

Mechanical and Antibacterial Properties of Modified Nano-ZnO/High-Density Polyethylene Composite Films with a Low Doped Content of Nano-ZnO

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ABSTRACT: Nano-ZnO/high-density polyethylene (HDPE) composite films were prepared via melt blending and a hot compression-molding process. The properties, including ultraviolet absorption, mechanical and antibacterial properties of the films, and plasticizing behavior of the composites, were investigated. The results show that the absorbance in the ultraviolet region of the HDPE films was enhanced after the addition of modified nano-ZnO to the HDPE matrix. Also, we found that improvement in the HDPE films of the tensile strength and elongation at break was achieved by the incorporation of modified ZnO nanoparticles up to 0.5 wt % in contrast

with the original nano-ZnO/HDPE composite films. Antibacterial testing was carried out via plate counting, and the results indicate that the HDPE films doped with modified ZnO nanoparticles showed favorable antibacterial activity, especially for *Staphylococcus aureus*. However, the low doped content of modified nano-ZnO in the HDPE matrix made the balance torque of the composites increase slightly. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2965–2969, 2010

Key words: composites; films; polyethylene (PE); nanocomposites

INTRODUCTION

High-density polyethylene (HDPE) is one of the most common packaging materials because of its excellent flexibility, good processability, and low cost. However, its use is restricted because of its lower strength, photodegradation, and so on.^{1,2} In recent years, nanocomposite materials have drawn considerable interest from both academics and industrialists because of their remarkable desirable functionalities, which are unavailable to micrometer structured materials. Much effort has been devoted to improving the properties of polymers by the addition of inorganic nanofillers, such as SiO₂,³ ZnO,^{4,5} CaCO₃,⁶ and carbon nanofibers.⁷ Nano-ZnO as a functional inorganic filler has been widely used in functional devices, catalysts, pigments, optical materials, cosmetics, and ultraviolet (UV) absorbers.^{8,9} In addition, after Sawai and coworkers^{10,11} found that ZnO powder had antibacterial activity against some bacteria strains in 1995, more and more researchers have embarked on studies of ZnO as an antibacterial

agent. Therefore, the introduction of nano-ZnO into polymers can not only enhance the mechanical properties of the polymers because of a strong interfacial interaction between polymers and nanoparticles but also endow polymers with some other functional capabilities, such as photostabilization^{12,13} and antibacterial activity.¹⁴

In this study, nano-ZnO/HDPE composite films were prepared via melt blending and a hot compression-molding process. Mainly, we investigated the effects of ZnO nanoparticles on the mechanical and antibacterial properties of the HDPE films.

EXPERIMENTAL

Materials

HDPE resin (5021D) was purchased from China National Offshore Oil Corp. (Beijing, China). The ZnO nanoparticles (ca. 50 nm average diameter, Shanxi Wenxiyaoxing Zinc Products Factory, Shanxi, China) were commercially available and were used as received. A surface modifier, γ -aminopropyltriethoxy silane [KH550; H₂NCH₂CH₂Si(OC₂H₅)₃], was purchased from Shuguang Chemicals Co. (Nanjing, China). The other reagents were analytical grade and were purchased from a chemical store.

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Modification of nano-ZnO

Nano-ZnO particles (0.10 g) and ethanol (100 g) were mixed with an ultrasonicator (KQ-300DV, Kunshan, China) for 30 min. Then, 0.5 g of modifier, which was prehydrolyzed for 1 h in an ethanol/water (1/10 w/w) solution, was slowly dripped into the system. After 1 h of reaction at a given temperature, the mixture was filtered to remove the solvent and dried to get solid particles, which were finally ground into powders.

Preparation of the nano-ZnO/HDPE composite films

The premixture ((ZnO/HDPE) wt. = 5 : 95) was fabricated first via a Haake internal mixer (PolylabRC.300P, Karlsruhe, Germany) at 180°C and 60 rpm for 10 min. Then, the final nano-ZnO/HDPE composite particles were prepared by the mixture of the premixture and HDPE at a certain ratio via a single-screw extruder (PLE330 Brabender OHG, Duisburg, Germany) and a granulator. The temperatures of the extruder from the feeding zone to the die were set at 150, 190, 200, and 195°C, and the turning speed of the screws was set at 40 rpm. Then, the composite particles were fabricated to a sheet via a two-roll mill (SK-160B, Shanghai Rubber Machinery Factory, Shanghai, China) at 180°C for 10 min. Test specimens were gauged from the final films (ca. 120 μm) and were compression-molded with the sheet by a press machine (SL-45, Shanghai Rubber Machinery Factory, Shanghai, China) at 180°C for 5 min.

Morphology

Cross sections of nano-ZnO/HDPE composite films fractured in liquid nitrogen were observed with a scanning electron microscope (SEM; JSM-6380, JEOL, Tokyo, Japan) to study the dispersion of the modified nano-ZnO in the HDPE matrix.

Mechanical properties

The tensile strength and elongation at break were tested with a universal material testing machine (SANS CMT4503, Shenzhen, China) at a crosshead speed of 200 mm/min at 23°C. The films for tensile measurement were cut into dumbbell shapes 4 mm wide and 25 mm long of the testing part. Six replicates were measured for each sample.

Antibacterial properties

The antibacterial properties against *Escherichia coli* (ATCC10536) and *Staphylococcus aureus* (ATCC6538) were determined by plate counting.¹⁵ The samples

(5 × 5 cm²) were first washed with 70% ethanol to kill all the bacteria on the surface. After drying, a 0.2-mL solution of bacteria (2.0–5.0 × 10⁶ cell/mL) was added onto the film surface, and the surface was then covered by a polyethylene film (4 × 4 cm²). These carrier films were kept at 37°C and at a relative humidity of 90% or greater. After 24 h, the bacteria were washed off with a 0.80% NaCl solution, and then, a 1-mL serial dilution of this suspension was plated onto nutrient broth agar. The colony forming units of bacteria were counted, and the antibacterial rate (*R*) was calculated with the following equation¹⁶:

$$R = \frac{B - C}{B} \times 100\% \quad (1)$$

where *B* is the number of colony forming units of the blank sample and *C* is the number of colony forming units of the antibacterial samples.

UV absorbance

Ultraviolet-visible (UV-vis) spectrophotometry (UV-2550pc, Shimadzu, Tokyo, Japan) was used to determine the UV absorption of the nano-ZnO/HDPE composite films. Transmittance spectra was recorded in the 200–800-nm wavelength range.

Plasticizing behavior

Plasticizing tests were conducted by the mixture of HDPE and nano-ZnO at a certain ratio with a Haake rheometer (PolylabRC.300P, Karlsruhe, Germany) at 180°C and a rotation rate of 60 rpm for 8 min.

RESULTS AND DISCUSSION

Morphology

Figures 1 and 2 show the fractured sections of the unmodified and modified nano-ZnO/HDPE composite films, respectively. At a 0.5 wt % content of nano-ZnO, we found that inorganic particles with a size of about 300 nm in the unmodified nano-ZnO/HDPE composite film appeared [see Fig. 1(a)]. This might have been due to the aggregation of the nanoparticles, although for the modified nano-ZnO composite film [see Fig. 2(a)], the nano-ZnO particles dispersed uniformly in the HDPE matrix. When the content of nano-ZnO was up to 1 wt %, the size of the inorganic particles rose to around 500 nm for the unmodified nano-ZnO/HDPE composite film [see Fig. 1(b)]. As a contrast, the inorganic particles in modified nano-ZnO composite film were far smaller than that in unmodified nano-ZnO/HDPE composite film [see Fig. 2(b)].

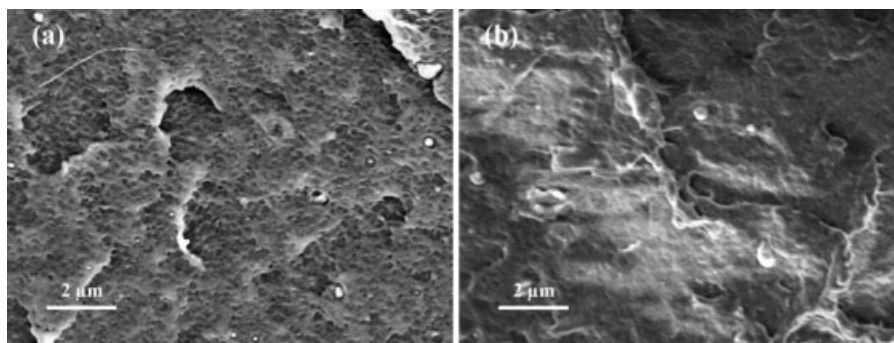


Figure 1 Cross sections of the unmodified nano-ZnO/HDPE composite films with nano-ZnO contents of (a) 0.5 and (b) 1 wt %.

It is well known that nonpolar and hydrophobic HDPE resin lacks a strong interaction with polar and hydrophilic nanoparticles. Silane treatment of inorganic nanoparticles is an usual and effective way to make a strong connection between a polymer and nanoparticles^{3,17} because of the unique bifunctional structure of the silane coupling agents with one end being capable of reacting with the hydroxyl groups on the nanoparticle surface and the other end being compatible with the polymer. The modification process¹⁸ is described as a hydrolysis and condensation reaction between the silane coupling agents and the nanoparticle surface in a polar medium. The bonding between the silane and the nanoparticle surface removes the surface hydroxyl groups and changes the hydrophilic surface into a hydrophobic surface. So the result of surface treatment is a reduction of the nanoparticle–nanoparticle interaction and an improvement in the dispersability of the nanoparticles in the polymer matrix. Therefore, the aggregation of nano-ZnO in the HDPE matrix decreased after it was modified by the silane coupling agent KH550. Moreover, at a relatively low doped content of modified nano-ZnO, such as 0.5 wt %, the nanoparticles showed good dispersability in the composite films, as shown in Figure 2(a).

Mechanical properties

Figure 3 shows the tensile strength of the modified nano-ZnO-doped HDPE films as a function of nano-ZnO content, with the tensile strength of the original nano-ZnO-doped HDPE films as a control. For the original version doped HDPE films, the tensile strength initially increased and then decreased when ZnO was greater than 0.2 wt %, and the tensile strength was even lower than that of the neat HDPE film when the content of ZnO was 2 wt %. However, for the modified nano-ZnO-doped HDPE films, the tensile strength increased abruptly and reached its maximum when the content of ZnO was 0.5 wt %; this was followed by a decrease. The maximum tensile strength was near twice that of the neat HDPE film.

It is known that the interface between nanoparticles and a resin matrix can transfer stress, which is beneficial for the improvement of the tensile strength of composite films. However, with increasing doped content of nanoparticles, aggregation occurs, which leads to a decrease in the contact area between the nanoparticles and resin matrix and creates defects in the composites. Therefore, the effective interfacial interaction is reduced, and the tensile strength of the films drops.

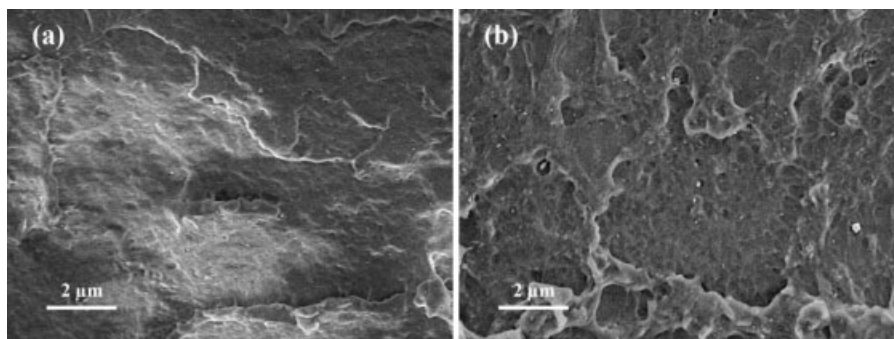


Figure 2 Cross sections of the modified nano-ZnO/HDPE composite films with nano-ZnO contents of (a) 0.5 and (b) 1 wt %.

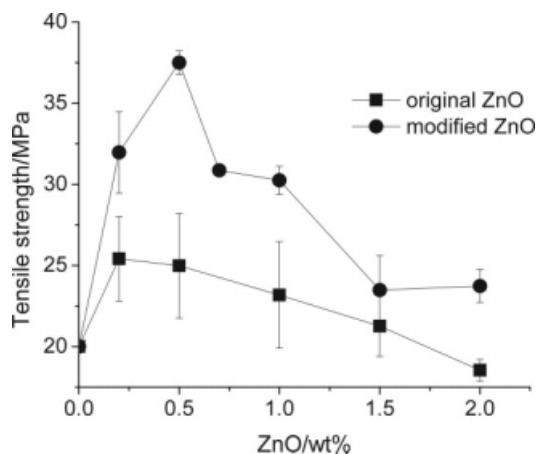


Figure 3 Tensile strength of the nano-ZnO/HDPE composite films as a function of the nano-ZnO content.

After modification by the coupling agent KH550, a better dispersion of nano-ZnO in the HDPE matrix was gained, as shown in Figure 2. The nanoparticles presented good interaction with the resin matrix through the coupling agent for the rigid particles to pass their tensile strength and modulus to the resin matrix.¹⁹ Thus, the tensile strength of the modified nano-ZnO/HDPE composite films was improved further in contrast to that of the original nano-ZnO/HDPE composite films.

Data of the elongation at break (Fig. 4) also showed that the toughness was improved for the modified version doped HDPE nanocomposite films over the filled original nanoparticles. For the modified nano-ZnO-doped HDPE films, the elongation at break had an initial increase and reached its maximum at a content of 0.5 wt %. Over 0.5 wt %, the aggregation of nanoparticles led to the decline of the elongation at break.

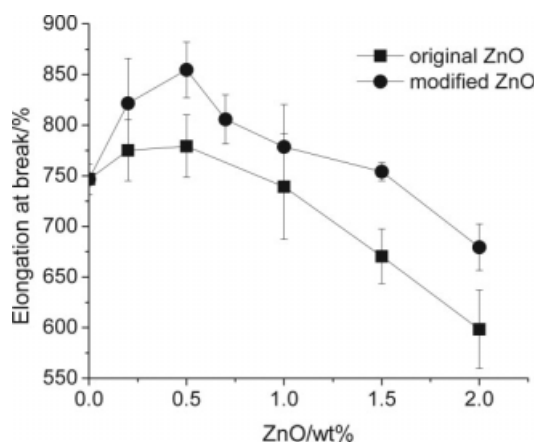


Figure 4 Elongation at break of the nano-ZnO/HDPE composite films as a function of the nano-ZnO content.

TABLE I
Antibacterial Rate of the Modified Nano-ZnO/HDPE Composite Films Against *E. coli* and *S. aureus*

Nano-ZnO (wt %)	Antibacterial rate (%)	
	<i>E. coli</i>	<i>S. aureus</i>
0	0	0
0.2	78.7	89.1
0.5	89.8	95.3
1	98.4	99.3
2	97.7	99.9

Antibacterial properties

Table I shows the results of the antibacterial experiments for the modified nano-ZnO/HDPE composite films. The antibacterial rate increased with increasing content of nano-ZnO. When the content was 0.5 wt %, the antibacterial rate was up to 89.8% against *E. coli* and 95.3% against *S. aureus*. The antibacterial rate showed a slow increase when the concentration was over 0.5 wt %. These results suggest that the composite films possessed obvious antibacterial properties and that the bacterial growth was effectively inhibited when the dosage of modified nano-ZnO was only 0.5 wt %.

On the other hand, we also found that the nano-ZnO/HDPE composite films inhibited the antibacterial activity for *S. aureus* much more effectively than for *E. coli*. It was reported²⁰ that H_2O_2 generated from the surface of ZnO can easily penetrate the cell wall of bacteria. *S. aureus* and *E. coli* are Gram-positive and Gram-negative bacteria, respectively. The structures and chemical compositions of the cell surfaces of these bacteria are quite different. That is, the thin layers of lipid A, lipopolysaccharide, and peptidoglycan exist in the cell surface of *E. coli*, and there is only a peptidoglycan layer for *S. aureus*. *S. aureus* is a Gram-positive bacterium and is generally

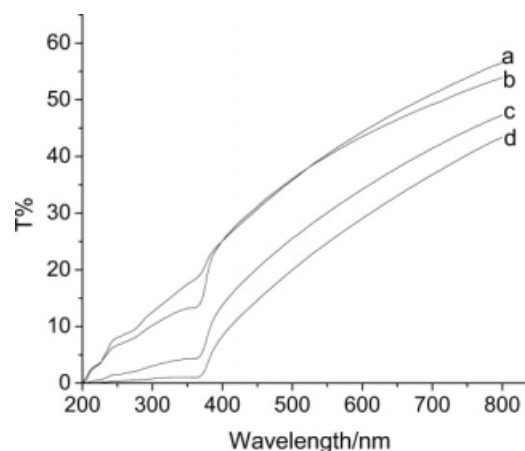


Figure 5 Transmission spectra of the modified nano-ZnO/HDPE composite films with nano-ZnO contents of (a) 0, (b) 0.2, (c) 0.5, and (d) 1 wt % (T = transmittance).

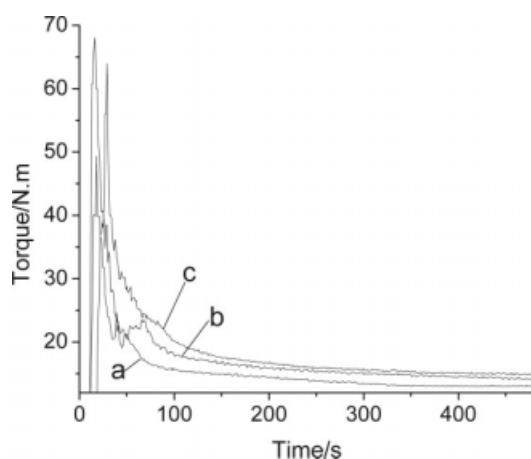


Figure 6 Torque variation of the modified nano-ZnO/HDPE composites as a function of the mixing time at 180°C with nano-ZnO contents of (a) 0, (b) 0.5, and (c) 1.5 wt %.

weak in chemical stress, and it is known that *E. coli*, which is a Gram-negative bacterium, shows a strong resistance for medicine such as antimicrobial medicine.^{21,22} Therefore, the reason that the composite films showed stronger antibacterial activity for *S. aureus* than that for *E. coli* is supposedly due to the high sensitivity for H₂O₂.

UV absorption

The UV-vis transmission of the nano-ZnO/HDPE films is shown in Figure 5. The neat HDPE film had a limited UV absorbance, whereas the absorbance in the UV region was enhanced with the addition of nano-ZnO because of a wide band gap with a large refractive index and exciton binding energy of ZnO.⁴ Nano-ZnO particles not only absorbed UV light but also scattered visible light. Therefore, the UV absorbance increased with increasing nano-ZnO content of the composite films, whereas the transmission of the visible light dropped.

Plasticizing behavior

Figure 6 presents the typical variation of torque versus mixing time for the neat HDPE and modified nano-ZnO/HDPE. It was apparent that the torque increased rapidly during initial mixing and then dropped to stabilize a line with increasing blending time. This revealed that the balance torque of the modified nano-ZnO/HDPE composites was higher than that of neat HDPE. This was mainly caused by the interfacial interaction between the nanoparticles and resin at 0.5 wt % nano-ZnO. Furthermore, a small increase in the content of the modified nano-ZnO gave rise to an elevation in the balance torque, which was attributed to the collision and friction among the

ZnO particles due to the aggregation of nano-ZnO particles,³ in addition to the interfacial interaction.

CONCLUSIONS

In this study, ZnO/HDPE nanocomposite films were prepared via melt blending and a hot compression-molding process. The addition of modified nano-ZnO to neat HDPE caused an increase not only in the tensile strength but also in the elongation at break of the HDPE films. The optimal ZnO content was 0.5 wt %. The antibacterial experiments showed that the composite films exhibited favorable activity against both *E. coli* and *S. aureus*. Also, the UV absorbance of the HDPE films was enhanced with the addition of modified nano-ZnO, which indicated that the resistance to photodegradation was improved. Finally, the torque curves showed that the addition of a low content of modified nano-ZnO to HDPE caused an increase in the balance torque of the nano-ZnO/HDPE composites.

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