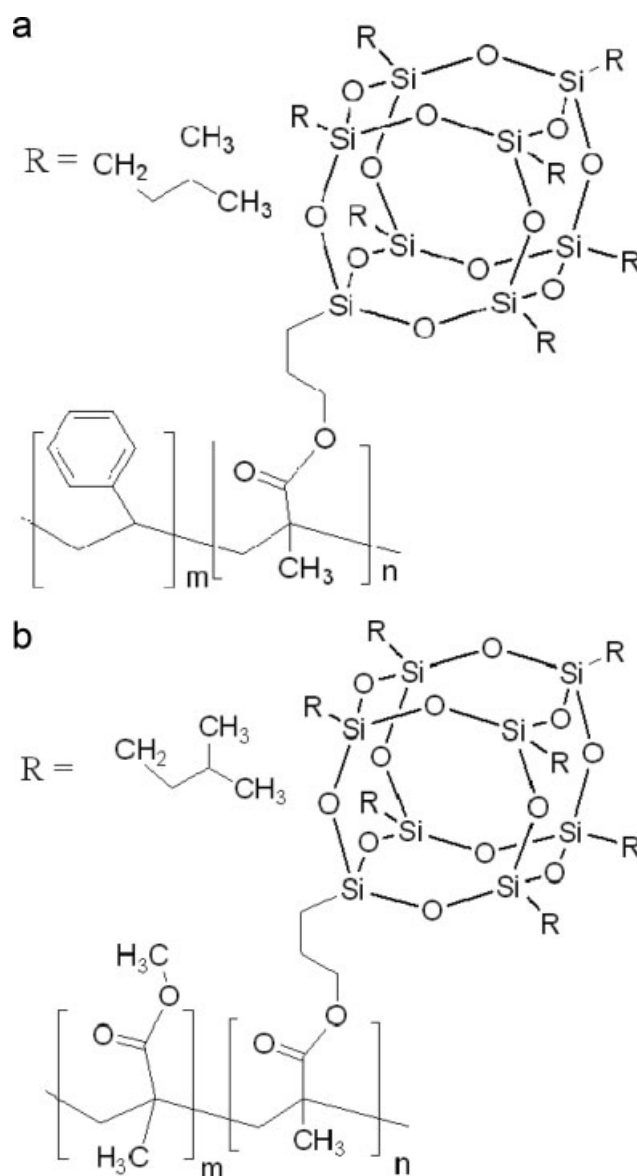


Figure 2 Chemical structure of POSS copolymers. (a) Poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-styrene] (POSScoPS). (b) Poly[(propylmethacryl-heptaisobutyl-POSS)-*co*-(methylmethacrylate)] (POSScoPMMA).

TABLE I
Composition of All the Blends

wt %	PS	PMMA	POSScoPS	POSScoPMMA
PS/PMMA100	0	100	0	0
PS/PMMA75	25	75	0	0
PS/PMMA50	50	50	0	0
PS/PMMA25	75	25	0	0
PS/PMMA0	100	0	0	0
POSScoPS/PS100	100	0	0	0
POSScoPS/PS75	75	0	25	0
POSScoPS/PS50	50	0	50	0
POSScoPS/PS25	25	0	75	0
POSScoPS/PS0	0	0	100	0
POSScoPMMA/PMMA100	0	100	0	0
POSScoPMMA/PMMA75	0	75	0	25
POSScoPMMA/PMMA50	0	50	0	50
POSScoPMMA/PMMA25	0	25	0	75
POSScoPMMA/PMMA0	0	0	0	100
POSScoPS/POSScoPMMA100	0	0	0	100
POSScoPS/POSScoPMMA75	0	0	25	75
POSScoPS/POSScoPMMA50	0	0	50	50
POSScoPS/POSScoPMMA25	0	0	75	25
POSScoPS/POSScoPMMA0	0	0	100	0
PS/PMMA75/POSScoPS5	25	75	5	0
PS/PMMA75/POSScoPS2.5/POSScoPMMA2.5	25	75	2.5	2.5
PS/PMMA25/POSScoPMMA5	75	25	0	5
PS/PMMA25/POSScoPS2.5/POSScoPMMA2.5	75	25	2.5	2.5

SEM

Morphology of nanocomposites was characterized with Hitachi scanning electron microscopy (SEM) at a voltage of 15 kV. Cryogenic fracture surfaces of blends were prepared under liquid nitrogen and were sputter-coated with gold before imaging.

DSC

Differential scanning calorimetry (DSC) using a TA Instruments Q100 DSC was performed to determine the glass transition temperature T_g of the blends. The value of T_g for each blend was determined from the inflection point of the heat flow temperature curves obtained with a scan rate 10°C/min at the first heating runs.

Density

The density of all the blends was measured with AccuPyc 1330 Pycnometer at 27°C with helium used both as the purge and measurement gas. The density was an average of 10 runs.

RESULTS AND DISCUSSION

Morphology

Figure 3 represents SEM micrographs of cryogenic fracture surfaces of solution-blended materials. In Figure 3(a), blends of the two homopolymers are

shown, where it can be seen that the blend is clearly immiscible and the interface is quite poor, with separation of the phases being clearly observable. The dispersed phase size on either extreme of the concentration range is quite small, between 1 and 2 μm in diameter, due to the small surface tension difference between the two homopolymers.

In Figure 3(b), the blends of the two copolymers are shown. It is clear here that the size of phase separation is greater across the whole concentration spectrum, being some 2–5 μm in diameter. Thus, despite the fact that both components have similar units attached (isobutyl POSS units), this has not driven the constituents to a particularly fine dispersion. In a sense, the POSS units decorating both the PS and PMMA chains appear to hinder more intimate packing miscibility, although it should be noted that the interface between the dispersed phase and matrix still appears good.

Likewise Figure 3(c) shows PS copolymer blended with its corresponding PS homopolymer. It can be seen again that despite similarity of moieties (polystyrene), strong immiscibility is once again observed, with phase separation leading to particles of size 3–6 μm , although once again with good interfaces. Perhaps, the most interesting blends are the POSScoPMMA and PMMA blends shown in Figure 3(d). Although there was difficulty in imaging these samples because of degradation under the SEM beam, it was clear that no phase separation could be observed. It appears that the isobutyl groups on the

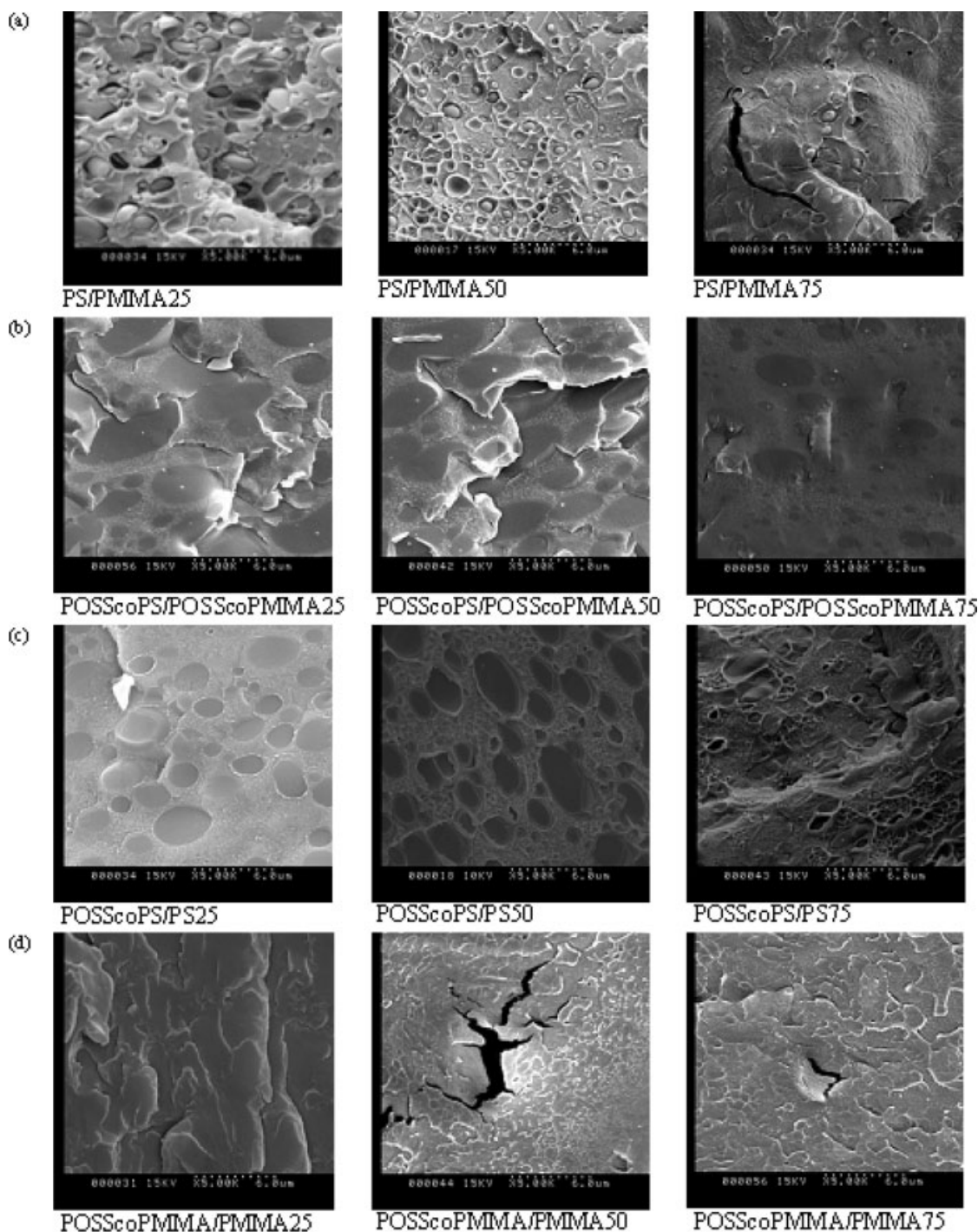


Figure 3 SEM of cryogenic fractured surfaces of blends after solution blending.

POSS unit are indeed sufficient to help attain molecular intimacy within the mixtures, contrasting with the immiscible PS and POSScoPS blends.

POSS copolymers have also been incorporated as an interfacial agent in PS/PMMA blend, and Figure 4 shows the SEM images of these cryogenic fractured surfaces. Five percent POSScoPMMA and 5% POSScoPS were used as compatibilizer in PS/PMMA25 and PS/PMMA75 systems, respectively. Good inter-

facial bonding between phases can be observed in both of them, and no particles can be found from POSScoPS in PS/PMMA75. With both 2.5% POSS copolymers in each PS/PMMA75 and PS/PMMA25, good interactions can be observed around the particles. This work indicates that the POSS copolymers can be used as interfacial agents and likely improves the interfacial adhesion of PS and PMMA. Because of the relatively low interfacial tension between PS

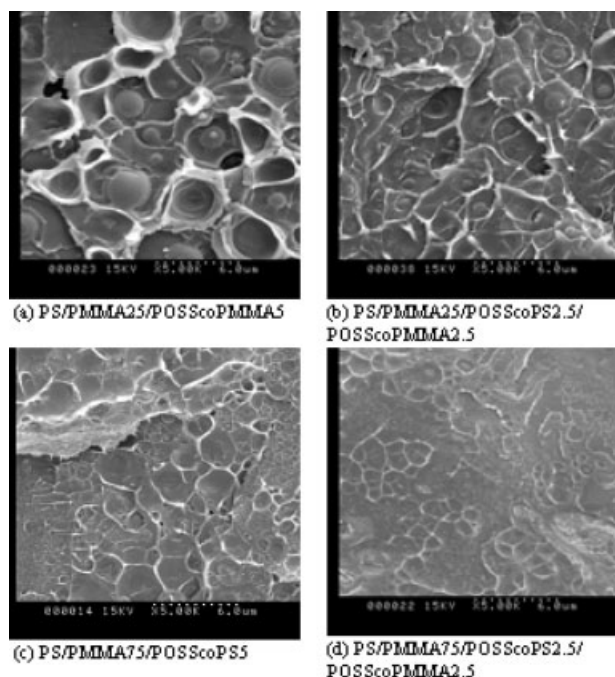


Figure 4 SEM of cryogenic fractured surfaces of blends after solution blending with POSS copolymer as interfacial agents.

and PMMA (e.g., PS/PMMA is 1.2–1.9 mN/m, but PE/PS is 5.2 mN/m¹⁵), the particle size is already quite small (around 1–2 μm). The incorporation of the copolymers with their attendant bulk appears to slightly increase the size when it is introduced (around 3–5 μm), but the effect is very small.

DSC

The DSC curves of all the blends are shown in Figure 5. Blends of PS/PMMA are typically immiscible, in which two glass transitions can be clearly seen [Fig. 5(a)]. This correlates well with the phase separation clearly observed in the SEM micrographs.

In the case of blends of POSScoPMMA and PMMA [Fig. 5(b)], there does appear to be some degree of compatibility. The experimental *T_g* data are higher than the *T_g* predicted by Fox equation, which indicates a lower degree of miscibility. A glass transition of the POSScoPMMA appears to be slightly decreased by some 10°C when 50% PMMA is added, whereas the PMMA glass transition is difficult to observe, even in the PMMA-rich blends. The

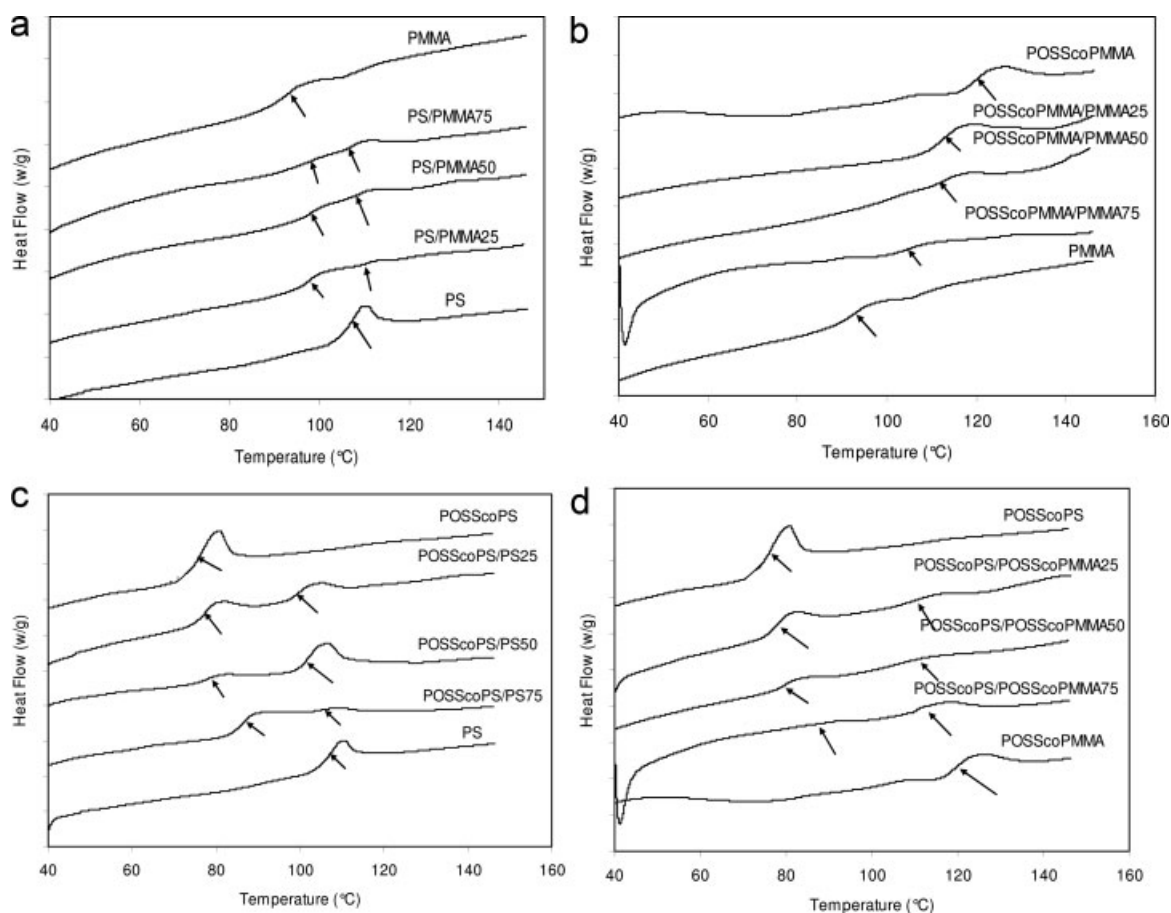


Figure 5 DSC curves of the blends, the arrows indicate the location of glass transition temperature. (a) PS/PMMA, (b) POSScoPMMA/PMMA, (c) POSScoPS/PS, and (d) POSScoPS/POSScoPMMA.

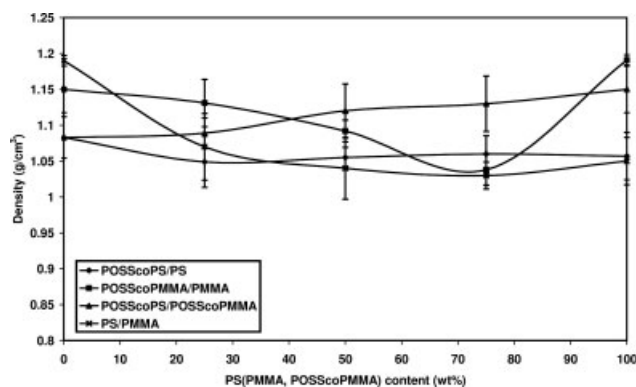


Figure 6 Density of the blends at 27°C.

strength of the transition also seems fairly suppressed in these blends. Conversely, in the blends of the PS copolymer with PS [Fig. 5(c)], a clear immiscibility is seen and two composition-independent T_g s occur but the T_g s shift to each other, indicating a certain degree of compatibility. This greater compatibility of POSScoPMMA with PMMA, compared with POSScoPS and PS, is striking, given the fact that the PMMA copolymer is of a very high molecular weight (which in itself would encourage immiscibility), whereas the PS copolymer is of quite low molecular weight and yet still remains immiscible. (It should also be noted that the POSScoPMMA shows a higher T_g than PMMA alone, whereas POSScoPS has a lower T_g than the PS alone. This may be due to the very low molecular weight of POSScoPS compared with PS, and the very high molecular weight of POSScoPMMA compared with the PMMA homopolymer).

The DSC curves of blends of the two POSS copolymers are shown in Figure 5(d), where two independent T_g s of POSScoPS and POSScoPMMA can be clearly seen, and a shift of T_g can be clearly observed. It appears that the interaction of POSS units on different chains encourages miscibility to some extent. On the other hand, the large bulky structure of the POSS unit in each copolymer means that the polymer chains do not entangle easily. This conclusion is in agreement with the density results: density of POSS copolymer blends increases linearly (in an additive fashion) from 1.07 to 1.17 g/cm³, which proved the compatibilization in the blends.

It does appear that the isobutyl groups on the apex of the POSS do encourage greater compatibility of that copolymer with the PMMA, as observed by DSC. The blends of the two POSS copolymers also appear, to a large degree to be immiscible, with little change in the PS's T_g in the POSScoPS-rich phase of the blend. This was the blend that showed the least negative deviation in blend density, an indication of a well-packed, immiscible blend. However, although DSC data are consistent in these con-

clusions, density results overall do not generally follow simple trends.

Density

The density of all components and blends is shown in Figure 6. Given that the density of neat POSS is similar to that of polymers (neat POSS density 1.10 g/cm³),¹⁶ the use of POSS additives allows for the possibility of increasing modulus without a significant increase in weight, compared with the use of denser fillers such as silica (ca. 2.2 g/cm³). In all cases, the blends investigated here showed a negative deviation, indication of a lower-than-expected density (poorer packing). This was found to be the strongest for the immiscible PS and PMMA blend, where such a decrease in density in such an immiscible blend is likely due to increased free volume at the interface.^{17,18}

Interestingly, the other blend pair that also showed a strong negative deviation was the pair of PMMA and POSScoPMMA, despite this appearing more miscible according to SEM micrographs. The POSScoPS/POSScoPMMA blend showed the greatest degree of additivity in density and is clearly immiscible. It appears that the density behavior of these materials is complex and likely related to free volume in the components themselves (strongly influenced by the POSS units), as well as the degree of interaction between the immiscible phases.¹⁹

CONCLUSIONS

Blends of PS, PMMA, and copolymers of these materials with each other were investigated in terms of compatibility using a range of techniques. PS and PMMA represent a clear immiscible blend with poor interfacial behavior as seen by SEM micrographs and two distinct glass transition temperatures measured by DSC. Interestingly, blends of the copolymers of these two materials themselves also appeared incompatible and the phase separation was more coarse (larger phase structure), despite the possibility of interaction between the POSS units. Although the copolymer of POSS and PS was immiscible with PS, it was found that the corresponding blend of POSScoPMMA with PMMA homopolymer showed some degree of compatibility, with strong shifts in the glass transition temperature on blending and no clear phase separation from SEM images, despite POSScoPMMA being of a particularly high molecular weight. It appears that in this instance, the isobutyl groups on the apex of the POSS cages encourage miscibility with the PMMA phase. The two POSS copolymers were used as a function of interfacial agent in PS/PMMA system, and the

interfacial adhesion appears improved based on examination of phase-separated SEM images from the initial work, although the particle size was little affected.

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