Polyurethane foams based entirely on recycled polyols derived from natural oils[*)]

Pavel Horák[1)], Hynek Beneš[1), **)]

DOI: dx.doi.org/10.14314/polimery.2015.579

Abstract: Flexible polyurethane (PUR) foam was chemically recycled using two types of oleochemical polyols based on rapeseed oil and waste fish oil. The functional hydroxyl groups of the oleochemical polyols reacted with the urethane and the disubstituted urea structures of flexible PUR foam at temperatures around 200 °C. The liquid recycled polyols with hydroxyl numbers *ca*. 175 mg KOH/g were obtained after 2 h of the reaction. Only the recycled polyols without additional virgin polyols were used for the preparation of low density PUR foams. PUR foams with free rise density of 30 and 50 kg/m^3 were prepared exhibiting semi-rigid character due to the presence of soft segments of fatty acid chains.

Keywords: polyurethane foam, recycled polyol, rapeseed oil, fish oil, recycling.

Pianki poliuretanowe wytworzone na bazie recyklowanych polioli pochodzących z olejów naturalnych

Streszczenie: Elastyczne pianki poliuretanowe (PUR) poddano chemicznemu recyklingowi za pomocą dwóch rodzajów oleochemicznych polioli na bazie oleju rzepakowego i odpadowego oleju rybnego. W wyniku reakcji (200 °C, 2h) hydroksylowych grup funkcyjnych oleochemicznych polioli z grupami uretanowymi i dipodstawionymi mocznikowymi, obecnymi w piankach PUR, otrzymano ciekłe recyklowane poliole o liczbie hydroksylowej 175 mg KOH/g. Półsztywne pianki poliuretanowe, o małej gęstości pozornej w zakresie 30—50 kg/m^3, wytworzone zostały jedynie z polioli recyklowanych, bez dodatku dostępnych w handlu polioli. Swoją strukturę zawdzięczają obecności miękkich segmentów łańcuchów kwasów tłuszczowych.

Słowa kluczowe: pianki poliuretanowe, recyklowane poliole, olej rzepakowy, olej rybny, recykling.

The polyurethane (PUR) industry has recently tended toward the replacement of petrochemical materials with renewable resources [1]. Natural (vegetable) triglyceride oils are a highly promising, renewable feedstock for the synthesis of oleochemical polyols with the potential to fully replace petrochemical polyols [2]. It is expected that vegetable oils will be significantly used in PUR chemistry in the future due to their hydrophobic character connected with improved moisture resistance and weatherability, as well as sufficiently good thermal and oxidative properties [3].

Various ways to transform the triglyceride oils into the oleochemical polyols are known [2, 4]. One of the simplest routes is the transesterification of oils with glycol, leading to the formation of a mixture of mono-, di- and tri-acylesters. Glycerol, as the cheap byproduct from biodiesel production, can be advantageously applied for the transesterification of oils. The resulting mixture of glycerides exhibits hydroxyl (OH) numbers typically from 150 to 350 mg KOH/g, depending on the oil/glycerol ratio used in the reaction.

Petrochemical polyols in the PUR industry can also be substituted with recycled polyols obtained from the glycolysis of PUR waste [5—7]. The current effort in the elimination of petrochemical feedstock led us to develop a new "green" recycling process of PUR waste utilizing renewable reagents for the transformation of solid PUR waste into liquid recycled polyols. Recently, it has been found [8] that oleochemical polyols based on castor or fish oil can be used as very efficient reagents for the transesterification reaction of urethane (UR) and disubstituted urea (DiUr) structures in PUR. The obtained polyols are composed uniquely of recycled and renewable components. The combination of recycled and renewable (oleochemical) polyols used in the preparation of new PUR has not frequently been mentioned in the literature. The mixture of recycled polyols from the glycolysis of PET waste and castor oil was tested for the preparation of PUR insulating coatings [9], waterborne PUR adhesives [10] and flame retardant rigid PUR foams [11]. In our last

---

[1)] Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162-06 Prague, Czech Republic.

[*)] Material presented at the conference „Polyurethanes 2015 — cooperation for innovation", September 9—11, 2015, Cracow, Poland.

[**)] Author for correspondence; e-mail: benesh@imc.cas.cz

study, recycled polyols based on castor oil and fish oil were used in the preparation of flexible cast PUR and high density rigid PUR foams, respectively [12]. However, the most desirable low density PUR foams were not successfully prepared due to cell-opening during the foaming process. Their formulation thus remains a challenging issue.

In this paper, two commercial polyols based on rapeseed oil (RP) and waste fish oil (FP) were used for the chemical recycling of a model, flexible PUR foam. The reactions of both polyols with the PUR foam were compared and discussed. The prepared recycled polyols were solely used as the polyol components in PUR formulation with the aim to prepare low density PUR foams. The influence of both polyols on the PUR preparation was compared and discussed. Both prepared recycled polyols were used for the preparation of new PUR foams and their foaming process and their properties were also evaluated.

EXPERIMENTAL PART

Materials

The model flexible PUR foam used for the chemical recycling was prepared according to our procedure described before [8]. A polyol based on rapeseed oil (NOP^{TM} 330, RP, kindly provided by SINPOL, Czech Republic) and a polyol prepared from waste fish oil (FP, kindly provided by IcePol, Iceland) were used as the decomposing reagents without further purification. Their basic properties and compositions determined in our laboratory are summarized in Table 1.

Table 1. Properties of the oleochemical polyols based on rapeseed oil (RP) and fish oil (FP)

		RP	FP
OH number, mg KOH/g		295	377
Acid number, mg KOH/g		2.4	7.3
Iodine number, mg I_2/100g		123	150
Fatty acid	Shorthand formula	Content, wt %	
Myristic acid	C14:0	0.0	7.2
Palmitoleic acid	C16:1	0.0	5.9
Palmitic acid	C16:0	1.7	9.4
Stearic acid	C18:0	0.6	0.0
Oleic acid	C18:1	97.5	11.1
Gondoic acid	C20:1	0.3	26.4
Erucic acid	C22:1	0	41.6

OH number, acid number and iodine number determined by titration methods, fatty acid composition determined by GC-MS (in the form of methylesters).

For the preparation of PUR foams based on recycled polyols, the following materials were used: 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, Germany) and dibutylbis[1-oxo(dodecyl)oxy]stannane (DBTL, Aldrich, Germany) as the catalysts, distilled water as the blowing agent, Tegostab 8870 (Evonik, Germany) as the surfactant and isocyanate, polymeric 1-isocyanato-4-[(4-isocyanatophenyl)methyl]benzene (PMDI, Suprasec^{TM} 2496 — kindly provided by Hunstman, Netherland), with NCO content of 32 %.

Chemical recycling of flexible PUR foam

Pieces of the model PUR foam were mixed with the reagent (RP or FP) and added into a triple-neck flask. The flask equipped with a reflux, a nitrogen inlet and a mechanical stirrer was placed into a pre-heated oil bath. The reaction was monitored using size exclusion chromatography (SEC). After the reaction, the mixture was cooled and filtered.

Preparation of polyurethane foams based on recycled polyols

Only the recycled polyol (based on RP or FP), without additional virgin polyol, was used for the preparation of PUR foams. The catalysts, distilled water and surfactant were put into a small plastic cup (*ca*. 150 cm^3) and fully homogenized (2 min at 2000 rpm). Then, isocyanate was quickly added and homogenized (10 s at 2000 rpm). The NCO index used in all formulations was 100. The free rise foams were prepared directly in a cup or poured into an open mold with a 10 dm^3 volume.

Methods of testing

Characterization of recycled polyols

SEC was performed using a modular GPC System equipped with a refractive index detector RIDK-102 (Laboratorní přístroje Praha, Czech Republic) and a UV-VIS photometric detector LCD 2084 (ECOM, Czech Republic) operated at λ = 254 nm, and a set of two columns 1000Å PLgel and 50Å PLgel (Polymer Laboratories, UK), 10 mm particle size, 300 × 7.5 mm. Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 1 cm^3/min.

The OH number was determined using the acetylating method according to ISO 2554:1999. The acid number was obtained according to ASTM D 4662-93. The water content was determined using Karl-Fischer titrations. The viscosity of the recycled polyols was measured at 25 °C using a rotational rheometer Bohlin Gemini HR nano (Malvern Instruments, UK) with cone-plate geometry (40 mm diameter) in the range of shear tension from 0.01 to 100 Pa.

Characterization of the foaming process

During the PUR foam preparation, the following parameters of foaming were evaluated: cream time — the time between isocyanate addition and the start of foam rise, gel time — the time between isocyanate addition and the point at which the foam had developed enough gel to withdraw a polymeric string by dipping a stick into the reaction mixture, free rise time — the time at which a freely rising foam stopped expanding, and tack-free time when the surface of the foam stopped being sticky.

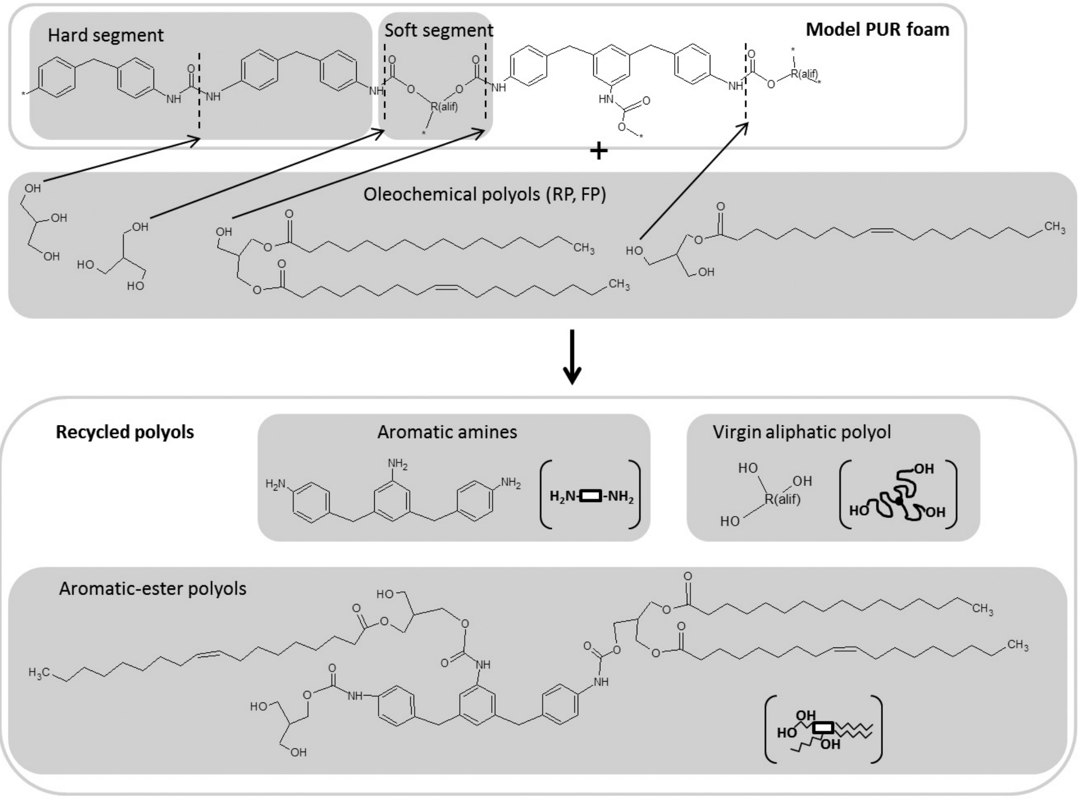
Characterization of prepared foams

Free rise density was calculated from the known weight and volume of the sample. Scanning electron microscopy *(*SEM*)* microphotographs were obtained using an electron microscope JSM 6400 (Jeol, Japan) with an acceleration voltage of 15 kV. The compression test was performed according to ISO 844. The specimens (50 mm side cubes) were cut from blocks of the foam. The tests were performed at room temperature in parallel or perpendicular to the foam rise at a speed of 5 mm/min using an Instron 6025/5800R tester (Instron, UK). The compressive stress at 10 % deformation (σ_{10}) or the compressive strength reached at lower deformations was evaluated. Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA thermogravimetric analyzer (Perkin Elmer, USA). The samples were heated at a rate of 10 deg/min from 40 °C to 800 °C under a flow of nitrogen (25 cm^3/min).

RESULTS AND DISCUSSION

Preparation of recycled polyols

In our last study, FP was deeply analyzed using MALDI-TOF MS and GC-MS [12]. The MALDI-TOF mass spectrum of RP (not shown here) contained the same structures. However, a detailed RP characterization is beyond the scope of this article. Shortly, both reagents were transesterified oils consisting of mono-, di- and triglycerides together with mono-, di- and tri- acylesters of 2-hydroxymethyl-1,3-propandiol. When RP or FP were heated with the PUR foam, the functional OH groups reacted with UR and DiUr structures of PUR and a mixture simply denoted as "recycled polyol" was formed. The obtained mixture contained (i) the original (virgin) aliphatic polyol, (ii) aromatic-ester polyols ending with acylester units bearing OH groups (called "carbamate polyols") and (iii) aromatic amines derived from the original PMDI (Scheme A).



Scheme A: Reaction scheme of the model flexible PUR foam with oleochemical polyols

The reaction between PUR foam and FP took place at 200 °C for 2 h with no added catalysts (Table 2). In order to minimize the content of unreacted FP in the produced recycled polyol (RFP), the slightly lower FP/PUR ratio of 1.15 was used in comparison with our last study [8]. After the reaction, the brown liquid, without any solid residues (polymeric or oligomeric PUR), was obtained.

Table 2. Reaction conditions for chemical recycling of model flexible PUR foam leading to preparation of recycled rapeseed oil-based polyol (RRP) and recycled fish oil-based

Conditions of reaction	Recycled polyols	
	RRP	RFP
PUR foam, g	100	100
RP, g	200	—
FP, g	—	115
Temperature, °C	210	200
PUR foam dissolution[a)], min	13	20
Reaction time, h	2	2
Solid residues after reaction, wt % [b)]	< 1	< 1

[a)] Determined visually, [b)] wt % from PUR weight.

The second reagent (RP) has not been tested for the PUR chemical recovery before. Therefore, the first preliminary experiments focused on finding suitable reaction conditions regarding the lowest consumption of RP. Similar reactivities of both reagents were evident since comparable reaction temperatures (around 200 °C) and times (2 h) were applied. The lower content of OH groups in the case of RP (compared to FP) demanded a higher reagent/PUR ratio (ideally 2/1) to reach the complete reaction (Table 2). The obtained recycled polyol (RRP) was again a brown homogeneous liquid.

Characterization of recycled polyols

The prepared recycled polyols were analysed using SEC (Fig. 1). The presence of original (virgin) polyol coming from the model flexible PUR foam was clearly seen in both recycled polyols (RRP and RFP) as a signal at 11.8 min on the RI detector. This gave evidence that the UR groups of PUR reacted with OH groups of RP and FP, respectively, according to the proposed reaction path (Scheme A). The UV SEC records of both recycled polyols were similar. The absence of UV signals at lower retention times excluded the presence of PUR oligomers in the products, which confirmed the complete PUR degradation. The triple peaks (from 11.5 min to 14.4 min) in UV SEC records (Fig. 1) were assigned to the carbamate polyols and the peak at 15.3 min corresponded to the formed aromatic amines, namely 4,4′-diaminodiphenylmethane (see Scheme A) [12].

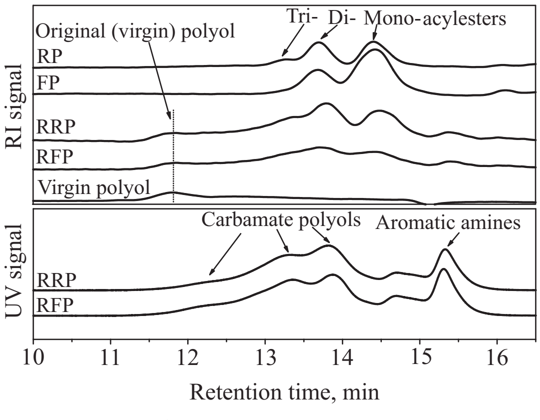


Fig. 1. SEC records of the recycled polyols (RRP and RFP), the original oleochemical polyols (RP and FP) and the aliphatic polyol used in formulation of model flexible PUR foam (virgin polyol)

The basic physicochemical properties of the prepared recycled polyols are summarized in Table 3. Both polyols had a similar content of OH groups as well as values of acid and iodine numbers. The experimentally determined OH numbers were significantly lower than the calculated (theoretical) values, which might indicate a partial dehydration of the oleochemical polyols during the reaction.

Table 3. Characteristics of the recycled polyols based on rapeseed oil (RRP) and fish oil (RFP)

	RRP	RFP
OH number, mg KOH/g	176±5[a)]/197[b)]	175±4[a)]/202[b)]
Acid number, mg KOH/g	1.6±0.1	1.6±0.2
Content of water, wt %	0.20	0.31
Viscosity at 25 °C, mPa·s	640	1480

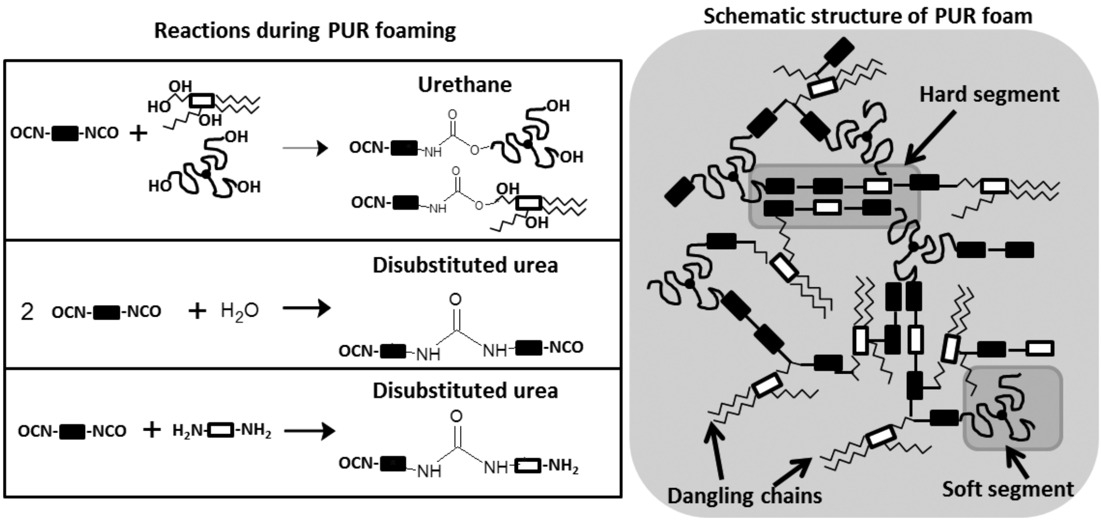
[a)] Determined, [b)] theoretical (calculated).

The two-fold increase in the viscosity of RFP might come from (i) the lower content of reagent (FP) used in the reaction with PUR foam and (ii) the presence of high molecular weight acylesters of C20:1 and C22:1 fatty acids uniquely included in the original FP (see Table 1).

A viscosity of polyol lower than 10 000 mPa·s (at 25 °C) is usually required for PUR foaming [13]. However, the recycled polyols obtained by conventional glycolyses might exhibit higher values of viscosity; *e.g.* Prociak *et al.* [13] reported that only 30 wt % of a virgin polyol can be substituted with a recycled one in order to prevent the undesirable increase in polyol viscosity. Contrary to that, in our case the both recycled polyols exhibited viscosity values low enough to be directly applied for the preparation of PUR foams without the necessity to be diluted by another polyol. To verify this, the PUR foams prepared in the following chapter were entirely based on the recycled polyols RRP and RFP (no addition of virgin polyol).

Polyurethane foams entirely based on recycled polyols

Three basic reactions leading to the creation of UR and DiUr structures were considered during PUR foaming (Scheme B). The created PUR network structure was complex, comprising (i) the hard aromatic segments bonded through DiUr units, (ii) the soft aliphatic segments from



Scheme B: Reactions involved during the formation of PUR foam and PUR foam schematic structure

the virgin polyol and the fatty acid chain connected through UR units, and (iii) the dangling fatty acid chains.

The formulation of PUR foams and their foaming characteristics are given in Table 4. Despite the similar properties of both polyols (see Table 3), RFP caused faster foaming compared to RRP. This acceleration might result from the increased amount of aromatic amines or catalytic residues originating either from the processed PUR foam or from the synthesis of FP.

Table 4. Formulations, processing parameters and properties of PUR foams based on recycled polyols derived from rapeseed oil (RRP) and fish oil (RFP)

	PUR foam ID			
	F-RRP1	F-RFP1	F-RRP2	F-RFP2
RRP, g	100	-	100	-
RFP, g	-	100	-	100
Water, g	2.8	2.8	11.3	11.2
Surfactant, g	1.0	1.0	1.0	1.0
DABCO, g	0.05	0.05	0.07	0.07
DBTL, g	0.05	0.05	0.07	0.07
PMDI, g	82.6	82.1	206.4	205.2
UR / DiUr molar ratio	2 / 1	2 / 1	0.5 / 1	0.5 / 1
Cream time, s	24	12	35	30
Gel time, s	40	25	160	90
Free rise time, s	90	50	230	160
Tack-free time, s	120	60	720	205
Free rise density, kg/m^3	50	53	30	28
σ_{10} (perpendicular to rise), kPa	52±12	57±11	23±1	32±3
σ_{10} (parallel to rise), kPa	58±8	63±6	18±4	18±1

The values of free rise density were comparable for both recycled polyols (Table 4). Contrary to our previous results [12], and despite the relatively low OH number of used polyols, the low density PUR foams with closed cells were prepared without undesirable cell-opening or collapse of cellular structure. The increasing amount of water in the formulation decreased the values of free rise density of the prepared PUR foams from 50 kg/m^3 to *ca.* 30 kg/m^3.

The size of cells and their shape varied with the type of used recycled polyol (Fig. 2). The PUR foams F-RFP1 and F-RFP2, based on RFP, exhibited fine and homogeneous cellular structures (Fig. 2b and 2d) with average cell diameters of 290±120 μm and 370±75 μm, respectively. Contrary to that, the PUR foams based on RRP comprised the higher content of larger cells created by disruption and interconnection of the cells (Fig. 2a and 2c); the average cell diameter of 500±145 μm and 540±115 μm was determined for the PUR foams F-RRP1 and F-RRP2, respectively.

The prepared PUR foams were evaluated by a compression test (Table 4). In the case of rigid PUR foams, the maximum on the stress-strain curve (compressive strength) or σ_{10}, if there is no clear maximum, are generally determined. For many rigid PUR foam applications, a compressive strength or σ_{10} value of 100 kPa is sufficient [14]. In our case, no maximum on the stress-strain curve occurred till 50 % deformation (Fig. 3). The low values of σ_{10} (Table 4), together with the more compliant stress-strain curve during the compression test, gave evidence that the prepared PUR foams might be classified as semirigid. This behavior probably resulted from the presence of flexible fatty acid chains forming long dangling chains (derived from the diacylesters) and the soft segments (derived from the monoacylesters) in the PUR network (Scheme B). Moreover, the relatively low OH number of both recycled polyol caused the formation of a less dense PUR network with semirigid behavior [15]. Generally, the mechanical properties of the cellular material mainly depend on its density [16, 17]. The values of σ_{10} of

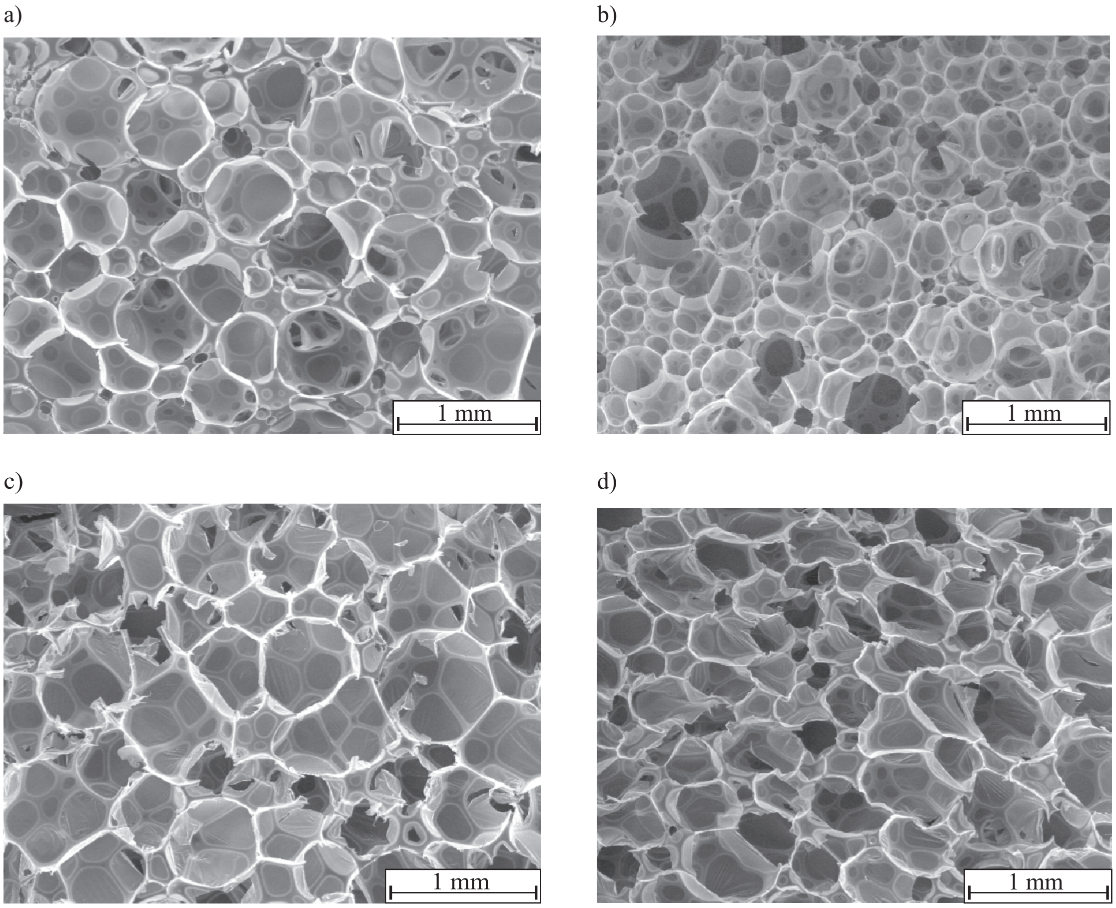


Fig. 2. SEM images of the prepared PUR foams: a) F-RRP1, b) F-RFP1, c) F-RRP2, d) F-RFP2 (scanned perpendicularly to foam rise)

all prepared PUR foams did not vary much with the nature of polyol as reflected in the density measurements. The slightly higher σ_{10} values of PUR foams derived from RFP compared to the PUR foams based on RRP might be caused by (i) the higher content of hard segments — the rigid aromatic structures from the chemical recycled model PUR foam — and (ii) the lower amount of soft segments (the fatty acid connections and the dangling chains) from FP [18].

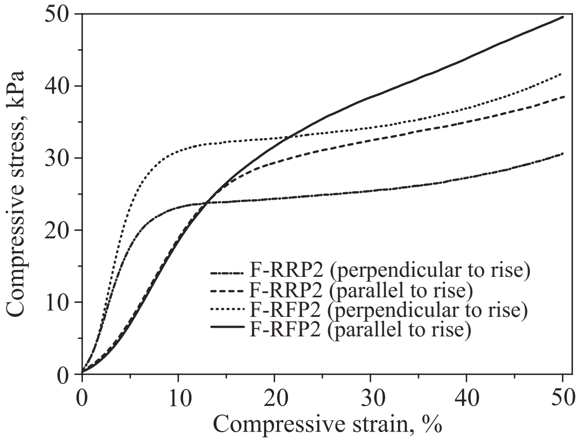


Fig. 3. Typical stress-strain curves of uniaxial compression tests of the prepared PUR foams F-RRP2 and F-RFP2

The thermal stability of prepared PUR foams was evaluated using TGA (Fig. 4). All foams were thermally stable up to *ca*. 200 °C. Above this temperature a spontaneous thermal degradation began. This behavior is typical for most rigid PUR foams [16].

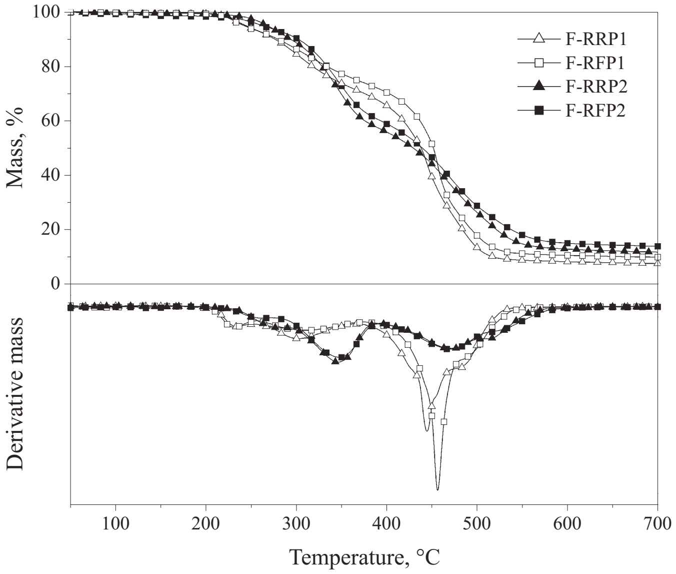


Fig. 4. TGA / DTG curves of the prepared PUR foams under nitrogen atmosphere

The denser foams (F-RRP1 and F-RFP1) started to degrade at lower temperatures compared to the less dense foams (F-RRP2 and F-RFP2) due to the presence of a higher content of free triacylesters and UR-bonded dangling chains. These structures began to degrade as first and the weight loss connected with their degradation corresponded to the first DTG peak at 233 °C — the case of F-RRP1 and F-RFP1 foams, and to the small shoulder on DTG peak (around 270 °C) with *ca*. 7 % mass loss in the case of F-RRP2 and F-RFP2 foams. The further two degradation stages were related to the breakage of UR and DiUr structures (the DTG peak at 300—350 °C) and the decomposition of ester bonds of polyol segments (the DTG peak at 440—470 °C) [12, 19]. The more dense foams (F-RFP1 and F-RRP1) exhibited a higher content of solid residues after TGA as the result of an increased content of DiUr aromatic structures. The slightly increased amounts of residues after TGA in the case of foams based on RFP were connected with the higher content of aromatic structures in RFP in comparison with RRP.

CONCLUSIONS

Two types of oleochemical polyols derived from rapeseed and fish oils were used as the renewable reagents for the chemical recycling of model flexible PUR foam. The reaction between the functional OH groups of reagents and the urethane and disubstituted urea structures of PUR foam took place at temperatures around 200 °C. After 2 h of the reaction, both reagents gave liquid products (the recycled polyols) with similar values of OH number (*ca*. 175 mg KOH/g).

Both prepared recycled polyols derived from rapeseed oil and fish oil were tested as the basic polyols for the preparation of low density PUR foams without additional virgin polyols. The recycled polyol based on fish oil was more reactive with the isocyanate resulting in faster PUR foaming. The PUR foams with free rise density of *ca*. 30 kg/m^3 were prepared from both types of recycled polyols. The prepared PUR foams exhibited the semirigid character due to the presence of soft fatty acid chains in the PUR network structure. The low values of compressive strength of the prepared PUR foams limited their potential use only to non-mechanically demanding applications, such as packaging or filling and sealing of spaces and cavities in the building industry.

ACKNOWLEDGMENT

Financial support from the Ministry of Industry and Trade of the Czech Republic (grant no. FR-TI4/133) is gratefully appreciated by the authors. The authors also gratefully thank Daniela Popelkova (Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic) for SEM images.

REFERENCES

[1] Babb D.A.: *Advances in Polymer Science* **2012**, *245*, 315. http://dx.doi.org/10.1007/12_2011_130

[2] Ionescu M: "Chemistry and technology of polyols for polyurethanes", Rapra Technology, Shropshire 2005, p. 435.

[3] Javni I., Zhang W., Petrovic Z.S.: *Journal of Polymers and the Environment* **2004**, *12*, 123. http://dx.doi.org/10.1023/B:JOOE.0000038543.77820.be

[4] Desroches M., Escouvois M., Auvergne R. *et al*.: *Polymer Reviews* **2012**, *52*, 38. http://dx.doi.org/10.1080/15583724.2011.640443

[5] Datta J., Janicka M.: *Przemysł Chemiczny* **2007**, *86*, 624.

[6] Datta J., Pniewska K.: *Polimery* **2008**, *53*, 27.

[7] Zhu P., Cao Z.B., Chen Y. *et al*.: *Environmental Technology* **2014**, *35*, 2676. http://dx.doi.org/10.1080/09593330.2014.918180

[8] Benes H., Cerna R., Durackova A., Latalova P.: *Journal of Polymers and the Environment* **2012**, *20*, 175. http://dx.doi.org/10.1007/s10924-011-0339-8

[9] Moeini H.R.: *Journal of Applied Polymer Science* **2007**, *106*, 1853. http://dx.doi.org/10.1002/app.26623

[10] Cakic S.M., Ristic I.S., Cincovic M.M. *et al*.: *Progress in Organic Coatings* **2015**, *78*, 357. http://dx.doi.org/10.1016/j.porgcoat.2014.07.012

[11] Li M.J., Luo J., Huang Y.H. *et al*.: *Journal of Applied Polymer Science* **2014**, *131*, 40857. http://dx.doi.org/10.1002/app.40857

[12] Benes H., Vlcek T., Cerna R. *et al*.: *European Journal of Lipid Science and Technology* **2012**, *114*, 71. http://dx.doi.org/10.1002/ejlt.201000123

[13] Prociak A., Pielichowski J.: *Polimery* **2005**, *50*, 682.

[14] http://www.excellence-in-insulation.eu/site/fileadmin/user_upload/PDF/Thermal_insulation_materials_made_of_rigid_polyurethane_foam.pdf (access date 06.01.2015).

[15] Firdaus F.E.: *World Academy of Science, Engineering and Technology* **2011**, *5*, 179.

[16] Backus J.K: "Handbook of Polymeric Foams and Foam Technology" (Klempner D., Frisch K.C.) Hanser, Munich, Germany 1991, p. 74.

[17] Thirumal M., Khastgir D., Singha N.K. *et al*.: *Journal of Applied Polymer Science* **2008**, *108*, 1810. http://dx.doi.org/10.1002/app.27712

[18] Narine S.S., Kong X., Bouzidi L., Sporns P.: *Journal of the American Oil Chemists' Society* **2007**, *84*, 65. http://dx.doi.org/10.1007/s11746-006-1008-2

[19] Trovati G., Sanches A.E., Neto S.C. *et al*.: *Journal of Applied Polymer Science* **2010**, *115*, 263. http://dx.doi.org/10.1002/app.31096