

# Impact of Natural Oil-Based Recycled Polyols on Properties of Cast Polyurethanes

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**ABSTRACT:** In this study, castor oil, rapeseed oil and medium chain triglycerides of coconut oil, were transesterified by means of 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane) and consequently used to convert polycarbonate waste from end-of-life vehicles into liquid polyols. The prepared recycled polyols, composed uniquely of renewable and recycled components, had a hydroxyl number of ca. 250 mg KOH·g<sup>-1</sup>. They were successfully applied as 100% replacement of a virgin polyol for preparation of solid crosslinked polyurethanes (PU) by solvent-free casting. The produced rigid cast PU exhibited the main transition temperature ranging from 44°C to 53°C, the hardness value from 46 to 61 Shore D and the beneficial low water absorption (0.4-0.5 wt.%). The PU network structure was highly influenced by the presence of aromatic structures of polycarbonate-units and fatty acid compositions. A suitable selection of natural oil thus enabled to adjust thermo-mechanical properties and promote excellent optical transparency of the produced PU.

**KEYWORDS:** Natural oil, cast polyurethane, bio-based, polycarbonate waste, recycling

## 1 INTRODUCTION

Cast crosslinked polyurethanes (PU) have been widely used as insulation materials in electrical and electronics industry competing with unsaturated polyesters, epoxy resins and silicone rubbers [1]. PU are often preferred over other plastics because of their low exotherm during curing, hardening at room temperature, no volatile product formation and structure versatility, which enables to prepare crosslinked materials ranging from hard and tough to soft and elastic and thus meeting the different customer requirements. By contrast, extreme sensitivity to moisture during curing and the increased water uptake are the main drawbacks of PU cast resins.

Recent sustainable chemistry concept has promoted investigations using various renewable resources (mainly natural oils) [2-4] as well as recycled polyols (obtained by decomposition of PU or PET) [5, 6] for synthesis of novel PU materials. These materials exhibit beneficial properties, e.g. the decreased moisture uptake thanks to hydrophobic nature of oils and aromatic structures presented in the recycled polyols [7, 8]. While the application of natural oils in solid crosslinked PU materials has been widely investigated [9-11], the use of recycled polyols has been mainly focused on PU foams [12-14] and thermoplastic PU [15-17]. Our last research showed

that incorporation of recycled polyols combining flexible glyceride units derived from vegetable oils with rigid aromatic segments derived from polycarbonate (PC) waste into rigid PU foams led to decrease of water absorption and simultaneous improvement in mechanical properties [8]. Despite the beneficial influence of recycled polyols on the end-use properties of rigid PU foams, the presence of both primary and secondary hydroxyl groups (due to the presence of glyceride structures) makes a polyol-isocyanate reaction difficult to control.

In this work we used 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane, TMP) bearing uniquely primary hydroxyl groups for reaction with glyceride backbone of different vegetable oils. The prepared transesterified oils were used for conversion of a PC waste into liquid recycled polyols. Subsequently, crosslinked cast PU based entirely on these recycled polyols were prepared and compared with transesterified vegetable oil-based PU. The main aim of this work was to evaluate the effects of fatty acid compositions of the used natural oils and PC-derived units of the recycled polyols on structure-property relationships in the prepared PU networks.

## 2 EXPERIMENTAL

### 2.1 Synthesis of Transesterified Oils

Castor oil (CO, puriss, Sigma-Aldrich), rapeseed oil (RO, Glencore Agriculture Czech Ltd, Czech Republic), and medium chain triglycerides of coconut oil (CCO, Environ Ltd., Czech Republic)-the byproduct from soap industry, were used as received and analyzed (Table 1).

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The oils were transesterified using 2-ethyl-2-hydroxymethyl-1,3-propanediol (trimethylolpropane, TMP, 98%, Sigma-Aldrich) according to the slightly modified procedure described before [18]. All transesterifications were carried out keeping the hydroxyl group (TMP)/ester bond (oil) molar ratio of 3/1. Typically, 200 g of CO, 86.6 g of TMP and 0.9 g (0.3 wt.%) of dibutylbis[1-oxo(dodecyl)oxy]stannane (dibutyltin dilaurate, DBTL, 95%, Sigma-Aldrich) were added into a 500 mL glass reactor equipped with a nitrogen inlet and a reflux. The transesterification was carried out at 200°C for 3 h. The obtained product (denoted as CO-TMP) was a transparent pale yellow liquid. Similarly, the transesterified RO and CCO, denoted as RO-TMP and CCO-TMP, respectively, were obtained.

**Table 1** Properties of castor oil (CO), rapeseed oil (RO) and medium chain triglycerides of coconut oil (CCO)

	CO	RO	CCO
Viscosity at 25°C [mPa·s]	650	58	26
Hydroxyl number [mgKOH·g <sup>-1</sup> ]	163	-	-
Acid number [mgKOH·g <sup>-1</sup> ]	0.9	1.3	1.5
M <sub>w</sub> [g·mol <sup>-1</sup> ] <sup>a</sup>	932	871	506
<b>Fatty acid composition [wt.%]<sup>b</sup>:</b>			
Caprylic acid, C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	-	-	57
Capric acid, C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	-	-	43
Palmitic acid, C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	-	7.8	-
Linolenic acid, C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	-	8.6	-
Linoleic acid, C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.3	17.1	-
Oleic acid, C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.3	57.1	-
Ricinoleic acid, C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>	99.4	-	-
Stearic acid, C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	-	9.4	-

<sup>a</sup> calculated from fatty acid composition

<sup>b</sup> determined from GC/MS (more details in [18])

The properties of obtained transesterified oils are summarized in Table 2. The prepared transesterified oils were used as the reagents for conversions of PC waste into recycled polyols and also applied for preparation of cast PU.

**Table 2** Properties of transesterified oils obtained from the reaction of trimethylolpropane (TMP) with i) castor oil (CO-TMP), ii) rapeseed oil (RO-TMP) and iii) medium chain triglycerides of coconut oil (CCO-TMP).

	CO-TMP	RO-TMP	CCO-TMP
Hydroxyl number [mgKOH·g <sup>-1</sup> ]	468	367	519
Viscosity at 25°C [mPa·s]	1700	390	310
Acid number [mgKOH·g <sup>-1</sup> ]	1.0	1.2	0.2
Monoacylestes [wt.%] <sup>a</sup>	39.3	46.6	49.9
Diacylesters [wt.%] <sup>a</sup>	27.2	29.1	21.9
Triacylestes [wt.%] <sup>a</sup>	15.2	7.0	1.2
Free TMP [wt.%] <sup>a</sup>	18.3	17.3	27.0

<sup>a</sup> from size exclusion chromatography (SEC)

## 2.2 Conversion of Polycarbonate Waste into Recycled Polyols Using Transesterified Oils

The prepared transesterified oils were used for the conversion of a post-consumer PC waste from end-of-life vehicles into recycled polyols according to the procedure described in details before [18]. In principle, the hydroxyl group of transesterified oils reacted with carbonate group of PC. In this study, the hydroxyl group/carbonate bond molar ratio of 2/1 was always used to ensure the complete PC decomposition.

Typically, CO-TMP (50 g) and granulated PC waste (52 g) were placed into a 250 ml three-neck flask equipped with nitrogen inlet, reflux and mechanical stirrer. The reaction mixture was heated in a multimode microwave reactor (Romill, Ltd., Czech Republic, f=2.45 GHz, maximum power of 1000 W). The temperature was controlled using a shielded Pt100-thermometer inserted directly into the reaction medium. After ca. 15 min of microwave heating with the constant power of 300 W, the temperature of such reaction mixture reached ca 215°C. Then, the temperature was kept constant at 215°C. The reaction was complete when no PC oligomers were found in the mixture (verified by SEC). The product was then cooled and solid impurities (<0.5 wt. %) containing mainly residues of polysiloxane coatings were filtered off. The obtained liquid recycled polyol was denoted as REC-CO-TMP. Similarly, the reactions between RO-TMP and the PC waste and between CCO-TMP and the PC waste led to the production of other recycled polyols denoted as REC-RO-TMP and REC-CCO-TMP, respectively.

## 2.3 Characterization of Recycled Polyols

SEC of recycled polyols was performed on a Modular GPC System equipped with a refractive index detector RIDK-102 (Laboratorní přístroje Praha, Czech Republic) and an UV-vis photometric detector LCD 2084 (ECOM, Czech Republic) operated at λ=254 nm, and a set of two columns PLgel 10E3 Å and 50 Å, 10 μm particle size, 300 mm×7.5 mm (Polymer Laboratories, UK). Chromatographic data were collected and treated using Clarity software (Data-Apex, Czech Republic). Tetrahydrofuran and toluene were used as a mobile phase and a flow marker (retention time of toluene was 17.72 min) respectively, at a flow rate of 1 mL/min. Polystyrene standards with weight-average molecular weights (M<sub>w</sub>) of 500, 1000, 3000 and 10 000 were used for calibration.

Viscosity of recycled polyols was measured using a Bohlin Gemini HR nano Rheometer (Malvern Instruments) with cone/plate geometry (40 mm diameter, 4° angle, 0.15 mm gap) at temperature 25°C in the range of shear rates 0.001-100 s<sup>-1</sup>.

Hydroxyl number and acid number of recycled polyols were determined according to ISO 2554: 1974 and ASTM D 4662-93, respectively.

## 2.4 Preparation of Cast Polyurethanes

A recycled polyol was mixed with a catalyst (DBTL, 80 ppm) and then trimer of hexamethylene diisocyanate (t-HDI, Desmodur N 3300, Covestro) with isocyanate content of 5.32 mmol/g was added. The reaction mixture was homogenized and degassed under vacuum (10 min at room temperature), then casted into an open aluminum mold and cured at room temperature. The NCO/OH molar ratio of 1.0 was kept constant for all PU. The complete reaction was checked using FTIR spectroscopy by disappearance of the isocyanate band at 2270 cm<sup>-1</sup>. Using this procedure, three cast PU based on REC-CO-TMP, REC-RO-TMP and REC-CCO-TMP recycled polyols were prepared and denoted as PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP, respectively. For comparison, cast PU based on CO-TMP, RO-TMP and CCO-TMP transesterified oils were also prepared and denoted as PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP, respectively.

## 2.5 Characterization of Cast Polyurethanes

**Equilibrium swelling measurement.** A piece of the PU sample of about 0.2-0.3 g was precisely weighed and put in a sufficient amount of dimethyl sulfoxide (DMSO, Sigma-Aldrich). The solvent volume was about 50 times larger than the sample volume. Weight of the swollen sample was determined at various time intervals until it was constant. The volume fraction of polymer in the swollen sample ( $\varphi_2$ ) was calculated from weights of the swollen sample ( $m_{sw}$ ) and dry sample after extraction ( $m_2$ ), PU ( $\rho_2$ ) and solvent ( $\rho_1$ ) densities:

$$\varphi_2 = \frac{m_2/\rho_2}{m_2/\rho_2 + (m_{sw} - m_2)/\rho_1} \quad (1)$$

The PU density was determined according to ISO 1183-1 using a titration method with water / aqueous solution of sodium bromide.

**Determination of equilibrium modulus and dynamic mechanical measurements.** Equilibrium shear modulus ( $G'_{sw}$ ) of equilibrium swollen samples in DMSO was measured using an ARES G2 rheometer (TA Instruments, USA) at 25°C. The rectangular sample (dimension ca 20×10×2 mm<sup>3</sup>) was quickly fastened between two clamps and immediately measured at frequency range of 0.1-10 Hz. Frequency measurements were done to be

sure that at the given temperature the material is in the rubbery state.

**Dynamic mechanical and thermal analysis (DMTA)** of dry samples was performed using the same equipment. The temperature dependencies of the complex shear moduli of dry samples were measured by oscillatory shear deformation at a frequency of 1 Hz in a temperature range of -80-200°C at a heating rate of 3 °C·min<sup>-1</sup> with 0.2% strain. The rubbery storage shear modulus ( $G'_R$ ) was determined in the rubbery plateau region at  $T=110^\circ\text{C}$ . The temperature of main (alfa) transition ( $T$ ) was evaluated as the maximum of  $\tan \delta$  peak. The typical precision of the measurements was  $T \pm 2^\circ\text{C}$  and  $G'_R \pm 5\%$ .

**The crosslink density**, i.e. the concentration of elastically active network chains ( $\nu_e$ ), of PU networks was determined using the following Equation [19]:

$$\nu_e = \frac{G'_{sw}}{RTA_f(\varphi_2^0)^{2/3}(\varphi_2)^{1/3}} \quad (2)$$

where,  $\varphi_2^0$  was the volume fraction of PU at network formation ( $\varphi_2^0=1$ , since no solvent was used during synthesis),  $\varphi_2$  was the volume fraction of PU in the swollen network,  $R$  is the universal gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>),  $T$  is temperature,  $A_f$  is the front factor ( $A_f=1$ ; an affine network) and  $G'_{sw}$  is the equilibrium shear modulus. The number average molar mass between crosslinks ( $M_c$ ) was calculated as:

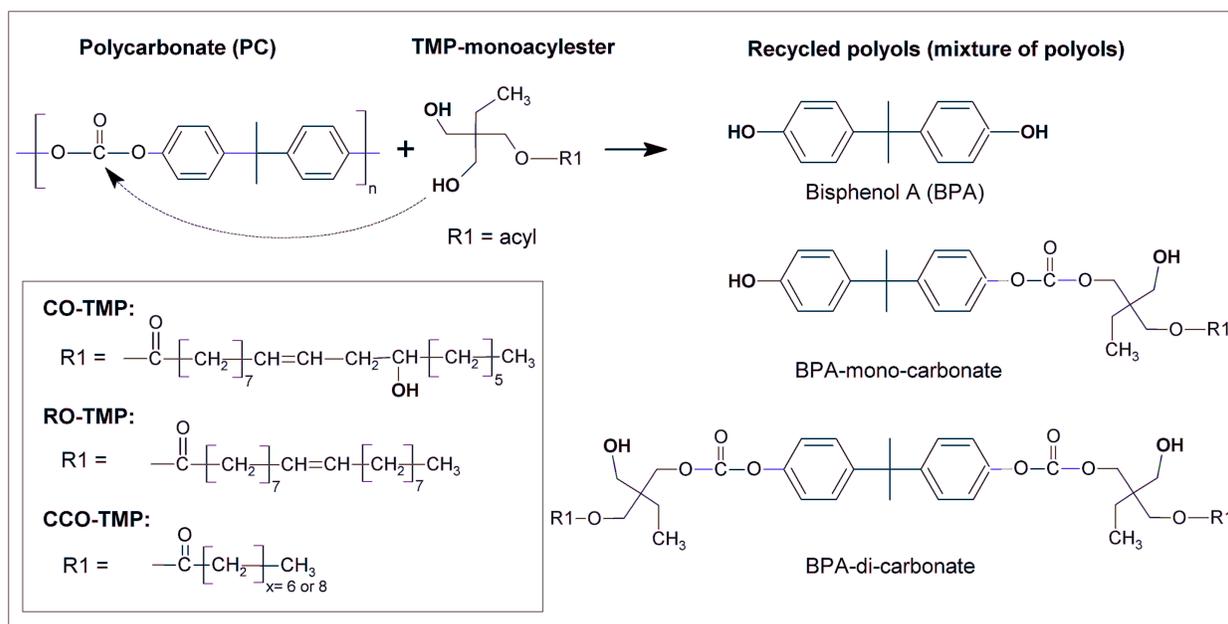
$$M_c = \rho_2/\nu_e \quad (3)$$

**Tensile tests** were carried out on an Instron 6025/5800R instrument (High Wycombe) equipped with a 100 N load cell at room temperature with a cross-head speed of 10 mm·min<sup>-1</sup>. Dumbbell shaped specimens were prepared according to the ISO 527-2/5B: Total specimen length 35 mm, length and width of the narrowed part: 12 mm and 2 mm, thickness ~1.50 mm. Reported values were the averages of at least five measurements. The Young modulus ( $E$ ), tensile strength ( $\sigma_b$ ), energy to break, and elongation-at-break ( $\epsilon_b$ ) were evaluated.

**Hardness (Shore D)** was determined according to ISO 868.

**Water absorption** was performed according to ISO 62 after 24 h exposure at 23°C and 50% relative humidity.

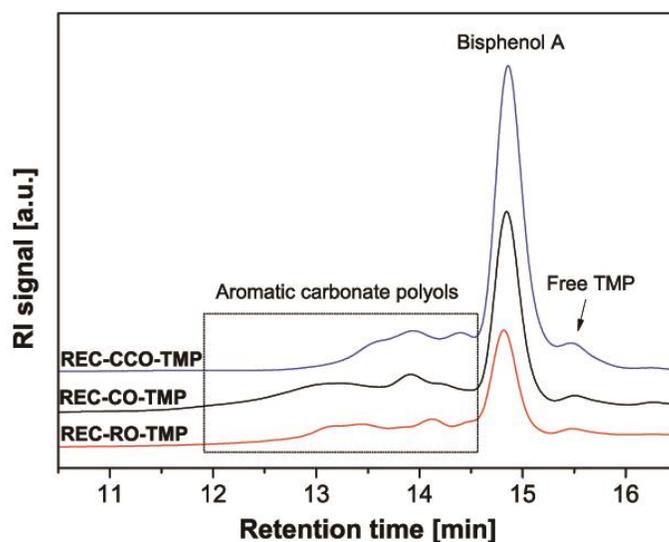
**Thermogravimetric analysis (TGA)** was performed on a Pyris 1 TGA thermogravimetric analyzer (PerkinElmer, USA). The samples were heated at a rate of 10 °C·min<sup>-1</sup> from 30°C to 800°C under nitrogen atmosphere. Temperature of 5% weight loss ( $T_{5\%}$ ) and char yield after TGA were evaluated.



**Figure 1** Reaction of transesterified oils (CO-TMP, RO-TMP and CCO-TMP) with polycarbonate (PC) waste. The reaction scheme is simplified considering only the reaction between PC and monoacylesters of trimethylolpropane (TMP-monoacylesters) representing the major oils' components. The inset frame shows acyl structures of the TMP-monoacylesters occurred in the transesterified oils.

**Table 3** Reaction conditions of polycarbonate (PC) conversion into recycled polyols using CO-TMP, RO-TMP and CCO-TMP as reagents, and the properties of produced REC-CO-TMP, REC-RO-TMP and REC-CCO-TMP recycled polyols.

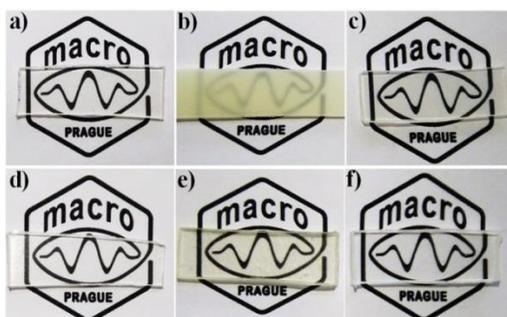
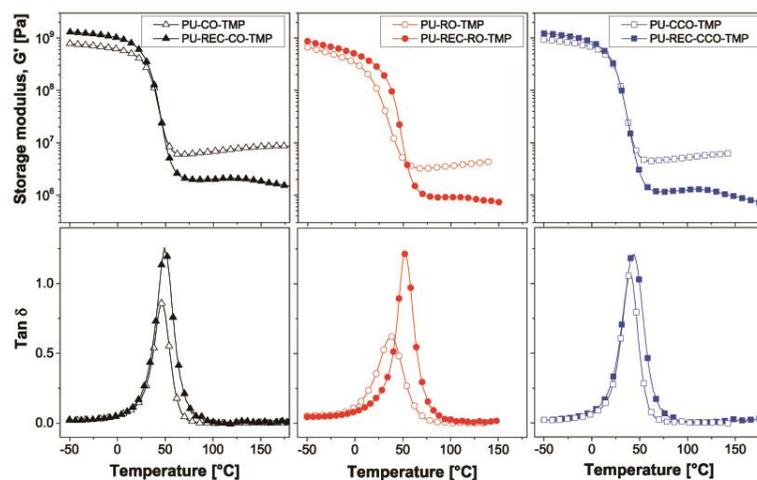
	REC-CO-TMP	REC-RO-TMP	REC-CCO-TMP
Mass ratio of PC/ reagent	52/50	42/50	60/50
Complete PC dissolution [min]	22	16	13
Reaction time [min]	33	25	19
Viscosity at 25°C [Pa·s]	220	12	32
Hydroxyl number [mgKOH·g <sup>-1</sup> ]	253	217	264
Acid number [mgKOH·g <sup>-1</sup> ]	2.2	1.4	1.9



**Figure 2** SEC chromatograms of the produced REC-CO-TMP, REC-RO-TMP and REC-CCO-TMP recycled polyols.

**Table 4** Network parameters at 298 K for the cast polyurethanes swollen in DMSO and prepared from the recycled polyols (PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP) and from the transesterified oils (PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP).

	$G_{sw}^+$ [MPa]	$\rho_2$ [g·cm <sup>-3</sup> ]	$\varphi_2$	$v_e$ [mol·dm <sup>-3</sup> ]	$M_c$ [g·mol <sup>-1</sup> ]
<b>PU-REC-CO-TMP</b>	<b>1.4</b>	<b>1.13</b>	<b>0.43</b>	<b>0.75</b>	<b>1508</b>
PU-CO-TMP	7.2	1.12	0.65	3.35	334
<b>PU-REC-RO-TMP</b>	<b>1.0</b>	<b>1.13</b>	<b>0.37</b>	<b>0.56</b>	<b>2031</b>
PU-RO-TMP	3.5	1.09	0.65	1.63	667
<b>PU-REC-CCO-TMP</b>	<b>1.3</b>	<b>1.13</b>	<b>0.37</b>	<b>0.73</b>	<b>1547</b>
PU-CCO-TMP	4.7	1.14	0.60	2.25	506

**Figure 3** Photographic images of the prepared cast polyurethanes: a) PU-REC-CO-TMP, b) PU-REC-RO-TMP, c) PU-REC-CCO-TMP, d) PU-CO-TMP, e) PU-RO-TMP and f) PU-CCO-TMP.**Figure 4** Storage modulus ( $G'$ ) and  $\tan \delta$  of the cast polyurethanes prepared from the recycled polyols (PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP) and from the transesterified oils (PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP).**Table 5** DMTA ( $T_\alpha$ ,  $G'_R$ ), hardness test (Shore D), water absorption and TGA ( $T_{5\%}$ , char yield at 650°C) of the cast polyurethanes prepared from the recycled polyols (PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP) and from the transesterified oils (PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP).

	$T_\alpha$ [°C]	$G'_R$ [MPa]	Hardness [Shore D]	Water absorption [wt.%]	$T_{5\%}$ [°C]	Char yield [wt.%]
<b>PU-REC-CO-TMP</b>	<b>49</b>	<b>2.1</b>	<b>61±1</b>	<b>0.5</b>	<b>277</b>	<b>2.9</b>
PU-CO-TMP	47	7.1	58±2	0.6	338	1.5
<b>PU-REC-RO-TMP</b>	<b>53</b>	<b>0.9</b>	<b>56±2</b>	<b>0.5</b>	<b>265</b>	<b>2.4</b>
PU-RO-TMP	37	3.8	35±2	0.7	328	1.3
<b>PU-REC-CCO-TMP</b>	<b>44</b>	<b>1.3</b>	<b>46±2</b>	<b>0.4</b>	<b>237</b>	<b>3.2</b>
PU-CCO-TMP	40	5.5	60±1	0.5	302	1.9

### 3 RESULTS AND DISCUSSION

#### 3.1 Preparation and Properties of Recycled Polyols

Three different transesterified oils (CO-TMP, RO-TMP and CCO-TMP) were used for conversion of PC waste into recycled polyols at 215°C. An idealized reaction scheme of PC conversion into the recycled polyols by means of monoacyl esters of TMP as the major components of transesterified oils is depicted in Figure 1. A mixture of aromatic diols composed of bisphenol A (BPA), BPA-mono-carbonate and BPA-dicarbonate diols containing one and two TMP-monoacyl ester units, respectively, was received.

The initial mass ratio of PC/transesterified oil varied (Table 3) to keep the molar ratio of OH groups of the transesterified oils/carbonate linkages of PC equal to 2/1. These conditions enabled us to compare reactivity of the used transesterified oils towards PC. The kinetics of PC-transesterified oil reactions were compared using a time to complete PC dissolution (Table 3). The shortest time to complete PC dissolution (13 min) was observed for the reaction between CCO-TMP and PC, which corresponded well to the composition of CCO-TMP comprising uniquely the medium-chain fatty acid esters. These esters were highly mobile and thus more reactive with PC than the long-chain fatty acid esters presented in CO-TMP and RO-TMP. RO-TMP was found to be more reactive than CO-TMP since it contained uniquely primary hydroxyl groups. CO-TMP thus exhibited the lowest reactivity with PC (the complete PC dissolution occurred after 22 min) due to a partial presence of secondary hydroxyls, which formed approx. 1/3 of all hydroxyl groups of CO-TMP. These secondary hydroxyls located at 12<sup>th</sup> carbon of ricinoleic acid chain were less reactive towards the carbonate linkages of PC due to steric hindrance of acyl chain [20].

All obtained recycled polyols were pale yellow transparent liquids with hydroxyl numbers ranging between 217-264 mgKOH·g<sup>-1</sup> and acid numbers below 2.2 mgKOH·g<sup>-1</sup> (Table 3). The viscosity values of individual recycled polyols were influenced by the oils' fatty acid compositions (Table 1) but mainly by the PC/reagent mass ratio used for the PC decomposition (Table 3). REC-CCO-TMP contained a large amount of aromatic carbonate polyols from the decomposed PC, which increased polyol viscosity. The lowest PC/reagent mass ratio used for the preparation of REC-RO-TMP decreased polyol viscosity. By contrast, the higher PC/reagent mass ratio together with the high viscosity of original CO-TMP caused that the REC-CO-TMP viscosity was one order of magnitude higher than viscosities of other polyols.

In all cases, the PC waste was completely converted into polyols since no polymeric or oligomeric residues were detected by SEC (Figure 2). The SEC records of recycled polyols contained signals of the final degradation products: The peak at 14.8 min was assigned to bisphenol A (BPA) and three broad peaks in the range of ~13-14.5 min corresponded to the aromatic BPA-carbonate polyols [18]. These polyols were composed of end-capping acylester-TMP units connected through carbonate linkages to BPA (Figure 1). Positions of their relevant SEC peaks were thus dependent on acylester chain lengths. Therefore, the REC-CCO-TMP polyol based on the medium chain acylesters (Table 1) comprised the aromatic carbonate polyols (the corresponding SEC peaks at 13.6 min, 13.9 min and 14.4 min) with the lower molecular weight than those contained in the REC-CO-TMP and REC-RO-TMP polyols (Figure 2) derived from the long chain acylesters (Table 1). Moreover, the MALDI TOF mass spectrum of REC-CO-TMP polyol (not shown here) revealed a covalent linkage of carbonate polyols probably via the hydroxyl groups' condensation of ricinoleic chain. The formation of linked carbonate structures in the REC-CO-TMP polyol was also evidenced from SEC as the broad peak at 13.2 min (Figure 2). The small SEC peak at 15.5 min showed the traces of free TMP in all recycled polyols.

#### 3.2 Cast Polyurethanes Based on Natural Oils and Recycled Polyols

According to environmentally-friendly concept, all cast PU were prepared without a solvent addition. Figure 3 shows that only the PU-REC-RO-TMP sample containing the recycled polyol based on RO was opalescent due to phase separation and incomplete miscibility of all components. The both polyols based on RO (RO-TMP and REC-RO-TMP) gave pale yellow-colored PU, while the polyols based on CO and CCO produced highly transparent and colorless PU. Advantageously, the low viscosity of CCO-based polyols enabled easy mixing of PU components and fast degassing.

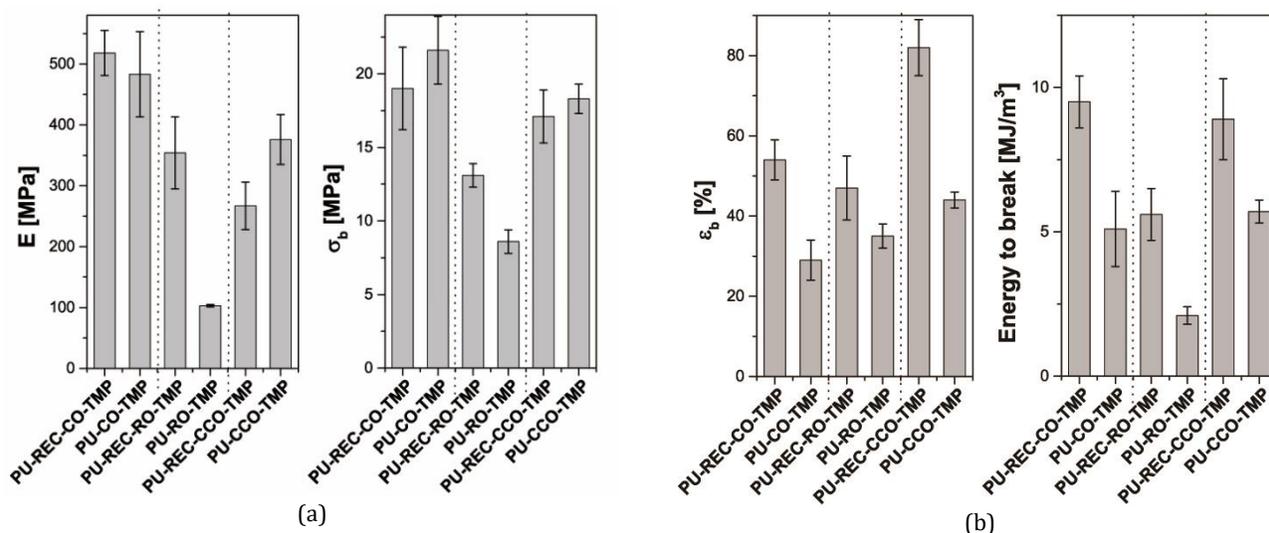
The effective crosslink density ( $\nu_e$ ) and the average molar masses between crosslinks ( $M_c$ ) of the prepared cast PU (Table 4) were determined from the equilibrium shear modulus of swollen samples ( $G'_{sw}$ ). As physical bonds in PU networks were disrupted at swollen state, the determined  $\nu_e$  and  $M_c$  values reflected the number of chemical crosslinks primary related to functionality and molecular weight of the used precursors, i.e. the polyols and t-HDI. It is seen that the addition of recycled polyols decreased the  $\nu_e$  values due to the major content of bifunctional BPA and the BPA-carbonate polyols acting as chain

extenders in the cast PU. The effect of hydroxyl group-bearing species with functionality ( $f$ ) equal to 2 (or <2) prevailed over the polyol components with  $f > 2$ , i.e. free TMP and CO-based species. Among the cast PU with recycled polyols, PU-REC-CO-TMP swelled at the lowest extent ( $\varphi_2=0.43$ ), which evidenced the most dense chemically crosslinked PU network due to an additional covalent bonding between the hydroxyls located at 12<sup>th</sup> carbon of ricinoleic chains of REC-CO-TMP and the isocyanate group of t-HDI.

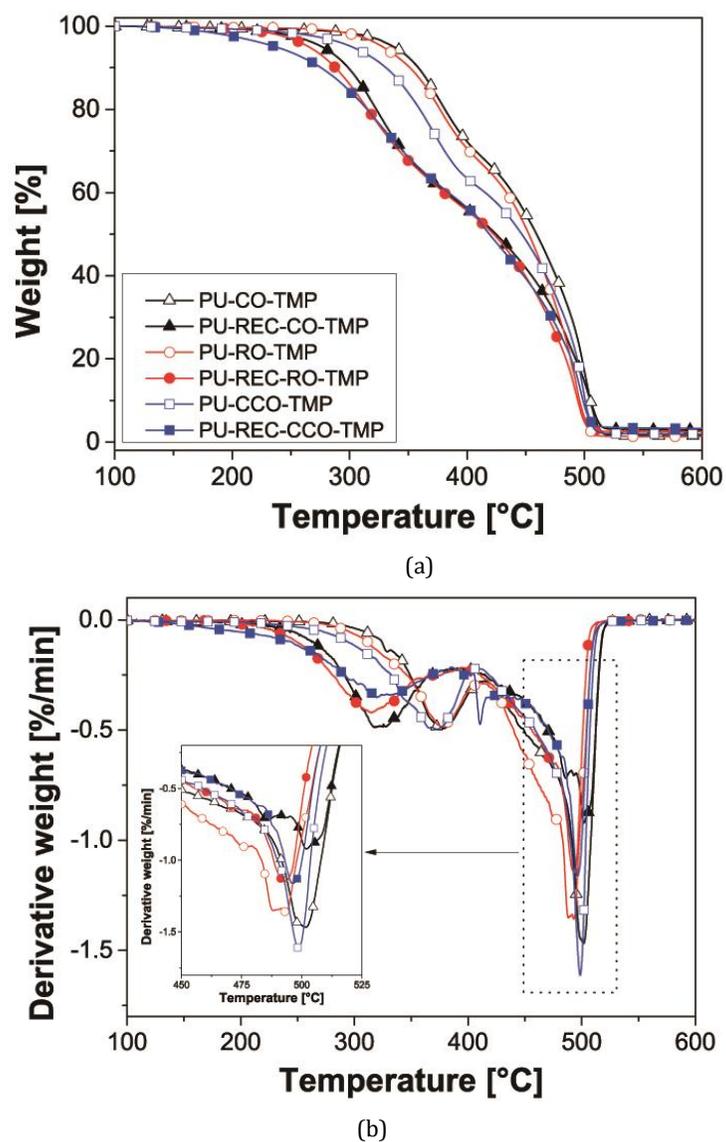
The DMTA behavior of crosslinked cast PU at dry state (Figure 4) was dependent on the mobility of chain segments driven by the number of chemical and physical crosslinks and network structure rigidity. The overall lower crosslink density of the recycled polyols-based PU over the PU based on transesterified vegetable oils decreased the values of storage shear modulus in the rubbery region ( $G'_R$ , Table 5). The  $G'_R$  values of dry PU networks were proportional to the number of effective network chains (i.e. chemical crosslinks—the  $\nu_e$  values in Table 4) and secondary (physical) bonds between the chains [21, 22]. The formation of latter was promoted by the addition of recycled polyols. The storage modulus curves of the recycled polyol-based PU (Figure 4) clearly indicated the existence of these physical crosslinks providing significant structural reinforcement up to ca 130°C. Above this temperature the rubbery plateau disappeared and the storage modulus started to decrease due to physical crosslink disruption.

The main transition temperature ( $T_\alpha$ ) of PU based on the recycled polyols was higher than the transesterified vegetable oil-based PU analogs (Table 5) due to the increased aromaticity (rigidity) of PU networks [23] resulting from the incorporation of BPA-derived units. An additional physical bonding, mainly hydrogen bonding of urethane and carbonate groups and  $\pi$ - $\pi$  interactions of aromatic segments took place [21]. The created pseudo-crosslink points [8, 24] caused that a less chemically cross-linked structure of the recycled polyol-based PU provided less free volume for network chain segment relaxation shifting the  $T$  values to higher temperatures.

Poor tensile properties of PU-RO-TMP (Figure 5) originated from a relatively high content of triacylestes in RO-TMP (ca 7%, Table 2) bearing no hydroxyl groups, which were incapable to react with t-HDI during PU network formation. The final PU network thus contained these triacylestes as diluents worsening its mechanical properties. The addition of recycled polyols improved dramatically the tensile properties of the cast PU based on RO (Figure 5). The substantial increase of all tensile characteristics (Young modulus,  $E$ , tensile strength,  $\sigma_b$ , energy to break and elongation-at-break,  $\epsilon_b$ ) of PU-REC-RO-TMP compared to the recycled polyol-free analog (PU-RO-TMP) demonstrated i) an improved incorporation of the polyol components into the PU network and ii) a reinforcing effect resulting from the increased non-covalent bonding (in accordance to the DMTA results) due to the presence of BPA-derived units of the recycled polyol.



**Figure 5** Tensile properties (Young modulus,  $E$ , tensile strength,  $\sigma_b$ , energy to break and elongation-at-break,  $\epsilon_b$ ) of the cast polyurethanes prepared from the recycled polyols (PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP) and from the transesterified oils (PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP).



**Figure 6** TGA and DTG curves of the cast polyurethanes prepared from prepared from the recycled polyols (PU-REC-CO-TMP, PU-REC-RO-TMP and PU-REC-CCO-TMP) and from the transesterified oils (PU-CO-TMP, PU-RO-TMP and PU-CCO-TMP).

For the cast PU derived from CO and CCO, the addition of recycled polyols significantly increased the energy to break and elongation-at-break compared to the cast PU based on the transesterified oils (Figure 5) due to the formation of less dense PU networks as the swelling measurements demonstrated (Table 4). Despite being less chemically crosslinked, the cast PU with the recycled polyols exhibited the similar values of Young modulus and tensile strength compared to the cast PU based on the transesterified oils, which evidenced (according to the DMTA results) the non-covalent bonding among the aromatic structures of BPA-derived units [8].

From the application point of view, all prepared materials (except PU-RO-TMP exhibiting poor mechanical properties) were classified as the rigid cast PU with the hardness values from 46 to 61 Shore D and the low water absorption (<0.6 wt.%, Table 5). The addition of recycled polyols slightly decreased the water absorption probably due to a less polar character of PU networks containing aromatic segments [8]. Commercially available cast PU exhibit the similar water absorption values [25]. However, it is known that these commercial PU are not pure polymers but composites containing inorganic fillers substantially decreasing the water uptake. Our materials thus might be advantageously designed as

filler-free transparent cast PU potentially applicable for electronic encapsulation.

The thermal stability of cast PU was evaluated using TGA under nitrogen atmosphere. The TG and DTG curves showed a two-step degradation (Figure 6), typical for PU [26]. The first degradation was significantly shifted to lower temperatures due to the incorporation of recycled polyols. This shift resulted from the more diluted PU network [27] and a presence of thermally labile pendant and entangled BPA-carbonate acyl chains [14]. The recycled polyols always contained a certain amount of BPA-carbonates bearing none or only one hydroxyl group. These structures were presented in the final cast PU either in the form of entangled molecules, i.e. not covalently bonded with polymer chains, or as the pendant units of the PU network. The presence of these thermally labile structures caused that the temperature of 5% weight loss ( $T_{5\%}$ , Table 5) of the cast PU based on the recycled polyols was shifted to lower temperatures. The second degradation step around 500°C was not influenced by the addition of recycled polyols (Figure 6). At this step, degradation products formed during the first step further degraded to form a char residue. The increased char yield after TGA of the cast PU based on recycled polyols (Table 5) was directly proportional to their aromatic contents [27]. PU-REC-CCO-TMP produced the maximal char yield (3.2 wt.%) due to the highest content of BPA-carbonates in the REC-CCO-TMP recycle polyol (the highest PC / reagent ratio used-see Table 3).

#### 4 CONCLUSIONS

It can be concluded that the transesterified natural oils can be used as the reagents for conversion of polycarbonate (PC) waste from end-of-life vehicles into polyols. The produced recycled polyols were successfully applied to prepare crosslink cast polyurethanes (PU) showing tunable thermo-mechanical properties and optical transparency depending on the fatty acid composition of the used natural oil. They can be classified as the rigid cast PU with the main  $\alpha$ -transition temperature ranging from 44°C to 53°C, the hardness value from 46 to 61 Shore D and the beneficially low water absorption (ca. 0.4-0.5 wt.%). The addition of recycled polyols on one hand decreased the crosslink density but on the other hand reinforced the PU network by increasing chain rigidity thanks to the presence of aromatic structures derived from the decomposed PC. Moreover, the rigid aromatic segments promoted the additional physical bonding via  $\pi$ - $\pi$  interactions of aromatic rings and hydrogen bonding of urethane and carbonate groups, which resulted in a glass transition increase and an

improvement of tensile properties. The prepared cast PU based on recycled polyols thus showed a better toughness than recycled polyol-free PU analogs, while a sufficiently high stiffness was preserved. These materials may find a suitable application in electrical and electronic casting and encapsulation.

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