

Synthesis, characterization and thermal properties of inorganic-organic hybrid

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Abstract. Poly (St-MAN-APTES)/silica hybrid materials were successfully prepared from styrene (St), maleic anhydride (MAN) and tetraethoxysilane (TEOS) in the presence of a coupling agent 3-aminopropyltriethoxysilane (APTES), by free-radical solution polymerization and in situ sol-gel process. The TEOS content varied from 0 to 25 wt%. Fourier transform infrared spectroscopy and ^{29}Si nuclear magnetic resonance spectroscopy were used to characterize the structure of the hybrids (condensed siloxane bonds designated as Q^1 , Q^2 , Q^3 , Q^4 , with 3-aminopropyltriethoxysilane having mono-, di-, tri-, tetra-substituted siloxane bonds designated as T^1 , T^2 and T^3). The results revealed that Q^3 , Q^4 and T^3 were the major microstructure elements in forming a network structure. The hybrid materials were also characterized by the methods of solvent extraction, Transmission Electron Microscopy (TEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for determining the gel contents, particle size and thermal performance. The results showed that gel contents in the hybrid materials were much higher, the SiO_2 phase were well dispersed in the polymer matrix, silicon dioxide existed at nanoscale in the composites, which had excellent thermal stability.

Keywords: polymer composites, organic-inorganic hybrid material, sol-gel process

1. Introduction

Over the past decade, the synthesis and characterization of inorganic-organic hybrid materials by the sol-gel process have received considerable attention. This is mainly due to the mild conditions, such as low temperature and pressure [1–3]. In addition, the sol-gel process is a convenient method for preparing oxide films from alkoxysilyl group containing materials via continuous reaction steps of hydrolysis and condensation. This technology has been a great achievement in making ceramic or organic modified hybrid materials in the past two decades, by which homogeneous materials with higher thermal stability, density, and hardness can be produced. These hybrid materials possess organic and inorganic properties [4] which can also be tuned through changing the functionality or seg-

ment size of each component, tailoring thermal, mechanical, electronic, optical and optoelectronic properties. Common applications of the hybrid materials as passive or active layer in optoelectronic devices have been reported, including protective coating [5], contact lenses [6], high refractive index films [7], thin film transistors [8], solar cells [9], light-emitting diodes [10], optical waveguides materials [11] and photo chromic materials [12]. These properties are associated with σ conjugation [13]. Many researchers have demonstrated that monolithic, transparent hybrid materials without macroscopic phase separation can be prepared by properly controlling the conditions of hydrolysis and condensation of sol-gel materials such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) [14–16]. Organic and inorganic constituents can be chemically bonded or just physi-

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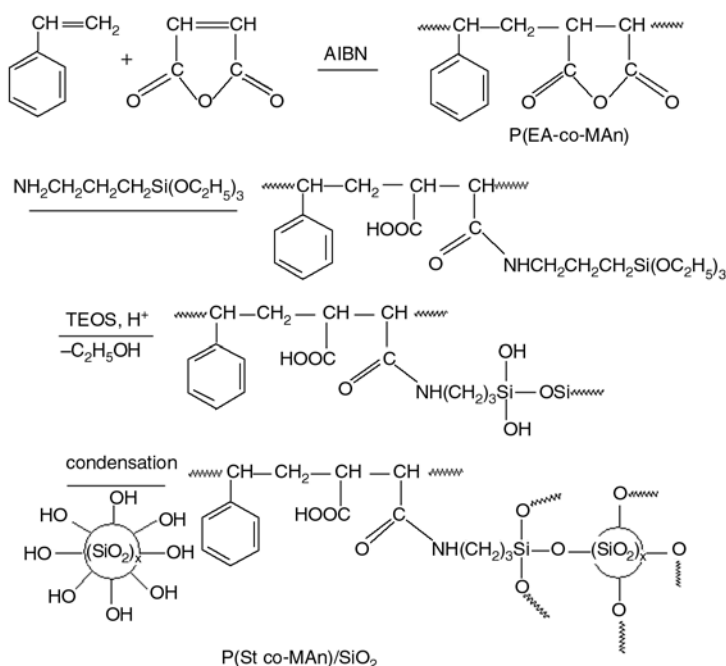


Figure 1. Preparation of organic-inorganic hybrid by sol-gel process

cally mixed in these hybrid materials. A significant feature to enhance the compatibility in the hybrid material, however, is the formation of covalent bonding between organic polymers and inorganic components.

In this study, copolymer was prepared by free radical copolymerization of styrene (St) with maleic anhydride (MAN). Copolymer precursor holding trimethoxysilyl-functionality was prepared by 3-aminopropyltriethoxysilane (APTES), coupling of the copolymer with miscible TEOS as an inorganic silica matrix for a sol-gel process. Then the copolymer precursor was hydrolyzed and condensed in the presence of an aqueous HCl catalyst to generate poly (St-MAN-APTES)-SiO₂ hybrid material as shown in Figure 1.

2. Experimental

2.1 Materials

Styrene (St), maleic anhydride (MAN), 2,2'-azobisisobutyronitrile (AIBN) and TEOS were purchased from Shanghai Chemical Reagent Company. Initiating agent AIBN was purified by recrystallization from alcohol and then dried in a vacuum oven. APTES was purchased from Nanjing Shuguang Chemical Plant. Tetrahydrofuran (THF) was purified by distillation and other reagents, solvents

were obtained commercially and were used as received.

2.2. Preparation of hybrid P (St-MAN-APTES)/SiO₂

Hybrid was prepared according to the scheme, as shown in Table 1. St and MAN were taken in a 500 ml three-neck round-bottomed flask. The THF and initiator AIBN were added under nitrogen purging. The reaction temperature was maintained at 70°C for 3 h and the copolymerization was carried out. Then APTES was added under nitrogen and stirred for 2 h at 70°C. The copolymer precursor for preparing the hybrid films was obtained. Then the TEOS homogeneous hydrolysate, prepared using deionized water, hydrochloric acid and THF, were added into the copolymer precursor solution. Meanwhile the sol-gel process was carried

Table 1. Monomer compositions for preparing hybrid thin films

Sample	St [g]	MAN [g]	APTES [g]	TEOS [wt%]
Z1	28.61	26.96	40.53	5
Z2	27.11	25.54	38.40	10
Z3	25.39	24.31	36.26	15
Z4	24.09	22.70	34.13	20
Z5	22.59	21.28	32.00	25

All of polymerization mixtures had the following fixed composition: [APTES]/[St] + [MAN] + [APTES] = 25 mol%; [AIBN]/[St] + [MAN] + [APTES] = 3.25 mol%

out. The synthetic route is shown in Figure 1. The homogeneous transparent sol can be obtained and then transferred to a conical flask. Solvents have been evaporated off the resulting gel slowly for 5 days and then was dried at 110°C under vacuum for 5 h to remove residual solvent and by-products (water and alcohol etc.). The thermally stable sol-gel hybrid material was obtained.

2.3. Measurement

FT-IR spectra of the prepared thin films were obtained on KBr pellets using Nicolet AVATAR 360 spectrometer. ^{29}Si NMR was performed using a Bruker DPX-400WB, Germany. HITACHI H-600 Transmission Electron Microscope (TEM) measured the particle sizes. Transmission electron microscopy (TEM) micrographs were obtained using a Hitachi H-600 operated at 80 kV with a 35 micron objective. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA 449C. The programmed heating range was from room temperature to 800°C, at a heating rate of 10°C/min under nitrogen atmosphere. The measurement was taken using 6–10 mg samples. TGA and DSC curves were recorded. The determination of sol fraction was to put the obtained hybrid materials in the sorbite extraction set and use acetone circulation reflux for 36 h. Then dried to constant weight in the vacuum drying oven. Sol fraction is calculated by Equation (1):

$$A = \frac{m_1 - m_2}{m_1} \cdot 100\% \quad (1)$$

where A is the sol fraction, m_1 and m_2 are the mass before and after extraction, respectively.

3. Results and discussion

3.1. Fourier transforms infrared spectra

The results of FT-IR spectra (4000–400 cm^{-1}) of hybrid materials Z1–Z5 are shown in Figure 2. It could be easily found that 1788 and 1850 cm^{-1} was attributed to stretching peaks of carbonyl in carboxylic ($-\text{COOH}$) groups. Transmissions at 1732 and 1700 cm^{-1} belonged to stretching peaks of carbonyl in amid ($-\text{CONH}$) groups. Therefore it could be confirmed that amino-group of coupling agent APTES broke maleic anhydride of copolymer to

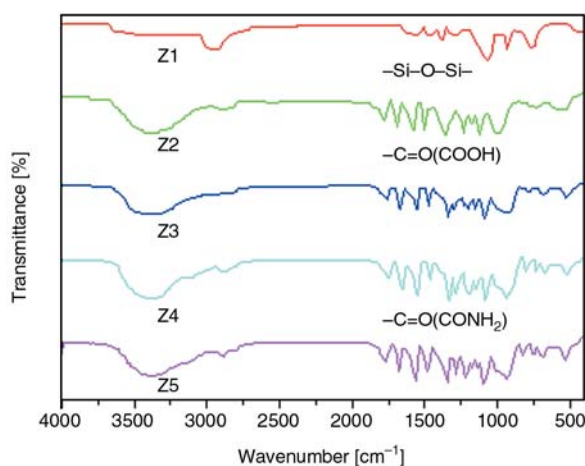


Figure 2. FT-IR spectra of hybrid materials

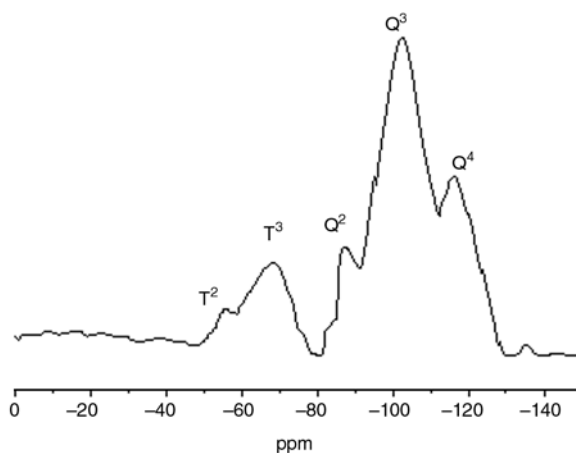


Figure 3. Solid-state ^{29}Si NMR spectrum of hybrid (Z3)

form carboxylic acid and amide. However the TEOS and triethoxy-silicon group of APTES formed inorganic network by hydrolysis and condensation, which could be demonstrated by the absorption, peaks of Si–O–Si asymmetric stretching (1100 to 1050 cm^{-1}) and symmetric stretching (728 cm^{-1}).

Figure 3 displays the solid-state ^{29}Si NMR spectra of the hybrid nanocomposite (Z3). The condensed siloxane species originating from TEOS, the silicon atoms through mono-, di-, tri-, and tetra-substituted siloxane bonds were designated as Q^1 , Q^2 , Q^3 , and Q^4 , respectively. The various Q^s were defined in Figure 4.

The 3-aminopropyltriethoxysilane, APTES, similarly with mono-, di-, tri-, tetra-substituted siloxane bonds were designated as T^1 , T^2 , T^3 , respectively. The various T^s are defined in Figure 5.

The chemical shifts from the ^{29}Si NMR spectra of Q^2 , Q^3 , and Q^4 were -87 , -102 , -116 ppm, respectively, and were similar to those reported in the lit-

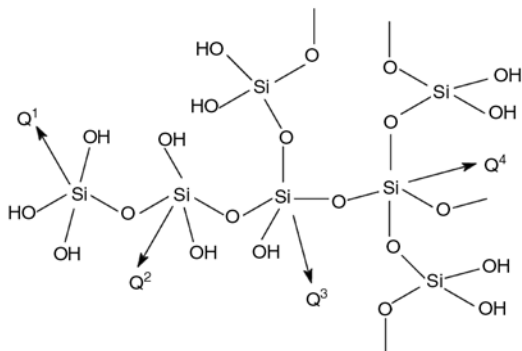


Figure 4. Abbreviations used for Si atoms attached to four oxygen atoms in various structural positions

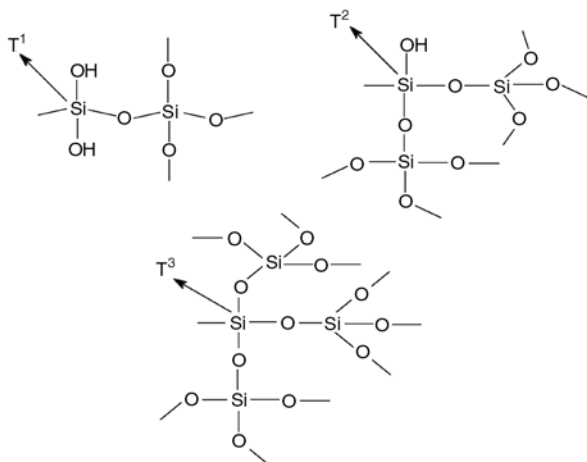


Figure 5. Abbreviations used for Si atoms attached to three oxygen atoms in various structural positions

erature [17]. The chemical shifts of T² and T³ were –54 and –68 ppm, respectively, and also in good agreement with the literature values [18]. Results revealed that Q³, Q⁴ and T³ were the major microstructures forming a network structure.

3.2. Determination of sol fraction

As is well known, good solvent will extract the part, which doesn’t cross link with chemical bond. After the synthetic hybrid materials were extracted

with acetone, the extraction sol is the copolymer, which doesn’t combine to inorganic network with the covalent bond. The results of extraction experiments were 5.8% (Z1), 5.5% (Z2), 5.1% (Z3) and 4.9% (Z4) and 4.7% (Z5) respectively. This shows combination with chemical bond between organic and inorganic parts. Coupling agent APTES could integrate between the organic unit of the copolymer and inorganic network with covalent bond and restrain the extracted hybrid materials.

3.3. Microstructure analysis

Figure 6 shows the TEM pictures of Z2 and Z5 respectively. The silica particle size was about 50–70 nm.

3.4. Thermal analysis

The results of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are shown by Figures 7, 8 and Table 2. The glass transition temperatures (*T_g*) and the thermal degradation temperatures (*T_d*) of the hybrids increased with the increase of APTES content. This is due to the fact that the plasticizing trimethoxysilyl groups have transformed to silica network during the sol-gel process. The large-scale cooperative movement

Table2. Thermal properties of hybrid materials

Hybrid material	<i>T_g</i> [°C] ¹	<i>T_d</i> [°C] ²
Z1	122	292
Z2	134	298
Z3	148	303
Z4	152	309
Z5	160	313

¹The glass transition temperature (*T_g*) was obtained from DSC curves

²The thermal degradation temperatures (*T_d*) were defined as weight loss of TGA thermogram at 5 wt%

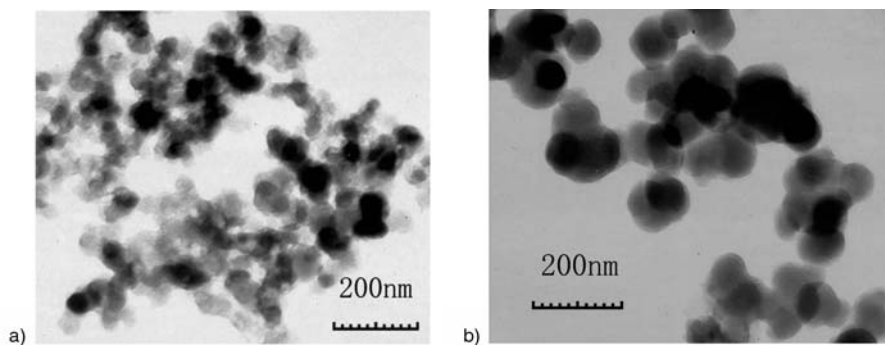


Figure 6. TEM pictures of poly (St-MAn-APTES)/SiO₂ for Z2 (a) and Z5 (b)

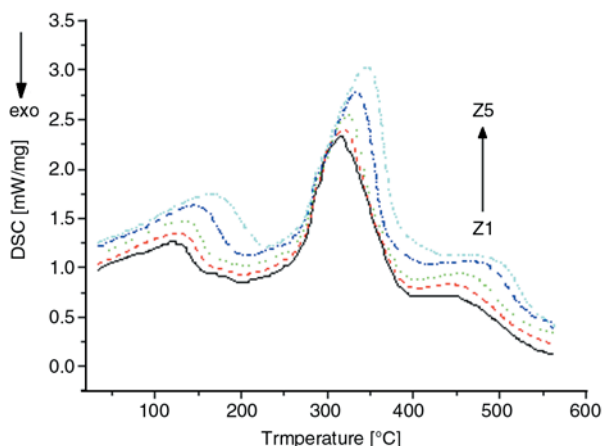


Figure 7. DSC curves of hybrid materials

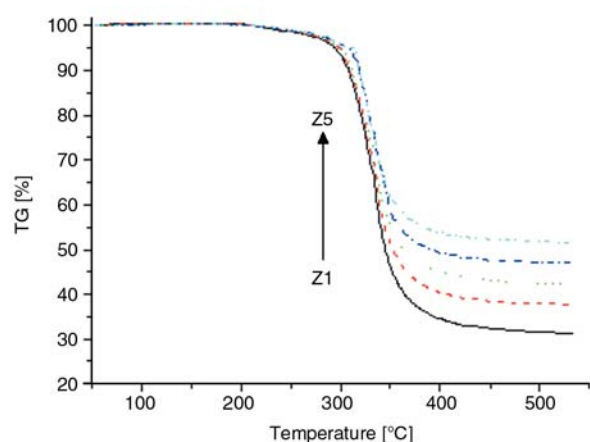


Figure 8. TGA curves of hybrid materials

of the polymer chain segments (i. e., glass transition) was highly restricted by the cross linking points that are generated from the formation of covalent bonds between the polymer chains and the silica network as well as by steric hindrance of the rigid silica (hydrolysis and condensation of TEOS) framework.

4. Conclusions

Different SiO₂ content hybrids were synthesized by the sol-gel process. FT-IR and ²⁹Si NMR were used to characterize the structure of the hybrids. The results show that Q³, Q⁴ and T³ are the major microstructures forming the network structure. The SiO₂ structures in TEOS based hybrid systems were completely condensed. So these hybrid materials have network structure and inorganic phases have a small size. The hybrids were nanocomposites. Covalent bonding between the organic and inorganic components enhanced miscibility between the silica and the copolymer, which was further

confirmed by TEM and the determination of sol content. Because the amino-group of coupling agent APTES breaks maleic anhydride of copolymer to form carboxylic acid and amide, the hybrids have new nanosystems with extremely good heat resistance, resulting from

Acknowledgements

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