

Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol)

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Received 16 September 2006; received in revised form 10 October 2006; accepted 21 October 2006

Available online 6 December 2006

Abstract

Polyurethane networks based on castor oil (CO) as a renewable resource polyol and poly(ethylene glycol) (PEG) with tunable biodegradation rates as potential candidates for biomedical implants and tissue engineering were synthesized through the reaction of epoxy-terminated polyurethane prepolymers (EPUs) with 1,6-hexamethylene diamine curing agent. EPUs themselves were prepared from reaction of glycidol and isocyanate terminated polyurethane prepolymers made from CO or PEG and 1,6-hexamethylene diisocyanate. All of the polymers were characterized by conventional methods, and their physical, mechanical and viscoelastic properties were studied. The results showed that the degradation rate and mechanical properties of final products could be controlled by the ratio of PEG or CO based EPUs in the final products. Increasing the PEG based EPU content caused an increase in hydrolytic degradation rate and mechanical properties. Evaluation of the L-929 fibroblast cells' interaction with prepared polymeric films showed nontoxic behavior and good cytocompatibility.
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Keywords: Polyurethanes; Biodegradation; Biocompatibility; Renewable resource

1. Introduction

Polyurethanes (PUs) have been used for various biomedical applications due to their appreciable physical and mechanical properties and good biocompatibility [1,2]. For some of these applications such as vascular prostheses, artificial skin, pericardial patches, soft-tissue adhesive, drug delivery devices, scaffolds for tissue engineering, besides biocompatibility, biodegradability is a must have factor [3–11]. Biodegradability of polyurethanes is generally achieved by incorporating labile and hydrolysable moieties into the polymer backbone [12–15]. The most common method for fulfilling this goal is the application of polyols (soft segments) with hydrolysable bonds as starting materials for the preparation of polyurethanes. Several hydroxyl terminated polymers such as polycarolactone, polyalkylene adipate, polylactides, polyglycolides

were used for the synthesis of hydrolytically degradable polyurethanes [16–23].

The preparation of polymers from renewable sources such as vegetable oil-based materials is currently receiving increasing attention because of the economic and environmental concerns [24–27]. Vegetable oils are triglycerides of fatty acids. In order to use these compounds as starting materials for polyurethane synthesis, it is necessary to functionalize them to form polyols. Epoxidation and ring opening reaction with hal-acids or alcohols, ozonolysis and hydration are some of the common methods for functionalization of unsaturated vegetable oils [28–32]. Among vegetable oils, castor oil (CO) represents a promising raw material due to its low cost, low toxicity, and its availability as a renewable agricultural resource. Its major constituent, ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid), is a hydroxyl containing fatty acid [33]. So castor oil can be used directly as a raw material for the preparation of polyurethanes without any future modification [34–37].

Presence of ester groups in the structure of plant oil renders prepared polyurethanes to be hydrolytically degradable.

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Surprisingly there have been little works published on the biodegradability of vegetable oil-based polyurethanes and most of them were based on the combination of these polymers with other natural resource materials such as soy dreg, soy protein, starch and cellulose triacetate [38–44]. Also majority of these works studied the degradation process under composting condition and little attention has been paid to the biodegradability of these materials under biological condition of human body and evaluation of their biocompatibility [45–50].

Because of the inherent hydrophobicity of vegetable oil-based polyurethanes low rate of hydrolytic degradation is expected for these materials, at biological environment of human body (pH 7.4, 37 °C). Introduction of hydrophilic polyols such as poly(ethylene glycol) (PEG) into the backbone of vegetable oil-based polyurethanes can increase the degradation rate as a result of enhancement in water permeability and increase in the surface and bulk hydrophilicities, which provide more water in vicinity of hydrolytically labile ester groups.

The objective of this work was to synthesize and characterize a series of biodegradable crosslinked polyurethane elastomers based on castor oil with tunable degradation rates and potential applications in soft-tissue engineering and elastomeric implants. Having this goal in mind two epoxy-terminated polyurethanes (EPUs) based on CO and PEG were prepared, characterized and mixed in various mass ratios and cured with 1,6-hexamethylene diamine curing agent. Physical and mechanical properties of prepared polymers were studied and related to their structure. The degradation rate profile of these polymers was established and short-term biocompatibility of these new biodegradable polyurethanes was evaluated *in vitro*. The results of this paper can provide some insight and scientific data for filling the gap present in the area of biomedical applications of renewable resource-based biodegradable polyurethanes.

2. Experimental

CO with hydroxyl number 144 mg KOH/g and acid number 1.14 mg KOH/g was supplied by Sigma and was dried at 80 °C under vacuum for 24 h. The hydroxyl equivalent weight of CO was 386. PEG with a molecular weight of 2000 from Merck was freed from moisture by an azeotropic distillation with toluene prior to use. 1,6-Hexamethylene diisocyanate (HDI) from Merck was purified via vacuum distillation. 2,3-Epoxy-1-propanol (glycidol) from Aldrich was vacuum distilled before use. THF from Merck was dried by distillation over sodium wire. 1,6-Hexamethylene diamine (HMDA) from Aldrich, streptomycin and fetal calf serum from Gibco BRL Laboratories, Germany, and L-929 fibroblast cells from Pasteur Institute of Iran were used as received. Phosphate-buffered saline (PBS) was prepared via dissolving NaCl (5.85 g), KH₂PO₄ (0.6 g), Na₂HPO₄ (6.4 g) all from Merck in distilled water and the volume adjusted to 1 l. The pH was then correlated to 7.4 by 0.2 M HCl or NaOH solutions.

FTIR and ATR-FTIR spectra were obtained on a Bruker IFS 48 instrument. ¹H NMR spectra were recorded on a Bruker

model AVANCE DPX 500 MHz using CDCl₃ as a solvent. Mechanical properties including tensile strength, initial modulus, and elongation at break were determined from stress–strain curves with MTS tensile tester model 10/M at a strain rate of 5 mm/min. The measurements were performed at 25 °C with a film thickness of about 1 mm and stamped out with an ASTM D638 Die. The data presented were average of five different measurements. Dynamic mechanical testing (DMTA) were carried out on a “UK Polymer Lab” dynamic mechanical thermal analyzer model MKII over a temperature range of –100 to 200 °C at a heating rate of 2 °C/min and frequency of 1 Hz. The dimension of samples was 30 × 10 × 1 mm. Kruss G10 contact angle measuring system was used for the measurement of the water droplet angle on polymeric film surface. The data presented were average of four measurements.

Gel content measurements were performed in a Soxhlet extractor using acetone as solvent. The OH number of castor oil was measured by a method reported in ASTM D-4294. NCO content of polyurethane prepolymers was determined according to the procedure reported in ASTM D-2572 and epoxy content of prepolymers was determined by the method reported in Ref. [51], and presented as mole of epoxy per kilogram of polymer. Density of polymers was measured according to the method reported in ASTM D-1817.

2.1. Synthesis of epoxy modified polyurethane prepolymer based on CO (EPU1)

HDI (13.36 g) and THF (15 ml) were placed into a four-necked reaction kettle equipped with a mechanical stirrer, heating mantle, reflux condenser, dropping funnel and N₂ inlet and outlet. Temperature was increased to 40 °C. CO (30 g) dissolved in THF was dropped into the reactor at a rate that the reaction temperature would not surpass 60 °C. The solid content was adjusted to 40 wt% by the addition of extra amount of THF. The reaction was continued till the NCO content reached the theoretical value as determined by dibutyl amine titration. Then the reaction kettle was cooled to 40 °C and glycidol (5.88 g) was added dropwise through the dropping funnel for over a period of 30 min and mixed. The temperature was increased slowly and maintained at about 60 °C to allow the termination reaction to take place. The reaction was continued until NCO peak at 2270 cm⁻¹ disappeared totally in the FTIR spectra of samples taken from the reaction kettle every 0.5 h. The final product was vacuum dried at 50 °C for 2 days.

Epoxy content: 1.2 (mol epoxy/kg resin).

2.2. Synthesis of epoxy modified polyurethane prepolymer based on PEG (EPU2)

EPU2 was prepared according to the procedure, shown in Scheme 2, and reported in our previous publication [52].

Epoxy content: 0.7 (mol epoxy/kg resin).

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