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Surface modification of poly(ethylene terephthalate) (PET) film by gamma-ray induced grafting of poly(acrylic acid) and its application in antibacterial hybrid film

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ABSTRACT

Acrylic acid (AA) was facilely grafted onto poly(ethylene terephthalate) (PET) film through gamma-ray induced graft copolymerization. Silver nanoparticles produced by the chemical reduction of silver ions were then immobilized by carboxylic anions and embedded on the surface of PET-g-PAA film. It was found that the DG of PAA on PET film increases with the absorbed dose and would finally control the amount of loaded silver nanoparticles. The prepared PET-g-PAA/Ag hybrid films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). The bactericidal activity of the PET-g-PAA/Ag hybrid film was evaluated by the efficiency of killing *Escherichia coli*. The results showed that the PET-g-PAA/Ag hybrid film has a strong and stable antibacterial activity.

1. Introduction

Poly(ethylene terephthalate) (PET) is a kind of well-known engineering plastic. Its application area has been expanded widely in household appliances, cosmetics, clothing, and medical materials because of its good mechanical strength, good stability in the presence of body fluids, and high radiation resistance (Bisson et al., 2002; Gupta et al., 2002; Jeon et al., 2004; Massia et al., 2000). Considering the health care in these applications, improving the antibacterial properties of PET is necessary. Thus, various types of modification methods have been developed to enhance the antibacterial properties of PET film and fabric (Cen et al., 2003; Huh et al., 2001; Jou et al., 2007; Kim et al., 2009; Shi et al., 2004, 2005). In recent years, silver nanoparticles have attracted considerable attention for their effective biocidal ability and non-toxicity to human beings (Koga et al., 2009; Kong and Jang, 2008; Morones et al., 2005; Nino-Martinez et al., 2008; Shi et al., 2004; Xu et al., 2006). Therefore, many research works have focused on how to load the silver nanoparticles on material surfaces. Kang et al. modified the surface of a PET film by grafting viologen groups and then precipitated silver nanoparticles on the film. They found that the antibacterial property of PET film had been significantly enhanced (Shi et al., 2004). Jin et al. embedded silver nanoparticles on silica nanospheres using poly(acrylic acid) as a soft template. The hybrid nanospheres exhibit excellent bactericidal activity (Jiang et al., 2007). Obviously, grafting polymer chains with functional groups on the surface of PET film is very important for the loading of bactericidal silver nanoparticles. But the molecular chains of PET have good chemical and thermal stability. It is difficult to modify PET chains through the traditional in situ radical graft polymerization.

γ-Ray induced graft copolymerization has been applied for many years to develop new functional materials (Bhattacharya and Misra, 2004; Chen et al., 2005, 2006; Gupta et al., 2008; Khayet et al., 2005). The major advantages of radiation grafting reaction are as follows: (a) the extensive radical penetration in the polymer matrix and rapid radical production to initiate graft polymerization; (b) the reactions can be conducted at room temperature and in gaseous, liquid or even solid-state phase. In the present paper, acrylic acid (AA) was grafted onto PET film by γ-ray induced graft copolymerization. The carboxylic anions on the grafted poly(acrylic acid) (PAA) chains can immobilize silver ions. After an in situ reduction process, silver nanoparticles can be embedded onto the surface of PET film and an antibacterial PET-g-PAA/Ag hybrid film can be prepared finally. The principle of the preparation of PET-g-PAA/Ag hybrid film is illustrated in Scheme 1. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) were used to characterize the modified PET film. The bactericidal activity of hybrid PET films was evaluated by the efficiency of killing *Escherichia coli* (*E. coli*).

2. Experimental

2.1. Materials

PET film with a thickness of 25 μm was provided by Shanghai BangKai Co., China. Chemical-grade acrylic acid (AA; Shanghai

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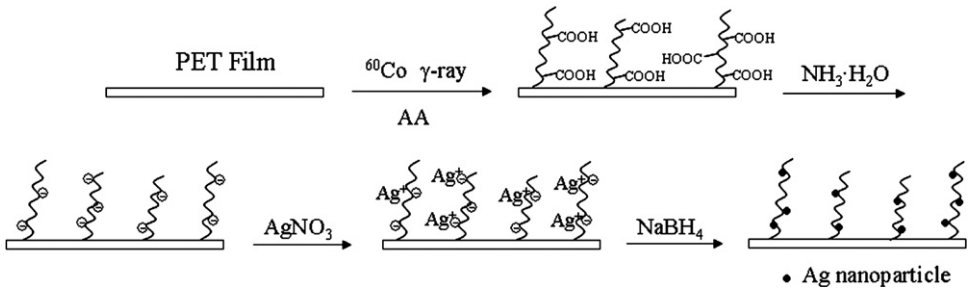

Scheme 1. Schematic illustration of preparation of PET-g-PAA/Ag hybrid film.

Chemical Reagents Co.) was purified by vacuum distillation and stored at −20 °C prior to use. Acetone, ferrous sulfate hydrate ($FeSO_4 \cdot 7H_2O$), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and aqueous ammonia ($NH_3 \cdot H_2O$, 25 wt%) were all purchased from Shanghai Chemical Reagents Co., China, and all reagents were analytical grade and used as received. De-ionized water (resistivity > 18.2 MΩ cm/25 °C) prepared by a Milli-Q 185 system (Millipore, USA) was used for all experiments. Peptone, yeast extract, and agar were obtained from Oxoid. *Escherichia coli* DH5α (Gram-negative bacteria) was obtained from Hefei National Laboratory for Physical Sciences at Microscale and School of Life Sciences (University of Science and Technology of China, Hefei, China).

2.2. Preparation of PET-g-PAA films by γ-ray induced graft copolymerization

PET film with a size of 2.5 cm × 2.5 cm was washed with acetone, and then dried in a vacuum oven at 60 °C for 12 h. The dried film was put in an ampoule and immersed in de-ionized water containing AA monomer. $FeSO_4 \cdot 7H_2O$ was added to the grafting solution at a concentration of 1 wt%. After bubbling nitrogen to the reaction solution for 10 min to remove the dissolved oxygen, the ampoule was sealed and irradiated by a 1.11×10^{15} Bq ^{60}Co γ-ray radiation source (located in USTC, China) under a dose rate of 1.46 kGy/h for a certain time. The film was then taken out of the solution and extracted in a Soxhlet system using de-ionized water as solvent for 24 h to remove PAA homopolymer and unreacted AA monomers. Finally, the grafted film was dried in a vacuum oven at 60 °C until a constant weight was obtained.

2.3. Loading silver nanoparticles on PET-g-PAA film

The PET-g-PAA film was placed in a beaker that contained 30 mL of de-ionized water and 0.5 mL of $NH_3 \cdot H_2O$. The solution was sonicated for 3 min and continuously stirred at room temperature for 2 h. Then the film was washed with de-ionized water until the pH of the aqueous phase approached 7.0 (at least three cycles with ca. 30 mL de-ionized water). Subsequently, the PET-g-PAA film was placed in a beaker that contained de-ionized water (20 mL). $AgNO_3$ aqueous solution (10 mL, 0.01 M) was added dropwise to the beaker under vigorous stirring. The mixture was stirred at room temperature for 3 h in a nitrogen atmosphere to ensure that the silver ion (Ag^+) was adsorbed on the PAA chains. Afterwards, the Ag^+ immobilized PET film was washed thoroughly using de-ionized water to remove residual $AgNO_3$ and re-immersed in de-ionized water (20 mL). A brownish color formed immediately after adding 10 mL of 0.05 M $NaBH_4$ under vigorous stirring. After stirring at room temperature for 3 h, the film was washed with de-ionized water to remove the residual salts at least four cycles in an ultrasonic bath for ca. 10 min per cycle. The PET-g-PAA/Ag hybrid film was then dried in vacuum oven at 50 °C until a constant weight was obtained.

2.4. Characterization

The degree of grafting (DG) of the PET film is defined by the following Eq. (A):

$$\mathrm{DG} = \frac{W_g - W_o}{W_o} \times 100\% \quad \text{(A)}$$

where W_g and W_o are the weight of the grafted and original PET films, respectively. X-ray diffraction patterns (XRD) were recorded on a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with monochromatized CuKα radiation ($\lambda = 1.54056$ Å). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using an MgKα line (1486.6 eV) as the excitation source under high vacuum (5×10^{-9} Pa). Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere at a scan rate of 10 °C/min with a Shimadzu DTG-60H thermal analyzer.

2.5. Antibacterial activity tests

E. coli was cultivated in sterilized Luria–Bertani (LB) medium (containing 10 g/L peptone, 5 g/L sodium chloride, and 5 g/L yeast extract at a pH of 7.0) at 37 °C. All glassware and polymer samples were sterilized in an autoclave at 121 °C for 20 min or with 70% ethanol solution before the experiments.

The bacterial suspension was centrifuged at 2700 rpm for 10 min. After removing the supernatant, the cells were washed twice with a sterile phosphate buffer solution (PBS) and resuspended in PBS at a concentration of 10^8 cells/mL. One piece of the PET film (original or grafted) with a size of 1 cm × 1 cm was immersed in 5 mL of the above prepared suspension in a test tube and shaken at 200 rpm at 37 °C. For the kinetic test, 0.8 mL of bacterial culture was taken from the test tube every 1 h, and diluted ten times (× 10) with PBS serially. 0.1 mL of the diluted sample was spread onto LB agar plates using a surface spread plate technique. After incubation of the plates at 37 °C for 12 h, the number of colony-forming units (CFU) was counted manually. The mean CFU per milliliter was expressed as the value of the counted CFU after multiplication with the dilution factor. The antibacterial efficacy (ABE) of the specimen was calculated according to Eq. (B)

$$\mathrm{ABE} = \frac{V_o - V_t}{V_o} \times 100\% \quad \text{(B)}$$

where V_o is the number of CFU in the blank solution (pure PBS buffer solution) and V_t is the number of CFU in the test specimen solution.

3. Results and discussion

3.1. PET-g-PAA films

It has been reported that the PET backbone can produce two kinds of free radicals under γ-ray radiation, but the predominant