

Preparation and Characterization of High Refractive Index Thin Films of TiO₂/Epoxy Resin Nanocomposites

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ABSTRACT: By using sol-gel method, amorphous titania was introduced into epoxy matrix to prepare a series of high refractive index TiO₂/epoxy resin nanocomposite films. To increase the refractive index of the hybrid films, triethoxysilane-capped trimercaptothioethylamine (TCTMTEA), a new kind of high refractive index coupling agent was synthesized from trimercaptothioethylamine (TMTEA). In the experiment, TCTMTEA acted as the solidification agent together with TMTEA except being used as the coupling agent. The hybrid films have been characterized via FTIR, AFM, DSC, TGA, etc. The experimental results showed that

the amorphous TiO₂ had been dispersed uniformly in the organic polymer matrix with the size smaller than 100 nm in each sample. More importantly, the refractive index of this kind of materials can be continuously adjusted from 1.61 to 1.797 with the content of TiO₂ increasing from 0% to 65% in mass, and the continuously adjusted refractive index is very important for the applications in optical antireflective films. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1631–1636, 2006

Key words: nanocomposites; transparency; thin films; resins; refractive index

INTRODUCTION

During the past decade, inorganic/polymer hybrid materials have been the research focus for their excellent electrical, optical, magnetic, optoelectronic, and enhanced mechanical properties.^{1–7} Since the hybrid materials can breach the limit of the refractive index of the pure polymer, the preparation of inorganic/polymer hybrid materials with high refractive index has attracted considerable attention.^{8–19} In particular, using TiO₂ as inorganic domains and incorporating it into a polymer matrix to synthesize high refractive index hybrid materials through a sol-gel process has been extensively studied.^{13–19} These hybrid materials combine the advantages of the organic polymers (lightweight, flexibility, good impact resistance, and good processability) and inorganic materials (good chemical resistance, high thermal stability, and high brittleness). Furthermore, the refractive index of the hybrid materials can be easily manipulated via adjusting the ratio of inorganic phase to organic phase.

The properties (optical, mechanical, and thermal) of the hybrid materials are relative to the properties of each component, and also to the composite phase morphology and interfacial properties. The mild characteristics offered by the sol-gel process allow inorganic and organic components to be mixed at the nanometric scale.²⁰ The nature of the interface between organic and inorganic components has been used recently to classify these hybrids into two different classes.²¹ Class I corresponds to all the systems in which there are no covalent or ionic-covalent bonds between the organic and inorganic components. There are only Van der Waals forces, hydrogen bonds, or electrostatic forces between them. In contrast, some of the organic and inorganic components are linked through strong chemical bonds (covalent or ionic-covalent), which are defined as class II materials. The interfacial force between organic and inorganic phases plays a major role in controlling the microstructure and properties of composite materials.^{20,22–24} The formation of the extensive covalent bonding between organic and inorganic phase can prevent phase separation effectively, which offered the possibility of preparing transparent hybrid materials.^{16,18,25} To obtain class II materials, it is necessary for many cases to introduce the coupling agent to produce strong interfacial force between organic and inorganic. At the same time, the coupling agent has introduced its own characters into the hybrid materials as a component. Synthesis of a new kind of coupling agent

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with good characters is an effective way to improve the properties of the hybrid materials.

Previously, we have prepared TiO₂-triethoxysilane-capped polythiourethane (TCPTU) hybrid optical films with high refractive index via an *in situ* sol-gel method.²⁶ In that work, TiO₂ acted as inorganic component in the high refractive index hybrid materials and exhibited its excellent properties. In this work, to increase the refractive index of the hybrid films, a new kind of sulfur-coupling agent, triethoxysilane-capped trimercaptothioethylamine (TCTMTEA) has been prepared, which is more appropriate for the preparation of high refractive index materials because of the introduction of sulfur element.²⁷ Due to the similar structure with TMTEA, TCTMTEA can also act as solidification agent together with TMTEA for the epoxy resin except being used as coupling agent between the TiO₂ and polymer. At the same time, both TCTMTEA and TMTEA can self-catalyze the epoxy resin curing system.²⁷ In this experiment, TiO₂ was still used as the inorganic component and trimercaptothioethylamine (TMTEA)/epoxy resin system was adopted as organic polymer component, which we had roundly studied before.^{27,28} These hybrid films were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis, (TGA) and atomic force microscopy (AFM). The refractive indices of the resulted films were measured at the wavelength of 632.8 nm by an ellipsometer. All the results showed that a series of high refractive index and transparency TiO₂/epoxy resin nanocomposite films have been obtained by using TCTMTEA as the coupling agent.

EXPERIMENTAL

Materials

Trimercaptothioethylamine (TMTEA) was synthesized according to the literature,^{29,30} $n_d = 1.59$. Anhydrous tetrahydrofuran (THF) was prepared by drying THF at reflux conditions with metal sodium. Diglycidyl ether of bisphenol A (DGEBA) was purified by fractionation in butanone/methanol solution, the epoxy equivalent weight (EEW) is 185 g equiv⁻¹. The chemicals (3-isocyanatopropyl)triethoxysilane (IPTEOS, 99%, Fluka), dibutyltin diaurate (DBTL), and titanium butoxide [Ti(OBu)₄, 99%] were all of analytical grade and were used without further purification.

Synthesis of the TCTMTEA

About 4.9352 g (0.025 mol) TMTEA, 200 mL anhydrous THF, and 0.1 g DBTL were added into a 500-mL four-necked round-bottomed flask under mechanical stirring and the protection of nitrogen at 45°C. Then the mixture of 6.1844 g (0.025 mol) IPTEOS and 20 mL

anhydrous THF was added dropwise into the flask within about 1 h. The temperature was held for another 2 h before finishing the reaction. The THF was removed by vacuum distillation, and the colorless and limpid liquid was obtained.

Preparation of TiO₂/epoxy resin hybrid films

Under vigorous stirring, the mixture of H₂O and anhydrous THF was added into a 50-mL reactor with titanium butoxide and anhydrous THF. The molar ratio of H₂O to Ti(OBu)₄ was fixed at 1 : 1. Then TCTMTEA was added into the mixture. After having reacted for 8 h at room temperature, TMTEA and DGEBA were added into the reaction system (the content of TCTMTEA in the organic part was 15% and the molar ratio of TMTEA to TCTMTEA was 2.68. At the same time, the molar ratio of epoxy group to hydrosulfide group was 1:1), and then the temperature was andante raised to 70°C for 30 min. At last, the reaction system was kept for 8–12 h at room temperature. Then the mixture was spin-coated on a silicon wafer at 1500–3000 rpm. The films were cured at 60°C for 1 h, 100°C for 1 h, 120°C for 2 h, and 150°C for 3 h.

Characterization

IR spectra were taken on an AVATAR 360 FT-IR infrared spectrophotometer. ¹H-NMR spectrum was obtained with a Bruker Avance 500-MHz NMR spectrometer. The glass-transition temperatures (T_g) were measured by a Netzsch 204 differential scanning calorimeter (DSC) with a heating rate of 10°C/min in nitrogen atmosphere. A Netzschsta449c thermogravimetric analyzer (TGA) with a heating rate of 10°C/min up to 800°C was used for the thermal degradation study of polymers under nitrogen. Atomic force microscopic (AFM) images were recorded with a Dimension 3100 of Digital Instrument, and operated in a tapping mode that measured topography. The refractive index of the hybrid films was measured on an Auel-III laser auto-ellipsometer at the wavelength of 632.8 nm.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectrum of TCTMTEA. The absorption peak of isocyanate group (—NCO) of IPTEOS at 2272 cm⁻¹ has completely disappeared and the absorption peak of —SH vibration of TMTEA at 2550 cm⁻¹ still can be observed. At the same time, the characteristic vibration of hydrogen-bonded N—H bonds and C=O bonds for the thiourethane linkages at 3311 and 1658 cm⁻¹ were observed. The absorption peaks of Si—OEt bands appeared at 1103 and 957 cm⁻¹. The structure of the TCTMTEA was further characterized by ¹H-NMR. The absorption peaks of

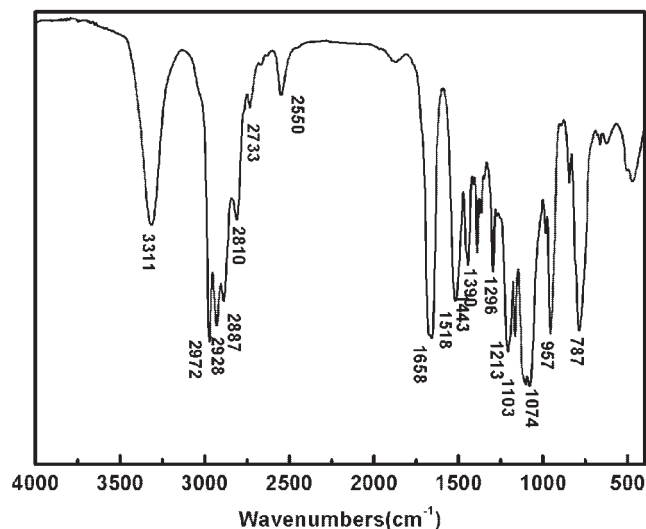


Figure 1 FTIR spectrum of the TCTMTEA.

methyl-substituted hydrogen on IPTEOS and the remainder mercapto-substituted hydrogen on TMTEA were observed at 1.23 and 1.77 ppm; the absorption peaks of thiocarbamate-substituted hydrogen appear at 5.88 ppm. All the results showed that the TCTMTEA has been obtained.

Figure 2 shows IR spectra of the hybrid films for Ti0-Ti50 (TiX was defined as a film with X wt % of titania in hybrid film). The absorption bands at 3036, 1606, 1506, and 829 cm⁻¹ are phenyl groups in DGEBA and the absorption peaks of epoxy group in DGEBA have disappeared. The broad absorption bands at 3200–3500 cm⁻¹ are N–H bands in TCTMTEA and the bands of Ti–OH or Si–OH residue groups. The absorption of Ti–O–Ti and Ti–O–Si appear at 613

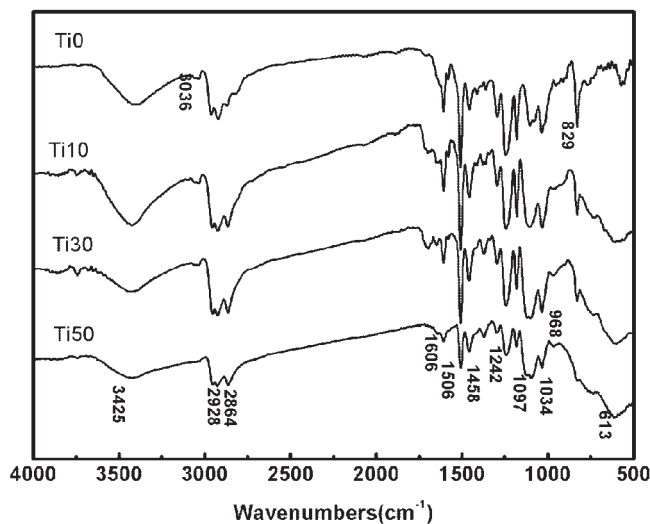


Figure 2 FTIR spectra of the TiO₂/epoxy resin hybrid films Ti0, Ti10, Ti30, and Ti50.

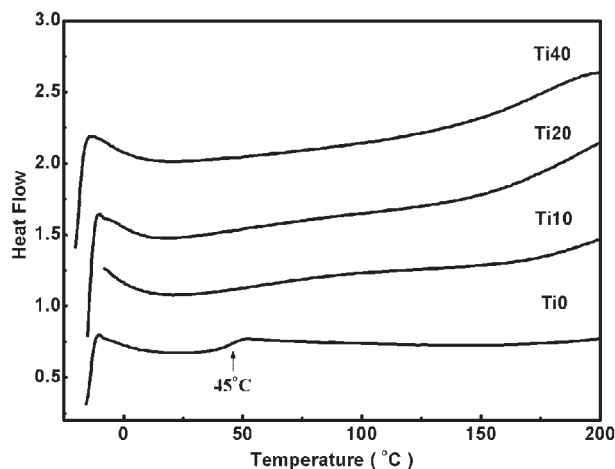


Figure 3 DSC curves of the TiO₂/epoxy resin hybrid films Ti0, Ti10, Ti20, and Ti40.

and 968 cm⁻¹. All the information proves that the epoxy resin has been completely cured and the interlaced network has been formed.

Figure 3 shows the DSC curves of the pure epoxy resins (Ti0) and TiO₂/epoxy resins hybrid materials Ti10-Ti40. The pure resin exhibits a glass-transition temperature (T_g) of about 45°C, which accords with the result in the literature.³¹ However, no any significant thermal transition points below 200°C were observed for the hybrid films. The hybrid films showed a good thermal stability in DSC analysis. These results suggest that the covalent bonds between TiO₂ and the polymer matrix have formed, which make the glass-transition temperature of the polymer close to its decomposition temperature.²⁵

Figure 4 shows the TGA curves of the pure epoxy resins (Ti0) and TiO₂/epoxy resins hybrid films (Ti10-

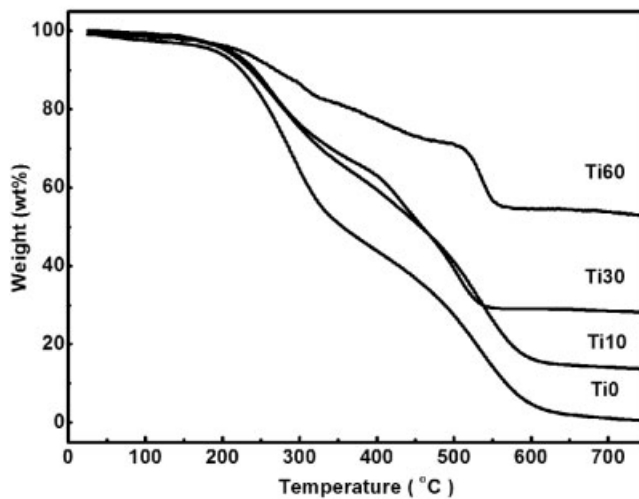


Figure 4 TGA curves of the TiO₂/epoxy resin hybrid films Ti0, Ti10, Ti30, and Ti60.

TABLE I
Properties of TiO₂/Epoxy Resins Hybrid Films

Film ^a	Residue ^b	Residue ^c	<i>h</i> (Å) ^d	<i>n</i> _{632.8 nm} ^e	<i>R</i> _q ^f (nm)	<i>R</i> _a ^g (nm)
Ti0	0.4	0	–	1.610	–	–
Ti10	13.6	10	1701	1.644	0.309	0.242
Ti20	–	–	1330	1.665	0.424	0.338
Ti30	27.9	30	1383	1.686	0.639	0.511
Ti40	–	–	1643	1.724	0.517	0.409
Ti50	–	–	1671	1.760	0.392	0.312
Ti60	52.9	60	1597	1.759	0.312	0.241
Ti65	–	–	1081	1.797	0.503	0.400

^a TiX was defined as a film with a X% wt % of titania in hybrid film.

^b Char yield of the hybrid films at 750°C after TGA.

^c Theoretical char yield of the hybrid films.

^d Thickness of the hybrid films.

^e Refractive index of the hybrid films at 632.8 nm.

^f Room mean square roughness of hybrid films.

^g Average roughness of the hybrid films.

Ti60). The initial decomposition temperature (about 200°C) of the hybrid films is relative to the decomposition of the pure epoxy resins matrix. As shown in Table I, the residues of 13.7% for the hybrid film Ti10 is higher than the theoretical content of titania. The reason may be that the covalent linkages between the inorganic phase and the polymer matrix trapped a part of organic moiety in the inorganic phase.¹⁸ Contrarily, the residues of Ti30 and Ti60 are 27.8% and 52.9% respectively, which are lower than the theoretical contents of the inorganic phase, particularly in the hybrid films with high content of titania. This is likely to be aroused by the insufficient hydrolysis and condensation of Ti(OBu)₄ because of no enough water existing in the hydrolysis system (there was only a quarter of the theoretical content of water in the system).

Figure 5 shows the AFM images of the hybrid films of Ti10 and Ti60. The height images are listed on the left and the phase images are put on the right. The phase images of the hybrid films show two kinds of obvious regions, dark (titania domain) and bright (polymer domain). However, no macrophase separation is observed in the hybrid films. Both the titania phase and polymer phase are uniformly mixed and the average sizes are less than 100 nm in Ti10 and T60. The surfaces of the hybrid films exhibit high degree of smoothness, and both the average roughness (*R*_a) and mean square roughness (*R*_q) of this series of hybrid films are in the range of 0.2–0.6 nm, which can be reflected in the height images and Table I.

Figure 6 shows the UV–vis spectra of the TiO₂/epoxy resins hybrid films Ti20, Ti30, Ti40, and Ti50. The transparencies of them are obtained, which is relative to blank slide. Depending on the well controlling of the titania phase size, the hybrid films exhibit excellent transparencies. Especially, in the range of 400–800 nm, all the transparencies of the hybrid films are

higher than 90%. And the transparencies of the hybrid films have reduced faintly, when the weight content of TiO₂ has increased from 20% to 50%. The curves of Ti20 and Ti40 show seasonal undulation as shown in Figure 6, which is brought by the appropriate thickness of the hybrid films relative to the wavelength of detective ray.

Figure 7 shows the refractive index variation of the TiO₂/epoxy resins hybrid films with the weight content of TiO₂. Because the titania synthesized by sol–gel method under low temperature is commonly amorphous, its refractive index is in the range of 2.0–2.2 according to the preparation condition.³² Figure 7 shows that the refractive index of the hybrid films increases from 1.61 for pure polymer²⁸ to 1.797 for Ti65 with increasing TiO₂ content and there is a linear dependence for the refractive index of hybrid films on the TiO₂ weight fraction. It offered the capability to adjust the refractive index of the hybrid films by controlling the content of TiO₂. In this system, as discussed earlier, the real content of amorphous titania is less than the theoretic content for insufficient hydrolysis and condensation of Ti(OBu)₄, and so the high-point of the refractive index of the hybrid films is 1.885 as shown in Figure 6, which is less than 2.0.

CONCLUSIONS

In summary, a series of TiO₂/TCTMTEA/epoxy resins hybrid optical films with high refractive index have been successfully prepared via sol–gel method. In this system, TCTMTEA acts both as the coupling agent and as the solidification agent of epoxy resin. At the same time, TCTMTEA has a high refractive index for the import of sulfur element. FTIR and DSC results demonstrate that the titania phase was effectively incorporated into the polymer matrix by covalent bonds. AFM images show that the titania phase and the poly-

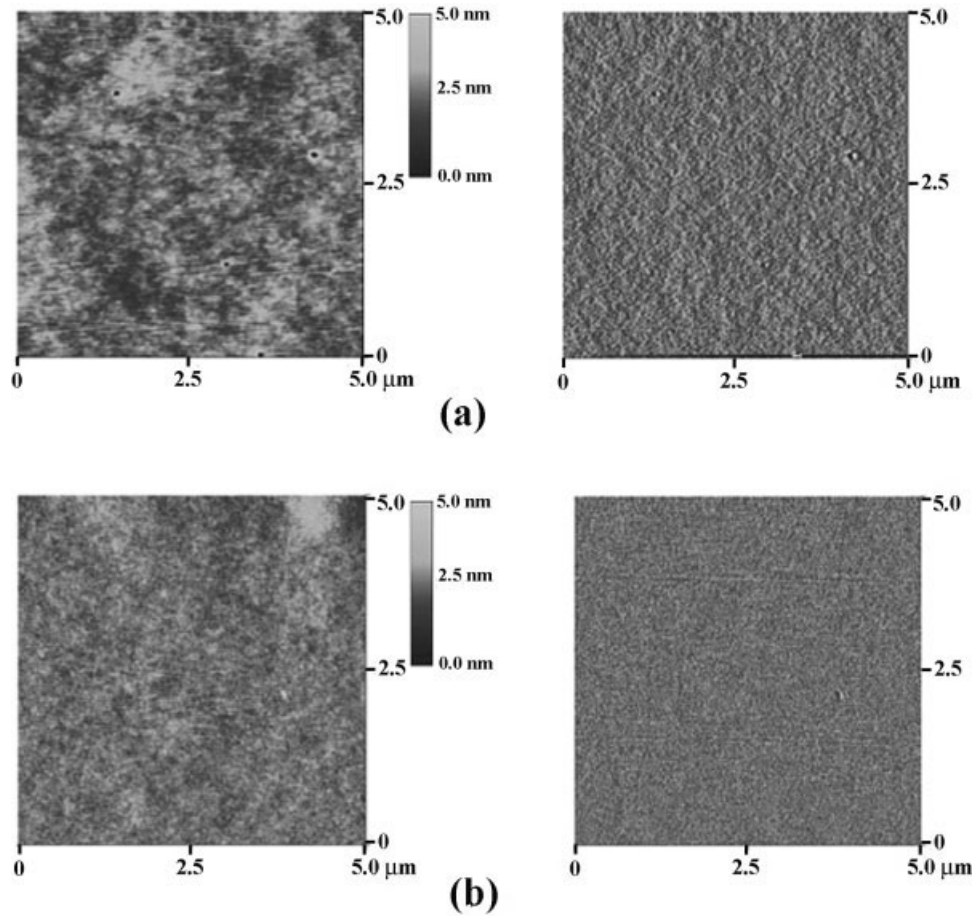


Figure 5 AFM images of hybrid films (a) Ti10 and (b) Ti60 (left images are height image and right images are phase images).

mer phase are in the nanometric scale and the hybrid films have excellent surface planarity. The covalent bonds between the inorganic phase and organic phase

are the most important factors for controlling the phase size of the hybrid films and making the hybrid films a good optical character. The hybrid films have higher refractive index than the pure polymer matrix. Because the refractive index of the hybrid films has a

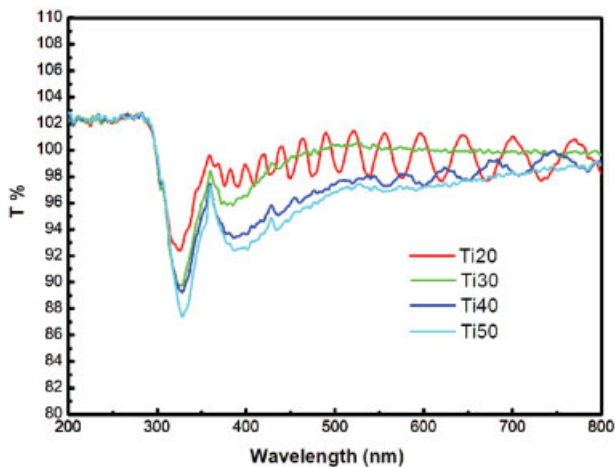


Figure 6 UV-vis spectra of the TiO₂/epoxy resin hybrid films Ti20, Ti30, Ti40, and Ti50. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

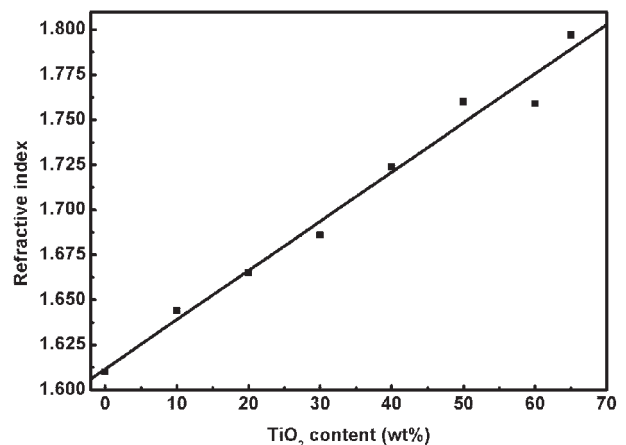


Figure 7 Refractive index variation of the TiO₂/epoxy resin hybrid films with the weight content of TiO₂.

well linear dependence on the TiO₂ weight fraction, the refractive index can be turned by changing the TiO₂ weight fraction easily. These hybrid materials can potentially be used as high refractive index optical films in the optical design.

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