

Fabrication of hybrid surface-modified titania–epoxy nanocomposite films

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ABSTRACT

This work reports the preparation of well-dispersed surface-modified titania nanoparticles in organic solvents. Different types of surface-modified titania nanoparticles can be incorporated into epoxy matrix to form hybrid nanocomposites. The hybrid nanocomposite films have higher refractive index than pure epoxy system. The refractive index can be tuned by using different forms of titania nanoparticles and by changing the titania solid content. The titania solid content in the epoxy matrix can be more than 70 wt% without affecting the optical transparency of the hybrid film.

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1. Introduction

Nanomaterials have been studied by both academic and industrial researchers recently. The physical and chemical properties of various polymer can be tuned by incorporating inorganic fillers. Zhang et al. [1] reported silica/PMMA hybrid materials with high transparency and heat stability via sol–gel process. Incorporating silica nanoparticles and corundum microparticles into UV-cured polyacrylate coatings exhibit improved scratch and abrasion resistance properties [2]. Surface-functionalized alumina nanoparticles filled polymeric nanocomposite show enhanced mechanical properties [3]. Surface modification of the nanoparticles is necessary in order to enhance the stability of nanoparticles in the polymer matrix. Colloidal titania nanorod with different surface ligands are used for tailoring the optical properties of PMMA thin films [4]. TiO₂–triethoxysilane-capped polythiourethane hybrid optical films with high refractive index via an in situ sol–gel method were reported [5]. A multilayer-graded refractive index structure for LED encapsulants with refractive index of 1.68 at wavelength 400 nm was also demonstrated recently [6].

In this work, titania nanoparticles with different surface coupling agents were prepared by modified sol–gel process. They were incorporated into the epoxy matrix to form transparent optical nanocomposite films. The effect of curing conditions to optical transmittance of different hybrids was also studied.

2. Experimental

2.1. Materials characterizations

The synthesized nanopowders were characterized by the X-ray diffractometer (Philips 1700) equipped with a graphite crystal monochromator for phase analysis. The particle size and morphology was studied by transmission electronic microscopy (JEM 2000EX). Refractive indexes were measured on a J. A. Woolam M44 Ellipsometer. The UV–vis transmission was measured by Hitachi ultraviolet–visible absorption spectrometer (UV–vis, U-2001).

2.2. Preparation of surface-modified titania nanoparticles

2.2.1. DBS-capped titania nanoparticles

28.43 g of TTIP was added dropwise into 500 ml of distilled water under stirring at room temperature for 15 min. Then 20.85 ml of 12 M hydrochloric acid was added into the mixture. The solution was stirred for 8 h at room temperature. The resulting TiO₂ nanoparticles were isolated by centrifugation. Desired amount of sodium dodecylbenzenesulfonate (DBS) solution was added into the mixture. DBS-capped titania nanoparticles (A) can be obtained after stirring the mixture for 1 day at room temperature.

2.2.2. DBS-capped titania and hexylamine/DBS-capped titania nanoparticles

28.43 g of TTIP was added dropwise into 500 ml of distilled water under stirring at room temperature for 15 min. Then,

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20.85 ml of 12 M hydrochloric acid was added to the mixture. Distilled water was added to the titania colloid in order to adjust the pH value > 0.7 . After that, 50 ml of toluene was added to 100 ml of titania colloid in water and slowly stirred for 30 min. 20 ml of 0.2 M DBS solution was added and stirred for 3 h. The organic phase was separated out and refluxed for 24 h. Dried

DBS-capped titania nanoparticles (B1) was obtained after evaporating the solvent. The DBS-capped titania nanoparticles (B1) was redispersed in the co-solvent of n-butanol and toluene with a weight ratio of 1:1 to obtain a dispersion with solid content of 5 wt%. Excess amount of hexylamine (10 ml) was added to the colloidal dispersion and stirred for 2 h. The precipitated solid was

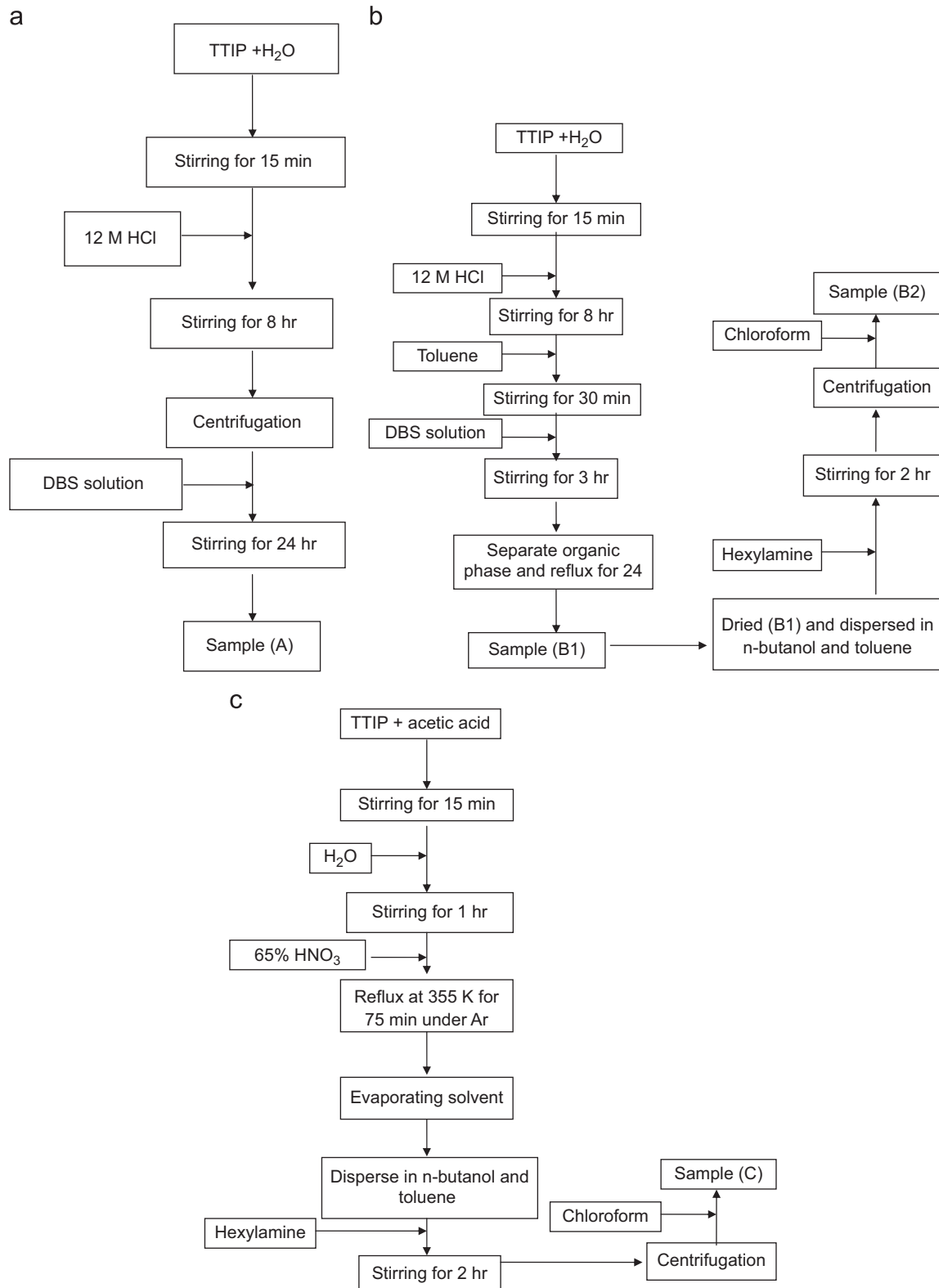


Fig. 1. Schematic procedures for preparing (a) sample A, (b) sample B1, B2 and (c) sample C.

isolated by centrifugation. The wet solid was added to chloroform to obtain hexylamine/DBS-capped titania nanoparticles dispersion (B2).

2.2.3. Hexylamine/acetic acid-capped titania nanoparticles

12 g of acetic acid was first mixed with 58.6 g of titanium isopropoxide. The solution was then poured into 290 ml of distilled water with vigorous stirring for 1 h. 4 ml of 65% nitric acid was added into the mixture. The solution was refluxed at 355 K for 75 min under argon atmosphere. The solvent was evaporated with a rotary evaporator at 318 K. The dried powder was redispersed in co-solvent of n-butanol and toluene with a weight ratio of 1:1 to obtain a colloidal dispersion with solid content of 5 wt%. Excess amount of hexylamine (10 ml) was added to 50 g of dispersion and stirred for 2 h. The precipitated solid was isolated by centrifugation. The wet solid was added to chloroform and sonicated for 2 h to obtain hexylamine/acetic acid-capped titania nanoparticles dispersion (C).

The procedures for preparing the surface-modified titania nanoparticles in organic solvents are shown in Fig. 1. The average particle size, crystal phase and solid content of titania nanoparticles dispersions (samples A, B1, B2 and C) were shown in Table 1. Figs. 2 and 3 show the TEM images and XRD patterns of surface-modified titania nanoparticles. TEM analysis shows that all titania nanoparticles synthesized have rod-shaped structure.

2.3. Preparation of hybrid titania–epoxy nanocomposite films

Diglycidyl ether of bisphenol A epoxy (DGEBA, Dow) and 4,4'-diamino-diphenylsulfone (DDS, Merck) were used as resin and curing agent, respectively. The weight ratio of epoxy to curing agent was fixed at 1:0.3342. Different amount of well-dispersed surface-modified titania nanoparticles was added into the epoxy system. The mixture was then stirred at room temperature for 2 h. After that, the mixture was spin-coated on silicon wafer at 1500–3000 rpm. The thickness of the hybrid films were controlled

Table 1
Compositions and physical properties of surface-modified-titania nanoparticles.

Sample	Surfactant	TiO ₂ content (%)	Solvent	TiO ₂ :surfactant (weight ratio)	Average size (nm)	Crystalline phase
TiO ₂ (A)	DBS	0.5	THF	1:0.8	34	Rutile
TiO ₂ (B1)	DBS	5	Pyridine	1:1.55	26	Amorphous+anatase
TiO ₂ (B2)	DBS+hexylamine	5	CHCl ₃	1:0.31	27	Anatase
TiO ₂ (C)	HOAc+hexylamine	5	CHCl ₃	1:0.20	14	Anatase

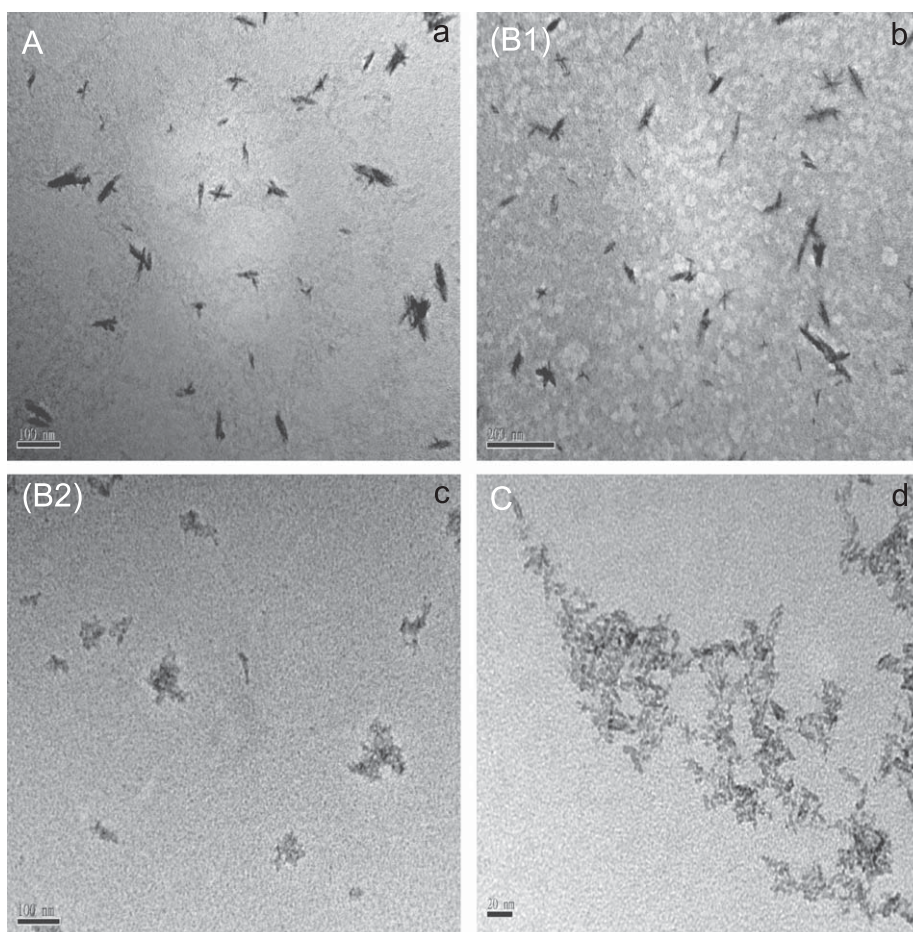


Fig. 2. TEM images of (a) sample A, (b) sample B1, (c) sample B2 and (d) sample C.

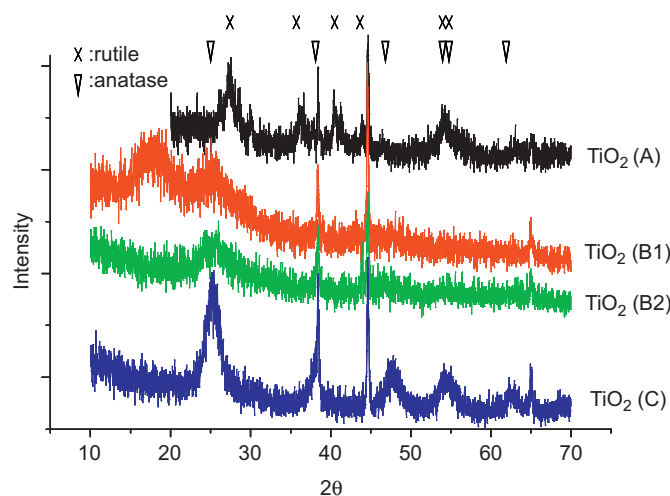


Fig. 3. XRD patterns of (a) sample A, (b) sample B1, (c) sample B2 and (d) sample C.

at about 1 μm . The films were cured at 493 K for 2 h in ambient or nitrogen environment.

3. Results and discussion

The titania nanoparticles after surface modification can be uniformly dispersed in organic solvent without precipitation. XRD examination shows that single-phase rutile can be synthesized by hydrolysis of TTIP in water at room temperature in the presence of hydrochloric acid as the catalyst in sample (A). DBS-capped titania nanoparticles obtained in sample B1 was further modified with hexylamine. Severe aggregation of particles can be reduced by surface modification using carboxylic acids and long chain alkyl amines in the process of preparing colloidal solution of TiO_2 nanoparticles [7]. Different acids can be used to increase the liability of protonated OR groups in the sol-gel process. Acetate can function as a chelating ligand and react with the titanium alkoxide precursor to form $\text{Ti}(\text{OR})_x(\text{AC})_y$. The condensation process can thus be initialized by the addition of water to the precursor. Highly crystalline single-phase anatase can be obtained by using the synthesis procedure for sample (C) according to the XRD data in Fig. 3. The acetic acid-capped titania nanoparticles was also modified with hexylamine to obtain hexylamine/acetic acid-capped titania nanoparticles dispersion.

Fig. 4 display the plot of refractive index of DGEBA/DDS epoxy system versus the weight percentage of different titania nanoparticles. If the curing agent was replaced by methylhexahydrophthalic anhydride (MHHPA), the pure DGEBA/MHHPA epoxy system has refractive index of 1.54. The pure DGEBA/DDS epoxy system has higher refractive index ($n=1.63$) due to the relatively heavier sulfur atom in 4,4'-diaminodiphenylsulfone (DDS) curing agent.

The hybrid nanocomposite with hexylamine/acetic acid-capped titania nanoparticles (C) have higher refractive index. The surface-modified titania nanoparticles maybe dispersed more uniformly due to the smaller average particle size of sample C. The refractive index of the nanocomposite increases from 1.63 for pure polymer to 1.795 for sample C with increasing titania weight content. However, for polymer filled with sample B1, the increase in refractive index is not so significant compared to other two hybrids. The amorphous phase of DBS-capped titania nanoparticles (B1) may reduce the refractive index of the resulting hybrid. However, for all kinds of hybrid systems, the refractive index increases with the solid content of titania nanoparticles irrespec-

tive of their surface modification processes. Fig. 5(a) and (b) display the transmittance spectra of hybrid nanocomposite films cured in air and nitrogen environment, respectively (insets

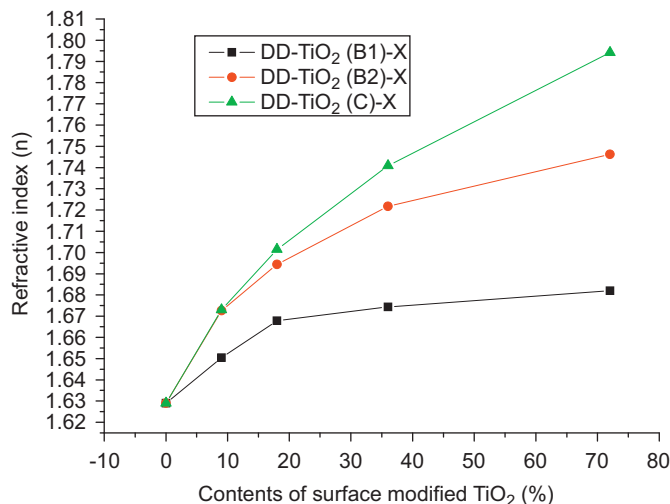


Fig. 4. Variation of the refractive index of hybrid nanocomposite films with different TiO_2 content.

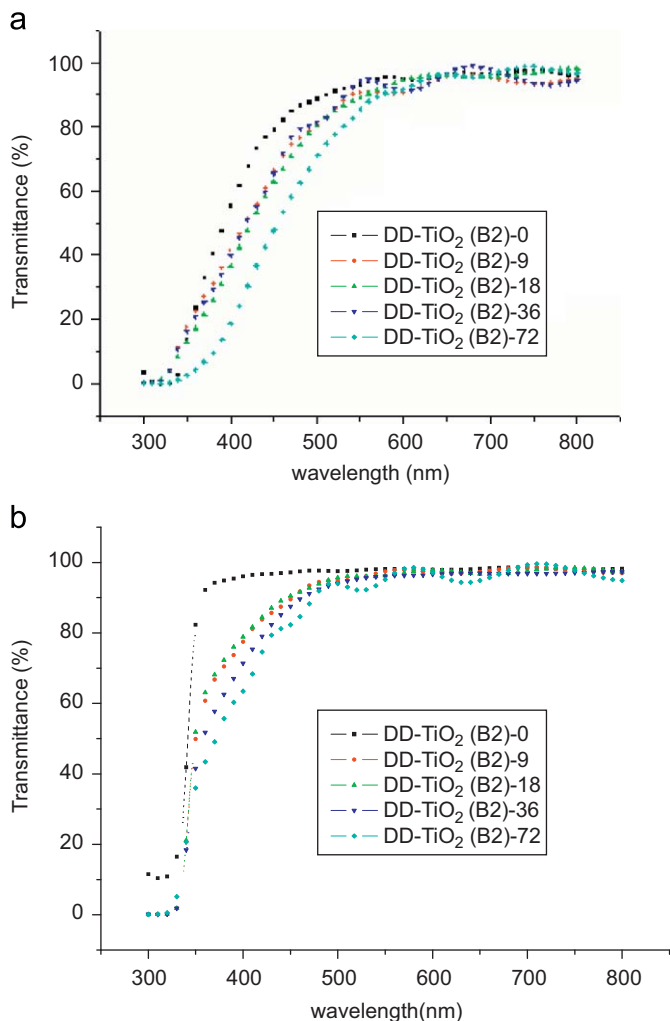


Fig. 5. Transmittance spectra of hybrid nanocomposite films with different titania content cured in (a) air and (b) nitrogen (insets indicate – the epoxy system-sample of titania nanoparticles-weight content of titania in the hybrid).

indicate – the epoxy system–type of titania nanoparticles–weight content of titania). It can be seen that samples cured in air exhibit transmission >80% at wavelength of 550 nm, while samples cured in nitrogen environment have transmission >90% at wavelength of 550 nm. The reason for this may due to the oxidation occurs at the amino functional group within the 4,4'-diamino-diphenylsulfone (DDS) curing agent when the epoxy system was curing in air. It should be noted that the nanocomposite films with high solid content of titania also absorb a significant portion of violet and blue light.

4. Conclusion

This work show that different types of surface-modified titania nanoparticles can be incorporated into epoxy system to form hybrid nanocomposites. The refractive index can be tuned by using different forms of titania nanoparticles and by changing the titania solid content easily. The solid content can be more than

70 wt% without affecting the optical transparency of the hybrid film. The highly transparent nature of these nanocomposite films can be potentially applied in filters, planar-gradient index lenses, reflectors, optical waveguides, antireflection films, and optical coupling materials.

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