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Preparation, antimicrobial, crystallization and mechanical properties of nano-ZnO-supported zeolite filled polypropylene random copolymer composites

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ABSTRACT

In order to increase the antimicrobial functionality of polypropylene random copolymer (PPR), nano-ZnO-supported on the surface of zeolite particles were prepared and used as functional fillers for PPR composites. The prepared nano-ZnO-supported zeolite particles were characterized by fluorescence and UV–Vis spectra, inductive coupled plasma and scanning electron microscopy. The crystallization behavior and crystalline morphology, antimicrobial ability and mechanical properties of zeolite, ZnO and nano-ZnO-supported zeolite filled PPR composites were investigated by differential scanning calorimeter, polarizing optical microscopy, antimicrobial and mechanical testing. The results indicated that the ZnO with flower-like morphology was formed on the surface of zeolite particles. The heterogeneous nucleation of zeolite and nano-ZnO-supported zeolite increase the crystallization temperature of PPR. The crystallization temperatures of nano-ZnO-supported zeolite filled PPR composites increase with increasing ZnO content in the nano-ZnO-supported zeolite. Incorporation of nano-ZnO-supported zeolite significantly decreases the size of spherulites of PPR. The nano-ZnO-supported zeolite filled PPR composites exhibit higher antimicrobial abilities than nano-ZnO filled PPR composite prepared by directly adding the same content of nano-ZnO into PPR matrix for the *Staphylococcus aureus* and *Escherichia coli* due to the flower-like morphology of ZnO in the nano-ZnO-supported zeolite. The nano-ZnO-supported zeolite content has little influence on the mechanical properties of PPR composites. nano-ZnO-supported zeolite as functional filler can be used to increase the antimicrobial ability of PPR.

1. Introduction

Polypropylene random copolymer (PPR) copolymerized by propylene and ethylene has received a great deal of attention from academics and industry due to the higher impact strength, excellent thermal stability, ageing resistance and mechanical properties [1]. It has been widely used for making pipes, packing plastic, automobiles and so on. The crystalline structure, morphology and mechanical properties of PPR have been reported [2–10]. However, PPR as well as iPP homopolymer materials are contaminated easily under appropriate temperature and humidity condition. It is well known that addition of nano particles is an effective method to offer the functionality and improve the physical and mechanical properties of polymer materials [11–14]. It has been reported that zinc oxide not only offers the antimicrobial ability and improves the mechanical properties but also significantly reduces photo-oxidation degradation of iPP induced by UV irradiation when it is incorporated in iPP matrix [15–22]. Chandramouleeswaran et al. [15] found that nano-ZnO reduced photo-oxidation degradation and improved antibacterial ability of iPP against two human pathogenic bacteria, *Staphylococcus aureus* and *Escherichia coli.* The physical and mechanical properties of ZnO filled PP composites vary with the morphology of ZnO [16–20]. Recently, Jiang et al. [20] prepared ZnO-supported zeolite filled iPP composites and found that ZnO-supported zeolite filled iPP composites exhibit better ultraviolet resistance and higher antibacterial ability than those of iPP composites filled by micro-ZnO. Meanwhile, the heterogeneous nucleation of ZnO-supported zeolite enhanced the crystallization temperatures of iPP.

Although the research in the field of zeolite or ZnO filled iPP composite have been reported [23–31], zeolite filled PPR composite and nano-ZnO-supported zeolite filled PPR composites have not been invested at present. In this article, nano-ZnO-supported

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zeolite particles and the filled PPR composites were prepared in the first time. The effect of zeolite and nano-ZnO-supported zeolite on the crystallization behavior and morphology of PPR was compared. The antimicrobial ability and mechanical properties of filled PPR composites were investigated.

2. Experimental

2.1. Materials

PPR (R200P, MRI = 0.23 g/10 min at 23 °C, 2.16 kg, the content of ethylene is 3.8%, Mn = 72.2 × 10^4 g/mol, Mw/Mn = 4.5 and the density is 0.91 g/cm^3) were provided by Hyosung Corporation. 13X Zeolite with average particle size of about 1.0 μm and porediameter about 1.0 nm was supplied by Wuxi Rongdeli Molecular Sieve Factory, China. Zinc chloride (AR) was supplied by Tianjin Fuchen Chemical Factory, China. NaOH (AR) was provided by Santou Guanghua Chemical Factory, China. Concentrated nitric acid (GR) was bought from Guangzhou Chemical Factory, China. Nano-ZnO with average particle size of about 30 ± 10 nm was supplied by Aladdin Chemistry Co. Ltd. *S. aureus* and *E.* coli obtained from Guangzhou Institute of Microbiology, China were used in the experiments.

2.2. Preparation of composites

2.2.1. Preparation of nano-ZnO-supported zeolite particles

Neat zeolite were pretreated at 400 °C in muffle furnace for 4 h, then added 10 g pretreated zeolite into four different three-neck flask, respectively. After the system was evacuated to 6.3 MPa and kept the pressure for 0.5 h, 50 ml of aqueous solution containing 1, 2, 3 and 4 wt% zinc chloride were respectively added into four three-neck flask and then stirred the mixture for 2 h. 1 mol/L NaOH was added and adjust the pH of mixture to 7.0, then stirred the mixture for 0.5 h. The filtered mixture was dried in vacuum oven for 1 h, in muffle furnace at 200 °C for 4 h and 500 °C for 2 h, respectively. The nano-ZnO-supported zeolite particles prepared with 1, 2, 3 and 4 wt% zinc chloride aqueous solution were respectively denoted as SZ_1, SZ_2, SZ_3 and SZ_4 and the content of ZnO in the nano-ZnO-supported zeolite particles were measured by inductive coupled plasma testing.

2.2.2. Preparation of zeolite filled PPR composites

PPR composites were prepared with an HL-200 internal mixer (Jilin University Science and Education Instrument Factory, China) at 170 °C and 50 rpm for 7 min. ZnO filled PPR composite was denoted as ZP. The nano-ZnO-supported zeolite filled PPR composites (SZP) prepared with 10 phr S, SZ_1, SZ_2, SZ_3 and SZ_4 were denoted as SP, SZ_1P, SZ_2P, SZ_3P and SZ_4P, respectively. The SZ_4 filled PPR composites prepared at the SZ_4/PPR ratio of 0/100, 5/100, 10/100, 15/100 and 20/100 were denoted as PPR, 5 SZ_4P, 10 SZ_4P, 15 SZ_4P and 20 SZ_4P, respectively.

2.2.3. Preparation of antimicrobial films

The film samples of neat PPR, nano-ZnO-supported zeolite filled PPR (SZ_4P) and nano-ZnO filled PPR composite (ZP) were pressed by plate vulcanizing press at 180 °C and 10 MPa. The content of ZnO in PPR, 5 SP, 5 SZ_4P, 10 SZ_4P, 15 SZ_4P, 20 SZ_4P, ZP are 0 phr, 0 phr, 0.71 phr, 1.42 phr, 2.13 phr, 2.84 phr, 2.84 phr, respectively.

2.2.4. Preparation of samples for mechanical testing

Before the sample preparation, all the materials were dried in a vacuum oven at 60 °C for 12 h. All the composites were prepared with SJ-30 co-rotating twin screw extruder (Nanjing Hengao Mechanical Company, China) at temperatures of 170/180/190/200/200/200 °C and 300 r/min. Extradites were cooled in a water bath and cut into pellets by a pelletizer. The dried pellets were injected for specimens of tensile, flexural and impact characterizations by using a F-120 vertical injection molding machine (Guangzhou Fengtie Mechanical Company, China) at temperature of 230 °C and injection pressure of 60 MPa and mould temperature of 60 °C. A single-edge V-shaped notch of 2 mm depth was milled in the molded specimens for the notched Charpy impact experiments.

2.3. Characterization

2.3.1. Zinc oxide contents

Nano-ZnO-supported zeolite of 3 mg was dissolved in concentrated nitric acid and the content of ZnO was obtained by inductive coupled plasma (Spectro Ciros Vision, Spectro Co. Germany).

2.3.2. Zeolite morphology

The morphology of zeolite and nano-ZnO-supported zeolite particles were observed with a scanning electron microscopy (SEM S4800, Hitachi, Japan).

2.3.3. Fluorescence spectra

The fluorescence spectra of zeolite, ZnO and nano-ZnO-supported zeolite particles were measured by X-ray fluorescence spectroscopy (RF-5301PC, Shimadzu, Japan) at excitation wavelength of 320 nm and emission wavelength of 330–800 nm. The slit width of excitation and emission is 10 nm and the optical filter of incident light and emitted light is 250–400 nm and 360 nm, respectively.

2.3.4. UV–Vis spectra

The UV–Vis spectra of zeolite and nano-ZnO-supported zeolite particles were characterized by a UV-3150 (Shimadzu, Japan) at slit width of 5 nm and scanning number of 200–600 nm. The $BaSO_4$ was used as reference sample.

2.3.5. Antibacterial property

The films of composites at 1 g with the dimensions of 1 cm length × 0.5 cm width × 0.38 cm thickness were putted in a plastic bag. The fluid nutrient medium at pH 7.2 is comprised of beef extract, peptone, sodium chloride and water with the weight ratio 1:2:1:200 [32,33]. After sterilization in an autoclave, the fluid nutrient medium was inoculated with S. aureus and *E. coli* respectively. The films were soaked in the fluid nutrient at 37 °C for 18 h in a shaker and the UV absorption of nutrient solution was measured by UV–Vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co. Ltd. China). It generally suggested that the more the antibacterial colony, the higher intensity of UV absorption is. The amount of antibacterial colony is obtained through the intensity of UV absorption, *A* value. The antibacterial reduction rate, *Y* value, was obtained with the following formula [20]:

$$Y\% = [(A_b - A_s)/A_b] \times 100\%, \tag{1}$$

in which, A_b and A_s are the intensity of UV absorption of blank and samples, respectively.

2.3.6. Crystallization and melting behavior

The crystallization behavior and melting characteristics of PPR and its composites were performed on a TA Q20 differential scanning calorimeter in a nitrogen atmosphere. About 5 mg of sample was heated to 220 °C at the rate of 30 °C/min and held at this temperature for 3 min to erase the thermal and mechanical history. Then samples were cooled to 50 °C and reheated to 220 °C at the rate of 10 °C/min. The crystallinity was determined