Original scientific papers UDK 66:678
doi: 10.7251/COMEN1301009R

NOVEL POTENTIALLY BIODEGRADABLE POLYURETHANES FROM BIO-BASED POLYOLS

Dragana Radojčić,[*] *Mihail Ionescu, Zoran S. Petrović*

Kansas Polymer Research Center, Pittsburg State University,
1204 Research Road, Pittsburg, KS, 66762

Abstract: Completely bio-based polyols, suitable for the preparation of rigid polyurethanes were synthesized from polyglycerol, lactic acid and fatty acids. Lactic units were introduced into the polyol structure by the ring opening addition of L-lactide to hydroxyl groups, in the presence of the titanium(IV) isopropoxide catalyst. To address the incompatibility issue of simple lactide–(poly)glycerol polyols with isocyanates, vegetable oil-based fatty acids were introduced into the polyol structure. Cast thermosetting polyurethane resins were prepared by reacting polyols with diphenylmethane diisocyanate. Polyurethanes were crosslinked glassy amorphous materials with tensile strength of ~ 60 MPa, flexural modulus of 0.9 - 2.3 GPa and notched Izod impact resistance of 30 - 80 J/m. These polyurethanes are potentially biodegradable.

Keywords: bio-based polyols, lactate polyols, polyglycerol, vegetable oil, polyurethanes.

1. INTRODUCTION

Polyurethanes (PU) are obtained by reacting polyols with polyisocyanates. Similarly to many polymeric materials, PU relies on petroleum as the feedstock for its major components. Developing bio-renewable feedstock for PU manufacturing and polymer industry as a whole is highly desirable for both economic and environmental reasons. Industry is increasingly involved in the production of bio-based polyols, mainly synthesized from vegetable oils [1]. Currently, polyether polyols are predominantly (75%) used for polyurethanes. Polyester polyols are the second most important group with 18% of the polyol market. They are obtained by polycondensation of dicarboxylic acids (or derivatives such as esters or anhydrides) and diols (or polyols), or by the ring opening polymerization of cyclic esters (lactones, cyclic carbonates) [2].

Polylactic acid (PLA) is commercial thermoplastic polyester known for its biodegradability [3]. Preparing polyols from lactic acid (lactate polyols) as precursors for polyurethanes would be beneficial in several ways. It would allow preparation of biodegradable foams, elastomers and other products where traditional urethanes are used, but also would also easy processing and casting complicated forms as with other thermosetting materials. They may be useful for biomedical applications such as scaffolding materials etc.

Lactate polyols are polyester polyols containing lactic acid units. Introducing lactic acid units into a polyol structure can be done in different ways. One possible route is the ring opening addition of lactide to hydroxyl groups. Other routes involve esterification of different polyols with lactic acid, or transesterification with esters of lactic acid (e.g., ethyl lactate, butyl lactate). The advantage of the addition of lactide to polyols is in short reaction times and avoidance of the removal of low molecular weight compounds (water or alcohols). Lactate polyols can be prepared from 100% bio-renewable feedstock.

As reported in literature, PUs prepared from lactate polyols were found to be biodegradable, and possibly biocompatible [4−8]. The GB patent 1,517,826 [4] describes the synthesis of hydrophilic crosslinked PU foams using a mixture of trimethylolpropane trilactate and polyethylene glycol. These biomedical foams of high absorptive ability of body fluids were readily biodegradable after disposal. Miao and coworkers [5] obtained a vegetable oil polyol with LA units by reacting epoxidized soybean oil (ESBO) with lactic acid. T_g of PUs derived from this polyol were higher than those of PU's derived from ESBO. The soybean

---

[*] Correspondig author: dradojcic@pittstate.edu

polyol with 5.2 OH groups / mol reacted with MDI to give a polyurethane with T_g of 31 ^{o}C, while the ESBO polyol containing LA units gave a polyurethane with $T_g = 96$ ^{o}C. Uiama et al.[5] prepared a polyol containing LA units by polyaddition of lactide to the hydroxyl groups of castor oil. The authors claimed that the PU foams and coatings obtained with this castor oil-based lactate polyol were biodegradable. Two different groups prepared block copolymers of polyethylene glycol (PEG)-poly (Lactic acid) (PLA) by polyaddition of lactides to the hydroxyl groups. These A-B type block copolymers (PEG-PLA) [6] and A-B-A type block copolymers (PLA-PEG-PLA) [7] were proven to be useful for drug delivery of poorly water soluble drugs. Wang et al. [8] prepared biodegradable polyurethanes by using a diol PLA-PEG-PLA block copolymer (A-B-A type) and an aliphatic bio-based diisocyanate (L-Lysine diisocyanate ethyl ester). They showed that aliphatic diisocyanates led to polyurethanes with excellent biodegradability.

Polyurethanes have been found to be susceptible to biodegradation by naturally occurring microorganisms, including fungi and bacteria. Microbial degradation of polyurethanes is dependent on many properties of polymer such as molecular orientation, crystallinity, cross-linking and chemical groups present in molecular chains, which determine the accessibility to degrading-enzyme systems [9−13]. Polyester-type PU is considered to be more susceptible to microbial attack than polyether-type PU. The hydrolysis of ester bonds in the polyester segments of PU has been shown to occur through esterase activity. Little information has been available on the degradation of the isocyanate segment of PU; however, the production of ammonia indicates that attack does occur. [9,14] Kim & Kim [15] investigated the biodegradation of diverse polyester type polyurethanes of different chemical structures. The authors concluded that the rate of biodegradation increased in accordance with the diisocyanates used: MDI < H_{12}MDI < HDI. The PU composed of aliphatic diisocyanates demonstrated a greater rate of biodegradation than the PU composed of aromatic diisocyanates.

The objective of the present work was to prepare high functionality polyester (PE) polyols containing lactic units (lactate polyols) suitable for preparation of rigid cast polyurethanes and foams. These PUs, apart from having high bio-based content, were expected to be biodegradable. The ring opening addition of L-lactide to hydroxyl groups was the reaction used for introducing lactic acid units into polyol structure. In order to obtain high functionality polyols with high bio-based content, different polyglycerols with high content of OH groups were used as starters. However, high concentration of OH groups in simple polyglycerol-lactate adducts and strong tendency to crystallization of lactate units result in strong intramolecular hydrogen bonding, which makes these polyols immiscible with isocyanates. Consequently, this issue was addressed by incorporation of hydrophobic fatty acid (FA) segments in the lactate polyol structure, which are known to have good affinity for isocyanates. Synthesized lactate polyols were reacted with isocyanate to obtain rigid cast polyurethanes.

2. EXPERIMENTAL

2.1. Materials

L-lactide (L-100, Nature Works Ingeo, LCC) of high purity (≥99%, MW = 144) was crushed into a fine powder prior to use. Glycerol (G) (≥99%), diglycerol (DG) and polyglycerol (PGL) were used as bio-based initiators in all synthesis. Properties of G, DG and PGL are given in *Table 1*. Methyl ricinoleate (MeRA) (>75%, Tokyo Chemical Industry), methyl soyate (MeSBO) and soybean oil (SBO) RBD from Cargill, castor oil (CO) from Alfa Aesar and soy-based polyol X-173 (OH# = 173 mg KOH/g, f = 3.3, EW = 324) synthesized at KPRC were used for attaching hydrophobic fatty acid chains to polyols. Titanium(IV) isopropoxide, 98+% (Acros Organics) was used as the catalyst. Modified monomeric methylene diphenyl diisocyanate (MDI) (Rubinate 9225, f = 2.06, EW = 135) from Huntsman was used in the preparation of cast polyurethanes. Soy-based polyol Bi-OH X-0210 (f = 4, EW = 249) from Cargill was used for the preparation of the reference PU.

2.2. Synthesis of lactate polyols by direct reaction of bio-based starters with L-lactide

Polyols was prepared by ring opening addition of L-lactide (L) to glycerol (G), diglycerol (DG) or polyglycerol 3 (PGL3), in the presence of anionic coordinative catalyst titanium(IV) isopropoxide or $Ti(OiPr)_4$ at the concentration of 0.3 wt%. Reactions were carried out in a 500 mL three-neck round bottom flask equipped with a mechanical stirrer, water condenser and coat heater under the constant flow of nitrogen. Reactants were charged at once, and the mixture was maintained at 140 °C for 4 h. General reaction scheme is presented in *Figure 1.*

Table 1. Properties of diglycerol and polyglycerols (from manufacturer data sheets).

Starters	n	MW	OH# (mg KOH/g)	EW	f	Viscosity at 25°C (Pa·s)	Manufacturer
Glycerol	1	92	1828	30.7	3	1	Sigma Aldrich
Diglycerol	2	166	1352	41.5	4	13	Solvay Chemicals (Germany)
Polyglycerol 3	3	250	1122	50.0	5	41	
Polyglycerol 4	4	314	1072	52.3	6	83	
Polyglycerol 5	5	388	1012	55.4	7	176	Daicel Chemicals (Japan)

n- average number of glycerol units f - average functionality

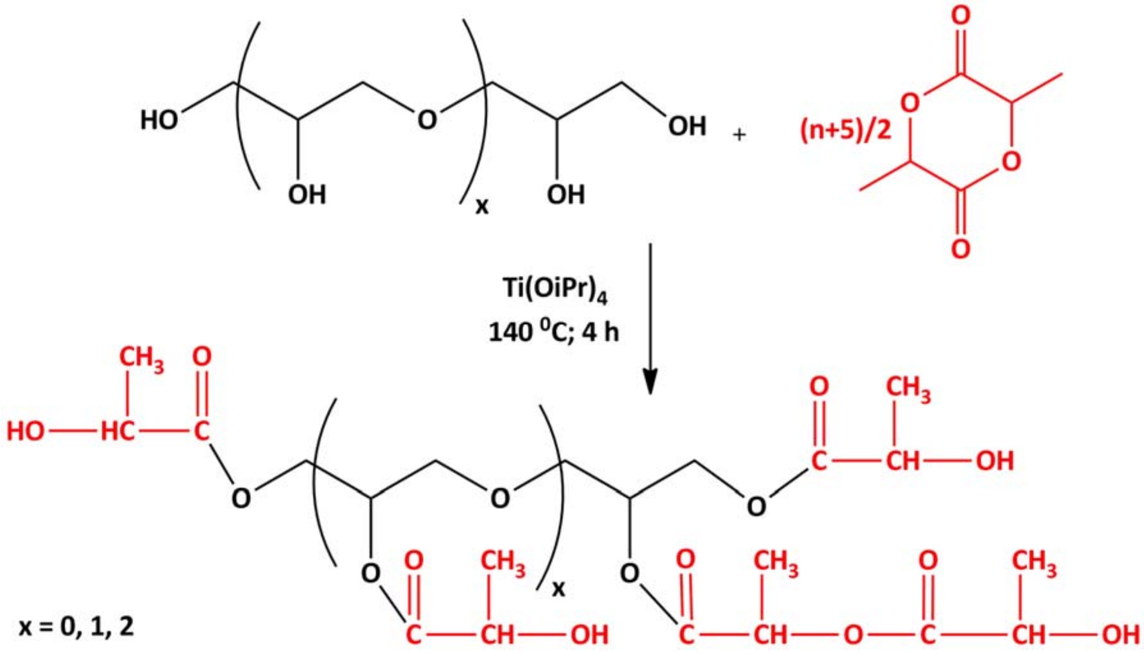

Figure 1. General scheme for synthesis of lactate polyols by direct addition of L-lactide to glycerol, diglycerol and polyglycerol.

2.3. Synthesis of fatty acid modified lactate polyols

Polyester polyols were prepared by ring opening addition of L-lactide (L) to partial (poly) glycerol- fatty acid esters. Reactions were carried out in a 500 mL three-neck round bottom flask equipped with a mechanical stirrer, water condenser, Dean Stark trap and coat heater under the constant flow of nitrogen. General reaction scheme is presented in Figure 2 and 3. The reactions were carried out in two steps. In the first step, DG or PGL (PGL4 or PGL5) was transesterified with fatty acid derivatives at 180 – 220 °C for 3 h, in the presence of 0.35 wt% $Ti(OiPr)_4$. When simple FAMEs were used the reaction was accompanied by methanol removal. In the case of vegetable oils, the first step was actually equilibration between polyglycerol and glycerol esters of fatty acids. The second step was ring opening addition of L-lactide to hydroxyl groups of the first step product. It was conducted at 140 °C during 4 h.

2.4. Preparation of rigid cast polyurethanes

Synthesized lactate polyols were used for preparation of rigid cast polyurethanes by reacting with Rubinate 9225 at isocyanate index 102. Calculations were made to total weight ($w_p + w_i$) of 22 g, using the following relation:

$$w_i = 1.02 \cdot EW_i \cdot (w_p / EW_p) \qquad (1)$$

where: w_p and w_i are weight of polyol and isocyanate, respectively. $EW_p = 56110/OH\#$ is the hydroxyl equivalent weight of polyol and $EW_i = 4200/NCO\%$ is the equivalent weight of isocyanate. The following procedure was applied: polyol was charged in a 50 mL round bottom glass flask and dried under high vacuum (5 mm Hg) at 70 °C for half an hour. Subsequently, isocyanate was added and mixed vigorously under high vacuum at 70 °C. Before reaching the gel point, the mixture was quickly poured into the preheated square aluminum mold (10x10x2 mm) and cured at 110 °C overnight. Prior to testing, samples were allowed to post-cure under ambient conditions for 7 days. Additionally, PU with commercial soy-based polyol X-210 was prepared for comparison.

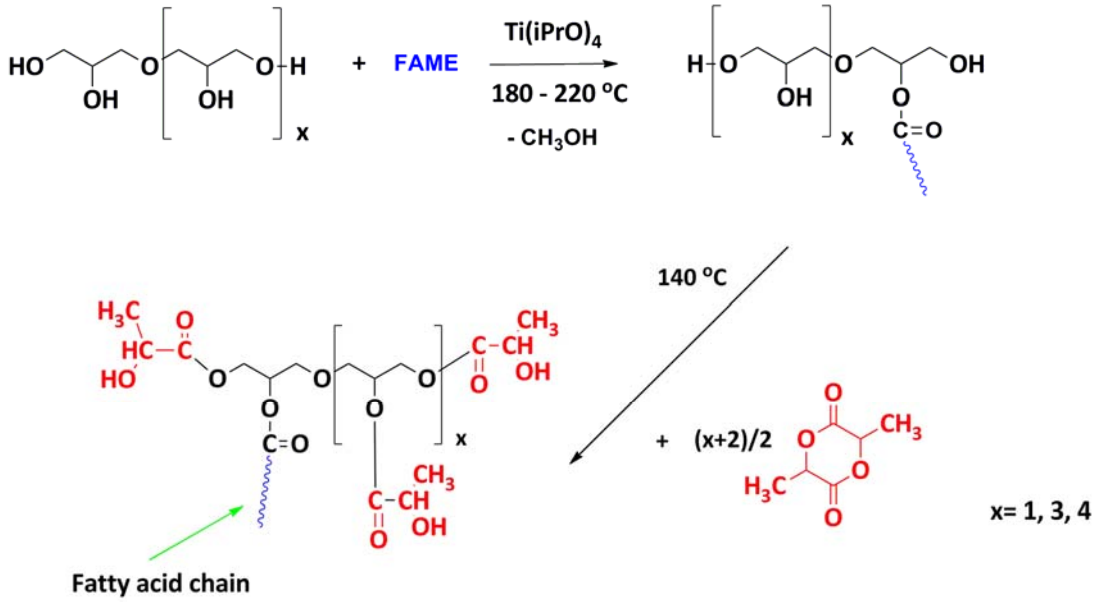

Figure 2. Generalized scheme for transesterification reaction of polyglycerol with fatty acid methyl ester (FAME) followed by addition of L-lactide.

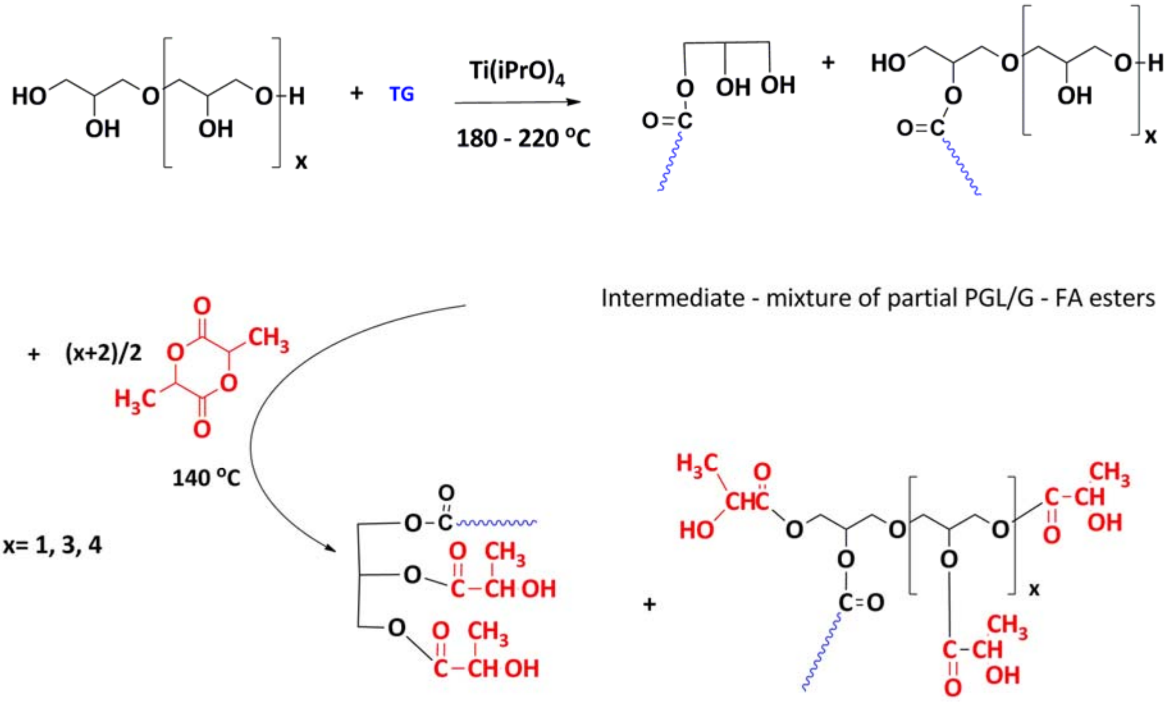

Figure 3. Generalized scheme for equilibration of polyglycerol with triglyceride (TG) followed by addition of L-lactide.

2.5. Methods

Acid value (AV) was determined according to the indicator method following IUPAC 2.201 standard. Hydroxyl number was determined by phthalic anhydride method (P.A.P.) according to ASTM D 4274. Total hydroxyl number (OH#) was calculated as the sum of OH# P.A.P. and AV.

An AR 2000 dynamic stress rheometer (TA Instruments, New Castle, DE, USA), equipped with a 2^o cone plate having 25 mm diameter and 55 μm truncation height, was used to measure polyol viscosities at 25 ^{0}C. Continuous shear stress ramp from 1 to 2000 Pa linear mode, 12 sample point procedure was applied. Results in Pa·s were obtained via TA Data Analysis software.

Gel permeation chromatography (GPC) was performed with a Waters gel permeation chromatograph (Milford, MA, USA), consisting of the 515 HPLC pump, a 2410 differential refractometer (Waters), set of four 300x7.8mm phenogel 5μ columns (50, 102, 103 and 104 Å) (all Phenomenex, Torrance, CA); autosampler (SIL-20A/20AC, Shimadzu); on-line degasser, JMDG-4 (JM Science, Grand Island, NY) and Millenium software. The flow rate of tetrahydrofuran (THF) eluent was 1 mL/min. at 30 ^{o}C. M_n, M_w, and polydispersity were calculated based on peaks present in each chromatogram compared to polyol standard calibration.

The number-average molecular weights of polyols, M_n, were also determined by a vapor pressure osmometer, Osmomat 070 (UIC Inc., Joliet, IL). Measurements were performed at 60 °C in toluene. Benzyl was used as the calibration standard.

Fourier transform Infrared (FT-IR) analysis was performed to identify the presence of characteristic functional groups. A liquid film spread on one KBr plate technique was used. Shimadzu IR Affinity-1 instrument (Kyoto, Japan) set to 16 scans and a resolution of 4 cm^{-1} was implemented. Acquired spectra (4000 – 600 cm^{-1}) were analyzed using Shimadzu IR Solution software.

Differential scanning calorimeter (DSC) model Q100, from TA Instruments (New Castle, DE, USA) was used for studying temperature transitions. DSC measurements were performed in nitrogen atmosphere (50 mL/min. purge flow) using hermetic aluminum pans, at a heating rate of 10 °C/min from -90 °C to 150 °C. TA Universal Analysis software was used for thermograph acquisition and processing.

Tensile properties were determined according to ASTM D882. The test was conducted on a Q-Test 2-tensile machine (MTS, USA) equipped with pneumatic head grips set to 50 mm distance, crosshead speed of 50 mm/min and maximum load cell of 1250 N. Five rectangular specimens (10 mm long, 8±1 mm wide and 1.5±0.3 mm thick) were cut out of each cast sheet and submitted to the test at room temperature. Stress at break (MPa), elongation at break (%) and tangent modulus (MPa) were recorded by the means of TestWorks QT software.

Flexural properties were investigated by 3 point bending test, according to ASTM D790. The test was conducted on a Q-Test 2-tensile machine equipped with loading anvil (crosshead speed of 0.85 mm/min and maximum load cell of 1250 N) and 2 point support span (32 mm distance). Specimens were prepared with the same dimensions as used in the tensile test. Flexural modulus was calculated from the initial slope of the load-deflection curve.

Izod impact test according to standard ASTM D256 was used to record energy to break a notched cantilever beam specimen upon impact by a pendulum. Five rectangle shape specimens (63.5x12.7 mm) were cut out of each PU cast sheet and notched to 10.2 mm width on the Tinius Olsen Specimen Notcher, Model 899 (Willow Grove, PA, USA). Testing was done on Resil Impactor (CEAST, Pianezza, Italy) at room temperature. A pendulum fitted with a striker head of 4 J, was released from a rest position of 150 deg to hit the specimen at a point above the notch. Displayed energy absorbed (J) was automatically corrected for windage and friction by the indicating system. The results of test methods were averaged and reported in terms of energy absorbed per unit of specimen width (J/m) along with the type of failure.

Density was measured by weight change of sample after immersion in water according to standard test method ASTM D 792. Three specimens of each sample were tested and results were averaged.

Equilibrium swelling was carried out in toluene (HPLC grade, Fisher Scientific) and methylene chloride (99.5%, Fisher Scientific) at room temperature for 72 hours. Two specimen of each PU cast were cut into 2x2 cm square samples and immersed in toluene. Weight measurement of swollen samples was carried out after 30 minutes and in 1 hour intervals during first 8 hours, and continued in 24 hour intervals. After 72 h, samples were transferred into pans and dried in a vacuum oven at 80 °C until constant weight. The degree of swelling (*DS*) or swelling ratio was calculated as the ratio of the volume of swollen polymer V_s to the volume of polymer before swelling V_0, according to equations 2-4. Sol fraction (%) was calculated based on the equation 5.

$$V_s = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \qquad (2)$$

$$V_0 = \frac{w_0}{\rho_2} \qquad (3)$$

$$\text{Swelling ratio} = \frac{V_s}{V_0} \qquad (4)$$

$$\text{Sol fraction, \%} = 100 \cdot \frac{w_0 - w_d}{w_0} \qquad (5)$$

Here w_0 is the initial sample weight, and w_s is the weight of a swollen sample, w_d is the weight of sample after drying; ρ_1 and ρ_2 are the densities of the solvent and polymer network, respectively.

Differential scanning calorimeter (DSC) model Q100, from TA Instruments (New Castle, DE, USA) was used for studying temperature transitions of PU cast. DSC measurements were performed in nitrogen atmosphere (50 mL/min. purge flow) using standard aluminum pans, at a heating rate of 10 °C/min from -90 °C to 220 °C. Prior to main heating cycle, samples were heated to 150 °C, held for 3 min to erase thermal histories and residual stress. TA Universal Analysis software was used for thermograph acquisition and processing.

Thermogravimetric analyzer (TGA) model Q50 (TA Instruments, New Castle, DE, USA) was used for examining thermal stability of PU cast and foams. All experiments were carried out under the nitrogen atmosphere (60 mL/min) with the heating rate of 10 °C/min from room temperature to 600 °C. Weight loss and derivative weight loss as a function of temperature was recorded by TA Universal Analysis software.

3. RESULTS AND DISCUSSION

In order to compete with petrochemical polyols, bio-based polyols for rigid PUs have to satisfy some structural requirements such as the right functionality (>3), molecular weight (<1000), and OH number (350 - 600 mg KOH/g). Since pure polyglycerols, due to high OH# and viscosity, are not applicable, the initial idea of this work was modification of PGL by grafting lactic acid units. This would give polyols with lower OH# while the functionality would remain unaffected. Three polyols were synthesized, starting from glycerol, diglycerol and polyglycerol 3. The quantity of L-lactide was calculated to obtain a hydroxyl number within the range 350 - 400 mg KOH/g. Properties of (poly)glycerol-lactate polyols (hydroxyl number, acid value, viscosity at 25 °C and polydispersity) are summarized in *Table 2*. Polyol prepared from glycerol appeared as clear, transparent liquid; polyol prepared from diglycerol was a high viscosity whitish liquid; while polyol prepared from polyglycerol 3 was white solid at room temperature.

Compared to starting materials, it can be observed that viscosity of polyols significantly increased. Viscosity increased with the molecular weight of the (poly)glycerol starter (PGL3>DG>G). However, all polyols had similar OH number, around 390 mg KOH/g, in the range of many petrochemical polyols for rigid PU foams (350 - 400 mg KOH/g).

Overlaid GPC curves of polyol PE-G-L and starting materials are shown in *Figure 4*. The GPC analysis of polyols revealed a small amount of residual L-lactide, about 1 % in PE-G-L and PE-PGL3-L and about 2 % in PE-DG-L polyol. Also, there was about 4 % of unreacted glycerol in PE-G-L polyol.

FT-IR spectra of polyols are shown in *Figure 5*. It can be noticed that all polyols displayed the same characteristic peaks. Peaks at 3427 cm^{-1} and 1747 cm^{-1} are assigned to OH group and ester carbonyl group, respectively; peaks in 1049 - 1269 cm^{-1} region are due to C-O stretching consistent with ester, ether and hydroxyl groups. Other bands are attributed to stretching (2880 - 2990 cm^{-1}) and bending (1379, 1454 cm^{-1}) of CH_3 and CH_2 groups.

Table 2. Properties of (poly)glycerol lactate polyols.

Polyol Name	**OH# (mg KOH/g)**	**AV (mg KOH/g)**	**Viscosity at 25°C (Pa·s)**	**M_w/M_n^{GPC}**
PE-G-L	389.13	6.44	63	1.206
PE-DG-L	383.81	12.62	438	1.136
PE-PGL3-L	393.44	18.72	solid	1.185

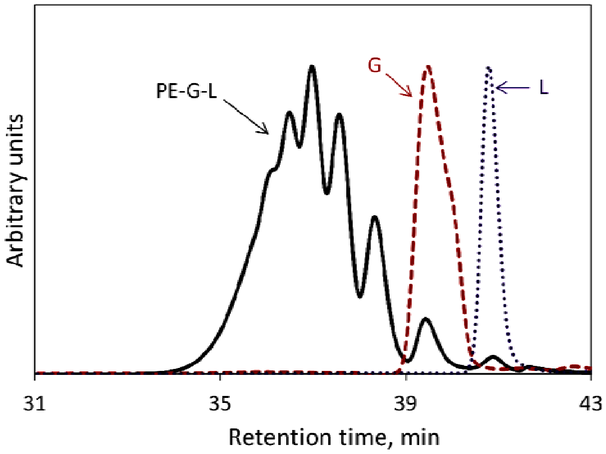

Figure 4. GPC curves overlay of the PE-G-L polyol, glycerol (G) and L-lactide (L).

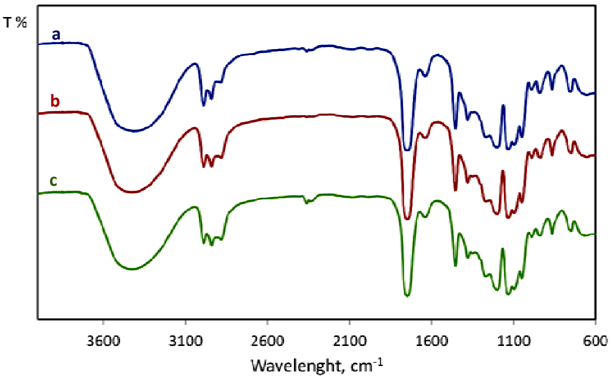

Figure 5. FT-IR spectra of PE-G-L polyol (a), PE-DG-L polyol (b) and PE-PGL3-L polyol (c).

The thermal behavior of polyglycerol-lactate polyols, investigated by DSC, showed only a glass transition in all cases. The glass transition temperature (T_g) increased with the molecular weight of starter, being the lowest for PE-G-L polyol (-21 °C) and the highest for PE-PGL3-L polyol (-8 °C).

Apart from having high viscosity, these simple polyglycerol-lactide adducts were incompatible with isocyanates, leading to phase separation when reacted. The reason for immiscibility lies in their high polarity. Consequently, further work was oriented towards improving the compatibility by incorporation of hydrophobic units in the lactate polyol structure, which are known to have good affinity for isocyanates. Among various choices for reducing polarity of polyols, we preferred fatty acids as modifiers, since vegetable oil based polyols have been utilized in PUs production for decades.

Properties of fatty acid modified polyglycerol-lactide polyols and their designations (ID) are summarized in *Table 3*. All polyols were yellow, clear liquids at room temperature. Molecular weight, polydispersity and number average functionality (f), are summarized in *Table 4*. Molecular weight was determined by two methods, GPC and VPO. Number average functionality was calculated by dividing experimentally determined M_n with hydroxyl equivalent weight (EW). EW was calculated from OH number (OH#). GPC of low molecular compounds does not give very good molecular weight assessment and was used as a qualitative tool to check for residual monomer, peak shape and molecular weight distribution.

Due to the dilution effect caused by introduction of relatively high molecular weight fatty acid chains, the hydroxyl numbers of these polyols were lower than of those from simple (poly)glycerol-lactate adducts. Except for the polyol "*A*" all others had OH# 10 - 30 units lower than theoretical. Much lower OH# than theoretical of polyol A is assigned to incomplete transesterification of DG and MeRA, which can be observed in GPC and possible side reactions of OH group on ricinoleic fatty acid chain. Theoretically, polyol functionality should be the same as that of the polyglycerol starter for simple PGL–lactide adducts. However, introducing fatty acid moiety can change the functionality, depending on the FA type. Fatty acids or functionalized fatty acids containing one OH group in the chain should not affect the functionality, since one reacted OH group is replaced by one created. This is the case with MeRA, CO and X-173 soybean oil polyol system. When simple fatty acid methyl esters (MESBO) or plain oil (SBO) are used, functionality decreases with the number of reacted FA chains. Lactic units do not change functionality as they generate terminal secondary OH group.

Table 3. Properties of polyols.

Polyol Name	**Polyol ID**	**OH# (mg KOH/g)**	**Theor. OH# (mg KOH/g)**	**AV (mg KOH/g)**	**EW**	**Viscosity at 25°C (Pa·s)**
PE-DG-MeRA-L	A	203.40	339	4.03	276	8.2
PE-PGL5-MeRA-L	B	245.90	285	1.07	228	15.3
PE-PGL5-MeSBO-L	C	175.90	209	1.62	319	30.9
PE-PGL4-SBO-L	D	197.24	208	10.4	284	2.7
PE-PGL4-CO-L	E	249.38	268	12.20	225	5.6
PE-PGL4-X173-L	F	246.33	271	23.70	228	12.8

Table 4. Molecular weight, polydispersity and number average functionality of polyols.

Polyol Name	**M_n^{VPO}**	**M_w/M_n^{GPC}**	**f^{VPO}**
PE-DG-MeRA-L	707	1.400	2.56
PE-PGL5-MeRA-L	1496	1.550	6.56
PE-PGL5-MeSBO-L	1395	1.530	4.37
PE-PGL4-SBO-L	n/d	1.381	n/d
PE-PGL4-CO-L	953	1.429	4.24
PE-PGL4-X173-L	807	2.118	3.54

The polyol *A* (PE-DG-MeRA-L) was synthesized from equimolar quantities of DG and MeRA. Theoretically, this means that a single OH group of DG tetrol should have been substituted with one ricinoleic fatty acid chain, leading to the final polyol with functionality 4. *Table 4* shows that experimental value f^{VPO} is lower, indicating that some side reactions occurred. Polyols *B* and *C* were synthesized starting from 1 mol of PGL5 and 2 mols of corresponding FA. The expected functionality for the polyol B when MeRA was used is 7. The experimentally determined functionality of 6.56 was lower. Theoretical functionality for the polyol *C* was 5, which is 2 units lower than that of the starting PGL5, since fatty acids from SBO have no OH groups on the chain. Here again, the real functionality was lower. For polyols *D, E* and *F,* the situation is more complicated since the final product is a mixture of structurally different polyesters (see *Figure 2).* In all three reactions, the component ratio was 1 mol of TG per 1 mol of PGL4. Calculated functionalities of the final mixtures were 3, 4.35, and 4.5 for polyols *D, E* and *F* respectively.

Viscosity is an important property of raw materials affecting processing. In foam preparation, low viscosity of components is a prerequisite for good mixing in the reaction system. The polyols had viscosity from about 3 to 31 Pa.s (*Table 3*), but all are in the range acceptable for PU processing. Generally, viscosity increases with increasing molecular weight and decreases with increasing double bond content.

High acid values are not acceptable, especially in rigid PU foams technology, where the reaction of polyol with polyisocyanates is catalyzed by tertiary amines. High AV of some polyols (*Table 3.*) could be attributed, in part, to the alkyl cleavage of L-lactide resulting in terminal carboxyl groups, and in part due to the presence of the unreacted lactide monomer.

Overlay of GPC curves of polyols PE-DG-MeRA-L and starting materials is displayed in *Figure 6.* Overlay of GPC curves of all other polyols is presented in *Figure 7*. PE-DG-MeRA-L, PE-PGL5-MeRA-L and PE-PGL5-MeSBO-L polyols show clear shift to shorter elution times (higher molecular weights) compared to starting materials. There was no residual L-lactide in PE-PGL5-MeRA-L and PE-PGL5-MeSBO-L, while integration of the discrete peak at 41 min gave the following content of L monomer: 0.4 % in PE-DG-MeRA-L and PE-PGL4-SBO-L, 0.6 % in PE-PGL4-CO-L and 1.4 % in PE-PGL4-X173-L polyol. The amount of the unreacted L-lactide correlates well with the acidity of the final polyol.

FT-IR spectra of polyols given in *Figure 8* are similar, displaying characteristic absorption bands at 3448 cm^{-1} for the OH group, ester carbonyl band at 1742 cm^{-1}, C-O vibration peaks in 1051 - 1261 cm^{-1} region are from ester, ether and hydroxyl group; 2857, 2928 cm^{-1} stretching and 1377, 1456 cm^{-1} bending of alkane C-H. Small peak at 3007 cm^{-1} present in the spectra of polyols *C* and *D* is due to C=C in FA chains. Hydroxyl peak intensities are in correspondence with polyols hydroxyl numbers.

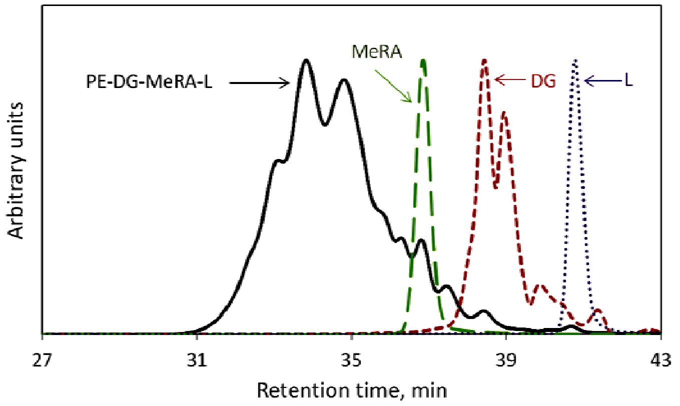

Figure 6. GPC curves overlay of PE-DG-MeRA-L polyol, DG, MeRA and L- lactide.

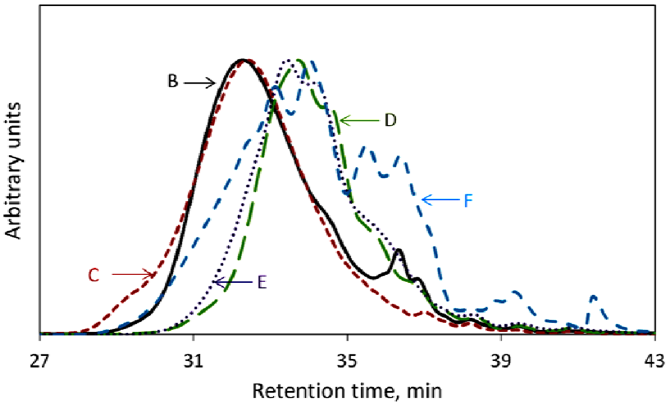

Figure 7. GPC curves overlay of PE-PGL5-MeRA-L, PE-PGL5-MeSBO-L, PE-PGL4-SBO-L, PE-PGL4-CO-L and PE-PGL4-X173-L polyol (for polyol ID refer to Table 1).

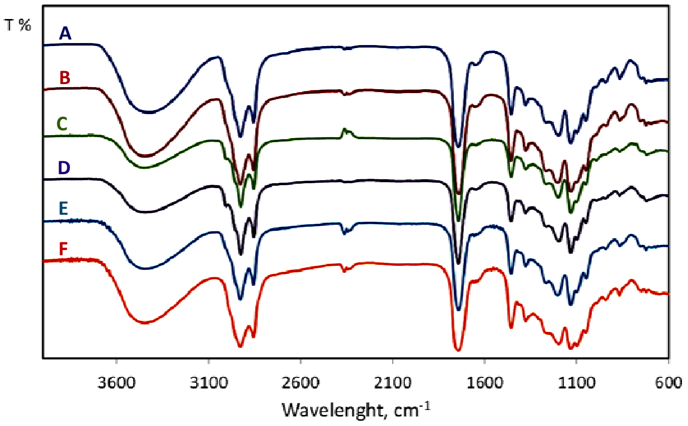

Figure 8. FT-IR spectra of polyols. (for polyol ID refer to Table 1).

DSC analysis (*Figure 9*) of lactate polyols derived from methyl ricinoleate (MeRA) and castor oil (CO) showed clear glass transitions, ranging from -48 to -20 °C. Polyols based on SBO showed more than one transition; with the first one being assigned to T_g. Broad and weak endotherms above glass transition temperatures were due to melting of crystallizing fatty acid chains in the polyol structure.

All cast polyurethanes were yellowish, transparent hard resins with smooth surface. The degree of swelling, calculated as the volume ratio of the swollen polymer network to the dry polymer network, is used as a measure of the degree of cross-linking. Soluble fraction consists of free chains (extracted by the solvent) not bound to the polymer network. It indicates whether the system is completely cured but it may arise from the linear polymers not bound to a starter molecule. Cross-linking density expressed as the number of cross-links per unit volume is in direct correlation to apparent density and reciprocal to molecular weight of network chains (M_c). Data obtained from equilibrium swelling and density measurements are presented in *Table 5*. Low swelling ratio in both toluene and methylene chloride indicates high cross-linking density. Higher sol fraction in some cast PUs indicates the presence of unreactive moieties, present in the polyol, which were extracted with the solvent. This is especially pronounced in PUs prepared from polyols A and D which had much lower functionality than expected. This proves that some side reactions on OH groups took place during polyol synthesis.

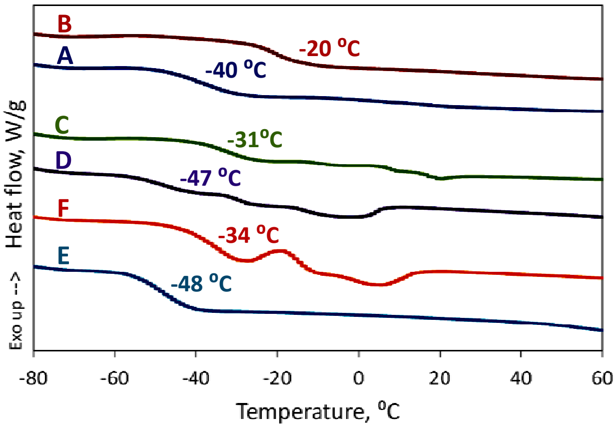

Figure 9. DSC curves overlay of polyols (for polyol ID refer to Table 1).

Table 5. Density, swelling ratio and soluble fraction of cast PUs prepared from lactate polyols and reference polyol.

PU Name	PU ID	Density (g/cm^3)	Swelling ratio^a	Sol fraction (%)^a	Swelling ratio^b	Sol fraction (%)^b
PU-PE-DG-MeRA-L	A	1.188	1.56	2.26	1.46	11.60
PU-PE-PGL5-MeRA-L	B	1.196	1.30	0.91	1.46	5.36
PU-PE-PGL5-MeSBO	C	1.175	1.51	2.50	1.48	4.14
PU-PE-PGL4-SBO-L	D	1.149	1.84	4.45	1.97	6.15
PU-PE-PGL4-CO-L	E	1.185	1.52	0.97	1.74	1.79
PU-PE-PGL4-X173-L	F	1.188	1.15	0.11	1.69	5.33
PU-X210	Re	1.128	1.52	0.70	1.70	3.06

a – in toluene; b – in methylene chloride

Mechanical properties are strongly dependent on the degree of crosslinking and network structure. Results obtained from tensile, flexural and impact test of cast PUs are summarized in *Table 6*. Stress-strain curves overlay from tensile test is given in *Figure 10*. Flexural stress vs. strain diagrams showed peak at low strain (5 – 7 %), while sample failure happened above 20 % strain for all.

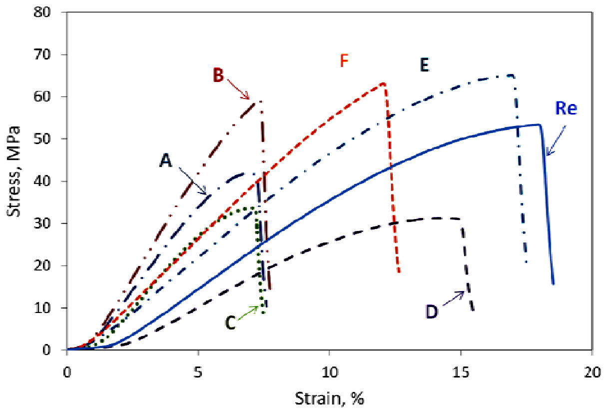

Figure 10. Tensile stress vs. strain curves overlay of cast PUs prepared from synthesized lactate polyols and reference polyol X210 (for PU IDs refer to Table 5).

Table 6. Mechanical properties of cast PUs prepared from lactate polyols and reference polyols.

SAMPLE ID	σ_b (MPa)	ε_b (%)	E_f (MPa)	I (J/m)
PU-PE-DG-MeRA-L	42	7	1366	76
PU-PE-PGL5-MeRA-L	60	7	2314	46
PU-PE-PGL5-MeSBO	33	7	1276	79
PU-PE-PGL4-SBO-L	30	15	947	89
PU-PE-PGL4-CO-L	64	16	2039	77
PU-PE-PGL4-X173-L	61	11	2204	29
PU-X210	53	17	1430	54

σ_b – tensile strength; ε_b – elongation at break; E_f –flexural modulus; I – Izod impact resistance, notched

Thermal stability in nitrogen was investigated by TGA. TGA curves are shown in *Figure 12*. All polyurethanes displayed lower thermal stability than the reference. The onset degradation temperature was around 175 °C for PU prepared from synthesized polyols and around 200 °C for reference PU. Degradation occurred in three steps, with the total residue ranging from 5 – 20 %. It can be observed that the lowest functionality polyol based PU (*A*) showed the highest degradation speed and the highest total wt. degradation, while the highest functionality polyol based PU (*B*) had the highest residue amount.

Properties of PUs prepared from synthesized polyols were comparable or better, in most cases than those of the reference. It is known that FA dangling chains have a plasticizing effect in PU network [16]. Generally, introduction of FA chains in lactate-PGL polyol structure is a tradeoff between miscibility with isocyanates and rigidity of the PU network. *Table 6* shows that PU-PE-PGL4-SBO-L stands out with the lowest tensile strength (30 MPa), tensile modulus (352 MPa) and flexural modulus (947 MPa). This was expected, considering lower polyol functionality combined with 18C long dangling chain. Other PUs showed better or comparable mechanical properties than the soy-based PU-X210 cast reference. This can be attributed to the higher polyol functionality and therefore higher crosslinking density as well as shorter dangling chains.

DSC curves with labeled T_gs of cast PUs prepared from lactate polyols and a reference polyol are displayed in *Figure 11*. The curves show only glass transitions in all PUs ranging from 28 °C for the cast prepared from lowest functionality polyol (PE-DG MeRA-L) to 85 °C for reference PU.

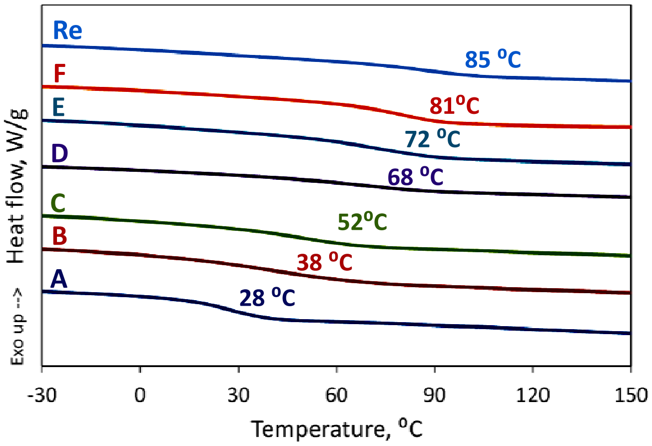

Figure 11. DSC curves overlay of cast PUs prepared from synthesized lactate polyols and reference polyol X210 (for PU IDs refer to Table 5).

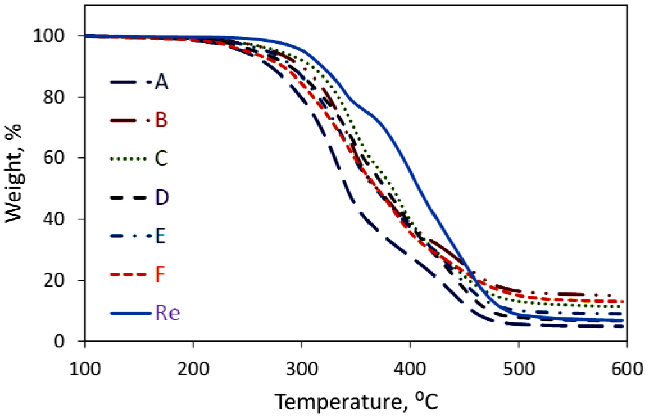

Figure 12. TGA thermograms of cast PUs prepared from synthesized polyols and a reference polyol X210 (for PU IDs refer to Table 5).

4. CONCLUSIONS

Simple lactic acid units modified polyglycerols are immiscible with isocyanates.

Polyester lactate polyols were prepared by the ring opening addition of L-lactide to bio-based fatty acid modified hydroxyl compounds of different functionality.

Depending on starting materials, polyols of different functionality were obtained. With the exception of PE-DG-MeRA-L polyol, all others had functionality higher than 3, which is suitable for preparation of rigid polyurethanes. The highest functionality polyol, 6.56 was obtained starting from PGL5 and MeRA.

Novel polyester polyols are applicable in the preparation of thermosetting polyurethane resins. Properties of PU depended not just on polyol functionality, but also on polyol architecture and the amount of incurable low molecular weight compounds. Tensile strength and modulus correlated well with OH number of polyols being the highest in systems with the highest OH numbers.

Novel PUs have significant content of renewables and are expected to have an increased degree of biodegradability.

5. REFERENCES

[1] M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, *From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products*. Polymer Reviews, 52−1 (2012) 38–79.

[2] M. Ionescu, *Chemistry and technology of polyols for polyurethanes*. Rapra Technology, Ltd.:Shawbury, Shrewsbury, Shropshire, UK, 2005.

[3] Y. Ikada, H. Tsuji, *Biodegradable polyesters for medical and ecological applications.* Macromolecular Rapid Communications. 21−3 (2000) 117–32.

[4] W. R. Grase, *A Method of Preparing a Biodegradable Foam of Cross-linked Polyurethane*. GB Patent 1517826; 1978.

[5] S. Miao, S. Zhang, Z. Su, P. Wang. *A Novel Vegetable Oil – Lactate Hybrid Monomer for Synthesis of High-T g Polyurethanes.* 48 (2010) 243–50.

[6] S. Min-Hyo, C. In-Ja, *Polymeric composition for solubilizing poorly water soluble drugs and process for preparation thereof.* WO 0112718(A1); 2001.

[7] K. S. Chul, C. Eun Ok, *Copolymeric micelle drug composition for the preparation thereof.* WO 9710849(A1) 1997.

[8] Z. Wang, L. Yu, M. Ding, H. Tan, J. Li, Q. Fu, *Preparation and rapid degradation of nontoxic biodegradable polyurethanes based on poly(lactic acid)-poly(ethylene glycol)-poly(lactic acid) and l-lysine diisocyanate*. Polymer Chemistry. 2−3 (2011) 601.

[9] G. T. Howard, *Biodegradation of polyurethane: a review.* International Biodeterioration & Biodegradation. 49−4 (2002) 245–52.

[10] R. Adhikari, P. A. Gunatillake *Biodegradable injectable polyurethanes: Synthesis and evaluation for orthopaedic applications. Biomaterials*. 28 (2008) 3762.

[11] J. R. Russell, J. Huang, P. Anand, K. Kucera, A. G. Sandoval, K. W. Dantzler, et al. *Biodegradation of polyester polyurethane by endophytic fungi*. Applied and environmental microbiology. 77−17 (2011) 6076–84.

[12] R. L. Shogren, Z. Petrovic, Z. Liu, S. Z. Erhan, *Biodegradation Behavior of Some Vegetable Oil-Based Polymers*. Journal of Polymers and the Environment. 12−3 (2004) 173–8.

[13] J. M. Cangemi, A. M. Santos, C. Dos, S. Neto, Chierice GO. *Biodegradation of polyurethane derived from castor oil. Polímeros*. 18−3 (2008) 201–6.

[14] G. T. Howard. Polyurethane Biodegradation. In: Singh SN, editor. *Microbial Degradation of Xenobiotics*. Berlin, Heidelberg: Springer Berlin Heidelberg; 2012.

[15] Y. D. Kim, S. C. Kim *Effect of chemical structure on the biodegradation of polyurethanes under composting conditions*. Polymer Degradation and Stability. 62−2 (1998) 343–52.

[16] Z. Petrovic, *Polyurethanes from Vegetable Oils*. Polymer Reviews. 48−1 (2008) 109–55.

* * *

НОВИ, ПОТЕНЦИЈАЛНО БИОРАЗГРАДЉИВИ ПОЛИУРЕТАНИ НА ОСНОВУ ПОЛИОЛА ИЗ ОБНОВЉИВИХ СИРОВИНА

Сажетак: Полиоли из потпуно обновљивих сировина погодни за тврде полиуретане синтетизовани су од полиглицерола, млечне киселине и масних киселина. Јединице млечне киселине су уведене у структуру адицијом лактида на хидроксилне групе уз отварање прстена, уз титан(IV)изопропоксид катализатор. Некомпатибилност лактид-полиглицерол полиола са изоцијанатима је решена тако што су у структуру уведене масне киселине. Ливене полиуретанске смоле прављене су реакцијом полиола са дифенилметан диизоцијанатом. Полиуретани су били умрежени, стакласти, аморфни материјали прекидне чврстоће од ~ 60 MPa, савојног модула 0.9 – 1.4 GPa и отпорности на удар са зарезом по Изоду 30 – 80 J/m. Ови полиуретани су потенцијално биоразградљиви.

Кључне речи: полиоли из обновљивих сировина, млечна киселина, полиглицерол, биљно уље, полиуретани.

* * *