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PEO-grafting on PU/PS IPNs for enhanced blood compatibility—effect of pendant length and grafting density

J.H. Kim, S.C. Kim*

Center for Advanced Functional Polymers, Korea Advanced Institute of Science and Technology, Yusong-gu, 373-1, Kusong-dong, Taejon 305-701, South Korea

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Abstract

Polyurethane (PU) homopolymers and PU/polystyrene (PS) interpenetrating polymer networks (IPNs) were successfully synthesized changing the length of the pendant poly(ethylene oxide) (PEO) chains and the grafting density of PEO chains. All the PU/PS IPNs had the microphase-separated structures in which the PS-rich phase domains were dispersed in the matrix of the PU-rich phase. The domain size decreased a little, as the degree of grafting with PEO chains was increased. The water swelling ratio increased, and the interfacial energy decreased, as the length of the pendant PEO chains, and the grafting density of PEO chains of the PEO-grafted PU/PS IPNs were increased, since the mobile hydrophilic pendant PEO chains effectively induced and absorbed the water, when they were contacted with water. The hydrophilic and highly concentrated pendant PEO chains could easily prohibit the adhesion of the fibrinogens and the platelets on the surface, and the blood compatibility of IPNs was enhanced by increasing of grafting with PEO chains. The adsorption of the fibrinogens and the platelets was suppressed, as the length of pendant PEO chains, and the grafting density were increased. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Blood compatibility; Hydrophilic–hydrophobic IPN; PEO-grafting; Fibrinogen; Platelet; Protein–biomaterial interaction

1. Introduction

Early in 1980s, Nagaoka and Mori proposed the use of a hydrated dynamic surface for better blood compatibility in a study of grafting poly(ethylene oxide) (PEO) onto poly(vinyl chloride) [1]. They demonstrated that the excluded volume effect, and the dynamic motion of the water-soluble PEO chains on the surface, suppressed protein adsorption and platelet adhesion. The movement of hydrated PEO chains induces the microflow of water, and the surface adsorption is inhibited. They reported that the PEO chains might be called ''molecular cilia''. Andrade et al. were stimulated by that work, and also found that pendant PEO chains on the surfaces of materials had an important role in reducing the adsorption of blood proteins onto the surfaces [2]. In their succeeding works, the protein resistance character of polyethylene oxide chains terminally attached on the substrate was investigated experimentally and also theoretically [3–6]. They considered the steric repulsion effect of PEO, van der Waals attraction between PEO and protein, hydrophobic interaction between substrate and protein, and found that the protein resistance character of PEO was dependant on the chain length and surface density of PEO, and a high surface density and long chain length of terminally attached PEO exhibited optimal protein resistance.

In this study, PEO pendant chains with various lengths were introduced to PU/polystyrene (PS) IPNs for enhanced blood compatibility.

2. Experimental methods

2.1. Materials

Poly(ethylene glycol) (PEG, $M_w = 200$, 600, 1000, Junsei Chemical Co., Ltd., $\geqslant$99.97%), poly(ethylene glycol) methylether (PEGME, $M_w = 350$, 750, 2000, Aldrich Chemical Company, Inc.), 1,4-butanediol (1,4-BD, Junsei Chemical Co., Ltd., $\geqslant$99.7%) and trimethy-

*Corresponding author. Tel./fax: +82-42-869-3910.
E-mail address: kimsc@mail.kaist.ac.kr (S.C. Kim).

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lolpropane (TMP, Acros Organics, 98%) as a cross-linking agent for the Polyurethane (PU) network were degassed at 65°C for 12 h under vacuum to remove moisture before use. Styrene monomer (SM, Showa Chemical Co., Ltd.) was purified to remove quinone, the inhibitor by the conventional method [7]. Hexamethylene diisocyanate (HDI, Tokyo Kasei Kogyo Co., Ltd. 98%), divinylbenzene (DVB, Aldrich Chemical Company, Inc., 80%) as a cross-linking agent for PS network, and benzoyl peroxide (BPO, Fluka Chemika ⩾97%) as an initiator for the polymerization of styrene were used without further purification.

2.2. Synthesis

The synthesis procedure of PU prepolymer was described in our previous paper published [8–10]. In this study, three kinds of PU prepolymer were prepared varying the molecular weight of PEG from 200 to 1000 to vary the crosslink density of PU network. Fig. 1 shows the synthetic scheme of Isocyanatemethoxy-terminated poly(ethylene oxide) (IMPEO), and dihydroxymethoxy-terminated poly(ethylene oxide) (DHMPEO), which were synthesized to graft PEO chains to PU network. IMPEO was prepared by reacting one equivalent of poly(ethylene glycol) methylether (PEGME) with one equivalent of HDI. Three kinds of PEGME's, of which the molecular weight were 200, 600, and 1000, respectively, were used to introduce the various length of PEO pendant chains to PU network. The DHMPEO was prepared by reacting 1 equiv. of IMPEO with excess TMP. The unreacted TMP would be used as the cross-linking agent in PU/PS IPN synthesis. The molecular structure of IMPEO and DHMPEO was investigated by NMR spectroscopy.

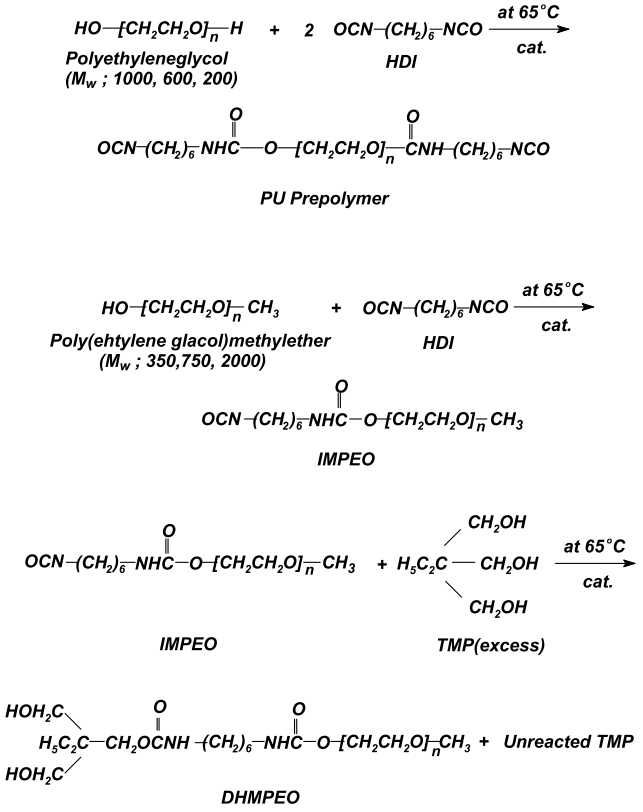

Fig. 1. Syntheses of IMPEO, and DHMPEO.

Ungrafted PU homopolymer was prepared by reacting the diisocyanate-terminated PU prepolymer with 1,4-butanediol (1,4-BD) as a chain extender, and TMP as a cross-linking agent. 0.05 wt% of dibutyltin diaurate (T-12) was added as a catalyst. 1,4-BD and TMP were mixed and degassed before reaction. After PU prepolymer, 1,4-BD, and TMP were mixed vigorously by a high-torque stirrer in a 250 ml beaker, the air bubbles entrapped during the mixing were then removed under vacuum for about 3 min. The mixture was cast in a glass plate mold, with a silicon spacer of 1 mm thick. The cast mixture was polymerized at 60°C for 5 h, and then postcured at 100°C for 2 h in a convection oven. PU homopolymers with PEO pendant chains were prepared in the same way as in the preparation of the ungrafted PU, but the DHMPEO was used instead of 1,4-BD. In the case of the preparation of PU homopolymers with long PEO grafts, the DHMPEO, synthesized with high molecular weight of IMPEO, was used instead of 1,4-BD. Three PU prepolymers with various lengths were also synthesized previously and used to prepare the PEO-grafted PU homopolymer samples with changing the distance between the PEO grafts. In the synthesis of interpenetrating polymer networks (IPNs), first, PU prepolymer, 1,4-BD, TMP, SM, DVB, and BPO were mixed by a high-torque stirrer in a 250 ml-beaker for about 5 min, and then the mixture was degassed under vacuum for about 3 min and cast in a glass mold with a silicon spacer. The PU network was formed in a convection oven at 60°C for 5 h, and then the PS network was formed in a convection oven at 80°C for 10 h. The samples were postcured in a convection oven at 100°C for 2 h. PU/PS IPNs with pendant PEO chains were prepared using DHMPEO instead of 1,4-BD as chain extender. Three kinds of PU prepolymers, and three kinds of DHMPEO of various molecular weights were used to change the grafting density, and the length of PEO grafts, respectively.

2.3. Morphology

The morphology of the fracture surface and the top surface of the PU/PS IPNs was investigated by using both the scanning electron microscopy (SEM, Philips 535 M) [8–10] as well as the scanning probe microscopy (SPM, DI NanoScope IIIa), respectively. SPM measurement was performed in air with an etched silicon probe of which the length was 125 μm, and the spring constant

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