

# New bio-polyol based on white mustard seed oil for rigid PUR-PIR foams

Joanna Paciorek-Sadowska, Marcin Borowicz\*, Bogusław Czupryński, Ewa Tomaszewska, Joanna Liszkowska

Kazimierz Wielki University, J.K. Chodkiewicza 30, 85-064, Bydgoszcz, Poland

\*Corresponding author: e-mail: m.borowicz@ukw.edu.pl

A new bio-polyol based on white mustard oil (*Sinapis alba*) and 2,2'-mercaptodiethanol (2,2'-MDE) was obtained. The synthesis was carried out by two-step method. In the first stage, the double bond of the unsaturated fatty acid residues was oxidized, and in the second step the epoxy rings were opened with 2,2'-MDE. The properties of the obtained bio-polyol for application as raw material in polyurethane-polyisocyanurate foams (PUR-PIR) - hydroxyl number, acid number, density, viscosity, pH, water content, FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR were investigated. Based on the obtained results, foaming formulations containing 0 to 0.6 R of the new bio-polyol were prepared. Significant impact of bio-polyol on apparent density, compressive strength, brittleness, flammability, water absorption and thermal conductivity of polyurethane composites were noted. Modified foam had better functional properties than reference foam e.g. lower brittleness, better thermal insulation properties and better fire resistance.

**Keywords:** polyurethane foam, white mustard seed oil, 2,2'-mercaptodiethanol, bio-polyol.

## INTRODUCTION

Polyurethanes are the important group of thermosets because of their wide application in everyday life. The use of these materials is directly related to their properties: physical (density), mechanical (brittleness, compressive strength), thermal (thermal conductivity) and flammability. Environmental aspects (e.g. reuse of waste from this materials) and economic aspects (e.g. price of the finished product) are also significant. Often, the desire to obtain specific properties of polyurethanes is related to the incorporation into the technological formulation of additives<sup>1-4</sup>. Many chemical companies strives to receive green product solutions and keep sustainable development strategies. Raw materials of plant origin are recently more and more used for the production of polyurethane materials, e.g. bio-polyols based on vegetable oils<sup>5-7</sup>. They are usually produced by pressing oil plants. The unrefined vegetable oil obtained is additionally subjected to a filtration process to remove solid seed residues<sup>8</sup>. In recent years there has been a huge interest in these raw materials because of their green nature and an alternative to shrinking oil and gas reserves<sup>1</sup>.

A number of studies on the synthesis of bio-polyols based on oils: soybean<sup>9-11</sup>, castor<sup>12-15</sup> and rapeseed<sup>16-19</sup> can be found in the literature. Studies on the use of polyols based on soya oil for rigid foam were conducted by Tu et al.<sup>20</sup>. The obtained materials were characterized by a low coefficient of thermal conductivity. Veronese et al.<sup>21</sup> used a mixture of petrochemical polyols and soybean-based polyol to obtain the resultant transesterification of the hydroxylated oil with tri-ethanolamine to produce rigid polyurethane foams. The resulting bio-composites exhibited better mechanical properties than their equivalents obtained from conventional raw materials. Prociak et al.<sup>22-25</sup> developed composites with bio-polyol based on rapeseed oil, which was characterized by higher content of closed cells and lower thermal conductivity. Horak and Benes<sup>26</sup> have used fish oil waste to chemically recycle flexible polyurethane foams. As a result of the process, the authors obtained liquid recycled polyols that were used to obtain new semi-rigid foams. The properties of these materials were, however, worse than these of pure raw materials. Liszkowska et al.<sup>27-28</sup> with the team used

polyols based on citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) and various glycols to obtain a rigid polyurethane-polyisocyanurate foams. These composites were characterized by good thermal insulation properties, high aging resistance and low flammability.

The aim of the study was to obtain a new bio-polyol based on crude mustard oil and 2,2'-mercaptodiethanol and to investigate its physicochemical properties. The effect of this bio-polyol on the properties of rigid polyurethane-polyisocyanurate foams was also investigated.

## EXPERIMENTAL

### Material and methods

For the synthesis of a new bio-polyol, the two-stage method used unrefined white mustard seed (*Sinapis alba*) oil, as a light yellow liquid with a density of 0.880 g/cm<sup>3</sup> and a viscosity of 160 mPa · s, produced by the company jedzpij.pl (Poland). The iodine value was 0.426 mol I<sub>2</sub>/100g of oil and the unsaturated fatty acid content was 95.88 wt% of total fatty acid in the oil. The fatty acid profile of the oil used is shown in Table 1.

**Table 1.** Fatty acid profile of white mustard oil

Fatty acid	Content [%]	Number of unsaturated bonds
Palmitic acid	1.65	0
Stearic acid	1.24	0
Oleic acid	34.13	1
Linoleic acid	19.28	2
Arachidic acid	0.69	0
Eicosene acid	10.47	1
lkazadienic acid	0.4	2
Decasenoic acid	0.54	1
Erucic acid	30.88	1
Nervonic acid	0.73	0

In the first stage of the synthesis, an oxidizing system was used: 99.5% acetic acid (Chempur, Poland) and 30% solution of hydrogen peroxide (Chempur, Poland). 96% sulfuric acid (VI) (POCh, Poland). Anhydrous magnesium sulphate (VI) (Chempur, Poland) was used to dry the purified epoxidized white mustard oil.

98% of 2,2'-mercaptodiethanol in presence of the acid catalyst (as above) was used to open the oxirane rings

(Sigma-Aldrich, USA). Anhydrous calcium chloride (POCh, Poland) was used to neutralize the catalyst and remove residual water.

Polyether polyol- Rokopol RF 551 – sorbitol oxypropylene product with HN = 420 mgKOH/g (PCC Rokita, Poland), was used for the synthesis of PUR-PIR foams. Purocyn B, a technical polyisocyanate (purchased in Purinova, Poland) was used as a isocyanate raw material. Main ingredient was 4,4'-diphenylmethane diisocyanate. NCO content was 31%.

The catalyst system for the preparation of PUR-PIR rigid foams was anhydrous potassium acetate (Chempur, Gliwice) used as a 33% solution in diethylene glycol (catalyst 12) and DABCO – 1,4-diazabicyclo [2.2.2] octane (Hülls, Germany) used as a 33% solution in diethylene glycol. The foam structure stabilizer was Silicone L-6900 – poly-siloxane poly-oxy-alkylene surfactant (Witco, Sweden). The foaming agent was Solkane HFC 365/227 (Solvay, Belgium) – a mixture of 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane in a weight ratio of 87:13. The flame retardant was Antiblaze TCMP - tri[2-chloro-1-methylethyl phosphate] (Albright and Wilson, UK).

### Synthesis of new bio-polyol

500 g of crude mustard oil (MO) with an iodine value of 0.426 mol I<sub>2</sub>/100g, 128.55 g of 99.5% acetic acid (AC) and 4.35g of 96% sulfuric acid (VI) (SA) were transferred into a 1000 cm<sup>3</sup> reactor equipped with a reflux condenser, thermometer, addition funnel and mechanical stirrer. The mixture was heated to 40°C at constant stirrer speed (700 rpm) and 362.10g of 30% hydrogen peroxide (HP) was added via dropping funnel. The molar ratio of the reactants was 1:1:1.5:0.02 for MO:AC:HP:SA. After adding all hydrogen peroxide solution, the mixture was heated to 60°C. Hydrogen peroxide in the presence of acetic acid produced peracetic acid *in situ*, which oxidized the double bonds contained in the oil to the epoxy groups. The reaction was carried out for 3 hours. During synthesis, the epoxy number of the mixture was determined all the time. Then the reaction system was cooled and allowed to stand for 24 hours to separate the oil phase from the aqueous phase. The oil phase was washed with distilled water to remove residual acetic acid and catalyst, and the remaining water was removed with anhydrous magnesium sulphate (VI). The obtained intermediate (epoxidized oil) was subjected to analytical tests and was used to further synthesis.

In the next step, 500 g of epoxidized white mustard oil (EMO), 234.24 g of 98% 2,2'-mercaptodiethanol (MDE) and 1.96 g of 96% sulfuric acid (VI) were transferred into a 1000 cm<sup>3</sup> reactor. The molar ratio of the reagents was 1:1:0.01 for EMO:MDE:SA. The mixture was heated to 120°C under continuous stirring (700 rpm). The synthesis was performed for 4 hours to open all epoxy rings (EV = 0). After synthesis, the obtained polyol was neutralized and dried with solid anhydrous calcium chloride.

The properties of the new bio-polyol (PG3) based on white mustard oil were studied. The reaction product was then used for the synthesis of rigid polyurethane-polyisocyanurate foams.

### Properties of bio-polyol based on mustard oil

New bio-polyol was subjected to physicochemical, analytical and spectroscopic studies to determine its suitability for the synthesis of rigid PUR-PIR foams. The properties are determined in accordance with the standards applicable to polyol raw materials:

- Hydroxyl number (HN), was determined in accordance with the factory standard of Purinova Chemical Plant No. WT/06/07/PURINOVA.

- Acid value (AV) was determined in accordance with PN-ISO 660 standard.

- Iodine value (IV) was determined in accordance with PN-ISO 3961:2013-10 standard.

- Epoxy value (EV) was determined in accordance with PN-ISO 3001:1999 standard.

- Viscosity of bio-polyol determined by Fungilab digital rheometer at 20°C (293 K). Measurements were made using a standard DIN-87 spindle co-operating with the ULA-DIN-87 bushing. Keeping the constant temperature is ensured by a thermostat connected to the water jacket of the sleeve.

- Density was measured at 25°C (298 K) in an adiabatic pycnometer in accordance with PN-92/C-04504.

- Water content was determined by Carl-Fisher method using Titraqual branded reagent in accordance with PN-81/C-04959.

- The pH was measured by Hanna Instruments microprocessor laboratory pH-meter (ORP/ISO/°C) with RS 22 C connector.

- Elemental analysis with the Elementar Vario EL III CHNSO.

- Spectroscopic analysis of the chemical structure of crude mustard oil, epoxidized oil and bio-polyol was also performed:

- In infrared spectroscopy was performed using the Brücker Vector Spectrophotometer with the KBr technique in the range of 400 to 4000 cm<sup>-1</sup>.

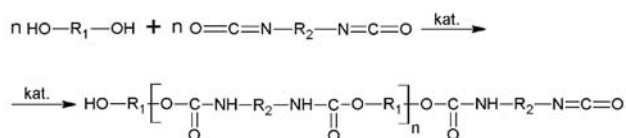
- <sup>1</sup>H NMR and <sup>13</sup>C NMR were performed using the Brücker Ascend III NMR spectrometer at 400 MHz in deuterated chloroform.

### Preparation of PUR-PIR foams

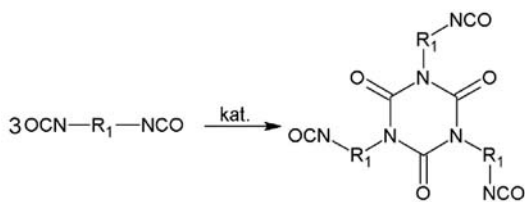
The preparation of rigid PUR-PIR foams with white mustard oil based bio-polyol required experimental studies to determine the optimal composition of additives (catalysts, surfactants, flame retardants and blowing agents). The basis for determining the amount of polyols raw materials was the hydroxyl number. Polyol formulation was developed to keep a constant isocyanate index. The addition of isocyanate was selected taking into account the equivalent (R) ratio of the NCO to OH groups in the reaction mixture, which for PUR-PIR rigid foams was set to 3:1. It is essential for the reaction of the NCO groups with OH to produce the urethane bond (Scheme 1) and the trimerization of the three NCO groups to the isocyanurate ring (Scheme 2).

The content of additives, i.e. catalyst of reaction between OH and NCO (1 wt%), catalyst of trimerization reaction (2.5 wt%), physical blowing agent (10 wt%), flame retardant (17 wt%) and surfactant (1.7 wt%).

The foams were prepared on a laboratory scale from two-component system by using one-stage method. Component A was obtained by precisely mixing the



Scheme 1. Reaction of urethane bond formation.



Scheme 2. The trimerization of isocyanate to isocyanurate ring.

appropriate amounts of polyols, catalysts, surfactant, blowing agent and flame retardant. Component B was Purocyn B. Components A and B were mixed for 10 s by using a mechanical stirrer (1800 rpm) at a suitable mass ratio. Then mixture was poured into a rectangular opened mould with an internal dimension of 25 x 25 x 30 cm, where was free rise of foam.

A series of P3 foams (P3.0-P3.6) was added with an increase in the equivalent of bio-polyol from 0 to 0.6 (0.1R increments) at the expense of the petrochemical polyol (Table 2). The synthesis of PUR-PIR foams was repeated twice. The resulting foam was cured for 4 hours at 120°C.

#### Assessing the properties of rigid PUR-PIR foams

The selected performance characteristics of the PUR-PIR foams have been determined according to the accepted standards for rigid polyurethane foam:

- Direction of the foaming process was analysed by measuring of typical foaming times: start, growth and gelation by electronic stopwatch<sup>29-30</sup>.

- Apparent density foam is marked in accordance with ISO 845-1988.

- Compressive strength was achieved on Instron's universal 5544 machine in accordance with PN 93/C-89071 (ISO 844).

- The brittleness of the obtained foams was determined in accordance with ASTM C-421-61.

- Aging tests of foam were determined after 48h thermostat at 120°C in accordance with ISO 1923:1981

(stability of linear dimensions, change of geometrical volume) and PN-ISO 4590:1994 (mass loss).

- The thermal conductivity of the foams was determined by Lasercomp FOX 200.

- Absorbability and water absorption were carried out in accordance with DIN 53433.

- Retention (Bütler's vertical test) was determined in accordance with ASTM D3014-73.

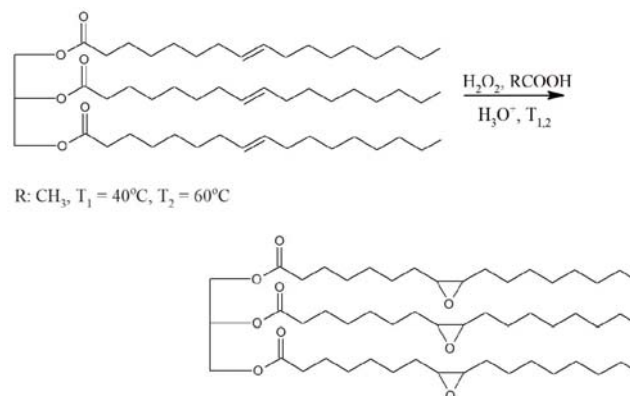
- Test of horizontal burning was determined in accordance with PN-78 C-05012.

- Oxygen index (OI) was determined by Concept Equipment apparatus in accordance with ASTM D2863-1970.

## RESULTS AND DISCUSSION

### Synthesis and characterisation of polyols

Milk-white epoxidized oil (EMO) with an iodine value of 0.039 mol I<sub>2</sub>/100g of oil and an epoxy number of 0.384 mol/100g of oil was obtained by reaction of white mustard oil (MO) with peracetic acid produced *in situ*. A simplified reaction on the example of an oleic acid triglyceride, was shown in Scheme 3.



Scheme 3. Epoxidation of unsaturated bonds in fatty acids

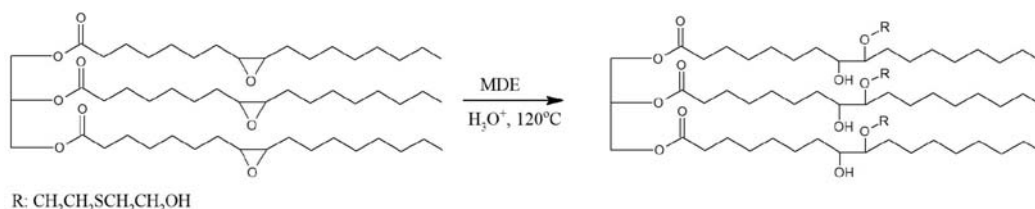
The efficiency of oxidation the double bonds was determined as the ratio of the epoxy number of EMO to the initial iodine number of MO. It was equal 89.67%<sup>31</sup>.

The epoxidized mustard oil was reacted to open the epoxy rings with the 2,2'-mercaptodiethanol according to Scheme 4.

The physicochemical properties of obtained light yellow bio-polyol (PG3) were shown in Table 3.

Table 2. Formulation of rigid PUR-PIR foams with bio-polyol

Foam symbol	Rokopol RF551 [R] [g]	PG3 [R] [g]	Silicone L6900 [g]	DABCO [g]	Catalyst 12 [g]	Antiblaze TCMP [g]	Solkane HFC365/227 [g]	Purocyn B [g]
P3.0	1.0 66.80	0.0 0.00	4.59	2.70	6.75	45.90	27.0	203.2
P3.1	0.9 60.12	0.1 7.33	4.60	2.71	6.77	46.04	27.1	203.2
P3.2	0.8 53.44	0.2 14.66	4.62	2.71	6.79	46.19	27.1	203.2
P3.3	0.7 46.76	0.3 21.99	4.63	2.72	6.81	46.34	27.2	203.2
P3.4	0.6 40.08	0.4 29.32	4.64	2.73	6.84	46.48	27.3	203.2
P3.5	0.5 33.40	0.5 37.67	4.66	2.74	6.86	46.63	27.4	203.2
P3.6	0.4 26.72	0.6 45.20	4.68	2.75	6.88	46.77	27.5	203.2



**Scheme 4.** Reaction of epoxy ring opening by 2,2'-mercapto-diethanol

The efficiency of the epoxy ring opening process was equal 100% because the epoxy value of the bio-polyol was 0 mol/100g of oil.

The results of the elemental analysis of the obtained bio-polyol (PG3) are presented in Table 4.

**Table 3.** Properties of bio-polyol based on white mustard oil

Parameter	HN [mgKOH/g]	AV [mgKOH/g]	IV [mol I <sub>2</sub> /100g]	EV [mol/100g]	$\eta^{20}$ [mPa·s]	$d^{25}$ [g/cm <sup>3</sup> ]	%H <sub>2</sub> O [%mas]	pH
PG3	371.70	4.71	0.039	0.000	10540	1.08	0.80	7.0

**Table 4.** Results of elemental analysis of oil and bio-polyol

Element	Carbon [%]	Hydrogen [%]	Oxygen [%]	Sulfur [%]
MO [%mas.]	77.48 ±0.19	16.24 ±0.15	6.28 ±0.04	0.00
PG3 [%mas.]	57.58 ±0.24	13.25 ±0.07	19.24 ±0.11	9.93 ±0.07

There was a significant increase in oxygen and sulphur content, at the expense of carbon and hydrogen. The increase in oxygen was due to the oxidation of double bonds and the opening of the rings with 2,2'-mercapto-diethanol. As a result, two -OH groups (one at the fatty acid carbon, the other at the end of the glycol chain) were obtained per a C=C bond. The increase in sulphur content is attributable to the attachment of the 2,2'-mercaptodiethanol molecule.

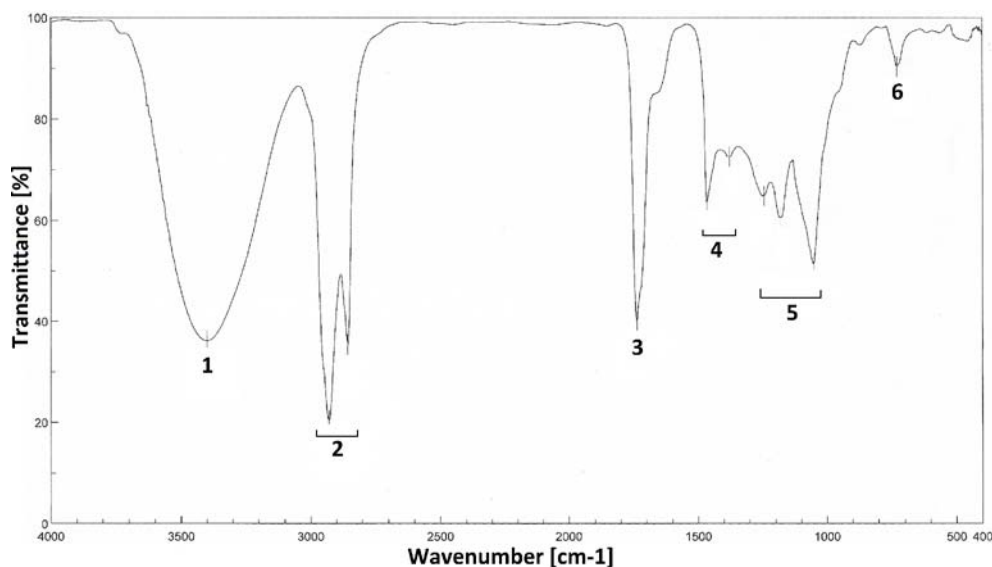
The presence of sulphur in the bio-polyol molecule also has other important implications. This element belongs to the so-called group flame retardant. This suggests that it can play a dual role in the polyurethane preparation process as a polyol component and as an internal flame retardant.

The chemical structure of synthesized bio-polyol was confirmed by spectroscopic analyses: FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. The FTIR method (Figure 1) showed the presence of band intensity at: (1) 3450 cm<sup>-1</sup> of hydroxyl

group (-OH) stretching, (2) 2950 and 2925 cm<sup>-1</sup> of C-H bond stretching in -CH<sub>2</sub>- and -CH<sub>3</sub>, (3) 1740 cm<sup>-1</sup> of carbonyl group (C=O) stretching, (4) 1465 and 1380 cm<sup>-1</sup> of C-H bond deformation in -CH<sub>2</sub>- and -CH<sub>3</sub>, (5) 1240,

1160 and 1089 cm<sup>-1</sup> of torsional vibration of the ester group and (6) 725 cm<sup>-1</sup> of oscillation of -CH<sub>2</sub>- group.

Analysis of <sup>1</sup>H NMR spectrum (Figure 2) showed characteristic chemical shift for: (1) protons of oleic groups of fatty acids -CH=CH-; (2) methane protons of glyceryl -CH<sub>2</sub>-CH-CH<sub>2</sub>-; (3) methylene protons of glyceryl -CH<sub>2</sub>-CH-CH<sub>2</sub>-; (4) protons of hydroxyl groups at the end of the chain -OH; (5) protons of α-CH<sub>2</sub> groups to the hydroxyl group -CH<sub>2</sub>-OH; (6) protons of the β-CH<sub>2</sub> group to the hydroxyl group -CH<sub>2</sub>-CH<sub>2</sub>-OH; (7) protons of α-CH<sub>2</sub> groups to the sulphide group -CH<sub>2</sub>-S-CH<sub>2</sub>-; (8) protons of the α-CH<sub>2</sub> group to the carbonyl group -CH<sub>2</sub>-CO-; (9) protons of hydroxyl groups inside the chain -OH; (10) protons of α-CH<sub>2</sub> groups with respect to olefin group -CH<sub>2</sub>-CH=CH-; (11) protons of the β-CH<sub>2</sub> group to the carbonyl group -CH<sub>2</sub>-CH<sub>2</sub>-CO-; (12) protons of CH<sub>2</sub> groups in the fatty acid chain; (13) protons of the end groups -CH<sub>3</sub>.



**Figure 1.** FTIR spectrum of bio-polyol based on mustard oil

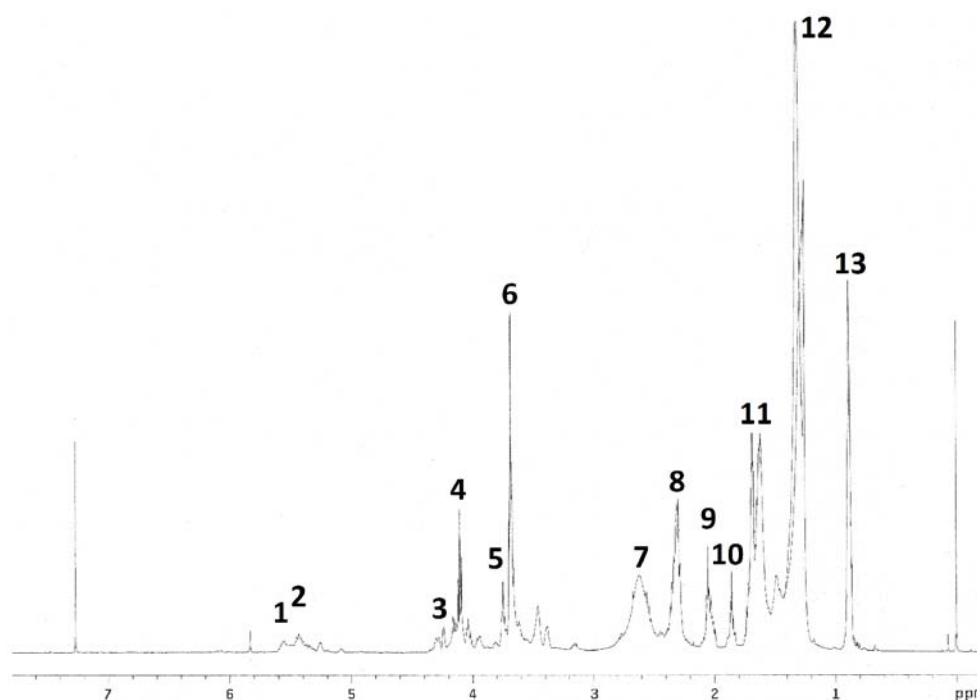


Figure 2.  $^1\text{H}$  NMR spectrum of bio-polyol based on mustard oil

Analysis of the  $^{13}\text{C}$  NMR spectrum (Figure 3) showed characteristic chemical shift for: (1) carbons of carbonyl groups  $>\text{C}=\text{O}$ ; (2) carbons of olefinic fatty acids  $-\text{CH}=\text{CH}-$ ; (3) carbons of  $\alpha\text{-CH}_2$  groups to the alkoxy group  $-\text{CH}_2\text{-O-CH}_2-$ ; (4) carbons of  $\alpha\text{-CH}$  groups linked to a hydroxyl group within the chain  $>\text{CH-OH}$ ; (5) methane carbons of glyceryl  $-\text{CH}_2\text{-CH-CH}_2-$ ; (6) methylene carbons of glyceryl  $-\text{CH}_2\text{-CH-CH}_2-$ ; (7) carbons of  $\alpha\text{-CH}_2$  groups to the hydroxyl group at the end of the chain  $-\text{CH}_2\text{-OH}$ ; (8) carbons of the  $\alpha\text{-CH}_2$  group to the sulphide group  $-\text{CH}_2\text{-S-CH}_2-$ ; (9) carbons of  $\beta\text{-CH}_2$  groups to the hydroxyl group at the end of the chain  $-\text{CH}_2\text{-CH}_2\text{-OH}$ ; (10) carbons of  $\alpha\text{-CH}_2$  groups to the carbonyl group  $-\text{CH}_2\text{-OOC-CH}_2-$ ; (11) carbons of  $\text{CH}_2$  groups in

the fatty acid chain; (12) carbons of penultimate groups  $-\text{CH}_2\text{-CH}_3$ ; (13) carbons of the terminal groups  $-\text{CH}_3$ .

FTIR spectroscopy,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR confirmed the assumed chemical structure of the synthesized bio-polyol.

#### Properties of rigid polyurethane-polyisocyanurate foams

The second part of the experiment consisted of the synthesis of polyurethane-polyisocyanurate foams using a new white mustard oil based bio-polyol (PG3) in an amount of 0 to 0.6 molar equivalents. The formulation of rigid PUR-PIR foams are shown in Table 2.

The effect of polyol on a number of properties of new polyurethane foams was investigated. Processing times,

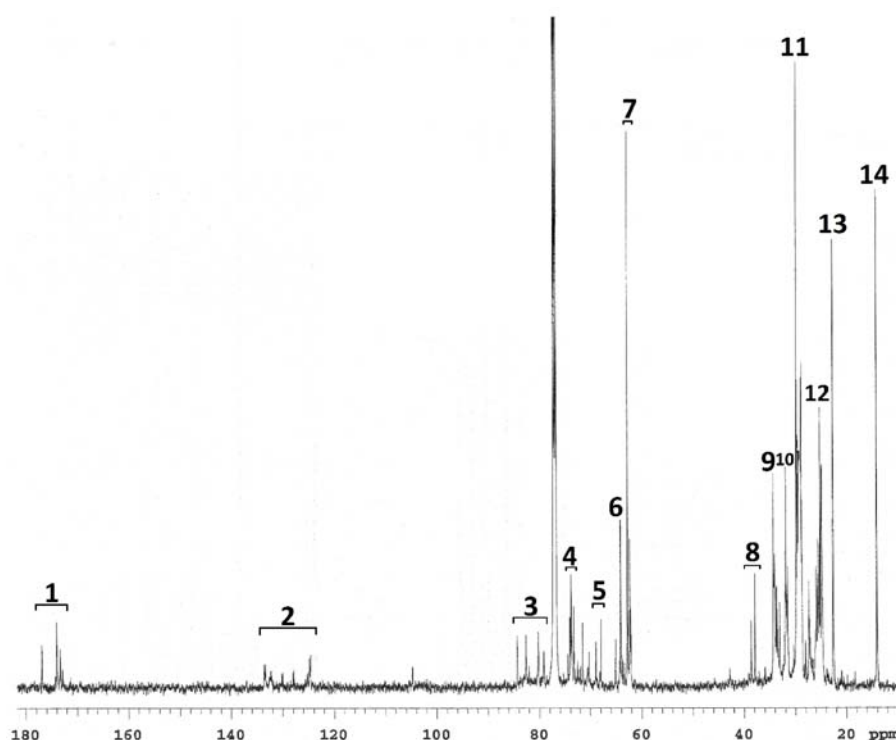


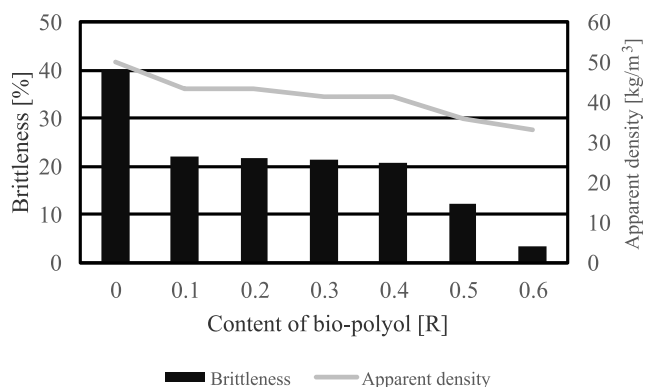
Figure 3.  $^{13}\text{C}$  NMR spectrum of bio-polyol based on mustard oil

measured during foaming, showed a tendency to elongate (Table 5). However, up to 0.4 R technology times were similar to the reference foam. With the use of more bio-polyol, a noticeable increase in start, growth and gelling time. This suggests that the new white mustard-based bio-polyols have less reactivity than petrochemical polyols. As long as its contribution to the formulation is less than 0.5 R, it does not significantly affect the reactivity of the polyol premix (component A).

**Table 5.** Processing times of PUR-PIR foams with bio-polyol

Foam symbol	Start time [s]	Growth time [s]	Gelation time [s]
P3.0	7	34	23
P3.1	8	35	23
P3.2	8	35	23
P3.3	8	35	23
P3.4	8	36	24
P3.5	10	46	29
P3.6	11	50	34

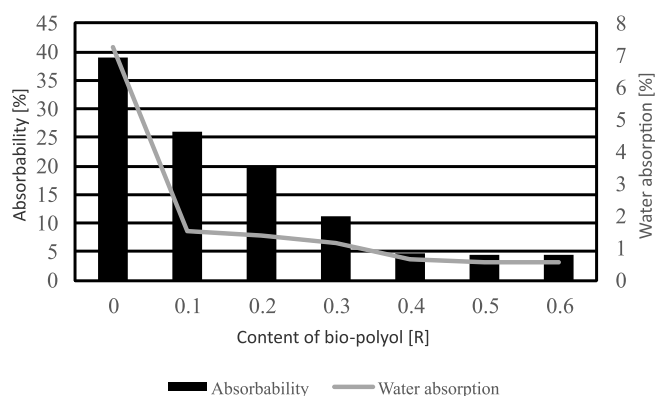
An important parameter for PUR-PIR rigid foams is the apparent density. It indirectly affects compression strength or brittleness. The increase in the share of the new polyol raw material resulted in a decrease in apparent density from 50.19 kg/m<sup>3</sup> for the reference foam to 33.07 kg/m<sup>3</sup> for the foam with 0.6 R. The incorporation to polyurethane, a component containing long linear chains results in a decrease in packing of the polymer macromolecules. It follows that fatty acid residues are flexible segments with low crosslinking. Also water content in the bio-polyol had an impact on apparent density. Free water molecule could react with NCO group and produce a chemical blowing agent – CO<sub>2</sub>. More blowing agent in the polyurethane formulation caused apparent density decrease. This phenomenon also significantly affected on the compressive strength of rigid foams. With the increase in the number of elastic segments and the apparent density decrease, this parameter decreased from 377.43 kPa (PG3.0) to 293.31 kPa (PG3.6). In spite of a marked decrease in compressive strength, the value of this parameter was at a satisfactory level. Another consequence of the decrease in degree of packing was slight decrease in stiffness. This leads to a reduction in the brittleness of the obtained PUR-PIR rigid foams. In case of application of bio-polyol based on white mustard oil, the parameter was reduced from 40.17% for P3.0 foam to 3.53% for P3.6 foam (Figure 4).



**Figure 4.** Dependence between brittleness, apparent density and bio-polyol content

Studies of accelerated aging i.e. change of linear dimensions ( $\Delta l$ ) and change of geometric volume ( $\Delta V$ ) showed that bio-polyol modified foam up to 0.4 R had the same value like a reference foam, 1.3% and 6%, respectively. The increase in bio-polyol content resulted in an increase of  $\Delta l$  to 5.6% and  $\Delta V$  to 10.8%. This was due to the migration of the blowing agent closed in the foam cells. The increased amount of long elastic segments encouraged easier escape from gas fumes such as 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane (Solkane HFC 365/227). Mass loss studies have shown that the addition of white mustard based bio-polyol was conducive to lowering this parameter from 3.09% for reference foam to 1.37% for foam with 0.6 R. This meant that the bio-polyol has a higher aging resistance than petrochemical polyol.

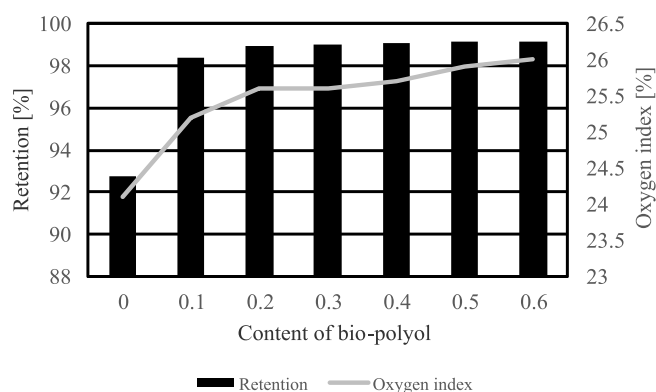
Absorbability and water absorption are important parameters in porous materials. The first one refers to the amount of water that is in the material immediately after being removed from the dipping. The second one refers to the water that has got into its interior. In both cases, a significant decrease in the value of this parameter was noted (Figure 5). In both cases absorbability and water absorption was due to the introduction of hydrophobic groups derived from vegetable oil into the polyurethane macromolecule.



**Figure 5.** Dependence between absorbability, water absorption and bio-polyol content

An important feature of porous polyurethane materials is their flammability. Rigid polyurethane-polyisocyanurate foams are characterized by lower flammability than polyurethane foams due to the presence of their isocyanurate ring. However, due to stringent fire safety requirements, they must have a flame retardant (Antiblaze TMCP in foam series P3). Flammability tests of obtained polyurethane materials (vertical test, horizontal test, oxygen index) showed that the increase of the content of bio-polyol based on white mustard oil influenced on the increase of fire resistance of these materials. The combustion residue increased from 92.77% for P3.0 to 99.15% for P3.6, the oxygen index from 24.1% to 26.0% (Figure 6) and the burning rate decreased accordingly from 0.167 mm/s to 0,033 mm/s.

Obtained results indicated that the increase in the proportion of bio-polyol based on white mustard oil had significantly influence of the retention of rigid PUR-PIR foams. The reason for this was the presence of sulphur atoms in the structure (about 10%, Table 3). This confirmed that this element is included in the group of fire



**Figure 6.** Dependence between retention, oxygen index and bio-polyol content

retardants. As a result new polyol raw material was also an internal flame retardant.

Thermal conductivity was reduced by using bio-polyol from 0.028 W/(m · K) for the reference foam to 0.024 W/(m · K) for modified foam. This meant that rigid polyurethane-polyisocyanurate foams based on white mustard oil and 2,2'-mercaptodiethanol were better insulates heat than foam containing petrochemical counterparts in the same formulation.

## CONCLUSION

New bio-polyol based on white mustard oil was synthesized in a two-step method: epoxidation of double bonds and opened it with 2,2'-mercaptodiethanol (Pat. Appl. PL422888). After testing, the obtained product showed suitability for the synthesis of rigid polyurethane-polyisocyanurate foams. It was characterized by i.e. a hydroxyl number of 371.70 mg KOH/g, an acid value of 4.71 mg KOH/g or a water content of 0.8%. The presented parameters were similar to those of commercial petrochemical polyols used in rigid foams. The bio-polyol was used as a raw material for PUR-PIR foams, in amounts of 0 to 0.6 equivalents in admixture with a polyol based on product of oxypropylation of sorbitol. Properties of the obtained materials were tested. Studies were shown that bio-polyol based foams had lower apparent density, compressive strength and brittleness. The presence of polyols containing sulphur significantly affected the flame retardancy of these materials.

The use of bio-polyol for the synthesis of PUR composites perfectly fits into the principle of sustainable development. It allows partial replacement of petrochemical polyols, and the ability to lower flammability by these compounds is an interesting issue that can lead to reduced use of expensive and toxic flame retardants.

## LITERATURE CITED

1. Prociak, A., Rokicki, G. & Ryszkowska, J. (2014). *Polyurethane materials*. Warszawa, Poland: Wydaw. Naukowe PWN. [in Polish].
2. Lubczak, J., Chmiel-Szukiewicz, E., Duliban, J., Głowacz-Czerwonka, D., Lubczak, R., Łukasiewicz, B., Zarzyka, I., Łodyga, A., Tyński, P., Kozioł, M., Majerczyk, Z. & Minda-Data, D. (2014). Polyurethane foams with 1,3,5-triazine ring of improved thermal stability. *Przem. Chem.*, 93 (10), 1690–1697. DOI: 10.12916/przemchem.2014.1690. [in Polish].

3. Król, P. (2009). Polyurethanes — A review of 60 years of their syntheses and applications. *Polimery*, 54 (7–8), 489–500. [in Polish].

4. Czupryński, B. (2004). *Issues in chemistry and technology of polyurethanes*. Bydgoszcz, Poland: Wydaw. Akad. Bydg. [in Polish].

5. Paciorek-Sadowska, J., Czupryński, B. & Liszkowska, J. (2011). Application of waste products from agricultural-food industry for production of rigid polyurethane-polyisocyanurate foams. *J. Porous Mater.*, 18, 631–638. DOI: DOI 10.1007/s10934-010-9419-8.

6. Kurańska, M., Prociak, A., Kirpluks, M. & Cabulis, U. (2013). Porous polyurethane composites based on bio-components. *J. Com. Sci. Tech.*, 75, 70–76. DOI: 10.1016/j.compscitech.2012.11.014.

7. Piszczyk, Ł., Strankowski, M., Danowska, M., Hejna, A. & Haponiuk, J. (2014). Rigid polyurethane foams from a polyglycerol-based polyol. *Eur. Polym. J.*, 57, 143–150. DOI: 10.1016/j.eurpolymj.2014.05.012.

8. Bartuzi, K. (2012). Vegetable oils, characteristics and production technology. *J. Nutri Life*, 9. Retrieved October 16, 2017 from <http://www.NutriLife.pl/index.php?art=52> [in Polish].

9. Miao, S., Sun, L., Wang, P., Liu, R., Su, Z. & Zhang, S. (2012). Soybean oil-based polyurethane networks as candidate biomaterials: Synthesis and biocompatibility. *Eur. J. Lipid Sci. Technol.*, 114, 1165–1174. DOI: 10.1002/ejlt.201200050.

10. Miao, S., Zhang, S., Su, Z. & Wang, P. (2013). Synthesis of bio-based polyurethanes from epoxidized soybean oil and isopropanolamine. *J. App. Polym. Sci.*, 10, 1929–1936. DOI: 10.1002/app.37564.

11. Garrison, T., Murawski, A. & Quirino, R.L. (2016). Bio-based polymers with potential for biodegradability. *Polymers*, 8 (7), 262. DOI: 10.3390/polym8070262.

12. Ibrahim, S., Ahmad, A. & Mohamed, N.S. (2015). Characterization of Novel Castor Oil-Based Polyurethane Polymer Electrolytes. *Polymers*, 7 (4), 747–759. DOI: 10.3390/polym7040747.

13. Abdolhossini, F. & Besharati Givi, M.K. (2016). Characterization of a Biodegradable Polyurethane Elastomer Derived from Castor Oil. *Am. J. Polym. Sci.*, 6 (1), 18–27. DOI: 10.5923/j.ajps.20160601.03.

14. Noreen, A., Zia, K.M., Zuber, M., Tabasum, S. & Zahoor, A.F. (2016). Bio-based polyurethane: An efficient and environment friendly coating systems: A review. *P. Org. Coat.*, 91, 25–32. DOI: 10.1016/j.porgcoat.2015.11.018.

15. Fu, C., Hu, X., Yang, Z., Shen, L. & Zheng, Z. (2015). Preparation and properties of waterborne bio-based polyurethane/siloxane cross-linked films by an in situ sol-gel process. *P. Org. Coat.*, 84, 18–27. DOI: 10.1016/j.porgcoat.2015.02.008.

16. Kong, X., Liu, G. & Curtis J. (2011). Characterization of canola oil based polyurethane wood adhesives. *Int. J. Adh. Adh.*, 559–564. DOI: 10.1016/j.ijadhadh.2011.05.004.

17. Prociak, A., Kurańska, M., Cabulis, U. & Kirpluks, M. (2017). Rapeseed oil as main component in synthesis of bio-polyurethane-polyisocyanurate porous materials modified with carbon fibers. *Polymer Testing*, 59, 478–486. DOI: 10.1016/j.polymeresting.2017.03.006.

18. Bueno-Ferrer, C., Hablot, E., del Carmen Garrigos, M., Bocchini, S., Averous, L. & Jimenez, A. (2012). Relationship between morphology, properties and degradation parameters of novative biobased thermoplastic polyurethanes obtained from dimer fatty acids. *Polym. Deg. Stab.*, 97, 1964–1969. DOI: 10.1016/j.polymdegradstab.2012.03.002.

19. Malewska, E., Bąk, S., Kurańska, M. & Prociak, A. (2016). The effect of various rapeseed oil-based polyols on selected properties of flexible polyurethane foams. *Polimery*, 61, 799–806. DOI: 10.14314/polimery.2016.799.

20. Tu, Y., Kiatsimkul, P., Suppes, G. & Hsieh, F. (2007). Physical properties of water-blown rigid polyurethane foams

from vegetable oil-based polyols. *J. Appl. Polym. Sci.*, 105, 453–459. DOI: 10.1002/app.26060.

21. Veronese, V.B., Menger, R.K., de C. Forte, M.M. & Petzhold, C.L. (2011). Rigid polyurethane foam based on vegetable oil. *J. Appl. Polym. Sci.*, 120, 530–537. DOI: 10.1002/app.33185.

22. Prociak, A. (2008). Heat-insulating properties of rigid polyurethane foams synthesized with use of vegetable oils – based polyols. *Polimery*, 53, 195–200. [in Polish].

23. Prociak, A. (2008). *New generation polyurethane thermal insulation materials*. Kraków, Poland: Wydaw. Politech.Krak. [in Polish]

24. Rojek, P. & Prociak, A. (2012). Effect of different rapeseed-oil-based polyols on mechanical properties of flexible polyurethane foams. *J. Appl. Polym. Sci.*, 125, 2936–2945. DOI: 10.1002/app.36500.

25. Kurańska, M. & Prociak, A. (2014). Environmentally friendly polyurethane-polyisocyanurate foams for applications in the construction industry. *Czasopismo techniczne Budownictwo*, 5-B, 149–152.

26. Horak, P. & Benes, H. (2015). Polyurethane foams based entirely on recycled polyols derived from natural oils. *Polimery*, 60 (9), 579–585. DOI: 10.14314/polimery.2015.579.

27. Liszkowska, J., Czupryński, B., Paciorek-Sadowska, J. & Michałowski, S. (2016). Thermal and flammable properties of rigid PUR-PIR foams obtained by using new compound based on 2-hydroxypropane-1,2,3-tricarboxylic acid. *J. Cell. Plast.*, 52 (3), 321–341. DOI: 10.1177/0021955X15570983.

28. Liszkowska, J., Czupryński, B. & Paciorek-Sadowska, J. (2016). Thermal properties of polyurethane-polyisocyanurate (PUR-PIR) foams modified with tris (5-hydroxypentyl) citrate. *J. Adv. Chem. Eng.*, 6, 2. DOI: 10.4172/2090-4568.1000148.

29. Paciorek-Sadowska, J., Borowicz, M., Czupryński, B. & Liszkowska, J. (2017). Composites of rigid polyurethane-polyisocyanurate foams with oak bark. *Polimery*, 62 (9), 666–672. DOI: 10.14314/polimery.2017.666. [in Polish].

30. Paciorek-Sadowska, J., Borowicz, M., Czupryński, B., Liszkowska, J. & Tomaszewska, E. (2018). Application of halloysite as filler in the production of rigid PUR-PIR foams. *Polimery*, 63 (3), 185–190. DOI: 14314/polimery.2018.3.3. [in Polish].

31. Smagowicz, A. (2011). *Obtaining of epoxidized rapeseed oil*. Published doctoral dissertation, Zachodniopomorski Uniwersytet Technologiczny, Szczecin, Poland. [in Polish].