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Preparation and property of polyurethane/nanosilver complex fibers

Rongjun Qu[a,b,*], Jingjing Gao[a,b,1], Bo Tang[b,2], Qianli Ma[c], Baohan Qu[d], Changmei Sun[a]

[a] School of Chemistry and Materials Science, Ludong University, Yantai 264025, China
[b] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China
[c] Yantai Spandex Co., Ltd, Yantai 264006, China
[d] College of Chemistry and Pharmacology, Qingdao Agricultural University, Qingdao 266109, Shandong, China

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ABSTRACT

Utilizing terminal reactive groups in polyurethane, nanometer silvers were reduced in situ. The formation mechanism of nanosilver in PU was under preliminary discussion. UV–vis spectroscopy and TEM analysis were used to monitor reduction process; and the PU/nanosilver complex fibers were produced by dry spinning, which were characterized by X-ray diffraction, Fourier transform infrared spectra, thermogravimetric analysis, differential scanning calorimetry and so on. The influence of nanosilver on the thermal, mechanical and antimicrobial properties of PU was studied. It is inferred that 0.030% Ag should be a proper concentration for the PU/nanosilver complex fibers with favorable mechanical properties and highly effective antibacterial activities.

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1. Introduction

Polymer nanocomposites have attracted a great deal of attention, due to their unique optical, electrical, catalytic and antimicrobial properties [1–3], which enable them to be used in novel applications such as sensors, catalysts and antibacterial materials [4–6]. Silver nanoparticles have attracted considerable interests for its potential application in photonics [7–9], microelectronics [10,11], lithography [12,13], especially in antibacterial medical device [14,15]. Researchs have shown that silver nanoparticle has good biocompatibility and good antimicrobial efficacy against bacteria, viruses and other eukaryotic micro-organisms [16]. The nano silver/polymer has been used as coatings in many areas such as food packaging and storage, water purification systems, and biomedical devices [17,18]. Alts et al. reported that bone cements loaded with 1% of silver nanoparticles revealed high antibacterial activity against *Staphylococcus aureus* and *Staphylococcus epidermidis* [19]. The silver/polymer nanocomposites have also been used in the textile industry to fabricate antibacterial fibers [20,21], which makes the research in preparation of polymer/nano silver fibers particularly significant.

Polyurethane (PU) is one of the most important engineering polymers and widely used in commercial applications, including construction, automotive, food packaging and storage, transportation, textiles, foot-wear and wound dressing materials. With the growing public health awareness of the pathogenic effects, malodors and stain formations caused by microorganisms, there is an increasing need to develop antimicrobial PU for improving the properties. Besides antibiotics, silver salts and silver nanoparticles can be used as filler or coating material in the preparation of antimicrobial PU. Comparatively speaking, silver nanoparticles show more efficient antimicrobial property than silver salts due to their extremely large surface area. The effective biocidal concentration of silver nanoparticles is at a nanomolar level in contrast to a micromolar level of silver ions. Therefore, application of nanosilver antibacterial agent would be a better alternative. The silver nanoparticles coated PU could serve as water filter to remove bacteria from water [22]. But the resulting silver nanoparticle-coated polyurethane foam was obtained by dipping in the nanoparticle solution. Then nanoparticles can easily fall off and result in the decrease of antibacterial performance. Thus, silver nanoparticles were prepared via in site reduction as a priority. A variety of routes were reported for the preparation of silver nanoparticles [23–25]. Usually, the most typical synthetic method is liquid chemical reduction method, the commonly used reductants such as sodium citrate, sodium borohydride, hydrazine hydrate, glucose, ascorbic acid, alcohol [26–31] and others. But something to be noticed, except hydrazine hydrate, the introduction of any external reducing agent

* Corresponding author. Tel.: +86 535 6699201; fax: +86 535 6699201.
E-mail address: rongjunqu@sohu.com (R. Qu).
[1] Tel: ++865356699146.
[2] Tel: +86 531 86180010; fax: +86 531 86180017.

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may produce residual substance in the course of reaction, which would sequentially influence the properties of the polyurethane. Therefore, several reports exist on the reduction of silver salt by organic solvents, particularly *N*,*N*-dimethylformamide (DMF), a powerful solvent and reductant [32,33]. But according to the data of epidemiological investigations, DMF is extremely toxic to the liver of human and animals. And so that *N*,*N*-dimethylacetamide (DMAC), an alternative common solvent in polyurethane industry, is used to replace DMF for the lower toxicity. There is no reductive group in DMAC, how to realize the reduction of silver ions without the addition of other reducing agent? In considering of the existence of terminal reactive groups-hydroxyl groups in polyurethane, we put forward a bold speculation that Ag^+ would be reduced in sit. Then during the reduction process, whether the structure of polymer chain would be disrupted and adversely affect the properties of the polyurethane? It is a considerable issue. However, most researchers have merely paid attention to the size, shape, and size distribution of nanoparticles, ignoring what happened to the polymer, which plays a very important role in later application process. In our previous study, it was reported that the degradation behavior of chitosan chains arise in the synthesis of gold nanoparticles [34]. Then in situ reduction of Ag^+ in PU, whether there is a similar degradation on polyurethane? So far, there are no relevant reports.

Nowadays, the preparation methods of polymer fibers include dry spinning, wet spinning, melt spinning and electrospinning. Electrospinning is more suitable for laboratory research, not for commercialized production [35–37]. A total of 80% of the spandex filaments worldwide are produced by dry spinning today. Whereas, researches respect to preparation and property of PU/nano silver fibers by dry spinning is relatively few.

In this paper, we put forward in situ reduction method for preparing PU/nanosilver spinning solution and preliminarily discusse the formation mechanism of Ag in PU. The PU/nanosilver fibers were prepared through dry spinning process and were subsequently characterized. The influences of the nanosilver on the structure and mechanical properties of PU fibers were discussed. The antibacterial activities of the fibers were assessed against both Gram-positive *Staphylococcus aureus* (*S. aureus* CVCC1882/CMCC26003) and Gram-negative *Escherichia coli* (*E. coli* CVCC1570/CMCC44102). The research shows that the introduction of nano Ag could not only improve the thermogravimetric and mechanical properties of PU, but also inhibit the growth of bacteria even at low concentrations of Ag nanoparticles embedded in the PU fibers.

2. Materials and methods

2.1. Materials

Polyurethane-40,000 (PU) was obtained from Yantai Spandex Co. Ltd. (China) and used as received. Analytical grade silver nitrate ($AgNO_3$) was supplied by Aldrich without further purification. *N*,*N*-dimethylacetylamide (DMAC) was purchased from Tianjin Chemical Regent Co., Ltd. Stock solutions of PU in DMAC has the same concentration of 31.8%. The $AgNO_3$ solution (1.23 mg/mL) was prepared by dissolving an appropriate amount of $AgNO_3$ in DMAC and was measured by UV–Vis spectroscopy to guarantee no metamorphism before usages. All glassware was treated with aqua regia, followed by copious washing with distilled water before drying in an oven.

2.2. Instruments

UV–Vis absorbance spectra of Ag nanoparticles were collected by a Unico7200 UV–Vis spectroscopy. The morphology of Ag nanoparticles was observed with a JEM1230 transmission electron microscope (TEM) operating at 200 kV. Over 50 particles for each sample are measured automatically and the data were treated with Image Pro-Plus 6.0 imaging software (Media Cybernetics, USA). UV–Vis absorbance spectra of Ag nanoparticles were collected using a Unico7200 UV–Vis spectroscopy. The X-ray diffraction (XRD) was determined on a rotating target X-ray diffractometer, D/max-2500VPC, Rigaku Corporation, Japan. The morphology of PU fibers containing silver nanoparticles was observed with a scanning electron microscope (SEM) (JEOL JSM 5610LV) after gold sputter-coating. The content of silver in fibers measured by an inductively coupled plasma atomic emission spectrometry (ICP AES, ICPE 9000, Japan). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms were recorded on a Netzsch TG 209 thermal analyzer. Test conditions: Sample mass 10 mg; heating rate: 10 K/min. Infrared spectra (IR) were recorded on a Nicolet MAGNAIR 550 (series II) spectrophotometer; test conditions: Potassium bromide pellets, scanning 32 times, resolution is 4 cm^{-1}. The data were treated with Thermo Nicolet Corporation OMNIC32 software of version 6.0a. The weight loss of the nano Ag/PU fibers was measured from ambient temperature up to 800 °C, at a rate of 10 °C/min. The pyrolytic temperatures (Tonset and Tp) were defined from the TGA curves. The glass transition temperature (T_g), and the hard-segment crystallization temperature (T_c) were further determined with a differential scanning calorimeter (DSC).

2.3. Fabrication of PU/nano Ag fibers

The PU/nanosilver spinning solution was prepared by in site reduction of Ag^+ ions in PU solution. In a typical experiment, different amounts of $AgNO_3$ solution (6.2 mL and 12 mL of 1.23 mg/mL, 3.1 mL of 12.3 mg/mL) was dropped into 100 g of 31.8% PU solution and was simultaneously stirred for 45 min at room temperature to form a homogeneous mixture. The mixture then reacted at 60 °C for 4 h. The resulted solution turned yellow indicating the formation of Ag nanoparticles. The reaction mixture was monitored by UV–visible spectroscopy to follow the nanoparticles growth process. The mass fraction of Ag represented the weight percentage of Ag to PU, so the mass fraction of Ag in the polymer solution was determined as 0.015%, 0.030% and 0.075%. The PU/nanosilver fibers (contain 0.015%, 0.030% and 0.075% nano Ag) were fabricated through dry spinning process by Yantai Spandex Co. Ltd. (China). The concentration of silver in fibers measured by ICP was consistent.

2.4. Mechanical property test

Tensile tests of PU/nanosilver fibers were performed using a China (Mainland) electromechanical universal testing aachine (Model CMT6101) with a 10 N load cell in a constant relative humidity (50%) room at 25 °C. Every sample was cut from the fibers (a length of 15 mm with intervals of two meters). A cross-head speed of 500 mm/min was used and at least ten samples were tested for each type of the fibers.

2.5. Determination of antibacterial activity

The nutrient media were prepared from the nutrient medium powder (Bacto, China) dissolved in distilled water and sterilized by an autoclave at 103 kPa for 20 min. *E. coli* and *S. aureus* were cultivated in sterilized LB broth and then incubated overnight at 37 °C with a shaking incubator (180 rpm). The bacterial suspension employed for the tests was diluted to 5×10^5–1×10^6 colony forming units (CFU/mL). Each fiber sample (0.3 g) was sterilized and placed into a sterilized erlenmeyer flask. 1 mL of bacterial

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