

# Preparation and Characterization of PS-PMMA/ZnO Nanocomposite Films with Novel Properties of High Transparency and UV-Shielding Capacity

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**ABSTRACT:** High transparent and UV-shielding poly(styrene)-co-poly(methyl methacrylate) (PS-PMMA)/zinc oxide (ZnO) optical nanocomposite films were prepared by solution mixing using methyl ethyl ketone (MEK) as a cosolvent. The films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-vis) spectra, high-resolution transmission electron microscopy (HR-TEM), and atomic force microscope (AFM). Cross-section HR-TEM and AFM images showed that the ZnO nanoparticles were uniformly dispersed in the polymer matrix at the nanoscale level. The XRD and FTIR studies indicate that there is no chemi-

cal bond or interaction between PS-PMMA and ZnO nanoparticles in the nanocomposite films. The UV-vis spectra in the wavelength range of 200–800 nm showed that nanocomposite films with ZnO particle contents from 1 to 20 wt % had strong absorption in UV spectrum region and the same transparency as pure PMMA-PS film in the visible region. The optical properties of polymer are greatly improved by the incorporation of ZnO nanoparticles. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1507–1512, 2010

**Key words:** nanocomposites; thin films; transparency; AFM; UV-vis spectroscopy

## INTRODUCTION

Nanocomposites are an exciting subject in the fields of both fundamental study and applied materials science.<sup>1</sup> The development of polymer-based composites, which exhibit various optical functionalities, such as high/low refractive index, tailored absorption/emission properties, or strong optical nonlinearities attracts great interest because of the potential optoelectronic applications.<sup>2</sup> These composites are typically obtained by the incorporation of functional inorganic particles into a transparent polymer matrix. Various types of metal oxide fillers, such as zinc oxide (ZnO),<sup>3–6</sup> ZnS,<sup>7,8</sup> SiO<sub>2</sub>,<sup>9–12</sup> TiO<sub>2</sub>,<sup>13,14</sup> and Al<sub>2</sub>O<sub>3</sub><sup>15</sup> have been incorporated into polymers to modify the optical properties of these polymers. Tiny ZnO nanoparticles are well-known multifunctional inorganic fillers that have unique properties, such as strong UV absorption combined with good transparency in the visible range, low-dielectric constant, large electromechanical coupling coefficient.<sup>16,17</sup> Thus,

polymer/ZnO nanocomposites can be used in various fields, such as UV-shielding, catalysis, field emission display, gas sensing, and thermoelectricity.

A great deal of research in recent years has focused on the development of polymer/ZnO nanocomposite materials. Demir and Koynov<sup>3</sup> prepared ZnO/PMMA composite films with strong UV absorption, light transmittance in visible by polymerization of the dispersions of the particles in the monomer. Chae et al. successfully fabricated PS/ZnO nanocomposite films, which exhibited UV-absorbance without losing transparency at low ZnO content by solution mixing.<sup>4</sup> However, these films showed transparency loss at high concentration because of aggregation of individual ZnO nanoparticles. Besides, ZnO has been incorporated into many other polymers, such as poly(hydroxyethyl methacrylate),<sup>18</sup> poly(amic acid),<sup>19</sup> polyimide,<sup>20</sup> Nylon,<sup>21</sup> poly(ethylene glycol),<sup>22</sup> poly(ethylene oxide),<sup>23</sup> Epoxy,<sup>24</sup> and so on. PS-PMMA is transparent, diffluent, and has better thermal and mechanical properties than PMMA or PS.<sup>25</sup> And it is widely used in architecture, automotive, air, and railway transport fields because of its favorable properties.<sup>26</sup> As far as we know, the incorporation of functional inorganic particles into PS-PMMA has rarely been reported to date.

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**TABLE I**  
**The Composition of the Nanocomposite Films Coded Polymer-X**

	Polymer-0	Polymer-1	Polymer-2	Polymer-5	Polymer-10	Polymer-20
ZnO (wt %)	0	1	2	5	10	20
PMMA-PS (wt %)	100	99	98	95	90	80

The physical properties of nanocomposites are certainly affected by many factors including filler size, size distribution, degree of dispersion, and filler contents.<sup>27</sup> Our materials of the 4–5 nm diameter ZnO nanoparticles were small enough and well-dispersed in methyl ethyl ketone (MEK) without aggregation. In this article, we incorporated ZnO nanoparticles into a transparent PS-PMMA matrix to obtain transparent PS-PMMA/ZnO nanocomposite films. The nanocomposites were prepared through solution mixing, which is suitable for industrial production, using MEK as cosolvent of PS-PMMA and ZnO nanoparticles. The nanocomposite films exhibited high UV-absorbance without reducing transparency even upon ZnO content to 10 wt %. The prepared composite films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-vis spectra, HR-TEM, and AFM, respectively.

## EXPERIMENTAL

### Materials

Poly(styrene-co-methyl methacrylate) (PS-PMMA, PS wt % = 70%, PMMA wt % = 30%) purchased from Shanghai Pen Chemical Factory was used as polymer systems. Modified ZnO nanopowder (average size = 4–5 nm) were supplied by NanoMaterials Technology of Singapore. MEK (Beijing Beihua Fine Chemical of China; AR) was selected as a co-solvent of PS-PMMA and ZnO.

### Sample preparation

A nano-ZnO dispersion (30 wt %) in MEK was prepared by dissolving 3 g ZnO in 7 g MEK under high shear stirring. 10 g PS-PMMA was dissolved in 90 g MEK for 2 h with vigorous stirring. Then a predetermined amount of 30 wt % ZnO/MEK dispersion was added into 10% PS-PMMA/MEK solution with continuous stirring. The mixture systems were stirred with sonication assistance for 10 min to ensure the ZnO nanoparticles dispersed well. ZnO contents (*X*) were 0, 1, 2, 5, 10, 20 wt % based on the polymer matrices, and they were coded Polymer-X below. The volume fraction of ZnO corresponded to 0, 0.2, 0.4, 1, 2.1, 4.7 vol %, respectively. The composition of the nanocomposite films coded Polymer-X was shown in Table I. To obtain nanocomposite films, the mixtures were poured into a glass mold. And then the films

with about  $200 \pm 10 \mu\text{m}$  thickness were fabricated by drying the mixtures at room temperature for 2 days.

### Characterization

The thickness of the films was characterized with a micrometer screw-gauge in five different places of each film. Absorption spectra of ZnO nanoparticles in MEK and transmission spectra of the nanocomposite films from 200 to 800 nm were recorded using a Shimadzu UV-2501 UV-vis Recording Spectrophotometer. AFM was obtained using Nanoscope IIIa Scanning Probe Microscope Controller to probe the surface morphology of the coated nanocomposite polymer films. XRD patterns were obtained using Shimadzu XRD-6000 X-ray Diffractometer equipment with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), using a scanning rate of  $5^\circ \text{ min}^{-1}$  in the  $2\theta$  ranging from  $5$  to  $80^\circ$ . FTIR spectra were characterized using a Nicolet Nexus-670 spectrometer. HR-TEM was carried out using JEM-3010 microscope. The HR-TEM slice samples of nanocomposite films were prepared by cryoultramicrotomy at liquid nitrogen temperature giving sections of nearly 100 nm in thickness.

## RESULTS AND DISCUSSION

### Characterization of the ZnO nanoparticles

Figure 1 shows the HR-TEM images of the ZnO nanoparticles dispersed in MEK. The ZnO nanoparticles with a diameter of 4–5 nm are uniform and monodisperse indicating that this polar solvent effectively breaks apart the agglomerate of ZnO nanoparticles.

Figure 2 shows the absorption spectrum of ZnO nanoparticles in MEK. The spectrum shows an obvious blue-shift excitation band at around 340 nm compared with that of bulk ZnO (373 nm).<sup>28</sup> The average size of the ZnO nanoparticles can be calculated according to the following equation reported by Meulenkamp<sup>29</sup>:

$$1240/\lambda_{1/2} = 3.301 + 294/D^2 + 1.09/D \quad (1)$$

where  $\lambda_{1/2}$  is the wavelength (nm) at 50% absorption of the excitonic peak (or shoulder) and  $D$  is the average diameter ( $\text{\AA}$ ) of ZnO particles. From the UV-vis absorption spectrum and Eq. (1), the average size of the ZnO nanoparticles was calculated to be about 4.2 nm in accordance with the result of the HR-TEM study.

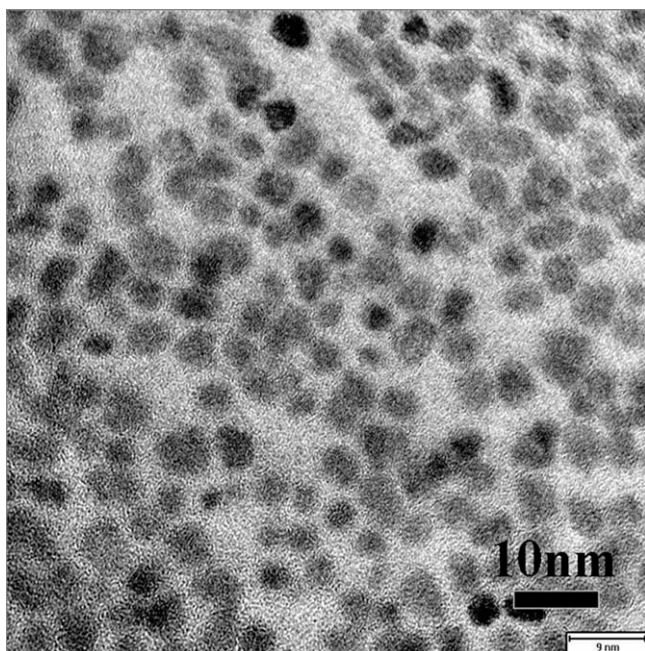


Figure 1 HR-TEM image of ZnO nanoparticles in MEK.

#### XRD and FTIR spectra of the PS-PMMA/ZnO nanocomposite films

To investigate the influence of grafting reaction on the crystalline structure of ZnO nanoparticles, X-ray diffraction patterns of pure PS-PMMA, and PS-PMMA composites were recorded. As shown in Figure 3, the XRD patterns show a broad noncrystalline peak (10–30°) of PS-PMMA and nanocrystalline diffraction peaks (30–80°) of ZnO. The peaks between 30–80° increase in their intensity with the increase of the ZnO content. All the diffraction peaks corresponding to (100), (101), (102), (110), (103), and (112) planes are in accordance with the typical wurtzite structure of bulk ZnO.<sup>5</sup> The incorporation of ZnO nanoparticles produces neither a new peak nor a

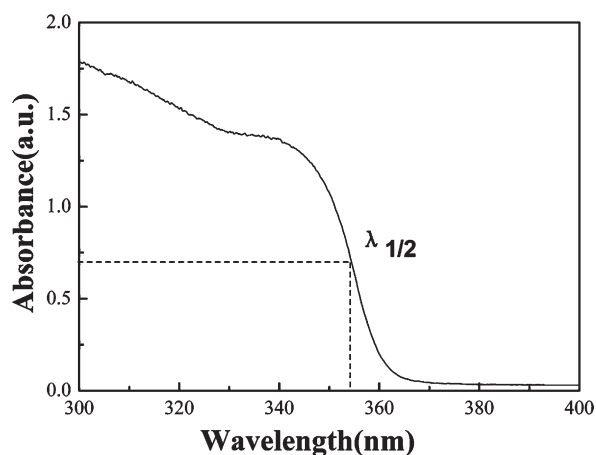


Figure 2 UV-visible absorption spectrum of ZnO nanoparticles in MEK.

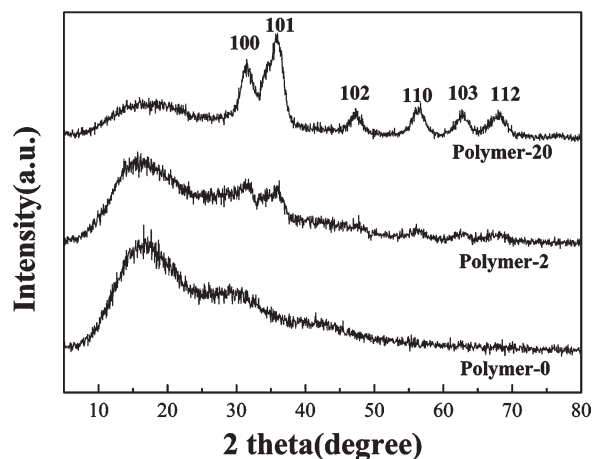


Figure 3 XRD spectra of PS-PMMA and PS-PMMA/ZnO nanocomposite films with different ZnO contents.

peak shift with respect to PS-PMMA indicating that ZnO-filled PS-PMMA nanocomposites consist of two phase structures.

FTIR measurements were carried out to evaluate the interface affinity between PS-PMMA and ZnO as shown in Figure 4. The spectra of the nanocomposite films are most similar except for the absorption peaks at 3410  $\text{cm}^{-1}$ , which are assigned to  $-\text{OH}$  on the ZnO surface.<sup>30</sup> It is found that the absorption peaks at 3410  $\text{cm}^{-1}$  gradually increase in intensity with increasing ZnO nanoparticle content, which indicates that an increasing content of ZnO is blended with the polymer matrix. However, when the content of ZnO decreases to 2 wt %, the intensity of the peak at 3410  $\text{cm}^{-1}$  is so low that it can not be seen in the curve. So it disappears at 2 wt % ZnO. The absorption peaks in the region 2800–3000  $\text{cm}^{-1}$  correspond to the  $\text{CH}_2$  and  $\text{CH}_3$  group. All the composite films exhibit the characteristic strong absorption peaks of 1742 and 1150  $\text{cm}^{-1}$ , which are caused

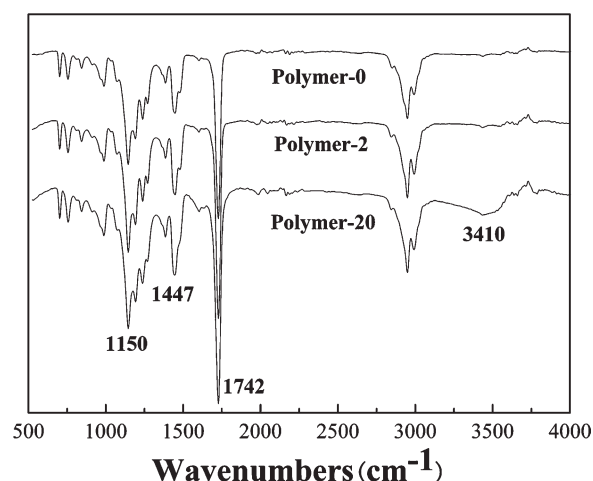
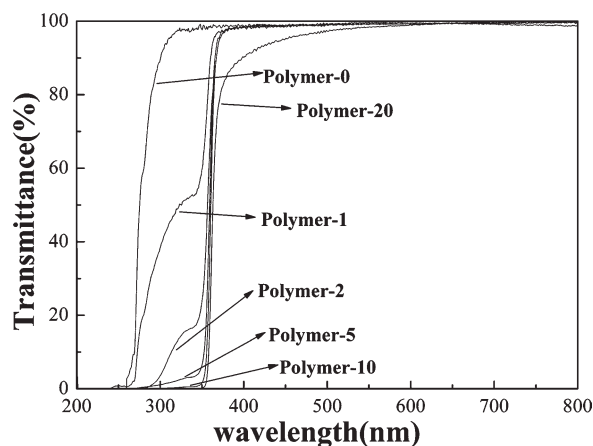


Figure 4 FTIR spectra of PS-PMMA and PS-PMMA/ZnO nanocomposites with different ZnO contents.



**Figure 5** UV-visible spectra of PS-PMMA and PS-PMMA/ZnO nanocomposite films with different ZnO contents.

by C=O and C—O—C stretching of the PS-PMMA linkages.<sup>31,32</sup> The absorption peak at near  $1447\text{ cm}^{-1}$  is attributable to represent the bending stretching of  $\text{CH}_2$  and  $\text{CH}_3$  group in PS-PMMA. It is not the group in the ZnO particle's surfactant. So, this absorption is also seen in PS/PMMA blends in the absence of ZnO. Neither shift nor new absorption peak is observed even when ZnO content is up to 20 wt %. Thus, there is no chemical bond or interaction between PS-PMMA and ZnO nanoparticles in the nanocomposites. The good dispersion of ZnO nanoparticles in polymer matrix is mainly because of the good compatibility between nanoparticles and polymer matrix in MEK cosolvent.

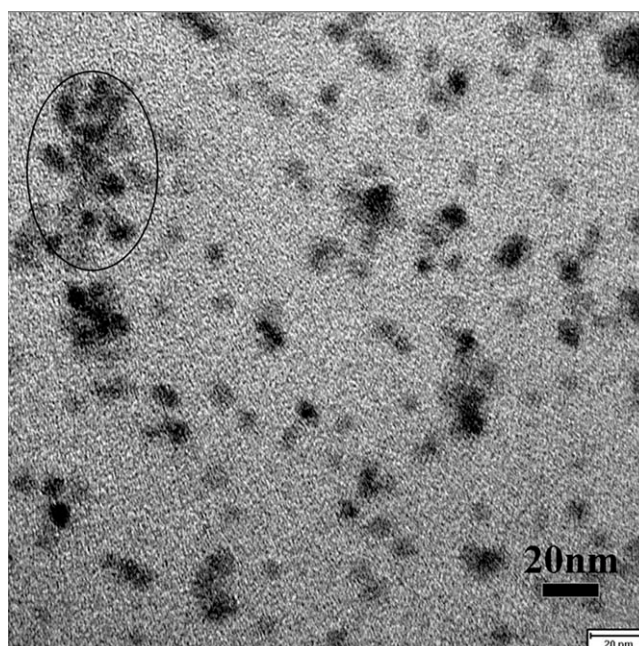
#### Optical properties of the PS-PMMA/ZnO composite films

To evaluate the influence of the ZnO content on the optical property of the composites, we studied a series of films in which the weight fraction of ZnO nanoparticles was varied from 0 to 20 wt %. The UV-vis spectra of PS-PMMA and PS-PMMA/ZnO composite films with blank quartz substrate as the reference are shown in Figure 5. A decrease in the transmittance, with an increase in the ZnO content, was observed in the UV region; however, their transmittances in the visible region were almost equal except for the Polymer-20. In addition, all the films are colorless and transparent in the visible range. ZnO is a wide band gap semiconductor, and it has a high-absorption coefficient in the UV. Thus, in contrast to the visible, the composite films are strongly absorbing in the UV region. The transmittance of the nanocomposite films is above 95% at 550 nm. Especially, when the content of ZnO is 5 wt %, the nanocomposite film exhibits high UV-shielding (>95%) property, whereas the transmittance of visible light is the same as that of film without ZnO

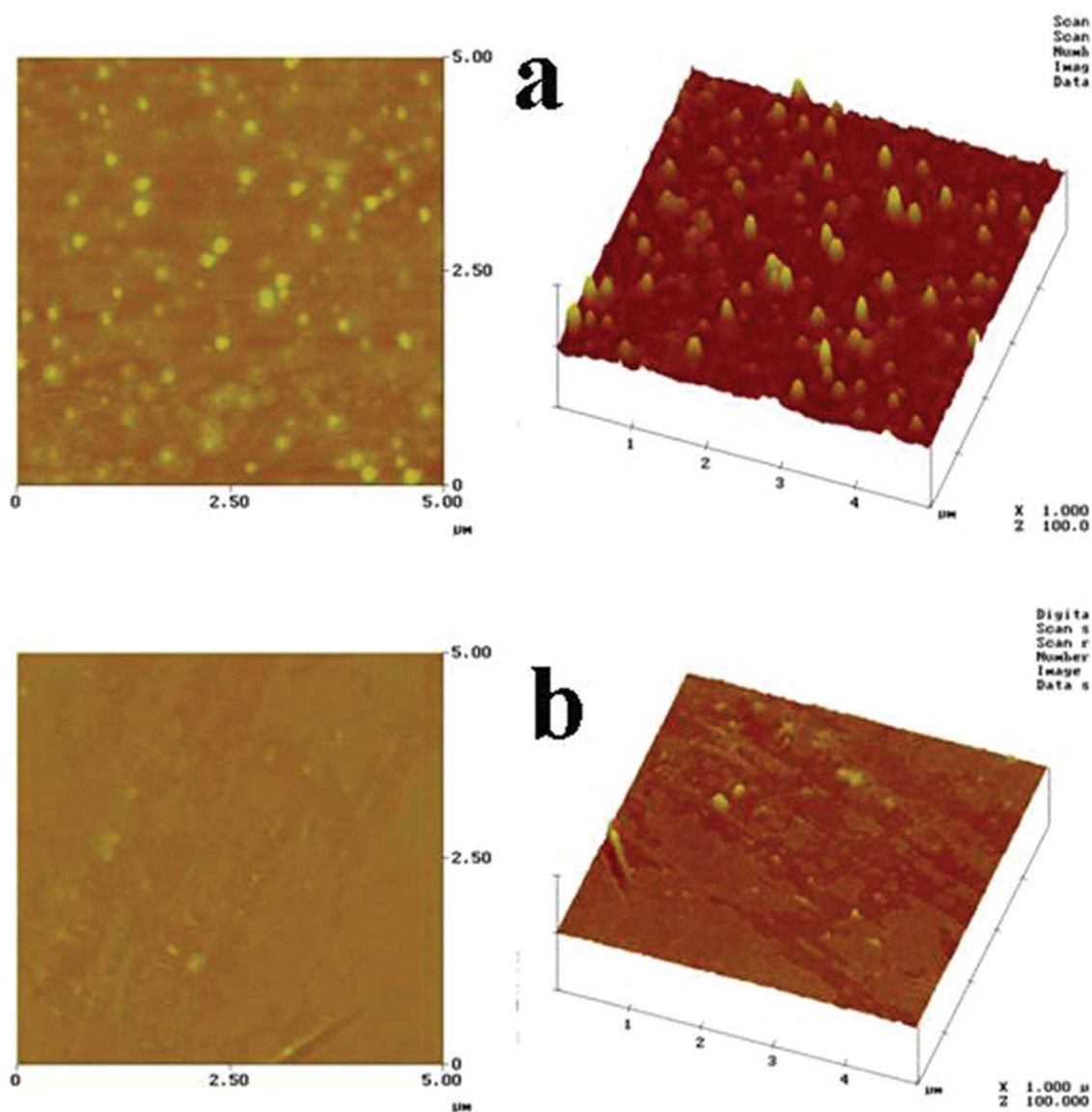


**Figure 6** Photograph of the transparent film with 5 wt % ZnO (background: tree). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

nanoparticles. It indicates that the nanoparticles are well-dispersed in polymer matrix, which is proved in Figures 7–8. The Rayleigh scattering caused by the aggregated NPs does not happen. Therefore, the nanocomposite film is transparent enough to be used as the optical materials with



**Figure 7** Cross-section HR-TEM image of nanocomposite film with 5 wt % ZnO.



**Figure 8** AFM phase (left) and (right) images ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ): (a) PS-PMMA/ZnO nanocomposite film with 5 wt % ZnO; (b) PS-PMMA pure film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

UV-shielding property. And the photograph of the transparent film with 5% under in the daylight is shown in Figure 6.

Size and dispersibility of inorganic domains in a polymer matrix have critical importance for transparency. As ZnO is not absorbing in the visible, only the scattering of the nanoparticles may cause a light intensity loss in this spectral region. Our particles are small enough so that scattering losses are negligible and the composite films are almost as transparent as pure PS-PMMA. It can be seen that the UV-shielding ratio is above 95% with ZnO contents above 5%. This suggests that the nanocomposite films have excellent UV-shielding properties. Therefore, these nanocomposite films are applicable as transparent coating with strong sunlight protection ability.

### The morphology of PS-PMMA/ZnO composite films

The distribution of the particles in the nanocomposite films was obtained from HR-TEM electromicrographs. Results of the measurements are presented in Figure 7 for ZnO weight fractions, 5 wt %. As shown in the image, the ZnO particles with their original size of about 4–5 nm exhibit good dispersibility in the polymers with little agglomeration, which is in accordance with the result of the HR-TEM of ZnO in MEK. The sizes of secondary particles are about 60 nm. The efficiency of the nanoparticles in improving the properties of the polymer materials is primarily determined by the degree of its dispersion in the PS-PMMA matrix. These nanoscale morphologies of ZnO in the polymer matrix may be definitely reflected by the changes in

thermal, optical and other properties of the final products.

To further gain the physical fundamentals of the topographical structures in more detail and the dispersion state of ZnO nanoparticles in the polymer matrix, the AFM technique is applied to investigate the surface profiles of the films. As shown in Figure 8, the images exhibit a 3D topographical feature of the PS-PMMA/ZnO nanocomposite films and the PS-PMMA pure film. Based on the images analysis, ZnO nanoparticles with sizes of about 60 nm are well dispersed, which is consistent with the secondary particles sizes of ZnO in Figure 7. In addition, the incorporation with 5 wt % loading of inorganic ZnO in the polymer brings the films a slightly smooth decrease of topography.

### CONCLUSIONS

In this article, we have prepared a series of transparent PS-PMMA/ZnO nanocomposite films with strong UV absorption using the solution mixing method. The XRD and FTIR studies indicate that there is no chemical bond or interaction between PS-PMMA and ZnO nanoparticles in the nanocomposite films. An increased absorption, with an increase in the ZnO content, was observed in the UV region, whereas the transmittance is almost equal in the visible region with lower than 20 wt % incorporation of ZnO. Especially, the PS-PMMA/ZnO composite films at a nanoparticle content of 5 wt % exhibit high UV-shielding (>95%), whereas a very high transmittance (>95%) in the visible range is observed. The light scattering does not happen because of the good dispersion of nanoparticles in polymer matrix. As-prepared nanocomposite films with strong UV absorption and high transmittance in visible are expected to be applied in the area of optically coating materials. We believe that the solution mixing method is a convenient and economical way for preparation of optical composite films and is suitable for industrial production.

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