Materials Science and Engineering C 33 (2013) 2871–2878

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Grafting of phosphorylcholine functional groups on polycarbonate urethane surface for resisting platelet adhesion

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ARTICLE INFO

Article history:
Received 11 October 2012
Received in revised form 12 February 2013
Accepted 3 March 2013
Available online 14 March 2013

Keywords:
Polycarbonate urethane
2-Methacryloyloxyethyl phosphorylcholine
Surface modification
Biomimetic
Biomaterials

ABSTRACT

In order to improve the resistance of platelet adhesion on material surface, 2-methacryloyloxyethyl phosphorylcholine (MPC) was grafted onto polycarbonate urethane (PCU) surface via Michael reaction to create biomimetic structure. After introducing primary amine groups via coupling tris(2-aminoethyl)amine (TAEA) onto the polymer surface, the double bond of MPC reacted with the amino group to obtain MPC modified PCU. The modified surface was characterized by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The results verified that MPC was grafted onto PCU surface by Michael reaction method. The MPC grafted PCU surface had a low water contact angle and a high water uptake. This means that the hydrophilic PC functional groups improved the surface hydrophilicity significantly. In addition, surface morphology of MPC grafted PCU film was imaged by atomic force microscope (AFM). The results showed that the grafted surface was rougher than the blank PCU surface. In addition, platelet adhesion study was evaluated by scanning electron microscopy (SEM) observation. The PCU films after treated with platelet-rich plasma demonstrated that much fewer platelets adhered to the MPC-grafted PCU surface than to the blank PCU surface. The antithrombogenicity of the MPC-grafted PCU surface was determined by the activated partial thromboplastin time (APTT). The result suggested that the MPC modified PCU may have potential application as biomaterials in blood-contacting and some subcutaneously implanted devices.

1. Introduction

Polycarbonate urethanes (PCUs) are one kind of the most biocompatible and hemocompatible biomaterials. They play a major role in the development of various medical devices ranging from catheters to total artificial heart [1–3]. However, the surface of conventional PCU materials may induce undesirable reactions caused by non-specific protein adsorption in some medical applications when PCU materials contact with blood over an extended period of time [4,5]. The hemocompatibility of biomaterials is usually and mainly affected by the physical and chemical characteristics of the surface. Therefore, surface modification is a rapid and effective approach to improve the hemocompatibility of biomaterials [6].

Poly(ethylene glycol) (PEG) as a kind of hydrophilic and biocompatible polymer has been widely used in surface modification [7,8]. PEG possesses many unique physical and biochemical properties, and has a long hydrophilic flexible chain which could form a fixed aqueous layer on the material surface to reduce the absorption of plasma albumen, protein and red blood cells. In our previous study, we have grafted poly(ethylene glycol) monoacrylates (PEGMAs) with a molecular weight between 400 and 1000 g/mol onto PCU surface by UV initiated photo-polymerization. The PEGMA layer could improve the hydrophilicity and effectively resist the platelet adsorption on the surface compared with the unmodified PCU [9,10].

Recently, zwitterionic monomers have been grafted onto PCU surface to improve the hemocompatibility, such as sulfobetaine and carboxybetaine [11–14]. Zwitterions possess an equal number of both positively and negatively charged groups, which can greatly resist nonspecific adsorption of protein and cells. In aqueous (blood) medium, the zwitterionic structure molecules are favorable to the maintenance of normal conformation of protein and its assembly due to avoid affecting the synergetic interaction between peptide chain and side groups [15,16]. In our previous studies, poly(3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate) (poly(DMAPS)) zwitterionic brushes have been successfully grafted onto PCU surface by UV polymerization. Poly(DMAPS) zwitterionic brush modified PCU has a lower hemolytic index and can effectively resist platelet adhesion [17].

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http://dx.doi.org/10.1016/j.msec.2013.03.007

Phosphorylcholine (PC) is a zwitterionic molecular segment and is similar in structure to the outer membrane of living cells. When PC groups are incorporated onto the surface of artificial materials, the surface becomes biomembrane-like structure [18–20]. The biomimetic PC surface could effectively resist the adhesion of platelets, and hence the blood compatibility of materials is significantly improved [21]. This modification method has contributed to the development of a wide variety of materials and surface treatments containing the PC head-group or structural analogs in order to produce systems that are better tolerated by the body [22].

More recently, we synthesized a novel phosphorylcholine-containing vinyl monomer and grafted it onto PCU surface by UV radiation-induced polymerization [23]. Yang et al. [24] used surface induced-atom transfer radical polymerization (SI-ATRP) to graft MPC onto PCU surface. Gao et al. [25] grafted phosphorylcholine glyceraldehydes (PCGA) onto PCU surface by the reductive amination between the amino group and the aldehyde group of PCGA, but the grafting density of PC group is very low. Until now, the functional PC group density on the surface is limited since the amino content is too low.

In this study, in order to increase PC grafting density, we presented an original method to graft MPC onto PCU surfaces via three steps shown in Fig. 1. Firstly, 1, 6-hexamethylene diisocyanate (HDI) was coupled onto PCU surface through an allophanate reaction [26]. Then, tris(2-aminoethyl)amine (TAEA) was linked to PCU surface through the coupling of the amino group of TAEA with the rest isocyanate group of HDI to create primary amine groups. Here, owing to three primary amino groups in one TAEA molecule, TAEA may introduce high amino content on PCU surface [27]. Finally, MPC was grafted onto PCU surface via Michael reaction of MPC and amino functional groups. Michael reaction is a simple and effective method to introduce functional groups [28]. The modification method we used is not only favorable for the polar head-group PC arranged onto PCU surface, but also greatly improves grafting density of PC functional groups, where the P content of modified PCU surface reached 1.3%. We introduced PC functional groups in order to create a biomimetic structure on PCU surface like bilayers of cell membrane and form a bound hydration layer when the zwitterionic groups directly contact with the aqueous phase on the exterior surfaces, which can resist platelet

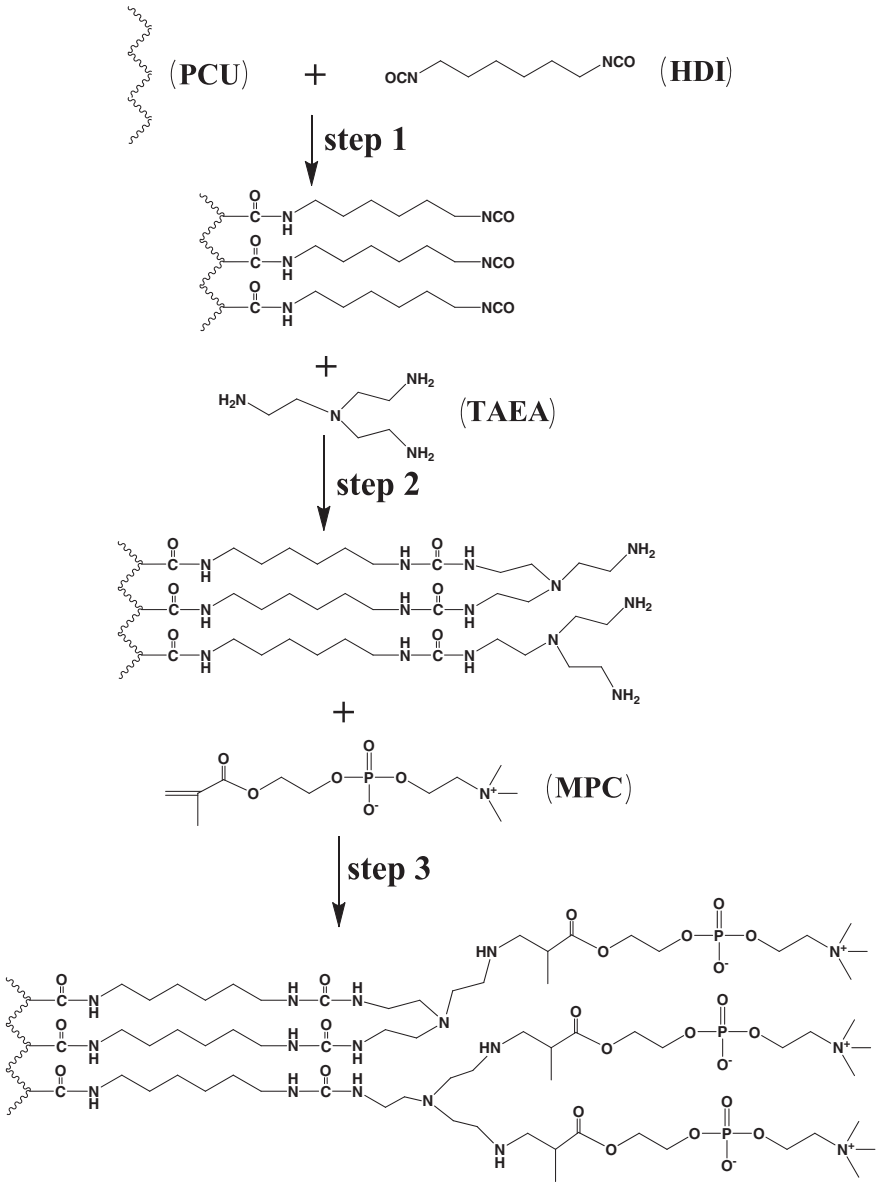

Fig. 1. Schematic diagram of grafting MPC onto PCU surface via Michael reaction.