



Imparting elastomeric properties to entirely lipid-derived thermoplastic poly(ester urethane)s: Molecular weight control



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ABSTRACT

High molecular weight, thermoplastic poly(ester urethane) (TPEU) elastomers were synthesized from oleic-acid derived polyester diols (PED)s and 1,7 heptamethylene diisocyanate (HPMDI). Functional group stoichiometry and polymerization time were used to control molecular weight and optimize thermal and mechanical properties. A targeted range of PEDs with controlled molecular weights and consistent dispersity were obtained in high yields using an induced stoichiometric imbalance method. The PEDs were reacted with HPMDI with different NCO:OH ratios (1.1–2.1) and polymerization times (2–24 h) to obtain high molecular weight TPEUs. Solvent-resistant TPEUs, displaying polyethylene-like behavior were obtained and characterized by GPC, FTIR, DSC, XRD, TGA, DMA and tensile tests in order to reveal the structure-property relationships. Melting temperatures, tensile strength and maximum strain scaled with molecular weight approaching saturation values, demonstrating a plateau effect of molecular weight on physical properties. The entirely lipid-derived TPEUs exhibited thermal and mechanical properties comparable to commercial, petroleum-based analogues.

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1. Introduction

Linear thermoplastic poly(ester urethane) (TPEU) elastomers are an attractive class of materials due to their elastic properties and reprocess-ability at melt. TPEUs are used in a wide variety of applications ranging from automotive parts and building construction to footwear, wire and cable insulation jackets, and biomedical devices [1]. TPEUs are copolymers of polyester diols (PEDs) and diisocyanates, and can demonstrate a versatile combination of chemical and physical properties such as biodegradability, flexibility, resistance to dilute acids and alkalis, thermal stability and mechanical strength. Recently, triacylglycerol (TAG) oil derivatives have received much attention as potential substitutes for petroleum for the synthesis of the polyurethane monomers including isocyanates constituents [2–5]. However, in contrast to their petroleum based counterparts, TPEUs derived from vegetable oils have shown low molecular weight and poor mechanical and

thermal properties due to the inherent structure and reactivity limitations of the TAG molecule [6–9].

The mechanical and thermal properties of a polymer such as the tensile strength and modulus, elongation, melt and glass transition temperatures are a function of molecular weight. At high molecular weight and above a critical value, the physical properties eventually attain a saturation value [10–12]. The molecular weight of TPEUs and subsequent properties depends on the structure and molecular weight of the urethane and the polyester segments, their functional group stoichiometry (NCO:OH ratio) and polymerization time [5,13,14].

The PED soft segments form the major component of TPEUs and strongly affect its crystal structure and therefore the properties [15–17]. The molecular weight and molecular weight distribution of PEDs is critical. PEDs with molecular weight in the range of 1000 and 6000 gmol^{-1} are typically preferred for optimal thermal and mechanical properties [10,14,18]. PEDs can be synthesized from lipid-derived diacid and diol monomers by solvent-free melt-condensation [15]. However, molecular weight control of polyesters by melt-condensation is difficult. It is complicated by inter and intra molecular side-reactions that lead to the formation of low molecular weight polyesters with cyclic by-products [10] and low yields [15]. Additionally, in the case of bifunctional molecules, the

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competing polyesterification reactions cause a shift in functional group stoichiometry resulting in polyesters with mixed end-groups; rendering them unsuitable as precursors for subsequent synthesis [10].

The control of polymerization time is also important for achieving specific molecular weight, since it determines the degree of polyesterification [10,19]. Therefore, for the successful synthesis of PEDs without mixed-end groups and specified molecular weights, an effective control of diacid: diol functional group stoichiometry and reaction time is essential. Kinetic studies on melt-condensation polyesterification have indicated that an initial diacid: diol stoichiometric ratio closer to unity, a high catalyst concentration and a range of high temperatures result in linear polyesters with high molecular weight and yields [10,20,21]. Specific molecular weights have also been achieved by using a monofunctional monomer to terminate the reaction at a selected time [22]. However the resultant polymers were unsuitable for further reaction because of their mixed end-groups composition.

The synthesis of linear TPEUs is also complicated by the rate of reaction of the diisocyanate with the PED; wherein the reactivity of the second NCO group of the diisocyanate varies when the first NCO group has reacted [13,23,24]. Furthermore, the possible diisocyanate side-reactions, such as allophanate formation, or the reaction with atmospheric moisture, lead to a decrease in the effective NCO:OH ratio during synthesis, resulting in a low degree of polymerization [25,26]. Valuev et al. [26] have shown through experiment and theoretical calculations that the molecular weight of TPEUs increases with increasing NCO:OH ratio and directly depends on the synthesis conditions that affect this ratio.

In the present work, hydroxyl terminated linear PEDs of target molecular weight between 1000 and 6000 g mol^{-1} with narrow PDIs were achieved in high yields by varying functional group stoichiometry and reaction time. This work builds on our previous study on TPEUs synthesized using lipid-derived PEDs and HPMDI [15]. Diacid and diol monomers were reacted with an initial stoichiometric imbalance, and in order to end-cap the polyesters with hydroxyl groups and mitigate polymerization; a further stoichiometric imbalance was induced by adding extra diol at selected reaction times. This is the first time, to the best of our knowledge, that such an induced stoichiometric imbalance approach has been applied to control molecular weight in lipid-derived PEDs. Two series of TPEUs were prepared from the PEDs and HPMDI. The NCO:OH ratio and polymerization time were optimized in order to achieve molecular weights above the critical value at which the TPEUs properties would reach saturation. The TPEUs were fully characterized for molecular weight, structural morphology, solubility and thermal and mechanical properties.

2. Experimental

2.1. Materials

Nonanedioic acid (azelaic acid, 85%), 1,9-nonanediol (ND, 98%) titanium (IV) butoxide (98%), stannous octoate ($\text{Sn}(\text{Oct})_2$) (98%), dibutylamine (98%), anhydrous tetrahydrofuran (THF), calcium hydride (98%), diethyl ether, chloroform (CHCl_3 , 99.8%), chloroform (HPLC grade) and methanol (99.8%) were purchased from Sigma Aldrich (Oakville, ON), Canada. All reagents except azelaic acid, DMF and THF were used as obtained. Azelaic acid was recrystallized from distilled water to a purity of 97% before use. DMF was dried overnight over calcium hydride followed by vacuum distillation (~300 Torr). THF was distilled after drying overnight over 4A molecular sieves. HPMDI was synthesized using a previously reported procedure [4].

2.2. Synthesis and purification of polyester diols

The PED, dihydroxypoly(nonanonenanoate), was synthesized by melt-condensation of oleic acid derived azelaic acid and 1,9 nonanediol (ND) in the presence of titanium (IV) butoxide as catalyst (Scheme 1). Azelaic acid, excess ND and titanium (IV) butoxide were added in bulk to a three necked 250 mL flask connected to a condenser, thermometer and vacuum outlet. The esterification reactions were carried out at 150 °C under constant stirring at 550 rpm. The excess ND relative to azelaic acid provided an initial molar diacid to diol stoichiometric imbalance, r , smaller than unity. The starting PED was synthesized with an initial azelaic acid: ND imbalance of $r = 0.8$. This value was chosen based on the results obtained with four different values of initial stoichiometric imbalance ($r = 0.9, 0.8, 0.7$ and 0.6). This preliminary work also involved the optimization of the reaction time for molecular weight and PDI. The results of this optimization are provided in the Supporting information. The PED synthesized with $r = 0.8$ and without further induced stoichiometric imbalance is labeled PED0.8.

Following the initial stoichiometric imbalance, the polyesterification reaction was arrested at a selected time (t_E) by inducing a secondary stoichiometric imbalance by adding an extra controlled amount of ND (diacid: ND = 0.1). The induced stoichiometric imbalance was fixed at $r = 0.1$ to achieve an r value between 0.8 and 0.7 at the arresting reaction time. Molecular weight development was monitored by GPC. Four reactions were conducted with 16 mmol (3.06 g) of azelaic acid and 20 mmol (3.27 g) of ND in the presence of 0.032 mmol (0.011 g) of catalyst. A fixed amount of extra diol, 4 mmol (0.64 g) and catalyst (0.0022 g) was added in each reaction at $t_E = 1, 3, 5$ or 7 h (Table 1). An inert atmosphere (N_2 gas) was supplied for an hour after the initial stoichiometric imbalance and for the hour following the induced stoichiometric imbalance. Vacuum (300 Torr) was applied when the N_2 supply was discontinued. The reaction was terminated four hours after t_E by cooling the system to room temperature.

Molecular weight and PDI of the PEDs were measured every hour with gel permeation chromatography (GPC). The structure of PEDs was confirmed by proton nuclear magnetic resonance spectroscopy (^1H NMR). The crude PEDs (6 g) were dissolved in 30 mL of chloroform and precipitated in methanol. The low molecular weight alcohols remained in solution while larger diols precipitated out. The optimum ratio of chloroform to methanol was determined by systematically varying the ratios of the PED solution in CHCl_3 with excess methanol until all impurities were consistently removed in a single step and PEDs achieved a target PDI of less than 2. The larger diols with molecular weights close to the target were procured by purification of PEDs with methanol: chloroform ratio of 15:1 (v/v).

For ease of presentation and discussion, the PEDs are coded based on the time of induced stoichiometric imbalance as shown in Table 1. **PED-1 h (3 h, 5 h or 7 h)** represents the PED produced when the stoichiometric imbalance was induced at **1 h (3 h, 5 h or 7 h)**.

2.3. Synthesis of thermoplastic poly(ester urethane) elastomers

2.3.1. Effect of NCO:OH ratio

PED-3h was selected for polymerization because it showed a molecular weight closest to the industry standard for TPEU synthesis of 2000 g mol^{-1} (1850 g mol^{-1} by ^1H NMR) and was produced with the highest yield (77%). The molecular weight of PED-3h is also comparable to that of the monomer polyethylene adipate diol (PEAD, DESMOPHEN 2000) that was used with HPMDI to obtain TPEUs with an ultra-high molecular weight (3,000,000 g mol^{-1}) [5].

The TPEUs were prepared by reacting PED-3h, in the presence of

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