



Polymer Communication

Effect of LiClO₄ on the thermal and morphological properties of organic/inorganic polymer hybridsYing-Chieh Yen^a, Yun-Sheng Ye^a, Chih-Chia Cheng^a, Hsiu-Mei Chen^b, Hwo-Shuenn Sheu^c, Feng-Chih Chang^{a,*}^a Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan, ROC^b Material and Chemical Research Laboratories, Industrial Technology Research Institute, Chutung, Taiwan, ROC^c National Synchrotron Radiation Research Center, Hsinchu Science Park, Taiwan, ROC

ARTICLE INFO

Article history:

Received 9 April 2008

Received in revised form 27 May 2008

Accepted 10 June 2008

Available online 19 June 2008

Keywords:

Hydrogen bonding

Polyhedral oligomeric silsesquioxane

Ion–dipole interaction

ABSTRACT

This paper describes the thermal properties, morphologies, and interactions within the binary and ternary blends of poly(methyl methacrylate) (PMMA), octa(phenol)octasilsesquioxane (OP-POSS), and LiClO₄. In the binary PMMA/OP-POSS blends, the OP-POSS molecules tend to aggregate and result in a decrease (19 °C) in the glass transition temperature. In the ternary PMMA/LiClO₄/OP-POSS blends, however, the OP-POSS molecules form small sphere-like domains (20 nm) leading to the composite's glass transition temperature increasing by up to 30 °C. Based on these FT-IR spectra, the addition of LiClO₄ influenced the probability of hydrogen bonds formed between PMMA and OP-POSS and these SEM micrographs, DSC, and XRD data indicated that the addition of LiClO₄ is a convenient and simple approach toward dispersing the OP-POSS nanoparticles within PMMA, where the presence of LiClO₄ changes the physical effect of OP-POSS from that of a diluent role to a cross-linker role.

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1. Introduction

Composite materials fabricated from organic polymers and inorganic materials are currently attracting great attention for both their fundamental scientific behavior and industrial applications. Polyhedral oligomeric silsesquioxanes (POSSs), which have the general formula (RSiO_{1.5})_n, are prototypical organic/inorganic systems because they are composed of inorganic cores with external organic substituents. Through appropriate control over the functionality of these organic substituents, both mono- and octa-functional macromonomers can be blended or attached covalently to linear thermoplastics or thermosetting networks to form high-performance hybrid materials [1–17]. Other interesting organic/inorganic blend systems are the polymer electrolytes formed via the dissolution of salts into polar and high-weight macromolecules where strong noncovalent interactions between the macromolecules and the cations of the salts result in changes in the polymers' properties, e.g., their miscibilities [18,19]. To our knowledge, the reports which described organic/inorganic composite system featuring both hydrogen bonding interactions, ion–dipole interactions by incorporating the POSS nanoparticles and LiClO₄ into polymers are still rare [20,21]. In addition, the interaction and conductivity

behaviors of poly(vinyl pyrrolidone-co-methyl methacrylate) (PVP-co-PMMA) with LiClO₄ were reported in our previous work [22] and we also indicated that the ionic conductivity of a LiClO₄/PMMA-co-PVP polymer electrolyte was enhanced after blending with OP-POSS [23]. To further realize the interaction mechanism within these polymer electrolytes incorporated by OP-POSS which is functionalized to behave as a strong proton donor and exhibits improved miscibility with host polymers containing proton acceptors [24–27], these blends comprising PMMA, LiClO₄, and POSS derivatives were prepared and their properties were described at various compositions.

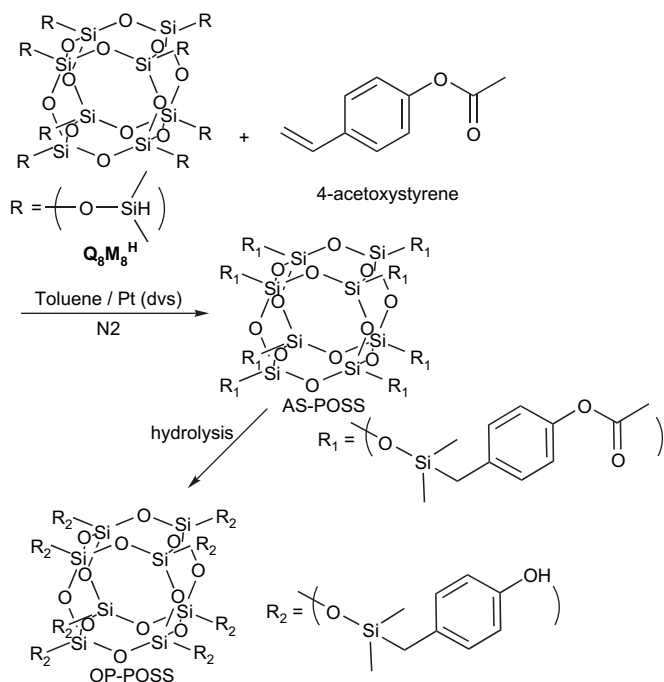
2. Experimental part

2.1. Materials

Toluene, tetrahydrofuran (THF), platinum divinyl tetramethyldisiloxane complex [Pt(dvs)], 4-acetoxystyrene (AS), lithium perchlorate (LiClO₄), and poly(methyl methacrylate) (PMMA) were purchased from Aldrich Chemical Co. Q₈M₈^H, C₁₆H₅₆O₂₀Si₁₆, was obtained from Hybrid Plastics Co. Toluene was fractionally distilled from calcium hydride under a nitrogen atmosphere. Q₈M₈^H, Pt(dvs) and AS were used as received. The oligomers octa(acetoxystyryl)octasilsequioxane (AS-POSS) and octa(phenol)octasilsesquioxane (OP-POSS) were synthesized (Scheme 1) according to a procedure described previously (see Supplementary data) [25].

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Scheme 1. Synthesis of OP-POSS.

Several PMMA/LiClO₄/OP-POSS blends were dissolved in THF (15 wt%) and stirred continuously for 8 h at 25 °C. To prepare the sample for XRD, SEM, and DSC measurements, the solutions were cast into Teflon dishes and dried under a nitrogen atmosphere at 25 °C for 24 h, under vacuum at about 0.2 torr at 60 °C for 12 h, and then at 120 °C for 8 h to completely remove any residual solvent or water. The compositions of the PMMA/LiClO₄/OP-POSS blends are summarized in Table 1. The unit phr is a concentration representation: e.g., 100/25/1 refers to a system formed from 100 g of PMMA, 25 g of LiClO₄ and 1 g of OP-POSS.

Table 1
Compositions, 2θ (degrees), and T_g of the binary and ternary blends

PMMA/LiClO ₄ /OP-POSS (phr)	2θ (degrees)	T_g^a (°C)
100/0/0	10.2	116
100/0/1	10.1	97
100/25/0	12.6	115
100/25/1	10.5	124
100/0/5	10.2	97
100/25/5	10.5	127

^a The glass transition temperature (T_g) was obtained as the inflection point of the heat capacity jump.

2.2. Characterization

Thermal analyses were performed using a DuPont TA 2010 DSC instrument operated at a scan rate of 20 °C/min from -50 to 200 °C. FT-IR spectra were recorded over the range 4000–400 cm⁻¹ using a Nicolet Avatar 320 FT-IR spectrometer (32 scans; 1 cm⁻¹ resolution) operated at 120 °C. To prepare the samples for the FT-IR observation, these solutions were cast onto KBr disks and dried as mentioned above. FE-SEM and SEM-DEX images were recorded using a Hitachi-S4200I microscope operated at acceleration voltage of 5–15 kV and ambient temperature. All samples were fractured under cryogenic conditions using liquid nitrogen. X-ray diffraction (XRD) experiments were performed at ambient temperature using the wiggler beamline BL17A1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan employing a monochromated

beam [wavelength (λ): 1.3329 Å]; the XRD pattern was collected by a curved imaging plate (IP: Fuji BAS III: area: 20 × 40 cm²) having a radius equivalent to the sample-to-detector distance (280 nm).

3. Results and discussion

3.1. Morphologies

Fig. 1 presents cross-sectional SEM images, which were employed previously to investigate the distribution of various functional POSS derivatives, of the (a) 100/0/5 and (b) 100/25/5 blends [5,28–34]. The POSS molecules in the 100/0/5 blend appear to aggregate into large domains (bright regions) within the PMMA matrix. In contrast, the OP-POSS molecules in the 100/25/5 blend have formed sphere-like domains having diameters of ca. 20 nm. In our previous studies [22,35], we examined blends featuring a range of competitive noncovalent interactions, including carbonyl (PMMA)···hydroxyl (OP-POSS), hydroxyl (OP-POSS)···hydroxyl (OP-POSS), carbonyl (PMMA)···Li⁺, and Li⁺···ClO₄⁻ interactions [36–38]. From the knowledge gained from those studies, we suspected that the morphological differences between the 100/0/5 and 100/25/5 blends resulted from the different types of noncovalent interactions within them. Fig. 2(a) presents IR spectra displaying the ν (ClO₄⁻) internal vibration modes of these blends. The bands centered at 626 and 636 cm⁻¹ correspond to the signals of the free anion and the contact ion pair, respectively [39,40]. The intensity of the blend for the contact ion pair increased upon increasing the content of OP-POSS, revealing that OP-POSS molecules tend to increase the formation of contact ion pairs. Fig. 2(b) displays the carbonyl stretching region of IR spectra of the PMMA/LiClO₄/OP-POSS blends. The bands at 1730, 1709, and 1700 cm⁻¹ correspond to the free C=O groups of PMMA, and those involved in hydrogen bonds (with the OH groups of OP-POSS) and ion–dipole interactions (with Li⁺), respectively. In the spectra of the 100/25/0 and 100/25/5 blends, the intensity of the shoulder at 1700 cm⁻¹ decreases dramatically in the latter, indicating that the presence of OP-POSS led to a decrease in the number of PMMA C=O groups involved in ion–dipole interactions. The intensities of the hydrogen-bonded C=O of PMMA were identical for the 100/25/5 and 100/0/20 blends, indicating that the fractions of such groups of PMMA were identical [35]. The presence of LiClO₄ salts in the ternary blend led to an increase of the probability of forming C=O (PMMA)···OH (OP-POSS) hydrogen bonds. Thus, there must have been a specific interaction occurring between LiClO₄ and OP-POSS. Fig. 2(c) displays the region from 2700 to 3700 cm⁻¹ in the IR spectra of the OP-POSS/LiClO₄ (phr) binary blends. LiClO₄ appears to interact with the OH groups of OP-POSS shifting their broad band to higher frequency. These IR spectra reveal that the interactions between OP-POSS and LiClO₄ coexist with the C=O (PMMA)···OH (OP-POSS), OH (OP-POSS)···OH (OP-POSS), C=O (PMMA)···Li⁺, and Li⁺···ClO₄⁻ interactions, with competition between these species resulting in the change in morphology [41–43]. Table 1 lists the values of 2θ obtained from XRD analysis of the various blends. The signal centered at 10.2° corresponding to the intermolecular distance between PMMA chains [44] remained unchanged after the incorporation of OP-POSS. In contrast, the addition of LiClO₄ (25 phr) to the PMMA matrix shifted the 2θ angle from 10.2° to 12.6° which suggests that Li⁺···O=C coordination resulted in contraction of the polymer chains. The presence of OP-POSS in the 100/25/5 blend resulted in a shift of the 2θ angle to 12.6° from that of 10.5° for the 100/25/0 blend. This finding implies that the addition of OP-POSS increases the contracted intermolecular distance between PMMA polymers. For the 100/25/5 blend, the 2θ angle was almost identical to that of 100/0/5, i.e., for the association of PMMA, LiClO₄, and OP-POSS. In the 100/25/5 blend, the OP-POSS molecules were dispersed well in the presence of LiClO₄, as the SEM image

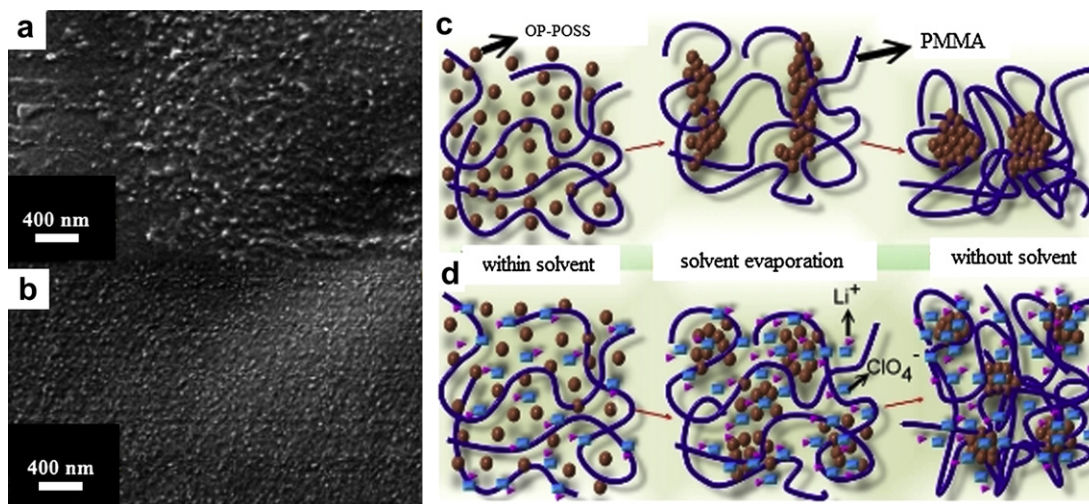


Fig. 1. FE-SEM micrographs of (a) PMMA/LiClO₄/OP-POSS (100/0/5) and (b) PMMA/LiClO₄/OP-POSS (100/25/5); (c and d) schematic representations of the proposed mechanisms of formation of the various OP-POSS domains.

revealed, which has the influence of increasing the contracted intermolecular distance between PMMA chains. As a result of these competing influences, the 2θ angle for the 100/0/5 and 100/25/5 blends remained virtually unchanged.

Fig. 1 illustrates the proposed mechanism leading to development of the morphologies of the 100/0/5 and 100/25/5 blends. During the initial stage, all of the components in the 100/0/5 and 100/25/5 blends were dissolved and distributed uniformly within the solvent. During the second stage, as the solvent evaporates partially, the LiClO₄ in the 100/25/5 blend interacts with both OP-POSS and PMMA and forms sphere-like OP-POSS/LiClO₄ domains. During the final stage, as the solvent and water molecules

are removed completely, the degree of phase separation in the PMMA/LiClO₄/OP-POSS is relatively lower – and, thus, the OP-POSS domains are relatively smaller – than in the PMMA/OP-POSS blends as a result of the competitive interactions.

3.2. Thermal properties

Table 1 lists DSC data of the PMMA/LiClO₄/OP-POSS blends. In the blends lacking the salt, the presence of OP-POSS decreases the glass transition temperature (T_g) of PMMA as a result of aggregation of OP-POSS. In contrast, for the 100/25/1 blend, the addition of 25 phr LiClO₄ salts to the 100/0/1 blend resulted in a 27 °C increase

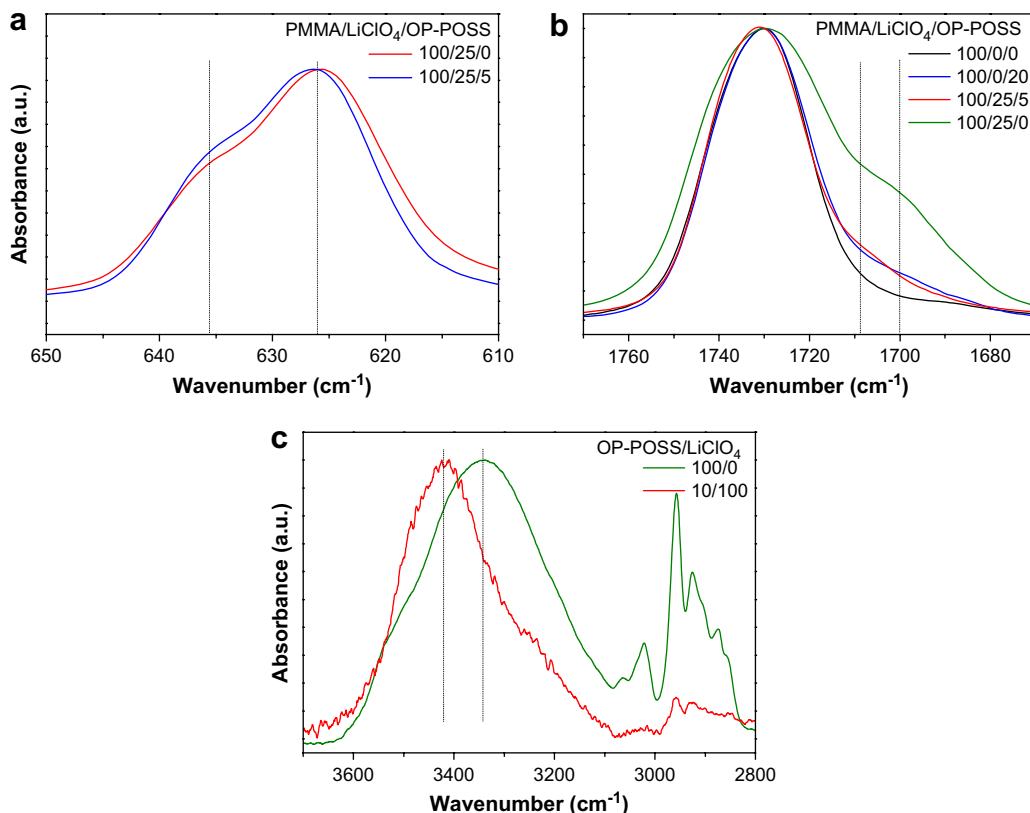


Fig. 2. IR spectra of various PMMA/LiClO₄/OP-POSS blends recorded at 120 °C.

in T_g . The change was much greater (30 °C) for the 100/0/5 and 100/25/5 systems. In the 100/25/0, 100/0/1, and 100/0/5 blends, the weak associations, i.e., $\text{Li}^+\cdots\text{O}=\text{C}$ (PMMA) and $\text{C}=\text{O}$ (PMMA) $\cdots\text{OH}$ (OP-POSS) had no effect or a slight decrease in the value of T_g of the composite [22,33,45,46]. In the 100/25/1 and 100/25/5 blends, the combination of the various noncovalent interactions resulted in the formation of OP-POSS/LiClO₄ aggregated domains, improving the probability of forming $\text{C}=\text{O}$ (PMMA) $\cdots\text{OH}$ (OP-POSS) hydrogen bonds, smaller and better-distributed OP-POSS molecules, and an increase in the value of T_g of the composites [47–50]. In previous studies [5,51], POSSs were found to affect the glass transition temperatures of nanocomposites through two different effects: one was a restricted effect that enhanced T_g , the other increased the free volume of the system, which reduced T_g . Based on our FT-IR, XRD, DSC data, and SEM micrographs, the presence of LiClO₄ in the 100/25/5 blend influenced the hydrogen bonds formed between PMMA and OP-POSS, dispersion of OP-POSS, and the intermolecular distance between PMMA chains; thus, the addition of LiClO₄ shifted the physical role of OP-POSS from that of a diluent to a restricted role (physical crosslinking). Additionally, the interactions between PMMA, LiClO₄, and OP-POSS enhanced the restricted effect of the OP-POSS toward PMMA. Therefore, the glass transition temperature of the composites was enhanced through the simultaneous incorporation of LiClO₄ and OP-POSS.

4. Conclusions

In the 100/0/1 and 100/0/5 blends, the OP-POSS molecules tended to aggregate into large domains because of the tendency of their OH groups to self-associate rather than form $\text{OH}\cdots\text{C}=\text{O}$ hydrogen bonds [35,52], resulting in a decrease in the value of T_g of the PMMA/OP-POSS composites. In the 100/25/1 and 100/25/5 blends, LiClO₄ and OP-POSS formed a better dispersion of sphere-like OP-POSS/LiClO₄ domains as a result of competition among the various interaction pairs. Based on these FT-IR spectra, LiClO₄ played critical roles through its ion–dipole interaction with PMMA and its specific interactions with OP-POSS, influencing hydrogen bonds formed between PMMA and OP-POSS and dispersion of OP-POSS; the result was an enhancement of the glass transition temperature of these PMMA/OP-POSS composites. Thus, the addition of LiClO₄ is a convenient and simple approach toward dispersing the OP-POSS nanoparticles within PMMA polymers, where the presence of LiClO₄ changes the physical effect of OP-POSS from that of a diluent to a cross-linker role.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.polymer.2008.06.025](https://doi.org/10.1016/j.polymer.2008.06.025).

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