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Fabrication of honeycomb-patterned poly(ε-caprolactone) composite films containing chemically modified silver nanoparticles

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ABSTRACT

Biocompatible composites containing poly(ε-caprolactone) (PCL) were prepared by incorporating different weight percentages of silver (Ag) nanoparticles with the particle size of about 10 nm modified by dodecanethiol. The synthesized PCL/Ag composites were characterized by Fourier transform infrared and UV–vis spectroscopy, and the surface morphology of these composites was identified by scanning electron microscopy and transmission electron microscopy. Honeycomb-patterned thin films with the film thickness of 20–30 μm was fabricated by casting the composite solution under humid conditions without separation of Ag nanoparticles due to the chemical modification. The dependence of the DC conductivity and pattern structure of the thin films on Ag concentration was studied.

1. Introduction

Over the past two decades, aliphatic polyesters, such as poly(ε-caprolactone) (PCL), have been intensively studied for their hydrolyzability in the human body and under natural circumstances [1,2]. PCL attracts considerable interest for its low cost, sustained biodegradability, and availability at a low molecular weight [3]. Owing to its hydrolyzability in the human body, PCL has been considered in a wide range of possible applications, such as biodegradable packaging materials, implantable biomaterials, and microparticles for drug delivery [4].

The PCL is a suitable material for forming composites with many functional materials, including conductive materials, by in-situ polymerization of ε-caprolactone in the presence of functional components [3,4].

The preparation of nanostructured PCL polymer composites using reinforcing materials, such as starch, clay, and carbon nanotubes metal nanoparticles has recently attracted significant attention because such composites exhibit excellent physical, mechanical, and electrical properties with biocompatibility [5]. Ag is typical among metal nanoparticles (NP) because it has high optical excitation efficiency and strong three-order nonlinear optical susceptibility $x^{(3)}$ [6]. Thus, Ag-dispersed polymers have received considerable attention [7] because the resulting nanocomposites can be used as catalysts, drug and wound dressings, optical information storage, and for surface-enhanced Raman scattering, among others [8]. However, the preparation of homogeneously Ag-dispersed PCL composites is not easy because the nanoparticles easily agglomerate. Thus, convenient and effective ways of preparing Ag-dispersed PCL composites are yet to be found.

In this study, conductive PCL polymer composites containing different weight percentages of chemically modified Ag nanoparticles were synthesized by the ring opening polymerization of ε-caprolactone. The synthesized PCL/Ag composites were characterized by Fourier transform infrared and UV–vis spectroscopic methods. Honeycomb-patterned polymer films were produced with the aid of water droplets in a volatile solvent under humid conditions. Room-temperature DC conductivity and pattern structure of the films depending on the concentration of Ag nanoparticle was studied.

2. Experimental

Materials: Sodium borohydride ($NaBH_4$ > 95.0%) and dodecyl trimethylammonium bromide (DTAB, ≥ 98.0%) were purchased from TCI Fine Chemicals. $AgNO_3$, 1-Dodecanethiol (≥ 98%), ε-caprolactone, stannousoctoate ($Sn(Oct)_2$, > 95%) and other reagents were purchased from Sigma-Aldrich and used as received.

Preparation of dodecanethiol-stabilized Ag nanoparticles: Dodecanethiol-stabilized Ag nanoparticles were synthesized according to a common two-phase procedure [9]. 30 mL aqueous solution of 0.5 M $AgNO_3$ was combined with 20 mL of toluene solution containing 0.2 M DTAB as a phase transfer agent and then vigorously stirred for 1 h. In the mixture, 150 μL of 1-dodecanethiol was added. After the

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mixture was stirred for 15 min, the Ag ions were reduced by introduction of 24 mL of aqueous 0.43 M $NaBH_4$ solution and then stirred for 24 h. The organic phase including Ag nanoparticles was isolated from the aqueous phase through phase separation. The Ag nanoparticles were washed in excess ethanol and acetone to remove the residual phase transfer catalyst and unbound thiol in the organic phase. The obtained Ag nanoparticles were well dispersed in organic solvents without aggregation due to the modification by 1-dodecanethiol. The particle size of Ag nano particles was about 10 nm, however, small varied in the range within 5 nm depending on the added amount of 1-dodecanethiol and stirring time with phase transfer agent.

Synthesis of PCL/Ag composites: An exactly determined amount of dodecanethiol-stabilized Ag nanoparticles and 20 mL of ε-caprolactone were placed in a three-neck round-bottom flask. The mixture was sonicated at room temperature for 1 h to produce a homogenous dispersion of Ag nanoparticles in ε-caprolactone, and 0.03 mL of $Sn(Oct)_2$ was added to the suspension. The flask was then transferred to a preheated oil bath at 170 °C, which was heated for 24 h by mechanical stirring under a nitrogen atmosphere. The resulting solidified polymer composites were filtered and dissolved in tetrahydrofuran. Thereafter, the synthesized PCL composite was precipitated by a large amount of cold methanol and washed with methanol and ethanol several times, after which it was dried at 40 °C for 48 h in a vacuum. The same procedure was also adopted for the PCL homopolymer without addition of Ag nanoparticles for comparison. PCL composites containing y wt% of Ag nanoparticles in the polymerization process are hereafter denoted as PCL/Ag-y. The overall experimental scheme for the synthesis of the PCL/Ag polymer composite is shown in Fig. 1.

Characterization: The infrared spectra of the PCL/Ag composite samples, which were pelletized with potassium bromide, were obtained using an FTIR spectrophotometer (Perkin-Elmer 1600). Approximately 60 scans were signal-averaged with a resolution of 2 cm^{-1} from 4000 to 400 cm^{-1}. The UV–vis spectra of the samples in chloroform were obtained using a spectrophotometer (Shimadzu UV-3101PC). The surface morphology of the synthesized PCL/Ag composite powders was investigated using a scanning electron microscope (SEM) (COXEM-CX100s) and a transmission electron microscope (TEM) (JEM-2000, JEOL).

Fabrication of honeycomb-patterned thin films for PCL and PCL/Ag composites: The fabrication procedure for honeycomb-patterned thin films by casting the polymer solution under humid conditions was introduced in our previous reports [10,11]. A solution of composites in chloroform was casted on a 40 mm diameter glass Petri dish at 20 °C and 60% relative humidity. An opaque film was obtained after the complete evaporation of the solution under humid conditions. To obtain a highly ordered honeycomb-patterned structure, water evaporation was applied to the solution

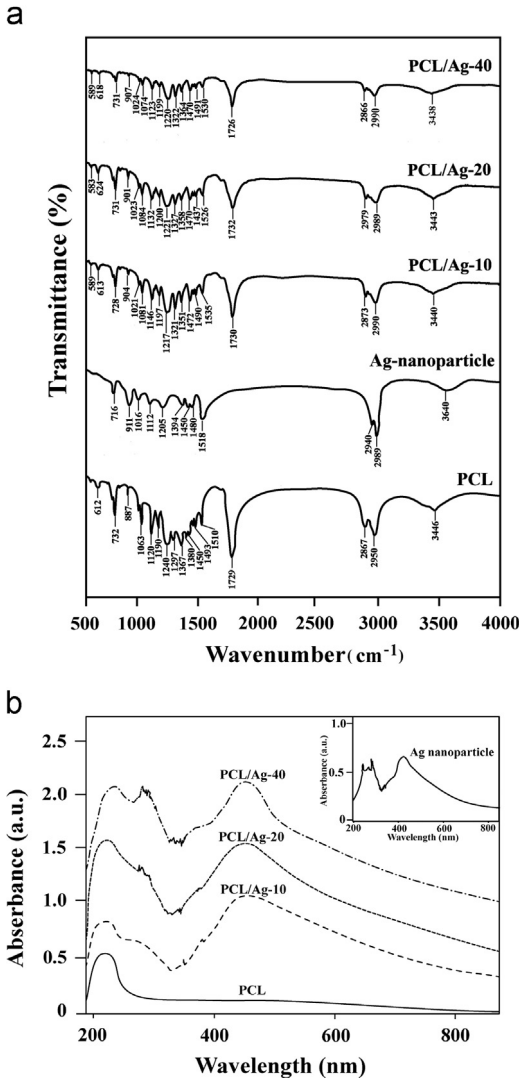

Fig. 2. (a) The FTIR spectra of PCL, Ag nanoparticles, PCL/Ag composites; (b) the UV–vis spectra of PCLand PCL/Ag composites. The inset figure shows the spectra of Ag nanoparticles.

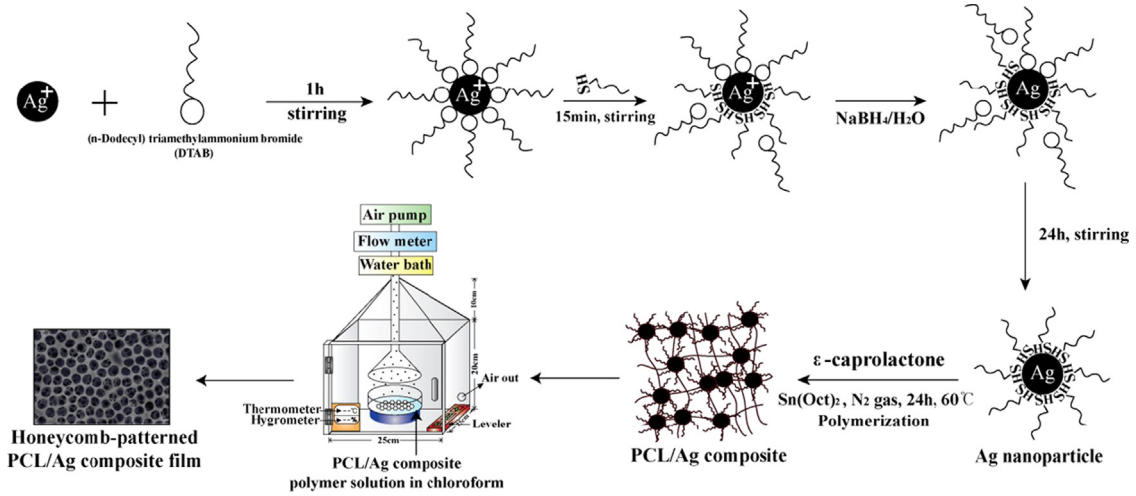

Fig. 1. Experimental scheme for the preparation of PCL/Ag composites.