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Antibacterial anionic waterborne polyurethanes/Ag nanocomposites with enhanced mechanical properties

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ABSTRACT

Antibacterial properties of anionic waterborne polyurethane (WPU) were obtained by the incorporation of silver nanoparticles via *in situ* reduction of silver ions. Formation of Ag nanoparticles in WPU was revealed by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). TEM results indicated that Ag nanoparticles had a spherical shape with particle size ranging from 5 – 30 nm depending on the $AgNO_3$ concentration. XRD patterns exhibited face-centered cubic structure of Ag nanoparticles in WPU, whereas XPS result showed Ag^0 oxidation state as a major component of the Ag 3d peak. The WPU/Ag nanocomposites could release silver ions and exhibited antibacterial property. The antibacterial activity tests of the nanocomposites showed the bacterial reduction of 99.99% for *Escherichia coli* and 53.97% for *Staphylococcus aureus*. Incorporation of Ag nanoparticles into WPU not only provided antibacterial properties but also enhanced mechanical properties. Tensile strength of the WPU/Ag nanocomposites was twice that of the control, whereas the Young's modulus of the nanocomposite was three times higher than that of the pure WPU. This WPU/Ag nanocomposite has potential to be used as a coating for antimicrobial products with enhanced mechanical properties.

1. Introduction

Antimicrobial products have gained considerable attention from both academic and industrial sectors. Hybrids of Ag nanoparticles with several polymers, such as hyperbranched polyethyleneimines [1], polydimethylsiloxane [2], poly(vinyl alcohol) [3] and polyurethanes [4–6], exhibit effective antimicrobial properties against various microorganisms. A convenient method to prepare polymer/Ag nanoparticle hybrids is by adding silver nanoparticles into a polymer matrix. However, in this case, preparation of Ag nanoparticles is required prior to preparing the hybrid. To produce Ag nanoparticles, chemical reduction of silver ion from silver salts is a widely used method because of its simplicity. The common reducing agents for silver ions are sodium borohydride ($NaBH_4$), hydrazine, *N,N*-dimethyl formamide (DMF), triethanolamine and ascorbic acid [7–11]. However, these organic reducing agents are toxic and non-environmentally friendly. Furthermore, the obtained silver nanoparticles have a strong tendency to agglomerate. An alternative method to prepare the polymer/silver nanoparticle hybrid is by *in situ* reduction of silver ions into silver nanoparticles in the presence of a polymer matrix, where the polymer or other chemicals in the system acts as a reducing and/or a stabilizing agents. In

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this case, good distribution and dispersion of Ag nanoparticles in the polymer matrix can be obtained [3].

Waterborne polyurethane (WPU) has been used in many applications such as coatings, medical and adhesive applications as a result of increase of environmental concerns. The WPU can be classified into three types that are anionic (*i.e.,* carboxylate or sulfonate groups), cationic (*i.e.,* quaternary ammonium groups) and non-ionic types. The anionic WPU was chosen in the present work since the anions are able to coordinate silver ions, as shown in the work of Francolini et al. [12].

WPU/silver nanocomposites have been investigated by various researchers [4–6]. Wu et al. prepared WPU/silver nanocomposites by incorporating silver colloid, prepared by the reduction of silver nitrate using $NaBH_4$, into WPU [4]. Their results showed that WPU matrix could prevent silver nanoparticle aggregation after solvent removal. Their nanocomposite films showed good antimicrobial activity against *E. coli.* Akbarian et al. investigated the effect of nano silver on thermal and antibacterial properties of a 2K WPU coating [5]. They prepared 2K WPU/silver coating by mixing a silver dispersion in monoethylene glycol with the polyacrylic component of 2K WPU. Dispersion of silver nanoparticles in the polyacrylic resin was enhanced by ultra-sonication. Their nanocomposite films showed higher glass transition temperature than that of the control and exhibited antimicrobial properties against *S. aureus* and *E. coli*. Hsu et al. studied the biocompatibility and antibacterial properties of WPU/silver nanocomposites [6]. Nano silver dispersed in distilled water was mixed with polyurethane dispersion. Their results showed that WPU/Ag nanocomposites had a lower number of *E. Coli*. adhered on the surface compared to that of the pure WPU. Chou et al. also prepared WPU/silver nanocomposites by adding silver nanoparticle suspension into an aqueous solution of polyether based PU to determine thermal, dynamic mechanical properties and biostability of the nanocomposites [13]. They found that thermal, dynamic mechanical properties and biostability of WPU were greatly enhanced by silver nanoparticles. So far, the influence of silver nanoparticles on tensile properties of WPU has not yet been determined, probably due to the small quantity of added silver nanoparticles. However, in the present work, significant improvement of tensile strength and Young's modulus of the anionic WPU was observed.

The purposes of the present work were to prepare the anionic WPU/Ag nanocomposites by *in situ* reduction of silver ions using the commercial anionic WPU and to investigate the effect of Ag nanoparticles on antibacterial and tensile properties of WPU. The influence of initial $AgNO_3$ contents on the formation of Ag nanoparticles and properties of the nanocomposites was also determined.

2. Experimental

2.1. Materials

A commercial carboxylate anionic waterborne polyurethane (WPU) containing N-methyl-2-pyrrolidone (5–10%) and triethylamine (1–5%) was purchased from Sincere Group Company (Bangkok, Thailand). This WPU is used as a finish coating. The weight average molecular weight (M_w) determined by Gel Permeation Chromatography, which consists of a Waters 2414 refractive index detector, Waters 1515 isocratic pump and Waters 2707 auto sampler, was about 107,900 Dalton. Silver nitrate ($AgNO_3$) was obtained from Sigma- Aldrich (Bangkok, Thailand). *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 6538) were used for determining the antimicrobial activity.

2.2. Preparation of WPU/Ag nanocomposites

Aqueous solutions of $AgNO_3$ were prepared by dissolving $AgNO_3$ in deionized water (DI water). The $AgNO_3$ solution was added to the WPU under stirring for 15 min at room temperature. Then, the mixture was left at room temperature for 30 min. The nanocomposite films were prepared by casting the solution onto glass substrates and allowing to dry in air over night. The samples were further heated in an oven at 50 °C for 6 h. The concentration of $AgNO_3$ reported in the present work was calculated based on the total solution content. "WPU/Ag 500 ppm" refers to WPU/Ag nanocomposite containing 500 ppm $AgNO_3$.

2.3. Characterization of WPU/Ag nanocomposites

WPU/Ag nanocomposites were characterized by a Transmission Electron Microscope (TEM) equipped with Energy-dispersive X-ray spectroscopy (JEM 2100, JEOL), X-ray diffraction (XRD, Rigaku DMAX) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos Analytical Ltd.). For TEM measurement, 20 μl portions of the WPU/Ag solutions were placed on formvar-coat Cu grids. The excess solution was removed by filter paper, and then the samples were dried at 50 °C overnight. Wide-angle x-ray diffraction (WAXD) patterns were collected on a Rigaku DMAX/rapid micro diffractometer in a transmission mode using a copper point focus source ($\lambda = 0.154$ nm) at 50 kV and 40 mA. XPS measurements were performed using an Al anode. The spectrum binding energies were referenced to the C 1s of hydrocarbon at 285.0 eV.

2.4. Measurement of antibacterial activity, silver ion release and mechanical properties of WPU/Ag nanocomposites

The antibacterial activity was determined according to ASTM E2149-01. The tested specimens were shaken in a concentrated bacterial suspension for one hour. Then, the suspension was serially diluted and cultured. The number of viable organisms in the suspension was determined and the percent reduction was calculated based on retrievals from the unfilled WPU. The antibacterial activity tests were repeated three times.

The silver ion release of WPU/Ag nanocomposites was measured by atomic absorption spectrometer (AAS, Analyst 200, Perkin-Elmer) having 1 ppb-detection limit of silver ions. WPU/Ag nanocomposite films were cut into 1.0 cm × 1.0 cm sheet. For each sample, six specimens were immersed into 20 ml of 0.2 v/v % HNO_3 solution. The samples were incubated at 37 °C. HNO_3 was used to protect the released silver ions from being reduced to metallic silver [14]. The solution was collected at a certain time and the