Synthesis, Structure and Properties of Poly(ester-Urethane-Urea)s Synthesized Using Biobased Diamine

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ABSTRACT: Modern polymer science and technology is focused on the development of partial or fully green polymers. This focus is related to green chemistry trends, which propose using natural and renewable resources as monomers in the synthesis of polymers. In this study, biobased diamine was used as a chain extender of ester-urethane prepolymer. Obtained poly(ester-urethane-urea) contains 16 wt% of biobased diamine. There is mention of an amine curing agent that is an amine derivative of dimerized fatty acids (obtained from vegetable oils). Application of two chain extenders, i.e., 1,4-butanediol and biobased diamine (applied separately or in mixture), with different molecular weights and chemical structures, resulted in obtaining materials with diversified properties. The chemical structure (by FTIR method), mechanical properties (tensile properties, hardness and elasticity), and thermomechanical properties (by DMTA method) were determined for the synthesized poly(ester-urethane-urea)s.

KEYWORDS: Poly(ester-urethane-urea), biobased diamine, chemical structure, mechanical properties, dynamic mechanical properties

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1 INTRODUCTION

A growing interest in polymers derived from renewable resources has been observed. A lot of natural substances—e.g., vegetable oils [1–3], glycerol [4, 5], terpenes [6], rosin [7] and tannins [8]—have been proposed as feedstock for the polymer industry. Compounds have been mentioned for use as substrates for the synthesis of polyesters, polyurethanes, epoxy resins and phenolic resins.

In the case of polyurethanes, there has been special interest concerning their use in the synthesis of biobased polyols, e.g., polyols based on vegetable oils, glycerol or sorbitol [9–13] and chain extenders, e.g., biobased 1,3-propanediol [14, 15]. In accordance with the literature, the synthesis and use of biobased diisocyanates (synthesized from dimers of fatty acids or lysine) are also known [16, 17].

The most important components for the synthesis of polyureas or poly(urethane-urea)s are diamines. Compounds with amine-functionality can also be synthesized from natural resources, e.g., cardanol, vanillin or dimers of fatty acids [18–21]. The biobased diamines mentioned are especially applied as curing agents for epoxy resins and cyclic carbonate intermediates, which are used in the synthesis of non-isocyanate polyurethanes.

The main aim of this work was to synthesize poly(urethane-urea)s using a biobased diamine (obtained from fatty acid dimers) as a chain extender. Chemical structure, mechanical and thermomechanical properties of obtained poly(ester-urethane-urea)s were determined.

2 EXPERIMENTAL

2.1 Synthesis of Ester-Urethane Prepolymer and Poly(ester-Urethane-Urea)s

The ester-urethane prepolymer was synthesized through a reaction between α,ω-dihydroxy(ethylene-butylene adipate) (POLES 55/20, Purinova, Poland) and 4,4′-diphenylmethane diisocyanate (MDI, Borsodchem, Hungary). The molar ratio of components POLES:MDI was equal to 1:2. Reaction was realized at 80 °C for 2 h, under vacuum. Synthesis of ester-urethane prepolymer is shown in Figure 1.

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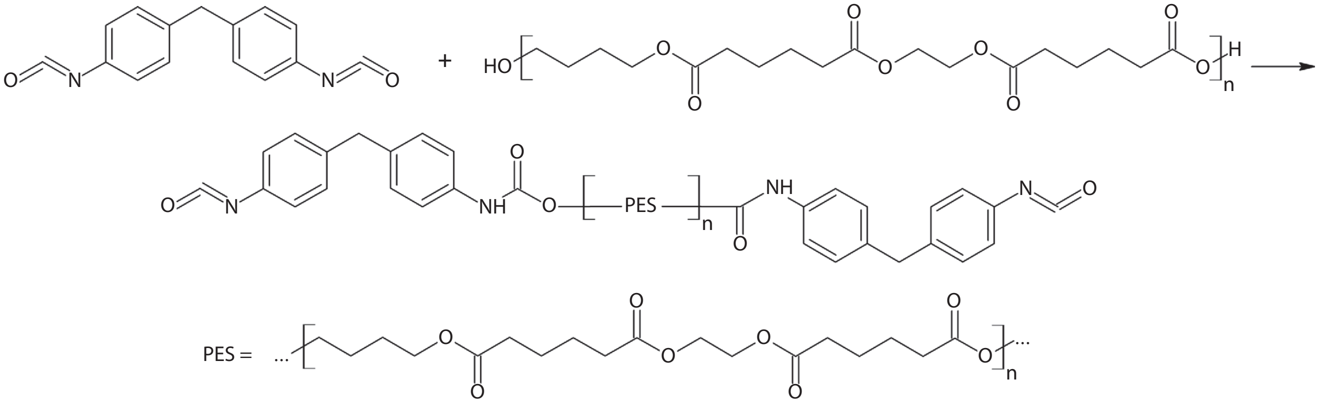

Figure 1 Synthesis of ester-urethane prepolymer.

Table 1 Codes for prepared poly(ester-urethane) and poly(ester-urethane-urea)s and formulations of applied chain extenders.

Polymer	Chain extender	Molar ratio of hydroxyl groups and amine groups to isocyanate groups during chain extending	
		nOH/nNCO	**$nNH_2/nNCO$**
PEsU poly(esterurethane)	1,4-butanediol	1	0
PEsUM-0.25BA poly(esterurethane-urea)	mixture of 1,4-butanediol with bio-based diamine	0,75	0,25
PEsUM-0.5BA poly(esterurethane-urea)		0,5	0,5
PEsUM-0.75BA poly(esterurethane-urea)		0,25	0,75
PEsUM-1BA poly(esterurethane-urea)	bio-based diamine	0	1

In the next step, prepared prepolymer was extended using: 1,4-butanediol (1,4-BDO, Brenntag, Netherlands), biobased diamine (Priamine 1071, Croda, Netherlands) or a mixture of both mentioned components. Formulations of applied chain extender agents are presented in Table 1.

The chain extending of ester-urethane prepolymer was carried out using a Brabender mixer (100 °C, 80 rpm, 5 min), due to high viscosity of reaction mixture. After that, the obtained materials were pressed by using a hydraulic press (120 °C, 5 MPa, 15 min). The reaction of ester-urethane prepolymer with biobased diamine is shown in Figure 2.

Priamine 1075 (Croda, Netherlands), which was used in this study as a curing agent, is a biobased and high purity C36 building block, which is an amine derivative of dimerized fatty acids. Two examples of the possible structure of mentioned biobased diamines are presented in Figure 3.

2.2 Testing Methods

Obtained poly(ester-urethane-urea)s were characterized by several methods. Chemical structure was determined by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 8700 FTIR spectrophotometer (Thermo Electron Corp.), and 64 scans was taken between 500 cm^{-1} and 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

Static tensile properties (tensile strength and elongation at break) were measured using a Zwick/Roell Z020 universal testing machine with crosshead speed equal to 100 mm/min. Static tensile tests were realized according to ISO 527-2. Hardness was measured using a Shore A Durometer (Zwick/Roell) according to ISO 868. Resilience was evaluated with a Schob type testing machine, according to ISO 4662.

Dynamic mechanical thermal anaysis (DMTA) was performed using a DMA Q800 Analyzer (TA

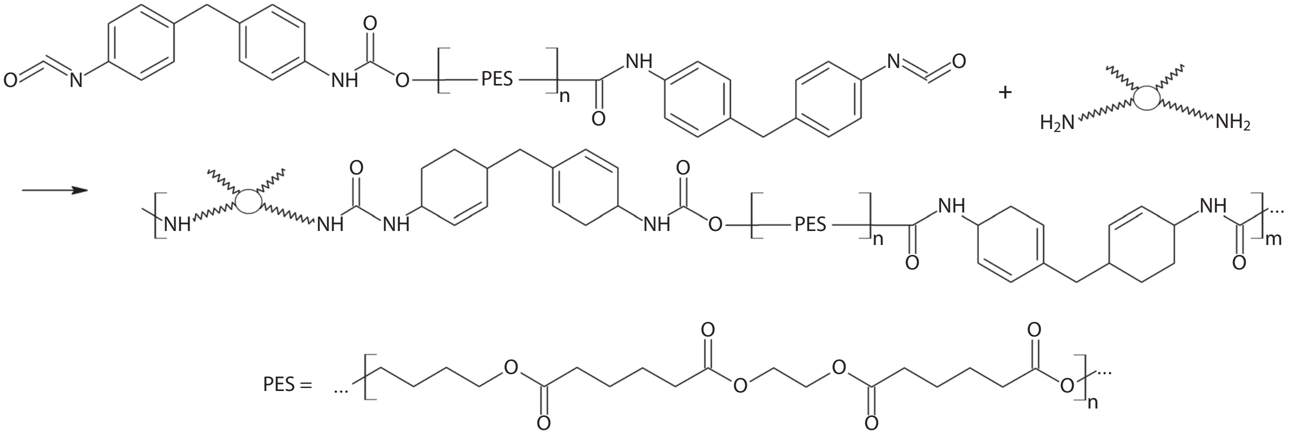

Figure 2 Synthesis of poly(ester-urethane-urea) (PEsUM-1BA) by reacting of ester-urethane prepolymer with biobased diamine.

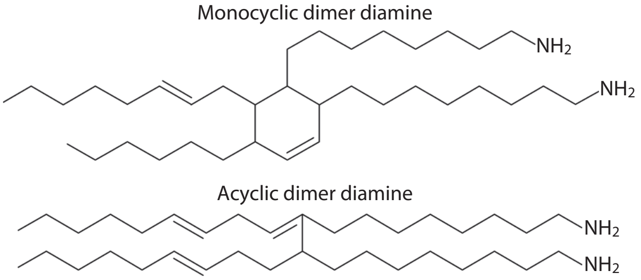

Figure 3 Possible chemical structure of amine derivative of dimerized fatty acids.

Instruments). Measurements were realized in the temperature range from −100 to 150 °C, at an operating frequency of 10 Hz, with a heating rate of 4 °C/min.

3 RESULTS AND DISCUSSION

Chemical structure analysis of obtained partially biobased materials (Figure 4) confirm the presence (characteristic vibrations) of expected chemical groups, i.e., carbonyl group in urethane groups and ester-based soft segments (υ C=O at 1725 cm^{-1}), carbonyl group in urea group (υ C=O at 1625 cm^{-1}), and amide group (υ C(O)NH at 1525–1535 cm^{-1} resulted from stretching vibrations of C-N). A higher amount of biobased diamine in the mixture of chain extenders results in an increase of intensity of the peaks connected with urea groups. Bands connected with stretching (υ C-O at 1165 and 1138 cm^{-1}) and bending (δ C-O at 1078 cm^{-1}) vibrations of C-O-C are also visible in the FTIR spectra, which are the result of the presence of urethane bonds and ester bonds (introduced by ester-based polyol) in the structure of prepared polymers. The increase of intensity of CH stretching vibrations (ca. 2950, 2920 and 2870 cm^{-1}) is the result of an increasing amount of biobased diamine (consisting of aliphatic chains) in the structure of prepared poly(ester-urethane-urea)s.

Generally, high content of soft segments resulted in low tensile strength, high elongation at break and low hardness. It is also a result of urea and urethane hydrogen bonding, which generates physical crosslinking and, as a consequence, prevents microphase separation. In the presented work, the situation is quite complicated due to the different molecular weights and structures of applied chain extenders. Biobased diamine (M_w = 586 g/mol), which was synthesized by dimerization of fatty acids, has in its structure long aliphatic chain with two aliphatic backbones. In the case of 1,4-butanediol, with a lower molecular weight (i.e., 90 g/mol) than that mentioned in the above diamine, the molecule has a short aliphatic chain.

The mechanical properties of obtained materials are shown in Figures 5 and 6. In the case of prepared poly(ester-urethane-urea), coded as PEsUM-1.0BA, soft segments are predominant constituents (81 wt%) in the structure and consist of high molecular weight (i.e., 586 g/mol) biobased diamine, and α,ω-dihydroxy(ethylene-butylene adipate). Hard segments are made up of 4,4′-diphenylmethane diisocyanate. Increasing the amount of 1,4-butanediol in the mixture of chain extender results in an increase of tensile strength, elongation at break, elasticity and a decrease of final material hardness. In the case of materials coded as PEsU, PEsUM-0.25BA, PEsUM-0.5BA and PEsUM-0.75BA, 1,4-butanediol (as a single chain extender or as part of a chain extender mixture) was used for extending prepolymer chains; therefore hard segments in the case of the mentioned materials are made up of 4,4′-diphenylmethane diisocyanate and 1,4-butanediol. The difference in molecular weight between 1,4-butanediol and the biobased diamine used results in higher content of hard segments in the case of

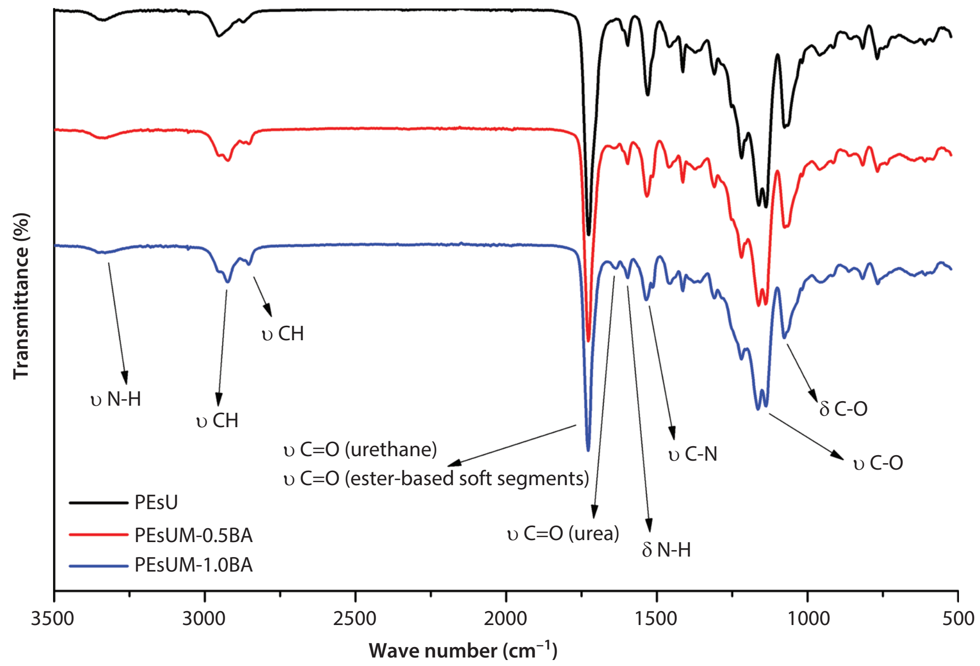

Figure 4 FTIR spectra of prepared poly(ester-urethane) (PesU) and poly(ester-urethane-urea)s, i.e., PEsUM-0.5BA and PEsUM-1.0BA.

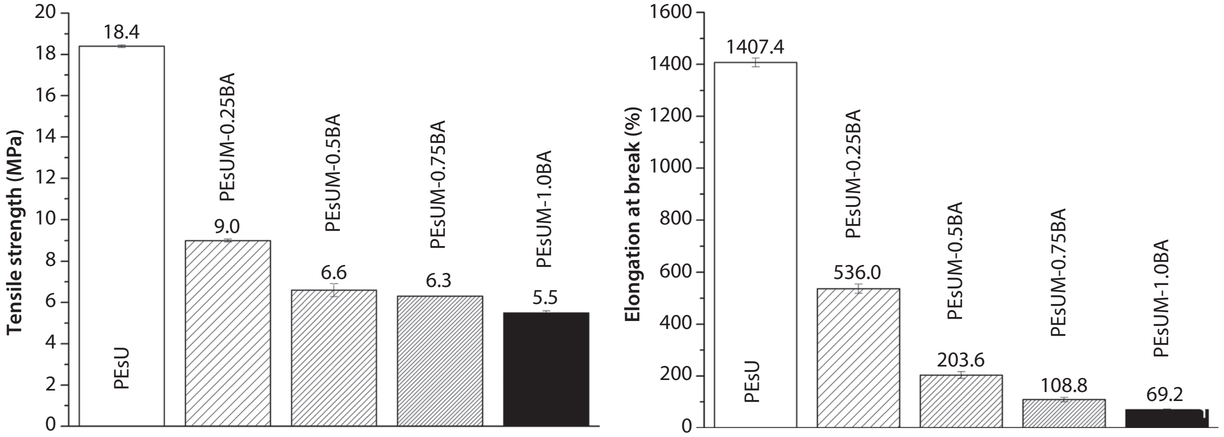

Figure 5 Tensile properties of prepared poly(ester-urethane) and poly(ester-urethane-urea)s.

PEsU in comparison to PEsUM-1.0BA, due to the soft nature of high molecular weight biobased diamine.

Generally, increasing the amount of soft segments is connected with increased elongation at break, but in the case of obtained poly(urethane-urea)s this trend is not visible. This probably results from the structure of applied diamine. The presence of aliphatic backbones in the structure of biobased diamine (Figure 3) can cause reduction of polymer chain movements, which results in faster fracture of material than in the case of polyurethane obtained without using diamine (PEsU).

Results from dynamic mechanical analysis of poly(ester-urethane-urea), obtained by using only biobased diamine as a chain extender (i.e., PEsUM-1.0BA), are shown in Figure 7. The storage modulus decreases abruptly between −35 and −15 °C, which is the region of glass transition of soft segments. The loss modulus cure displays well-defined peak with a maximum (318 MPa) at around −25 °C. The glass transition temperature is equal to −28.1 °C (defined as a temperature, when the loss factor reaches maximum value).

4 CONCLUSIONS

Poly(urea-urethane), obtained by using only biobased diamine as a chain extender, is composed of 16 wt%

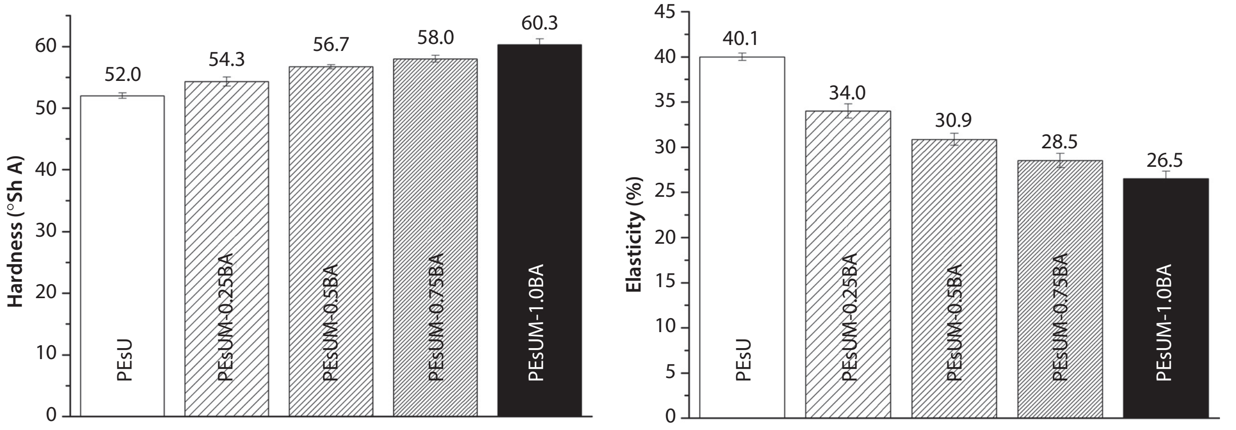

Figure 6 Hardness and elasticity of prepared poly(ester-urethane) and poly(ester-urethane-urea)s.

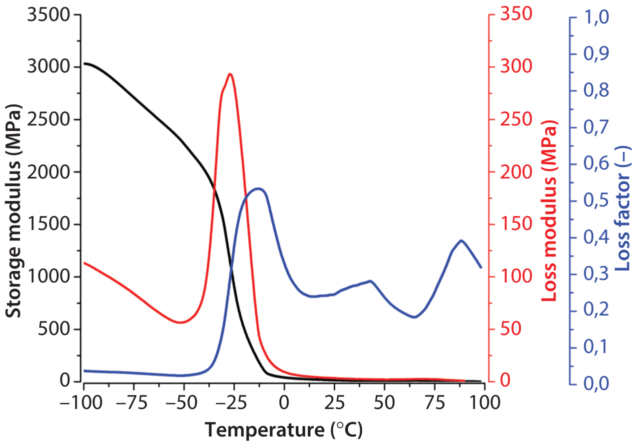

Figure 7 DMTA results for obtained poly(ester-urethane-urea).

biobased component, i.e., diamine obtained from dimerized fatty acids (derived from vegetable oils). Application of biobased diamine as a chain extender agent (which is necessary to crosslink such materials), reduces curing time of polyurethanes, due to the higher reactivity of primary amine groups in comparison to hydroxyl groups. The different molecular weights and structures of applied chain extenders, i.e., 1,4-butanediol and biobased diamine (applied separately or in mixture), results in obtaining materials with diversified properties. Further studies will be focused on preparation of high renewable content poly(urethane-urea)s using biobased polyol and diamine reactants.

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