Preparation and characterization of polyhedral oligomeric silsesquioxane/polystyrene nanocomposites

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(Received: 02 August, 2011; published: 09 August, 2012)

Abstract: Several inorganic/organic nanocomposites were prepared via solution-blending of cage-like octahexyl-polyhedral oligomeric silsesquioxane (Oh-POSS) with polystyrene (PS) in THF solvent. FTIR and ²⁹Si-NMR were employed to characterize the structures of the nanocomposites. SEM pictures showed that the sample films were smooth and no POSS aggregation was observed when POSS content was lower than 1.0 wt%. TGA and DSC were used to investigate the thermal property. The results showed that the incorporation of nanosized Oh-POSS enhanced the thermal stability of PS with low POSS content. When 1.0 wt% of Oh-POSS was incorporated into PS matrix, the *T_g* and *T_d* increased by 7.7 °C and 8.2 °C, respectively. However, higher POSS contents (>1.0 wt%) would deteriorate the thermal property of the nanocomposites due to the severe congregation of POSS..

Introduction

Organic-inorganic nanocomposites have attracted great attention in recent years because they may combine the advantages of both inorganic materials (e.g., rigidity and stability) and organic polymers (e.g., toughness and processability) [1]. The successful preparation of organic-inorganic nanocomposites depends much on the dispersive state of inorganic nanoparticles in polymer matrix. Traditional inorganic particles, like silica, clay and montmorillonite, are difficult to achieve even dispersion due to their strong trend to aggregate together. Therefore, the exploration of new method to prepare organic-inorganic nanocomposites is of great significance.

Polyhedral oligomeric silsesquioxane (POSS) is a kind of valuable molecule with general formula (RSiO_{1.5})_n. When n=8, POSS possesses a cube-like structure with its eight corners linked with organic groups, which are either reactive or inert. POSS is considered as the minimal SiO₂ particle because of its 0.53 nm of core size [2]. The incorporation of POSS into polymer matrix often leads to a remarkable enhancement of thermal property compared to the mother polymer due to the strong interactions between nanosized POSS and polymer chains. This is because the nanosize POSS cages have found an easy way to disperse in polymeric matrix. Therefore, POSS/Polymer nanocomposites have become one of the hot topics in the materials community.

POSS/Polymer nanocomposites can be prepared either via physical blending [3-6] or chemical copolymerization [7-12]. The latter one usually takes advantage of the reactive functional groups on POSS surface to copolymerize with organic monomers,

facilitating the dispersion of POSS at molecular level. Generally, it is hard for the physical blending to achieve even dispersion due to the easy aggregation of common inorganic nanoparticles. However, POSS is special. It could have excellent solubility in ordinary organic solvents because of its corner organic groups. In this paper, a facile solution-blending method was employed, in which POSS was modified in advance to improve its solubility, and then mixed with PS in THF to form a homogenous solution. POSS/PS nanocomposites were obtained simply by evaporating the solvent and the enhancement of thermal property of PS by incorporation of POSS was studied.

Results and discussion

Octahexyl-POSS (Oh-POSS) was synthesized via the hydrosilylative reaction between Octahydridosilsesquioxane (H_8 -POSS) and 1-hexene (Scheme 1). Fig. 1 shows the FTIR spectra of Oh-POSS as well as H_8 -POSS. The pure H_8 -POSS shows a characteristic Si-O-Si stretching absorption band at $\sim 1109\text{ cm}^{-1}$, and the stretching and bending absorption bands of Si-H at 2290 cm^{-1} and 860 cm^{-1} , respectively. The Oh-POSS has a quite different IR spectrum to that of H_8 -POSS except that a strong absorption band still remains at $\sim 1109\text{ cm}^{-1}$, which is the characteristic Si-O-Si stretching absorption of silsesquioxane cages.

Scheme 1. Synthesis of Oh-POSS from H_8 -POSS.

Fig. 1. FTIR spectra of H_8 -POSS and Oh-POSS measured with a spectral resolution of 1 cm^{-1} using KBr powder at room temperature.

Fig. 2. ^{29}Si -NMR spectrum of Oh-POSS measured from CDCl_3 solutions in a 10-mm glass tube spinning at 20 Hz and using an 8-s pulse delay.

The absorption bands of Si-H at 2290 cm^{-1} and 860 cm^{-1} disappear, while the stretching absorption bands of methylene groups at 2930 and 2855 cm^{-1} appear in the FTIR spectra of Oh-POSS, revealing that all the vinyl groups of hexene and Si-H groups of H_8 -POSS may have been consumed in the hydrosilylative addition reaction, hinting that Oh-POSS have been formed. This is further confirmed by the ^{29}Si -NMR spectra of Oh-POSS (Fig. 2). There are two resonance peaks at -67 and -85 ppm , which are respectively ascribed to Si-C and Si-H on POSS. Peak at -67 ppm is much higher than peak at -85 ppm , indicating that most Si-H bonds have been consumed in the hydrosilylative reaction to form Si-C bonds. By calculating the peak area ratio, we estimate that about 7.5 Si-H on each H_8 -POSS cage have been transformed to Si-C, implying that Oh-POSS has been successfully synthesized.

Fig. 3. FTIR spectra of Oh-POSS/PS nanocomposites, Oh-POSS and pure PS.

Fig. 3 indicates the FTIR spectra of Oh-POSS/PS nanocomposites with different POSS contents. For comparison, FTIR spectra of PS and Oh-POSS are also showed in Fig. 3. The FTIR spectra of Oh-POSS/PS are much similar to that of PS, all showing the characteristic absorption bands of PS such as the phenyl skeleton vibration peaks at 1600 cm^{-1} , 1492 cm^{-1} and 1448 cm^{-1} . And meanwhile, the characteristic Si-O-Si stretching vibration peak at $\sim 1109\text{ cm}^{-1}$ are all observed in the FTIR spectra of Oh-POSS/PS nanocomposites, and the Si-O-Si peak becomes larger from Oh-POSS/PS 0.1% to Oh-POSS/PS 4.0%, implying that Oh-POSS has been incorporated into the PS matrix, and Oh-POSS/PS nanocomposites have been successfully prepared.

The dispersive state of POSS cages in the polymeric matrix has much influence on the properties of the nanocomposites. In order to investigate the morphology or the homogeneity of the resultant nanocomposites, the as-prepared Oh-POSS/PS mixture solutions were spun on Si wafers to form thin films. It was observed that the prepared films with low POSS contents were clear and transparent, suggesting that the nanocomposites are uniform.

The morphologies of the nanocomposites were further investigated by scanning electronic microscopy (SEM). Fig. 4 shows the SEM images of the thin films of Oh-POSS/PS nanocomposites at a magnifying scale of 10000. When Oh-POSS content is relatively low (less than 1.0 wt%), POSS particles evenly disperse in the PS matrix. The thin films are rather smooth and uniform, and no cracks or flaws appear. When content is increased to 4.0 %, however, the aggregation of Oh-POSS is observed (Fig. 4c).

Fig. 4. SEM images of Oh-POSS/PS nanocomposites ($\times 10000$). (a) Oh-POSS/PS 0.1 %; (b) Oh-POSS/PS 1.0 %; (c) Oh-POSS/PS 4.0 %.

Figure 5 shows the DSC thermograms of Oh-POSS/PS nanocomposites with various POSS contents. For comparison, PS homopolymer thermogram is also displayed. As is seen in Table 1, T_g 's of Oh-POSS/PS nanocomposites with POSS content less than 4.0 wt% are higher than that of PS homopolymer. The T_g of the nanocomposite increases gradually with the increase of the POSS contents. For example, the T_g of Oh-POSS/PS with 0.1 wt% of POSS (Oh-POSS/PS0.1%) is $101.6\text{ }^{\circ}\text{C}$, which is $5.9\text{ }^{\circ}\text{C}$ higher than that ($95.7\text{ }^{\circ}\text{C}$) of the PS homopolymer. When content of POSS in the nanocomposite is increased to 1.0 wt%, the T_g reaches as high as $103.4\text{ }^{\circ}\text{C}$, which is $7.7\text{ }^{\circ}\text{C}$ higher than the T_g of the PS. With the further increase of POSS content, however, T_g shows a decreasing trend.

The T_g of a linear polymer is much related to the interaction strength between polymer chains. The T_g 's of Oh-POSS/PS nanocomposites differ from that of PS implies that

the incorporation of Oh-POSS nanoparticles have changed the original interaction strength in the polymer matrix. When POSS content is less than 1.0 wt%, Oh-POSS cages disperse evenly in the system (Fig. 4a, 4b), enhancing the interactions between POSS cages and PS chains due to the strong nanoeffect from POSS. Therein, POSS cages play roles of cross-linking points, which hinder the movement of PS chains, and therefore promote the T_g of Oh-POSS/PS nanocomposites [13]. When POSS content is higher than 1.0 wt%, however, the T_g of Oh-POSS/PS nanocomposites begins to decline due to the decrease of nanoeffect caused by the aggregation of POSS cages (Fig. 4c).

Fig. 5. DSC thermograms of Oh-POSS/PS nanocomposites and pure PS measured under a continuous nitrogen purge (50 mL/min) at a scanning rate of 10 °C/min.

Tab. 1. Thermal properties of Oh-POSS/PS nanocomposites.

Samples	POSS content (wt %)	T_g (°C)	T_d^a (°C)	Char ^b (%)
PS	0.0	95.7	345.8	0.2
Oh-POSS/PS 0.1%	0.1	101.6	348.4	1.7
Oh-POSS/PS 1.0%	1.0	103.4	354.0	3.5
Oh-POSS/PS 4.0%	4.0	93.7	339.9	7.9

a. The temperature at 5% weight loss. b. The remained weight at 600 °C.

Fig. 6 shows the TGA curves of Oh-POSS/PS nanocomposites as well as PS homopolymer. Pure PS shows one-step degradation at 345.8 °C. Similarly, Oh-POSS/PS nanocomposites also indicate one-step degradation, implying that the incorporation of small amount of POSS does not essentially change the thermal properties of PS. However, the decomposition temperatures (T_d) of Oh-POSS/PS nanocomposites do differ from PS. For example, when POSS content is 1.0 wt%, the T_d is 354.0 °C, which is 8.2 °C higher than that of PS homopolymer, indicating that

incorporation of small amount of POSS into PS could improve the thermal stability of PS.

Fig. 6. TGA curves of Oh-POSS/PS nanocomposites and pure PS obtained with a heating rate of 20 °C /min under a continuous nitrogen purge (100 mL/min).

Conclusions

A series of Oh-POSS/PS nanocomposites were prepared via solution-blending method. It reveals that when small amount of POSS (less than 1.0 wt%) is incorporated into PS homopolymer, the thin films of nanocomposites show rather smooth and uniform surfaces, and POSS molecules disperse evenly in the PS matrix. The thermal properties of Oh-POSS/PS nanocomposites are substantially improved due to the strong nanoeffect from POSS cages, which restrict the movement of PS chains.

Experimental part

Materials

PS ($M_n \approx 13000$) was synthesized in our lab. Octahydridosilsesquioxane (H_8 -POSS) was purchased from Amwest Technology Company. Platinum dicyclopentadiene (Pt(dcp), as the catalyst) was synthesized according to the procedures described in Ref. [14]. Hexene were bought from Sigma-Aldrich Co. The 1,4-dioxane were dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl immediately prior to use. All other reagents were used without further purification.

Syntheses of Oh-POSS

Oh-POSS was synthesized using a standard Schlenk vacuum-line system under a N_2 atmosphere. Typically, 4.25 g of H_8 -POSS, 1 mL of hexene and 4 mg of Pt(dcp) were added in a three-necked flask. The system was degassed and purged with N_2 three times. Anhydrous 200 mL of 1,4-dioxane were injected to dissolve the solid. The hydrosilylation was carried out for 8 h at 80 °C under N_2 . The mixture was cooled down to room temperature. The white crystalline powder was filtered out, washed with

cyclohexane, and recrystallized from tetrahydrofuran/methanol (1:3) to give white crystal powder.

Preparation of Oh-POSS/PS nanocomposites

PS and Oh-POSS were mixed up with POSS contents of 0.1 %, 0.5 %, 1.0 %, 2.0 % and 4.0 %, respectively, and dissolved in THF. After vigorous stirring for 1 h, most THF was driven off, and further dried under vacuum.

Measurements

FTIR spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet NEXUS 870 FTIR spectrophotometer using KBr powder at room temperature. ^{29}Si -NMR spectra were carried out using a **BRUKER** AVANCE/DMX 300 spectrometer. Solution ^{29}Si -NMR samples were measured from CDCl_3 solutions in a 10-mm glass tube spinning at 20 Hz and using an 8-s pulse delay. The sample solutions also contained a 0.02 M concentration of chromium tris(acetylacetonate) as a spin relaxing agent. All ^{29}Si -NMR shifts are referenced to tetramethylsilane (TMS). SEM images were obtained on a FEI Sirion 400 microscope. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 9000 under a continuous nitrogen purge (50 mL/min). The scan rate was $10\text{ }^{\circ}\text{C}/\text{min}$ at a temperature range of $30\text{--}300\text{ }^{\circ}\text{C}$. The glass-transition temperature (T_g) was taken as the midpoint of the specific heat increment. Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ from 30 to $600\text{ }^{\circ}\text{C}$ under a continuous nitrogen purge (100 mL/min). The thermal degradation temperature (T_d) was defined as the temperature of 5% weight lost.

Acknowledgements

This work was financially supported by the Natural Science Foundation of Anhui Educational Department (No. KJ2011A247) and the Natural Science Foundation of Anhui Province (No.1208085MB24)."

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