Effect of Crosslinking Density on the Physical Properties of Interpenetrating Polymer Networks of Polyurethane and 2-Hydroxyethyl Methacrylate-terminated Polyurethane

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Abstract: Interpenetrating polymer networks (IPNs) of 2-hydroxyethyl methacrylate-terminated polyurethane (HPU) and polyurethane (PU) with different crosslinking densities of the PU network were prepared by simultaneous solution polymerization. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) show that compatibility of component polymers in IPN formation depends on the crosslinking density of the PU network. Physical properties such as density and water absorption rely on the subtle balance between the degree of phase separation and the crosslinking density of the PU network. In spite of the occurrence of phase separation, the tensile moduli and tensile strength of the IPNs increase with the crosslinking density of the PU network. Morphological observation by scanning electron microscopy revealed different fracture surfaces between the compatible and incompatible IPNs. Surface characteristics of the IPNs, indicated as hydrogen bonding index and hard-to-soft segment ratio, are altered considerably by varying surface morphologies. Improved blood compatibility of IPN membranes is due to the variation of the hydrophilic and hydrophobic domain distribution.

Keywords: IPNs, Polyurethane, Crosslinking density, Phase separation, Blood compatibility.

Introduction

Polyurethanes (PUs) are a versatile family of materials whose properties can vary widely from glassy thermoplastics to elastomers by choosing certain monomers and processing techniques [1-3]. In addition to their high mechanical strength, flexibility, and fatigue resistance, PUs have been found to exhibit excellent blood compatibility [4,5]. Because of the intrinsic incompatibility of the hard urethane segments and the soft polyol segments and thus the formation of the hard and soft domains, phase separation of PU materials occurs. As the urethane groups tend to form strong intermolecular hydrogen bonds, segregated hard segment domains function as physical crosslinks which behave like chemical crosslinks within the vulcanized rubbers. Due to the polar character of the urethane groups, the hard urethane domains are hydrophilic, in contrast to the soft polyol domains. Various combinations of both hydrophilic and hydrophobic surface characteristics that appear in such microphase-separated structures have been shown to be crucial for blood compatibility [6,7]. Therefore, PUs are a prominent class of synthetic polymers used in a wide range of biomedical applications including artificial organs, blood tubings, pacemaker lead insulators and soft tissue implants [8-11].

After the pioneer works of Klemper [12]
and Sperling [13] on interpenetrating polymer networks (IPNs). IPNs have become a relatively novel branch of polymer alloys consisting of two or more crosslinked polymers locked together by permanent entanglements. If the reacting components are well mixed and permanent interlocking of polymer segments of different networks occurs, IPNs are able to limit the degree of phase separation. It has been reported that the formation of an IPN structure can significantly improve the mechanical properties of polymers [14-17]. This synergistic effect can be attributed to better bonding at interfaces and an increase in crosslinking density where the two networks are formed by interpenetration of each other [18,19]. Previous studies indicated that IPNs containing PUs were capable of achieving better blood compatibility as a result of the microphase separated morphology induced by intimately and permanently interlocking of polymer chains of different polymer networks [20-23].

In this work, two different types of PU prepolymers were used to prepare IPNs. The first component was a PU based on a general isocyanate-terminated PU prepolymer. Alteration of the crosslinking density of the PU network was achieved by varying the equivalent ratio of a triol to a diol. One-component PU prepolymers or UV-curable urethane prepolymers [24,25] were employed as the second component of the IPNs. The terminal isocyanate groups of the PU prepolymers were end-capped with 2-hydroxyethyl methacrylate (HEMA) to prepare HEMA-terminated PU (HPU) prepolymers. They possess a double bond at each chain end (functionality = 4) and are able to form a network structure via radical polymerization. Simultaneous solution polymerization was adapted to achieve a better mixing of these high molecular weight prepolymers (both with molecular weight ca. 1500). Effects of crosslinking density on physical properties, surface characteristics and blood compatibility of HPU/PU IPNs were investigated.

### Methods

#### 1. Materials

Table I lists all the chemicals employed in this work. The ether-type polyols (PPG1000 and PTMG1000), 1,4BD and TMP were stirred and degassed in a flask at 70 °C under reduced pressure for 16 hours. DMF and HEMA were dried for at least a week using 4 Å molecular sieves. MDI was melted in an oven at 55 °C and the upper-layer clear liquid was used for reaction.

#### 2. Preparation of HPU/PU IPNs

Details on the syntheses of PU and HPU prepolymers can be found elsewhere [21,22]. To prepare HPU/PU IPNs, (i) HPU prepolymer, (ii) PU prepolymer (with weight ratio of HPU : PU = 1 : 1), (iii) BPO (at a concentration of 2 wt% of HPU prepolymer), (iv) TMP/1,4BD mixture (with TMP/1,4BD equivalent ratio varying from 1/4 to 2/1) and (v) T-12 were dissolved in DMF to form a 40 wt% solution. The reaction was carried out at 70 °C in a 4-necked reaction vessel equipped with a mechanical stirrer, and purged with dry nitrogen for 40 minutes. In order to remove the trapped bubbles, the viscous solution was degassed before being cast into a glass dish. It was left for further reaction and vaporization of solvent in an oven at 70 °C for another 24 hours. The IPN membrane formed was postcured at 110 °C for 12 hours. All samples were vacuum dried for 24 hours at 70 °C before use. Figure 1 depicts the synthetic processes for the production of PU prepolymer, HPU prepolymer and their IPNs.

#### 3. Testing methods

Dynamic mechanical analysis (DMA) was carried out on a Du Pont 983 DMA unit at a frequency of 1 Hz and amplitude of 0.3 mm over a temperature range from -120 to 100 °C by the single cantilever mode. The heating rate was 5 °C/min. The specimen dimensions were 50 mm × 10 mm × 1 mm.