

# Study of Poly(methyl methacrylate–maleic anhydride)/Silica Hybrid Materials

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**ABSTRACT:** Poly(methyl methacrylate–maleic anhydride) [P(MMA–MAn)] with active groups, anhydrides, was synthesized by radical copolymerization. Using P(MMA–MAn) as a basic polymer, the P(MMA–MAn)/SiO<sub>2</sub> hybrid materials were obtained by a sol–gel process in different ways. The structures of the materials were characterized by IR spectra, and their properties were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and dynamic analysis (DA). The results show that the hybrids prepared in different ways have different properties, and the contents of SiO<sub>2</sub> also have influence on the properties of the hybrids. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 379–383, 2000

**Key words:** sol–gel process; inorganic–organic hybrid materials; P(MMA–MAn); tetraethoxysilane; 3-aminopropyltrimethoxysilane

## INTRODUCTION

In recent years, a new kind of inorganic–organic hybrid material has been prepared by the sol–gel process.<sup>1–4</sup> This kind of material has excellent application prospects due to its mechanical, optical, heat-resistant, and other properties. However, as the polymers are incompatible with SiO<sub>2</sub>, there exists separation between inorganic and organic species in the hybrid systems. To solve the problem, one can use special polymers with active groups which can react with functional metal alkoxides such as 3-aminopropyltrimethoxysilane (APTMS) and 3-glycidylpropyltrimethoxysilane

(GPTMS) to form chemical bonds to inorganic species, so making the two species homogeneous.

Huang and Qiu<sup>1</sup> prepared poly(methyl methacrylate) [P(MMA)]/TiO<sub>2</sub>–SiO<sub>2</sub> hybrid materials from the copolymer of methyl methacrylate (MMA) and methacryloxypropyltrimethoxysilane (MPTMS) with tetrabutyl titanate and tetraethoxysilane (TEOS). These materials have high transparency and a high glass transition temperature ( $T_g$ ). Also, Huang and Qiu<sup>5</sup> prepared hybrids incorporating the ethylene–propylene–non-conjugated diene terpolymer (EPDM–ENB) with tetrabutyl titanate and TEOS. These hybrids are also highly transparent and are found to have improved properties over pure EPDM–ENB in the modulus, etc. Noell et al.<sup>6</sup> and Surivet et al.<sup>7</sup> also did a great deal of work in this field.

In our work, we first synthesized P(MMA–MAn) with active groups, anhydrides, and, then, using it as a prepolymer, hybrid materials were prepared by the sol–gel process by the following

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**Table I** Preparation of P(MMA–MAn)/SiO<sub>2</sub> Hybrid Materials

Sample	Method	#4 SiO <sub>2</sub> (% wt)	SiO <sub>2</sub> <sup>a</sup> (% wt)	APTMS <sup>b</sup> (mol %)	Production Description
1		0	0	0	Transparent
2	I	10	0	0	White and opaque
3	II	0	10	0	Half-transparent
4	III	0	10	10	Slightly yellow and transparent
5	III	0	15	10	Slightly yellow and transparent
6	III	0	20	10	Slightly yellow and transparent

Preparation conditions: [H<sub>2</sub>O] : [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>] = 4 : 1 (mol ratio).

<sup>a</sup> Contents of SiO<sub>2</sub> calculated as absolute hydrolysis of TEOS and APTMS.

<sup>b</sup> Relative to the monomers of P(MMA–MAn).

ways: (1) mixing P(MMA–MAn) with #4 fumed SiO<sub>2</sub> in an acetone solution, (2) incorporating P(MMA–MAn) with TEOS in an acetone solution followed by hydrolysis, and (3) reacting P(MMA–MAn) with APTMS in an acetone solution followed by cohydrolysis with TEOS. In this article, the properties of hybrid materials prepared by different methods are compared and studied. The influence of SiO<sub>2</sub> contents on the properties of the materials is also discussed.

## EXPERIMENTAL

### Materials

MMA and APTMS, purified grade, were distilled under a vacuum before use. MAn was fractionally distilled under a nitrogen pressure of 12 mm of mercury and the middle fraction, bp 154°C, collected. AIBN was recrystallized three times from ethanol and once from ethyl acetate. TEOS, butanone, methanol, and acetone, purified grade, were used without any further treatment.

### Synthesis of P(MMA–MAn)

An appropriate amount of MMA, MAn, and AIBN was added to a 250-mL, three-necked, round-bottom flask equipped with a reflux condenser, a nitrogen inlet, and a thermometer. After aspirating with N<sub>2</sub> for 3 min, the reaction mixture was heated at 60 ± 0.2°C in a thermostatic water bath until the mixture became viscous. The viscous liquid was then transferred into a tube, sealed with plastic film, and kept at room temperature for 7 days and then heated at 80°C for 1.5 h, 90°C for 1.5 h, and 100°C for 1.5 h. After the tube was cooled, the mixture was dissolved in butanone.

The polymer was isolated by precipitating from methanol, filtering, and drying and then it was dissolved in acetone for the following experiment.

### Preparation of P(MMA–MAn)/SiO<sub>2</sub> Hybrid Materials

P(MMA–MAn)/SiO<sub>2</sub> hybrid materials were prepared by the following three methods:

Method I. An appropriate amount of P(MMA–MAn) and #4 fumed SiO<sub>2</sub> was mixed in an acetone solution and stirred for 6 h; then, the mixture was transferred into a mold and covered with a plastic film to allow low-boiling compounds to evaporate. After being heated at 60°C for 12 h in an oven, the hybrid material was obtained.

Method II. An appropriate amount of distilled water, TEOS, and acetone was mixed with the P(MMA–MAn) solution. After stirring the mixture for 6 h, the following operation proceeded as for Method I.

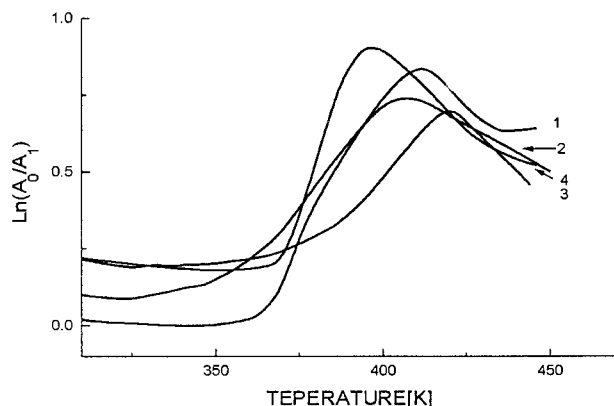
Method III. An appropriate amount of APTMS was dropped into the P(MMA–MAn) solution under stirring and reacted for 30 min. Then, a certain amount of distilled water was mixed with the solution. After vigorous stirring for 8–10 min, the following operation proceeded as for Method I.

The results are listed in Table I.

### Measurement of Properties of Materials

Solubility of the materials was observed visually after dissolving them in a good solvent, butanone, for 1 week. The FTIR spectra was recorded on a

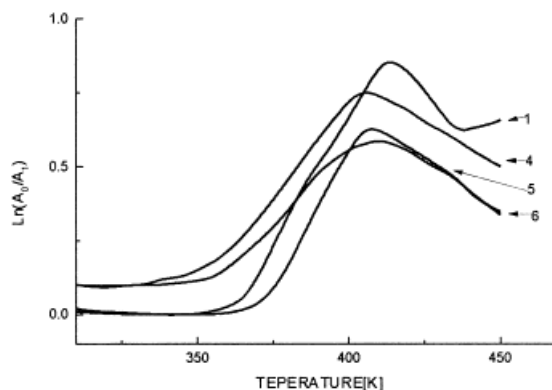




**Figure 2** Dynamic mechanical spectra of P(MMA-MAn)/SiO<sub>2</sub> hybrids by different processes.

glass transition temperatures ( $T_g$ 's) of Samples 2 and 4 are lower than that of P(MMA-MAn). For Sample 2, the microparticles of SiO<sub>2</sub> filled in among the polymer molecules and the particles are too big to infiltrate into the free volumes in the polymers, making not only the interaction among the polymer molecules to decrease but also the free volumes of the system to increase, therefore making the chain segments move more easily and the  $T_g$  decrease. For Sample 4, the long chains of APTMS connected with the polymer chains by amide bonds form the flexible interfaces between the organic and inorganic species, and the SiO<sub>2</sub> particles from the hydrolysis of TEOS are filled in among the molecules of the polymers, making the interaction of the polar molecules weaker, which causes the  $T_g$ 's of the hybrids to be lower. On the other hand, the crosslinks hinder the chain-segment motion to make the  $T_g$  increase. The overall effect makes the  $T_g$  decrease. However, for Sample 3, the  $T_g$  increases. This is because, during the process of hydrolysis, the molecules of TEOS diffused into the free volumes of the polymers and then hydrolyzed to form microparticles, which decreases the free volumes of the system and makes the  $T_g$  increase, whereas the SiO<sub>2</sub> particles filled in among the molecules make the  $T_g$  decrease. However, the former effect is larger than the latter, making the  $T_g$ 's of the hybrids increase.

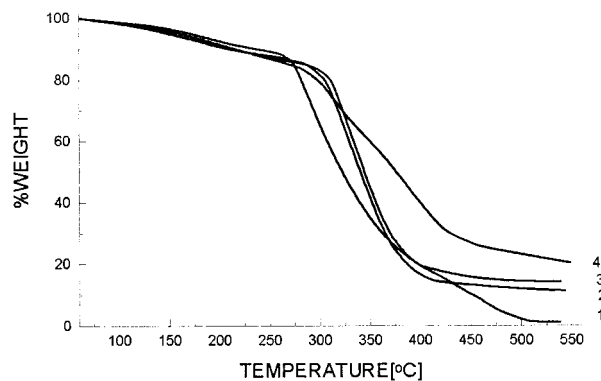
Figure 3 shows the dynamic mechanical behaviors of Samples 4, 5, and 6. All the  $T_g$ 's are lower than that of P(MMA-MAn) (lower about 2–5 K). The  $T_g$  increases with the SiO<sub>2</sub> content increase. This can be attributed to decrease of the free volumes of the systems with increasing contents of SiO<sub>2</sub>.



**Figure 3** Dynamic mechanical spectra of P(MMA-MAn)/SiO<sub>2</sub> hybrids with different SiO<sub>2</sub> contents.

## TGA OF HYBRIDS

Figure 4 shows the thermogravimetric behaviors of the hybrids. From Figure 4, we can see that all samples have the same rate of weight loss over the temperature range from 160 to 260°C. This may be attributed to the condensation of the unreacted Si—OH and the dehydration of —COOH with —CONH—. The subsequent rates of weight loss (above 260°C) of Samples 2, 3, and 4 are all lower than that of P(MMA-MAn), and that of Sample 4 is the lowest. The crosslinks between the polymer and silica decrease the degree of thermodegradation of Sample 4. The residues of Samples 2 and 3 are equal to the theoretical contents of SiO<sub>2</sub>, but that of Sample 4 is larger, showing that the connection of the organic molecules with the inorganic network by chemical bonds can improve the heat-resistant ability.



**Figure 4** TGA curve of P(MMA-MAn)/SiO<sub>2</sub> hybrids by different processes.

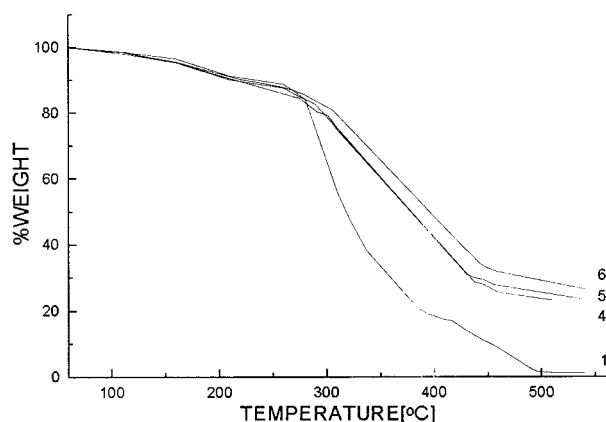
From Figure 5, we can see that the rate of weight loss above 260°C decreases with the increasing of content of SiO<sub>2</sub> in the systems. This is probably because the inorganic network prevents the chain segments of the polymers from the motion and degradation of the molecules. To provide energy, to make the molecular chains break in the heating process, one needs higher temperatures.

### Mechanical Properties of the Hybrids

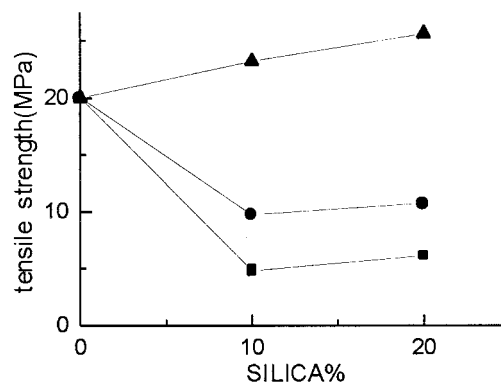
Figure 6 shows the relationship between the tensile strength and SiO<sub>2</sub> content. The results show that at low SiO<sub>2</sub> content ( $\leq 20\%$  wt) the hybrid materials prepared by Methods I and II, in which there are no chemical bonds between inorganic and organic species, have lower tensile strength than that of P(MMA-MAN), but the tensile strength of hybrids prepared by Method III is higher than that of P(MMA-MAN) and the tensile strength increases with increasing SiO<sub>2</sub> contents in all the materials. So, we can draw the conclusion that the hybrids with chemical bonds between inorganic and organic species prepared by the sol-gel process have higher mechanical properties than those from the coblending of inorganic-organic species, because the dispersion and reinforcement of inorganic particles in the latter are different from that in the former.

### CONCLUSIONS

The hybrid materials prepared by modified polymers of P(MMA-MAN) have high transparency.



**Figure 5** TGA curve of P(MMA-MAN)/SiO<sub>2</sub> hybrids with different SiO<sub>2</sub> contents.



**Figure 6** Relationship of tensile strengths with SiO<sub>2</sub> contents: (▲) hybrids prepared by cohydrolysis of modified P(MMA-MAN) and TEOS; (●) hybrids prepared by cohydrolysis of P(MMA-MAN) and TEOS; (■) hybrids prepared by coblending of P(MMA-MAN) and #4 SiO<sub>2</sub>.

However, the hybrid materials prepared by the coblending of the inorganic-organic species are opaque.

The hybrid materials prepared in different ways have different dynamic mechanical, thermogravimetric, and mechanical behaviors. The hybrids in which there are chemical bonds between the inorganic and organic species have improved properties over pure P(MMA-MAN) and coblends of the polymers and SiO<sub>2</sub> in regard to heat-resistant, mechanical, optical, and other properties.

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