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Surface modification on polyethylene terephthalate films with 2-methacryloyloxyethyl phosphorylcholine

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ABSTRACT

In this study, the surface of polyethylene terephthalate (PET) was modified to improve the protein and cell adhesion behavior with low temperature ammonia plasma treatment followed by 2-methacryloyloxyethyl phosphorylcholine (MPC) grafting. The x-ray photoelectron spectroscopy (XPS) results showed that the $-COO^-$, $-N-C{=}O$ and $-P-O-H$ groups were successfully incorporated onto the sample surface after MPC grafting. Furthermore, formation of new bonds, $-N{=}$ and $N-H$ on the sample surface grafted with MPC was recorded by Fourier transform infrared spectroscopy (FTIR). A large number of spherical particles at submicron to nanometer scale were also observed on the surface by atomic force microscopy (AFM). The cell adhesion experiments on PET film surfaces were evaluated and the highly hydrophilic surfaces could not promote cell adhesion and spreading. All results achieved in this study have clearly indicated that the method combining low temperature ammonia plasma treatment and MPC grafting is an effective way of producing a suitably hydrophilic PET surface with the capability of weakening the protein adsorption greatly.

1. Introduction

Surface properties of biopolymers are believed to be crucial in defining the interaction between cells and materials, which influence the formation of new tissues around the materials. Functionalization of biopolymer surfaces using plasma-induced graft polymerization is a feasible, simple and economic method to modify material surfaces with relatively thin layer of chemical groups or monomers without impairing materials' bulk properties [1–3]. Graft polymerization is defined as a process which begins with the activation of certain chemical groups of polymers acting as reaction centers on the polymer surface by exposing to the plasma irradiation, followed by the reactions between the activated groups and functional monomers which are triggered on the polymer surface[4]. Only stable free radicals retained on polymer surfaces can serve as active sites to initiate subsequent graft polymerization, since unstable free radicals will rapidly combine to form stable species, i.e. so called the termination of a chain reaction.

Polyethylene terephthalate (PET) is a type of polymer with highly symmetrical molecular structure which has been used and studied widely as biomaterials for its excellent physical and mechanical properties and chemical stability in human body fluid. It is often used to construct artificial vessel, heart ale closure, cardiac patches, artificial ligaments and surgical suture [5]. Yet the hydrophilicity and blood compatibility of PET are relatively poor due to its symmetrical molecular structure, high crystallinity and the absence of high polar groups on the surface. Modification of such material by introducing active groups on the surface is therefore desired for enhancing the hydrophilic and anticoagulant properties [6]. An effective way to achieve surface anti-aggregation functionality of PET films is the polar group graft. 2-Methacryloyloxyethyl phosphorylcholine (MPC) is a methacrylate monomer having a zwitterionic phosphorylcholine head group in its side chain, which is expected to provide hydrophilic surfaces and prevent cell/bacterial adhesion. Goda et al. [7] studied the biomimetic phosphorylcholine polymer grafting from polydimethylsiloxane surface using photo-induced polymerization. In Sugiyama's study [8], the vinyl monomers on the surface of PET film were grafted using Ar plasma-post polymerization technique to improve its biocompatibility. The MPC grafted surface was later evaluated and showed an excellent surface hydrophilicity, anti-biofouling property and oxygen permeability. The improved biocompatibility by MPC grafting is contributed by the phosphorylcholine groups which exist at the interface between the polymer and the biological environment [9].

It was reported previously that the hydrophilicity of PET film can be enhanced by modifying its surface using low temperature ammonia plasma, which could reduce the protein adsorption greatly [10]. In this paper, MPC was integrated on the ammonia plasma modified PET surface to improve its hydrophilicity furthermore. The human serum albumin (HSA) was used to evaluate the material protein

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adsorption behavior on the material surfaces which were immersed in a biological medium [11]. X-ray photoelectron spectrometer (XPS), contact angle measurements, Fourier Transform Infrared Spectroscopy (FTIR), atomic force microscope (AFM) and scanning electron microscope (SEM) were employed to characterize the chemical structure, hydrophilicity and the morphology of the film surface. Compared with the PET films treated by ammonia plasma only, the sample surface modified with both plasma and MPC grafting exhibited improved hydrophilicity and anti-adhesion ability of proteins or cells.

2. Experiment

PET films (DuPont) with a thickness of 250 μm were supplied by DuPont Teijin Films TM. They were ultrasonically cleansed in acetone and absolute ethyl alcohol separately for 15 min and then washed with distilled water and dehydrated at room temperature before plasma treatment. MPC was provided by Joy-Nature Institute of Technology (China) with a purity of 95%. HSA solution was purchased from Sigma and used without further purification, which was prepared in phosphate buffer saline (PBS; 6.44 mM KH_2PO_4, 8 mM Na_2HPO_4, 140 mM NaCl), stored at 8 °C and used within a week. The DL-01 model plasma generator (Suzhou Omega Machinery Electronic Technology Co., Ltd. China) was used in this study. PET films were treated in the plasma chamber with ammonia atmosphere at the pressure of approximately 20 Pa for 30 to 300 s with the plasma power ranging from 25 to 150 W.

The PET films were first treated by ammonia plasma under certain vacuity, plasma power and exposure time and then immersed into MPC aqueous solutions with different concentrations of 5, 10 and 15 mg/ml for more than 2 h with magnetic stirring. Next, the samples were flushed with double-distilled water to remove the extra homopolymer, dehydrated under room temperature and stored in desiccators.

The wetting tests were studied by contact angle measurement (Data Physics OCA15, Ger.) with 1 μl distilled water injection. X-ray photoelectron spectroscopy (XPS) spectrometer (Axis Ultra^{DLD} system, Kratos Analytical, UK) was used with a monochromatic Al Kα X-ray source (1486.7 eV). The survey spectra were collected with pass energy of 160 eV under scanning rate of 1 eV/step over a range of 1110 eV, while high-resolution region scans were collected with pass energy of 40 eV under scanning rate of 0.1 eV/step. Binding energy was calibrated by C 1s of C–C (C–H) as 284.8 eV. FTIR characterizations were performed at ambient temperature with a Nicolet 5700 spectrometer (Thermo Electron, Madison, WI, US) in transmission mode. The adsorption of HSA onto the grafted PET films was carried out with the concentration of 40 mg/ml at pH 7.4 PBS solutions. The surface morphology of samples with MPC grafting was characterized using AFM (MFP-3D-S, Asylum Research, US) under Tapping Mode. Cell attachment was assessed through a field emission scanning electron microscopy (Leo 1530 VP) study with accelerating voltage of 15 kV. The ATDC5 cell line was obtained from the RIKEN cell bank (Tsukuba). The cells were cultured in maintenance medium consisting of a 1:1 mixture of Dulbecco's modified Eagle's medium and Ham's F-12 medium (Invitrogen) supplemented with 5% fetal bovine serum (Gibco) at 37 °C in a humidified 5% CO_2/95% air atmosphere. ATDC5 cells were seeded at 1×10^4 cells/cm^2 on the film surfaces, and cultured in maintenance medium. After seeding for 24 h, the cell-film constructs were washed twice with PBS and fixed in 2.5% glutaraldehyde, dehydrated in a graded ethanol series to 100% ethanol, air dried and sputtering-coated with gold palladium before observing.

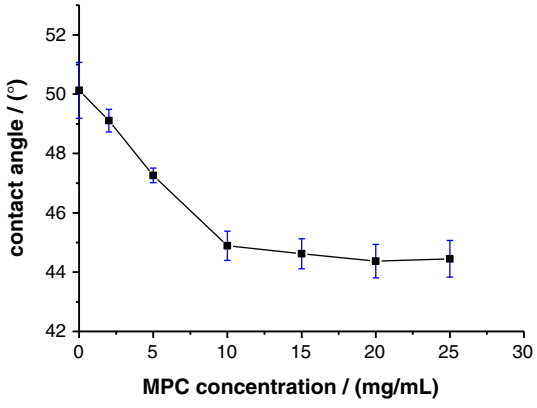

Fig. 1. Changes of surface contact angle with different MPC concentration grafting (50 W, 120 s, 30 Pa).

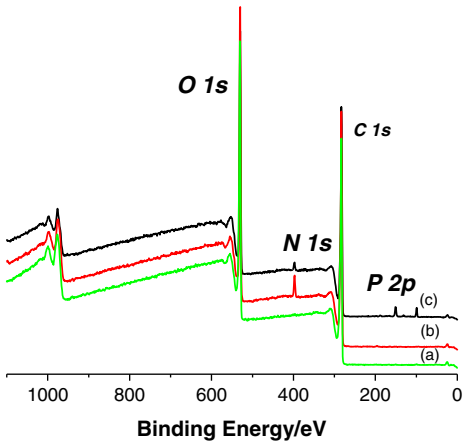

Fig. 2. XPS spectra of PET films before and after MPC grafting: (a) untreated, (b) treated by NH_3 plasma only, and (c) with 10 mg/ml MPC grafting.

3. Result and discussion

3.1. Water contact angle

The method of static contact angle was used to evaluate the hydrophilicity of the samples throughout the experiments. The water contact angles of PET films were recorded to decrease sharply after ammonia plasma treatment in previous studies [10]. A series of oxygen, nitrogen-containing polar groups were generated on PET surface with the active particles from highly excited ammonia plasma via etching or crosslinking effects. The effect of plasma on improving the wettability of PET films was shown in Fig. 1. The water contact angle decreased from 50.1 before ammonia plasma treatment only to 49.1° when the samples were treated with 2.5 mg/ml MPC, and then the angle dropped further to 44.9° by increasing the MPC

Table 1
Surface elemental compositions (at. %) of PET before and after MPC grafting.

	C	O	N	P	O/C	N/C	O/N	O/P
1	76.50	23.50	–	–	0.31	–	–	–
2	74.56	22.62	2.81	0	0.40	3.77	8.05	–
3	71.87	22.59	1.96	0.42	0.31	2.73	11.53	53.79

1. blank sample; 2. sample treated by NH_3 plasma only; 3. sample modified by 10 mg/ml MPC grafting.