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The influence of polyethylene terephthalate surfaces modified by silver ion implantation on bacterial adhesion behavior

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Abstract

The prevention of medical device related infection remains an important concern because of the high risk of complications. Efforts to prevent bacterial colonization of biomaterials have focused on surface modification. This paper investigates the antibacterial behavior of polyethylene terephthalate (PET) surfaces modified by ion implantation with silver ions (Ag^+). PET films were modified by silver ion implantation at a dose of 1×10^{16} ions/cm^2. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the surface structure and composition. The results indicate that silver was successfully implanted into the surface of the PET. The static contact angle of water decreased from an original value of 83.5° to 67.6° following Ag^+ implantation, which suggests that the hydrophilic property of the modified PET is improved. The quantity of *Staphylococcus epidermis* (SE) adhered onto the different PET films was quantitatively determined using colony forming units (CFU) plate counting *in vitro*. The results indicate that the quantity of SE adhered onto PET films implanted with Ag^+ is 5.3×10^6 CFU/ml, but the quantity of SE adhered onto virgin PET films is 2.23×10^7 CFU/ml. The releasing concentration of silver ions from the implanted PET is 0.22 mg/ml over 2 h. The release of antibacterial silver ions may be an important reason for less SE adhered to the PET surface modified by Ag^+ implantation. The free energy of adhesion (DF_{Adh}) of SE on the PET surfaces modified by Ag^+ implantation is positive, which means that this adhesion is energetically unfavorable.

Keywords: Polyethylene terephthalate (PET); Bacterial adhesion; Surface modification; Ion implantation; Silver ion

1. Introduction

Poly (ethylene terephthalate) (PET) has been widely used as an important biomedical material in cardiovascular implants such as artificial heart valve sewing rings [1,2] and artificial blood vessels [3,4] because of its excellent mechanical properties and moderate biocompatibility. However, Biomaterial Centered Infection (BCI) turns out to be a serious problem that frustrates clinical application of implanted biomedical materials [5]. BCI occurs with high probability and the problem causes high rates of mortality and morbidity and significant increases health care costs [6–8]. In particular, the incidence of prosthetic valve endocarditis (PVE) is about 2%–3% in patients undergoing valve replacement, with *Staphylococcus epidermis* (SE) accounting for about 30% overall of these infections [9]. Such devices generally involve artificial materials in contact with living matter at a surface, which is an easy channel for bacterial proliferation. In order to prevent bacterial adhesion and colonization of biomaterials, some studies have focused on modification of the polymer surfaces to induce bactericidal properties and preserve at the same time the bulk mechanical properties of the device. Silver coating [10–12], surface-immobilized polyethylene oxide [13], surface thiocyanation [14], and surfaces modified by various gas plasmas (such as oxygen and H_2O) [15,16] have been proposed to improve the antibacterial properties. Surface engineering techniques such as ion implantation induce new surface

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properties without altering the bulk properties as only a small thickness of the material is involved. Thus ion implantation has been widely used to modify the surfaces of biomedical materials. Silver is often applied as an antibacterial material because it possesses antimicrobial activity and low human toxicity.

This paper focuses on silver ion implantation into PET films. The bacterial properties of the original and the Ag^+-implanted PET films were evaluated by CFU plate counting *in vitro*. Other characterization tests, such as static contact angle measurement, XPS, XRD and atomic absorption spectrometry (AAS) were also carried out to study the Ag^+-modified PET surfaces. This work may provide an approach to design modified polymer surfaces to repel bacteria and consequently reduce the infection risk.

2. Materials and methods

2.1. Materials

PET films 0.1 mm thick supplied by 3M were cut into rectangular shape 14×10 cm^2 in size and washed successively and ultrasonically in methanol, acetone and distilled water for 10 min and dried in a purified biological desiccator.

2.2. Ion implantation

The PET films were laid on stainless-steel substrates attached to an insulated negative electrode in the center of the vacuum chamber. A negative voltage was then applied to the electrode. A DLZ-100 ion implanter made by the Southwestern Institute of Physics of China was used with a 10 mm diameter silver (99.99%) cathode. The base pressure was 1.0×10^{-3} Pa. The substrates were cooled during implantation by a water-cooling system. The implantation process adopted interval implantation (implantation time 10 min; interval time 1 min) at 20 kV acceleration voltage and a dose of 1.0×10^{16} ions/cm^2.

2.3. Surface characterization

XRD measurements were carried out with a Philip X'Pert Pro diffractometer using Cu K_a at 1° glancing angle. X-ray photoelectron spectroscopy analysis was performed to characterize the surface composition of the PET films using the XSAM800, KRATOS system. The energy of the X-ray source was 1253.6 eV operated at 14 kV, 350 W.

2.4. Contact angle measurements

Static contact angle measurements by sessile drop technique using a JY-82 contact angle goniometer were conducted at 25 °C with doubly distilled water, formamide and diodomethane as wetting agents. Each droplet was about 10 ml. Every determination was obtained by averaging the results of at least 6 measurements. In the case of bacterial cells, the measurements were performed on the bacterial layers deposited on filter membranes according to the method described by Busscher et al. [17].

2.5. Silver ion release rate measurements

Atomic absorption spectroscopy (AAS) was used for the quantitative determination of the silver ion concentration released from the PET surface. PET films modified by silver ion implantation were cut into square 15×15 mm^2 in size and immersed in 100 ml doubly distilled water stirred by a magnetic stirrer at 120 rev/min. The liquids were taken out at designated times and the concentration of Ag^+ was measured by atomic absorption spectrophotometer (316MC, Shanghai Analytical Instrument Factory, China).

2.6. Quantification of bacteria adhesion in vitro

Bacterial adhesion testing was performed *in vitro* by the CFU plate counting method, which is the most basic method for bacterial enumeration. The bacterium used in this study was *Staphylococcus epidermis* (SE) (ATCC8023).

PET films were cut into 10 mm × 10 mm size and sterilized at 121 °C temperature and 0.15 Pa. The samples were put into the bacterial suspension and incubated at 37 °C. A control plate

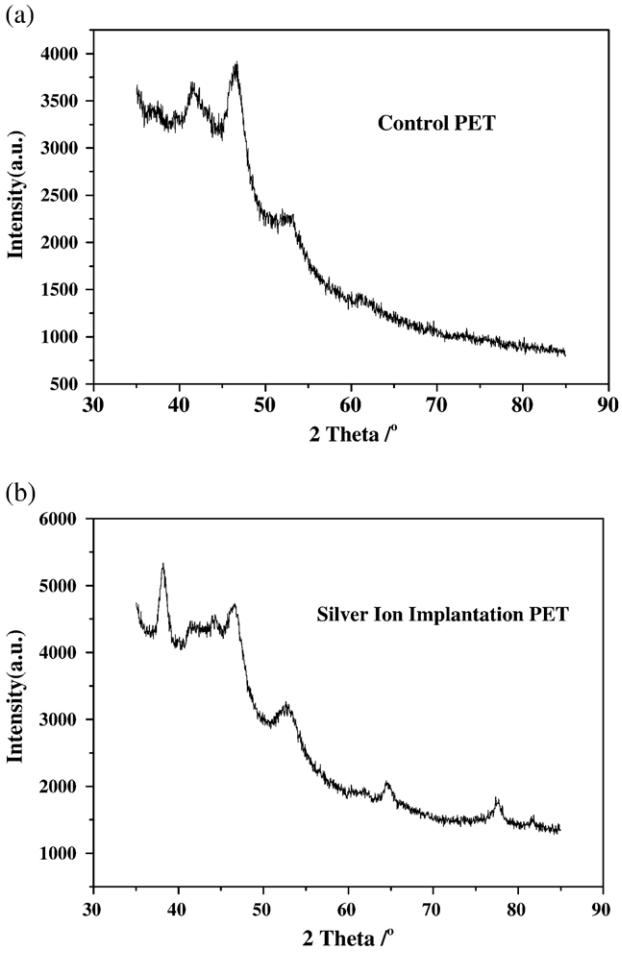

Fig. 1. XRD patterns of PET sample: (a) control; (b) silver ion implantation.