Hybrid networks based on poly(styrene-co-maleic anhydride) and N-phenylaminomethyl POSS

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Abstract

Novel PSMA-POSS nanocomposites were prepared, in which N-phenylaminomethyl polyhedral oligomeric silsesquioxane (POSS) was conducted as crosslink agent to incorporate to poly(styrene-co-maleic anhydride) (PSMA). POSS was introduced by one-step reactive solution blend in amounts of 1–30 wt%. FTIR measurement evidenced the occurrence of amidation reaction between the anhydride group of PSMA and the secondary amino group of POSS. This reaction turned out to promote POSS well dispersed in the polymer matrix, and the PSMA-POSS hybrids showed no macro phase separation even if POSS concentration was up to 30 wt%. DSC results showed that the glass transition temperature ($T_g$) increased to 168°C with the increase of POSS loading. Dynamic mechanical thermal analysis (DMTA) revealed the storage modulus at high temperature increased with the addition of POSS due to the formation of a permanent network. Incorporation of POSS also improved the thermal properties of PSMA-POSS composites.

1. Introduction

Nanoscopic organic-inorganic hybrids are receiving considerable attention as reinforcement in composites due to the excellent chemical and physical properties, such as reduced flammability, increased oxidation resistance and improved mechanical properties [1–4]. Among various nano reinforcements, POSS has received extensive research interests due to the unique molecular structures with robust inorganic silica core surrounded by organic groups (such as alkyl, aryl, or any of their derivatives), precisely controlled mono-dispersed nanometer size and diverse synthetic strategies for organic functionalization [5–7]. All these make POSS molecules attractive candidates for a wide range of application. Many researches had studied on the enhancements of the mechanical, thermal and some special surface properties of hybrid materials by incorporating POSS with different functional groups into traditional polymers [8–18].

In general, POSS can be introduced into polymer matrix through (1) chemical tethering to the polymer chains as pendant groups [19–30] or (2) chemical bonding to the polymer chains as new kinds of crosslinker [31–41] or (3) physical blending [42–48]. Among kinds of POSS, multifunctional ones are preferred since the formed branched, star-shape and crosslink structures can be more tightly tethered the polymers, and thereby significantly improve the properties of polymers. Wang et al. [49] synthesized multi-functional methacrylate-OPS macromonomers, which were polymerized with methylmethacrylate (MMA) to yield crosslinked POSS/PMMA hybrid materials. Octamethacryl-POSS was also used as a new kind of photo-crosslink agent of poly(propylene fumarate) to prepare novel injectable, crosslinkable, non-toxic and biodegradable polymeric systems for objectives in bone repair and regeneration by Wang et al. [32]. In our earlier work, multifunctional N-phenylaminomethyl POSS was made through hydrolytic condensation, and a series of polyurethane-POSS composites were prepared thereafter. Both the stress and elongation at break of POSS-PU hybrids were well improved at the same time [50].

Maleic anhydride copolymers provide strong polarity, high compatibility and reactivity between polymers or polymer and fillers [51–53]. Among those, PSMA, a transparent amorphous thermoplastic engineering material, is widely used as a compatibility booster. For example, the miscibility and mechanical properties of the blends of nylon 6 and ABS were dramatically improved when PSMA was used as a reactive compatibilizer [54]. Recently, Monticelli et al. [25] prepared a novel hybrid system based on PSMA and a mono-functional POSS (aminopropyl heptaisobutyl-POSS) by one-step reactive blending. The hybrids showed high reactivity and compatibility between POSS and PSMA, as well as improved mechanical properties compared with the non-reactive PSMA/POSS system. Even so, there were still some aspects

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needed to be improved to meet the increasing demands for high performance materials. In a variety of methods, chemical crosslinking introduced by multifunctional POSS was one of the most effective ways to increase comprehensive properties of materials [49]. The aim of the present work is to synthesize a series of PSMA-POSS networks based on PSMA and N-phenylaminomethyl POSS, with an expectation to achieve better overall properties of PSMA in contrast with other cases.

2. Experimental

2.1. Materials

N-phenylaminomethyl POSS (referred as POSS in the following) was homemade which was mainly T10 and T12 structures, and the procedures of synthesis were detailed in our previous work [50]. PSMA (XIRAN SZ 26080, Mw = 80,000) with a concentration of maleic anhydride 26 mol%, was supplied by Shanghai Zhaocheng Scientific Development Corporation, China and used as received. Tetrahydrofuran (THF) were purchased from Shanghai Guoyao Corporation. N,N-Dimethylacetamide (DMAC) and N,N-Dimethylacetamide (DMAC) with a concentration of 25 wt%, followed by POSS dissolved in DMAC with a selected concentration. The mixture was then stirred for 4 h and poured into a PTFE plate to remove the solvent at 70 °C for 6 h and 90 °C for 4 h. The temperature was further raised to 130 °C for another 3 h to make the reaction complete. The samples were finally dried under vacuum at 120 °C for 24 h and 180 °C for 2 h respectively. The synthesis procedures of PSMA-POSS hybrids were shown in Scheme 1. There was an amidation reaction between the anhydride group of PSMA and the secondary amino group of POSS, with the consequent formation of an amide linkage binding POSS to the polymer backbone and a new generation of a carboxyl group. Neat PSMA and PSMA-POSS hybrids with 1–30 wt% of POSS were prepared. The final number of sample names indicated the content of POSS in weight percent. For example, PSMA-POSS8 was consists of 8 wt% of POSS and 92 wt% of PSMA.

2.2. Preparation of PSMA/POSS nanocomposites

To prepare the nanocomposites, PSMA was firstly dissolved in DMAC with a concentration of 25 wt%, followed by POSS dissolved in the PSMA/DMAC solution with a selected concentration. The mixture was then stirred for 4 h and poured into a PTFE plate to remove the solvent at 70 °C for 6 h and 90 °C for 4 h. The temperature was further raised to 130 °C for another 3 h to make the reaction complete. The samples were finally dried under vacuum at 120 °C for 24 h and 180 °C for 2 h respectively. The synthesis procedures of PSMA-POSS hybrids were shown in Scheme 1. There was an amidation reaction between the anhydride group of PSMA and the secondary amino group of POSS, with the

2.3. Characterization methods

2.3.1. Molecular structure characterizations

The Fourier transform infrared spectra (FTIR) were recorded on a NICOLET NEXUS 870 spectrophotometer at room temperature in the 400–4000 cm⁻¹ region. 20 scans were taken for each spectrum with a resolution of 2 cm⁻¹, and the samples were prepared by dispersing the sample in KBr and compressing the mixtures to tablets.

Solid state ¹³C NMR spectra were recorded on a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer at a proton frequency of 399.7 MHz using a 7 mm T3 double resonance CPMAS probe and a zirconia PENCIL rotor. All of the NMR data were processed with Varian Spin sight software and the experiments were carried out at room temperature.

2.3.2. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were recorded in transmission with a Bruker D8 Advance X-ray diffractometer. The wavelength used was Cu Kα (λ = 0.154 nm), and spectra were recorded in the 2θ range of 4–40° (step size 0.01°).

2.3.3. Morphological characterizations

Morphologies of composite films were examined using a scanning electron microscopy (SEM, Hitachi S-4800). Samples were prepared by cryogenic fracture to observe a representative section (cross-section). An accelerating voltage of 10 kV with an Au coating of the sample was used to image the sections.

High-resolution transmission electron microscopy (HRTEM, JEM-2100) was also carried out for a further study of the morphologies. The materials were embedded in epoxy resin, and ultra-thin sections were made by using a Leica ULTRACUT UC6 with tens of nanometers thick. The sections were collected onto copper grids and then imaged at 200 kV.

2.3.4. Mechanical measurements

The dynamic mechanical tests were carried out on a dynamic mechanical analyzer (DMTA) (Rheometric Scientific IV). The viscoelastic properties were measured from 70 °C to 220 °C under a nitrogen atmosphere, at a heating rate of 2 °C/min and frequency of 1 Hz.

2.3.5. Swelling experiments of the samples

The pre-weighed dry specimens were immersed in acetone at 25.0 °C, a good solvent for POSS. After equilibrating for 24 h, the samples were blotted with laboratory tissue and weighed. The acetone swelling ratio (SR) was expressed as the weight percentage of acetone in the swollen sample.

\[
\text{Swelling ratio (SR)} = \left( \frac{W_S - W_D}{W_D} \right) \times 100\%
\]

where \(W_S\) is the weight of the swollen sample, and \(W_D\) is the weight of the dry sample.

The samples were weighed \(W_1\) and placed in tubes filled with acetone in triplicate. The samples in acetone were refluxed in the thermostatic shaker for 2 h. Then the samples were taken out and dried at vacuum oven at 45 °C until constant weight was attained and weighed \(W_2\). The loss weight was calculated as follows.
Loss weight (LW) = \( \frac{(W_1 - W_2)}{W_1} \times 100\% \)

2.3.6. Thermal characterization

Differential Scanning Calorimeter (DSC) analyses were run using a Perkin Thermal Analysis (Pyris 1 DSC) instrument. Samples (5 mg) were loaded in aluminum pans, and tests were performed from 50 to 210 °C at a heating rate of 20 °C/min under nitrogen flow of 50 ml/min.

Thermal gravimetric analysis (TGA) was examined using a Perkin–Elmer TGA-7 thermogravimetric analyzer. Samples (2 mg) were loaded in platinum pans and measured from 25 °C to 700 °C under a nitrogen environment at a heating rate of 20 °C/min.

TGA-IR was examined using a NETZSCH STA409PC/PG thermogravimetric analyzer combined with Nicolet IS10 FTIR instrument. All the evolved gases from the TGA instrument were sent to FTIR spectrometer using a heated transfer line.

2.3.7. Static contact angle

Static contact angle measurements were performed by CAM 200 (KSV Instrument, Finland) at room temperature using distilled water. In this work the Sessil Drop Method was used. Five drops were considered and the average contact angle was then calculated.

3. Results and discussion

3.1. FTIR studies on PSMA and PSMA-POSS hybrids

Fig. 1 showed the portion of amplificatory FTIR spectra of PSMA-POSS4 as well as those of neat POSS and PSMA for comparison. The PSMA showed two characteristic absorptions at \( \sim 1774 \text{ cm}^{-1} \) and \( \sim 1850 \text{ cm}^{-1} \), which were assigned as the symmetric and asymmetric stretching vibrations of the anhydride carbonyl group. The peaks at 1500 cm\(^{-1}\) came from the skeletal vibration of aromatic ring. The FTIR spectrum of PSMA-POSS4 was very similar to that of PSMA, except two new bands appeared at \( \sim 1640 \text{ cm}^{-1} \) and 1710 cm\(^{-1}\) respectively, which were the characteristic peaks of the secondary amide and carboxyl group. These results confirmed that the POSS cage was incorporated into the hybrid nanocomposites. The spectra of other hybrids which were not shown here were almost the same.

3.2. Solid \(^{13}\text{C} \) NMR studies on PSMA and PSMA-POSS hybrids

Solid \(^{13}\text{C} \) NMR was carried out to further study of the reaction between PSMA and POSS. Fig. 2 showed a portion of amplificatory

3.3. Morphological characterization of the nanocomposites

In order to investigate the distribution of POSS particles in the PSMA matrix, SEM images from the cross-section of the fractured surfaces were obtained. Fig. 3(a–c) showed the SEM micrographs of neat PSMA, PSMA-POSS4, PSMA-POSS8. Fairly homogeneous distributions of particles in the PSMA matrix could be observed from the pictures of PSMA-POSS4 and PSMA-POSS8.

For PSMA-POSS30, heterogeneous microstructure with some POSS aggregations could be formed in Fig. 3d, which were sized of 200–400 nm. The membrane looked translucent.

HRTEM was carried out to further study microstructure of the hybrids. Fig. 4 presented the TEM micrographs of the neat PSMA, PSMA-POSS4 and PSMA-POSS8. It could be seen that considerable amounts of dark spherical particles with a range of 20–30 nm were dispersed in the PSMA-POSS4 hybrid. These dark particles could be attributed to POSS aggregations because of the high electron density of the POSS cages. It revealed that POSS was nano dispersed in the matrix. The good dispersion was attributed to POSS aggregations because of the high electron density of the POSS cages. It revealed that POSS was nano dispersed in the matrix.

3.4. WAXD pattern of POSS, PSMA and PSMA-POSS hybrids

The wide-angle X-ray diffraction (WAXD) measurements between 4° and 40° were applied to examine the crystalline structure of nanocomposites. The diffraction patterns of PSMA-POSS hybrids were shown in Fig. 5. For comparison, the XRD
curves of neat POSS and PSMA were also introduced. The diffraction pattern of the neat POSS showed intense, characteristic crystalline peaks at 5.42°, indicating that POSS was highly crystalline. For neat PSMA, the XRD pattern implied a characteristic amorphous structure. The broad peaks at 2θ = 10° and 19.2° could be attributed to the copolymer of St and MA [55]. As for all the PSMA-POSS hybrids, the WAXD profiles turned out to be similar to that of neat PSMA, and there was nearly no reflections of POSS. It suggested that POSS were well dispersed in the PSMA matrix and no long-range order of POSS formed during the crosslink process [56,57]. Although WAXS data showed the absence of POSS crystallites in the hybrids, SEM photographs showed 20–30 nm spherical formations. It might be attributed tentatively to single network junctions including POSS and attached polymer segments. The phenomenon was also found in some other hybrids with grafted POSS [58].
3.5. Thermal characterization of PSMA and PSMA-POSS hybrids

Fig. 6a showed the DSC curves for neat PSMA and the hybrids with different amounts of POSS (1–30 wt%), and Fig. 6b gave the summary of \( T_g \) according to the percentage of POSS by weight. The \( T_g \) of the hybrids increased from 156 °C to 168 °C with the increment of POSS at low filler concentration, and the raise of \( T_g \) was contributed to the crosslink between POSS and PSMA which tended to restrict the segmental mobility of PSMA chains near \( T_g \) temperature. However, the raise of \( T_g \) gradually slowed when POSS loading was higher than 4 wt%. Wu et al. indicated that higher POSS content might increase free volume [59]. In the case of high POSS loading, it could be thought that the combined influences of the competing factors led to a slower raise of \( T_g \) for the hybrids.

TGA results of the neat PSMA and the hybrids were shown in Fig. 7a, and the decomposition temperatures were summarized in Fig. 7b. The values of \( T_{d,25\%} \) and \( T_{d,70\%} \) were found to increase with the increase of POSS, and the char yield of the hybrids was well improved than that of neat PSMA. It was contributed to the network formed by the reaction between PSMA and POSS. However, it was clear that the values of \( T_{d,5\%} \) decreased with the increase of POSS. As mentioned in the Scheme 1, new carboxyl groups in the hybrids were generated in the reaction between secondary amine of POSS and maleic anhydride of PSMA, which were not stable enough and released carbon dioxide at about 200 °C. Therefore, it could be deduced that the first step of mass loss came from the release of CO\(_2\). In order to confirm it, TGA-IR characterization of PSMA-POSS was further performed (Fig. 8). It allowed the analysis to be performed on the same specimen, thus minimizing the experimental errors. As shown, after 20–30 min heating at the rate of 10 °C/min, there was a small absorption peak at 2400 cm\(^{-1}\) which could be ascribed to the characteristic peaks of CO\(_2\), and there were no other absorptions at the same time.

3.6. Dynamic mechanical properties of PSMA and PSMA-POSS hybrids

Incorporation of POSS and formation of networks were expected to have a great influence on the dynamic mechanical properties of PSMA-POSS hybrids, especially the modulus in the high temperature region. The dynamic mechanical tests for neat PSMA and the hybrids containing 4, 8, 18, 30 wt% of POSS were performed (Fig. 9). As expected, the storage modulus of the hybrids was gradually enhanced with the increase of POSS content. The storage modulus of neat PSMA started to decrease from glassy state to rubber state at about 155 °C, and the rubber plateau was kept from 155 to 180 °C, then neat PSMA went into terminal region. For PSMA-POSS hybrids, the glassy states were similar to that of neat PSMA with just a little higher modulus, while the rubber states showed much higher storage modulus. The trends of the storage modulus at high temperature for the hybrids were not the same either. The hybrids with low POSS concentration (PSMA-POSS4 and PSMA-POSS8) went into the terminal region after 190 °C. This suggested that the crosslink of the hybrids with low POSS loading was not enough to form a 3-dimensional network, or just partly. However, the storage modulus of high POSS concentration (PSMA-POSS18 and PSMA-POSS30) almost kept constant at high temperature, which could be contributed to the well formed 3-dimensional permanent network. It should be pointed that the activity of POSS and the reaction between POSS and PSMA were mild because the functional group of POSS was a secondary amine. When the POSS content was low, only a part of the functional groups of POSS participated in the reaction, while more functional groups of POSS would participate in the reaction when POSS content was high. The crosslinking density was increased with the increase of POSS concentration, therefore, the hybrids showed obvious enhanced properties.

3.7. Acetone swelling and loss weight ratio test

Table 1 listed the results of the swelling ratio and the loss weight ratio of the hybrids. The loss weight ratio showed the amounts of un-crosslinked PSMA and unbonded POSS which could be
extracted in acetone. As compared with PSMA-POSS18, the physical blend of PSMA and POSS with the same components was prepared in acetone. After all solvent was removed, a yellow and transparent film was made. The physical blend film could be dissolved in the acetone again while the hybrid could not. The difference of solubility suggested that POSS in PSMA-POSS18 was reacted with the PSMA. It was found that as POSS content increased, the swelling ratio of the hybrids increased as well and the loss weight ratio decreased. Hence, according to the Flory-Rehner theory [60,61], in the PSMA-POSS system, the crosslinking density was increased as POSS concentration increased. The results came into agreement with the DMA results.

3.8. Macro-morphology and surface property

In order to provide a better comparison on the stability of PSMA-POSS hybrids and blends, samples that kept for a month at room temperature were compared. Fig. 10 showed the macroscopic morphologies of PSMA-POSS4 and the physical blend sample with 4 wt% of POSS. As represented, the film of PSMA-POSS4 looked transparent while the physical blend sample was opaque which was caused by the heavy aggregation of POSS. The difference indicated that the chemical reaction turned out to promote POSS well dispersed in the polymer matrix.

Moreover, incorporation of POSS molecules had a great influence on the surface properties of the films as evidenced by the large change in water contact angle. As displayed in Fig. 11, incorporating of 4 wt% POSS (PSMA-POSS4) resulted in an increase of the contact angle from 78° to 101°, and higher loadings further increased the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Swelling ratio in acetone (%)</th>
<th>Loss weight ratio in acetone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PSMA</td>
<td>Absolutely dissolved</td>
<td>Absolutely dissolved</td>
</tr>
<tr>
<td>PSMA-POSS8</td>
<td>94.8</td>
<td>16.5</td>
</tr>
<tr>
<td>PSMA-POSS18</td>
<td>88.3</td>
<td>0.3</td>
</tr>
<tr>
<td>PSMA-POSS30</td>
<td>32.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Fig. 10. Macro-morphologies of physical blend sample and PSMA-POSS4.
contact angle to 108°. This phenomenon was quite commonly observed for POSS modified polymers with as surface tension preferentially drove the lower energy POSS residues to the air interface [62,63].

4. Conclusions

N-phenylaminomethyl POSS was incorporated to modify the PSMA resin. A series of crosslinked hybrids were prepared using various amounts of POSS as nano scale crosslink agent. The hybrids showed no macro phase separation even when the POSS concentration was up to 30 wt%. HRTEM measurements showed the POSS was well dispersed in PSMA matrix. DSC results indicated that Tg increased with the addition of POSS. DMA revealed that the storage modulus of the hybrids at high temperature was much improved compared with that of neat PSMA, especially with high POSS loadings. TGA revealed the values of T4,25% and T6,70% of the hybrids were increased and the char yields were much improved as well.

The enhanced properties were ascribed to the chemical interaction between POSS and PSMA, acted as a crosslinker could be dispersed into PSMA matrix in nano scale. PSMA chains would be restricted by the nano scale crosslinker and resulted in the great enhancement of mechanical and thermal properties. Besides, as POSS concentration increased, the crosslinking density also increased, at last a permanent network formed to a certain extent.

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