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Preparation and properties of UV-curable polymer/nanosized indium-doped tin oxide (ITO) nanocomposite coatings

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Abstract UV-curable polymer/nanosized indium-doped tin oxide (ITO) nanocomposite coatings were fabricated by blending ITO slurry and oligomer and reactive monomers. The preparation of ITO slurry and the effect of the ITO content on the electrical conductivity, hardness and optical properties of the nanocomposite coats were investigated. It was found that the electric conductivity and UV absorbance of the nanocomposite coats increased while the hardness and refractive index first increased then decreased with increasing ITO concentration since too high ITO resulted in the incomplete curing of the coatings.

Introduction

Indium-doped tin oxide (ITO) has the optical properties of high transparency in the visible light range, high reflectance in the IR region and high absorbance in the ultraviolet region and high electric conductivity besides the advantages of inorganic oxides such as high rigidity, excellent chemical inertness, etc. It has been widely used as the functional coatings in displays [1–4], solar cells [5], optoelectronic devices [6], gas sensors [7], heat reflection mirror [8, 9], UV-shields and so on. Usually, ITO coatings are prepared by physical vapor deposition (PVD), chemical vapor deposition (CVD) and sol–gel method [10–13]. But the PVD and CVD methods are high cost and cannot be applied for large objects while the sol–gel method has to undergo treating at high temperature, which limits its applications on polymer substrates. To overcome these shortcomings, organic–inorganic (O/I) nanocomposite coatings may be the ideal substituent, which have both the advantages of easy applying of organic coatings and the analogous functions of inorganic coatings. For examples, ferroelectric nanocomposite coatings [14] and conductive nanocomposite coatings [15] were successfully fabricated via embedding barium titanate ($BaTiO_3$) nanoparticles and nanosized antimony-doped tin oxide (ATO) particles into polymer coatings, respectively. However, the nanocomposite coatings containing ITO nanoparticle, especially UV-curable polymer/ITO nanocomposite coatings are seldom reported although functional UV-curable coatings are becoming one of the fastest growing coatings.

In this article, we firstly prepared nano-ITO slurry with butyl acetate as the dispersing media by ball milling from ITO nanopowder. Then, UV-curable polymer/ITO nanocomposite coatings were prepared by mixing the nano-ITO slurry with UV-curable monomers and oligomer then cured under UV ray. The electric conductivity, hardness and optical properties of the nanocomposite coats were investigated.

Experimental

Materials

Blue ITO nanopowder (primary particle size: 20 nm) was purchased from Ningxia Orient Tantalum Industry Co. Ltd.

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of China. Polyester polyol based, aliphatic urethane diacrylate (UVU6219) was kindly supplied by Shanxi Xilaiwu Industry Co. Ltd. of China. *n*-Butyl acetate (BA,98%) 2-hydroxyethyl methacrylate (HEMA, 98%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. of China Trimethylolpropane triacrylate (TMPTA) was the product of UCB Chemical Company and 1-hydroxycyclohexyl acetophenone (Irgacure 184) a gift of Ciba Specialty Chemicals. All dispersants (Disperbyk 106, 170, 171, 183) were supplied by BYK Chemie. All these chemicals were used as received.

Preparation of ITO slurry

First, 7 g of dispersant was dissolved in 270 g of butyl acetate and then 30 g of nano-ITO powder was dispersed into this solution by vigorous stirring. The dispersion was further ground to obtain ITO slurry in an agitator bead miller (Minizeta, Netzsch Machinery and Instruments Co. Ltd., Germany) with a grinding speed of 2,600 rpm and the ZrO_2 beads of 0.6–0.8 mm.

Preparation of UV-curable polymer/ITO nanocomposite coatings

35 g of UVU 6219, 10 g of TMPTA and 5 g of HEMA were thoroughly mixed. Then, 1 g of the ITO slurry and 0.1 g of Irgacure 184 were added into 4 g of the mixture in turn and ultrasonically treated for 20 min to obtain ITO-containing UV curable coatings.

The resulted nanocomposite coatings were cast on glass substrates at room temperature using a drawdown rod and dried at room temperature for 20 min, followed by irradiation-cured in the air using a medium pressure mercury lamp (2 kW and 365 nm of the main wavelength) to form dried coats.

Characterization

Particle size analysis

Particle size of ITO slurry was determined by N4 Plus submicron particle size analyzer (Beckman Coulter Company, USA). The SDP (size distribution processor) model was adopted to analyze the data.

Morphology observation

The morphologies of ITO nanoparticles in ITO slurry were characterized by a transmission electron microscope (Hitachi H-600, Japan). The sample for TEM observation was dried on carbon-coated copper grids with ethanol as the diluent.

Electrical conductivity measurement

The volume resistivity of the composite coats was measured with ultra high resistance instrument (Changzhou Tonghui Electro Co. Ltd). The measurements were conducted according to Fig. 1. The volume resistivity ρ can be calculated from the measured sheet resistance R based on the equation $\rho = Rhd/L$ where h, d and L are the width, thickness and length of the coats, respectively.

Hardness measurement

Hardness measurements were performed on the pendulum hardness tester (BYK Gardner Company, Germany) using the coats with thickness of 5 μm. The damping time required to slow the oscillations down from 6° to 3° was regarded as the Konig hardness.

UV–vis spectroscopy

The absorbance and transmittance spectra of the films with thickness of 1 μm in the range of 200–700 nm wavelengths light were determined on an ultraviolet–visible (UV–vis) spectrophotometer (Hitachi UV-3000, Japan) with the scan speed of 300 nm/min.

Ellipsometry

A variable angle spectroscopic ellipsometer (V-VASE, J. A. Woollam Company, AutoRetarder, USA) was used to determine the refractive index. Diameter of focus facula

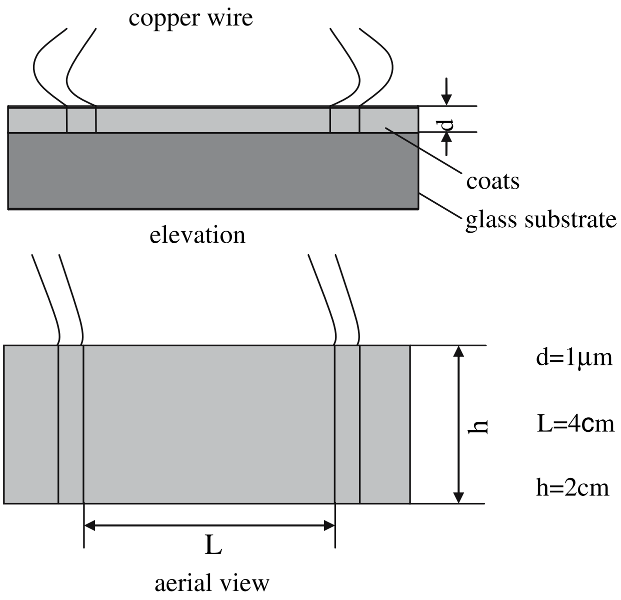

Fig. 1 Illustration of the measurement of the volume resistivity of coats

was 100 nm and wavelength with incident angle ranging from 20° to 90° was changed from UV to NIR spectral region (200–1,700 nm).

Results and discussion

Dispersion of ITO in butyl acetate

Butyl acetate was employed as the media for preparation of ITO slurry since it is one of the commonly used solvents in organic coatings. The ITO dispersions without/with different dispersants were ultrasonically treated and their mean particle sizes were shown in Fig. 2. It could be seen that the mean particle size of ITO greatly reduced once the dispersant was used, and the mean particle size of the ITO dispersions containing dispersants were generally smaller than those dispersions of TiO_2 [16] and ZnO nanopowders [17], suggesting the relatively easier grinding and dispersion of ITO nanopowder than TiO_2 and ZnO nanopowders. Figure 2 also indicated that the ITO dispersion with Disperbyk 106 had the minimum particle size (120 nm), thus this dispersant was always employed in the following experiments.

The ITO dispersion with Disperbyk 106 was further ground to obtain ITO slurry in an agitator bead miller. Figure 3 demonstrated the effect of the ball milling time on the average particle size of the slurries. Obviously, as the milling time increased, the mean particle size of ITO slurry decreased, and even to 32 nm after the slurry was milled for 120 min, which was very close to the primary particle size (20 nm) of ITO nanopowder, suggesting that the ITO nanopowder was almost completely ground. TEM image of slurry, as shown in Fig. 4, further indicated ITO nanoparticles had very good dispersion in butyl acetate although some aggregates were still seen. Based on these results, the aftermentioned UV-curable polymer/ITO nanocomposite coatings were obtained using the ITO slurries, which were prepared using 3 wt% Disperbyk 106 (based on the total weight of ITO slurry) for 0.5 h ultrasonic treatment and 2 h ball milling time.

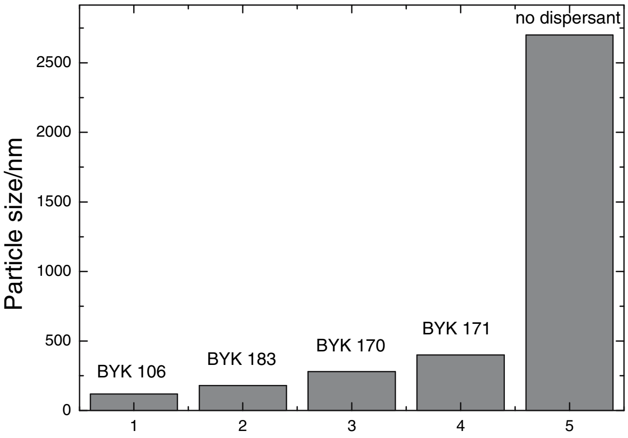

Fig. 2 The average particle sizes of ITO dispersion without/with different dispersants prepared by only ultrasonic treatment for 0.5 h

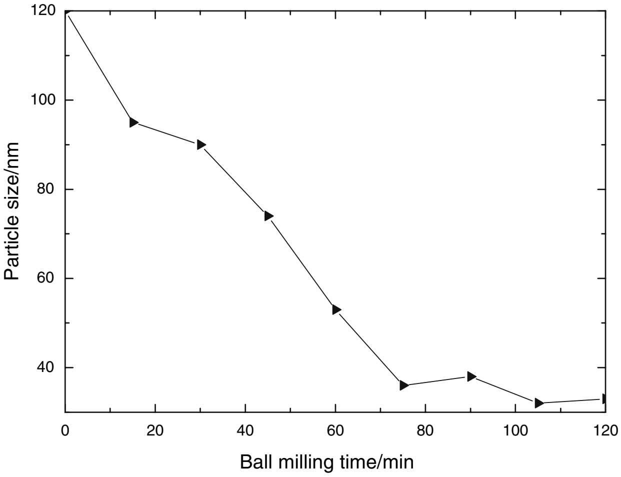

Fig. 3 Average particle size of ITO slurry as a function of ball milling time

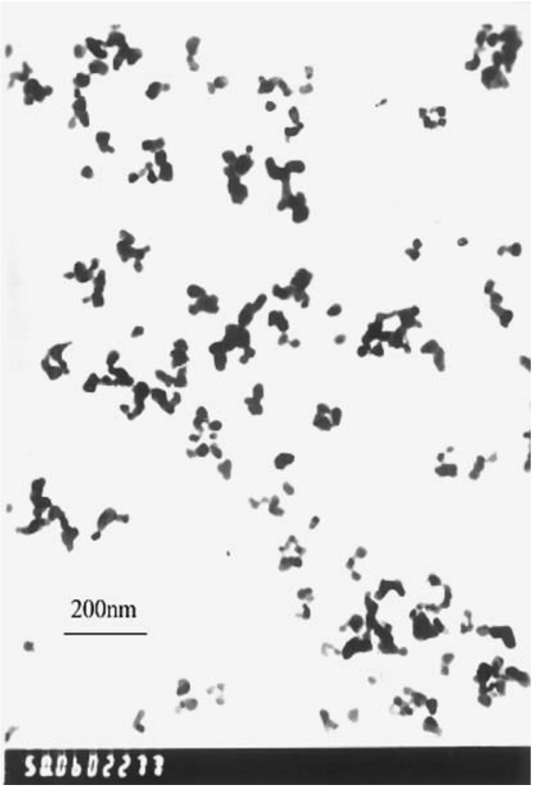

Fig. 4 TEM image of ITO slurry (milling time = 2 h)

Electrical conductivity of UV-cured polymer/ITO nanocomposite coats

Figure 5 illustrated the dependence of the volume resistivity of nanocomposite coats on the ITO concentrations. It was clearly found that the volume resistivity decreased quickly with increasing ITO content, suggesting that more conductive paths formed by ITO nanoparticles in the composite coats at higher ITO concentration. When the ITO content exceeded 30 wt%, the volume resistivity was lower than 10^6 Ω m, that is, the composite coats possessed the antistatic property when more than 30 wt% ITO was used. However, even if the ITO was further increased up to 80 wt%, the volume resistivity could only reduce to 10^4 Ω m, which was still tremendously higher than the volume resistivity of pure ITO nanoparticles (10^{-6} Ω m), this should be attributed to the barrier role of polymer phase and dispersant against electron transfer.

Hardness of UV-cured polymer/ITO nanocomposite coats

Figure 6 presented the variation of the hardness of the nanocomposite coats with ITO content. It could be seen that the hardness of the coat increased with the increase of ITO concentration when the ITO content was below 15 wt%, which was consistent with the hardness variation of the nanocomposite coats of acrylic based polyurethane/ silica [18], biodegradable plant oil/silica [19], epoxy/SiO_2 [20]. But the hardness obviously decreased when more than 15 wt% ITO was employed. This was probably resulted from the incomplete curing of the coatings since higher ITO content (absolute ITO amount in the unit area in thick film for hardness measurement was more than that in the thin film for UV–vis spectra) could shield more UV ray. Generally, complete curing was almost impossible when more than 15 wt% ITO was embedded in the coat with thickness of 5 μm even if the irradiation time was extended based on our experience.

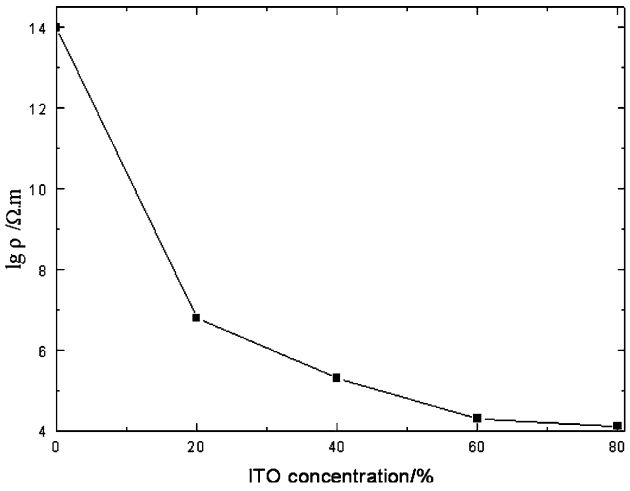

Fig. 5 Logarithm of volume resistivity as a function of ITO content

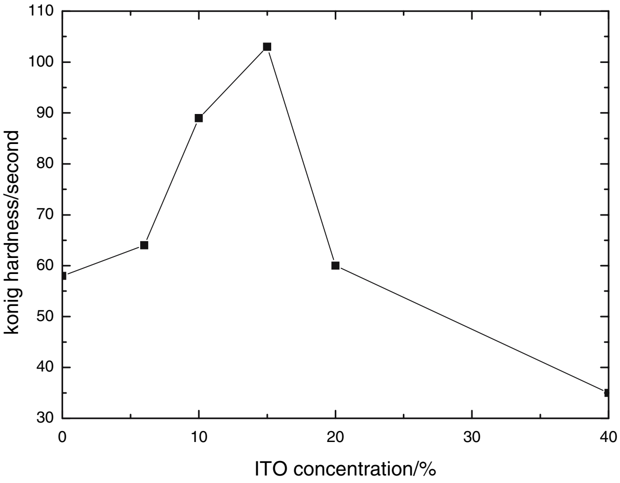

Fig. 6 The hardness of the coats with different ITO content

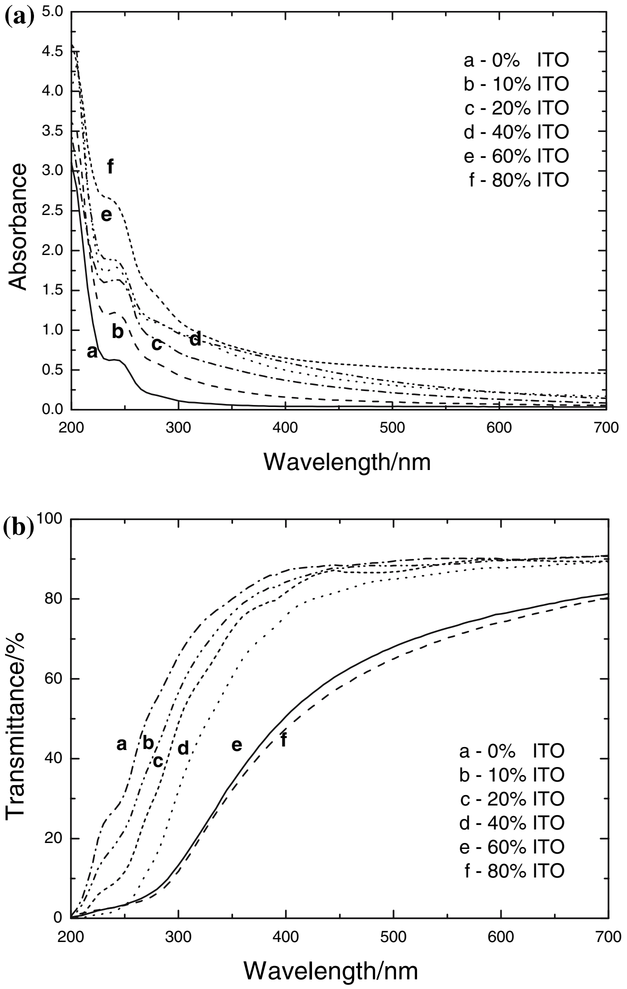

Fig. 7 The UV–vis spectra of the nanocomposite coats: (**a**) absorbance (**b**) transmittance

Optical property of UV-cured polymer/ITO nanocomposite coats

Figure 7 manifested the UV–vis spectra of the nanocomposite coats with thickness of 1 μm. It was found that introducing ITO could enhance the UV absorbance, and as ITO content increased, UV absorbance increased, suggesting that ITO could improve the durability of organic coats, just as other nanoparticles such as TiO_2, SiO_2, ZnO, etc. in our previous reports [21–26]. The nanocomposite coats had more than 80% transmission in visible region when less than 40 wt% ITO was embedded, indicating that the coats still had very good transparency.

Figure 8 demonstrated the variation of the refractive index of the nanocomposite coats at different wavelength with the ITO content. As the ITO content increased, the refractive index of the nanocomposite coat first increased then decreased. For example, the refractive index increased from 1.48 (at the wavelength of 550 μm) for pure polymer coat to 1.59 for the nanocomposite coat containing 20 wt% ITO, suggesting that the UV-cured polymer/ITO nanocomposite coatings could be potentially used as the high refractive index layer in the preparation of a double-layer anti-reflection films. The decrease in the refractive index after more than 20 wt% used should be attributed to the incomplete curing of the coatings due to higher UV-shielding property at higher ITO concentration, just as discussed above.

Conclusions

UV-curable polymer/ITO nanocomposite coatings with different ITO concentration were prepared by mixing monomers and oligomer with ITO slurries, which were first prepared using butyl acetate as the media. It was found that choosing correct dispersant and milling time could grind ITO close to its primary size. As ITO content increased, the electric conductivity and UV absorbance of the nanocomposite coats increased while the hardness and refractive index of the coats first increased then decreased. Based on the electric and optical properties of the UV-curable polymer/ITO nanocomposite coats, it could be found that the ITO-based UV-curable polymer coatings should have some potential applications for preparing functional films such as antistatic films, anti-reflection films, etc.

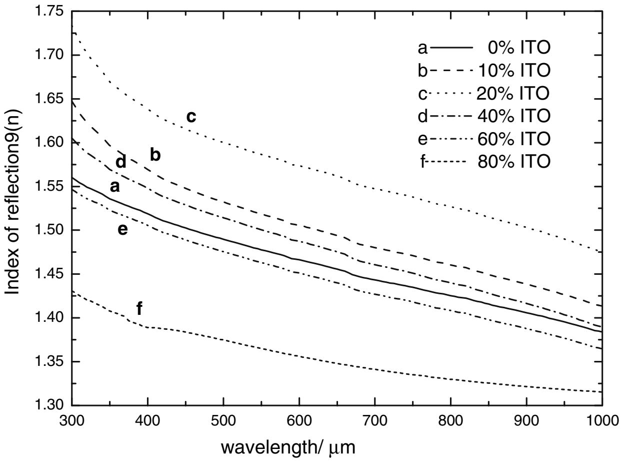

Fig. 8 The refractive index of UV-cured polymer/ITO nanocomposite coats

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