Production and characterization of poly(urea-urethane) elastomers synthetized from rapeseed oil-based polyols
Part I. Structure and properties

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DOI: dx.doi.org/10.14314/polimery.2016.490

Abstract: Poly(urea-urethane)s (PUUR), wherein the polyol substrates of petrochemical origin, partly replaced by vegetable polyols, were synthesized. Various contents of polyols derived from rapeseed oil – from 0 to 50 wt % were used. In order to determine the chemical structure of the obtained samples, they were examined using Fourier transform infrared spectroscopy (FT-IR). Physicochemical and mechanical properties were determined using, among others, methods of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), as well as the tribological tests were performed. Studies have shown that new material obtained using the highest content of the polyol of vegetable origin (50 wt %) was characterized by the best storage modulus and friction coefficient. This material can be applied where low abrasive wear and volume resistivity is required.

Keywords: urea-urethane elastomers, polyol from rapeseed oil, dicyandiamide.

Wytwarzanie i charakterystyka elastomerów uretanowo-mocznikowych z poliolu na bazie oleju rzepakowego
Cz. I. Struktura i właściwości

Streszczenie: W ramach pracy zsyntetyzowano poliuretanomoczniki (PUUR), w których substraty poliolowe pochodzenia petrochemicznego zastępowano częściowo poliolami pochodzenia roślinnego. Zastosowano różne zawartości polioli pochodzących z oleju rzepakowego – od 0 do 50 % mas. substratów poliolowych. Metodą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) określono strukturę chemiczną otrzymanych próbek PUUR. Właściwości fizykochemiczne i mechaniczne określano, odpowiednio, metodą różnicowej kalorymetrii skaningowej (DSC) i dynamicznej analizy mechanicznej (DMA). Przeprowadzono również testy trybologiczne. Badania wykazały, że najlepszą wartością składowej rzeczywistej modułu zespolonego (*E'*) i współczynnika tarcia charakteryzował się materiał zawierający 50 % mas. poliolu pochodzenia roślinnego. Materiał ten może znaleźć zastosowanie w wyrobach, dla których wymagane jest małe zużycie ścierne i mała rezystywność skrośna.

Słowa kluczowe: poli(uretano-moczniki), poliol z oleju rzepakowego, dicyjanodiamid.

Polyurethanes (PUR) are produced from a polyol, a diisocyanate, extenders and other auxiliary factors to obtain foams, coatings, elastomers and adhesives [1]. PUR is used in a number of applications such as footwear, machinery industry, coatings and paints, rigid insulations, elastic fibers, soft flexible foam, and medical devices. The PUR market currently accounts for about 5 % of the global polymer market [2]. PURs are the sixth most widespread group of polymers [3]. Petroleum was the first feedstock for polyols and isocyanates for the production of PUR, but for many years plant oils as well as fatty acids have been used in PUR technology. In contrast to petrochemical resources, the availability of these renewable natural raw materials is practically unlimited. Vegetable oils are considered to be one of the

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cheapest and most abundant biological sources available [4–6]. In recent years, due to the increasing cost of crude oil, global warming and other environmental problems, the interest in the polymers from non-petrochemical resources [6] has been growing. The growing interest in polyols from renewable resources also results from their simple preparation yet greatly promising applications [7], inherent biodegradability and limited toxicity [8, 9]. The latest advances in PUR research have focused on the replacement of petro-based polyols, isocyanates and extenders with bio-based molecules. Current trends are for the use of chemical platforms based on vegetable oils and involving the valorization of natural oil polyols [10–13]. Lately, considerable research has concentrated on the development of bio-based polyurethane using natural oils. These polyols were developed for the manufacture of PUR foams, ranging from flexible to rigid, with a broad range of properties [14–18], less frequently for the manufacture of elastomers [19–22] or coatings [23–27]. Vegetable oils are triglycerides and often have at least one unsaturated fatty acid molecule in their chemical structure [28, 29]. Many types of vegetable oils (from rapeseed, tung, linseed, canola, sunflower, and soybean) have been tested and reported for polyol synthesis as polyurethane precursors [7, 17, 30–31].

Foams obtained from plant oil polyols, such as soya, exhibited comparable mechanical, and insulating properties and better thermal resistance properties than foams from petrochemical feedstocks [15]. In the process of foam manufacture from vegetable oil-based polyols the recipe needs changes due to low reactivity of the secondary functional groups [17]. Another problem can also be the high viscosity of polyol [17].

The purpose of the work was the assessment of manufacture possibilities of urea-urethane elastomers using dicyandiamide (DCDA) and polyol from vegetable oil, as well as characteristics of the produced materials. It was envisaged that the analyzed materials would be used in applications, in which increased abrasive wear resistance, rigidity and low electrical conductivity would be required.

EXPERIMENT PART

Materials

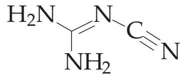
Poly(urea-urethane) (PUUR) was produced from the following substrates:

– poly(ethylene-butylene) adipate (EBA), characterized by hydroxyl value of 47.8 mg KOH/g, acid number of 0.8 mg KOH/g and number-average molar mass of 2320 g/mol was purchased from Purinova (Poland);

– rapeseed oil based on polyol MK ISO 52N (MK) having a molar mass *ca.* 2230 g/mol and functionality of 2, which was manufactured at Cracow University of Technology;

– methylene diphenyl-diisocyanate (MDI) used in this study were supplied by Sigma-Aldrich Co. (Poznań, Poland);

– dicyandiamide (DCDA) with trade name OMNICURE 5 provided by Emerald Performance Materials Company (USA) was used as chain extender [the structure of DCDA is presented by formula (I)].



(I)

Preparation of PUUR

PUUR was synthesized using a one-shot method in a 250-mL duralumin reactor with polytetrafluoroethylene coating equipped with a mechanical stirrer. The mole ratio of the substrates (EBA+MK):MDI:DCDA was 2:5:3 and isocyanate index was 1.05. Five samples with various EBA:MK weight ratio were prepared. Their compositions and symbols are listed in Table 1. EBA and DCDA were degassed for 1.5 h at 160 ± 5 °C and 6 hPa with intense stirring, then at 100 °C polyol MK was added and mixed under vacuum for 1 h. The mixture was cooled to 60 ± 3 °C before the MDI was added. The blend was then stirred for 5 min. The prepared mixture was then poured into a closed duralumin mold and annealed for 8 h at 150 °C. The samples were tested after 30 days of seasoning under ambient conditions. On the basis of the molar composition of the starting materials and their molar mass the content of hard segments in the prepared materials was calculated.

Table 1. Symbols and composition of the obtained PUUR samples

Symbol of sample	EBA:MK weight ratio	Hard segments content, %
RM1	100:0	24.5
RM2	90:10	24.5
RM3	80:20	24.6
RM4	70:30	24.6
RM5	50:50	24.7

Experimental methods

The Fourier transform infrared spectroscopy (FT-IR) spectra of PUUR were recorded on Nicolet 7600 apparatus (Thermo Electrone Corporation, USA), at spectral range between 4000 and 400 cm^{-1}, with resolution of 4 cm^{-1} and a count of 64. The data analysis was performed using Omnic software. A baseline correction with CO_2 and H_2O was performed to eliminate the impact of the compound residues from the analysis.

The thermal properties were determined using differential scanning calorimetry (DSC) on TA Instruments DSC Q1000 calorimeter. Samples of 5–10 mg were subjected to a helium atmosphere and examined under heat. Test cycle consisted of cooling to -90 °C, soaking for 5 min and heating at the rate of 10 deg/min to about 250 °C. Characteristic temperatures were designated from the first heating cycles.

The viscoelastic properties of PUUR were measured on a TA DMA Q800 instrument (TA Instruments, New Castle, DE, USA), using the two single cantilever bending mode. The experiments were carried out by heating of the sample from -100 °C to 110 °C at the heating rate of 3 deg/min, frequency of 1 Hz and amplitude of 25 μm.

Static tensile test was performed on Instron 1115 tensile machine according to PN-EN ISO 527-1:2012 standard. The paddle-shaped samples were stretched at the speed of 500 mm/min.

The density was determined using analytical balance produced by Radwag with an attachment for measuring of the density using Archimedes principle according to PN-C-04215:1983 standard.

The hardness was measured on Durometer A (Wilson Wolpert Company), according to DIN 53505, ASTM D2240 and ISO 7619 standards.

Resilience was determined using Schob apparatus in conformity with ASTM D1054 Method B (Schob).

The tribological tests were carried out using two methods. The first method determined wear resistance (V) using the apparatus Schopper-Schlobach according to ISO 4649:2010 standard. Measurements for five samples of each PUUR were performed, and the results were averaged. Measurements using a tester of pin-on-disk type (Type T-11) were also performed. The tribological pair contained a pin made of a material under test and the counter-sample was represented by a steel disk. On the basis of preliminary studies and reports in the literature, the following parameters of tribological tests were assumed: linear friction velocity v = 0.1 m/s, the diameter of the end face of the sample ϕ = 3 mm, pressure 2 MPa, time t = 1 h [32]. The results were averaged from three measurements for each PUUR.

Antistatic qualities of tested materials were evaluated using an antistatic ohmmeter Eurostat Tom 600 from Eurostat Company. At the same time the measurement of air humidity and temperature was carried out as well as the resistance (resistance to $2 \cdot 10^{12}$ Ω at the voltage of up to 100 V).

RESULTS AND DISCUSSION

PUUR samples were obtained using polyols from rapeseed oil. In the first step of rapeseed oil-based polyol synthesis, unsaturated fatty acids in triglycerides reacted with acetate peroxyacid to form epoxidized oil. In the second step the epoxidized oil was converted into a polyol using isopropanol. The amount of isopropanol was taken stoichiometrically to epoxy groups.

The FT-IR analysis confirmed the presence of groups characteristic for the polyols and polyurethane. The FT-IR spectra of the analyzed materials are shown in Fig. 1. Signals in the range of 3341–3352 cm^{-1} are the result of symmetric and asymmetric stretching vibrations of the N-H groups present in urethane groups [33]. The signals at 2920–2960 cm^{-1} and at 2846–2873 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of C-H bonds of -CH$_2$- groups, respectively. The signals at the 1451–1462 cm^{-1} were connected with scissoring vibrations of -CH$_2$- groups. The signal at 2275–2277 cm^{-1} corresponding to unreacted isocyanate [34] was observed only on the spectrum of RM5 sample. The presence of isocyanate groups is related to an excess of isocyanate used relative to MK polyol. The signal at 1725–1739 cm^{-1} indicates the presence of C=O carbonyl bonds in urethane groups [36]. The aromatic groups in materials correspond to 1595–1600 cm^{-1}. The signals at 1524–1530 cm^{-1} represent the bending vibrations of the N-H groups present in urethane groups [34]. Signals in the range of 1212–1217 cm^{-1} are the result of C-N stretching vibrations. The multiplet band in the range of 1070–1262 cm^{-1} is assigned to C-O bonds in flexible segments [35].

The spectroscopic analysis results of materials are listed in Table 2. Observed signal displacements are the result of the differing weight ratios of the polyols used (EBA:MK). With increasing amount of MK polyol the absorbance of bands

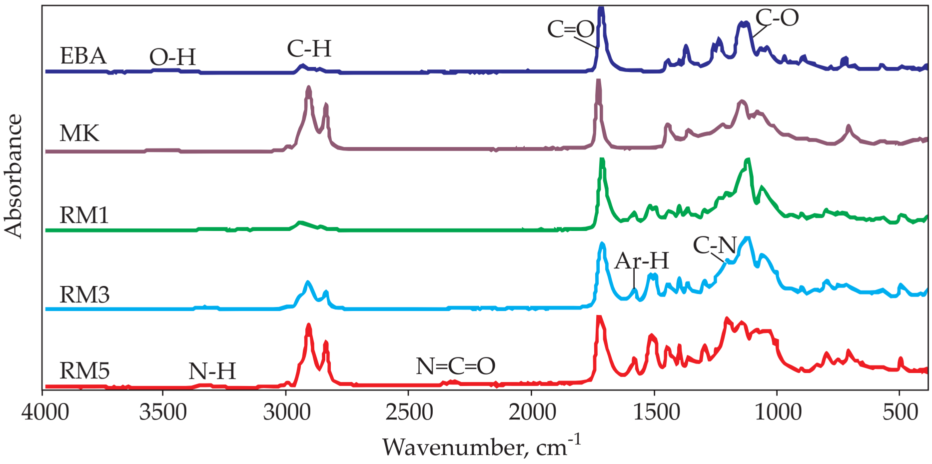


Fig. 1. FT-IR spectra of obtained PUUR materials

Table 2. Analysis of signal displacements in FT-IR spectra of obtained PUUR samples

EBA	MK	RM1	RM2	RM3	RM4	RM5	
wavenumbers, cm^{-1}							bond (vibration)
3520	3538	–	–	–	–	–	O-H (stretching)
–	–	3344	3341	3341	3350	3352	N-H (stretching) [35]
3017	3005	–	–	–	–	–	C-H (asymmetric stretching)
2946	–	2960	–	–	–	–	C-H (asymmetric stretching)
–	2923	2920	2926	2920	2923	2920	C-H (asymmetric stretching)
2873	2846	2870	2849	2852	2849	2849	C-H (symmetric stretching)
–	–	2269	2269	2266	2269	2266	N=C=O (stretching)
1736	1733	1725	1728	1730	1730	1739	C=O (stretching)
–	–	1595	1598	1600	1595	1595	Ar-H (deformation)
–	–	1530	1530	1527	1524	1530	N-H (bending)
–	–	1504	1510	1510	1513	1510	H-N-C=O Amide II Combined motion
–	–	1451	1460	1460	1458	1462	C-H (scissoring)
–	–	1303	1307	1310	1306	1304	Y-CH$_2$
–	–	1256	1262	1259	1258	1260	C-O (stretching)
–	–	1215	1212	1212	1217	1212	C-N (stretching)
–	–	1071	1080	1077	1070	1088	C-O (stretching)

originating from symmetric and asymmetric stretching of bonds C-H (2960, 2923, 2852 cm^{-1}) increases. A decrease in absorbance of bands originating from the stretching vibrations of bonds C-O (1133, 1260 cm^{-1}) is also observed. This is the result of reducing the amount of ester groups in PUUR soft segments, after introducing of MK polyol.

The use of polyols from rapeseed oil in the manufacture of PUR brings about a shift in the bands deriving from various bonds (Table 2) and also changes its absorbance. To compare absorbance bands in the PUUR spectra all the bands were calibrated with respect to the band related to vibrations of bonds in the aromatic ring (Ar-H, 1595 cm^{-1}) and selected results are shown in Fig. 2.

With increasing amount of MK increases the absorption of bands originating from vibrations: bending N-H bonds (1524–1530 cm^{-1}), combined motion of Amide II bonds (1504–1513 cm^{-1}) and stretching C-N bonds (1212–1218 cm^{-1}). A significant increase in absorbance of bands derived from the vibrations of C-N bonds and strands of Amide II is one of the reasons for the observed decrease in absorbance of bands derived from the vibrations of carbonyl bond C=O (1725–1739 cm^{-1}). These changes affect also the absorbance of the multiplet band derived from carbonyl bonds.

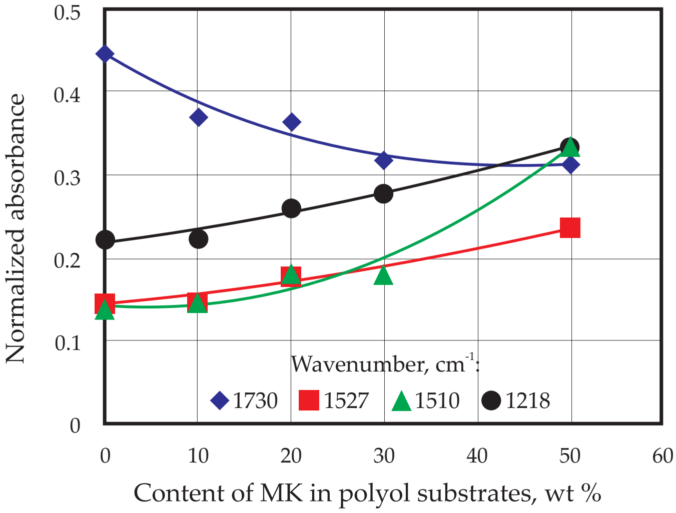


Fig. 2. Effect of MK content on absorbance of the selected bands of FT-IR spectra

Based on FT-IR spectra, the index of hydrogen bond ($R_{C=O}$) and degree of phase separation (*DPS*) were analyzed. These values were taken from the bands in the range of 1630–1750 cm^{-1} corresponding to the stretching vibrations of the C=O group. The share of C=O bonds of urea and urethane groups linked by hydrogen bonds was defined by equation [36]:

$$R_{C=O} = \frac{A_{B1} + A_{B2}}{A_{F1} + A_{F2}} \tag{1}$$

where: A_{B1}, A_{B2} – the surface of the bands from the vibrations bound to the hydrogen bond of the carbonyl groups of urea (B1, 1640–1680 cm^{-1}) and urethane (B2, 1705–1727 cm^{-1}), respectively; A_{F1}, A_{F2} – the respective areas of bands from vibrations unbound with the hydrogen bond of the carbonyl groups of urea (F1, 1690–1701 cm^{-1}) and urethane (F2, 1736–1745 cm^{-1}) bonding, respectively.

On the basis of the resulting index $R_{C=O}$ the value of *DPS* of hard segments was calculated from the following equation:

$$DPS = \frac{R_{C=O}}{1 + R_{C=O}} \tag{2}$$

Values of $R_{C=O}$ and *DPS* determined for obtained PUUR samples are listed in Table 3. It can be concluded that increasing content of MK caused a decrease in $R_{C=O}$

Table 3. The results of phase separation analysis of PUUR samples

Symbol of sample	$R_{\mathrm{C=O}}$	*DPS*	$U_{\mathrm{NH\text{-}O}}$, %
RM1	0.834	0.455	19.0
RM2	0.683	0.406	12.2
RM3	0.521	0.343	5.4
RM4	0.485	0.327	12.5
RM5	0.347	0.258	17.5

and *DPS*. The changes in $R_{\mathrm{C=O}}$ and *DPS* affect the properties of the polyurethanes, as presented in the work by Pretsch *et al*. [36].

For PUR there is observed a multiplet band derived from stretching vibrations of N-H group at wave number of 3200–3500 $\mathrm{cm^{-1}}$ [36]. Within this band there is a band component, which is connected with the vibrations of N-H group in the hard segment (urea and urethane) linked by hydrogen bonding with oxygen of the flexible segment at the wavenumber of 3295 $\mathrm{cm^{-1}}$ and resonance band at 3260 $\mathrm{cm^{-1}}$. The formation of hydrogen bonds complicates the phase separation in PUUR [36]. The share of that component band ($U_{\mathrm{NH\text{-}O}}$) at 3260 $\mathrm{cm^{-1}}$ (B1) and 3290 $\mathrm{cm^{-1}}$ (B2) in the multiplet band in the range of 3250–3400 $\mathrm{cm^{-1}}$ (B) was calculated from the surface areas of the bands B1, B2 and B (A_{B1}, A_{B2} and A_{B}, respectively) using the following equation:

$$U_{\mathrm{NH-O}} = \frac{A_{\mathrm{B1}} + A_{\mathrm{B2}}}{A_{\mathrm{B}}} \qquad (3)$$

The calculation results are provided in Table 3.

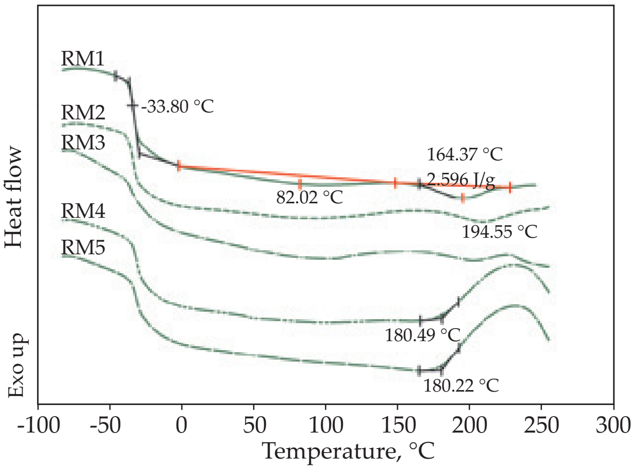


Fig. 3. Thermogram of DSC analysis of the examined PUUR

DSC measurements were performed under heating/cooling/heating mode to explain phenomena that occur in the analyzed materials. The thermograms obtained in the first heating cycle (Fig. 3) for all of the analyzed PUUR materials showed inflection corresponding to the glass transition temperature of soft segments (T_g). This temperature was also observed in the curves obtained during the second heating cycle. In the curves obtained in the first cycle for materials RM1, RM2, RM3, RM4 there was occurrence of a broad endothermic peak [with first transition temperature (T_1) and first enthalpy of transition (ΔH_1)]. For materials RM1, RM2 and RM3 another endothermic peak of the second transition temperature (T_2) and its enthalpy (ΔH_2) occurred. The characteristic temperatures and enthalpies of transitions are summarized in Table 4. In order to facilitate the interpretation of the results for PUUR samples a DSC analysis of polyols EBA and MK was also performed. For both polyols DSC thermograms show a visible inflection characteristic for the glass transition and endothermic peak associated with melting of the crystalline phase (T_m – melting temperature, ΔH_m – enthalpy of melting, Table 4). For MK polyol exothermic transition at approx. 170 °C was also observed. This temperature, designated by T_r can be associated with polymerization temperature of unsaturated fatty acids in polyol MK.

Indirectly, T_g gives information on the structure of the soft phase in the tested materials. Values of T_g determined for PUUR samples in the first heating cycle were within the range between -34.5 and -30.8 °C. The introduction of smaller amounts of MK (RM2 and RM3) causes that soft phase to be characterized by a little lower T_g values in comparison to the value observed for RM1 (without MK). When more MK was introduced (RM4, RM5), then T_g increased by about 2.9 deg higher than observed for RM1. This indicates that microparticle fragments forming the soft phase of such PUUR have somewhat lower flexibility. Probably in these materials the influence of rigid segments of macromolecules introduced with MK is higher. The consequence of changes in the chemical structure of PUUR is the difference in the phase separa-

Table 4. Results of DSC analysis for obtained PUUR samples

Symbol of sample	T_g °C	T_{m1} °C	ΔH_{m1} J/g	T_{m2} °C	ΔH_{m2} J/g	T_r °C
EBA	-46.7	53.8	94.5	–	–	–
MK	-44.6	-17.5	6.5	–	–	170
RM1	-33.7	82.7	3.6	195	3.3	–
RM2	-34.1	90.4	3.6	209	2.8	–
RM3	-34.5	81.9	6.7	201	1.0	–
RM4	-30.8	86.8	3.0	–	–	179
RM5	-30.8	–	–	–	–	179

tion shown by *DPS* values determined in the course of spectroscopic analysis (Table 3). *DPS* values of prepared samples decrease with increase in MK content.

With the hard phase in the analyzed materials there are connected endothermic peaks appearing at temperature above 80 °C in DSC thermograms of the investigated materials (T_{m1} and T_{m2}). These peaks are probably a result of the dissociation of hydrogen bonds formed in the hard phase of PUUR. In the case of RM4 sample the peak at T_{m1}, was observed, but no second peak occurred at T_{m2}. For RM5 sample, neither of both peaks was observed. This confirms the difference in the level of hydrogen bonds in RM4 and RM5 in comparison to other materials, which were also stated using spectroscopic analysis. Introduction of higher amount of MK during PUUR synthesis may limit the process of phase separation in obtained materials. Possibly, they favor the formation of hydrogen bonds between N-H groups and the oxygen ($U_{\text{NH-O}}$) of the flexible segment (Table 3). DSC thermograms of polymers RM4 and RM5 indicated the occurrence of an exothermic peak starting at approx. 180 °C. This peak, similarly to that observed in MK, can be associated with polymerization of unsaturated fatty acids introduced with polyol MK into PUUR mixtures. According to literature, transesterification process of polyols from rapeseed oils can be conducted at 180–240 °C [37].

To confirm this hypothesis, the RM5 sample was heated for 30 min at 200 °C and FT-IR analysis of this sample was performed prior to and after heating. Both spectra obtained with correction of CO_2 and H_2O are shown in Fig. 4. A comparative analysis of these spectra was conducted, taking into account the intensity of the 1595 cm^{-1} band, derived from aromatic groups' vibrations. As a result of this analysis, it was concluded that there was a slight change in the multiplet band in the range of 1650–1745 cm^{-1}. After heating the fraction of non-bonded urea and urethane groups increased and the fraction of these bounded groups decreased. Such changes result in a slight increase in the degree of the separation phase. However, the sum of the urethane and urea bonds, remains unchanged. The absorption of bands originating from vibrations: symmetric and asymmetric stretching bonds C-H (2990, 2965, 2925, 2896, 2852 cm^{-1} and 1453 cm^{-1}), bending N-H bonds (1528 cm^{-1}), combined motion bonds Amide II (1514 cm^{-1}) increases. The intensity of the band in the range of 1000–1200 cm^{-1} increases but for the next band 1240 cm^{-1}, assigned to C-O bonds in flexible segments of PUUR, the intensity decreases. Observed changes are the result of polymerization of unsaturated fatty acids and confirm that no significant changes took place in the hard phase of RM5 sample, but there were changes in its soft phase composed of flexible segments formed by MK.

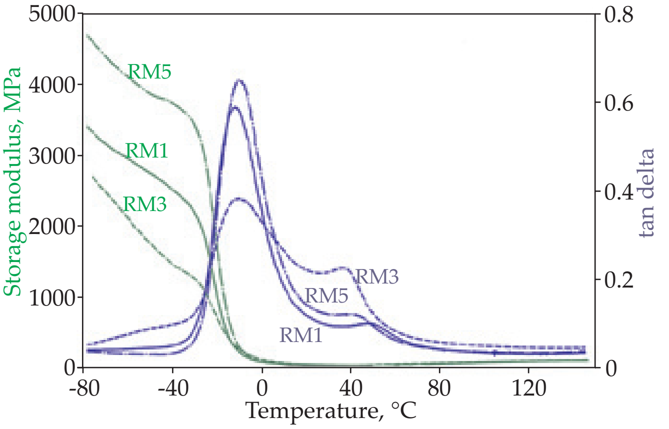


Fig. 5. DMA curves (*E′* modulus and tan delta) for RM1, RM3 and RM5

The viscoelastic properties of the PUUR samples were investigated using DMA. The variation of the storage modulus (*E′*) and of the tan delta as a function of temperature for selected samples are shown in Fig. 5. In the glassy region *E′* can be decreased by adding a higher amount of MK. In the rubbery plateau, a similar trend is found for all samples. The temperature corresponding to the first maximum in the tan delta curve (T_β) indicates the glass transition of soft phase and the temperature of second maximum indicates the melting of soft phase (T_α) of PUUR. Values of T_α and T_β as well as modulus *E′* values at -50 and 20 °C for prepared PUUR samples are listed in Table 5.

Values T_α of tested PUUR samples vary in the range between -6 and -12 °C. The higher content of MK results in

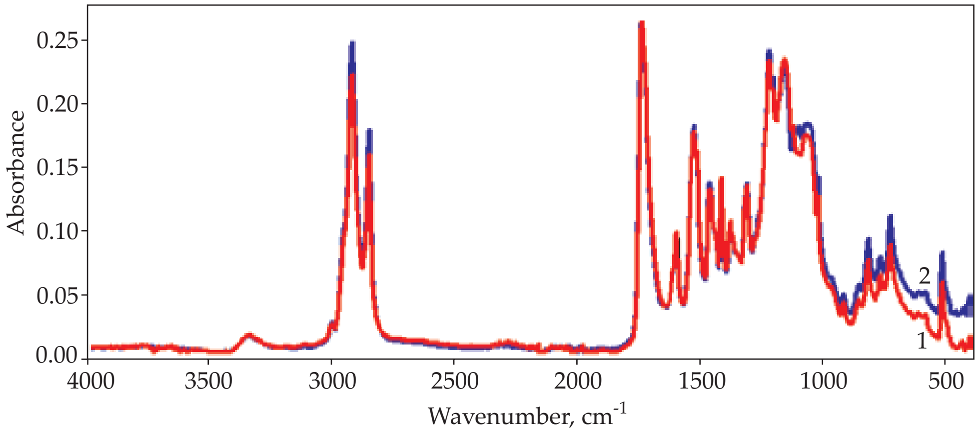


Fig. 4. Comparison of FT-IR spectra of RM5 sample before (1) and after (2) heating

Table 5. The results of the DMA for obtained PUUR samples

Symbol of sample	T_α, °C	T_β, °C	E', MPa	
			-50 °C	20 °C
RM1	-12.5	49	2715	24.5
RM2	-10.6	38	3845	20.6
RM3	-10.9	37	1715	26.6
RM4	-6.1	20	2068	10.3
RM5	-6.3	–	5800	53.5

Table 6. Mechanical properties of prepared PUUR samples

Symbol of sample	σ_{100} MPa	*Rm* MPa	*E* MPa	ε_r %	ε_t %	ϱ g/cm^3	η %	*H* °ShA
RM1	4.6 ± 0.2	42.8 ± 0.2	28.3 ± 0.9	1005 ± 35	14.4 ± 0.1	1.246 ± 0.007	32 ± 1	80.4 ± 0.5
RM2	4.2 ± 0.1	31.7 ± 0.1	47.5 ± 1.2	844 ± 45	15.6 ± 0.2	1.224 ± 0.005	26 ± 2	79.4 ± 0.6
RM3	3.2 ± 0.2	15.9 ± 0.2	21.9 ± 0.7	696 ± 35	7.5 ± 0.1	1.182 ± 0.009	25 ± 1	70.1 ± 0.6
RM4	3.4 ± 0.2	16.0 ± 0.2	29.2 ± 0.3	657 ± 24	7.5 ± 0.1	1.163 ± 0.012	24 ± 2	67.3 ± 0.3
RM5	5.5 ± 0.2	6.2 ± 0.1	98.8 ± 3.6	148 ± 23	3.8 ± 0.1	1.124 ± 0.009	20 ± 2	78.8 ± 0.3

the higher value of T_α indicated on the tan delta curve. This shows that there is a decrease in the flexibility of soft segments of the materials macromolecules. The introduction of higher MK content reduces the value of T_β. The decrease in that temperature may promote the formation of more hydrogen bonds between flexible and rigid segments in these materials. For RM5 sample with highest content of MK the highest E' value was observed. This is probably the result of the formation in these materials of additional bonds linking the macromolecules of such materials.

The results of mechanical properties measurements are presented in Table 6. In the examined materials very high modulus of elasticity (*E*) and favorably low permanent deformations (ε_r) as well as a decrease in their elongations at break (ε_t) were observed. Unfortunately, the tensile strength (*Rm*) and elasticity (η) were weakened. The stress at elongation of 100 % (σ_{100}), E', and hardness (*H*) of RM2 and RM3 samples decreased in comparison to RM1, but for RM4 and RM5 increases in comparison to RM3. The increase of MK amount caused a decrease in density (ϱ) of prepared materials, which was due to low density of MK in comparison to EBA.

In many applications of polyurethanes a highly important element is their behavior in tribological tests whose results are shown in Figs. 6 and 7. During the material consumption analysis, differences in density of the analyzed materials were taken into account. Low friction coefficient was characteristic for RM4 and RM5 materials (Fig. 6), while materials RM1, RM2 and RM3 shared a similar friction coefficient of approx. 0.65. Materials with MK polyol manifested much lower abrasive wear (*V*1) in pin-on-disk test than PUUR without MK (Fig. 7). Abrasive wear in Schopper-Schlobach test (*V*2) of PUUR samples increased with the increase in MK content.

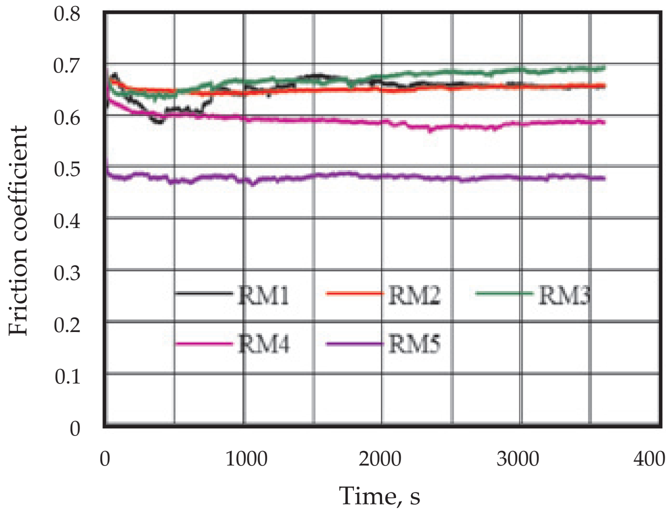


Fig. 6. The friction coefficient of PUUR samples during tribological test

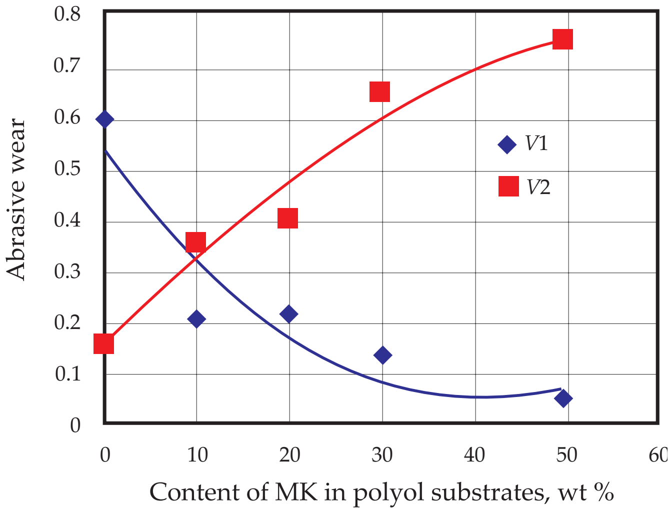


Fig. 7. Abrasive wear of PUUR samples in pin-on-disk (*V*1) and in Schopper-Schlobach (*V*2) tests

Table 7. Impact of added polyol MK on the resistance of PUUR

Symbol of sample	*VR* 10^9 Ω · m	Temperature °C	Humidity %
RM1	3.8 ± 0.6	33	32
RM2	3.8 ± 0.4	32	34
RM3	3.6 ± 0.3	32	34
RM4	2.3 ± 0.2	32	35
RM5	1.8 ± 0.2	32	35

PUUR investigations were finalized with an analysis of their antistatic properties [38] and results are presented in Table 7. The use of a higher content of MK reduces the volume resistivity (*VR*) of PUUR, which leads to better electrical conductivity. *VR* value is reduced to $1.8 \cdot 10^9$ Ω · m for RM5.

CONCLUSIONS

The paper presents the results of research on the impact of supramolecular structure of PUUR produced using vegetable-based polyol on their physicochemical and mechanical properties.

The use of polyol with rapeseed oil for the preparation of PUUR results in a change of phase separation degree in these materials. As the content of MK increases, the number of hydrogen bonds connecting the rigid segments of these materials is reduced. For smaller quantities of MK, the number of hydrogen bonds linking the rigid segments with the flexible segments drops down when compared to PUUR with petrochemical polyol. However, in polyols with more vegetable-based components, the number of these bonds increases.

As a consequence of differences in the course of separation phase and its chemical structure in PUUR, a change in the thermal characteristics of these materials takes place.

Among all the materials tested, best *E'* modulus and friction coefficient were displayed by PUUR containing about 50 wt % of MK in polyol substrates. This material has the lowest volume resistivity and abrasive wear in pin-on-disk test.

Obtained PUUR materials can be used in applications, in which low abrasive wear and low volume resistivity are required, *e.g.* in mining.

The study has been financed within the framework of the project Nr PBS1/A5/3/2012, entitled: "Elastomer composite materials for applications in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment".

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Received 18 VIII 2015.