



Synthesis, characterization and degradation of biodegradable thermoplastic elastomers from poly(ester urethane)s and renewable soy protein isolate biopolymer

Wenshou Wang^a, Yanlin Guo^b, Joshua U. Otaigbe^{a,*}

^a School of Polymers & High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406-0076, United States

^b Department of Biological Sciences, The University of Southern Mississippi, Hattiesburg, MS 39406-0076, United States

ARTICLE INFO

Article history:

Received 30 July 2010

Received in revised form

15 September 2010

Accepted 18 September 2010

Available online 27 September 2010

Keywords:

Poly(ester urethane)s

Soy protein isolates

Biodegradable polymers

Thermoplastic elastomers

ABSTRACT

New biodegradable poly(ester urethane)/soy protein isolate (PEU/SPI) hybrids were prepared by *in situ* polymerization. The chemical incorporation of the SPI into the backbone chain of the PEU was facilitated by the reaction of the amine functional groups of SPI with methylene diphenyl diisocyanate (MDI). X-ray diffraction results showed that the chemical incorporation of SPI into PEU significantly changed the molecular structure of the PEU. The PEU/SPI hybrids exhibited higher thermal decomposition temperature and significant increase in the modulus compared with that of pure PEU. Microscopic examination of the morphology of PEU/SPI hybrids confirmed very fine and homogeneous SPI dispersion in PEU. The hydrolytic degradation of the PEU in a phosphate buffer solution was accelerated by incorporation of SPI, which was confirmed by water absorption and scanning electron microscopy of the samples after up to 10 weeks immersion in the buffer solution. This study provides a facile and innovative method of controlling the biodegradation rate of pure PEU with the additional advantage of environmentally-benign biodegradation of the hybrid PEU/SPI polymer, making the concept potentially widely applicable.

Published by Elsevier Ltd.

1. Introduction

The development of synthetic petroleum-based polymer materials (such as polyethylene and polypropylene) has resulted in a number of serious environmental problems that is exacerbated by the fact that several metric tons of consumer plastics waste are designed to be discarded after use and need to be safely disposed [1]. A number of plastics waste disposal methods such as combustion and landfill are known to cause environmental pollution. For example, combustion of plastics waste can generate toxic air pollution and landfill can lead to underground water pollution and soil contamination. In this context, biodegradable polymers could help solve the above problems because they can be made to degrade in an environmentally-benign way by the action of humidity and microorganisms. Consequently, research efforts towards developing environmentally-friendly and biodegradable polymers and their hybrids with other compatible materials for

various applications have gained significant attention in recent years in academia and industry.

Examples of biodegradable polymers include polyester, polycarbonate, protein, starch, and cellulose [2–5]. In the class of polymers just mentioned, polyurethane is a very important industrial material because of its special properties and relatively mature production equipment and technology in industry [6–9]. It is well known that the glass transition temperature and mechanical properties of polyurethanes can be tuned by changing the composition and ratio of the soft and hard segments to yield a wide range of polyurethanes that varies from thermoplastic elastomers to rigid thermoset foams. Poly(ϵ -caprolactone)-based polyurethane is one example of a widely studied biodegradable elastomer because of its good mechanical properties and biocompatibility that are highly desirable in a number of uses such as cardiovascular stents and scaffolds in biomedical engineering [10–12]. One major drawback of the poly(ϵ -caprolactone) (PCL)-based polyurethane in the applications just mentioned is that it degrades very slowly (i.e., it may take years to degrade completely) in natural environments because of its intrinsic hydrophobic nature. Another limitation of the PCL-based polyurethane is its relative high cost compared with that of natural renewable biodegradable polymers such as

* Corresponding author. Tel.: +1 601 266 5596.

E-mail address: Joshua.Otaigbe@usm.edu (J.U. Otaigbe).

cellulose, starch, soy protein, and chitin that are derived from agricultural biopolymers [13–16].

In the class of biodegradable polymers already mentioned, soy protein isolate has been studied extensively as an alternative material to petroleum-based polymers due to its relative low cost, availability, and biodegradability [17–22]. Soy protein isolate (SPI) is prepared from soybean seeds that contain at least 90% proteins with molecular weights ranging from 8 kDa to about 600 kDa. The various components of SPI are identified as 2S, 7S, 11S, and 15S (S denotes Svedberg unit), and are respectively found in 20–27%, 37%, 31–40%, and 10–11% of the total weight in the SPI [23]. The 7S or β -conglycinin (42–58 kDa) and 11S or glycinin (360 kDa) are reported to be the two major globulins present in SPI. These proteins can react with each other to form various crosslinkages such as disulphide, lysinoalanine, and lanthionine. The resin obtained from SPI is very brittle and hence difficult to process and use. Another inherent characteristic of SPI is its strong tendency to absorb moisture, leading to its relatively fast degradation in moist environments [24]. A number of researchers have reported attempts to improve the processability of SPI plastics by using relatively high concentrations of plasticizers (e.g., water, glycerol and waterborne polyurethane) in the SPI plastic batch formulation [25–28].

In previous articles, we reported innovative synthesis and processing of useful biodegradable and bioabsorbable polymers such as poly(ester urethane)s [10,12] and soy protein isolates [18,29,30] with improved properties. The work described in this current article aims to extend our prior research into feasibility of developing new poly(ester urethane)/soy protein hybrids that combines in one material the advantages of polyurethanes (excellent mechanical properties and biocompatibility) and SPI (low cost, environmentally-benign degradation in humid environments, and availability from renewable natural resources). In this paper, we specifically report an innovative method of chemically incorporating SPI into the backbone chain structure of poly(ester urethane) via *in situ* polymerization. The resulting thermomechanical properties, degradation behavior, and interaction between the poly(ester urethane) and SPI in the hybrids are studied to assess the benefits of the new PEU/SPI hybrid materials. It is hoped that the current results reported in this article may stimulate a better understanding of the behavior of the materials in a number of applications requiring the biocompatibility and bioabsorbability of the hybrid components.

2. Experimental section

2.1. Materials

Poly(ϵ -caprolactone) diol (TONE[®] Polyol 5249; Mn = 2000) was purchased from Dow Chemical Company (Midland, MI). Methylene diphenyl diisocyanate, toluene, dibutyltin dilaurate, 1,4-butanediol and phosphate buffer solution (1 M, pH = 7.4) were obtained from Sigma Aldrich. Soy protein isolate was purchased from the Solae Company (St. Louis, MO).

2.2. Synthesis of polyurethane/soy protein isolate (SPI) hybrids

The desired amount of the soy protein isolate was dispersed in toluene in a dry reaction flask. The flask was subsequently placed in an ultrasonic bath for 2 h in order to homogeneously disperse the SPI in toluene. Subsequently, PCL diol was added to the flask and the flask was placed in an isothermal oil bath (65 °C) under stirring. After the PCL diol was dissolved completely, dibutyltin dilaurate and methylene diphenyl diisocyanate were added to the reaction system. After 3 h, 1,4-butanediol was added to the system and the

Table 1

The feed ratio of the synthesized PEU/SPI hybrids.

Code	PCL diol (g)	MDI (g)	1,4-Butanediol (g)	Soy Protein Isolate (g)
PEU	5	2.21	0.5	0
PEU/3% SPI	5	2.21	0.5	0.23
PEU/6% SPI	5	2.21	0.5	0.46
PEU/10% SPI	5	2.21	0.5	0.77
PEU/20% SPI	5	2.21	0.5	1.54

reaction was allowed to continue for another 3 h to yield the final product. The feed ratios of the reactants and starting materials are summarized in Table 1. All the as-polymerized samples were dried under vacuum oven for 24 h and compression molded at 150 °C into the film configurations used for the following measurements.

2.3. Measurements

2.3.1. FT-IR and XRD

IR spectroscopy was conducted on the samples using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, NH). The crystallinity of the PEU/SPI hybrids was evaluated using X-ray diffraction (XRD) analysis. A Rigaku Ultima III powder diffractometer was used, employing Cu K α radiation (at 40 kV and 44 mA). The XRD data were collected over the range of $2\theta = 3\text{--}40^\circ$ at a rate of $1^\circ/\text{min}$.

2.3.2. Thermal analysis

Differential scanning calorimetry (DSC) was carried out on the samples over a temperature range of -80°C to 250°C using a TA Instruments (TA Q100) operating under a nitrogen atmosphere. The DSC heating or cooling rate was $10^\circ\text{C}/\text{min}$. The midpoint of the transition zone was taken as the glass transition temperature (T_g) of the sample. Thermogravimetric analysis (TGA) tests were conducted on the samples using Perkin–Elmer (Pyris 1 TGA) equipment operating over a temperature range of $50\text{--}800^\circ\text{C}$ and a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Thermal decomposition temperature was defined as the temperature corresponding to the maximum rate of weight loss.

2.3.3. Static and dynamic mechanical properties

Static mechanical tensile stress–strain measurements were performed on the samples using a Material Testing System Alliance RT/10 and a MTS Testworks 4 computer software package for automatic control of test sequences and data acquisition and analysis. Dumbbell-shaped test specimens (with an effective cross section of $4 \times 0.7 \text{ mm}^2$) were cut from the compression molded PEU/SPI films and tested at room temperature and using a cross-head speed of $20 \text{ mm}/\text{min}$ according to the ASTM D882–88 standard method. The tests were performed in triplicate to give the mean values reported in this paper. The temperature dependencies of the dynamic storage modulus E' and mechanical damping ($\tan\delta$) of the compression molded rectangular test specimens ($20 \times 5 \times 1 \text{ mm}^3$) were determined using a PYRIS Diamond Dynamic Mechanical Analyzer (DMA) operating at temperatures ranging from -80°C to 150°C , a heating rate of $3^\circ\text{C}/\text{min}$, a frequency of 1 Hz, and a linear strain amplitude of 10%.

2.3.4. Hydrolytic degradation in buffer solution

The degradation test was conducted in a phosphate buffer solution of pH = 7.4 at 37°C following procedures reported elsewhere [31]. The samples were cut into disks (diameter = 15 mm and thickness = 1 mm) and placed into the buffer solution (pH = 7.4) at 37°C . The original weight of the sample was recorded as W_0 . When the sample was taken out of the buffer solution and

Download English Version:

<https://daneshyari.com/en/article/5184604>

Download Persian Version:

<https://daneshyari.com/article/5184604>

[Daneshyari.com](https://daneshyari.com)