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Polymer Degradation and Stability 91 (2006) 1017–1024
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Enhanced thermal and mechanical properties and biostability of polyurethane containing silver nanoparticles

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Received 4 May 2005; received in revised form 27 July 2005; accepted 3 August 2005
Available online 22 September 2005

Abstract

A polyether-type polyurethane (PU) containing silver (Ag) nanoparticles (4–7 nm, 1.51×10^{-3}–1.13×10^{-2} wt-%) was prepared by mixing the waterborne PU with the nanoparticle suspension, casting and drying at 60 °C. The Ag nanoparticles were found to be well dispersed in PU. A significant increase in the thermal stability and mechanical properties of the polymer was demonstrated in the nanocomposite PU films, which was believed a result of induced crystallization in the presence of Ag nanoparticles. The biostability was tested in a rat subcutaneous model. After 19 days of implantation, the PU containing Ag showed enhanced biostability and lowered foreign body reaction. The effect of Ag on the stability of the PU polymer was even more remarkable over a wider range of particle contents than that of the gold nanoparticles previously studied.

Keywords: Biodegradation; Biostability; Foreign body reaction; Microphase separation; Thermostability

1. Introduction

Numerous studies have been performed on the preparation of new polymer–metal hybrid materials and nanocomposites. They have been reported to exhibit markedly improved properties as compared to the pure polymers [1–10], including an increase in modulus and strength, and in chemical and heat resistance. As a consequence, such hybrid materials may offer various potential applications in different fields such as catalysts, non-linear optical materials, conductive composites, and biomaterials [11–14].

Polyurethanes are commonly used as biomaterials due to their good biocompatibility and mechanical properties. Device-associated oxidative biodegradation, however, is common [15,16]. The oxidative biodegradation is associated with the highly reactive oxygen species produced by the macrophages and other phagocytes during inflammation [17]. Various techniques such as modification of the chemical structure or fabrication of hybrid inorganic materials have been proposed to enhance their thermal properties and biostability [18–22]. We have previously reported that the physical properties as well as the biostability of PTMO-based waterborne polyurethane were enhanced by gold nanoparticles [9,10].

In this paper, the effect of silver nanoparticles, 4–7 nm in diameter, on PTMO-based waterborne polyurethane films (1.51×10^{-3}–1.13×10^{-2} wt-% Ag) was

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doi:10.1016/j.polymdegradstab.2005.08.001

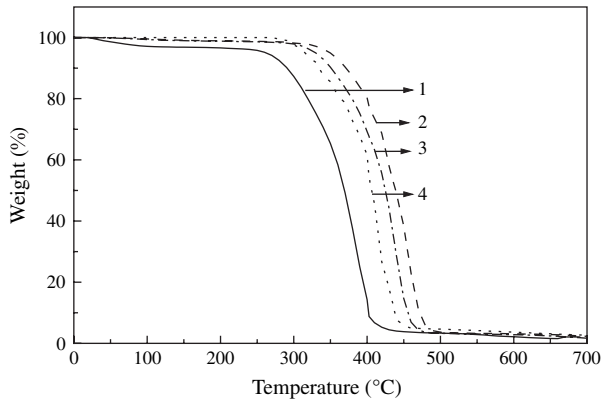

Fig. 1. Thermal properties of PU-Ag nanocomposites TGA curve (pure PU (1) and the nanocomposites filled with 3.02×10^{-3} wt-% (2), 7.55×10^{-3} wt-% (3) and 1.13×10^{-2} wt-% (4) of Ag nanoparticles).

studied by thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA) and a rat subcutaneous model. The effect of Ag on PU was compared with that previously reported for Au.

2. Experimental

2.1. Polyurethane synthesis

The waterborne PU used in this study was prepared from an acetone process as described earlier [9]. Briefly, poly(tetramethylene glycol) (PTMO: 2000 g/mol; Coating Chemical Industrial Co., Taiwan) and methylene dicyclohexane diisocyanate (H_{12}MDI; Jiuh Yi Chemical Industrial Co., Taiwan) were charged into a four-neck kettle reactor equipped with nitrogen inlet, outlet, mechanical stirrer and a thermometer. The reaction took place under nitrogen flow at 70 °C. When the end-point of the reaction had been reached, acetone was added to the reaction kettle and the reaction mixture was cooled to room temperature. It was followed by the addition of *N*-(ethylene sulfonate sodium salt) ethylene diamine (EES-200L; 45% aqueous solution; Jiuh Yi Chemical Industrial Co., Taiwan) and allowed to stir for an additional 30 min. Deionised water was introduced into the reaction mixture with vigorous stirring. After the addition of deionised water, ethylene diamine (TCI) was put into reaction mixture for further chain extension. Finally, acetone in the reaction mixture was removed under vacuum.

2.2. Preparation of PU-Ag composites

PU-Ag nanocomposite films (1.51×10^{-3}–1.13×10^{-2} wt-%) were prepared by adding a certain calculated volume of Ag nanoparticle (27.2 ppm/ml; 4–7 nm; Global Nanotech Industries Ltd., Taiwan) suspension into 10% aqueous solution of PU. The mixture was cast onto Teflon plates, dried at 60 °C for 48 h, followed by further drying in a vacuum oven at 60 °C for 72 h to remove any residual solvent. The films were stored in a desiccator at room temperature.

2.3. Morphology, thermal properties and storage modulus

Thermogravimetric analysis (TGA) was carried out with a thermogravimetric analyser (TA Instrument, TGA 2050). Samples of 5 mg each in a Pt crucible were used with a heating rate of 10 °C/min under nitrogen. A JEOL JSM-6700F field emission scanning electron microscope (FESEM) was used for studying the microstructure of the PU-Ag nanocomposites. It was operated at a working distance of 11 mm, an acceleration voltage of 5 kV and a beam current of 1×10^{-10} A. The specimens were made conductive with a 3-nm layer of gold using a Cressington Rotating Magnetron Sputter Coater operated at a working distance of 150 mm and a current of 20 mA. The morphology was examined by means of transmission electron microscopy

Table 1
A comparison of mechanical and thermal properties of pure PU, PU-Ag and PU-Au nanocomposites

	Storage modulus, E' (MPa)				T_g (°C)	T_{onset} (°C)	T_p (°C)
	−100 °C	−20 °C	37 °C	60 °C			
Pure PU	1040	21.5	14.3	10.9	−56.2	310	370
1.51×10^{-3} wt-% Ag	1110	27.8	15.8	13.0	−52.0	335	379
3.02×10^{-3} wt-% Ag	2840	61.4	31.1	23.6	−39.5	387	438
7.55×10^{-3} wt-% Ag	1910	33.1	17.9	15.5	−45.2	377	426
1.13×10^{-2} wt-% Ag	1650	30.6	16.3	14.3	−50.2	357	406
1.74×10^{-3} wt-% Au[a]	2330	45.5	23.5	20.9	−35.6	370	417
4.35×10^{-3} wt-% Au[a]	3020	66.2	33.0	29.9	−36.0	379	423
6.50×10^{-3} wt-% Au[a]	719	12.1	6.1	4.9	−50.6	338	380

T_{onset}: onset temperature of pyrolysis; T_p: peak pyrolytic temperature; T_g: glass transition temperature; E': storage modulus.
[a] Some of the data from ref. [9].