

# Thermal and Optical Properties of PMMA–Titania Hybrid Materials Prepared by Sol-Gel Approach with HEMA as Coupling Agent

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**ABSTRACT:** A series of sol-gel derived organic–inorganic hybrid materials consisting of organic poly(methyl methacrylate) (PMMA) and inorganic titania (TiO<sub>2</sub>) were successfully synthesized by using 2-hydroxyethyl methacrylate (HEMA) as coupling agent. In this work, HEMA is first copolymerized with methyl methacrylate monomer at specific feeding ratios by using benzoyl peroxide (BPO) as initiator. Subsequently, the as-prepared copolymer (i.e., sol-gel precursor) is then cohydrolyzed with various contents of titanium butoxide to afford chemical bondings to the forming titania networks to give a series of hybrid materials. Transparent organic–inorganic hybrid materials with differ-

ent contents of titania are always achieved. Effects of the material composition on the thermal stability, optical properties, and morphology of neat copolymer and a series of hybrid materials, in the form of both coating and free-standing film, are also studied by differential scanning calorimetry, thermogravimetric analysis, UV–Vis transmission spectra, refractometer, and atomic force microscopy, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 400–405, 2004

**Key words:** hybrid; sol-gel; titania; coupling agent; atomic force microscopy (AFM) film; PMMA

## INTRODUCTION

Lately, lots of researchers have devoted great effort in sol-gel technique to prepare ceramic precursors and inorganic glasses at relatively low temperatures. This technique has evoked intense research interest because of its potential for developing new ceramics or glasses. In sol-gel technology, organo-silicate, -titanates, and -aluminates, etc. are typically hydrolyzed to multi-hydroxy compounds, which then further condensed into gellike structures that can be dried and subsequently fired into ceramic coatings, foams, or monolithic objects. A typical example for representing sol-gel reaction is the reaction of tetraethoxysilane (TEOS) [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>] to yield silica (SiO<sub>2</sub>) and ethanol as a volatile and easily removed byproduct. Various acids and bases, and even some salts, can be employed to effectively catalyze the process.

Recently, many researchers have demonstrated the successful combinations of various polymers and co-

polymers with inorganic structures (such as the SiO<sub>2</sub>) at the molecular level to form a class of organic–inorganic sol-gel materials. Typically, organic-modified sol-gel materials can be classified into the two following major families: (1) organic–inorganic composites in which the organic/polymer components are trapped in the inorganic networks and (2) organic–inorganic hybrid materials in which the organic/polymer components are covalently bonded to the inorganic networks. Accordingly, many physical properties of these hybrid materials could be designed and tuned by varying the nature and composition of both the polymer and the inorganic components.

Lots of polymers were incorporated into inorganic SiO<sub>2</sub> networks, including poly(dimethylsiloxane),<sup>1</sup> polyimides,<sup>2</sup> poly(arylene ether ketone) and poly(arylene ether sulfone),<sup>3</sup> polymethacrylate,<sup>4–5</sup> and polyoxazolines.<sup>6</sup> The as-prepared composites can be changed from soft and flexible to brittle and hard materials depending on the chemical structure of the organic components and the overall composition ratio between organic and inorganic moiety. They can be applied in many different fields. For example, they have been demonstrated to be used in dental restorative materials, coatings, membranes, catalysts, reaction templates, and lithography.<sup>7–14</sup>

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TABLE I  
Monomer Mixtures (wt %) for Preparing Hybrid Thin Films PMH-PMH-Ti-60

Code No.	MMA (g)	HEMA (g)	Ti (OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub>	BPO	0.1N HCl (g)	ACAC (g)
PMH-Ti-60	3.0	3.0	9.0	0.128	0.93	2.65
PMH-Ti-50	3.75	3.75	7.5	0.160	0.79	2.20
PMH-Ti-40	4.50	4.5	6.0	0.192	0.64	1.47
PMH-Ti-30	5.25	5.25	4.5	0.224	0.46	1.30
PMH-Ti-20	6.0	6.0	3.0	0.256	0.32	0.88
PMH-Ti-10	6.75	6.75	1.5	0.285	0.144	0.44
PMH	7.5	7.5	—	0.318	—	—

Notes. Molar ratio of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>/ACAC = 1/1; ACAC is chelating agent. Concentration of solution about 26% in IPA. Molar ratio of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>/H<sub>2</sub>O (0.1N HCl) = 1/2.

However, the inorganic phase used currently in the majority of publications associated with the preparation of organic-inorganic hybrid materials is silica (SiO<sub>2</sub>). Recently, organic-inorganic hybrid materials containing inorganic titania (TiO<sub>2</sub>) have gradually evoked obvious research attention because of its characteristic of high refractive index. By investigating the publications in terms of the preparation and properties of organic-inorganic hybrid materials, some literature associated with the studies of the polymer-TiO<sub>2</sub> hybrid system have been reported. For example, Mark et al.<sup>15</sup> reported the preparation and properties of poly(phenylene terephthalamide)-titania hybrid materials. Wang and Wilkes<sup>16</sup> reported the preparation and properties of poly(tetramethylene oxide)-titania hybrid materials. Innocenzi et al.<sup>17</sup> reported the preparation and properties of 3-(glycidoxypropyl)-trimethoxysilane-TiO<sub>2</sub> hybrid materials. Lee and Chen<sup>18</sup> reported the preparation and high refractive index of poly(methyl methacrylate) (PMMA)-TiO<sub>2</sub> hybrid materials with 3-(trimethoxysilyl)propyl methacrylate (MSMA) as coupling agent.

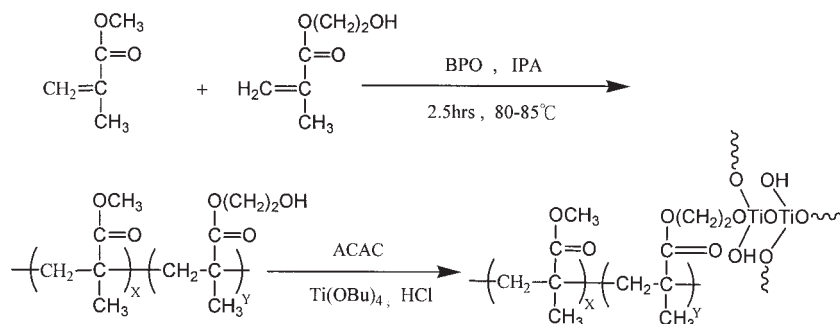
In this work, we prepared a series of PMMA-titania hybrid materials with a chemical bond between the PMMA and the titania network by using 2-hydroxyethyl methacrylate (HEMA) as coupling agent. Effects of the material composition on the thermal stability, optical properties, and morphol-

ogy of PMMA and a series of hybrid materials, in the form of free-standing film and coating, are studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), UV-Vis transmission spectra, refractometry, and atomic force microscopy (AFM), respectively.

## EXPERIMENTAL

### Chemicals and instrumentations

Methyl methacrylate (MMA; Riedel-dehaen, 99%) was doubly distilled prior to use. HEMA (Aldrich, 97%), isopropyl alcohol (IPA; Tedia, 99.9%), benzoyl peroxide (BPO; Riedel-dehaen), acetylacetone (ACAC; Merck, reagent grade), titanium(IV) *n*-butoxide (Acros, 99%), and HCl were used as received without further purification. Thermal analysis of TGA and DSC was performed under air flow by using a Seiko thermal analysis system with a model TG/DTA 220 and Perkin-Elmer thermal analysis system with a model 7 DSC. The programmed heating rate was 20°C/min in most cases. The TGA and DSC samples were prepared by spin-coating the precursor solution onto a glass substrate, followed by curing at different stages of temperature. AFM (Digital Instrument, Inc., model DI 5000 AFM) was used to probe the surface morphology of the coated hybrid films. The UV-Vis



Scheme 1 Flow chart for the preparation of poly(methyl methacrylate)-titania hybrid materials with HEMA as coupling agent.

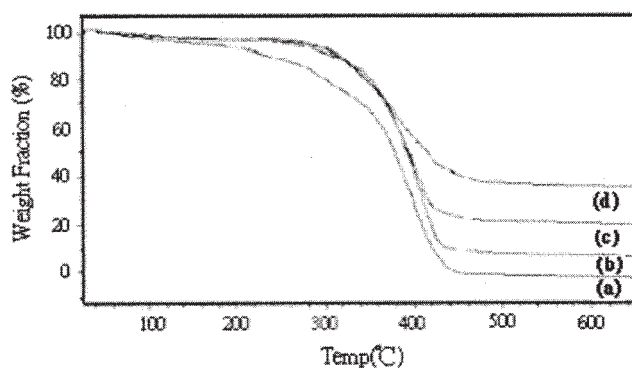
transmission spectra of a hybrid free-standing film were recorded on a Hitachi U-2000 UV-Vis spectrometer at room temperature. A refractometer (Metricon, model 2010-WLG2) was used to measure the refractive index.

### Synthesis of P(MMA-HEMA) copolymer

The typical synthesis procedure of copolymer poly(methacrylate-co-2-hydroxyethyl methacrylate) [P(MMA-HEMA)] obeyed the following procedure.<sup>5</sup> A typical procedure to prepare the copolymer P(MMA-HEMA) containing 50% MMA and 50% HEMA units by weight was given as follows: 7.5 g MMA and 7.5 g HEMA monomers, 0.318 g benzoyl peroxide (BPO), and 40 mL dry IPA were put in a 250-mL three-necked round-bottomed flask connected with a condenser, a thermometer, and a nitrogen gas inlet/outlet. Nitrogen gas was bubbled into the flask throughout the reaction. Under magnetic stirring, the solution was heated to 80–85°C and refluxed for 2.5 h. The reaction mixture solution was then poured into ~ 800 mL hexane to precipitate the copolymer. After filtration, the as-prepared copolymer was dissolved in 50 mL dry IPA and then followed by reprecipitation in 800 mL hexane. The purification procedure was repeated twice, and the purified copolymer was dried under vacuum at room temperature for 48 h. Copolymer (9.0 g) P(MMA-HEMA) was obtained in ~ 60% yield.

### Preparation of PMMA-TiO<sub>2</sub> hybrid films

The representative procedure to prepare PMMA-TiO<sub>2</sub> hybrid films with 10 wt % TiO<sub>2</sub> was listed as follows: The compositions of the monomer mixture by weight percentage for preparing polymer films were listed in Table I. PMH-Ti-X indicated the amount (wt %) of Ti (OBU)<sub>4</sub> in the reaction mixture. For example, PMH-Ti-10 represented the weight ratio of the monomer Ti(OBU)<sub>4</sub> in the monomer mixture MMA + HEMA + Ti (OBU)<sub>4</sub> was 10%. The monomer, MMA and HEMA, and the initiator, BPO, were added into the reaction flask and polymerized at 80–85°C under nitrogen flow for 2.5 h. Several drops of 0.1N HCl were added into the reaction mixture to catalyze the sol-gel process. Subsequently, a homogeneous solution of Ti(OBU)<sub>4</sub> and acetylacetonate (ACAC) (functioned as chelating agent) was added dropwise over 10 min into the reaction mixture with vigorous magnetical stirring to avoid local inhomogeneities. The reaction was allowed to proceed at 70°C for 1 h, and then the mixture was spin-coated at 1500 rpm on a silicon wafer for 30 s. The coated hybrid film was then baked at 100°C for 5 h. The typical flowchart for the



**Figure 1** TGA curves of hybrid materials with different titania contents: (a) PMH; (b) PMH-Ti-10; (c) PMH-Ti-30; (d) PMH-Ti-50.

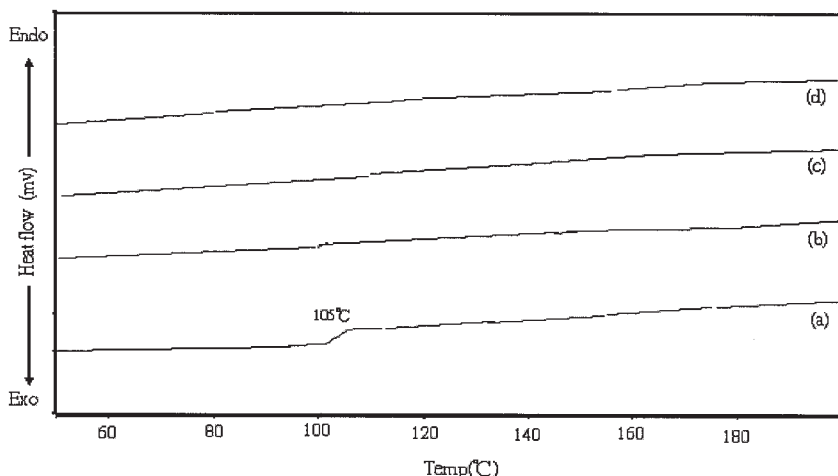
preparation of PMMA-titania hybrid materials with HEMA as coupling agent was given as Scheme 1.

## RESULTS AND DISCUSSION

### Thermal properties of PMMA-titania hybrid films

Figure 1 illustrates the TGA thermograms of weight loss as a function of temperature for the as-synthesized materials, as measured at a heating rate of 20°C/min under an air-flow. In general, there appears to be one stage of weight loss starting at ~ 200°C and ending at ~ 650°C, which may correspond to the structural decomposition of the polymers. Evidently, the thermal decomposition of these hybrid materials shifts toward the higher temperature range than that of neat PMMA, which confirms the enhancement of thermal stability of hybrid PMMA. Furthermore, the char yields of as-synthesized PMMA-titania hybrid materials at 600°C increase with increasing titania content in the hybrid materials. This implies that the Ti(OBU)<sub>4</sub> has successfully incorporated into the framework of the hybrid materials. The black color of the char residue after the TGA running also proves that the organic chains have been trapped in the inorganic titania matrix.<sup>18</sup>

Figure 2 shows the DSC curves of copolymer P(MMA-co-HEMA) and as-synthesized hybrid materials at a heating rate of 20°C/min under nitrogen flow. The copolymer P(MMA-co-HEMA) exhibits a glass-transition temperature ( $T_g$ ) at ~ 105°C. However, all the hybrid materials do not exhibit any clear thermal transition peak that can be attributed to neat PMMA. This may be associated with the trapped inorganic moiety making the polymer chain segment immobile and leading to the  $T_g$  being probably very close to the decomposition temperature.<sup>18</sup> Moreover, the DSC study also implies good thermal stability of the as-prepared films and successful



**Figure 2** DSC curves of hybrid materials with different titania contents: (a) PMH; (b) PMH-Ti-10; (c) PMH-Ti-30; (d) PMH-Ti-50.

bonding of the organic and inorganic moieties in the hybrid films.

**Optical properties of PMMA-titania hybrid films**

**Optical clarity**

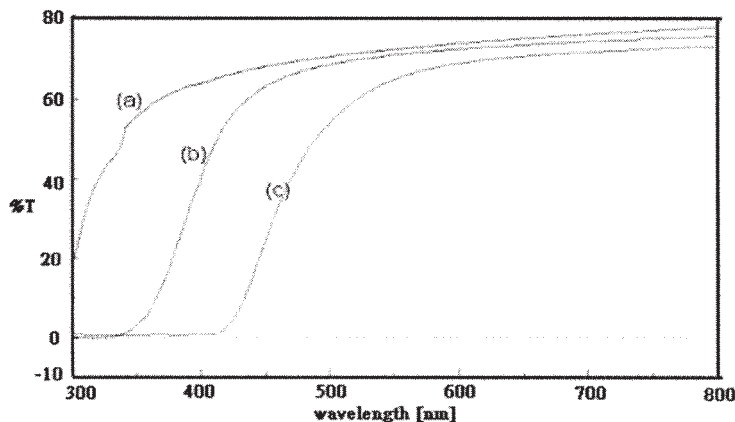
Figure 3 shows the UV-Vis transmission spectra of the PMMA-TiO<sub>2</sub> hybrid films at different titania contents. The appearance of copolymer P(MMA-co-HEMA) film exhibits higher transparency. When the weight percentage of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> in hybrid materials is increased to 10 wt %, the transparency of the hybrid film is slightly affected by the introduction of titania content. However, transparency of the copolymer PMMA-co-HEMA hybrid film is significantly affected by the incorporation of 30 wt % titania loading, leading to an obvious decrease in optical transparency. In conclusion, the incorporation of inorganic titania into organic PMMA leads to a lowering of transparency of hybrid PMMA.

**Refractive index**

Figure 4 shows the refractive index (*n*) of P(MMA-co-HEMA) hybrid films. The refractive index (RI) of hybrid film at 632.8 nm increases from 1.515 for Ti-20 to 1.550 for Ti-60, as shown in Table II. The refractive indices of the prepared films Ti-20 to Ti-60 are higher than neat copolymer film (RI = 1.5022). This suggests that increasing the incorporation of titania into the copolymer matrix results in an increment of the refractive index.

**Morphology studies**

To further gain the physical fundamentals of the topographically structures in more detail, an AFM is applied to investigate the surface profiles of the samples. As shown in Figure 5, that exhibits a 3D topographical feature of the neat copolymer PMH and hybrid film PMH-Ti-40. Based on the 3D image analysis, it demonstrates a slightly smooth decrease of



**Figure 3** UV-Visible transmission spectra of (a) PMH; (b) PMH-Ti-10; (c) PMH-Ti-30.

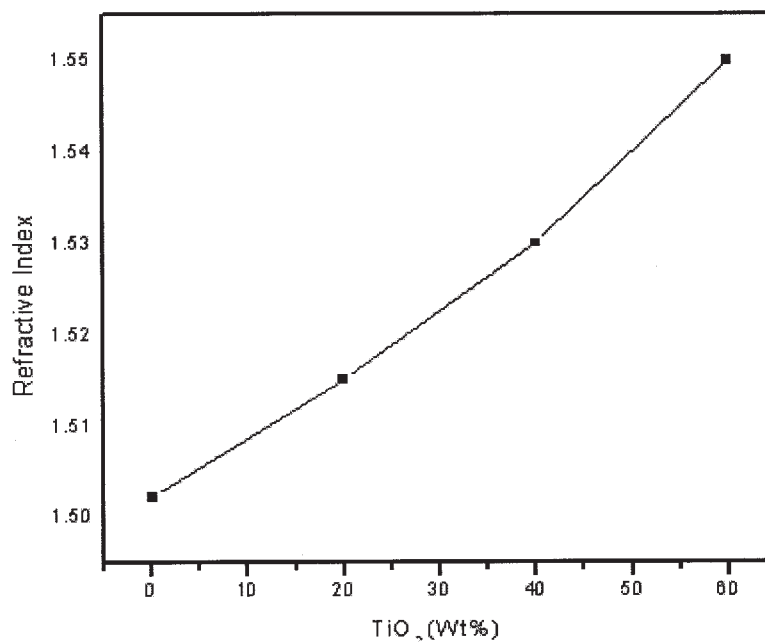


Figure 4 Refractive index of the hybrid films as a function of the titania content in the hybrid materials.

topography as the copolymer PMH matrix incorporated with 40 wt % loading of inorganic titania.

### CONCLUSION

In this study, a series of sol-gel-derived organic-inorganic hybrid materials consisting of organic PMMA and TiO<sub>2</sub> was successfully synthesized by using HEMA as coupling agent. In this work, HEMA is first copolymerized with methyl methacrylate monomer at a specific feeding ratio by using BPO as initiator. Subsequently, the as-prepared copolymer (i.e., sol-gel precursor) is then cohydrolyzed with various contents of titanium butoxide to afford chemical bondings to the forming titania networks to give a series of hybrid materials. Transparent organic-inorganic hybrid ma-

terials with different contents of titania are always achieved. The thermal decomposition of these hybrid materials shifts toward the higher temperature range than that of neat PMMA based on the TGA studies, which confirms the enhancement of thermal stability of hybrid PMMA. The copolymer P(MMA-co-HEMA) exhibits a  $T_g$  at  $\sim 105^\circ\text{C}$  based on the DSC studies. However, all the hybrid materials do not exhibit any clear thermal transition peak that can be attributed to pure PMMA. This may be associated with the trapped inorganic moiety that made the polymer chain segment immobile, and thus, the glass transition temperature is very probably close to the decomposition temperature. Furthermore, increasing the incorporation of titania into the PMMA matrix results in an increment of the refractive index. The topographical feature of

TABLE II  
Thermal and Optical Properties of the Prepared Materials

Code No.	Thermal properties			Optical properties	
	$T_g^a$	$T_d^b$	Char yield (wt %) <sup>b</sup>	RI <sup>c</sup>	UV-vis <sup>d</sup>
PMH	105°C	159.13°C	0	1.5022	78%
PMH-Ti-10	—	185.96°C	4.10	—	75%
PMH-Ti-20	—	277.62°C	12.63	1.515	—
PMH-Ti-30	—	279.85°C	19.47	—	70%
PMH-Ti-40	—	274.26°C	33.24	1.530	—
PMH-Ti-50	—	264.20°C	32.90	—	—
PMH-Ti-60	—	287.68°C	43.66	1.550	—

<sup>a</sup> As measured by differential scanning calorimeter (DSC).

<sup>b</sup> As measured by thermogravimetric analysis (TGA).

<sup>c</sup> As measured by refractometer at 632.8 nm.

<sup>d</sup> As measured by UV-visible spectroscopy.

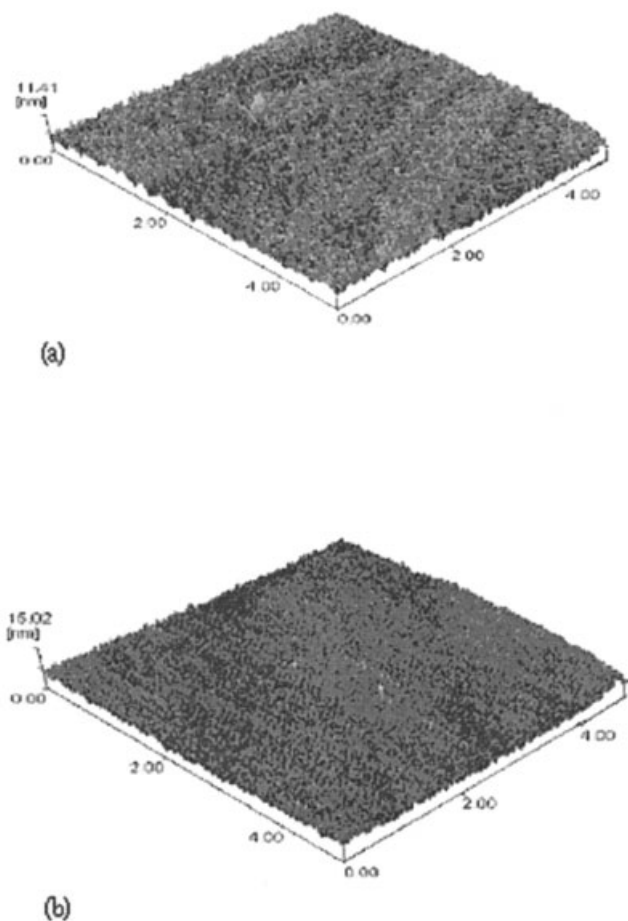


Figure 5 AFM surface images ( $500 \times 500 \text{ nm}^2$ ) of films: (a) PMH; (b) PMH-Ti-40 baked 5 h at  $100^\circ\text{C}$ .

hybrid film demonstrates a slightly smooth decrease of morphology as the PMH matrix incorporated with inorganic titania.

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