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Synthesis and characterization of biodegradable acrylated polyurethane based on poly(ε-caprolactone) and 1,6-hexamethylene diisocyanate

M. Alishiri [a], A. Shojaei [a,*], M.J. Abdekhodaie [a], H. Yeganeh [b]

[a] Department of Chemical and Petroleum Engineering, Sharif University of Technology, P. O. Box 11155-9465, Tehran, Iran
[b] Department of Polyurethane, Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

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ABSTRACT

A series of biodegradable acrylic terminated polyurethanes (APUs) based on poly(ε-caprolactone) diol (PCL), aliphatic 1,6-hexamethylene diisocyanate (HDI) and hydroxyethyl methyl acrylate (HEMA) was synthesized as potential materials for hard tissue biomedical applications. PCLs with low molecular weights of 1000 and 2000 g/mol were employed to provide different amounts of end capped urethane acrylate in APUs. To control crosslink density, a mixture of two different reactive diluents including mono-functional HEMA and bi-functional ethylene glycol dimethacrylate (EGDMA) with different weight ratios was incorporated into the APUs, called here PUAs. Morphological characteristics and mechanical properties were investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DMA results indicated some degree of microphase separation between hard and soft segments; however, the microphase separation is more prominent for PUAs with higher molecular weight PCL. It was also found that the degree of crosslinking dominated greatly the formation of crystalline structure. PUAs with low crosslink density exhibited crystalline microstructure. The results also indicated that the mechanical properties of PUAs were governed considerably by crystalline microstructure, and hard segment content. All PUAs demonstrated hydrophobic behavior and were able to be degraded hydrolytically. The degradation process was closely related to the microstructure and surface tension of PUAs.

1. Introduction

The unique properties of polyurethanes (PUs) undoubtedly have placed these materials among the most appreciable polymers. PUs actually offer diverse properties such as high flexibility, large abrasion strength, good chemical resistance, excellent mechanical properties and adequate biocompatibility. These make them appropriate candidates in building materials, sport goods, adhesives, coatings and biomedical devices [1–3]. Typically, PU macromolecular chains are composed of soft and hard segments originated from the chemical structure of starting monomers/prepolymers. The incompatibility and thermodynamic immiscibility between the soft and hard segments often result in phase separation, leading to two-phase morphology. The composition, chemical structure and the molecular weight of the starting monomers/prepolymers dominate the morphology of the separated phases and consequently govern the final properties of PU products [4–6].

Crosslinking is one of the versatile ways to improve the mechanical properties and final performance of PU. The presence of crosslinked network provides thermoset PU with superior mechanical properties compared to initial uncrosslinked PU [7,8]. Typically, PU molecules can be end capped with an appropriate acrylic functionality [9,10], providing carbon double bond at both ends of PU chains. Such acrylic terminated PU (APU) is able to be crosslinked easily by thermal or photo-polymerization in the presence of a suitable initiator. Normally, the soft segments of APU can be polyether- or polyester-based polyol and the hard segments consist of isocyanate groups along with acrylic chemical units. Moreover, acrylic monomers are often added to the APU prepolymers to reduce the viscosity of prepolymers and to improve the properties of final crosslinked polymer [11]. Incorporation of acrylic monomers such as hydroxyethylacrylate (HEA) or hydroxyethyl methyl acrylate (HEMA) as reactive diluents combines inherent properties of these materials into PUA properties, while preserves the biocompatibility of initial prepolymer.

APU has received a great deal of attention in the past decades, and therefore its structural characteristics have been investigated extensively in different fields such as: coatings with high impact and high tensile strength, environmental friendliness, abrasion resistance and toughness combined with excellent resistance to chemicals and solvents [12–15]; holographic polymers dispersed liquid crystals for reflective flat panel technology [16–18]; polymer electrolytes for rechargeable lithium-ion batteries having compatibility with lithium metal as inferred from

* Corresponding author. Tel./fax: +98 21 66166432.
E-mail address: akbar.shojaei@sharif.edu (A. Shojaei).

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impedance measurements with a good cationic transference number [7], printing inks [19,20]; adhesives [19,20]; membranes for biosensor devices with good adhesion of the membrane [21]; adhesive films for humidity sensors with achieving low-cost and high-reliable optical property [11,22].

We believe that APUs can also be considered as potential polymeric materials for biomedical applications because of their unique mechanical properties as well as inherent capability for *in situ* photo and/or thermal crosslinking. However, the chemical units of such PUAs must be biocompatible without any toxic or tumorogenic responses to biological systems. These characteristics lead researchers to choose special kinds of polyol and isocynate units suitable for biomedical applications. With this in mind, the research works devoted to APUs in biomedical applications is very rare, and therefore much effort is required to explore their performance in such applications. Recently, Pereira et al. [10] synthesized APUs as potential biomaterials using a one-step polymerization method. Their studies have been concentrated on the synthesis and characterization of photo-polymerizable polymer systems as injectable materials for soft tissue applications, with little efforts on their microstructure and the mechanical properties. However, the mechanical properties of APUs are essential factors for hard tissue applications.

In this work, biodegradable APU based on polyester, i.e. polycaprolactone diol (PCL), polyol with two different molecular weights (M_n) of 1000, 2000 g/mol, aliphatic diisocyanate (hexamethylene diisocyanate, HDI) and HEMA (2-hydroxyethyl methacrylate) were synthesized as potential materials for hard tissue engineering. PCL is a biocompatible polymer with aliphatic ester linkage that is susceptible to be hydrolyzed (biodegradation). The degradation product of PCL is 6-hydroxyhexanoic acid, which is a naturally occurring metabolite in the human body [23]. Furthermore, it is believed that the degradation of aliphatic diisocyanate in polyurethanes leads to nontoxic amine [24,25]. The two-step polymerization method was used in this study which was believed to get better control on molecular weight, molecular weight distribution and chemical structure of APU compared with one-step method mentioned by Pereira et al. [10] To prevent any possible side effects of solvent and catalyst residues in the final APU as a biomedical product, the synthesis reaction was performed in bulk state without utilizing any catalyst. It was aimed to explore the correlation between the characteristics of chemical constituents such as PCL molecular weight and the reactive diluents functionality (average vinyl group in the system) with the microstructure, mechanical properties and biodegradation of the final crosslinked acrylated polyurethane. In order to achieve such goal appropriately, a systematic characterization on morphological, physical, mechanical and *in vitro* degradation properties of the final product was implemented.

2. Experimental

2.1. Materials

PCL-diol CAPA 210, and CAPA 225, with molecular weights of 1000 and 2000, respectively, were obtained from Interox Chemicals. 1,6-Hexamethylene diisocyanate (HDI) and ethylene glycol dimethacrylate EGDMA (used as the crosslinking agent and a comonomer) were purchased from Merck. 2-Hydroxyethyl methacrylate (HEMA) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Sigma-Aldrich. PCLs were dehydrated in a vacuum oven at 85 °C for 24 h before use. HEMA was dried by a 4 Å molecular sieve with stirring at room temperature over-night to eliminate the trace water. Other chemicals were employed as received.

2.2. Synthesis of isocyanate terminated polyurethane prepolymer (IPU)

Isocyanate terminated prepolymers were synthesized by PCL and HDI according to a standard two-step polymerization as follows. A 250-ml four-necked glass reaction flask equipped with a heating mantle, reflux condenser, mechanical stirrer, dropping funnel and nitrogen gas inlet system was used. Briefly, the stoichiometry of the synthesis reaction was 2:1 of hard segment (HDI) to soft segment (PCL). Precalculated amount of PCL 1000 (IPU-1) or PCL 2000 (IPU-2) was placed into the reactor and HDI was then added dropwise to the reactor with vigorous stirring, while the temperature is maintained at about 60 °C under N_2 atmosphere. The temperature then increased to 85 °C, and the reaction continued till the NCO content reached the theoretical value, as determined by dibutyl amine titration [26]. NCO content of polyurethane prepolymers were determined according to procedure reported in ASTM D-2572.

2.3. Synthesis of acrylic terminated polyurethane prepolymer (APU)

Upon completion of IPU synthesis, the reaction flask was cooled down to 40 °C, and 2 equiv of HEMA was added to the reaction mixture in a dropwise manner through a dropping funnel over a 30-min period while the mixture was stirred continuously. The mole ratio of PCL/HDI/HEMA during synthesis was kept on 1:2:2 in this step. This introduced reactive vinyl group at the end of IPU prepolymer molecule. The flask was heated slowly in an oil bath up to 80 °C to allow the termination reaction to be completed. The reaction was continued until the absorption peak of the NCO group at 2270 cm^{-1} (traced by Fourier transform infrared spectroscopy, FTIR) has disappeared entirely resulting in viscous stable acrylic terminated prepolymers (APUs). The APUs were kept in fridge until the next step. Molar compositions of the feed raw materials for the APUs synthesized in this work are collected at Table 1.

2.4. Preparation of test specimens

The acrylic terminated prepolymers (APUs) are highly viscous liquid which necessitates the use of reactive diluents. The reactive diluents are often acrylic monomers which can also take part in the crosslinking reaction and promote the network structure. The reactive diluents used in this study are a combination of mono-functional (HEMA) and bi-functional (EGDMA) acrylic monomers at two different weight ratios, i.e. HEMA/EGDMA of 70:30 and 30:70. These offer reactive diluents with varying vinyl functionality between 1 and 2. As-synthesized APU oligomers were heated slightly above ambient temperature and then mixed with predefined amount of combined reactive diluents, i.e. 30 wt.%, for 2 h. Finally, AIBN (1 wt.%) was added to the above-mentioned mixtures for initiating crosslink reaction through the vinyl end groups. After homogenous mixing, the mixture was degassed under vacuum for 5–10 min at ambient temperature and then it was poured into a glass mold. The mold was placed in an oven at 80 °C for 3 h to crosslink the prepolymer/diluent mixture. The crosslinked samples were designated as PUA-M-Y where M indicates the PCL molecular weight and Y stands for the weight ratio of HEMA in HEMA/EGDMA mixture. For instance, PUA-1-70 indicates that the PUA contains PCL1000 as soft segment and reactive diluent HEMA/EGDMA of 70/30. The polymerization reaction procedure and chemical structures of the final product are schematically illustrated in Fig. 1.

2.5. Characterization

FTIR was carried out using ABB Bomem MB100 spectrophotometer (Canada) on a KBr pellet at room temperature to characterize the chemical functional groups of synthesized polymers. ^1H NMR spectra were recorded on a Bruker model AVANCE DPX 500 MHz in $CDCl_3$ as solvent. The molecular weights and the molecular weight distributions of the prepolymers were determined using gel permeation chromatography (GPC) with an Agilent 1100 modular system with an RI (refractometer index) detector instrument. Tetrahydrofuran (THF) was used as diluent at a flow rate of 1.0 ml/min at 30 °C. The system was calibrated with