Synthesis of antibacterial polyurethane film and its properties

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Polyurethane (PU) is a polymer widely used in the biomedical field with excellent mechanical properties and good biocompatibility. However, it usually exhibits poor antibacterial properties for practical applications. Efforts are needed to improve the antibacterial activities of PU films for broader application prospect and added application values. In the present work, two PU films, TDI-P(E-co-T) and TDI-N-100-P(E-co-T), were prepared. Silver nanoparticles (AgNPs) were composited into the TDI-N-100-P(E-co-T) film for better mechanical properties and antibacterial activities, and resultant PU/AgNPs composite film was systematically characterized and studied. The as-prepared PU/AgNPs composite film exhibits much better antibacterial properties than the traditional PU membrane, exhibiting broader application prospect.

Keywords: polyurethane, Ag nanoparticles, antibacterial, composite film.

INTRODUCTION

Polyurethane (PU) is a general term of the macro-molecular compounds containing repeated carbamate groups (-NHOOC-) in the backbone chain. It is the product of the addition polymerization of polyisocyanate with oligomeric polyol. Due to its good comprehensive properties, such as diverse forms and properties, excellent strength and toughness, oil resistance, chemical corrosion resistance and so on, PU has been applied to the medical field as a dressing material⁴⁻⁵. The backbone chain of hydroxy-terminated ethylene oxide tetrahydrofuran copolymer ether (P(E-co-T)) is composed of methylene (-CH2-) and ether bond (R-O-R) groups, which endows PU medical films good flexibility, excellent mechanical properties and environmental adaptability⁶.

During the usage and storage, the surface of PU material is prone to grow and reproduce bacteria at appropriate temperatures and humidity because of its nutrient bases, which can break and decolor the material, and shorten the service life of the material⁷. In addition to the nutrient bases, various modification additives in PU material, such as plasticizers, stabilizers and fillers, can also serve as the nutrient sources of microorganisms. The nutrients provided by these additives allow bacteria to multiply to large numbers under suitable conditions and eventually deteriorate the PU material⁸. Improving the antibacterial activities of PU material is highly desired for broader application prospect and added application values.

For many years, scientists have committed to developing antibacterial agents and studying the antibacterial mechanism. Among various antibacterial agents, antibiotics possess the best antibacterial properties, yet are easily subject to drug resistances⁹. Most of organic antibacterial agents, such as quaternary ammonium salt, perform poorly upon the broad-spectrum antibacterial activities. ZnO nanoparticles have been successfully composited into a PU film to improve its antibacterial properties. However, the antibacterial activity is significantly affected by light irradiation⁷,⁸.

Ag is an important inorganic antibacterial agent that can destroy the inherent components or cause functional disorder and even death of bacteria upon contact⁹⁻¹⁰. It can also catalyze and activate the reaction of water with the oxygen in air to produce hydroxyl radicals (·OH) with strong oxidizing ability and reactive oxygen ion (O₂⁻) under light irradiation to enhance the sterilization ability¹¹⁻¹². In addition, Ag antibacterial agents are low toxic, strongly antibacterial and easy to be composited with a variety of matrices. Several composites of Ag and PU have been prepared by simply combining Ag with PU. For example, Wang et al.¹³ fabricated a PU/keratin nanofibrous by electrostatic spinning. Ag nanoparticles (AnPs) were in situ composited into the nanofibrous to form a novel nanofibrous composite mat. The mat exhibited better biocompatibility, antibacterial properties and wound healing performance, as compared with the conventional gauze sponge dressings. Prashant et al.¹⁴ obtained a uniformly coated PU foam by immersing a PU foam in nanosilver solution overnight. The nanosilver coated PU foam was test for water filtration using E. coli as the water pollution index. No bacteria were detected in the output water due to the excellent antibacterial ability of the foam. However, these methods rarely produce the composites directly during the preparation of PU. P(E-co-T) is a class of polyether prepolymers with good flexibility and low glass transition temperatures¹⁵. The PUs prepared from P(E-co-T) also possess good flexibility, good low temperature mechanical properties and excellent environmental adaptability¹⁶. In the present work, AgNPs were directly dispersed in P(E-co-T) by physical mixing method, and then subjected to the one pot reaction to yield PU/AgNPs composite films. The properties of the composite films were systematically characterized and analyzed.

EXPERIMENTAL

Materials

P(E-co-T) (hydroxyl value, 25.2 mg KOH/g) of chemical grade was obtained from Luoyang Liming Chemical Industry Research Institute (Luoyang, China) and was dried in a vacuum oven at 60°C for 2 h before use. Analytical grade toluene-2, 4-diisocyanate (TDI) and polyfunctional urea-isocyanate (N-100) were purchased from Luoyang Liming Chemical Industry Research Institute and stored.
in a desiccator before use. The molar ratio of 2,4-isomer to 2,6-isomer of TDI is 8:2 and the -NCO content of N-100 is 22.0±0.3%. Dibutyltin dilaurate (T-12) and triphenylbismuth (TPB) (analytical grade) were supplied by Beijing Chemical Reagent Co., Ltd (Beijing, China). They were respectively dissolved in dibutyl phthalate to form 1.5 wt% solutions. AgNPs with the purity of 99.5% and average particle size of 120 nm were purchased from Shanghai Aladdin Reagent Co., Ltd (Shanghai, China). Analytical grade dibutyl phthalate was obtained from Beijing Chemical Factory (Beijing, China).

Preparation of PU film

Twenty grams of P(E-co-T) were added into a three-necked flask that was pre-purged with nitrogen to remove water vapor and stirred at the constant temperature of 85°C for 30 minutes. A certain amount of TDI or the mixture of TDI and N-100 was added into the flask at the desired [-NOC][-OH] ratios (R) and stirred for 1 h. The composition of each experimental sample is shown in Table 1. Catalyst T-12 and TPB were then added into the flask and stirred for 30 min. The resultant product was vacuumed to remove bubbles, poured into a polytetrafluoroethylene (PTFE) mold, vacuumed until no new bubbles appeared and solidified in an oven at 75°C for 7 days to obtain a PU film.

Synthesis of TDI-N-100-P(E-co-T)PU/AgNPs film

AgNPs (0.2 g, 0.5 wt%) were dispersed into dibutyl phthalate (8 g, 20 wt%). The suspension was mixed with P(E-co-T) polyether at 85°C under the protection of nitrogen atmosphere in a 100 mL three-mouth flask and stirred for 30 min. TDI/N-100 was added to the mixture at the desired [-NOC][-OH] ratios (R) and stirred for 1 h. The composition of each experimental sample is shown in Table 1. Catalyst T-12 and TPB were then added into the flask and stirred for 30 min. The resultant product was vacuumed to remove bubbles, poured into a polytetrafluoroethylene (PTFE) mold, vacuumed until no new bubbles appeared and solidified in an oven at 75°C for 7 days to form a TDI-N-100-P(E-co-T) PU/AgNPs film.

Characterizations

FTIR measurements were performed with a NEXUS-470 FTIR infrared spectrometer ( Nicolet company, USA) in the scanning range of 500–4000 cm–1 using KBr pellets. The XRD patterns of the as-prepared PU films were recorded on an X-ray diffractometer (XRD-6000, Shimadzu company, Japan) using CuKα radiation (wavelength λ = 0.154 nm) at the voltage of 40 kV and the current of 30 mA in the scanning range from 10° to 50°. The scanning rate was set to 5 °/min. The glass transition temperature of each film product was determined by DSC using a DSC200PC differential scanning calorimeter (NETZSCH company, Germany) at the heating rate of 5°C/min from −100°C to −20°C. PU film samples were respectively mounted on a metal stub with a conductive tape, sputter-coated with a thin layer of gold and imaged under a scanning electron microscope (Hitachi X650, Japan) for the dispersion of AgNPs.

The mechanical properties of each sample were tested according to the GB/T528-92 standard. The samples were respectively cut into 20 mm long, 5mm wide and ~1mm thick dumbbell-shaped specimens. Stress-strain curve was measured with an Instron 6022 series material testing machine at the strain rate of 100 mm/min and temperature of 25°C. The maximum tensile strength (σm (MPa)), maximum elongation (εm (%)) and elongation at break (εb (%)) of each sample were obtained from the stress-strain curve. Each test was repeated five times and the mean value was reported.

The antibacterial efficacy of TDI-N-100-P(E-co-T) PU/AgNPs film was evaluated with Gram negative E. coli ATCC 25933 by the zone of inhibition test. The bacterial species on an inclined surface were selected and shaken in sterile water with glass beads for several minutes to obtain a suspension of baceria. An aliquot of 0.1 mL suspension was uniformly dispersed on a cured luria-bertani medium under aseptic operation. The sample with the diameter of 3 cm was disinfected by ultraviolet light, placed in the medium and cultivated at 37°C for 18 h. The bacteriostatic circle around the sample was imaged.

RESULTS AND DISCUSSION

Characterizations of PU film

The TDI-N-100-P(E-co-T) PU film was first characterized by FTIR. The reaction between isocyanate monomer and P(E-co-T) produces a carbamate ester group (-NH-CO-O-). The stretching vibration and bending vibration of N-H are observed at 3433.59 cm–1 and 3372.78 cm–1, respectively (Fig. 1). The film also exhibit a peak at 1729.38 cm –1 due to the stretching vibration of C=O. No peak of the -NCO is found at 2270 cm –1 due to the stretching vibration of C=O. No peak of the -NCO is found at 2270 cm–1 on the spectrum, indicating that TDI and N-100 have been completely reacted.

The stress-strain curves of TDI-P(E-co-T) PU and TDI-N-100-P(E-co-T) PU films prepared at different

| Film type | No. | R value | Molar ratio of TDI/N-100 | Mass content of AgNPs |
|-----------|-----|---------|-------------------------|-----------------------|
| TDI-P(E-co-T) | TP-1 | 1.20 | – | – |
| | TP-2 | 1.30 | – | – |
| | TP-3 | 1.41 | – | – |
| | TP-4 | 1.50 | – | – |
| | TP-5 | 1.65 | – | – |
| TDI-N-100-P(E-co-T) | TNP-1 | 1.38 | 0.8/0.2 | – |
| | TNP-2 | 1.50 | 0.8/0.2 | – |
| | TNP-3 | 1.63 | 0.8/0.2 | – |
| | TNP-4 | 2.62 | 0.8/0.2 | – |
| TDI-N-100-P(E-co-T)/AgNPs | TNP/AgNPs-1 | 1.50 | 0.8/0.2 | 0.5 |
| | TNP/AgNPs-1 | 1.50 | 0.8/0.2 | 1.0 |
| | TNP/AgNPs-1 | 1.50 | 0.8/0.2 | 1.5 |
The crystallinity of the TDI-P(E-co-T) and TDI-N-100-P(E-co-T) PU films with different hard segment contents was determined by XRD. The TDI-P(E-co-T) film cured with TDI contains more regular hard segments and thus exhibits higher crystallinity than the film cured with N-100 due to the asymmetry of N-100 (Fig. 3). In addition, the crystallization degrees of both PU films increase first and then decrease with the increase of hard segment content. The hard segment cannot be crystallized or crystallized very slowly at low contents. The formation of an orderly arranged concentrated hard segment area out of soft segments is a very slow process, and the hydrogen bonding interaction between the hard and soft segments also hinders such “separation”. The degree of aggregation between hard segments increases with the increase of content, and the effects of hydrogen
bonding are enhanced, resulting in the orderly accumulated hard segments and better crystallization. However, a large amount of hard segments can be mixed with the soft segments, which destroys the orderly stacked structure of soft segment and significantly reduces the crystallization degree\textsuperscript{18, 19}.

The glass transition temperatures (T\textsubscript{g}) of the TDI-P(E-co-T) and TDI-N-100-P(E-co-T) films with different structures were determined by DSC. As shown in Figure 4 for their DSC curves, the TDI-P(E-co-T) and TDI-N-100-P(E-co-T) films prepared at the R of 1.5 exhibit the glass transition temperatures (T\textsubscript{g}) of −79.8 and −78.1°C. The higher T\textsubscript{g} of TDI-N-100-P(E-co-T) film is due to its higher degree of crosslinking. The T\textsubscript{g} of the TDI-N-100-P(E-co-T) film raises to −77.3°C as the R value increased to 1.63. These results suggest that higher R values of PU film result in higher T\textsubscript{g}. The low T\textsubscript{g} of the PU films prepared in the present work is due to the good flexibility of P (E-co-T) skeleton.

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The distribution of AgNPs in PU film was imaged by SEM. Figure 5 shows the SEM images of TDI-N-100-P(E-co-T) PU film and the PU/AgNPs film containing 1% AgNPs. It is clear that the AgNPs are uniformly distributed in the TDI-N-100-P(E-co-T) PU film.

The tensile strengths and elongations at break of the PU/AgNPs films with different AgNPs contents were measured to evaluate their mechanical properties. The tensile strength of the composite film remains stable with the increase of AgNPs content up to 1.0% and dramatically decreases as the content of AgNPs further increased to 1.5% (Black line in Fig. 6). The elongation at break gradually increases with the increase of AgNPs content (Blue line in Fig. 6).

The AgNPs in TDI-N-100-P(E-co-T) PU film can function as the reinforcing particles. They afford a certain load, absorb part of the energy accumulated from stress, and cause crack bifurcate or change the direction as an external force imposed on the film. Therefore, they can disperse stress, prevent the continued development of crack, delay fracture, and improve the mechanical properties of the material. Compositing the inorganic NPs during the preparation of TDI-N-100-P(E-co-T) PU can increase the confusion degree of the soft and hard segments in the PU matrix\textsuperscript{20}. The chemical bonds or hydrogen bonds formed between the surface groups of AgNPs and the isocyanate group of TDI-N-100-P(E-co-T)
circles are formed on the PU/AgNPs composite evaluated by the zone of inhibition test with the toughness than PU energy. Therefore, the composite films exhibit better toughness than PU film.

The antibacterial efficacy of the PU/Ag film was evaluated by the zone of inhibition test with the film samples containing no AgNPs and 0.5% AgNPs. Antibacterial circles are formed on the PU/AgNPs composite film containing 0.5% AgNPs and no obvious antibacterial circle is observed on the film containing no AgNPs (Fig. 7), suggesting the strong antibacterial activity of the composite film against E. coli. The positive Ag⁺ and the negatively charged cytomembrane attract each other by Coulomb force, which adheres the bacteria onto the composite film surface. Ag⁺ then penetrates the cytoderm into bacterial cells to inhibit the activity of cell synthesize, and damages the microbial electronic transport system, respiratory system and material transfer system. Eventually the cells lose the ability to divide and multiply and die. The excellent antibacterial properties of PU/AgNPs composite film can significantly promote the application of PU film as a medical dressing material.

Figure 7. Antibacterial efficacy of the PU/Ag film containing 0.5% AgNPs and 0% AgNPs (insert image)

CONCLUSION

TDI-P(E-co-T) and TDI-N-100-P(E-co-T) PU films were respectively prepared and characterized for their structures, crystallization properties and mechanical properties. AgNPs were successfully composited with TDI-N-100-P(E-co-T) PU film in situ by one-pot reaction. The AgNPs are evenly dispersed in the composite film, and can enhance the tensile strength and elongation at break of the composite film. In addition, the AgNPs endow the film excellent antibacterial activity against E. coli. The PU/AgNPs composite film with the excellent antibacterial and mechanical properties can potentially improve the poor antibacterial property of PU medical membrane and have broad application prospect.

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