1 INTRODUCTION

In order to protect the environment and to reduce our dependence on fossil fuels, a great deal of research effort has been, and is still being, devoted to the development of innovative technologies using renewable resources. Vegetable oils are abundant and cheap renewable resources that represent a major potential alternative source of chemicals suitable for developing safe, environmentally products. The use of vegetable oils and natural fatty acids as starting raw materials offers numerous advantages: for example, inexpensive, abundant, low toxicity, and inherent biodegradability, thus they are considered to be one of the most important classes of renewable resources for the production of bio-based polymeric materials. Polyurethanes (PUs) form a versatile class of polymers, which are used in a broad range of applications, for example, as elastomers, sealants, fibers, foams, coatings, adhesives, and biomedical materials. The industrial production of PUs is normally accomplished through the polyaddition reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Comparing with polyurethanes derived from petrochemical polyols, the vegetable-oil-based polyols used to produce polyurethanes have been the subject of many studies. Moreover, due to the hydrophobic nature of triglycerides, vegetable oils produce PUs that have excellent chemical and physical properties, such as enhanced hydrolytic, high tensile strength and elongation, high tear strength, and thermal stability.

Vegetable oils are one of the most important sources of renewable raw materials for the chemical industry and provide versatile opportunities for a transformation to meet specific applications. In the 1980s, H. Baumann et al. mainly focused on the carboxyl group of fatty acids, these include the hydrolysis of fats to make soaps, and synthesis of fatty amines from fatty acids. Recently, increasing interest in industrial and academic research has been focused on reactions on the hydrocarbon chains of fatty acids, especially on the double bonds of unsaturated fatty acids. Guo et al. applied the epoxidation of the double bonds of fatty acids, followed by nucleophilic ring opening of the epoxide to make polyols for producing polyurethanes.

To further expand applications of the bio-based polymeric materials, previous studies were focusing on converting vegetable oils into useful PUs. Based on these studies, now it has become a main research field to functionalize vegetable oils by the introduction of aromatic

PREPARATION OF BIO-POLYMERIC MATERIALS, THEIR MICROSTRUCTURES AND PHYSICAL FUNCTIONALITIES

PRIPRAVA BIOPOLIMERNIH MATERIALOV TEC NJIHOVE MIKROSTRUKTURE IN FIZIČNE FUNKCIONALNOSTI

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In this work, three kinds of bio-based aromatic triols were prepared based on vegetable oils. Furthermore, PUs were synthesized using the three triols and 4,4'-methylenebis(phenyl isocyanate), 1,4-butanediol as a chain extender. The chemical structures, molecular characteristics, and physical functionalities were studied and compared using nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetry-differential thermal analysis (TG-DTA). Results showed that the poly-(oxypropylene)-based polyurethanes degrade in a single step, whereas the vegetable-oil-based polyurethane shows one-step decomposition. The present study therefore suggests a feasible synthesis route for the use of the biomaterials for the production of polyurethanes.

Keywords: polymers, microstructures, functionalities

1 INTRODUCTION

In order to protect the environment and to reduce our dependence on fossil fuels, a great deal of research effort has been, and is still being, devoted to the development of innovative technologies using renewable resources. Vegetable oils are abundant and cheap renewable resources that represent a major potential alternative source of chemicals suitable for developing safe, environmentally products. Vegetable oils are one of the most important sources of chemicals suitable for developing safe, environmentally products. The use of vegetable oils and natural fatty acids as starting raw materials offers numerous advantages: for example, inexpensive, abundant, low toxicity, and inherent biodegradability, thus they are considered to be one of the most important classes of renewable resources for the production of bio-based polymeric materials. Polyurethanes (PUs) form a versatile class of polymers, which are used in a broad range of applications, for example, as elastomers, sealants, fibers, foams, coatings, adhesives, and biomedical materials. The industrial production of PUs is normally accomplished through the polyaddition reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Comparing with polyurethanes derived from petrochemical polyols, the vegetable-oil-based polyols used to produce polyurethanes have been the subject of many studies. Moreover, due to the hydrophobic nature of triglycerides, vegetable oils produce PUs that have excellent chemical and physical properties, such as enhanced hydrolytic, high tensile strength and elongation, high tear strength, and thermal stability.

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To further expand applications of the bio-based polymeric materials, previous studies were focusing on converting vegetable oils into useful PUs. Based on these studies, now it has become a main research field to functionalize vegetable oils by the introduction of aromatic
co-monomers into the polymer structure, which could be suitable in the search for new viable polymeric materials.12 The transition-metal-catalyzed trimerization of alkyne fatty acid compounds provides an alternative method for the preparation of highly functionalized aromatic polyols.10,11

In the present study, we have synthesized three kinds of bio-based aromatic triols prepared by oleic acid, 10-undecenoic acid, and erucic acid, which could be obtained from sunflower oil, castor oil, and rapeseed oil, respectively. PUs were synthesized by these aromatic triols and 4,4'-methylenebis(phenyl isocyanate), 1,4-butanediol as a chain extender. The chemical structures, molecular characteristics, physical properties, and thermal properties were studied and compared using nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetry-differential thermal analysis (TG-DTA).

2 EXPERIMENTAL PART

2.1 Materials

The following chemicals were obtained from the sources indicated: Oleic acid (AR, from Sinopharm), 10-undecenoic acid (from Sinopharm), erucic acid (from Aldrich), copper (II) chloride, CuCl2 (99 %, from Sinopharm), palladium (II) chloride, PdCl2 (AR, from Aldrich), palladium on carbon, Pd/C (10 % of mass fractions, from Aldrich), potassium hydroxide, KOH (AR, from Kerml), n-propanol (AR, from Kerml), dimethyl sulfoxide, DMSO (AR, from Kerml), bromine (AR, from Xilong), chlorotrimethylsilane, TMSCl (CP, from Aldrich), lithium aluminum hydride, LiAlH4 (97 %, from Aldrich), 1,4-butanediol, BD (AR, from Bodi) and 4,4'-methylenebis(phenyl isocyanate), MDI (98 %, from Aldrich) were used as received.

2.2 Synthesis of aromatic triol 4 from oleic acid

2.2.1 Dibromide carboxylic acid

To a solution of oleic acid (10.6 g, 33.6 mmol) in diethyl ether (150 mL) that was cooled to 0 °C in an ice-water bath, bromine (2.7 mL, 52.3 mmol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. A saturated sodium sulfate (Na2SO4) solution (20 mL) was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow powder 1 (yield 73 %).

IR (thin film): 3446 (OH), 2356 (C=O) cm–1.
1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.34 (s, 1H, COOH), 2.33 (t, 2H, CH2-COOH), 2.12 (m, 4H, CH2-CC), 1.26-1.62 (m, 22H), 0.88 (t, 3H, CH3).

2.2.2 Stearic acid

The dibromide compound 1 (5.5 g, 15 mmol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 mmol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N hydrochloric acid (HCl) (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow powder 2 (yield 76 %).

IR (thin film): 3454 (OH), 2356 (C=O) cm–1.
1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.24 (s, 1H, COOH), 2.33 (t, 2H, CH2-COOH), 2.12 (m, 4H, CH2-CC), 1.26-1.62 (m, 22H), 0.88 (t, 3H, CH3).

2.2.3 Stearoyl alcohol

Stearoyl alcohol 3 (1.05 g, 4.0 mmol) was dissolved in tetrahydrofuran (THF) (50 mL). 0.25 g of Pd/C (10 % of mass fractions) and TMSCl (0.75 mL, 6.0 mmol) were added. The reaction mixture was heated at 65 °C refluxed for 8 h. The resulting mixture was cooled to room temperature and filtered to remove the Pd/C. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow oil 3 (yield 82 %).

IR (thin film): 3392 (OH), 2360 (C=O) cm–1.
1H NMR (CDCl3/TMS, δ, 0.0001 %): 3.65 (t, 2H, CH2OH), 2.14 (t, 4H, CH2-CC), 1.58-1.48 (m, 6H, 1H NMR (CDCl3/TMS, δ, 0.0001 %): 1.41-1.23 (m, 1,8H), 0.90 (t, 3H, CH3).

2.2.4 Aromatic triols

Stearoyl alcohol 3 (1.05 g, 4.0 mmol) was dissolved in tetrahydrofuran (THF) (50 mL). 0.25 g of Pd/C (10 % of mass fractions) and TMSCl (0.75 mL, 6.0 mmol) were added. The reaction mixture was heated at 65 °C refluxed for 8 h. The resulting mixture was cooled to room temperature and filtered to remove the Pd/C. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a dark-yellow oil 4a and 4b (yield 58 %).

IR (thin film): 3438 (OH), 1652 (C=O of benzene) cm–1.
1H NMR (CDCl3/TMS, δ, 0.0001 %): 3.56 (t, 2H, CH2OH), 2.43 (m, 12H, CH2Ph), 1.49-1.20 (m, 72H), 0.83 (t, 9H).
13C NMR (CDCl3/TMS, δ, 10–4 %): 136.77 (Ph-CH2), 62.94 (CH2OH), 31.94, 31.86, 29.68, 29.64, 29.57, 29.33, 29.26, 25.72, 22.68, 22.66, 14.12 (CH3).
2.3 Synthesis of aromatic triol 4’ from 10-undecenoic acid

2.3.1 Dibromide carboxylic acid 1’

10-Undecylenic acid (9.2 g, 50 m mol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath. Bromine (2.7 mL, 52.3 mmol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. A saturated Na2S2O3 solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a white solid 1’ (yield 78 %).

IR (thin film): 3433 (OH), 1705 (C=O) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.58 (s, 1H, COOH), 3.85-3.80 (q, 1H, CH-CHBr), 3.64-3.57 (t, 2H, CH-Br), 2.35-2.30 (t, 2H, CH2-COOH), 2.17-2.05 (m, 1H), 1.84-1.50 (m, 3H), 1.30-1.23 (m, 8H).

2.3.2 10-Undecyn-1-ol 3’

10-Undecyn-1-ol (3.3 g, 21 mmol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath. Bromine (4.2 mL, 81 m mol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. A saturated Na2S2O3 solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over MgSO4. The solution was treated with hydrogen chloride (30 mL) aqueous solution was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a gray solid 3’ (yield 78 %).

IR (thin film): 3440 (OH), 2360 (C=C), 1710 (C=O) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.54 (s, 1H, COOH), 2.31 (t, 2H, CH2-COOH), 2.17-2.11 (m, 2H), 1.92 (t, 1H), 1.55-1.44 (m, 4H), 1.33-1.23 (m, 8H).

2.3.3 10-Undecyn-1-ol 3’

10-Undecynic acid 2’ (1.6 g, 8.8 m mol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 m mol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N HCl (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a white solid 2’ (yield 63 %).

IR (thin film): 3440 (OH), 2360 (C=C), 1710 (C=O) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.52 (s, 1H, COOH), 2.31 (t, 2H, CH2-COOH), 2.17-2.11 (m, 2H), 1.92 (t, 1H), 1.55-1.44 (m, 4H), 1.33-1.23 (m, 8H).

2.4 Synthesis of aromatic triol 4” from erucic acid

2.4.1 Dibromide carboxylic acid 1”

Erucic acid (15.88 g, 33.6 mmol) in diethyl ether (150 mL) was cooled to 0 °C in an ice-water bath. Bromine (2.7 mL, 52.3 mmol) was added dropwise over 30 min. Then the ice-water bath was removed and the solution was stirred for another 2 h at room temperature. A saturated Na2S2O3 solution (20 mL) was added to reduce the excess bromine. The resulting organic phase was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a gray solid 1” (yield 78 %).

IR (thin film): 3425 (OH), 1706 (C=O) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.89 (s, 1H, COOH), 4.27-4.18 (m, 2H, CH2-CHBr), 2.35 (t, 2H, CH2-COOH), 2.10-1.95 (m, 2H, CH2-CHBr), 1.65-1.54 (m, 2H), 1.47-1.26 (m, 30H), 0.89 (t, 3H, CH3).

2.4.2 Behenolic acid 2”

The dibromide compound 1” (7.5 g, 15 mmol) was dissolved in DMSO (18 mL, 250 mmol). KOH (20 g, 360 m mol) and 1-propanol (150 mL) were added. The mixture was heated at 110 °C under reflux for 4 h. Then the solution was poured into 2N hydrochloric acid (HCl) (150 mL) at room temperature. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow powder 2” (yield 72 %).

IR (thin film): 3454 (OH), 2361 (C=C), 1705 (C=O) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 11.62 (s, 1H, COOH), 2.37 (t, 2H, CH2-COOH), 2.15 (m, 4H, CH2-CC), 1.69-1.23 (m, 30H), 0.90 (t, 3H, CH3).

2.4.3 Behenolic ester 3”

To a solution of behenolic acid 2” (4.5 g, 12.9 mmol) in methanol (100 mL) was added about 5 mL concentrated sulphuric acid. The reaction mixture was heated at 95 °C and refluxed for 3 h. The resulting organic layer was separated, washed with brine (20 mL) and filtered to remove the PdCl2 and CuCl2. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated by reduced pressure to give a dark-yellow oil 4’a and 4’b (yield 68 %).

IR (thin film): 3456 (OH), 1639 (C=C of benzene) cm−1.

1H NMR (CDCl3/TMS, δ, 0.0001 %): 6.40 (s, 3H, Ph), 3.64 (t, 6H, CH3-Ph), 2.29 (t, 6H), 1.61-1.24 (m, 42H).

13C NMR (CDCl3/TMS, δ, ppm): 138.22 (Ph-CH2), 120.35 (Ph-H), 64.11 (CH2-CH3), 39.86, 34.35, 30.68, 29.70, 29.08, 28.54, 27.46, 24.96.
dried over MgSO4. The solvent was evaporated under reduced pressure to give pale-yellow oil 3" (yield 62%).

IR (thin film): 2360 (C\equiv\text{N}), 1745 (C=O), 1170 (C-O) cm\(^{-1}\).

\(^1\)H NMR (CDCl3/TMS, δ, 0.0001 %): 3.66 (s, 3H, CH3-O), 2.56-2.40 (m, 12H), 1.64-1.26 (m, 96H), 0.89 (t, 3H, CH3).

\(^13\)C NMR (CDCl3/TMS, δ, 0.0001 %): 174.41 (C=O), 1170 (C-O), 51.48 (CH3-O), 34.13, 33.76, 31.96, 31.46, 30.69, 30.17, 29.71, 29.52, 29.42, 29.36, 29.31, 29.10, 24.97, 22.72, 14.16 (CH3).

2.4.4 Aromatic triester 4"a and 4"b.

Behenolic ester 3" (2.8 g, 8.0 mmol) were dissolved in n-butyl alcohol (9 mL) and benzene (150 mL). PdCl2 (0.15 g, 0.85 mmol) and CuCl2 (2.05 g, 12 mmol) were added. The reaction mixture was heated at 40 °C and refluxed for 12 h. The resulting mixture was cooled to room temperature and filtered to remove the PdCl2 and CuCl2. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow oil 4"a and 4"b (yield 68%).

IR (thin film): 2360 (C\equiv\text{N}), 1745 (C=O), 1170 (C-O) cm\(^{-1}\).

\(^1\)H NMR (CDCl3/TMS, δ, 0.0001 %): 3.68 (s, 9H, CH3-O), 2.54-2.43 (m, 2H, CH2-COOCH3), 2.13 (m, 4H, CH2-CC), 1.68-1.20 (m, 30H), 0.88 (t, 3H, CH3).

\(^13\)C NMR (CDCl3/TMS, δ, 0.0001 %): 136.71 (Ph-CH2), 51.48 (CH3-O), 34.13, 33.76, 31.96, 31.49, 30.68, 29.70, 29.51, 29.42, 29.26, 25.75, 24.97, 22.70, 22.70, 19.15, 14.13(CH3).

2.4.5 Aromatic triols 5"a and 5"b.

Aromatic triol 5" (2.1 g, 2.0 mmol) were dissolved in n-butyl alcohol (9 mL) and benzene (150 mL). PdCl2 (0.15 g, 0.85 mmol) and CuCl2 (2.05 g, 12 mmol) were added. The reaction mixture was heated at 40 °C and refluxed for 12 h. The resulting mixture was decomposed by adding 20 mL of water dropwise. A 2N HCl (30 mL) aqueous solution was added until the pH was neutral. The resulting organic layer was separated, washed with brine (20 mL) and dried over MgSO4. The solvent was evaporated under reduced pressure to give a pale-yellow oil 5"a and 5"b (yield 88%).

IR (thin film): 3430 (OH), 1465 (C=C of benzene), 1364 (C-O), 1174 (C-O) cm\(^{-1}\).

\(^1\)H NMR (CDCl3/TMS, δ, 0.0001 %): 3.66 (t, 6H, CH2-CH2), 2.56-2.43 (m, 2H, CH2-COOCH3), 1.70-1.26 (m, 90H), 0.90 (t, 9H, CH3).

\(^13\)C NMR (CDCl3/TMS, δ, 0.0001 %): 174.41 (C=O), 1170 (C-O), 51.48 (CH3-O), 34.13, 33.76, 31.96, 31.46, 30.69, 30.17, 29.71, 29.52, 29.42, 29.36, 29.31, 29.10, 24.97, 22.72, 14.16 (CH3).
For thermal stability analysis, 10 mg of the dried polyurethane powders were used in TG-DTA thermal analyzer (type PerkinElmer Diamond TG/DTA, America) at a heating rate of 10 °C/min from 20 °C to 800 °C in an inert-gas atmosphere.

3 RESULTS AND DISCUSSION

3.1 Synthesis of bio-based aromatic triols

The synthesis of triol monomers from oleic acid, erucic acid and 10-undecenoic through a cyclotrimerization reaction yielded a mixture of asymmetrical and symmetrical molecules (Chart 1). Bio-based aromatic triols oleic acid-based aromatic triols (O-BAT), erucic acid-based aromatic triols (E-BAT) and 10-undecenoic-based aromatic triols (U-BAT) were synthesized by two different methods. Alkyne alcohol derivatives were obtained in moderate yields from the corresponding fatty acids by bromination, dehydrobromination, and reduction of carboxylic acid using well-established procedures (Scheme1). Alkyne fatty derivatives were obtained in moderate yields from the corresponding fatty acids by bromination, dehydrobromination, and esterification using well-established procedures (Scheme1).\(^{9,12}\) Cyclotrimerization of the 10-undecyn-1-ol 3’ and behenolic ester 3’’ were carried out using PdCl\(_2\) as a transition-metal catalyst. However, when cyclotrimerization of stearoyl alcohol 3 was carried out under the same conditions, some side products were slowly generated or no indication of the trimer formation was obtained. The reaction was then carried out using Pd/C as a transition-metal catalyst, and the expected product was obtained in moderate yields.\(^{10,11}\)

Transition-metal-catalyzed cyclotrimerization of alkynes can be considered as one of the most powerful and general methodologies used to assemble arene rings, and a large number of transition-metal catalysts have been developed for alkyne cyclotrimerization in organic media.\(^{12,24–25}\) A simple method utilizes a heterogeneous Pa/C catalyst in a nitrogen atmosphere with refluxing THF as the solvent and commercial grade chlorotrimethylsilane.\(^{10,26}\) Cyclotrimerization of Stearoyl alcohol 3 was carried out following this procedure, and the symmetric and asymmetric isomers, such as aromatic triols 4a and 4b, have almost identical IR or \(^{13}\)C NMR spectra in CDCl\(_3\). The formation of the aromatic derivative was confirmed by the appearance of the signal at 0.013677 % in the \(^{13}\)C NMR spectrum corresponding to the aromatic core. The two compounds could not be separated by flash chromatography due to their similar polarities. Therefore, the presence of two compounds could not be ruled out.

The preparation of benzene derivatives via the palladium-chloride-catalyzed cyclotrimerization of alkynes in the presence of CuCl\(_2\) has been described as a smooth and regioselective method.\(^{15}\) When the cyclotrimerization of 10-undecyn-1-ol 3’ was carried out using PdCl\(_2\) and CuCl\(_2\) as transition-metal catalysts, a 1,3,5-trisubstituted benzene derivative was obtained regioselectively in a moderate yield. The appearance of signals at 0.000639 % in the \(^1\)H NMR spectrum and 0.012035 % and 0.013763 ppm in the \(^{13}\)C NMR spectrum confirms the formation of the symmetric product.

(A) Oleic acid and derivatives: n=5, R=(CH\(_2\))\(_n\)CH\(_3\)

(B) Erucic acid and derivatives: n=9, R=(CH\(_2\))\(_n\)CH\(_3\)

(C) 10-undecenoic acid and derivatives: n=6, R=H

Chart 1: Chemical structures of aromatic triols monomers obtained by oleic acid, erucic acid and 10-undecenoic, respectively

Grafikon 1: Kemijske strukture aromatičnih triol monomerov, dobljenih z oleinsko kislino, eruka kislino in 10-undekenojsko kislino

Scheme 1: Synthesis of aromatic triols from oleic acid, erucic acid and 10-undecenoic acid, respectively

Shema 1: Sinteza aromatičnih triol iz oleinske kislino, eruka kislino in 10-undekenojske kislino
The attempt to cyclotrimerize behenolic ester 3” via Pa/C catalyst in nitrogen atmosphere with refluxing THF as the solvent and chlorotrimethylsilane, some side products were slowly generated. The preparation of benzene derivatives via the palladium-chloride-catalyzed cyclotrimerization of alkynes in the presence of CuCl2 has been described as a smooth and regioselective method.12,27–28 When we applied the reaction to behenolic ester 3”, the symmetric and asymmetric isomers, such as aromatic triols 4”a and 4”b, have almost identical IR or 13C NMR spectra in CDCl3. The formation of the aromatic derivative was confirmed by the appearance of the signal at 0.013671 % in the 13C NMR spectrum corresponding to the aromatic core. The two compounds could not be separated by flash chromatography due to their similar polarities. Therefore, the presence of two compounds could not be ruled out. The reaction can also proceed with behenolyl alcohol. However, when cyclotrimerization of the behenolyl alcohol was carried out in the same conditions, a lot of side products were slowly generated and the yields of aromatic triester 4”a and 4”b were lower. So, aromatic ester derivatives were used as a starting material for the reduction of the carboxylate groups to synthesize two triols with primary hydroxyl groups.

3.2 Synthesis and characterization of polyurethanes

Vegetable-oil-based polyols have been widely used to produce segmented and non-segmented polyurethanes.19–22 Segmented polyurethanes are elastomeric block copolymers that generally exhibit a phase-segregated morphology made up of soft rubbery segments and hard glassy or semi-crystalline segments.23,24 The soft segment usually consists of polyether or polyester diols, whereas the hard segment consists of the diisocyanate component and a low molecular weight consists of the diisocyanate component and a low-molecular-weight chain extender. The advantage of segmented polyurethanes is that their segmental and domain structure can be controlled over a considerable range through the selection of the materials, their relative proportions, and the processing conditions.12

In the study, bio-based polyurethanes were prepared using the one-shot technique from O-BAT, E-BAT or U-BAT, BD as a chain extender, and MDI as a coupling agent. The bio-based aromatic triols/MDI part is considered as the soft phase, even though its glass transition is above room temperature (Table 1). These hard segments are polar, crystallizable and likely to form a separate phase if the hard-segment content is high enough. The chemical composition and hard-segment content of the synthesized polyurethanes are also shown in Table 1. The OH/NCO molar ratio was kept at 1.5. Reactants were mixed at 75 °C and cured at this temperature for 2 h and post-cured at 110 °C for 18 h to give the polyurethanes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Ratio (OH:NCO)</th>
<th>Ratio (Polyol/BD/MDI)</th>
<th>% Hard segment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-BAT-PU</td>
<td>0.9</td>
<td>1:3:3</td>
<td>56.9</td>
</tr>
<tr>
<td>E-BAT-PU</td>
<td>0.9</td>
<td>1:3:3</td>
<td>52.1</td>
</tr>
<tr>
<td>U-BAT-PU</td>
<td>0.9</td>
<td>1:3:3</td>
<td>67.6</td>
</tr>
</tbody>
</table>

*The hard-segment percentage is calculated as the w/% of BD and MDI per total material weight

To investigate the molecular structure of polyurethanes WAXD and FTIR were employed. The amorphous character of both the asymmetric and symmetric polyurethanes was verified by WAXD (Figure 1). All the samples show similar WAXD curves with a broad peak at about 2θ ≈ 22°. This broad peak is a typical characteristic of amorphous polymers12,13,15–17, which confirms that there are no crystals in O-BAT-PU, E-BAT-PU and U-BAT-PU.

![Figure 1](image1.png)

**Figure 1:** Wide-angle X-ray diffraction patterns of: a) O-BAT, b) E-BAT and c) U-BAT polyurethane

**Slika 1:** Sirokokotna rentgenska difrakcija: a) O-BAT, b) E-BAT in c) U-BAT poliuretana

![Figure 2](image2.png)

**Figure 2:** FTIR spectra of: a) O-BAT-PU, b) E-BAT-PU, and c) U-BAT-PU

**Slika 2:** FTIR-spekttri: a) O-BAT-PU, b) E-BAT-PU in c) U-BAT-PU
The FTIR spectra for O-BA T-PU, E-BA T-PU, and U-BA T-PU are shown in Figure 2. From Figure 2, it is clear that the spectra are similar for the PUs prepared from the same diisocyanate but different aromatic triols sources. The unreacted diisocyanate (NCO group) is clearly shown by a peak centered at 2362 cm⁻¹. A strong stretching band located at around 3317 cm⁻¹ characteristic of the N-H group and a stretching vibration band centered around 1708 cm⁻¹ characteristic of the C=O group are present in the FTIR spectra.7,8,15 There are also two stretching regions attributed to the C=O group. The band centered at around 1768cm⁻¹ corresponds to the free carbonyl group. These results indicated that the three kinds of PU materials undergo physical bonding.16,18

3.3. Thermal stability of polyurethanes

Thermal analysis of the polyurethanes obtained was performed to provide insights into the morphological structure of the material. Figure 3 shows the DSC thermogram for the polyurethanes. There were two endothermic peaks at about 45–50 °C and 175–190 °C. The glass-transition temperature of the samples measured by DSC was 45–50 °C. The transition appeared in the region from 45 °C to 50 °C and were attributed to the soft-segment glass-transition temperature \(T_g\). The \(T_g\) value is a measure of relative purity of the soft-segment regions; when there are hard segments dispersed in the soft domains, the \(T_g\) is raised.12 The addition of bifunctional components such as MDI/BD reduces the cross-linking density, but increases the phenyl ring content. In principle, a reduced cross-linking density should decrease the \(T_g\), but an increased aromatic content should have the opposite.12 The peak in the region from 175 °C to 190 °C was ascribed to the melting point of hard-segment domains, which supports the development of a phase-separated morphology and indicates that the hard-segment content is high enough to achieve phase separation.12

TGA is the most favored technique for the evaluation of the thermal stability of polymers. Polyurethanes have a relatively low thermal stability, mainly because the presence of urethane bonds. From the DTG curves it can be seen that in nitrogen only one process occurs during thermal degradation. G. Lligadas et al.12 observed a similar behavior in the case of vegetable-oil-based polyurethanes. They showed that poly-(oxypropylene)-based polyurethanes degrade in a single step, whereas vegetable-oil-based polyurethane shows one-step decomposition.4,7,15 Figure 4 shows the DTG curve and Figure 5 shows the TGA curves of different polyurethanes, which reveals a degradation stage at temperatures between 300 °C and 400 °C. The results are similar to the three bio-based polyurethanes systems. That can be associated with the decomposition of urethane bonds, which takes place through the dissociation to diisocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines.16,18
4 CONCLUSIONS

Bio-based aromatic triols, O-BAT, E-BAT and U-BAT have been synthesized using two different methods. It is demonstrated that alkylz alcohol derivatives can be obtained in moderate yields from the corresponding fatty acids by bromation, dehydrobromination, and reduction of carboxylic acid, and alkylz fatty derivatives can also be obtained in moderate yields from the corresponding fatty acids by bromation, dehydrobromination, and esterification. Such a synthesis methodology has indicated a practical feasibility of utilizing the new bio-based aromatic triols for the production of bio-based polyurethanes. The crystalline structure and thermal stability of these polyurethanes have been compared to their counterparts made from a similar O-BAT, E-BAT, and U-BAT, respectively. The corresponding polyurethane networks with hard-segment have been further prepared by the reaction of the polyol, BD, and MDI. The synthesized materials have been characterized using the spectroscopic techniques, WAXD, DSC and TG-DTA. The results have showed that it is possible to exploit renewable resources to achieve environment-friendly green materials.

5 REFERENCES