

Preparation and characterization of titania/silicone nanocomposite material

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Abstract. The preparation and properties of high refractive index nanocomposite material were studied. The TiO₂ nanoparticles were synthesized by sol-gel method using acetic acid as a chelating ligand. The nanoparticles were dispersed directly into the polymer matrix to prepare transparent high refractive index nanocomposite thin films. The refractive index of films will be enhanced with the increase of titania contents. The particles were characterized by X-ray diffraction (XRD), Transmission Electron Microscope (TEM), and Fourier Transform Infrared Spectroscopy (FTIR), respectively. The results showed that all samples with different amounts of TiO₂ exhibit good optical transparency. Furthermore, the pattern of the TiO₂ NPs shows a pure anatase phases. From TEM image, the TiO₂ has little agglomeration. The FT-IR spectrum indicated that acetate ions and titanium ions show good chelation.

1. Introduction

Polymer–inorganic nanocomposites have attracted much attention due to the excellent properties in optics, mechanics, and physics [1-6]. Especially in the light-emitting diode (LED) field, a high refractive index and transparency is needed to increase light-extraction efficiency. The light-extraction efficiency will double increase, when the encapsulant refractive index rises from 1.5 to 2.0 [7]. However, the refractive indices of most organic materials do not exceed 1.5. On the other hand, some of the polymers have a greater refractive index than 1.7, but they usually have a high optical dispersion and strong absorption in the visible region. Therefore, if a high refractive index of inorganic material is incorporated into polymers, the problems will be solved, and the polymer can adjust refractive indices over a wide range.

In recent years, there have been a large number of reports about polymer–inorganic hybrid materials with high refractive indices [3, 4, 8-20]. There are many kinds of inorganic particles, and TiO₂ has been studied a lot [10, 11, 16-18]. For example, Joseph et al. [4] reported the preparation of acetic acid-modified TiO₂ nanoparticles by sol–gel synthesis method, and the refractive index of hybrid nanocomposite thin film reached to 2.38. Liu et al. [10] synthesized anatase titania nanocrystals (NCS), which was then incorporated into (3-glycidyoxypropyl) trimethoxysilane organic silica sol followed by a sol–gel process. The refractive index at 632.8 nm increased from 1.502 to 1.663 as the TiO₂ weight content went from 10% to 50%; Tao et al. [14] prepared grafting polymer chains onto anatase TiO₂ nanoparticles by a combination of phosphate ligand engineering and alkyneazide “click”

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chemistry. The refractive index of the composite material increased linearly from 1.5 up to 1.8 by increasing the loading of TiO₂ particles to 30 vol%.

In this study, acetic acid was utilized as a chelated agent to synthesize TiO₂ NPs, then directly incorporated into silicone to prepare TiO₂/silicone nanocomposite. Acetic acid can improve the dispersion of TiO₂ in the organic matrix, and reduce the agglomeration of nanoparticles. The particles were characterized by XRD, TEM, and FTIR, respectively. The results showed that all samples with different amounts of TiO₂ exhibit good optical transparency. Furthermore, the pattern of the TiO₂ NPs shows pure anatase phases. From TEM image, the TiO₂ had little agglomeration. The FT-IR spectrum indicated that acetate ions and titanium ions showed good chelation.

2. Experimental

2.1. Material

Tetrabutyl titanate (98%, Sinoreagent) was the precursor of TiO₂ in the sol-gel process. Other materials are listed as follows: acetic acid (HAc, 99.5%, Sinoreagent), nitric acid (65-68%), dimethylacetamide (DMAC, 99%), deionized water, silicone resin and curing agent.

2.2. Synthesis of TiO₂ NPs

In the experiment, 17 g tetrabutyl titanate and 6 g HAc were mixed for 10 min. at room temperature. Then, mixture was rapidly poured into deionized water with stirring. Further, a few drops of nitric acid were added into the solution, and heated to 80 °C, maintained under reflux for 90min. The as-synthesized TiO₂ sol was centrifuged and washed three times with DMAC. Finally, TiO₂ sol was dispersed into DMAC through ultrasonication for 1 h. The crystal structure of the nanoparticles was characterized by XRD with Cu K α radiation. TEM was used to observe the agglomeration of TiO₂.

2.3. Preparation of high-refractive-index hybrid films

First, 1 g of silicone and 1 g of curing agent were mixed for 10min, then various amounts of TiO₂ solution(10, 20 and 30 wt.% of TiO₂ respectively) were added, and stirred for 1 h. Then the mixture was spin-coated on glass or silicon wafer. The sample was put in a vacuum oven for 80 °C until the DMAC solvent had been evaporated, and then cured at 120 °C for 4 h.

3. Results and discussion

Figure 1 shows the XRD pattern of the TiO₂ NPs dominant peaks with values of 2 θ being located at 25.3 (101), 38 (004), 48 (200), 54 (105) and 62.4 (204). It belongs to an anatase phase. Thus, the as-prepared TiO₂ NPs was pure anatase phase. Figure 2 shows the particle size of the TiO₂ NPs, which was about 10 to 20 nm.

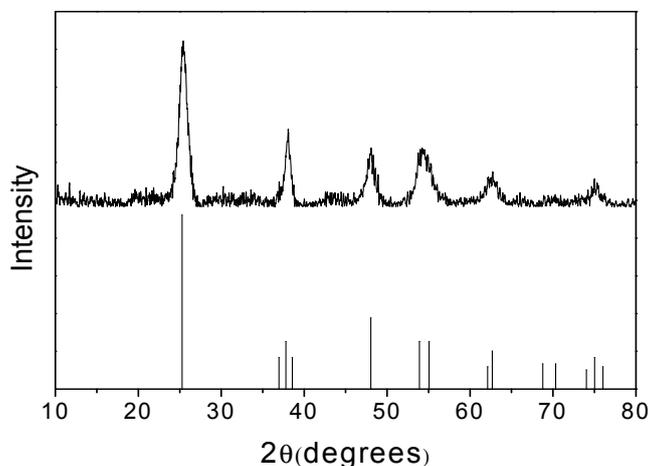


Figure 1. XRD pattern of TiO₂ nanoparticles.

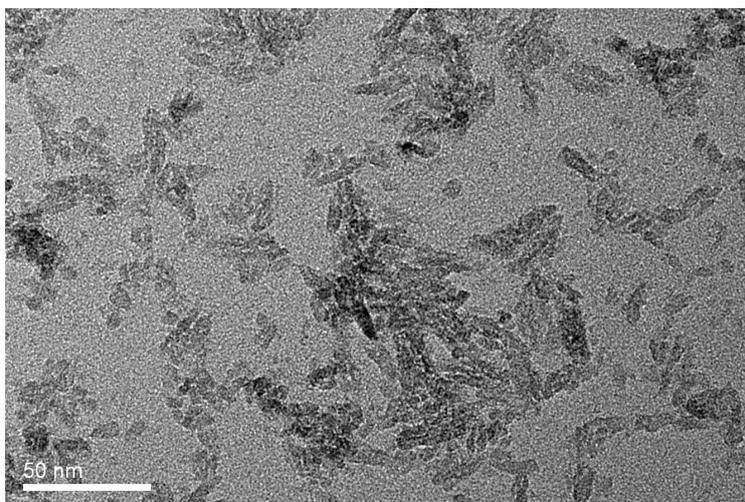


Figure 2. TEM image of TiO₂ nanoparticles.

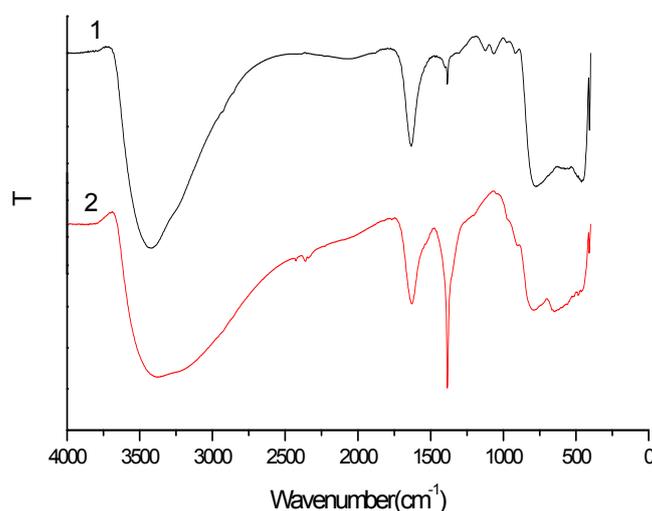


Figure 3. FTIR spectra of (1) TiO₂ and (2) the TiO₂-HAc NPs.

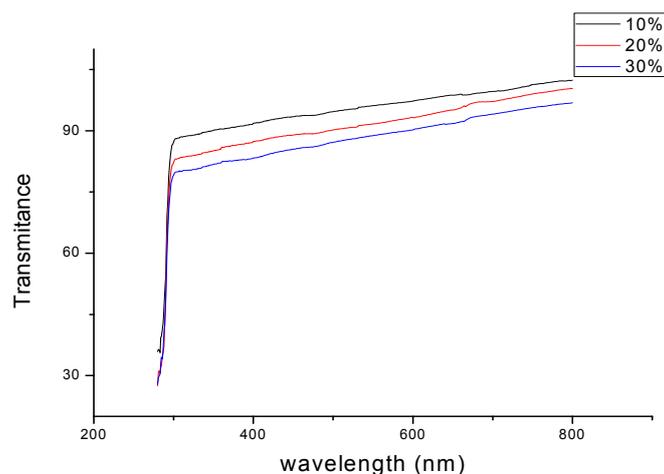


Figure 4. Variation of the transmittance of nanocomposite films with different TiO₂ concentrations.

Figure 3 presents FTIR spectra of TiO₂ and TiO₂-HAc NPs; both exhibit an absorption at 3200–3000 cm⁻¹ for –OH units, a peak near 1633 cm⁻¹ for H-O-H bending vibrations, and Ti-O bond at 800–450 cm⁻¹. Line 2 reveals the peak of C-H stretching vibration at 3000–2800 cm⁻¹. New peak

appears at 1500 cm^{-1} , and 1430 cm^{-1} peak is strengthened, the acetate ions and titanium ions show good chelation. Figure 4 shows the transmittance of the nanocomposite films with different concentrations of TiO_2 which exhibits good optical transparency. The lowest transmittance exceeds 80%.

4. Conclusion

The TiO_2 nanoparticles, modified by acetic acid, are prepared by the sol-gel method. The modified nanoparticles have well dispersion in epoxy resin. The hybrid thin film exhibits excellent optical transparency in the visible region, so the nanocomposite material can be used in optical components potentially.

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