Effect of 3-Aminopropyltriethoxysilane on Properties of Poly(butyl acrylate-*co*-maleic anhydride)/Silica Hybrid Materials

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ABSTRACT: The transparent poly(butyl acrylate-co-maleic anhydride)/silica [P(BA-co-MAn)/SiO₉] has been successfully prepared from butyl acrylate-maleic anhydride copolymer P(BA-co-MAn) and tetraethoxysilane (TEOS) in the presence of 3-aminopropyltriethoxysilane (APTES) by an in situ sol-gel process. Triethoxysilyl group can be readily incorporated into P(BA-co-MAn) as pendant side chains by the aminolysis of maleic anhydride unit of copolymer with APTES, and then organic polymer/silica hybrid materials with covalent bonds between two phases can be formed via the hydrolytic polycondensation of triethoxysilyl group-functionalized polymer with TEOS. It was found that the amount of APTES could dramatically affect the gel time of sol-gel system, the sol fraction of resultant hybrid materials, and the thermal properties of hybrid materials obtained. The decomposition temperature of hybrid materials and the final residual weight of thermogravimetry of hybrid both increase with the increasing of APTES. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed that the morphology of hybrid materials prepared in the presence of APTES was a co-continual phase structure. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 419-424, 1999

Key words: sol-gel; hybrid material; poly(butyl acrylate-*co*-maleic anhydride); tet-raethoxysilane; 3-aminopropyltriethoxysilane

INTRODUCTION

The hydrolysis and polycondensation of metal alkoxides to produce glasses and creamers at relatively low temperatures is commonly referred to as the sol-gel process. Under controlled reaction conditions, large-scale, optically transparent monolithic samples can be obtained. For systems containing a mixture of inorganic components, the final products are usually hard and brittle. The incorporation of organic components (elastomer, in particular) would be expected to impart flexibility to the inorganic glasses. On the other hand, the introduction of inorganic components can improve the hardness and modulus of the organic compounds. This multicomponent system could show some characteristics of the inorganic glass network as well as some properties of the organic components.

A convenient route for preparation of organic/ inorganic hybrid materials through the sol-gel process involves the hydrolysis and condensation reactions of metal alkoxide in the presence of an organic polymer.¹⁻⁶ Some articles⁷⁻¹⁴ have re-

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ported the preparation of hybrid materials with excellent mechanical properties and optical transparency. Among these hybrid materials, it was revealed that macrophase separation can be prevented either by formation of hydrogen bonding between the organic polymers and the silicate networks or by formation of covalent bonds between organic and inorganic phases.

The common method is to incorporate the trialkoxysilvl moieties into the polymers either as the end groups or pendant groups, and then, via hydrolytic polycondensation of trialkoxysilyl group-functionalized polymer with TEOS, the resulting hybrid materials with covalent bonds between two phases can be formed. Mark and Sun¹⁵ report that a platinum-catalyzed hydrozilation reaction on terminal carbon-carbon double bonds can introduce trialkoxysilyl groups at the end of polymers, such as PDMS/SiO₂. Poly(methyloxazoline) capped at both ends with trimethoxysilyl groups has been prepared by quenching the growing chains with APTES for the preparation of $poly(methyloxazoline)/SiO_2 \quad hybrid \quad material.^{16}$ However, the trialkoxysilyl groups incorporated on the polymer in advance are unstable. The more convenient method is using an *in situ* sol-gel process in the presence of a coupling agent with trialkoxysilyl groups, such as 3-isocyanatopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane (GOTMS), or APTES. Novak et al.¹⁷ used 3-isocyanatopropyltrimethoxysilane as a coupling agent for synthesis of cellulose/SiO₂ hybrid material with covalent bonds between organic and inorganic phases. SEBS/TiO2 and or SiO2 hybrid materials have been synthesized using GOTMS coupling agent.¹⁸ $EPDM/TiO_2$ and/or SiO_2 and poly(styrene-co-maleic anhydride)/SiO2 hybrid materials have been prepared using APTES coupling agent.^{19,20} In addition, copolymerization of vinyl monomer-bearing trialkoxysilyl group, such as methacryloxypropyltrimethoxysilane, has also been reported by some research groups.^{13,21–25}

In this article, we describe the preparation of poly(butyl acrylate-*co*-maleic anhydride)/SiO₂ hybrid material by *in situ* sol–gel process in the presence of APTES, as well as the effect of APTES on the reaction and the properties of P(BA-*co*-MAn)/SiO₂ hybrid materials obtained.

EXPERIMENTAL

Materials

Butyl acrylate and maleic anhydride are the domestic chemical products and were used after purification by vacuum distillation and sublimation, respectively. Tetraethoxysilane (TEOS) was purchased from Union Chimique Belge, S.A., Belgium, and was used without further purification. APTES domestic chemical product was purified by distillation, and the fraction at 85°C/2 mmHg was collected. The solvents used were purified by common methods.

Synthesis of Poly(butyl acrylate-co-maleic anhydride)

Poly(butyl acrylate-*co*-maleic anhydride) was prepared by radical copolymerization of 38.45 g (0.3 mol) butyl acrylate and 9.8 g (0.1 mol) maleic anhydride in 15 mL tetrahydrofuran (THF) at 65°C for 10 h, using 25 mg (0.05 wt % of monomers) BPO as initiator. The yield is 85% after purification using methanol as precipitation agent. The content of maleic anhydride unit in copolymer is 15 mol %, as determined by ¹H-NMR spectroscopy, and the number average molecular weight and molecular dispersity of copolymer were 3.4×10^4 and 3.2, respectively, as determined with gel-permeation chromatography (GPC) calibrated with polystyrene standards.

Preparation of Hybrid Materials

10.0 mL THF solution of poly(butyl acrylate-comaleic anhydride) (0.10 g/mL) was mixed with 0.3 mL APTES at room temperature under nitrogen. After stirring for about 1 hour, 1.0 g TEOS was added to the solution under continuous agitation. Then, stoichiometric amounts of water (0.32 mL) and 0.05 mL 5N NH₄OH were added. After being stirred for another 2 hours at ambient temperature under nitrogen, the reaction mixture was covered with parafilm. One week later, several pin holes was made in the parafilm. The mixture was left to dry at room temperature for 1 month, and then cured at 60°C under vacuum for 1 day to expel any residual alcohol or solvent. A yellowish, transparent hybrid was obtained. The reaction for the synthesis of hybrid material is shown in Scheme 1.

Measurements

Infrared spectra were taken with a Nicolet Mag DXB FT-IR spectrometer. ¹H-NMR spectra were recorded using Bruker ARX 400 spectrometer. The thermogravimetry analysis (TGA) was performed on a Shimadzu DT-30 under nitrogen. The heating rate was 20°C/min. The fracture surfaces



of hybrid materials were examined by AMRAY-1910FE field emission scanning electron microscope (SEM), and the AFM photographs were taken with a Digital Instruments Nanoscope III atomic force microscope (AFM) in the contact model with SiN probe tips.

RESULTS AND DISCUSSION

Effect of Coupling Agent APTES on Gel Time of Sol–Gel Solution

The effect of coupling agent APTES on gel time of sol-gel solution is shown in Table I. It can be seen that the gel time is 42 days in the system without APTES in the sol-gel solution. However, the gel time of the system decreases to 30 min when the molar ratio of APTES to maleic anhydride unit of copolymer is 1. The dramatic decrease of gel time results from the degree of the aminolysis of the anhydride groups on the copolymer chain. The more APTES employed, the more connections of



Figure 1 SEM of the surface of P(BA-co-MAn)/SiO₂ (K20) prepared without APTES.

organic polymer with the SiO_2 network form. The appearances for all hybrid materials prepared in the presence of APTES were yellowish transparent. However, without APTES, opaque solid was obtained. It is thought that macrophase separation occurs. Therefore, the addition of coupling agent APTES can prevent the macrophase separation, thus transparent hybrids can be obtained.

Effect of APTES on Morphology of P(BA-co-MAn)/SiO₂

Figures 1 and 2 are the SEM of the fracture surface of samples K20 and K24, which were prepared without APTES and with APTES, respectively. The surface of K20 differs greatly from that of K24, and the diameter of inorganic particles in K20 is more than 400 nm. This large particle size causes light scatter and results in opac-

Sample Code	Molar Ratios of APTES Over Maleic Anhydride Unit of Copolymer	Gel Time (h)	Gel ^b (wt %)	Appearance
K20	0.0	1022	24.71	Opaque
K21	0.1	48	47.16	Transparent
K22	0.2	12	56.90	Transparent
K23	0.5	1	91.54	Transparent
K24	1.0	0.5	93.24	Transparent
K25	1.5	0.3	96.75	Transparent

 Table I
 Effect of Molar Ratios of APTES Over Maleic Anhydride on Gel Time Sol-Gel Reactions of P(BA-co-MAn) with TEOS^a

^a The silica content of P(BA-co-MAn)/silica is 21%, calculated from the stoichiometry under the assumption of TEOS is totally changed into SiO_2 .

^b Gel content after acetone extraction of samples at 60°C for 48 h.



Figure 2 SEM of the surface of $P(BA-co-MAn)/SiO_2$ (K24) prepared with APTES.

ity of the hybrids. However, the size of inorganic particles in K24 is difficult to identify because of the Au coating on the surface of the nonconductor sample, as shown in Figure 2. This shows that the size of inorganic particles is no more than 20 nm, because the Au particles are under 20 nm. The much smaller size of particles than the wavelength of visible light (400–700 nm) made the hybrid material highly transparent. Figure 3 is the AFM of K24. It is difficult to identify the size of inorganic particles from this figure. It reveals that a co-continunual phase structure is formed.

Effect of APTES on Thermal Properties of P(BA-co-MAn)/SiO₂

Figure 4 shows TGA curves of samples K20, K21, K23, K24, and K25, respectively. The two-step



Figure 3 AFM of the surface of $P(BA-co-MAn)/SiO_2$ (K24).



Figure 4 TG curves of P(BA-co-MAn)/SiO₂ hybrids: (K20, K21, K23, K24, and K25).

weight loss processes can be observed. The onset of the first weight loss step began at 160°C. This may be attributable to the elimination of ethanol and water by the further hydrolysis and polycondensation between Si—OH and Si— OC_2H_5 or themselves, which happened during the increase of temperature.²⁵ The onset of the second weight loss step began at 370°C. It is caused by degradation of P(BA-co-MAn).

It can be seen from the TGA curves that the decomposition temperatures of hybrid materials increase with the increasing of APTES. Figure 5 shows the correlation of the residual weight of hybrids with APTES. From the figure it can be seen that the residual weight increases with increasing of APTES. This result indicates that thermal behavior of hybrids can be improved with APTES.

Evidence of Covalent Bonds Between Organic and Inorganic Phases

 $P(BA-co-MAn)/SiO_2$ with covalent bonds between organic and inorganic phases has been successfully prepared as mentioned above. Covalent bonds between two phases were formed through the aminolysis of maleic anhydride unit of P(BAco-MAn) with APTES and then via the hydrolytic polycondensation of triethoxylsilyl group-functionalized copolymer with TEOS. Several experiments have been performed to prove the formation of covalent bonds between organic and inorganic phases.



Figure 5 Effect of APTES on the residual weight of P(BA-co-MAn)/SiO₂.

Solvent extractions of samples were carried out in acetone for 2 days. The gel content of sample K20 prepared without APTES is 24.71% (wt %), which is approximately comparable to the calculated value of the silica content, and that of sample K24 prepared with APTES is 93.24% (wt %). The obvious difference of two samples is attributable to the effect of chemical bonding between organic copolymer and silica. This result reveals that P(BA-co-MAn) organic copolymer in K20, which is physically trapped in the silica network, can be removed by solvent extraction, and organic copolymer in K24, which is incorporated covalently in the silica network, cannot be removed by solvent extraction. Therefore, the gel content of samples increases with increasing of APTES. as shown in Table I.

It can be further demonstrated by FTIR spectra of gel samples of $P(BA-co-MAn)/SiO_2$ hybrids, such as K20–K25 and SiO₂, sample K00 prepared by sol–gel process, as shown in Figure 6. The similarity of FTIR spectra of K00 and gel of K20 reveals that most of P(BA-co-MAn) has been extracted. Comparing the intensity of two absorption peaks at 1160 cm⁻¹ and 1085 cm⁻¹, the characteristic stretching vibrations of C—O—C and Si—O—Si, it was observed that the intensity of the peak at 1160 cm⁻¹ increases from K21 to K25. In other word, the absorption peak at 1160 cm⁻¹ increases with the increasing of APTES. This is because more covalent bonds were formed as the APTES increased.

As mentioned before, the covalent bond between organic and inorganic phases is formed by two step reactions, and the first step reaction is the aminolysis of maleic anhydride unit of copolymer with APTES. The appearance of new absorption peaks around 1730 and 1701 cm⁻¹ corresponding to the C=O stretching vibration in amide and carboxyl groups in the P(St-co-MAn)/SiO₂ hybrids prepared with APTES was observed in a previous article.²⁰ However, in the case of P(BA-co-MAn)/ SiO_2 hybrids, these peaks are overlapped, with the absorption peak of C=O stretching vibration of ester groups of the butyl acrylate unit; therefore, the existence of amide groups cannot be confirmed directly by FTIR spectroscopy. However, the aminolysis reaction can be proved by measurement of ¹H-NMR spectroscopy on the reaction of APTES and succinic anhydride, the model compound of maleic anhydride unit of copolymer, at similar condition of preparation of P(BA-co-MAn)/SiO₂. As shown in Figure 7, the appearance of new peak around 8 ppm, the characteristic chemical shift of H of amide groups, and thus the occurrence of aminolysis of anhydride is confirmed.

CONCLUSIONS

P(BA-co-MAn)/SiO₂ hybrid materials with covalent bonds between organic and inorganic phases has been successfully prepared by an *in situ* sol-gel process in the presence of a coupling agent APTES. The P(BA-co-MAn) was incorporated into an inorganic network through the aminolysis of maleic anhydride unit of P(BA-co-MAn) with APTES and then hydrolytic polycondensation of the triethoxysi-



Figure 6 Infrared spectra for the pure silica gel (K00) and gel of K20, K21, K22, K23, K24, and K25.



Figure 7 ¹HNMR spectrum of product of APTES and succinic anhydride in DMSO-d6 reaction at ambient temperature for 18 days.

lyl group-functionalized polymer with TEOS. It was observed that the gel time of sol-gel solution was dramatically affected by the presence of APTES, and macrophase separation in hybrid materials can be prevented by the existence of covalent bonding between the copolymer and inorganic network. The yellowish, transparent, glass-like hybrids can be obtained with APTES. The higher gel fraction for solvent extraction of hybrid materials with APTES further proved the formation of covalent bond between the organic and inorganic phases. The thermal properties of P(BA-co-MAn)/SiO₂ hybrids can be improved with APTES. Scanning electron micrographs indicate that the average diameter of inorganic particles in the hybrids prepared with APTES decreases with increasing of APTES, and AFM shows the morphology of hybrid is a co-continunual phase structure.

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