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Poly(acetoxystyrene-*co*-isobutylstyryl POSS) Nanocomposites: Characterization and Molecular Interaction

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Abstract

The poly(acetoxystyrene-*co*-isobutyl styryl polyhedral oligomeric silsesquioxanes)s (PAS-POSS) were synthesized by free radical polymerization and characterized by FTIR, high resolution NMR, FTIR, GPC, and DSC. The results show that the POSS content can be controlled by varying the POSS feed ratios. The interactions between organic components and inorganic POSS core, and the effects of inorganic POSS core on the properties of the resulting hybrids were investigated by high resolution solid state ^{13}C NMR, ^{29}Si NMR and FTIR spectra. The results provide detailed understandings of the effects of POSS moiety on properties of hybrid polymers.

Introduction

Synthetic polymeric materials often face application limitations because of poor inherent properties such as low modulus and/or low thermal stability. To overcome these drawbacks to meet the increasing use requirements, the development of new plastics possessing unique or enhanced properties has attracted much attention. Many new materials have been developed, such as the polymer-filler macroscopic composites, hybrid materials, and nanocomposites. Polymer-filler macroscopic composites usually exist the compatibility problem, which strongly affects the global properties [1, 2]. Hybrid materials bridge covalently two dissimilar type of materials (organic and inorganic) and have properties intermediate between those of traditional organic systems (i.e. polymers) and those of traditional inorganic system (i.e. ceramics) [3, 4]. Nanocomposites are typically referred to discontinuous particulate inclusion with one component dimension on the scale of 1–100 nm. Their properties are strongly affected by the interfacial interactions rather than by the bulk phase properties [5, 6] and often endow the materials novel properties.

Polyhedral oligosilsesquioxanes (POSS) has recently generated great interest because of its unique structure [7]. POSS is a well-defined nano-cluster with an inorganic silica-like core (Si_8O_{12}) surrounded by eight organic corner groups. These organic groups can be functionalized with a wide variety of organic groups. It has been commonly employed in polymerization as a building block for hybrid inorganic/organic nanocomposites. More importantly, these POSS nanoparticles can be monodispersed in the polymer with tailorable interfacial properties. Many POSS based hybrid materials have been reported and show some novel properties [8–26]. For examples, epoxide-POSS, POSS-acrylalte hybrid polymer, and POSS-norborne, POSS-styrene, POSS-siloxane copolymers and POSS based polyurethane show improved thermal or mechanical properties [8–16]. POSS based polyolefin nanocomposites show improved thermal oxidative properties [17]. Photocurable POSS based hybrids possessing improved solvent resistant property and highly porous properties have been investigated by Lain et al. [18, 19].

We have reported syntheses and characterization of the vinylpyrrolidone- isobutylstyryl POSS and hydroxystyrene-vinylpyrrolidone-isobutylstyryl POSS copolymers with significant T_g increase [23, 24]. In this paper, we deal with the synthesis and molecular characterization of a series of the new acetoxystyrene-POSS copolymers and the special emphasis is placed on the interactions between the organic component and the inorganic POSS cube and the effects of POSS content on their thermal properties.

Experimental

Materials

The isobutyl styryl polyhedral oligosilsesquioxanes (POSS) was purchased from Hybrid plastic Co. Inc. of United States and kept in a dry box before use. Acetoxystyrene was purchased from Aldrich Chemical Co, distilled from calcium hydride under reduced pressure and stored in sealed ampuls in a refrigerator. High purity azobisisobutyronitrie (AIBN) also from Aldrich Chemical Co. was kept in dry box and used as received. Spectroscopic grade THF and toluene were predried over 4. A molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were purchased from Aldrich chemical Co. and used without further purification.

Instrumentations

Thermal analyses were performed on a DSC from Du-Pont (DSC-9000). The sample was quickly cooled to 0 °C from the melt for the first scan and then scanned from 20 to 280 °C at 20 °C/min. The glass transition temperature is at the midpoint of the specific heat increment. FTIR spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet Avatar 320 FTIR spectrophotometer using KBr disks or film samples at room temperature. Weight average (M_w), number average molecular weights (M_n) and polydispersity index (M_w/M_n) were determined by a Water 510 gel permeation chromatograph (GPC). ^{1}HNMR spectra were recorded on a Brucker ARX300 Spectrometer using chloroform-*d* solvent. High resolution solid state ^{13}C NMR and ^{29} Si NMR experiments were carried out at room temperature using a Bruker DSX-400 spectrometer operating at resonance frequency of 100.46 MHz and 79.38 MHz, respectively.

Polymerization

All polymerization reactions were carried out under nitrogen using a vacuum-line system. These poly(acetoxystyrene-*co*-isobutylstyrylPOSS)s (PAS-POSS) copolymers were prepared by a free radical polymerization method. For comparison, a pure poly(acetoxystyrene) (PAS) was also synthesized. A typical example of experimental procedure for these polymers is given below. In a typical reaction, 810.00 mg of acetoxystyrene (AS, 5.00 mmol) and 161.00 mg of isobutylstyryl polyhedral oligosilsesquioxane (POSS, 0.18 mmol) monomers in 10 mL dried toluene were polymerized using the azobisisobutyronitrile (AIBN) initiator (1 wt% based on monomer) at 80 °C under nitrogen atmosphere for 24 hours. The product was poured into excess cyclohexane under vigorous agitation to precipitate the copolymer, then was purified in THF/cyclohexane and was dried in a vacuum oven. A 40.0 wt% yield was obtained through this procedure.

Results and Discussion

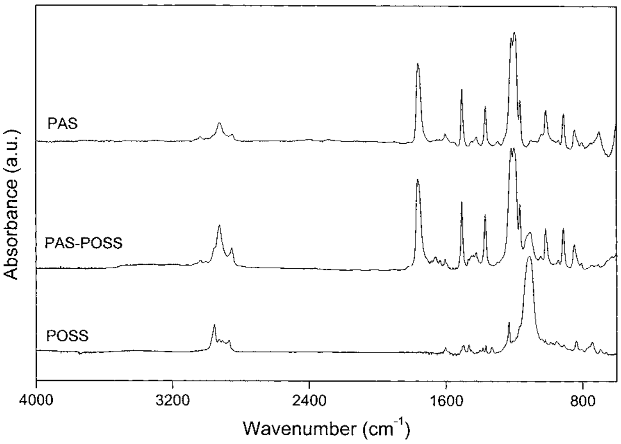

Figure 1. FT-IR spectra in the region of 4000–700 cm^{-1} recorded at room temperature of pure POSS, parent PAS and PAS-POSS1.38.

Figure 1 shows the FTIR spectra of PAS-POSS, pure POSS and pure PAS. The pure POSS shows a characteristic symmetric Si–O–Si stretching absorption band at 1109 cm^{-1}. The PAS shows a characteristic carbonyl vibration absorption at 1760 cm^{-1} and a strong ν_s (Ph–O) stretching absorption band at 1210 cm^{-1}. The ν_s (O–C=O) stretching absorption is at 1370 cm^{-1}. The *para*-substituted aromatic ring shows the characteristic peaks at 1490 cm^{-1}, 910 and 848 cm^{-1} which are assigned as the ν_s (C=C of Ar ring) stretching and two out-of-plane bending δ_s (C–H). The spectrum of the PAS-POSS is very similar to that of the PAS. However, A sharp, strong, and symmetric Si–O–Si stretching peak [νs (Si–O–Si)] appear at ~1109 cm^{-1} in all PAS-POSS hybrids which is from the silsesquioxane cage [18, 19]. The consistent presence of this Si–O–Si strenching peak confirms that the POSS cube structure is incorporated into these formed hybrid copolymers. The relative intensity of this characteristic absorption band in the copolymer increases with POSS feed ratio, indicating that the mole fraction of the POSS in the resulting hybrid increases with the POSS feed ratio. To further confirm that the POSS is indeed incorporated into the PAS rather than as a mixture, the following procedures were carried out. The prepared PAS-POSS hybrid polymer is re-dissolves in THF to form a homogenous and transparent solution. This solution was then added dropwise into cyclohexane which is a nonsolvent for the PAS-POSS hybrid polymer but is a good solvent for the POSS. The precipitated product was collected by filtration to remove the unreacted POSS. Such redissolution and reprecipitation procedure were repeated more than three times and the final product still displays the characteristic spectral peak in the region from 1150–1050 cm^{-1} with the same absorption intensity before and after purification. Similar redissolution and reprecipitation procedures were also carried out on a mixture of the POSS and the parent PAS, the finally obtained product does not give the siloxane characteristic peak (1150–1050 cm^{-1}), implying that the POSS macromer is indeed incorporated into the PAS polymer to produce the PAS-POSS copolymer.

^{1}H NMR Spectra

The PAS-POSS hybrid copolymer is soluble in most common solvents and its structure can therefore be characterized by the solution ^{1}HNMR spectra. Figure 2 shows ^{1}HNMR spectra of POSS, PAS and PAS-POSS (4.18 mol% of POSS) in *d*-chloroform solvent. For the pure POSS macromer, the resonances of methyl (**9**), methylene (**7**) and methine (**8**) protons from the substituted isobutyl group at a mole ratio of 6 : 2 : 1 are observed at δ 0.92, 0.60, 1.85 ppm, respectively. Doublet and the quartet resonance proton resonance peaks from the vinyl group (**2**, **1**H_a and **1**H_b) in the POSS are lo-

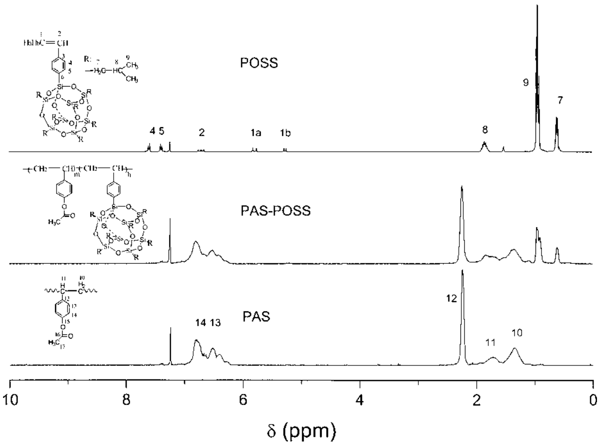

Figure 2. The ^{1}H NMR spectra of the pure POSS, parent PAS and PAS-POSS4.18.

cated at 5.26, 5.77 and 6.98 ppm with relative mole ratio of 1 : 1 : 1, corresponding to *iso*-, *trans*- and *substituted* vinyl protons. However, these peaks disappear after copolymerization with acetoxystyrene as an evidence of the complete reaction of the POSS. These doublet aromatic proton peaks of POSS with relative mole ratio of 1 : 1 are present at 7.38 (**5**) and 7.59 ppm (**4**). These aromatic proton peaks shift to a higher field after copolymerization with acetoxystyrene to form the PAS-POSS copolymer, further confirming that POSS was incorporated into the PAS. In the pure PAS, the methine proton (**11**) peak in the backbone is at δ 1.74 ppm and overlaps with methine protons in the backbone of the POSS segment in the PAS-POSS copolymer. The resonance observed at δ 1.35 ppm is assigned to the methylene protons (**10**) in the PAS backbone which overlaps with the methylene proton in the backbone of the POSS segment in the PAS-POSS copolymer. The methyl proton (**17**) from the acryl group is at 2.25 ppm which is still present in the PAS-POSS hybrid. The broad resonance band at 6.23–7.00 ppm in the pure POSS is attributed to the aromatic protons (**14**, **13**) and shows peaks at 6.82, 6.54 ppm with a mole ratio of 1 : 1. These aromatic proton peaks become wider in the PAS-POSS hybrid. All PAS characteristic resonances are clearly present in all PAS-POSS copolymers. All these resonant proton peaks from the PAS segment, except the methyl proton resonance at δ 2.25 ppm, are enhanced over that of the pure PAS due to the overlap with the resonance of related protons from the POSS segment of the PAS-POSS.

The ^{1}H NMR spectra of all copolymers clearly show that the methyl and methylene protons come from the isobutyl group. However, these vinyl protons from the original POSS completely disappear, further confirming that POSS has copolymerized with acetoxystyrene. The ratio of PAS to POSS is estimated by directly comparing the peak areas associated with the methyl protons (**17**) in the PAS segment (δ 2.25 ppm) and peak area associated with methyl (**9**) protons from isobutyl group of the POSS segment ($\delta = 0.92$ ppm). Table 1 summarized the POSS content in the PAS-POSS copolymer.

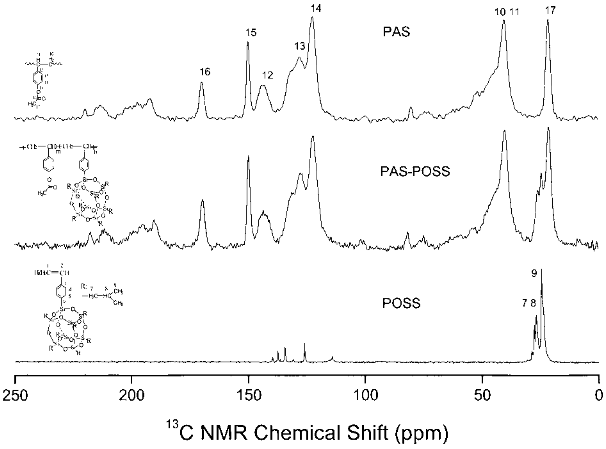

Figure 3. The high resolution solid state ^{13}C NMR spectra of the pure POSS, parent PAS and PAS-POSS4.18.

High Resolution Solid State ^{13}C NMR Analyses

High resolution solid state ^{13}C NMR spectroscopy provides further insight into the copolymerization of acetoxystyrene and the POSS macromer. Figure 3 shows the high resolution solid state ^{13}C NMR spectra of various PAS-POSSs, pure PAS and the pure POSS. The pure POSS possesses three strong resonance peaks at 24.4 (**C-9**), 26.7 (**C-7**), 27.6 (**C-8**) ppm, associated with the isobutyl group of the POSS macromer, and six weak resonance peaks in the low field at 114.2, 125.9, 130.7, 134.4, 137.4 and 139.7 ppm from the styryl group in the POSS. PAS also shows eight resonance peaks at 169.4, 149.4, 143.2, 127.7, 122.1, 40.0, and 21.1 ppm, in which the **C-10** and **C-11** resonances in the backbone overlap each other and show a peak maximum at 40.0 ppm. The resonance peak at 169.4 ppm comes from the carboxyl carbon. Figure 3 assigns all other resonance peaks.

^{13}C NMR spectra of all PAS-POSS copolymers clearly show these PAS resonance peaks. The PAS-POSS shows two new strong resonances at about 24.6 and 26.7 ppm, typical of isobutyl group of the POSS macromer. The intensities of these new resonance peaks (24.6 and 26.7 ppm) increase with the increase of the POSS content, further confirming that the POSS moiety is indeed incorporated into the PAS. Figure 4 shows expanded ^{29}Si NMR spectra of pure POSS and PAS-POSS hybrid (1.27 mol% of POSS). Pure POSS shows two characteristic silica resonance bands at −67.8 and −80.0 ppm, corresponding to the substitution of silicas in the POSS core by isobutyl and styryl group, respectively. The two characteristic resonances are present in all PAS-POSS hybrids, further providing additional evidences that the POSS moiety is attached to the PAS.

Thermal Properties and Molecular Interaction

Table 1 shows that the PAS-POSS0.41 (0.41 mol% of POSS) has a T_g at 113.6 °C which is 8.5 °C lower than the T_g of the non-POSS parent PAS (122.1 °C). It appears that the small POSS content in the hybrid copolymer is unable to increase the T_g of the parent polymer and actually reduces its T_g due to the diluent effect to reduce the dipole-dipole interaction of PAS molecules. The T_g of the PAS-POSS

Table 1. Effect of POSS feed ratio on the result of PAS-POSS

Sample No.	PAS (mol%)	POSS[a] (mol%)	POSS[b] (mol%)	yield (wt%)	T_g[c] (°C)	M_w[d] ($\times 10^3$ g/mol)	M_n ($\times 10^3$ g/mol)	PDI
1	100.00	0.00	0.00	56.2	122.12	46.23	17.71	2.61
2	99.02	0.98	0.41	40.0	113.60	40.06	18.84	2.13
3	98.73	1.27	1.38	19.1	105.79	16.40	9.34	1.76
4	98.53	1.47	2.66	19.5	104.71	22.75	13.03	1.74
5	96.77	3.23	4.18	14.5	103.15	14.86	10.34	1.44
6	95.97	4.03	5.43	9.2	107.80	15.59	11.21	1.39

[a] Data were obtained based on IR standard curve.
[b] Determined by ^{1}H NMR.
[c] Data were gathered on the second melt using a heating and cooling rate of 20 °C/min.
[d] Determined by GPC using PS standard curve.

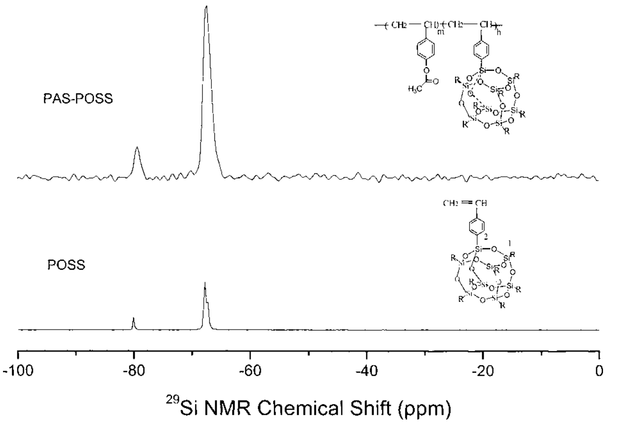

Figure 4. The high resolution solid state ^{29}Si NMR spectra of the pure POSS and the PAS-POSS4.18.

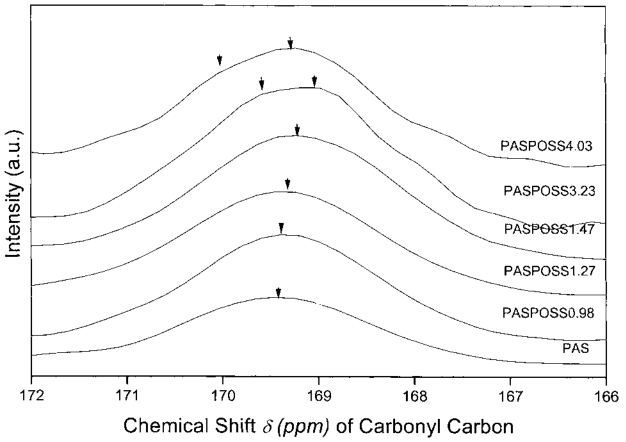

Figure 5. Expanded solid state ^{13}C NMR spectra of the pure POSS, parent PAS and PAS-POSS4.18 in the region of 172–166 ppm.

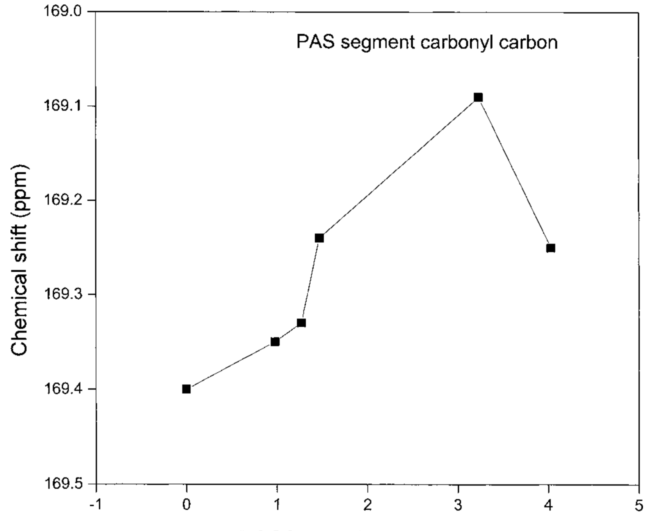

Figure 6. The relationship of the chemical shift of the carbonyl carbon resonance and the POSS fraction in the hybrid.

further decreases with the increase of the POSS content in the hybrid polymers and approaches a minimum at POSS = 4.18 mol% (T_g = 103.1 °C) (Table 1). At a higher POSS content (5.43 mol%), the T_g of the PAS-POSS hybrid increases with the increase of the POSS content. Similar effect of POSS on T_g behavior was also found in *p*-methylstyrene-POSS [10] and vinylpyrrolidone-POSS [24] copolymers. A new factor causing T_g increase must become dominant over the dilution effect when the POSS content is greater than 4.18 mol%.

Figure 5 shows the expanded carboxyl carbon resonance spectra of pure PAS and various PAS-POSSs in the region of 172.0–166.5 ppm. The carboxyl carbon resonance peak of the pure PAS is at 169.4 ppm and this resonance peak in the PAS-POSS with relatively low POSS fraction shifts slightly to higher field. For example, the PAS-POSS4.18 shows a high field shift of 0.3 ppm compared with that of the pure PAS. Chemical and physical environmental variations of the molecules are well known to cause a chemical shift. The high field shift means that the carboxyl-carboxyl dipole-dipole interaction is decreased. The POSS plays a diluent role when it is incorporated into the PAS with a relatively small POSS content. However, further increasing the POSS content to 5.43 mol%, the resonance peak does not further shift to higher field. On the contrary, it actually reduces the high field shift. For example, the PAS-POSS5.43 has only high shift of 0.1 ppm compared with that of the pure PAS. A new shoulder resonance peak at 169.9 ppm down field region is also observed at a relative higher POSS content, resulting from an interaction between the POSS and the PAS. The plot of chemical shift of carbonyl carbon verses POSS content is shown in Figure 6. The result is coincidentally consistent with the T_g behavior. Figure 7 shows the expanded

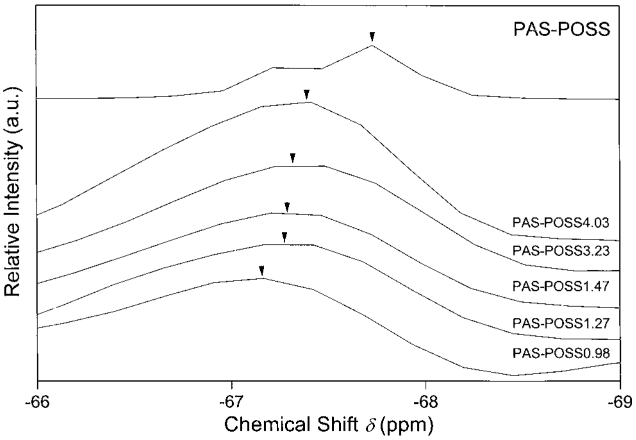

Figure 7. The expanded solid state ^{29}Si NMR spectra of the pure POSS and various PAS-POSSs from −66 to −69 ppm.

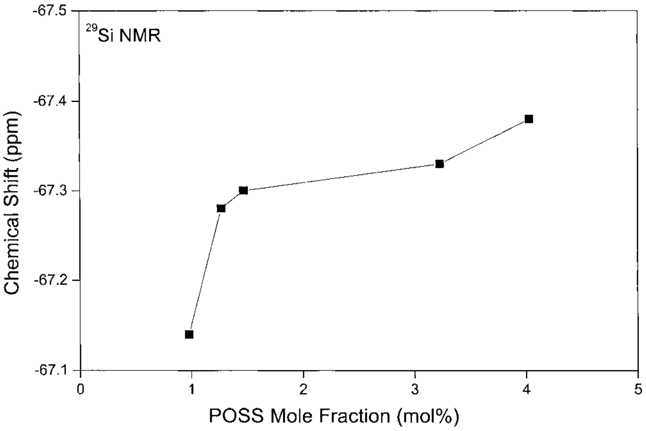

Figure 8. The relationship between the silica chemical shift and the POSS mole fraction in the hybrid.

^{29}Si NMR spectra of pure POSS and various PAS-POSSs in the region from −66 to −69 ppm. The pure POSS shows a resonance peak at −67.8 ppm and a shoulder peak at −67.2 ppm, which is assigned as the isobutyl substituted silica. This characteristic resonance band shifts to down field in these PAS-POSSs compared to the pure POSS. For example, the PAS-POSS0.98 (0.98 mol% of POSS) shows a 0.6 ppm down field shift, indicating that an interaction exists in the PAS-POSS. The interaction may come from the dipole-dipole interaction between siloxane of the POSS and the carbonyl group of PAS segment in PAS-POSS. The high POSS content results in POSS macromer aggregation because the silica resonance shifts to the high field. This observation is consistent with the result from solid state ^{13}C NMR spectra of carbonyl carbon in PAS segment, providing further evidence of the interaction between POSS siloxane and PAS carboxyl group. These results also support the T_g increase mechanism previously proposed [24]. Figure 8 clearly shows the dependence of the chemical shift on POSS content and the relationship between POSS content thermal properties of these PAS-POSS hybrids.

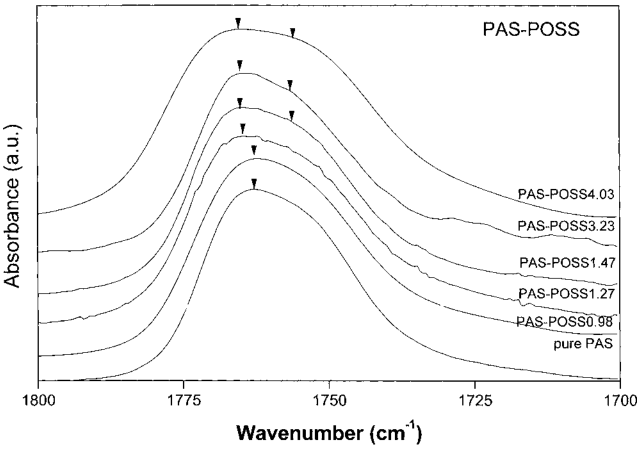

Figure 9. The expanded FT-IR spectra ranging from 1800 to1700 cm^{-1} of the POSS, pure PAS and various PAS-POSSs recorded at room temperature.

Figure 9 shows the expanded FTIR spectra of various PAS-POSS, pure POSS and parent PAS ranging from 1800 to 1700 cm^{-1}. Parent PAS shows a characteristic carboxyl vibration band at 1760 cm^{-1}. This absorption peak maximum shifts slightly toward higher frequency when the POSS moiety is incorporated into the PAS due to the inert diluent effect of the POSS to reduce the self-association interaction of PAS molecules. This vibration band is obviously broadened asymmetrically on the low-frequency side and a significant absorption shoulder appears at the lower wavenumber. This absorption shoulder intensity increases with the increase of the POSS content. For example, the PVP-POSS with 4.03 mol% POSS exhibits a significant strong absorption shoulder 1756.2 cm^{-1}, which is assigned to the dipole-dipole interaction between the POSS siloxane and the PAS carbonyl.

The interaction potential between two dopoles, A and B, can be written in the following form [27]:

$$V_{dd} = -\mu_A \mu_B X_{AB}, \tag{1}$$

$$X_{AB} = \left[\hat{e}_A \cdot \hat{e}_B - 3(\hat{e}_A \cdot r_{AB})(\hat{e}_A - r_{AB})\right]/r_{AB}^3 \tag{2}$$

while ê is a unit vector describing the direction of the dipole moment and r_{AB} is the distance between the centers of the dipoles.

When we consider only the first order (i.e., neglecting interactions between different norma; modes), the frequency shift (and intensity) of ith normal mode in the infrared spectrum determined by the transition dipole moment due to V_{dd} is expressed as following [28]:

$$\Delta\nu_i = \frac{V_{dd}}{hc}. \tag{3}$$

The frequency shift (and intensity) is determined mainly by the transitional dipole moment and obviously also depends on the orientation of the transitional dipoles with respect to one another and the proximity of the molecules (or polar species). The dipole interaction plays a role through their effect on the geometry-dependent term, X_{AB}.

When the POSS is attached to the polymer chain, the nanosize POSS will impose the barrier to the rotation of a molecule or segment relative to the parent polymer molecules and increases the distance between polar species. The presence of POSS reduce the dipole interaction potential

V_{dd}, which is responsible for carbonyl vibration band shifting to higher frequency. The dipole interaction between POSS and POSS is relatively small because of its monodispersion chemically into the polymer chain. Thus, a new dipole interaction occurs between the POSS siloxane and its immediate neighboring polar carbonyl and results in the new vibration shoulder of the POSS based hybrid. Higher POSS content decreases the distance of POSS units that makes the POSS-POSS interaction possible and thus results in the POSS aggregation. The POSS aggregation and the dipole interaction between the POSS siloxane and PAS carbonyl tend to hinder the molecular chain motion and result in the T_g increase.

Conclusion

The hybrid poly(acetoxystyrene-co-isobutylstyryl polyhedral oligomeric silsesquoixane) hybrid nanocomposites are prepared by one step polymerization reaction. The nanosize well-defined POSS content can be controlled simply by varying the POSS feed ratio. Microstructures of these PAS-POSS hybrid nanocomposites were characterized by high resolution NMR, FTIR, DSC and GPC. The high resolution NMR spectra provide important information to explain the T_g increase mechanism. At a low POSS content, the POSS moiety mainly plays a diluent role to reduce the PAS self-interaction. At a high POSS content, the interaction between the siloxane of the POSS and the dipole carbonyl group of the PAS in these hybrids becomes dominant and results in high T_g. In addition, the nanoscale POSS physical aggregation also partically contributes the observed T_g increase.

Acknowledgment

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References

1. F. L. Mathews and R. D. Rawlings, *Composites Materials: Engineering and Science*, Champman & Hall, London, UK, 1994, p. 14.
2. G. V. Jackson and M. L. Orton, *In Particulate-Filled Polymer Composites*, R. Rothon (ed.), Longman Scientific & Technical, Essex, UK, 1995, p. 317.
3. L. Mascia, *Trends Polym. Sci.*, **3**, 61 (1995).
4. C. Sanchez and F. Ribot, *Nouv. J. Chem.*, **18**, 1007 (1995).
5. D. A. Loy and K. J. Shea, *Chem. Rev.*, **95**, 1431 (1995).
6. P. M. Ajayan, *Chem. Rev.*, **99**, 1787 (1999).
7. F. J. Feher, D. Soulivong and G. T. Lewis, *J. Am. Chem. Soc.*, **119**, 11323 (1997).
8. J. D. Lichtenhan, N. Q. Vu, J. A. Carter, J. W. Gilman and F. J. Feher, *Macromolecules*, **26**, 2141 (1993).
9. J. D. Lichtenhan, Y. Otonari and M. J. Carri, *Macromolecules*, **28**, 8435 (1995).
10. T. S. Haddad and J. D. Lichtenhan, *Macromolecules*, **29**, 7302 (1996).
11. J. D. Mantz, P. F. Jones, K. P. Chaffee, J. D. Lichtenhan, J. W. Gilman, I. M. K. Ismail and M. J. Burmeister, *Chem. Mater.*, **8**, 1250 (1996).
12. A. Romo-Urbie, P. T. Mather, T. S. Haddad and J. D. Lichtenhan, *J. Polym. Sci., Part B: Polym. Phys.*, **36**, 1857 (1998).
13. J. J. Schwab and J. D. Lichtenhan, *Appl. Oganometal. Chem.*, **12**, 707 (1998).
14. P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad and J. D. Lichtenhan, *Macromolecules*, **32**, 1194 (1999).
15. J. J. Schwab, J. D. Lichtenhan, P. T. Mather, A. Romouribe and F. J. Feher, *211th meeting of the American Chemical Society*, New Orleans, LA, 1996.
16. E. G. Shochey, A. G. Bolf, P. F. Jones, J. J. Schwab, K. P. Chaffee, T. S. Haddad and J. D. Lichtenhan, *Appl. Organometal. Chem.*, **13**, 311 (1999).
17. L. Zheng, R. J. Farris and E. B. Coughlin, *Macromolecules*, **34**, 8034 (2001).
18. A. Sellinger and R. M. Laine, *Macromolecules*, **29**, 2327 (1996).
19. C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov and A. F. Yee, *J. Am. Chem. Soc.*, **120**, 8380 (1998).
20. N. Auner, J. W. Bats, D. E. Katsoulis, M. Suto, R. E. Tecklenburg and G. A. Zank, *Chem. Mater.*, **12**, 3402 (2000).
21. R. A. Mantz, K. Jones and M. J. Brumeister, *Chem. Mater.*, **8**, 1250 (1996).
22. T. E. Gentle and A. R. Bassindale, *J. Inorg. Organomet. Polym.*, **5**, 281 (1995).
23. H. Xu, S. W. Kuo, C. T. Lee and F. C. Chang, *Macromolecules*, **35**, 8788 (2002).
24. H. Xu, S. W. Kuo, C. T. Huang and F. C. Chang, *Polymer*, **43**, 5117 (2002).
25. D. Hoebbel, I. Pitsch, D. Heldemann, H. Jancke and W. Z. Hiller, *Anorg. Allg. Chem.*, **583**, 133 (1990).
26. J. Yun and K. Matyjaszewski, *Macromolecules*, **33**, 217 (2000).
27. P. C. Painter, G. J. Pehlert, Y. Hu and M. M. Coleman, *Macromolecules*, **32**, 2055 (1999).
28. T. C. Cheam and S. Krimm, *Chem. Phys. Lett.*, **107**, 613 (1984).