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Transparent high refractive index nanocomposite thin films

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Abstract

This work reports the preparation of acetic acid-modified TiO_2 nanoparticles by sol–gel synthesis method. The nanoparticles can be incorporated directly into the polymer matrix to form transparent high refractive index nanocomposite thin films. The result shows that increasing the titania content in the hybrid nanocomposite thin films can significantly increase the refractive index. Hybrid nanocomposite thin film with refractive index value of 2.38 had been prepared. All prepared films also exhibit excellent optical transparency in the visible region.

Keywords: Nanocomposites; High refractive index; Hybrid; Films; Optical materials and properties

1. Introduction

Organic–inorganic hybrid materials have attracted considerable attention in recent years due to their novel physical and chemical properties. Incorporating nanoparticles into the polymer matrix becomes the most common method in producing these hybrid materials. The nanocomposite can have specialized properties that cannot be found in their respective single phase. Hybrid materials with enhanced electrical, mechanical and optical properties have been reported [1–3]. High refractive index nanocomposites have attracted considerable interests in light emitting diodes (LEDs) encapsulation [4–6]. If an encapsulating resin with an index of 1.80 or more can be prepared, the light extraction efficiency will be greatly enhanced due to internal reflection phenomena occurring at the interface between the light emitting semiconductor layer and the resin.

Inorganic nanoparticles can be embedded in polymer matrix to form high refractive index nanocomposite. For example, incorporating PbS nanoparticles into gelatin or poly(ethylene oxide) has been reported [7,8]. Their studies prove that the PbS particle loading affects significantly the overall refractive index of the nanocomposite. Refractive index of 1.60–1.76 prepared from a solvent based polyarylether(sulfone) containing SiO_2–TiO_2–ZrO_2 has also been reported [9]. Titania nanoparticles/polymer hybrid materials have been widely studied for their novel optical properties. Trialkoxysilane-capped PMMA–TiO_2 hybrid thin films with refractive index of 1.51–1.87 were prepared using in situ sol–gel method [10]. The dispersion property of the TiO_2 nanoparticles in the polymer matrix becomes one critical issue in the successful preparation of these transparent hybrid nanocomposites. Particle agglomeration can significantly reduce the transparency of the nanocomposite.

In this study, transparent high refractive index TiO_2–epoxy nanocomposite was prepared. Homogeneous acetic acid-modified TiO_2 nanoparticles were synthesized by using the sol–gel method. The refractive indexes of our prepared hybrid thin films were in the range of 2.18–2.38.

2. Experimental

2.1. Synthesis of TiO_2 nanoparticles

Titanium tetraisopropoxide (97%, Aldrich) was the precursor of TiO_2 in the sol–gel process. Titanium tetraisopropoxide

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(117.2 g) was first mixed with 24 g of acetic acid (99.8%, Acros) to form a clear solution at room temperature. The titanium alkoxides can react with carboxylic acid to form hexa-coordinated Ti species with compact Ti–O–Ti framework. The mixture was then rapidly poured into distilled water under vigorous stirring. After that, a few drops of nitric acid (65%, Merck) were added into the mixture. The resulting solution was heated at 355 K for 75 min under reflux condition. The hydrolysis–condensation process is dependent on the relative concentrations of the respective component in the solution. The as-synthesized TiO_2 sol was centrifuged. The product was thoroughly washed three times with THF and finally dispersed into THF to form TiO_2 colloidal solution. Dynamic light scattering (Mastersizer 2000, Malvern Instruments) was used to determine the mean particle size and distribution. The crystal structure of the nanoparticles was characterized by X-ray diffractometer (XRD) equipped with a graphite crystal monochromator (Philips PW-1700).

2.2. Preparation of TiO_2–epoxy hybrid nanocomposite

1 g of Diglycidyl ether of bisphenol A (DGEBA) and 1 g of Methyl hexahydrophthalic anhydride (MHHPA) were first dissolved in THF and stirred for 2 h at room temperature. A fixed amount of TiO_2 sol (10, 20 and 30 wt.% of TiO_2 respectively) was then added into the mixture and stirred for 3 h. The acetic acid-modified TiO_2 nanoparticles can be easily dispersed in THF solvent and incorporated into the polymer matrix by mechanical stirring. The mixture was then spin-coated on a silicon wafer. The thickness of the film can be controlled by the coating speed and time during the spin-coating process. The resulting sample was put in a vacuum oven until all the THF solvent had been evaporated. The coated film was then cured in the vacuum oven at 398 K for 2 h. The thickness of the prepared hybrid nanocomposite thin films was in the range of 25–82 nm. TiO_2–epoxy nanocomposite thin films can be obtained. For the refractive index measurements, the thickness of the nanocomposite thin films was controlled at 50 nm.

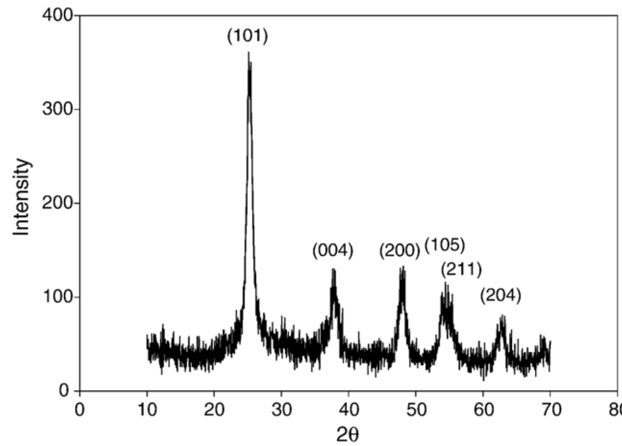

Fig. 2. XRD pattern of anatase TiO_2 nanoparticles.

Refractive indexes were measured on a J. A. Woolam M44 Ellipsometer. Data were collected at wavelengths between 400 and 750 nm. The UV–Vis transmission spectra was measured by Hitachi Ultraviolet–Visible Absorption Spectrometer (UV–Vis, U-2001).

3. Results and discussion

In this work, acetic acid modified-TiO_2 nanoparticles were first prepared before adding into the polymer matrix. Fig. 1 shows the particle size distribution of the TiO_2 nanoparticles. Fig. 2 displays the XRD pattern of the TiO_2 nanoparticles. The result shows that the particles prepared by the sol–gel process had pure anatase crystal structure. The particle diameters were distributed in a narrow range and no aggregation was observed in the sample. The use of acid catalyst in the hydrolysis of titanium alkoxides to manipulate the hydrolysis reaction rate had been reported [11]. Different acids can be used to increase the liability of protonated OR groups in the sol–gel process. Acetate can act as a chelating ligand and react with the titanium alkoxide precursor to form $Ti(OR)_x(AC)_y$. The condensation process can thus be initialized by the addition of water to the precursor. The nitric acid can act as catalyst to enhance the reaction rate. The acetic

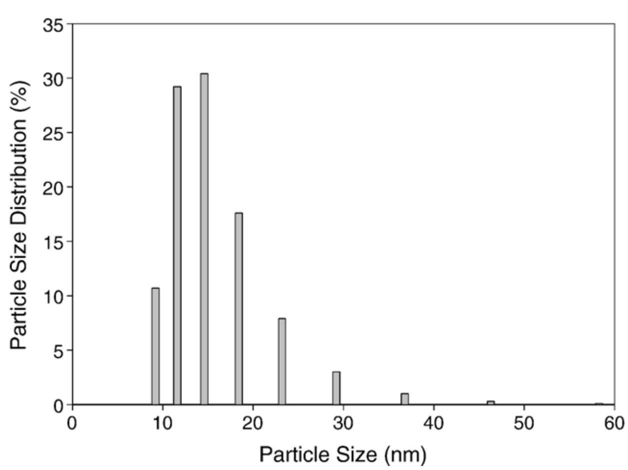

Fig. 1. Particle size distribution obtained by dynamic light scattering from TiO_2 colloidal solution.

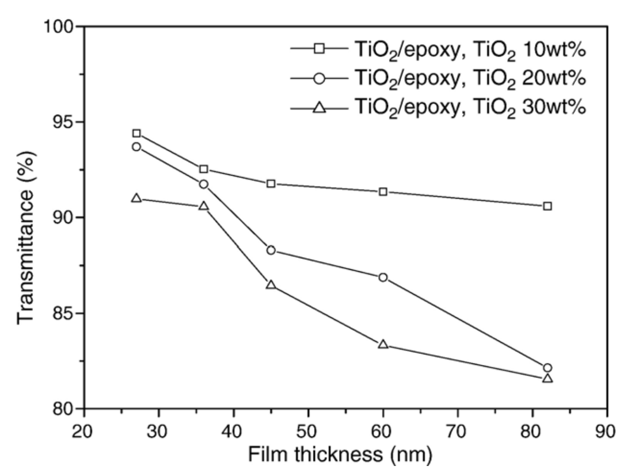

Fig. 3. Variation of the transmittance of the nanocomposite films with different thickness.

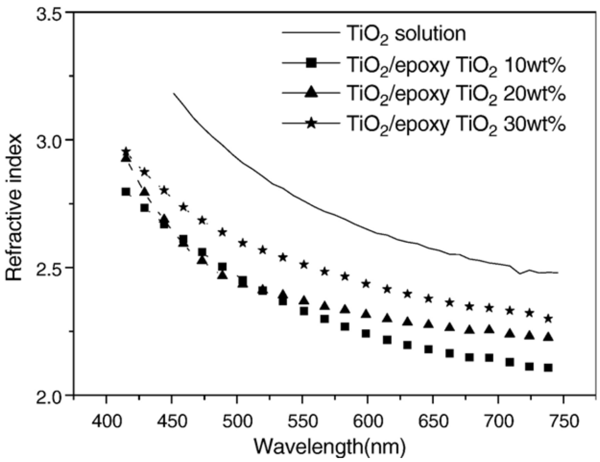

Fig. 4. Variation of the refractive index of nanocomposite films (with TiO_2 content of 10, 20, 30 and 100 wt.%) in the wavelength range of 400–750 nm.

acid modified-TiO_2 nanoparticles can be dispersed and incorporated easily into the polymer matrix.

Different amounts of TiO_2 nanoparticles (10, 20 and 30 wt.% respectively) were added into the polymer matrix. Fig. 3 displays the effect of film thickness to the transmittance at wavelength of 550 nm. Increasing the TiO_2 content and the film thickness causes the decrease in transparency of all samples. The nanocomposite sample (10 wt.% TiO_2 content) with film thickness of 50 nm exhibited more than 90% transmission in the visible region. Fig. 4 shows the refractive index distributions of the nanocomposite samples (with 10 wt.%, 20 wt.% and 30 wt.% TiO_2 content respectively) in the wavelength range of 400–750 nm. The optical transmittance and refractive index of pure epoxy resin were 99% and 1.48 respectively. The refractive index of pure TiO_2 nanoparticles (i.e., 100 wt.% TiO_2 content) was measured to be 2.6. The refractive index of the hybrid nanocomposite films at 633 nm increases from 2.19 (10 wt.% TiO_2 content) to 2.38 (30 wt.% TiO_2 content). This result shows that increasing the titania content in the nanocomposite can significantly increase the refractive index. All samples also exhibit excellent optical transparency in the visible region.

4. Conclusion

Acetic acid-modified TiO_2 nanoparticles were prepared by the sol–gel method. The TiO_2 nanoparticles can be incorporated easily into the polymer epoxy resin. Ellipsometric results show that increasing the TiO_2 content (wt.%) can increase the refractive index of the nanocomposite films. This paper describes the preparation of high refractive index hybrid nanocomposite thin films with values as high as 2.38. The prepared hybrid thin films exhibit excellent optical transparency in the visible region and can potentially be used as high refractive material in optical components.

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