

Effect of coupling agent on nano-ZnO modification and antibacterial activity of ZnO/HDPE nanocomposite films

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Abstract. Commercial zinc oxide nanoparticles were modified by silane coupling agent of KH550 and KH560, respectively. The obtained nanocomposite was characterized by scanning electron microscopy (SEM), Thermogravimetric analyses (TGA) and apparent sedimentation stability (Sapp). Then, nano-ZnO/high-density polyethylene (HDPE) composite films were prepared via melt blending and a hot compression-molding process. The antibacterial testing of the films against *E. coli* and *S. aureus* was carried out via plate counting. SEM, TGA and Sapp suggest the modifier of silane changed the surface hydrophilicity and effectively broke the agglomerations of nanoparticles. Antibacterial testing results indicated the antibacterial rate of the films increased with increasing nano-ZnO content. At a low doped content of 0.2 wt %, the types of coupling agent influenced the antibacterial property with that of KH560-modified nano-ZnO/HDPE KH550-modified nano-ZnO/HDPE unmodified nano-ZnO/HDPE films. When the dosage nano-ZnO was over 0.2 wt %, the differences of antibacterial activity resulted by modification was concealed by the strong antibacterial activity with near 100% of the nano-ZnO/HDPE composite films.

1. Introduction

When Sawai and his colleagues found that ZnO powders had antibacterial activities against some bacteria strains in 1995 [1, 2], more and more researchers have embarked on the studies on ZnO nanoparticles as an antibacterial agent. In recent years, polymer/nano-ZnO composite [3-5] has attracted great attention because of its remarkable desirable properties, including mechanical strength, photostabilization, antibacterial activity, etc.

At the same time, it is well known that, to enhance the dispersion of nanoparticles in polymer matrix, the surface modification for ZnO nanoparticles is a necessity [6]. Silane coupling agents are often used to treat the zinc oxide filler due to their unique bifunctional structure with one end capable of reacting with the silanol groups on ZnO surface and the other end compatible with the polymer [7]. And researches showed that the types and amounts of silane coupling agents influence the properties of nanocomposites, such as morphology, processability, mechanical and barrier properties [8-10].

However, there are few detailed articles so far on the coupling agent on the antibacterial activity of the ZnO reinforced polymer to our knowledge. In this work, ZnO treated with aminoethyl aminopropyl-trimethoxy silane (KH550) and γ -aminopropyl-triethoxy silane (KH560) respectively

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filled high density polyethylene (HDPE) nanocomposite films were prepared via melt blending and hot compression molding process. The surface treatment of the ZnO nanoparticles was characterized by SEM, TGA and sedimentation experiment. Moreover, the effect of coupling agent as well as the ZnO content on the antibacterial properties of HDPE films was investigated.

2. Experimental

2.1. Materials

The HDPE resin (5021D) was from China National Offshore Oil Corporation in Beijing. The ZnO nanoparticles (around 50 nm average diameter, from Nanjing Haitai nano materials Co., China) were commercially available. Surface modifier, silane coupling agent of 3-aminopropyl-trimethoxysilane (KH550) and γ -glycidoxypropyl-trimethoxysilane (KH560) was bought from Shuguang Chemicals Company of Nanjing, China. The other reagents were analytical grade and were bought from chemical store.

2.2. Modification of nano-ZnO

Nano-ZnO particles (10g) and ethanol (100 g) were mixed with ultrasonicator (KQ-300DV, China) for 30min. The modifier (0.5 g), pre-hydrolysed for 1h in ethanol/water (1/10, wt) solution, was slowly dripped in the system. After 1h reaction at a given temperature, the mixture was filtrated to remove the solvent and then get dry solid particles and grind them into powders.

2.3. Preparation of nano-ZnO/HDPE composite films

The master batch ((ZnO/HDPE) wt.=5:100) was fabricated firstly through HARRK internal mixer (PolylabRC.300P, Germany). The nano-ZnO/HDPE composite particles were prepared by mixing master batch and HDPE with a single-screw extruder (Brabender PLE330, Germany) and a granulator. Then the composite particles were made to a sheet via a two-roll mill (SK-160B, China). Test specimens (about 120 μ m) were compression-molded with the sheet by a press machine (SL-45, China).

2.4. Particle characterization

The observation of the nano-ZnO morphology was carried out using a scanning electron microscope (SEM, JSM-6380, JEOL Company, Japan). The sample was prepared by dropping the solution of nano-ZnO in ethanol on the electric conductive adhesive and making it evaporated at room temperature.

Thermogravimetric analyses (TGA) were performed with a TGA instrument (TGA Q500, TA Company, American) to study surface modification of nano-ZnO. The nano-ZnO powder, which had been dried on 120°C for 6 h, was heated under nitrogen from room temperature to 800°C at a ramping rate of 10°C/min. The weight loss of the nano-ZnO powder as a function of temperature was recorded.

The apparent sedimentation stability (S_{app}) was assessed by measuring the sedimentation speed of ZnO dispersion in water mixture with the aging time [11]. 10 wt.% ZnO nanoparticles-containing water dispersions were prepared and located in a glass tube of 0.5 cm inner diameter and 20 cm length with a scale and a cover. Then, the sedimentation stability of ZnO particles in the mixture was monitored at a given aging time, as equation (1):

$$S_{app} (\%) = \frac{l_{(t)}}{l_0} \times 100 \quad (1)$$

where, l_0 is the length of initial opaque dispersion and $l_{(t)}$ is the length of sediment part at a given time t in the tube, respectively.

2.5. Antibacterial tests

The antibacterial test of the composite films against *Escherichia coli* (ATCC10536, *E. coli*) and *Staphylococcus aureus* (ATCC6538, *S. aureus*) was according to the reference [12]. The antibacterial ratio was calculated using equation (2):

$$R = \frac{A - B}{A} \times 100\% \quad (2)$$

where R, antibacterial ratio (%); A, the CFU of the blank sample; B, the CFU of prepared samples.

3. Results and discussion

3.1. Characterization of ZnO nanoparticles

3.1.1. SEM. Scanning electron micrographs of original ZnO and modified ZnO nanoparticles are showed in figure 1. Figure 1(a) reveals that the original commercial ZnO nanoparticles are aggregated severely in ethanol solution. This should be attributed to the high surface energy of nanoparticles. From figures 1(b) and 1(c), it can be found that the dispersion of nanoparticles was greatly improved. That suggests that the modifier of silane effectively broke the agglomerations. However, the SEM pictures show no difference of the effect of the type of silane on the dispersion of nano-ZnO.

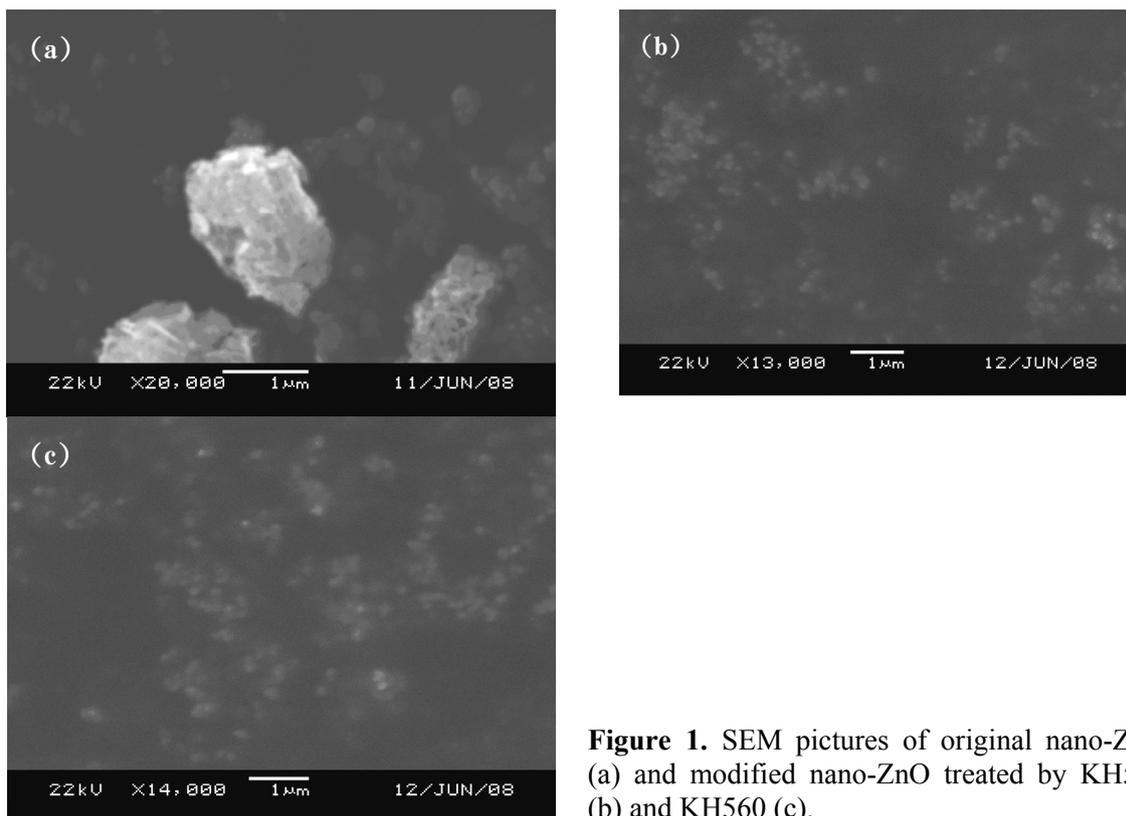


Figure 1. SEM pictures of original nano-ZnO (a) and modified nano-ZnO treated by KH550 (b) and KH560 (c).

3.1.2. Thermogravimetric analyses of nano-ZnO. The surface modification on the nano-ZnO was also characterized by TGA. It can be seen from figure 2 that the unmodified nano-ZnO has a weight loss (about 5wt%) around 100°C, which relates to the elimination of physically absorbed water on the surface [13]. The nano-size fillers possess a large surface area which makes it easy to pick up the moisture in a typical laboratory environment even after they are dried at 120°C for 6 h. The weight loss above 150°C for original nano-ZnO may be due to the chemically bonded water and residual organics from the process of the nano-ZnO synthesis [7]. On the other hand, it is found that the nano-

coupling agent and form poly (zinc silane) complex on the surface of ZnO nanoparticles. Consequently, the oligomers are initially grafted or anchored on the surface of the nanoparticle through one or several spots. The other terminal of silane is organic chain, which fulfill steric hindrance between inorganic nanoparticles [15]. This indicates that the grafting silane chain reduces the aggregation of ZnO nanoparticles (shown in figure 1) and increases the compatibility with organic solvent.

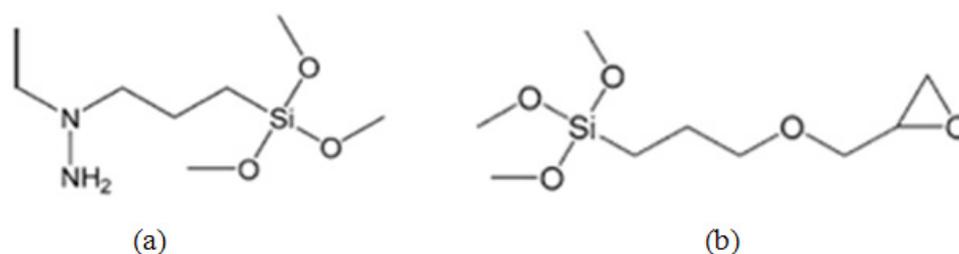


Figure 5. Chemical structure of KH550 (a) and KH560 (b).

In addition, the chemical structures of silane coupling agents are shown in figure 5. Compared with epoxy group on KH560, the amino group on KH550 is still hydrophilic [7]. On the other hand, the amino group in the silane is easily to form hydrogen bonding with hydroxyl groups on the ZnO surface [16], which also influences the proceeding of reaction between ZnO and hydrolyzed silane. Those may lead to the lower S_{app} after 4d and visually significantly more precipitation at 8 d of the KH550-modified nano-ZnO due to the slightly worse effect of surface modification of KH550 in contrast with KH560.

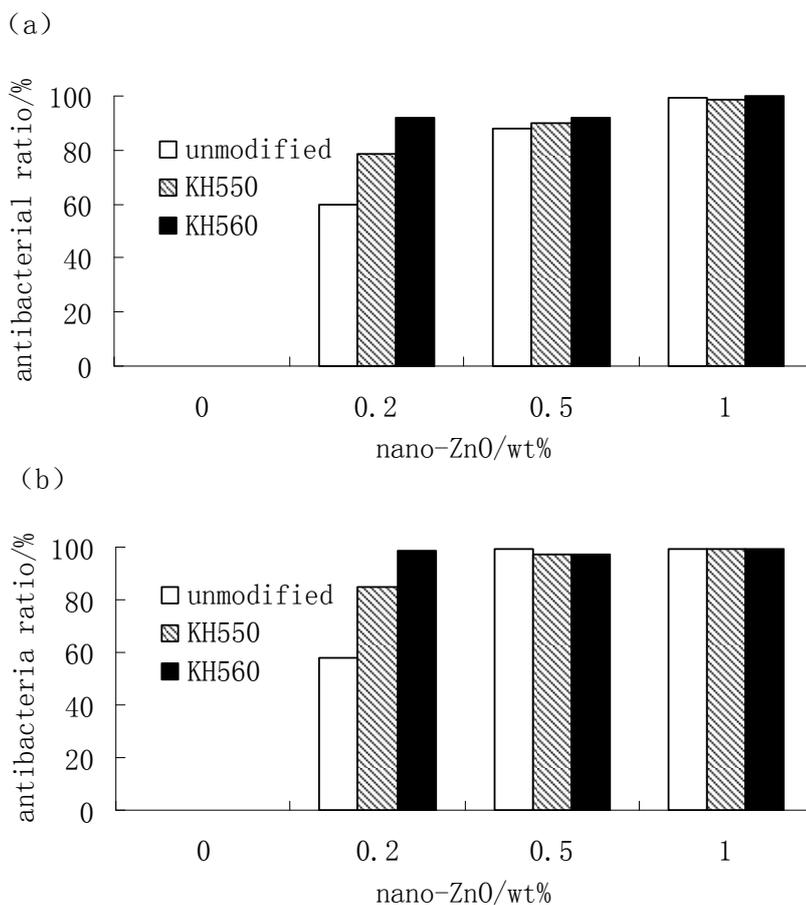


Figure 6. Antibacterial activity of nano-ZnO/HDPE composite films, (a) *E. coli*; (b) *S. aureus*.

3.2. Antibacterial property

The antibacterial activity of nano-ZnO/HDPE composite films against *E. coli* and *S. aureus* is shown in figure 6. It can be seen that the antibacterial ratio increased with the increase of nano-ZnO content, while the HDPE films had no any bacterial effect in this research with the antibacterial rate of 0%. When the concentration of nano-ZnO was 0.5wt %, the antibacterial ratio exceeded 90% against both *E. coli* and *S. aureus*. The films showed a stable strong antibacterial rate of near 100% when the content of nano-ZnO was over 0.5 wt %. That indicates that the composite films of nano-ZnO/HDPE possessed of excellent antibacterial property and the bacterial growth was effectively inhibited when the addition of nano-ZnO was only 0.5 wt %.

It was also found that for the low doped nano-ZnO with the content of 0.2wt %, the modification of nano-ZnO dramatically improved the antibacterial activity of the composite films against both *E. coli* and *S. aureus* compared with the unmodified nano-ZnO-doped HDPE films. In which, the antibacterial activity of KH560-modified nano-ZnO/HDPE films was better than that of KH550-modified nano-ZnO/HDPE films. The films showed a high antibacterial rate of near 100% against both *E. coli* and *S. aureus* when the concentration of ZnO nanoparticles was above 0.5 wt % with no influence by the surface modification of nano-ZnO and the type of coupling agents.

It is well known that nonpolar and hydrophobic HDPE resin lacks a strong interaction with polar and hydrophilic ZnO nanoparticles. Silane treatment improves the dispersability of nanoparticles in polymer matrix resulted from the reduction of the nanoparticle aggregation and enhancement of the interaction between HDPE and nano-ZnO [12, 17]. Therefore, at a relatively low doped content of modified nano-ZnO, such as 0.2 wt %, the aggregation of nano-ZnO in the HDPE matrix decreased after it was modified by the silane coupling agent. Moreover, from the result of sedimentation stability of nano-suspensions, the nanoparticles treated by KH560 would show better dispersability in the HDPE matrix than treated by KH550. Hence, the antibacterial activity of KH560-modified nano-ZnO/HDPE films was the best at a nano-ZnO content of 0.2 wt %. When the content of nano-ZnO was over 0.2 wt %, the differences of antibacterial activity resulted by modification was concealed by the strong antibacterial activity of the nano-ZnO/HDPE composite films.

4. Conclusions

- The modifier of silane changed the surface hydrophilicity and effectively broke the agglomerations of nanoparticles from SEM images and TGA curve. The effect of surface modification of KH560 was better than KH550 from the result of sedimentation experiment.
- The antibacterial rate of nano-ZnO/HDPE increased with increasing content of nano-ZnO. The composite films of nano-ZnO/HDPE possessed excellent antibacterial properties and that the bacterial growth was effectively inhibited when the dosage of nano-ZnO was only 0.5 wt %.
- The effect of surface modification influenced the antibacterial property due to dispersability of nanoparticles in HDPE matrix. The antibacterial activity of KH560-modified nano-ZnO/HDPE films was the best compared with KH550-modified nano-ZnO/HDPE and unmodified nano-ZnO/HDPE films at a low nano-ZnO content of 0.2 wt %. When the dosage nano-ZnO was over 0.2 wt %, the differences of antibacterial activity resulted by modification disappear due to the strong antibacterial activity with near 100% of the nano-ZnO/HDPE composite films.

Acknowledgment

The authors thank Wuhan Polytechnic University Scientific Research Funding (2013d13) and Research Funding of Hubei Provincial Education Department (D20151703) for the financial support.

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