

# Synthesis and Characterization of Poly(methyl acrylate-*co*-itaconic anhydride)/TiO<sub>2</sub> Hybrid Materials via Sol–Gel Process

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Received August 1999; accepted November 1999

**ABSTRACT:** In the presence of 3-aminopropyltriethoxysilane (APTES), the transparent and yellowish poly(methyl acrylate-*co*-itaconic anhydride)/TiO<sub>2</sub> [P(MA-*co*-Itn)/TiO<sub>2</sub>] hybrid materials were prepared from the copolymer of methyl acrylate and itaconic anhydride [P(MA-*co*-Itn)] and tetrabutyl titanate (TBT) via a sol–gel process. At first, the triethoxysilane groups were incorporated into the copolymer P(MA-*co*-Itn) as pendant side chains by the aminolytic reaction between the itaconic anhydride units of the copolymer and the amino group of 3-aminopropyltriethoxysilane (APTES), and then the covalent bonds between the organic and inorganic phases were introduced by the hydrolysis and polycondensation of the triethoxysilane groups on the copolymer with TBT. FTIR analysis proved the existence of the covalent bonds. The influences of APTES on glass transition and morphology of the hybrid materials was studied by differential scanning calorimetry, scanning electron microscope, and atomic force microscope. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1763–1768, 2000

**Key words:** sol–gel process; hybrid material; poly(methyl acrylate-*co*-anhydride); tetrabutyl titanate; 3-aminopropyltriethoxysilane

## INTRODUCTION

The sol–gel process has proved to be versatile and has been widely used in the preparation of organic/inorganic hybrid materials,<sup>1–3</sup> nonlinear optical materials,<sup>4–7</sup> and mesoporous materials.<sup>8–9</sup> The sol–gel chemistry is based on the hydrolysis and

polycondensation of metal alkoxides  $M(OR)_x$ , where  $M = \text{Si, Sn, Ti, Al, Mo, V, W, Ce}$ , and so forth. The following sequence of reactivity is usually found:  $\text{Si}(OR)_4 \ll \text{Sn}(OR)_4 = \text{Ti}(OR)_4 < \text{Zr}(OR)_4 = \text{Ce}(OR)_4$ .<sup>3</sup> Because silicon alkoxides are not very reactive, the sol–gel process of the silicon alkoxides is slow and easy to control in order to produce a transparent gel. However, in the case of titanium alkoxides, the hydrolysis and polycondensation reactions are too fast and always give opaque precipitate under the same condition with silicon alkoxides. In order to prepare the transparent hybrid materials in which TiO<sub>2</sub> is the inorganic part, measures must be taken to slow down the hydrolysis and polycondensation reactions of titanium alkoxides. So far, as re-

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Contract grant sponsor: National Institute of Health (K.Y.Q. and Y.W.); contract grant numbers: 29674001, 19810760343.

Contract grant sponsor: National Natural Science Foundation of China (to Y.W.); contract grant number: DE09848.

*Journal of Applied Polymer Science*, Vol. 78, 1763–1768 (2000)  
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ported in the literatures, there are four ways to do this.

The first way is to add chelating agents.<sup>10</sup> It has been found that some strong complexing ligands (such as  $\beta$ -diketones, organic acids, polyhydroxylated ligands,  $\beta$ -hydroxy acids) are very efficient at controlling the reactivity of  $M(OR)_x$ , where  $M = \text{Ti, Zr, Ce}$ , and so forth. However, the resident chelating agents in the materials prepared this way are difficult to get rid of and limit the refractive index. In order to improve the refractive index, a second method was developed: By slowly adding water containing acidified isopropanol instead of water and acid, Wang et al.<sup>11</sup> prepared transparent poly(tetramethylene oxide)/TiO<sub>2</sub> and poly(tetramethylene oxide)/ZrO<sub>2</sub> hybrid materials.

The third route to transparent TiO<sub>2</sub> hybrid materials is to control the humidity. In this way, Mauritz et al.<sup>12</sup> limited the water-giving rate and at last synthesized a transparent poly(*n*-butyl methacrylate)/TiO<sub>2</sub> hybrid.

The fourth way is to add concentrated inorganic acid. In this way, Lantelme et al.<sup>13</sup> prepared poly(vinyl acetate)/TiO<sub>2</sub> hybrid materials.

In our laboratory, using 3-aminopropyltriethoxysilane (APTES) as the coupling agent to introduce the covalent bond between the organic and inorganic phases, we successfully prepared ethylene-propylene nonconjugated diene terpolymer/TiO<sub>2</sub>/SiO<sub>2</sub> hybrid materials,<sup>14</sup> poly(styrene-*co*-maleic anhydride)/SiO<sub>2</sub> and poly(styrene-*co*-maleic anhydride)/TiO<sub>2</sub> hybrid materials,<sup>15–17</sup> and poly(methyl acrylate-*co*-itaconic anhydride)/SiO<sub>2</sub> hybrid materials.<sup>18</sup> For this article, which reports on our studies of the effect of APTES on the properties of materials, we prepared the transparent [P(MA-*co*-Itn)/TiO<sub>2</sub>] hybrid materials in the presence of APTES.

## EXPERIMENTAL

### Materials

Itaconic acid, with a purity of 99%, came from Aldrich Chemical Company (Milwaukee, WI). APTES (Gaixian, Liaoning, China), a domestic product, was purified by vacuum distillation. The collected fraction was 80°C/0.27 kPa. Methyl acrylate (MA), 2,2'-azo-*bis*-isobutyronitrile (AIBN), and tetrahydrofuran (THF) (all from Beijing, China) were domestic chemical products and purified using common methods. TBT (Beijing, Chi-

na), solvents, and other agents were also domestic products and used without further purification.

### Synthesis of Poly(methyl acrylate-*co*-itaconic anhydride)

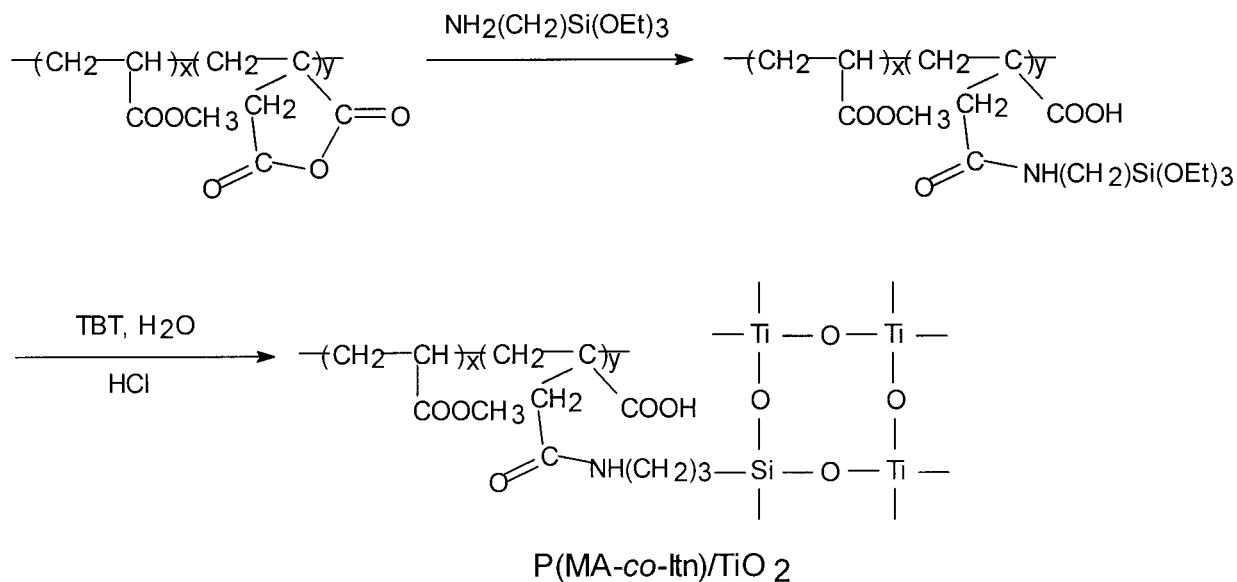
In a polymerization tube, 6 g of itaconic anhydride was prepared according to the method used by Qiu and Zhao<sup>19</sup>; 25 mL methyl acrylate, 20 mL dehydrated THF, and 150 mg AIBN were added. Nitrogen was introduced into the solution for 10 min in order to get rid of the effect of oxygen. After that, the tube was sealed and heated to 65°C. The tube was unsealed 36 h later, and the copolymer was dissolved and precipitated three times in THF and ethyl ether. The yield was 85% after purification. The weight average molecular weight and the polydispersity index were  $3.1 \times 10^4$  and 3.1, respectively, as determined with gel permeation chromatography calibrated with a polystyrene standard. The content of the itaconic anhydride unit was determined by <sup>1</sup>H-NMR to be 16.7 wt %.

### Preparation of P(MA-*co*-Itn)/TiO<sub>2</sub> Hybrid Materials

In a 50-mL beaker, TBT was mixed with THF at a TBT:THF volume ratio of 1:9. In another beaker, a stoichiometric amount of 0.14 mol/L HCl (the molar ratio of TBT:H<sub>2</sub>O:HCl was 1:4:0.01) was mixed with 2 mL THF. Then the diluted HCl was added to the first beaker very slowly. This mixture was stirred for 2 h, and a clear yellowish sol was obtained (if there were any precipitate, concentrated HCl was added until a clear sol was obtained). In the third beaker, a P(MA-*co*-Itn) solution (0.1 g/mL, THF) and a stoichiometric amount of APTES were added and stirred at room temperature for about 1 h. After that, the content of the third beaker was poured into the first. After stirring for 5 min, the reaction mixture was covered with a piece of parafilm. After gelling, several pinholes were made in the film, and the mixture was left to dry at room temperature for a month and cured at 70°C under vacuum for 24 h in order to expel the residual alcohol or solvent. The reaction for the synthesis of hybrid materials is shown in Scheme 1. The names and descriptions of samples are listed in Table I.

### Measurements

The FTIR spectra were recorded with a Nicolet Magna-IR 750 spectrometer. Differential scanning calorimetry (DSC) was performed on a TA



DSC2010, and the heating rate and nitrogen flow rate were 10°C/min and 30 mL/min, respectively. The sample for FTIR and DSC analysis was dried at 100°C/0.27 kPa for 1 h just before measuring. The fraction surfaces of hybrid materials were examined by a Hitachi S-4200 scanning electron microscope. The AFM photographs were taken on a Digital Instrument Nanoscope IIa in the contact mode with SiN tips.

## RESULTS AND DISCUSSION

### FTIR Analysis of P(MA-co-Itn)/TiO<sub>2</sub> Hybrid Materials

The FTIR spectra of P(MA-co-Itn), sample O10, TiO<sub>2</sub> gel prepared via the sol-gel process and

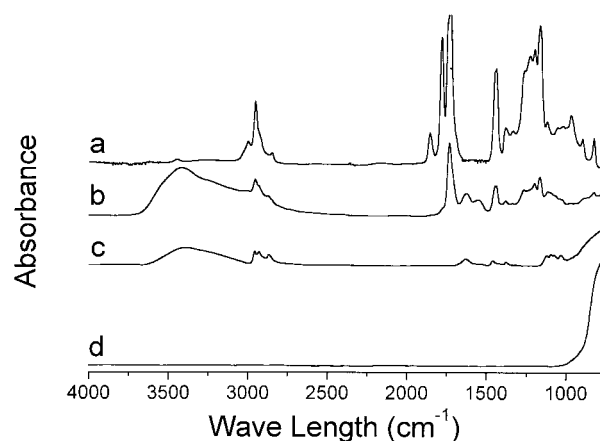
**Table I** Preparation and Description of P(MA-co-Itn)/TiO<sub>2</sub> Hybrid Materials

Sample Code <sup>a</sup>	Molar Ratio of APTES over Itaconic Anhydride Unit of Copolymer	Product Description <sup>b</sup>
O10	1	T
O08	0.8	T
O06	0.6	T
O04	0.4	T
O02	0.2	T
O00	0	O

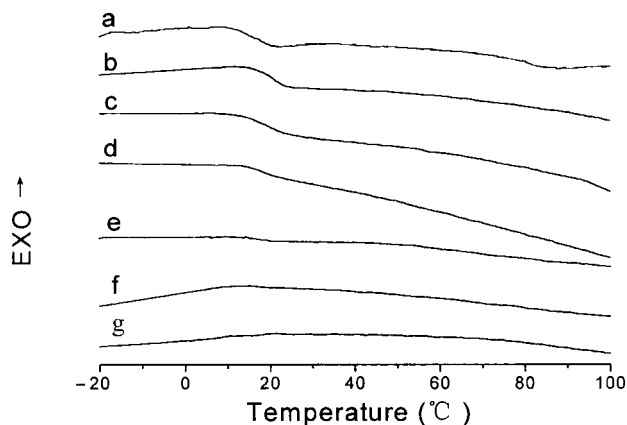
<sup>a</sup> The inorganic content is 20 wt.%, calculated from the stoichiometry under the assumption of the TBT changed into TiO<sub>2</sub> completely and the omission of the effect of APTES.

<sup>b</sup> T: Transparent; O: Opaque.

titanium white are shown in Figure 1. In the spectrum of P(MA-co-Itn) there are three peaks—at 1736 cm<sup>-1</sup>, 1782 cm<sup>-1</sup> and 1868 cm<sup>-1</sup>. The peak at 1736 cm<sup>-1</sup> corresponds to the stretching vibration of the C=O groups of the MA units of the copolymer, while the other two are due to the Itn units. In the spectrum of O10, the two peaks of anhydride groups disappear, but two new peaks appear, at 1650 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>. According to Socrates,<sup>20</sup> the two peaks can be attributed to amide I and amide II bands. This shows the existence of the aminolytic reaction between the Itn units in the copolymer and the amino group of APTES, as shown in Scheme 1. Compared with the spectrum of titanium white, the TiO<sub>2</sub> gel has



**Figure 1** FTIR spectra of (a) P(MA-co-Itn), (b) O10, (c) TiO<sub>2</sub> prepared via sol-gel process, and (d) titanium white.



**Figure 2** DSC curves of (a) P(MA-co-Itn), (b) O00, (c) O02, (d) O04, (e) O06, (f) O08, and (g) O10.

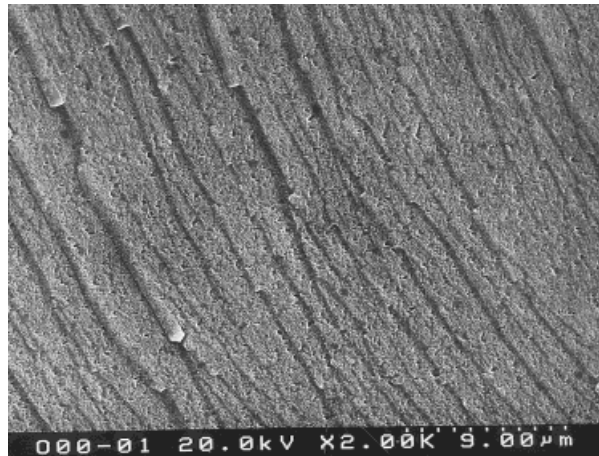
additional peaks, at  $3400\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$ ,  $1460\text{ cm}^{-1}$ ,  $1150\text{ cm}^{-1}$ . The peaks at  $3400\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  are a result of the adsorbed water and Ti—OH groups, while the other peaks are attributed to the residual Ti—OC<sub>4</sub>H<sub>9</sub> groups.

#### Effect of APTES on the Glass-Transition Temperature of P(MA-co-Itn)/TiO<sub>2</sub>

Figure 2 shows the DSC curves of P(MA-co-Itn)/TiO<sub>2</sub> hybrid materials prepared with different APTES amounts. Without APTES, the sample O00 (Curve b) has a glass-transition temperature of about 17°C, which is similar to the  $T_g$  of P(MA-co-Itn) (Curve a). As the amount of APTES increased, as shown in Curves c–g, the glass-transition temperatures were broadened and at last disappeared because the copolymer and inorganic phases were crosslinked into a network by the use of APTES. The DSC analysis provided strong evidence of the process shown in Scheme 1.

#### Effect of APTES on Morphology of P(MA-co-Itn)/TiO<sub>2</sub>

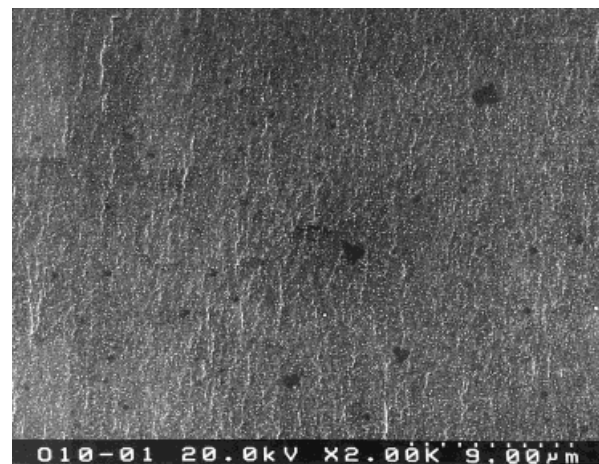
Table I shows that without APTES, an opaque hybrid material (O00) was obtained, from which the existence of phase separation beyond nano scale can be inferred. From the SEM photographs of the fresh fracture surface of O00 and O10 (Figs. 3 and 4), it can be seen that without APTES, the fracture surface of O00 is coarse, and there are some bar-shaped protrusions about  $1\text{ }\mu\text{m}$  wide. Because these protrusions are larger than the wavelength of visible light (400–700 nm) and can cause the scattering of visible light, the sample



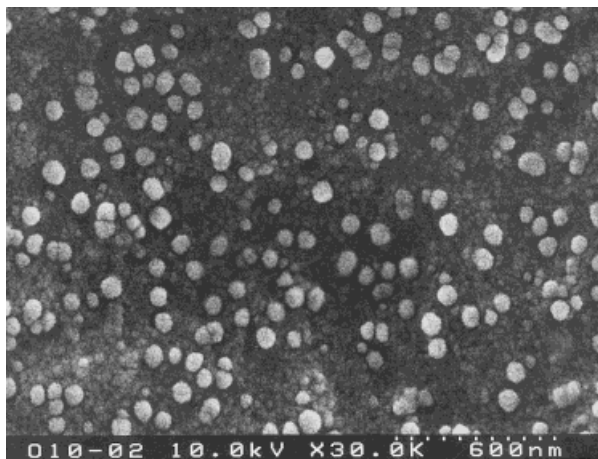
**Figure 3** SEM photograph of O00 magnified to 2000 times.

O00 is opaque. In contrast with this, the fracture surface of O10 is smooth, and no protrusion is observed. Magnified 30,000 times (Fig. 5), many particles around 60 nm in size can be seen. In agreement with the literature,<sup>21,22</sup> we think these particles are inorganic particles. Because these particles are much smaller than the wavelength of visible light, they will not cause the scattering of visible light, and the sample O10 is transparent.

AFM has been proven to be useful in evaluating the morphology of hybrid materials.<sup>23</sup> In order to confirm the conclusions drawn above, we observed the fracture surface of O00 and O10 with AFM as well (Figs. 6 and 7). Some bar-shaped protrusions can be found in the AFM photograph



**Figure 4** SEM photograph of O10 magnified to 2000 times.

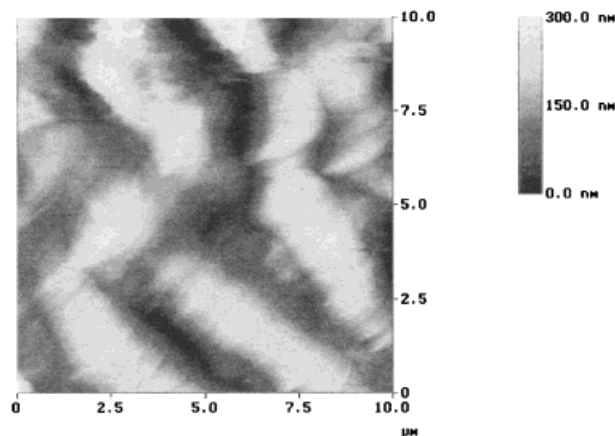


**Figure 5** SEM photograph of O10 magnified to 30000 times.

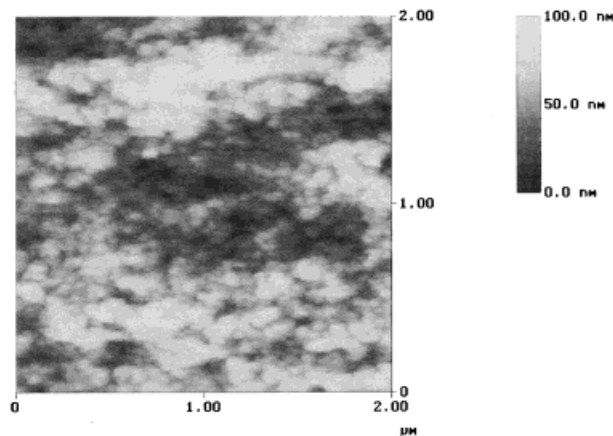
of O0. In the AFM photograph of O10, the sample is observed at greater magnification, and so many particles are observed. The outcomes using AFM conform well to those using SEM and are similar to the literature.<sup>22</sup> All the outcomes from both SEM and AFM show that without APTES, there are phase separations in macro scale, while in the presence of APTES, the hybrid material is a kind of nanocomposite.

## CONCLUSIONS

Transparent P(MA-co-Ita)/TiO<sub>2</sub> hybrid materials were prepared in the presence of APTES. The copolymer P(MA-co-Ita) was incorporated into the inorganic network by covalent bonds through the aminolytic reactions between the itaconic anhy-



**Figure 6** AFM photograph of O00.



**Figure 7** AFM photograph of O10.

dride unit of the copolymer and the amino group on APTES and the subsequent hydrolytic polycondensation of the triethoxysilyl group bearing polymer with TBT. The FTIR analysis showed the existence of amide groups in the hybrid materials. DSC showed that as APTES increased, the glass-transition temperature of the hybrid material broadened and at last disappeared, from which it was inferred that the copolymer is incorporated into the inorganic network. Without APTES, opaque hybrid material was obtained, and phase separation was observed through SEM and AFM. In the presence of APTES, the hybrid material obtained was transparent, and many particles of around 60 nm in size were observed. These results show that the material is a kind of nanocomposite.

The authors are grateful to Prof. Xincheng Zhao and Prof. Liming Ying of Peking University for taking AFM photographs.

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