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Synthesis and Characterization of Sol-Gel Processed Organic/ Inorganic Composite Materials

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ABSTRACT

Organic/inorganic composite materials consisting of polystyrene (PS) and silica (SiO_2) were synthesized by the sol-gel process, using styrene monomer and methacrylic acid 3-(trimethoxysilyl)propyl ester (MAMSE) as precursors. Three styrene/MAMSE ratios by mol were prepared, namely PS/SiO_2 = 80/20, 60/40 and 50/50. The copolymer precursors were then hydrolyzed and condensed to generate PS/SiO_2 composite materials. The copolymer precursors and composite materials were characterized by FT-IR, DSC, TGA and SEM. It was found that thermal properties of composite materials were improved as silica content increased. The compatibility between organic polymer and inorganic particles mainly derived from incorporating the polymer matrix with the silica covalently. To investigate the distribution of silica and microphase separation in the hybrid matrix, the morphology of the fractured surfaces was observed by SEM image. The silica particles are uniformly dispersed in the copolymer matrix. These results show that silica networks are restrained under molecular level in the PS-SiO_2 hybrid copolymers.

Key words: organic/inorganic, composite material, polystyrene, sol-gel process

INTRODUCTION

The possibility of combining properties of organic and inorganic materials was explored several years ago. The presence of finely dispersed inorganic particles in the polymer matrix has proven to be very useful in the improvement of material performances. Many new types of organic/inorganic composite materials have the potential to combine the desired properties of inorganic and organic systems, improving the mechanical and thermal properties of inorganic ones with the flexibility and ductility of organic polymers. These materials can be readily prepared by using a sol-gel process, which offers several advantages over other techniques (Zulfikar *et al*., 2006).

The sol-gel process is a versatile alternative method to produce a great variety of ceramic and glass compound materials. One of the great advantages of this process is that by controlling the chemical composition of the precursor solution, it is possible to obtain the materials in different forms such as fibers, monoliths or thin films. The sol-gel process can also be applied to the preparation of inorganic-organic composite materials. The purpose to produce materials is to combine the comple-

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mentary properties of the inorganic and organic phases which constitute them. The micro- and macrostructure of a composite material can be controlled by the optimization of several synthetic parameters, for example: pH, concentration, water-to-alkoxide ratio, temperature, pressure, type of catalyst and solvent at low temperature (Avila-Herrera *et al*., 2006; Zulfikar *et al*., 2006).

The specific mechanical and thermal properties of the sol-gel materials are affected by particle sizes and interfacial interactions between the dispersed and the continuous phases. Further, more the compatibility of the organic and inorganic composite materials is influenced by solvent, coupling agent, aging history, the percent of shrinkage accrued and the network microstructures. A significant feature to enhance the compatibility in the composite materials is the formation of covalent bonding between organic polymers and inorganic components. Not only do the hybrid materials exhibit tunable properties of both organic polymers and inorganic glasses, but also they have a blur interface (Hsiue *et al*., 2000).

In this work, a series of polystyrene (PS)/ silica (SiO_2) composite materials were prepared. Copolymer precursors of trimethoxysilyl-functionality were prepared by free radical copolymerization of styrene with methacrylic acid 3-(trimethoxysilyl)propyl ester (MAMSE). The copolymer precursors were then hydrolyzed and condensed in the presence of an aqueous hydrochloric acid catalyst to generate PS/SiO_2 composite materials. These copolymer precursors and composite materials were characterized with Fourier-transform infrared spectroscope (FT-IR: Bruker Optics FTIR Vertex 70), differential scanning calorimeter (DSC: Perkin-Elmer Pyris 1) and thermogravimetric analysis (TGA: Perkin-Elmer TGA 7). The compatibility and morphology of the materials were investigated by using the scanning electron microscope (SEM: Camscan-MX 2000).

MATERIALS AND METHODS

Materials preparation

All chemicals used were analytical grade reagents. Styrene monomer was purchased from Fluka Chemie A.G. and purified by treating with 5% aqueous NaOH, drying over anhydrous sodium sulfate and calcium hydride, followed by distillation under reduced pressure. Methacrylic acid 3-(trimethoxysilyl)propyl ester (MAMSE) was used as received. Benzoyl peroxide (BPO) was purified by recrystalization from acetone. Toluene and tetrahydrofuran (THF) were used as received.

Synthesis of copolymer precursors

Several copolymer precursors were produced via copolymerization of styrene with methacrylic acid 3-(trimethoxysilyl)propyl ester at various feed compositions (copolymer precursors containing monomer MAMSE at 20, 40 and 50 mol %, respectively). The copolymerization was carried out using BPO as a free radical initiator in a 250 mL three-neck flask at 78 °C under nitrogen. The concentration of comonomers was maintained at 2 M in toluene and the reaction time was about 6 h. These copolymer precursors were purified by reprecipitation in methanol. The synthetic route is shown in Figure 1.

Preparation of the composite materials

The PS-SiO_2 composite materials were prepared via the sol-gel process. The synthetic route is shown in Figure 2. The materials were dissolved in THF solution and the concentrations were controlled at 20 (W/V)%. A trace of the aqueous solution of hydrochloride was then added. The solution was stirred for 30 min and then casted onto Teflon coated plate. After drying for 2 days, transparent films were obtained. Further curing of the glass was performed in an oven at 200 °C for

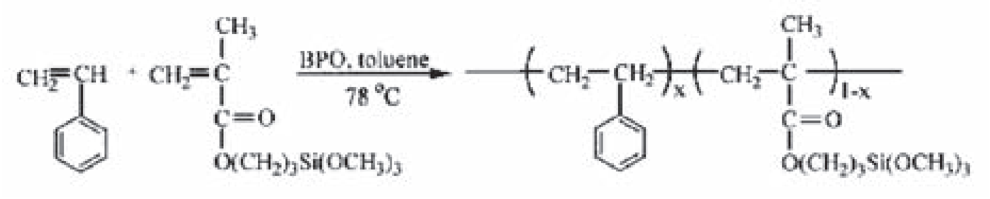

Figure 1 Synthesis of copolymer precursors by copolymerization.

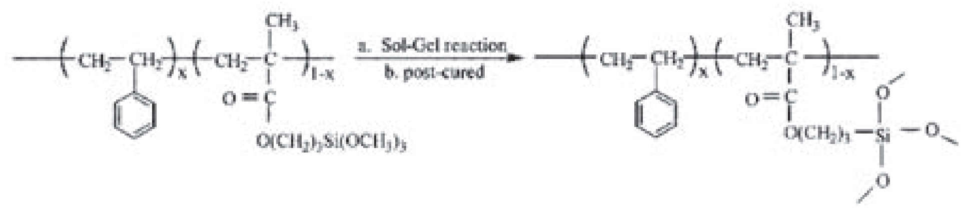

Figure 2 Synthesis of composite materials by sol-gel process.

2 h. After heat treatment, thermally stable sol-gel films without cracks were obtained.

Characterization of materials

The chemical structures were identified by FT-IR which was recorded on a Bruker Optics FTIR Vertex 70 Spectrometer. The samples for FT-IR analyses were mixed with KBr powder and pressed into pellets. The thermal properties were characterized by DSC and TGA which were performed on Perkin-Elmer Pyris 1 and Perkin-Elmer TGA 7 Equipped, respectively. The DSC and TGA measurements were performed at a heating rate of 10 °C /min. The composite materials were measured under air atmosphere. The temperature range for TGA measurements is from 40 to 600 °C. The samples for the thermal analyses were treated at 200 °C for 2 h and then ground into fine powder. The morphology of the fractured surfaces of the composite materials was observed by SEM (Camscan-MX 2000 Equipped).

RESULTS AND DISCUSSION

Identification and characterization of copolymer precursors and composite materials

The typical FT-IR spectra for the copolymer precursor and composite materials were shown in Figure 3 and 4, respectively. The characteristic bands of 3-(trimethoxysilyl)propyl methacrylate units appeared at 1735 cm^{-1} for the C=O bond and at 1087 cm^{-1} for the Si–OCH$_3$ bond. The characteristic bands of the aromatic ring contributing from styrene units were observed at 1600, 1490 and 1450 cm^{-1} (Daimay *et al.*, 1995). The characteristic absorption bands of Si–OCH$_3$ in the copolymer precursors became vague, whereas the characteristic absorption bands of Si–O–Si bond around 1000-1200 cm^{-1} of the

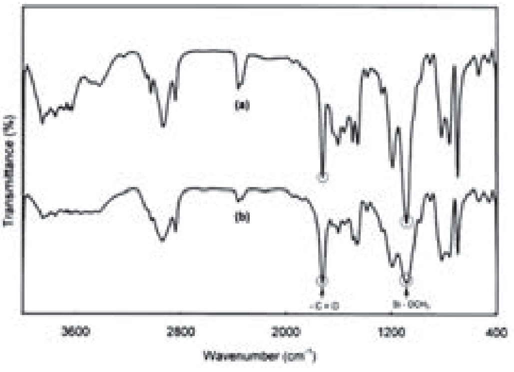

Figure 3 FT-IR spectra of copolymer precursors: (a) MAMSE 20 mol % and (b) MAMSE 40 mol %.

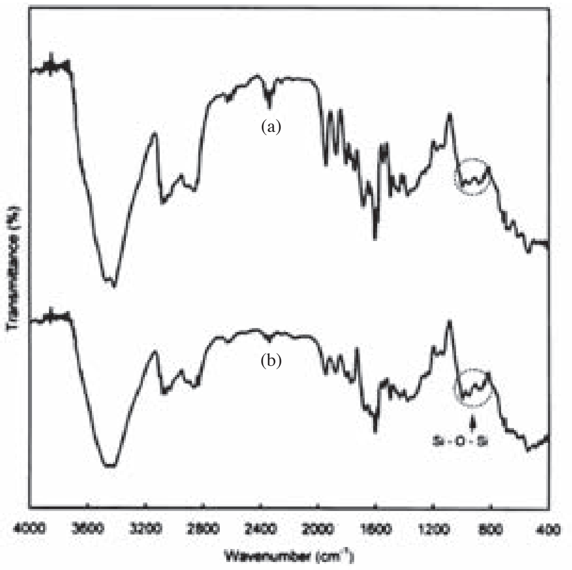

Figure 4 FT-IR spectra of composite materials: (a) MAMSE 20 mol % and (b) MAMSE 40 mol %.

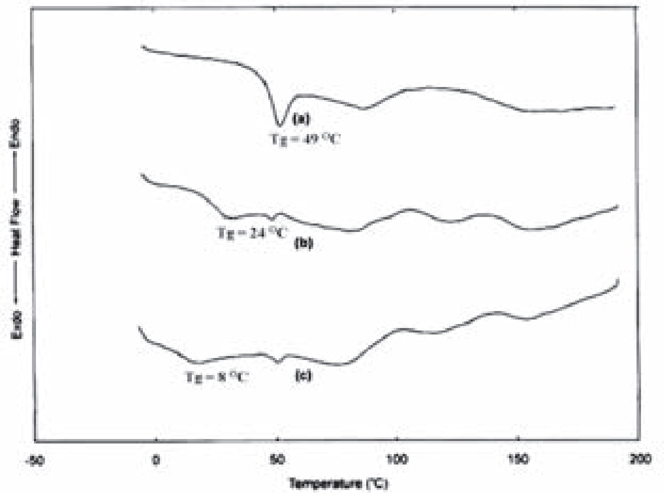

Figure 5 DSC thermograms of copolymer precursors: (a) MAMSE 20 mol % (b) MAMSE 40 mol % and (c) MAMSE 50 mol %.

composite materials after heat treatment emerged and their intensities increased with increasing MAMSE content. This implied that a more complete sol-gel reaction occurred during heat treatment.

Figure 5 showed the DSC thermogram of the copolymer precursors. The glass transition temperature (Tg) decreased as the MAMSE content increased. This indicated that the pending alkoxysilyl group had a plasticization effect on the copolymer precursors.

After heat treatment, the thermal stability increased significantly. The Tg of the PS/SiO_2 composite materials increased with increasing

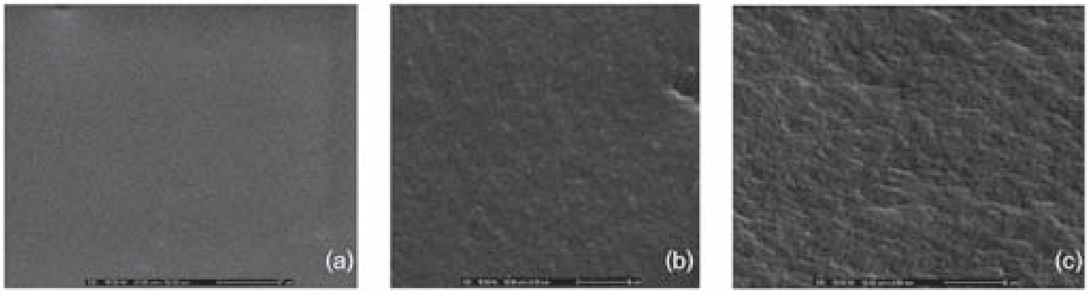

Figure 6 SEM images of composite materials: (a) MAMSE 20 mol % (b) MAMSE 40 mol % and (c) MAMSE 50 mol %, magnification 3,000 x.

MAMSE content. This result was different from that of the copolymer precursors. It was due to the fact that the plasticizing trimethoxysilyl groups had transformed to silica network during the sol-gel process. The silica contents in the composite materials were determined from the residual weight at 600°C in the TGA thermograms under air atmosphere, as listed in Table 1. The thermal degradation behaviors of the composite materials were divided into two stages. The primary degradation stage could be caused by the cleavage of copolymer chains, and the secondary degradation stage could be brought about by further oxidization of silicate. The degradation temperature (Td) of the composite materials increased as the low content of styrene was covalently incorporated. However, as the styrene content increased, Td decreased. This phenomenon was probably due to variation in morphology or chemical structures of the composite materials (Hsiue *et al.*, 2000).

The compatibility between the organic copolymer and silica had a great effect on the thermal, mechanical and optical properties. To investigate the distribution of silica and microphase separation in the polymer matrix, the morphology of the fractured surfaces was observed by SEM (Figure 6). In micrographs, brittle structures were observed. The roughness of the fracture surfaces also increased as increasing MAMSE content (Hsiue *et al.*, 2000; Sun *et al.*, 2007). Moreover, microphase separations were also observed on the fractured surfaces of these matrixes. The silica particles were uniformly dispersed in the copolymer matrix. These results showed that silica networks were restrained under molecular level in the PS/SiO_2 composite materials.

CONCLUSION

In this study, a series of alkoxysilane-containing prepolymers were prepared by a copolymerizing alkoxysilane-containing monomer and styrene. After curing, the silica particles were uniformly dispersed in the polymer matrix. Miscibility between the silica and the polymer was enhanced by covalent bonding between the organic

Table 1 Thermal properties and residual content of composite materials.

Composition of feed (Mol %)		Tg	Td	Residual contents
Styrene	MAMSE	(°C)	(°C)	(wt %)
100	0	80	291	0.3
80	20	82	299	9.1
60	40	107	305	15.8
50	50	133	308	20.0

and inorganic components. The thermal stability of the composite materials was also increased with increasing silica content.

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