

MARIA KURAŃSKA, ALEKSANDER PROCIAK\*

## ENVIRONMENTALLY FRIENDLY POLYURETHANE- -POLYISOCYANURATE FOAMS FOR APPLICATIONS IN THE CONSTRUCTION INDUSTRY

### PRZYJAZNE ŚRODOWISKU SZTYWNE PIANKI POLIURETANOWO-POLIIZOCYJANUROWE DO ZASTOSOWAŃ W BUDOWNICTWIE

#### Abstract

In this paper, the influence of raw materials from renewable sources in the form of rapeseed oil-based polyols on thermal conductivity and the cell structure of rigid polyurethane-polyisocyanurate foams was presented. Bio-polyols were prepared by the following methods: transesterification, transamidization and two-steps method of epoxidation and oxirane rings opening.

*Keywords: polyurethane-polyisocyanurate rigid foams, rapeseed oil-based polyols, thermal conductivity*

#### Streszczenie

W artykule przedstawiono wpływ surowców ze źródeł odnawialnych w postaci polioli z oleju rzepakowego na współczynnik przewodzenia ciepła oraz strukturę komórkową sztywnych pianek poliuretanowo-poliizocyanurowych. Poliiole z oleju rzepakowego były otrzymywane następującymi metodami: transestryfikacja, transamidyacja oraz dwuetapowa metoda epoksydacji i otwarcia pierścieni oksiranowych.

*Słowa kluczowe: sztywne pianki poliuretanowo-poliizocyanurowe, poliiole z oleju rzepakowego, współczynnik przewodzenia ciepła*

\* Ph.D. Eng. Maria Kurańska, D.Sc. Ph.D. Eng. Aleksander Prociak, prof. CUT, Department of Chemistry and Technology of Polymers, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

## 1. Introduction

Rigid polyurethane (PUR) and polyurethane-polyisocyanurate (PUR-PIR) foams have excellent properties such as low thermal conductivity, low apparent density, good mechanical resistance and low permeability. Such foams play an important role in buildings as insulating materials and in other industrial uses such as transportation, refrigeration, packaging, and automotive industry. The rigid PUR foams have the lowest thermal conductivity among heat-insulating materials which are commercially available.

Currently in the industry, there is an increasing interest in modern technologies, which are based on renewable raw materials. The introduction of vegetable oil-based polyols components to PUR-PIR systems meets all the requirements of sustainable development [1]. Natural oil-based polyols made from vegetable oils such as soybean, castor, palm and rapeseed oil are under intensive development and available on the small scale [2, 3].

In literature, different methods of the synthesizing polyols from natural oils such as hydroformylation, ozonolysis, transesterification, amidization [4] and epoxidation and opening oxirane ring are described. In this work, the three latter methods were used to prepare rapeseed oil-based polyols, which were next applied in the synthesis of PUR and PUR-PIR foams.

## 2. Experimental part

The rigid PUR and PUR-PIR foams were obtained by mixing two components (*A* and *B*). The reference chemical compositions of component *A* (REF) consisted of a petrochemical polyol, catalyst, water (as a chemical blowing agent) and surfactant. The mixture was stirred for 7 s. The isocyanate indexes were 110 and 250. This formulation was modified by replacing the petrochemical polyol with a rapeseed oil-based polyol in the amount of 70 wt. %. Three different rapeseed oil-based polyols were prepared using the following methods: epoxidation with opening oxirane rings ( $P_{\text{epox}}$ ), transesterification with triethanolamine ( $P_{\text{tr-est}}$ ) and transamidization with diethanolamine ( $P_{\text{tr-am}}$ ). The most important properties of obtained bio-polyols (hydroxyl number and water content) are shown in Table 1.

Table 1

**The characteristic of polyols used in the synthesis of foams**

	Petrochemical	$P_{\text{epox}}$	$P_{\text{tr-est}}$	$P_{\text{tr-am}}$
Hydroxyl number [mg KOH/g]	490.0	259.0	365.1	395.4
Water content [wt. %]	0.10	0.49	0.05	0.13

The foams were conditioned at 22°C and 50% relative humidity for 24 hours, before being cut to analyze their cellular structures and thermal conductivity. The initial (after 24 hours) thermal conductivity –  $\lambda$  values (mW/m·K) were measured using Laser Comp Heat Flow Instrument Fox 200. The measurements were also carried out after 7 days. The average temperature of measurements was 10°C (temperature of cold plate 0°C and warm plate 20°C).

The morphology of cells was analyzed using a scanning electron microscope (HITACHI S-4700). The samples were sputter coated with graphite before testing to avoid charging.

### 3. Results and discussion

The modifying reference formulation (based only on petrochemical polyols) with rapeseed oil polyol slightly increases the thermal conductivity of foams  $FP_{\text{epox}}$  and  $FP_{\text{tr-est}}$  (Fig. 1). Much higher deterioration of thermal conductivity was observed in the case of foam  $FP_{\text{tr-am}}$ . This is due to overly high reactivity of the polyol  $P_{\text{tr-am}}$  with the participation of diethanolamine, which causes processing problems and the considerable increase of apparent density of final foams.

More beneficial heat insulating properties of reference foam are an effect of more regular cellular structure of this material in comparison to the foams modified with bio-polyols (Fig. 2).

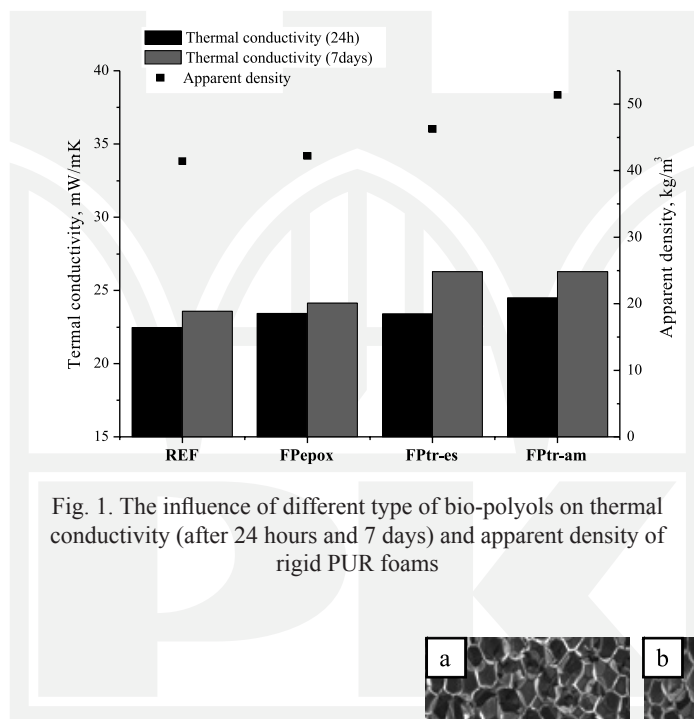


Fig. 1. The influence of different type of bio-polyols on thermal conductivity (after 24 hours and 7 days) and apparent density of rigid PUR foams

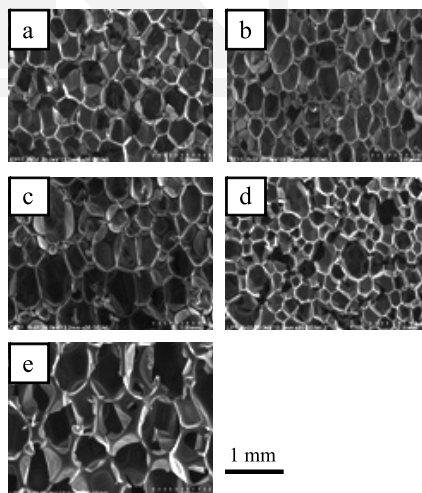


Fig. 2. SEM images of PUR foams (a –  $FP_{\text{epox}}$ , b –  $FP_{\text{tr-est}}$ , c –  $FP_{\text{tr-am}}$ , and d – REF); e – PUR-PIR foam. Magnification x35 in case of all images

The impact of the cellular structure on the thermal conductivity of foams was confirmed in the case of PUR-PIR foam. The cells of this material are considerably much larger compared with REF foam and affect the high value of thermal conductivity ca. 24.5 mW/m·K.

The results of thermal conductivity measured after 7 days showed that the smallest changes occur in the case of  $FP_{\text{epox}}$  foams, which is very important taking into account the long-term application of such materials.

#### 4. Conclusions

The investigations have shown that rapeseed oil-based polyol as, the renewable raw material, can be used in obtaining of rigid polyurethane foams of low density. Two types of oil-based polyols synthesized by epoxidation with opening oxirane rings ( $P_{\text{epox}}$ ), transesterification with triethanolamine ( $P_{\text{tr-est}}$ ) make production of good quality PUR foams possible. The replacement of petrochemical polyol with the amount of 70 wt. % of rapeseed oil derivatives allows to obtain PUR foams with comparable thermal conductivity after 7 days, as in the case of reference foam.

*The research leading to these results has received funding from the ERA-Net MATERA project BBPM "Bio-Based Polyurethane Materials".*

#### References

- [1] Kurańska M., Prociak A., Kirpluks M., Cabulis U., *Porous polyurethane composites based on bio-components*, Composites Science and Technology, 75, 2013, 70-76.
- [2] Zhao Y., Yan N., Feng M., *Polyurethane foams derived from Liquefied mountain pine beetle-infested barks*, Journal of Applied Polymer Science, 123, 2012, 2849-2858.
- [3] Pawlik H., Prociak A., Pielichowski J., *Synteza polioli z oleju palmowego przeznaczonych do otrzymywania elastycznych pianek poliuretanowych*, Czasopismo Techniczne, 1-Ch/2009, 111-117.
- [4] Stirna U, Fridrihsone A, Lazdina B, Misane M, Vilsone D., *Biobased polyurethanes from rapeseed oil polyols – structure, mechanical and thermal properties*, J Polym Environ, 21, 2013, 952-962.