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Synthesis of vegetable oil-based waterborne polyurethane/silver-halloysite antibacterial nanocomposites

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ABSTRACT

Castor oil-based waterborne polyurethane/silver-halloysite (WPU/Ag-HNT) antibacterial nanocomposites were prepared by incorporating silver-halloysite composite (Ag-HNT) into WPU via *in situ* polymerization. Ag-HNT was successfully synthesized by modification of halloysite nanotubes (HNTs) with 3-(2-Aminoethylamino) propyldimethoxymethylsilane (AEAPTMS) and chitosan, and then mixed with silver nitrate for combining silver ions, finally the silver nanoparticles were loaded on the surface of HNTs by reducing silver ions with $NaBH_4$. The morphology, thermal properties and mechanical properties of WPU/Ag-HNT nanocomposites films were characterized by SEM, TGA, DMA, DSC and tensile testing. The results were shown that the thermal and mechanical properties of WPU/Ag-HNT nanocomposites were improved. The antibacterial test indicated that the nanocomposites exhibited excellent antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. The obtained nanocomposites will have promising applications in high performance antibacterial coatings.

1. Introduction

Waterborne polyurethane (WPU) is a kind of environmentally friendly material with excellent elasticity, flexibility, abrasion resistance and broad substrate suitability, which make it is wildly used in many fields, such as adhesives, printing inks and coatings [1]. The coatings used in food industrial, marine structure and wastewater treatment are required to have high resistance to biodegradation, because they are often in different kinds of bacterial environments. Therefore, it is necessary to develop high performance WPU coatings with excellent thermal, mechanical and antibacterial properties. In recent years, various techniques have been used to enhance thermal and antibacterial properties of WPU. Among these methods, fabricating inorganic/organic hybrid nanocoatings is a good method [2]. Nanofillers such as TiO_2 [3], Ag [4], ZnO [5] were introduced into polyurethane matrix for their antibacterial properties. Compared with other nanomaterials, silver nanoparticles were the best antibacterial agent due to their wide antibacterial spectrum and good antimicrobial efficacy against bacterial and other eukaryotic micro-organisms [6]. It has been reported that the small size and good dispersion state of silver nanoparticles are crucial for their antibacterial properties [7]. Nanosilver particles have been incorporated into polyurethane matrix to prepare polyurethane/Ag nanocomposites with antibacterial properties [8]. However, it was found that it is difficult for the silver nanoparticles disperse into the polymer matrix homogeneously due to their easy agglomeration and incompatibility of inorganic and organic phases. Halloysite nanotubes (HNTs) are good candidate for reinforcing polymer nanocomposites [9]. HNTs can be easily dispersed in polymer matrices due to their unique crystal structure, tubular shape and low density of surface hydroxyl groups. In this study, HNTs were used as carries for silver nanoparticles to prevent silver nanoparticles from aggregating together. HNTs were first modified with silane coupling agent AEAPTMS and chitosan. And then, monodispersed silver nanoparticles were loaded on the surface of HNTs by reducing silver ions. The obtained silver-halloysite nanotubes (Ag-HNTs) were incorporated into WPU matrix via *in situ* polymerization. Castor oil was used as the polyol component. The aim of this study is to prepare a novel castor oil-based waterborne polyurethane/silver-halloysite antibacterial nanocomposites. At the same time the antibacterial mechanism of WPU/Ag-HNT nanocomposites was analyzed.

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2. Experimental

2.1. Materials

Halloysite nanotubes (HNTs) were purchased from Shunhe Packing Factory were purchased Shunhe Packing Factory (Danjiangkou, Hubei province, China) silver nitrate was purchased from Sinopharm Chemical Reagent Co., Ltd, China. 3-(2-Aminoethylamino) propyldimethoxymethylsilane (AEAPTMS, 96%), sodium borohydride (98%), glutaraldehyde (50%) and chitosan with a deacetylation degree of 90% were purchased from Aladdin (Shanghai, China). Isophorone diisocyanate (IPDI) and hexamethylene diisocyanate were purchased from Bayer, Germany. Castor oil was purchased from Damao Chemical Reagent Factory (Tianjin, China). Acetone was provided by Guangzhou Fine Chemical Factory, China. Dimethylolpropionic acid was supplied from YIP'S CHEMICAL. Triethylamine (TEA, Lingfeng, China), dibutyltin dilaurate (DBTDL, Lingfeng, China) and other chemicals were all obtained in AR grade.

2.2. Synthesis of silver-halloysite nanoparticles

Reaction principle of preparing Ag-HNT nanoparticles was showed in Fig. 1. First, the hydroxylated halloysite nanotubes were modified with a coupling agent AEAPTMS. 2 g of HNTs powder were dissolved into 200 mL of 75 vol % aqueous ethanol solution under a 10 min ultrasound. Then, the mixture was poured into a 500 mL flask stirring and stirred for 30 min. Subsequently, 2 mL of AEAPTMS was added into the mixture dropwise, and the suspension was refluxed at 70 °C for 8 h under constant stirring. The silylated HNTs were obtained by centrifugation and washed with ethanol for 3 times and was dried in a vacuum at 60 °C. 2 g of silylated HNTs were soaked into 100 mL glutaraldehyde (25 wt %) with magnetic stirring for 3 h at room temperature. Then, the solid was isolated by centrifugation and added into chitosan-acetic acid solution. The mixture was stirred with magnetical rotor for 4 h at 50 °C, and then the solid was isolated by centrifugation and added into 0.1 M $NaBH_4$ solution. After vigorously stirring for 2 h, the modified HNTs (mHNTs) were collected by centrifugation, then washed with deionized water for 3 times, and dried in a vacuum oven overnight at 60 °C. In order to deposit silver nanoparticles on the surface of HNTs, 0.8 g of silver nitrate was dissolved in 100 mL of methanol with mechanical stirring, and then 2 g of mHNTs were added. The mixture was stirred continuously for 8 h at room temperature. The precipitation was collected by centrifugation and washed with methanol and deionized water for several times. Subsequently, the precipitation was added into 0.1 M $NaBH_4$ solution and stirred vigorously for 2 h. The final product (Ag-HNT) was obtained by centrifugation, then washed with deionized water and dried in vacuum.

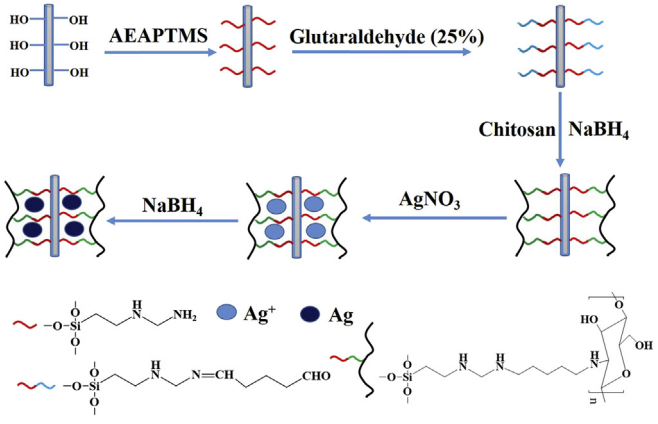

Fig. 1. Reaction principle of preparing Ag-HNT nanoparticles.

2.3. Preparation of castor oil-based waterborne polyurethane/halloysite-silver hybrid dispersions

The castor oil (40 g, 0.1162 mol of OH groups), 25.83 g of IPDI (0.1162 mol) and different contents of Ag-HNT were added to a four-necked flask equipped with a condenser, mechanical stirrer, thermometer and nitrogen inlet, and the reaction was carried out at 80 °C for 2 h under N_2 atmosphere. After that, 7.0 g of DMPA (0.0523 mol) dissolved in NMP was added into the flask and the reaction continued at 75 °C. The reaction was then cooled to 45 °C and 40 g of acetone was added to reduce the viscosity of prepolymer when the residual NCO content reached the expected value (determined by the dibutylamine back-titration method). Then the PU was neutralized by 5.29 g of TEA, followed by dispersion at high speed with 200 g of deionized water to prepare waterborne polyurethane dispersion. The castor oil based WPU with 30% solid content was obtained after removal of the acetone under vacuum. By changing the contents of Ag-HNT particles in the range 0, 1, 2 and 3, a series of WPU/Ag-HNT nanocomposites were prepared and coded as WPU/Ag-HNT-0, WPU/Ag-HNT-1, WPU/Ag-HNT-2, and WPU/Ag-HNT-3, respectively.

2.4. Preparation of waterborne polyurethane nanocomposite films

The WPU nanocomposites films were prepared by casting the hybrid emulsions on the polytetrafluoroethene (PTFE) moulds and dried at room temperature for 7 days.

2.5. Characterization

The TEM micrographs were obtained on a TEM (JEOL 2100, Japan). The average particle size and zeta potential were characterized by a Malvern Nano-ZS laser particle sizer. FTIR spectra were detected by a Bruker 550 infrared spectrophotometer in the wavenumber range from 4000 to 400 cm^{-1} at 25 °C. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 595 Multiprobe System with an Al Kα source (1486.6 eV). X-ray fluorescence analysis (XRF) was analyzed by a PANalytical Axios PW4400 (Netherland). Thermogravimetric analysis (TGA) was investigated by STGA 449C (Netzsch, Germany). Scanning electron microscope (SEM) imaging was performed on a Leo 1530 Compact to investigate the morphology of the nanocomposite films. The thermal property was detected by a Netzsch DSC204 differential scanning calorimeter analyzer (DSC, Germany). DMA was analyzed by the DMA242C (Netzsch, Germany) under the tension mode from −100 to 100 °C with a frequency of 1 Hz and a heating rate of 2 °C/min. The tensile properties were measured by Instron tension meter Model 3367 at room temperature. The antibacterial properties were measured according to ASTM E2149-01. Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* were selected for bactericidal testing. The number of viable microorganism colonies was determined using the method of plate counting and the antibacterial ratio was calculated as follows:

$$\text{Antibacterial ration}(\%) = \frac{N_0 - N}{N_0} \times 100\% \quad (1)$$

where N_0 is the mean number of bacterial on the film of neat WPU, and N is the mean number of bacterial on the film of WPU/Ag-HNT