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Effect of hydrothermal ageing on structure and physical properties of one-phase and two-phase entirely lipid-derived thermoplastic poly(ester urethane)s

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ABSTRACT

The hydrothermal degradation of a one-phase and a two-phase segmented thermoplastic poly(ester urethane) (TPEUs) made entirely from lipids was studied by accelerated ageing in water at 80 °C. Extensive alteration to the morphology, hydrogen bonding index and phase separation of the TPEUs were observed in one day of immersion in the water. The TPEU also achieved a tensile half-life of one day. The evolution of the physical properties of the TPEU such as the thermal decomposition, thermal transition and tensile characteristics was directly linked to the changes caused by hydrolysis to their phase morphology and microstructure. The degradation occurred in three stages depending on the degree of phase separation and hydrogen bond density. The formation of aliphatic carboxylic acid and amine degradation products following hydrolysis of both the soft and hard segments was identified by ^{1}H-NMR.

The controlled life-cycle properties combined with the adequate thermal and mechanical properties of the materials demonstrate the viability of lipid derivatives as alternatives to petroleum for manufacturing TPEUs and credible potential in biomedical applications especially as bioresorbable implants or tissue scaffolds.

1. Introduction

In recent years, sustainable bio-based monomer feedstocks such as vegetable oils and their derivatives have gained considerable interest as precursors for the manufacture of a wide range of materials including thermoplastic poly(ester urethane)s (TPEUs). Bio-based TPEUs are very attractive because of renewability and positive environmental impact. They are increasingly investigated for biomedical applications where adequate function, biocompatibility, nontoxicity and controlled degradation are required [1–3].

Segmented TPEUs consist of alternating “soft” polyester and “hard” polyurethane blocks linked together via covalent bonds. The polyester and the urethane segments of the TPEU respectively form crystalline domains which serve as a load bearing phase and amorphous domains which provide extensibility [4]. In the typically phase separated segmented TPEUs, diol or diamine chain extenders are used with a diisocyanate to form alternating structures which yield *two-phase* structures in contrast to the *one-phase* or mixed-phase polyurethanes which are synthesized without chain-extenders [5]. The micro-phase morphology and related properties of segmented TPEUs are determined by several competing factors related to the nature of the hard and soft segments and their ratio in the copolymer, particularly hydrogen bonding [6]. A wide range of bio-based precursor blocks are available for the manufacture of diverse functional TPEUs. Additionally, the molecular weight, phase composition, phase structure and related physical properties can be beneficially manipulated by educated synthesis and polymerization protocols [7].

The presence of the hydrolytically labile polyester groups which provide controlled degradation is desired in applications where degradation and resorption are important [1,8–10]. Aliphatic diisocyanates are preferable over aromatic diisocyanates for biomedical applications, especially for resorbable polyurethanes, as they lack the cytotoxic degradation products that are associated with aromatic diisocyanate degradation [8,11] and degrade into benign carboxylic acid by-products [12]. One of the main challenges of aliphatic TPEUs for biomedical applications such as implantable scaffold materials for tissue regeneration has been the compliance

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of mechanical properties to native tissue typically requiring high elongation at break and adequate tensile strength. More recent studies have employed the tunable chemistry of segmented polyurethanes to allow for formulations with elongations at break of approximately 900% and tensile strength of 29 MPa and enhanced burst pressure and suture retention [8,13,14].

Because the use of live models is not always practical, in vitro experiments are designed to provide information about the in vivo degradation of polyurethanes [2]. A common technique to study the long term hydrothermal degradation in a reasonable time span is ageing at elevated temperatures to accelerate hydrolysis [2,8]. It has been demonstrated that above 70 °C, hydrolysis is sufficiently accelerated to allow for observable effects on structure and properties in a reasonable time, typically within 10–30 days [15–18]. Hydrolytic ageing studies performed at 80 °C on TPEUs based on polyethylene adipate diols, MDI and butane diol [19] as well as at 90 °C [20] showed observable differences after 11 and 8 days of immersion. Tensile test parameters such as the modulus, elongation and particularly the tensile half-life; which is the time at which the tensile strength of the hydrolyzed polymer reaches half the tensile strength of the untreated polymer, have been widely used to rank the utility of polymers exposed to hydrolysis [21–23].

The present work is part of a series of investigations aimed at making functional aliphatic TPEUs from lipid-derived precursors. It concerns the study of the accelerated hydrothermal ageing of two different TPEUs made in our laboratory entirely from lipids, including the diisocyanate component. The first is a one-phase TPEU (coded PU2.1-24h). TPEU PU2.1-24h was prepared without a chain extender in a single-stage polymerization of 1,7-heptamethylene diisocyanate (HPMDI) and a linear long chain polyester diol (PED), dihydroxypoly(nonane nonanoate), under optimized conditions. The second is a two-phase TPEU (coded ND-B) that was prepared with HPMDI, PED and a chain extender (1,9-nonanediol, ND) in a customized two-stage polymerization [24,25]. PU2.1-24h and ND-B were prepared in our laboratory and have been fully characterized. Their structure and properties are detailed in Refs. [24] and [25], respectively. The hydrolytic ageing was conducted at 80 °C, a temperature in the range of what is recommended by ASTM D3137. The pathways of hydrothermal degradation and the impact of hydrolysis on the two microstructures were examined and contrasted using ^{1}H-NMR, FTIR, GPC, SEM, TGA, tensile measurements and DSC.

2. Experimental

2.1. Materials

Chloroform ($CHCl_3$) was obtained from ACP chemical Int. (Montreal, Quebec), Canada. Clear glass laboratory bottles, 60 mL, with polyethylene cone-lined caps were purchased from Fisher Scientific (Whitby, Ontario). All reagents were used as obtained. PU2.1-24h and ND-B were synthesized by procedures previously described [24,25].

2.2. Hydrothermal ageing testing

The hydrothermal tests were conducted following a previously reported procedure [19]. The polymers were melt-pressed into films of dimension 6.0 × 3.0 × 0.6 mm and cut into samples. For DSC and TGA and FTIR analyses rectangular samples of 6.0 ± 0.6 mg, 10.0 ± 0.5 mg and 20 ± 0.2 mg were used respectively. For tensile tests dumb-bell shaped specimens 0.60 ± 0.3 were cut from the films. Samples were immersed in 25 mL deionized water (pH 7.12) in sealed laboratory bottles then placed in an oven set at 80 ± 5 °C for 30 days. Samples were extracted and characterized at 1 day (1D), 5D, 10D, 15D, 20D, 25D and 30D. The samples were dried with lint-free paper before testing. Prior to the DSC, TGA and tensile tests, the sample was taken out of the laboratory bottles and allowed to cool down to room temperature (20 °C), which took about 5 min. Prior to solubility, SEM, FTIR and GPC analysis, the sample was further dried to constant weight under vacuum for three days at room temperature.

2.3. Characterization techniques

The solubility tests of the aged specimens were performed in $CHCl_3$. The sample, 2 mg of TPEU, was mixed with 2 mL of solvent in a 15 mL glass laboratory bottle, stirred for 30 min and left in the solvent for two days. The mixture was then brought to the boiling point of the solvent at least three times for at least 5 min each.

Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo Scientific Nicolet 380 FTIR spectrometer (Thermo Electron Scientific Instruments, LLC, Fitchburg, WI) equipped with a PIKE MIRacle™ attenuated total reflectance (ATR) system (PIKE Technologies, Madison, WI). The sample was placed onto the ATR crystal area and held in place by the pressure arm. The spectrum was acquired in the 400-4000 cm^{-1} scanning range using 64 scans at a resolution of 4 wavenumbers. All spectra were recorded at ambient temperature.

The carbonyl stretching region (1780 cm^{-1} to 1660 cm^{-1}) was fitted with three Gaussians as already described for polyurethanes [26,27]. The fit was performed after baseline correction using OriginPro (v9.2) software. The iterative least-squares method was used to obtain the best fit by varying the frequency, width at half height and the intensity of the peaks. The residuals of the fit were all better than 2%. The carbonyl hydrogen bonding index (R, equation (1)) was determined as a ratio of the intensities of the normalized hydrogen-bonded carbonyl stretching peaks (disordered at ~1715 cm^{-1} and ordered at ~1690 cm^{-1}) and the free (~1732 cm^{-1}) carbonyl stretching peaks [28,29]. The degree of phase separation (DPS, equation (2)) was calculated from R [19,30].

$$R = \frac{A_{bonded}}{A_{free}} = \frac{C_{bonded} \times \varepsilon_{bonded}}{C_{free} \times \varepsilon_{free}} \quad (1)$$

$$DPS = \frac{C_{bonded}}{C_{bonded} + C_{free}} = \frac{R}{R+1} \quad (2)$$

Where A_{bonded} and A_{free} are the absorbance of hydrogen-bonded and free carbonyl peaks, C_{bonded} and C_{free} are the concentrations and ε_{bonded} and ε_{free} are the extinction coefficients. although slightly different due to the wide distribution of hydrogen bond strengths, ε_{free} has not been observed to be significant from ε_{bonded} and according to Seymour et al. [29], $\frac{\varepsilon_{bonded}}{\varepsilon_{free}}$ may be set to approximately 1 so that R is directly equal to the ratio of $\frac{A_{bonded}}{A_{free}}$.

Scanning Electron Microscopy (SEM) was performed on a Phenom ProX apparatus (Phenom-World, The Netherlands) at an accelerating voltage of 15 kV and map intensity. Uncoated thin rectangular samples were fixed to the charge reduction sample holder with conductive tape. Composite images were captured using the Automated Image Mapping software (Phenom-World, The Netherlands).

Thermogravimetric analysis (TGA) was carried out on a Q500 TGA model (TA instrument, Newcastle, DE, USA) under purge flow of dry nitrogen. The sample was loaded in an open TGA platinum pan then heated to 600 °C at 10 °C/min.

Tensile properties of the TPEUs were measured at room temperature (RT = 20 °C) with a texture analyzer (Texture Technologies Corp, NJ, USA) fitted with a 2-kg load cell following the ASTM D882