Preparation and characterization of poly(urea-urethane) elastomers synthetized from rapeseed oil-based polyols. Part II. Thermal properties

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Abstract: Fourier transform infrared spectroscopy (FT-IR) studies revealed that the content of urethane, urea, and allophanate groups in hard segments depends on the amount of biopolyol used for the synthesis of elastomers (Table 2). Replacement of polyol of petrochemical origin with a natural material can reduce greenhouse gas emissions, but it should not deteriorate heat resistance and fire resistance, which determine the suitability of obtained elastomers for technical applications (*eg.* in the mining industry). The thermogravimetric analysis (TGA) under atmosphere of nitrogen and air atmosphere as well as combined analysis TGA/FT-IR of the obtained PUUR samples in air (Tables 3–4, Figs. 1–3) have shown that use of a polyol rapeseed oil resulted in only a slight reduction in their heat resistance as compared to the sample prepared without biopolyol. Use of biopolyol slightly worsens the fire resistance (Tables 5–6, Figs. 4–6).

Keywords: poly(urea-urethane) elastomer, polyol from rapeseed oil, dicyandiamide, thermal degradation, flammability.

Wytwarzanie i charakterystyka elastomerów uretanowo-mocznikowych z poliolu na bazie oleju rzepakowego. Cz. II. Właściwości termiczne

Streszczenie: Przedmiotem badań były poliuretanomoczniki (PUUR) wytworzone z zastosowaniem poliolu z oleju rzepakowego, którym zastępowano częściowo poliol pochodzenia petrochemicznego. Badania metodą spektroskopii w podczerwieni z transformatą Fouriera (FT-IR) pozwoliły stwierdzić, że zawartość ugrupowań uretanowych, mocznikowych i allofanianowych w segmentach sztywnych otrzymanych materiałów zależy od ilości biopoliolu użytego do syntezy elastomerów (tabela 2). Zastąpienie poliolu pochodzenia petrochemicznego surowcem naturalnym pozwala ograniczyć emisje gazów cieplarnianych, ale nie powinno przy tym pogarszać odporności termicznej i odporności na działanie ognia, które decydują o przydatności otrzymanych elastomerów do zastosowań technicznych (np. w górnictwie). Przeprowadzona analiza termograwimetryczna (TGA) w atmosferze azotu i atmosferze powietrza oraz analiza połączona TGA/FT-IR w atmosferze powietrza otrzymanych próbek PUUR (tabele 3–4, rys. 1–3) dowiodła, że zastosowanie poliolu z oleju rzepakowego spowodowało tylko nieznaczne zmniejszenie ich odporności termicznej w porównaniu z próbką otrzymaną bez biopoliolu. Użycie biopolioli nieznacznie pogorszyło również odporność na działanie ognia (tabele 5–6, rys. 4–6).

Słowa kluczowe: elastomer uretano-mocznikowy, poliol z oleju rzepakowego, dicyjanodiamid, degradacja termiczna, palność.

An increase of the concentration of greenhouse gases (GHG) in atmosphere influences the observable climate changes. Most of the amount of GHG is carbon dioxide from fossil resource use. Currently, most of raw materials for polymers production are based on fossil sources. A transition to the use of renewable resources for the pro-

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duction of polymers would allow reducing carbon dioxide emissions into the atmosphere [1].

For this reason efforts are made to implement the production of various polymer materials using renewable resources. In the report presented by Nova-Institute it is foreseen that worldwide production capacity of bio-based polymers will triple from 5.7 million tons in 2014 to nearly 17 million tons in 2020 [2].

One of the raw material groups being of recent interest of scientists are vegetable oils, due to their low cost, ready availability, and versatile applications. Nowadays, increasing attention has been paid to vegetable oil-based polymeric materials due to both economic and environmental concerns [3]. Several studies are focused on a replacement of fossil-based polyols with renewable-based ones [4–6], which allow decreasing the petroleum dependency as well as reducing the greenhouse gas emissions.

Polyols constitute one of the basic components for polyurethane manufacturing. Vegetable oil-based polyols are good candidates for polyurethane synthesis due to their functionality and other properties that are different comparing to polyether and polyester polyols used for this purpose [7–9].

Most of the published papers related to the applications of bio-based polyols concerns polyurethane foams [10–18]. In the previous article the results of mechanical and tribological properties of poly(urea-urethane) (PUUR) elastomers synthetized using the bio-polyols have been presented [19]. Their suitability for many technical applications, in particular in mining, is determined by the thermal and fire resistance [15, 20–22]. The aim of this part of work was study of thermal properties of PUUR elastomers prepared using rapeseed oil-based polyols.

EXPERIMENTAL PART

Materials

The subject of the study were PUUR samples produced using poly(ethylene-butylene)adipate (EBA) and rapeseed oil, based on bio-polyol MK ISO 52N (MK). A detailed description of the components used for PUUR manufacturing and the preparation method is contained in the previous paper [19]. The samples of PUUR have various contents of EBA and MK. These samples are described with symbols defined in Table 1.

Table 1. Characterization of the obtained PUUR

Symbol of sample	RM1	RM2	RM3	RM4	RM5
EBA:MK weight ratio	100:0	90:10	80:20	70:30	50:50

Methods of testing

The analyses of Fourier Transform Infrared Spectroscopy (FT-IR) were carried out using Nicolet 7600 (Thermo Electrone Corporation, USA). The spectra were recorded in spectral range from 4000 to 400 cm^{-1}, with a 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 degradation was investigated using thermogravimetric analysis (TGA) using TA Instruments TGA Q500. Samples of 10 mg were heated from room temperature to 800 °C with an increment of 10 °C/min. Tests were carried out in both air and nitrogen atmosphere. On the basis of TGA thermograms the temperature at 2 % mass loss ($T_{2\,\%}$) and temperature at 5 % mass loss ($T_{5\,\%}$) as well as the mass remaining after annealing at 600 °C (R_{600}) were determined. First derivative of TGA curves (DTG) were the basis to determine the temperature of the maximum degradation rate of the first stage (T_1), the temperature range in which this transformation occurs ($\Delta T_{\text{O-E1}}$), the mass loss in this step (Δm_1), and the maximum rate of mass loss at T_1 temperature (V_1). Furthermore, parameters were determined for three consecutive stages of the process of degradation, respectively, the temperatures of the maximum rate in subsequent stages of degradation (T_2, T_3, T_4), and the corresponding maximum rate of degradation (V_2, V_3, V_4) as well as the mass loss at each of the steps (Δm_2, Δm_3, Δm_4).

TGA/FT-IR combine experiments were carried out on a TGA Q500 (TA Instruments) coupled to a FT-IR instrument type Nicolet 7600 (Thermo Electrone Corporation, USA). Samples of about 15 mg were heated from room temperature to 1000 °C at a rate of 20 deg/min in air atmosphere. The IR spectra were recorded in the spectral range of 4000–400 cm^{-1} with a 4 cm^{-1} resolution and eight scans.

The limiting oxygen index (*OI*) for the samples was determined according to EN ISO 4589-3:1999 standard at room temperature using an instrument of Fire Testing Technology Ltd. (United Kingdom).

Heat release rate (*HRR*) during sample combustion as well as peak heat release rate (*PHRR*), percentage mass loss, time to ignition, and smoke coming off the sample characterizing flammability were evaluated for composite plates 100 x 100 x 10 mm in size using a cone microcalorimeter, a product of Fire Testing Technology Ltd. (United Kingdom), according to ISO 13927:2015-05 standard, by applying the heat flow of 25 kW/m^2 and the distance from ignition source 25 mm.

The flammability tests using UL-94 method were carried out in a chamber produced by Fire Testing Technology Ltd. (United Kingdom). The measurements were made according to PN-EN 60695-11-10:2014-02 standard with vertical sample beam position and methane fed burner of 25 mm height. In the test the flammability class according to the total burning time, *i.e.*, the sum of times t_1 and t_2 of burning the sample after first and second ignition, was determined, respectively. Each sample was fixed vertically *ca.* 300 mm above a cotton layer (used as a marker).

RESULTS AND DISCUSSION

The chemical constitution analysis

The FT-IR qualitative description of investigated PUUR samples is shown in the first part of the article [19]. The thermal degradation is largely dependent on the participation of the individual segments in the macromolecules, for which reason theoretical content of urethane, urea, and allophanate groups in the hard phase of the investigated elastomers was calculated.

From the FT-IR spectra values of A_{B1} and A_{B2} which are the respective areas of the bands from the vibrations bound by the hydrogen bond of the carbonyl groups of urea (B1, 1640–1680 cm^{-1}) and urethane (B2, 1705–1727 cm^{-1}) were determined. Similarly were specified A_{F1} and A_{F2}, meaning the respective surface areas of bands from vibrations unbounded with the hydrogen bond of the carbonyl groups of urea (F1, 1690–1701 cm^{-1}) and urethane (F2, 1736–1745 cm^{-1}) bonding. To compare absorbance bands in PUUR samples spectra, all the bands were calibrated with respect to the band related to vibrations of bonds in the aromatic ring (1595 cm^{-1}). Based on the results obtained in the multiple bandwidth distribution the participation of carbonyl groups was calculated, derived from urea (as the sum of A_{B1}, A_{F1}) and urethane groupings in the band (as the sum of A_{B2} and A_{F2}) and the field of bands of vibrations of carbonyl groups in the allophanate grouping (band at 1755 cm^{-1}) [23]. The results of this analysis are listed in Table 2.

T a b l e 2. The share of different groups in analyzed PUUR, calculated on the basis of substrate ratio and FT-IR spectra analysis

Sample symbol	Hard segments, wt %			Soft segments wt %	
	urethane	urea	allophanate	EBA	MK
RM1	16.3	6.8	1.4	75.5	0.0
RM2	17.7	6.5	1.1	68.0	7.6
RM3	17.5	5.9	1.2	60.3	15.1
RM4	16.8	5.8	1.3	52.8	22.6
RM5	16.5	5.7	2.5	37.6	37.6

It was found that in RM1 more urea linkages are formed than in the other polymers. The introduction of a small amount of MK bio-polyol to the formulation promotes the formation of urethane linkages in RM2. However, with the increasing amount of MK bio-polyol used in polymerization, the amount of generated bonds both urethane and urea ones is reduced. There has been a slight increase in the amount of allophanate bonds observed.

The thermal degradation analysis

The thermal stability of elastomers was analyzed by TGA. The details of the TGA data for PUUR samples under nitrogen atmosphere are presented in Fig. 1 and in Table 3.

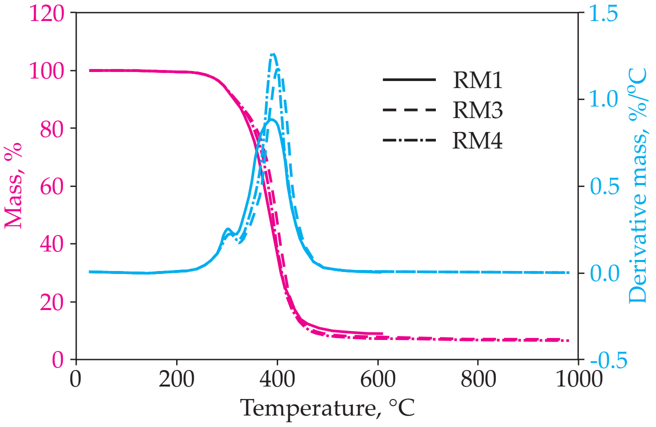

Fig. 1. Thermograms of TGA and DTG in nitrogen atmosphere

It has been established that the hard segments decompose at lower temperature than the soft segments, and furthermore urethane decomposes at lower temperature than urea hard segments [24]. It is known that the first stage of degradation is related to urethane and urea bonds decomposition [25]. In the second stage the degradation of soft segments occurs. Furthermore, in the third stage it is possible to observe another weight loss at higher temperatures associated with other segments of the remaining structure [26] or might be due to a C-C bond cleavage probably [27].

Thermal resistance of fossil-based polyol (EBA) is higher than that of rapeseed oil-based bio-polyol. However, $T_{2\,\%}$ and $T_{5\,\%}$ for samples with bio-polyol (RM2, RM3, RM4 and RM5) are higher than that of PUUR with only fossil-based polyol (RM1).

The first step of degradation process of PUUR (Fig. 1) shows a small intense peak. This peak appears at the temperature range of 283–326 °C ($T_{O\text{-}E1}$) during which there is

T a b l e 3. The results of TGA (conducted in nitrogen atmosphere) curve analysis

Sample	$T_{2\,\%}$, °C	$T_{5\,\%}$, °C	T_1, °C	$T_{O\text{-}E1}$, °C	Δm_1, %	V_1, %/°C	T_2, °C	Δm_2, %	V_2, %/°C	R_{600}, %
EBA	262	316	–	–	–	–	406	97	1.73	2.1
MK	211	255	222	156–278	6	0.08	405	91	1.50	0.8
RM1	265	291	302	283–318	11	0.25	391	76	1.21	9.1
RM2	267	294	303	285–320	11	0.22	405	77	1.16	8.8
RM3	265	292	308	287–326	11	0.22	400	77	1.19	7.8
RM4	267	294	309	283–324	11	0.23	390	78	1.27	7.5
RM5	272	298	310	288–325	10	0.21	400	80	1.30	7.4

a loss of approx. 11 % of initial mass of sample (Δm_1) in the case of all the samples (Table 3). The temperature of the maximum rate of PUUR degradation (T_1) increases in the range of 302–310 °C with increasing content of MK bio-polyol. Individual samples slightly differ in the maximum rate of material degradation in the first step (V_1), but stay within the limits of measurement error. This can be connected to the decreasing number of urea linkages occurring in these materials. In the second step connected with the degradation of soft segments it comes into the loss of approximately 76–80 % mass of the sample (Δm_2). At this stage a degradation of the soft phase and a part of the degradation of the hard phase takes place. The temperature of the maximum degradation rate in this stage varies in the range of 390–405 °C (T_2) and this value is higher for PUUR samples contained MK bio-polyol than for RM1 sample based only on petrochemical polyol. The degradation rate in this stage (V_2) is reduced for the materials slightly modified with MK bio-polyol in relation to the petroleum-derived polyol material, but its larger quantities accelerate the decomposition process (RM4 and RM5). Probably, these materials hold compounds vulnerable to faster degradation at these temperatures, that can be fatty acids. After degradation at 600 °C there remains 7.4–9.1 % mass of samples. Thermal resistance of RM1 obtained from the petrochemical polyol, is higher comparing to PUUR samples contained MK bio-polyol. In general, the elastomers modified with MK bio-polyol have thermal stability similar to materials based on petroleum-derived polyols [28–30].

The thermal stability of synthesized elastomers has also been analyzed in air atmosphere. The shapes of the weight loss curves in air are slightly different than thermograms achieved in nitrogen atmosphere, what is shown for the sample RM3 in Fig. 2.

The sample shows similar stability in both nitrogen and air atmospheres up to *ca.* 400 °C. However, different degradation steps were noticed indicating that the various degradation mechanism may occur in the range of temperatures of 400–650 °C. For RM3 sample at higher temperature in nitrogen atmosphere, the degradation process is completed at *ca.* 460 °C but in air atmosphere at 650 °C. The details of the TGA data for PUUR samples in air are presented in Table 4.

Similar to TGA analysis conducted in nitrogen the thermal resistance determined during analysis in the air of fossil-based polyol (EBA) is higher than that of rapeseed oil-based bio-polyol. The temperatures $T_{2\,\%}$ and $T_{5\,\%}$ for PUUR with fossil-based polyol (RM1) are similar to that obtained for PUUR samples modified with MK bio-polyol. The first stage of the degradation process carried out in an atmosphere of nitrogen and air is similar. The second stage of degradation occurs at 349–386 °C, *i.e.*, it occurs in lower temperature than the second step during degradation in nitrogen. Higher content of vegetable-based bio-polyol in PUUR causes the lower the temperature of degradation at this stage. In the case of RM1 made from petrochemical polyol approximately 40 % of its mass undergoes during degradation at this stage. It indicates that during this stage the process of soft phase's degradation is already starting. In the cases of PUUR samples obtained with using vegetable-based polyol, less mass of samples is degraded (roughly 12 to 20 %) at this stage. This is probably due to a higher thermal resistance of the bio-polyol.

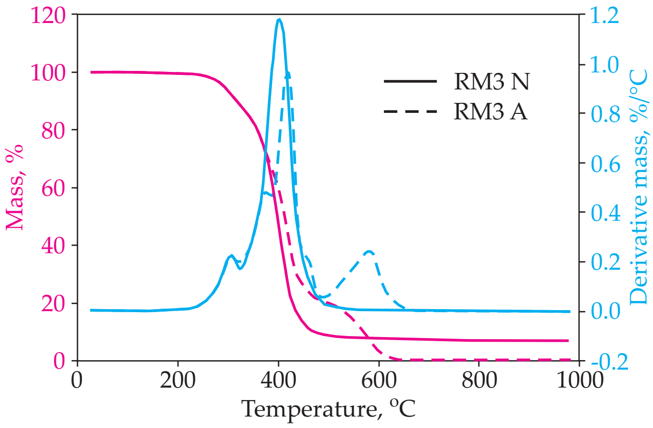

Fig. 2. Thermograms of RM3 sample in air (RM3 A) and nitrogen (RM3 N)

The total percentage mass loss at the first and second stage of degradation in PUUR samples obtained with bio-polyol is close to the content of different types of hard segments in these samples, *i.e.*, approx. 25 wt %. This indicates that during the both first stages of materials degradation these hard segments degrade mostly. During the second stage of RM1 sample degradation the mass loss is largely affected by degradation of the soft segments.

The third degradation stage for studied samples takes place at temperature range 396–414 °C. These tempera-

Table 4. The results of TGA (conducted in air atmosphere) curve analysis

Sample	$T_{2\,\%}$, °C	$T_{5\,\%}$, °C	T_1, °C	Δm_1, %	T_2, °C	Δm_2, %	T_3, °C	Δm_3, %	T_4, °C	Δm_4, %	R_{800}, %
EBA	266	300	331	16	389	77	–	–	496	7	0.1
MK	218	253	339	49	–	–	417	43	493	6	0.3
RM1	266	293	304	11	386	40	414	13	552	26	0.1
RM2	265	293	308	11	380	14	416	42	565	23	0.1
RM3	268	293	304	11	374	12	420	46	582	21	0.1
RM4	267	293	309	11	359	13	410	39	578	22	0.1
RM5	262	291	308	10	349	20	396	34	543	25	0.1

tures are lower when the vegetable-based polyol share in the blend is higher. During this third stage of degradation the mass loss observed for PUUR modified with MK bio-polyol (RM2, RM3, RM4 and RM5) was higher (34–42 %) than that for RM1 (13 %). A higher vegetable-based polyol heat resistance determines the course of the degradation process in this stage. During the third stage degradation of the PUUR sample the mass loss is largely affected by degradation of the soft segments coming from bio-polyol.

In the fourth stage of the PUUR degradation process mass loss of 21–26 % takes place. The mass loss at this stage is much larger than the one in the final stage of polyol degradation (6–7 % of weight). It can be assumed that degrading residues in this stage come mainly from the degradation of hard segments.

After degradation carried out under nitrogen atmosphere at 600 °C still a significant amount of samples' mass (7.4–9.1 %) remains. In contrast, in the degradation conducted under air atmosphere the step of degradation occurs with a maximum at 543–582 °C.

This temperature range is attributed to the decomposition of the unstable structures in the char, and the last step may result from the oxidation of the exposed matrix as well as the further oxidation of the char residue formed before [31]. This degradation can be explained also by an oxidative reaction of double bonds on the long fatty acid chains of the rapeseed oil [32].

The TGA/FT-IR technique can give direct information about the products of thermal degradation. The 3D TGA/FT-IR spectra of the gas phase formed during thermal degradation of samples RM1 and RM5 are shown in Figs. 3a and 3b, respectively. The FT-IR spectra of the pyrolysis products at the maximum decomposition rate of samples RM1 and RM5 are presented in Figs. 3c and 3d, respectively. Results for sample RM1 show four steps of thermal decomposition of the material, while thermal degradation of the sample RM5 took place in five steps. The results obtained from TGA measurement are a little different, but it should be noted that the measurements of TGA/FT-IR were made with another heating rate. In all spectra the bands at 2359 cm^{-1} and 2322 cm^{-1}, attributed to carbon dioxide, are observed [33]. In the case of RM1 spectra signals 2963 cm^{-1} and 2887 cm^{-1}, relating to C-H stretching vibrations, are confirmed, while for the material RM5 they are much more intense and shifted (2934 cm^{-1} and 2865 cm^{-1}). In the range of 4000–3500 cm^{-1} small signals were noticed, which could be related to O-H stretching vibrations from water or hydroxyl terminated compounds and N-H stretching vibrations (from urea and amine group) [33]. The 1757 cm^{-1} peak and signals in the range of 1044–1149 cm^{-1} correspond to -C-O-C- and C-O stretch vibration [33–34].

Flammability characterization

Flammability properties of obtained PUUR materials were measured using micro cone calorimeter [35]. Average flammability properties of the elastomers are summarized in Table 5.

The time to sustained ignition (t_{ig}) of samples modified with MK bio-polyol decreases by *ca.* 22 % comparing with the reference RM1 material. But the peak heat release rate (*PHRR*) of the PUUR samples unfavorably grows by 40 % for polymers containing up to 30 % of MK bio-polyol and as much as by 60 % for RM5 containing 50 % of this bio-polyol. The average *HRR* over 180 s from ignition (HRR_{180}) and total heat release (*THR*) for PUUR samples with MK bio-polyol are slightly higher than that for RM1.

The results of *HRR* measurements for obtained materials are shown in Fig. 4. These data indicate that PUUR resistance to fire decreases as the effect of higher content of the bio-polyol in elastomer.

A certain relationship between *DPS* values of PUUR samples and properties determined in a cone calorimeter for these materials have been shown in Fig. 5. The method of *DPS* calculation and results for obtained PUUR samples were presented in the first part of article [19]. It was found that the increase of *DPS* brings along a decrease in their *PHRR*, HRR_{180}, and *THR*.

The fire behavior was studied by means of oxygen index (*OI*) test. The effect of MK bio-polyol content on the flame retardant properties was studied in comparison with neat PUUR. The *OI* values of PUUR materials are shown in Table 5. The higher *OI* value represents the better flame retardancy [36]. It can be seen that the *OI* values decrease with the increase of MK bio-polyol content in PUUR sample. However, *OI* values for all investigated samples are higher than 21 %.

The analysis of relationship was conducted between t_{ig} as well as *OI* and participation of NH group in the

T a b l e 5. Summary of cone calorimetry data at irradiance of 25 kW/m² and oxygen index*)

Sample	t_{ig}, s	*PHRR*, kW/m²	HRR_{180}, kW/m²	*THR*, MJ/m²	*OI*, %	*DPS*	U_{NH-O}, %
RM1	127	141	113	40.6	23.7 ± 0.1	0.455	19.0
RM2	101	185	121	40.4	22.2 ± 0.1	0.406	12.2
RM3	99	186	126	41.4	21.8 ± 0.2	0.343	5.4
RM4	102	211	129	47.9	22.3 ± 0.1	0.327	12.5
RM5	107	267	138	51.3	22.1 ± 0.1	0.258	17.5

*) t_{ig} – time to sustained ignition, *PHHR* – peak heat release rate, HRR_{180} – average heat release rate over 180 s from ignition, *THR* – total heat release, *OI* – oxygen index, *DPS* – degree of phase separation, U_{NH-O} – share of NH group in the hard segment linked by hydrogen bonding with oxygen of the flexible segment.

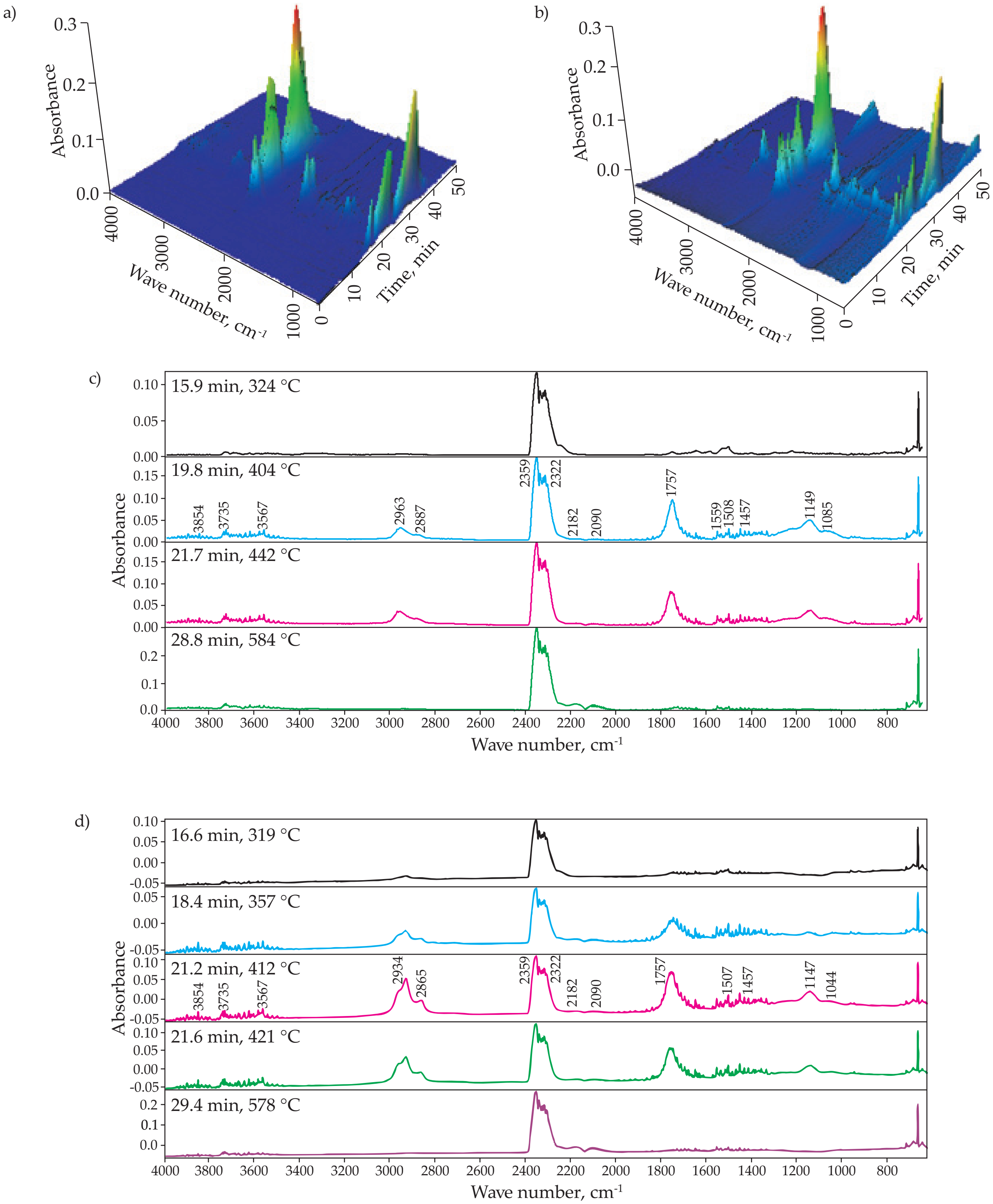

Fig. 3. The 3D TGA/FT-IR spectra of RM1 (a) and RM5 (b) together with the FT-IR spectra of volatilized pyrolysis products emitted at the maximum evolution rate from RM1 (c) and RM5 (d)

hard segments (urea and urethane) linked by hydrogen bonding with oxygen of the flexible segments (U_{NH-O}) and presented in Fig. 6. The method of U_{NH-O} calculation and results for studied PUUR samples were presented in the first part of article [19]. Along with the increasing U_{NH-O} a tendency of increasing their *OI* as well as t_{ig} for the materials was noticed.

Flammability of materials was also studied using UL 94 method and the results are listed in Table 6. All the analyzed materials belong to class V2. The samples

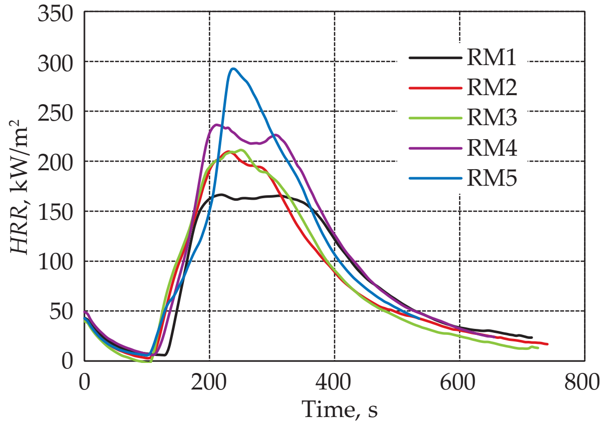

Fig. 4. Heat release rate of PUUR

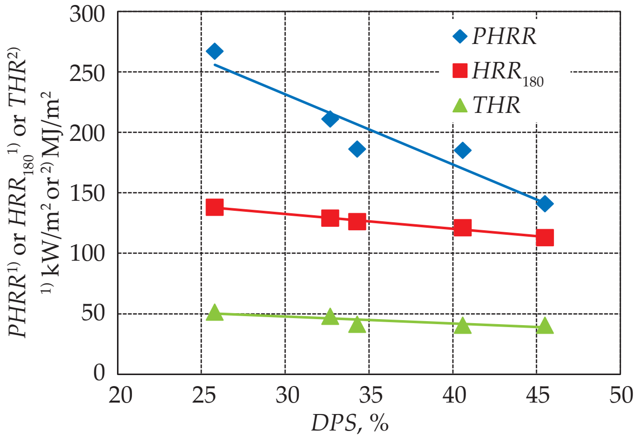

Fig. 5. Relationship between *DPS* and *PHRR*, HRR_{180}, and *THR*

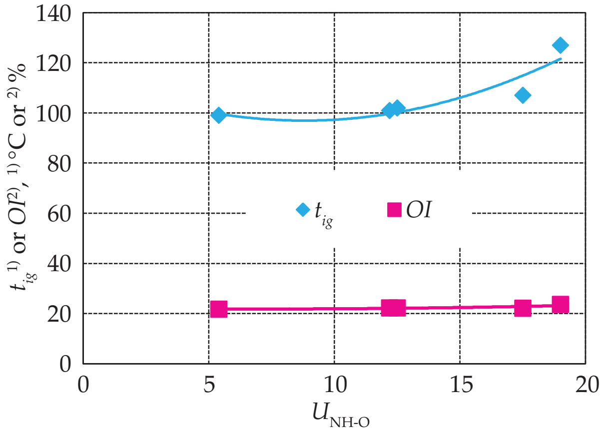

Fig. 6. Relationship between U_{NH-O} and t_{ig} and *OI*

belong to this class, when it burned for a short time and began dripping. In the case of PUUR materials obtained with MK bio-polyol we observed a lower mass loss, however, their ignition time is considerably shorter than that of fossil-based polyol material.

Table 6. Summary of the flammability results of the UL 94 test[*)]

Sample	U_{mas}, %	t_1, s	t_2, s	Class
RM1	16.7 ± 3.1	9.53 ± 0.9	0.83 ± 0.6	V2
RM2	8.8 ± 1.2	2.33 ± 0.4	3.03 ± 0.4	V2
RM3	4.7 ± 0.4	0.23 ± 0.4	1.53 ± 1.1	V2
RM4	7.5 ± 2.5	3.43 ± 1.5	4.03 ± 1.2	V2
RM5	4.3 ± 0.7	2.53 ± 2.3	1.83 ± 0.4	V2

[*)] U_{mas} – the percentage mass loss during the test UL 94, t_1 – burning time after first ignition, t_2 – burning time after second ignition.

CONCLUSIONS

The use of bio-polyol based on rapeseed oil for the preparation of poly(urea-urethane) elastomers results in a change of phase separation degree in these materials and the share of different groups as urea, urethane, and allophanate. When the higher content of vegetable oil-based polyol was applied for the synthesis of elastomers, the lower share of urethane and urea bonds but a higher one for allophanate groups was observed.

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

The use of vegetable oil-based polyol shortens t_{ig} and causes a slight decrease in *OI* and an increase in total *THR*. The materials examined fall under the V2 flammability class.

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