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Characterisation of ureaurethane elastomers with rapeseed oil-based polyol

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Abstract. The purpose of this study was to evaluate the effect of rapeseed oil-based (RO) polyol on the thermal and mechanical properties of the tested ureaurethane elastomers (EPUUs) produced with poly(ethylene adipate) (PEA). The bio-polyol was synthesized by epoxidation and opening of oxirane rings using diethylene glycol (DG). The use of RO polyol in the amount 40 wt.% in polyol premixes changed the chemical structure of EPUUs with different hard segments (HS) content, what in a consequence indicates the change in quantity of the number of hydrogen bonds and degree of phase separation (DPS). The consequence of these changes are variation in the thermal characteristics of these materials. The DSC analysis showed that an addition of the RO polyol causes the increase in the glass transition temperature of the soft phase with an increase of HS content in EPUUs. An introduction of the RO polyol also resulted in an decrease in the elongation at break with an increase of HS content in the modified elastomers.

1. Introduction

In recent years, the introduction of plant components to polyurethane (PUR) systems meets all the ideas of sustainable development and is an important challenge for chemical companies [1]. PURs are well known and widely used because of their very good properties and applications. The production of PURs is based on the two most important components: polyols and isocyanates. Nowadays, one of the problems of PUR industry, is facing is their dependence on petroleum feedstock [2]. The increasing interest of industry of polyols from vegetable oils is observed [3]. In the PUR production the natural oil polyols can be used to replace petrochemical materials [4]. Polyols can be synthesized from natural materials, such as plants, oils or wood [5,6]. There are many publications about obtaining PURs with polyols from different vegetable oils based on soybean oil [7-9], rapeseed oil [10], sunflower oil [11], linseed oil [12], or castor oil [13]. Most of PUR materials from vegetable oil polyols are foams [14], coatings [15], films [16] and adhesives [17]. To obtain PURs from renewable vegetable oils there are some aspects that have to be considered – hydroxyl value, functionality, dangling chains and structure of polyol and their effect on properties of PUR network [16].

Polyurethane elastomers (EPUs) are the most distinguished group of polymers, because of their excellent properties such as good resistance to abrasion and to oils, grease and weather conditions



[17]. They are used for many applications: from flexible to rigid foams, to thermoplastic polyurethane and elastomers [18]. Currently, polyurethanes industry is highly dependent on oil as its two main raw materials, polyols and isocyanates, are largely petroleum. Because of global warming and the oil crisis, began to look at alternative substrates [19].

In this work, we examine bio-based ureaurethane elastomers (EPUUs) with a 40% wt. of rapeseed oil-based (RO) polyol with a different content of hard segments (HS). The bio-polyol was synthesized using epoxidation and opening of oxirane rings using diethylene glycol. The different content of rapeseed oil-based polyol was applied in order to evaluate influence on thermal stability as well as mechanical properties of the EPUUs in comparison with the reference EPUU based only on petrochemical polyol.

2. Experimental

2.1. Materials

Ureaurethane elastomers (EPUUs) were prepared by using a polyester poly(ethylene adipate) (PEA) - Polios 60/20, with molar mass of 2318 g/mol (Purinova, Bydgoszcz, Poland) and 4,4'-diphenylmethane diisocyanate (MDI) (Sigma Aldrich Co., Poznan, Poland). As chain extender the dicyandiamide (DYDI) - Omnicure 5, with molar mass of 84 g/mol (Emerald Performance Materials Company, USA) was used. During the production of EPUUs, rapeseed based polyol (RO) in an amount of 40 wt. % was added. Rapeseed polyol (RO) characterized by hydroxyl value 42.9 mgKOH/g, acid value 4 mgKOH/g, content of water 0.06 wt. % and number molecular weight 2387 g/mol was synthesized using at the Cracow University of Technology according to method described in our previous publication [20].

2.2. Synthesis of the ureaurethane elastomers

Ureaurethane elastomers (EPUUs) were synthesized by one step method, with isocyanate index $I_{NCO} = 1.07$. The content of hard segment (HS) of produced EPUUs was different and it is shown in table 1.

The PEA with DYDI were melted and degassed for 1.5 h at $150 \pm 5^\circ\text{C}$ and 6 hPa with intense stirring. Then the PEA was cooled to $80 \pm 3^\circ\text{C}$ before the RO polyol was added. The mixture was then stirred for 30 min. Next, the mixture was cooled to $60 \pm 3^\circ\text{C}$ and MDI was added and stirred for 10 min. The prepared mixture was then poured into a duraluminium mould and annealed for 18 h at 110°C . The samples were tested after 30 days of seasoning under ambient conditions.

2.3. Test methods

The Fourier Transform Infrared Spectroscopy (FTIR) was carried out using a Nicolet 7600 (ThermoElectrone Corporation, USA). Spectra were recorded as a sum of 64 scans using a spectral range from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} . The data analysis was performed using Omnic software. A baseline correction for CO_2 and H_2O was performed to eliminate the impact of the compound residues from the analysis.

The DSC analysis was performed using a differential scanning calorimeter Q1000 (TA Instruments, USA). Samples (5 mg) were closed in hermetic aluminum cups and heated at $10^\circ\text{C}/\text{min}$ in the temperature range -90°C to 250°C .

The thermal stability was defined by thermogravimetric analysis using a Q500 analyzer (TA Instruments, USA). The tested 10 mg samples were heated from room temperature to 800°C for EPUUs with a heating rate of $10^\circ\text{C}/\text{min}$. Tests were carried out in a nitrogen atmosphere with a flow rate of 90 ml/min.

The dynamic mechanical thermal analysis (DMTA) was carried out on a TA Instruments DMA Q800 (USA). This study was conducted using cast rectangular-shaped samples with dimensions $60 \times 10 \times 2\text{ mm}$ and a two-point bending method. Samples were heated at $3^\circ\text{C}/\text{min}$ in a temperature range between -100°C to 110°C , using a constant frequency of 1 Hz and an amplitude of $25\text{ }\mu\text{m}$. The test was carried out in a nitrogen atmosphere.

The static tensile test was performed on a tensile machine (Instron 1115) according to PN-EN ISO 527. The cast paddle-shaped samples with dimensions 2,5x2 mm and measuring length 20 mm, were stretched at a speed of 500 mm/min.

Wear resistance was measured using the Schopper–Schlobach method. The cast samples had a cylindrical shape with dimensions 16 × 6mm² and were tested according to ISO 4649.

3. Results and discussion

3.1. The chemical constitution

The FTIR analysis confirmed the occurrence of groups characteristic for EPUUs. The FTIR spectra of RO polyol and the obtained materials are compared in figure 1.

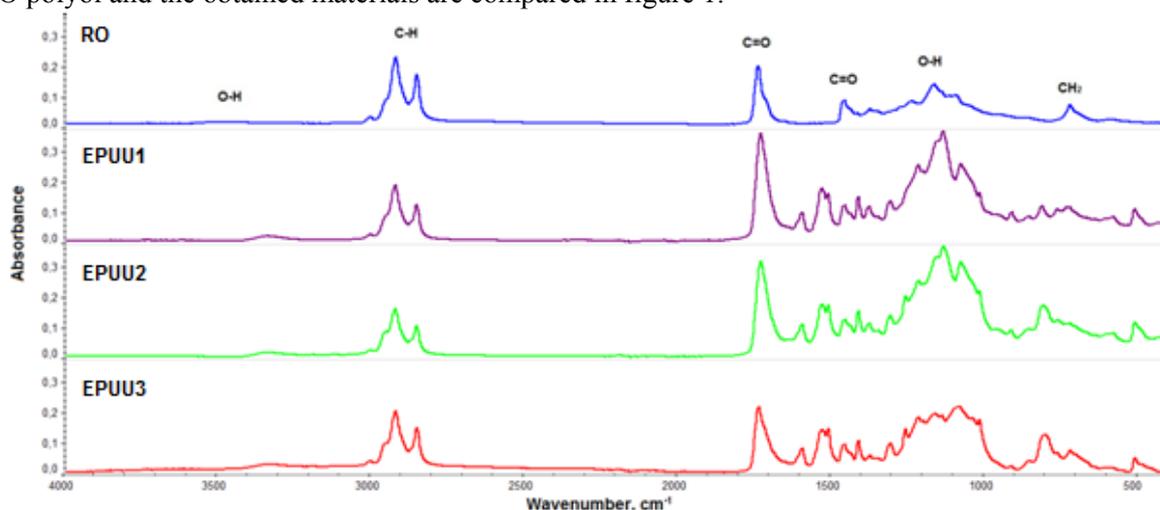


Figure 1. Fourier transform infrared spectroscopy (FTIR) spectra of RO polyol and tested EPUUs

The interpretation of the FTIR spectra of tested EPUUs shows signals in the range of 3349–3342 cm⁻¹, which are the result of symmetric and asymmetric stretching vibrations of the N-H groups present in urea and urethane derivatives. This bond is involved in the formation of hydrogen bonds. The signals at 2960–2953 cm⁻¹ and 2874–2872 cm⁻¹ are corresponding to symmetric and asymmetric CH₂ stretching vibrations, respectively. The multiplet signal at 1728–1727 cm⁻¹ indicate the presence of C=O bond stretching vibrations of the carbonyl groups in hard segments. The signal at 1598–1597 cm⁻¹ are corresponding to aromatic groups. In the range of 1534–1530 cm⁻¹ the urethane N-H bending vibrations and C-N stretching vibrations are observed. The signals at 1460–1455 cm⁻¹ are corresponding to scissoring vibrations of C-H bond. Signals in the range of 1212–1219 cm⁻¹ are the result of C-N stretching vibrations. The signals in the range of 1260–1060 cm⁻¹ are corresponding to the C-O bond, attributed to the flexible segments.

For RO polyol the signal at 3468 cm⁻¹, 3006 cm⁻¹, 2922 cm⁻¹, 2853 cm⁻¹, 1741 cm⁻¹ and 722 cm⁻¹ are observed and was discussed in our previous work [21].

With the increasing amount of HS content, the absorbance of bands originating from symmetric and asymmetric stretching of bonds C-H decreases, for tested materials. The absorbance of the bands originating from the stretching vibrations bonds C-O at 1159–1156 cm⁻¹ also decreases with the higher HS content. The intensity of bands originating from the vibrations of the carbonyl bonds C=O, also decreased with the increase of HS content.

The data analysis was performed using Omnic software. A baseline correction for CO₂ and H₂O was performed to eliminate the impact of the compound residues from the analysis. On the basis of the intensity of the bands, hydrogen bonding index (R) was calculated by equation:

$$R = \frac{A_1 + A_2}{A_3 + A_4}$$

where: A_1 and A_2 are the areas originating from vibrations bound by the hydrogen bond of the carbonyl groups of urea $1630\text{-}1680\text{ cm}^{-1}$ and urethane $1705\text{-}1727\text{ cm}^{-1}$; A_3 and A_4 are the areas originating from vibrations unbonded with the hydrogen bond of the carbonyl groups of urea $1690\text{-}1701\text{ cm}^{-1}$ and urethane $1736\text{-}1760\text{ cm}^{-1}$.

The value of degree of phase separation (DPS) was determined based on the R index and calculated by equation:

$$DPS = \frac{R}{R + 1}$$

Calculated values of R and DPS were calculated and are summarized in table 1.

Table 1. Hard segments (HS) content, hydrogen bond index (R) and degree of phase separation (DPS) for the tested EPUUs

Sample	HS, %	R	DPS
EPUU1	24	1.13	53.1
EPUU2	28	1.32	56.9
EPUU3	33	1.04	51.0

The DPS is the highest for EPUU2. For this material the highest formation of hydrogen bonds between rigid segments is observed. The characteristic of DPS values are related with physical cross-linking of the examined EPUUs.

3.2. Thermal properties

The Tg temperature determined from DSC analysis gives an information about structure of the soft phase in the tested materials. Values of Tg determined for EPUUs were within the range between -28.5°C and -26.2°C (table 2). The highest Tg value indicates that macroparticle fragments forming the soft phase of EPUUs have somewhat lower flexibility.

On the basis of TGA thermograms of tested EPUUs the temperature at 5% mass loss ($T_{5\%}$) as well as the mass remaining after annealing at 800°C (U_{800}) were determined (table 2).

No significant changes were observed in temperature associated with the beginning of degradation of materials ($T_{5\%}$). After degradation at 800°C (U_{800}) there remains 6.0-8.3% mass for EPUUs. The residue at 800°C decreased with an increase of HS content in EPUUs.

Table 2. Thermal and mechanical properties of tested EPUUs

Sample	Tg, °C	T _{5%} , °C	U ₈₀₀ , %	T _α , °C	δ _M , MPa	ε, %	E' ₋₃₀ , MPa	E' ₂₀ , MPa	E' ₆₀ , MPa	ΔV, mm ³
EPUU1	-27.0(0.2)	289(0.1)	6.0(0.1)	-20.1(0.2)	11.64	444	7559	39	15	184.1(0.1)
EPUU2	-28.5(0.3)	288(0.4)	8.1(0.3)	-21.8(0.1)	13.02	292	10440	124	77	139.0(0.2)
EPUU3	-26.2(0.1)	290(0.1)	8.3(0.1)	-18.7(0.1)	17.42	167	4366	180	91	169.7(0.4)

*Values between the parenthesis are standard deviations

3.3. Mechanical properties

The viscoelastic properties of the tested EPUUs were investigated using DMTA. The curves of EPUUs obtained from measurement using DMTA are shown in figure 2, storage modulus (E'), loss modulus (E'') and loss tangent (tan δ), respectively. The results from the DMTA curves are listed in table 1.

Storage modulus E' at three different temperatures: -30°C , 20°C and 60°C (E'₋₃₀, E'₂₀ and E'₆₀) were determined (table 1). The E' in minus temperatures is highest for EPUU2. The E'₂₀ (above glass transition temperature Tg) increased with the increase of RO polyol content (table 2). The storage

modulus at high temperature (E'_{60}) also increased with the increase of RO polyol content. These result allows for the application of materials of high mechanical demanding.

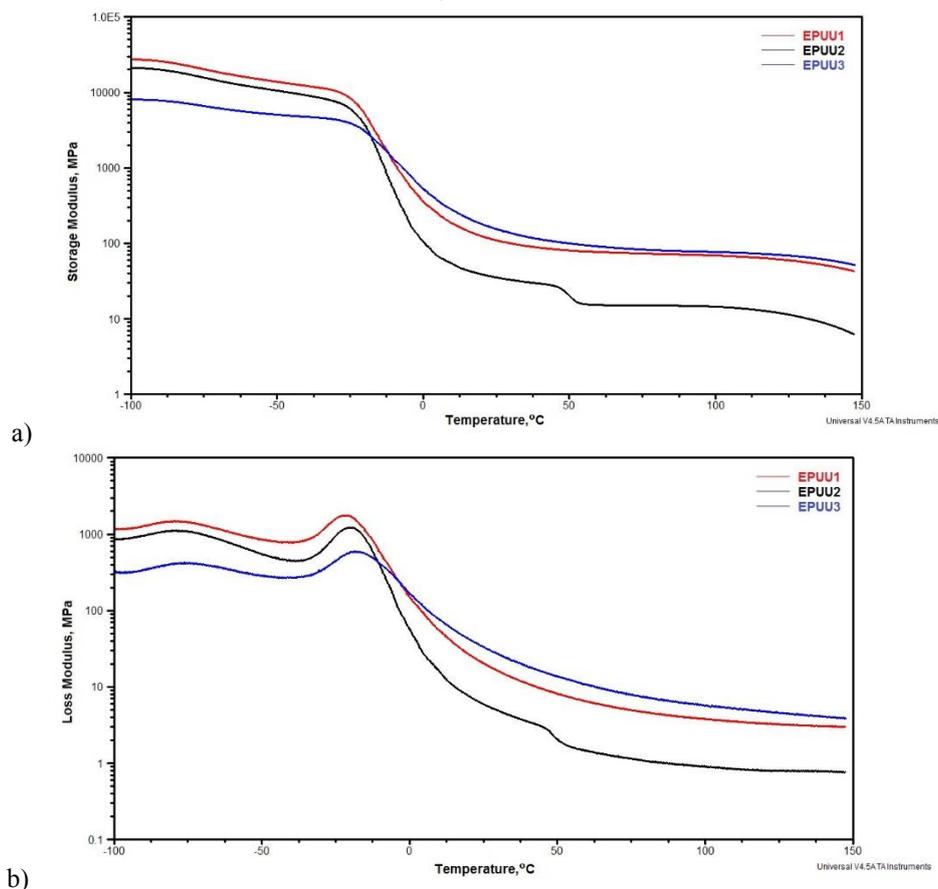
From the analysis of the curve of loss modulus (E'') (figure 2), taking into account the shape, position and height of the peak, it is possible to determine the degree of order and a free movement of the polymer chains. From this curve the α relaxation temperature, related to the glass transition temperature of soft segments ($T\alpha$) was determined as a maximum peak (table 2). The lowest temperature $T\alpha$ for EPUU2 is observed. This shown that for this material, the increase in the flexibility of the soft segments of the material microdomains, is observed.

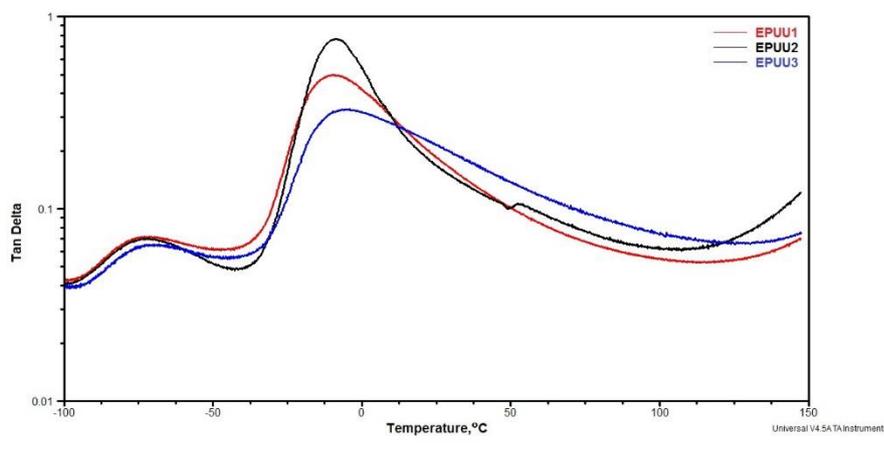
$\tan \delta$ value corresponds to the ratio of loss modulus (E'') to the storage modulus (E'). On the basis of $\tan \delta$ curves, the ability of a material to absorb and accumulate energy can be evaluated. Materials with high vibration-absorption and energy accumulation capacity are considered to have $\tan \delta > 0.3$ across a wide temperature range [21]. For all tested EPUUs the maximum peak of $\tan \delta$ is higher than 0.3.

Both DSC and DMTA analysis showed significant differences between the soft phase characteristic for tested materials. Both methods showed an increase in T_g and $T\alpha$ for material EPUU3, with the highest content of HS.

The tensile strength (δ_M) increased with an increase of HS content. Elongation at break (ϵ) decreased with an increase of HS content (table 2).

The usefulness of EPUUs in many applications is evaluated by wear resistance. The abrasive wear (ΔV) is lowest for EPUU2. This material have highest wear resistance.





c)

Figure 2. The DMTA curves of (a) storage modulus, (b) loss modulus and (c) $\tan \delta$ of tested EPUUs

4. Conclusions

According to the conducted study, the introduction of rapeseed oil-based polyol into the ureaurethane elastomers have different influence on their properties. The addition of RO polyol causes changes in the structure of soft phase in tested materials. The analysis of the DSC thermograms suggested that the increasing content of hard segments, results in higher glass transition temperature of the soft phase in EPUUs. This relationship has been confirmed by DMTA analysis. Wear resistance was highest for material EPUU2 with a 28 wt. % of HS content.

These studies showed that it is possible to control the properties of EPUUs with RO polyol by changing the hard segments content.

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