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FLAX FIBERS AS NATURAL FILLER FOR RIGID POLYURETHANE-POLYISOCYANURATE FOAMS BASED ON BIO-POLYOL FROM RAPESEED OIL

WŁÓKNA LNIANE JAKO NATURALNY NAPEŁNIACZ DO SZTYWNYCH PIANEK POLIURETANOWO-POLIIZOCYJANUROWYCH Z UDZIAŁEM BIO-POLIOLU Z OLEJU RZEPAKOWEGO

A b s t r a c t

The influence of flax fibers on the physical and mechanical properties and the flammability of rigid polyurethane-polyisocyanurate foams obtained from rapeseed oil-based polyol was analyzed. The rigid polyurethane-polyisocyanurate foams with apparent density of 40−48 kg/m^3 were prepared. It has been found that the introduction of flax fiber has a beneficial effect on selected properties of obtained foams.

Keywords: polyurethane- polyisocyanurate rigid foams, rapeseed oil-based polyols, thermal conductivity, mechanical properties, flammability, thermal stability, cellular structure

S t r e s z c z e n i e

Analizowano wpływ włókien lnianych na właściwości fizykomechaniczne oraz palność sztywnych pianek poliuretanowo-poliizocyjanurowych otrzymanych z udziałem bio-poliolu z oleju rzepakowego. Otrzymano porowate materiały poliuretanowo-poliizocyjanurowe o gęstościach pozornych w zakresie 40−48 kg/m^3. Stwierdzono, że wprowadzenie włókien lnianych wpływa korzystnie na wybrane właściwości otrzymanych pianek.

Słowa kluczowe: sztywne pianki poliuretanowo-poliizocyjanurowe, poliole z oleju rzepakowego, współczynnik przewodzenia ciepła, właściwości mechaniczne, palność, stabilność termiczna, struktura komórkowa

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1. Introduction

Nowadays, polyurethanes (PURs) are everywhere in everyday life, in such applications as car seats, insulation materials, packaging, foot wear, construction, furniture and so on [1]. PUR can be used mainly as foams, surface coatings, elastomers, adhesives, artificial and synthetic leathers and fibers. Polyurethane foams can be divided into three major classes: rigid, semi-rigid and flexible [2].

Rigid PUR foams are useful as insulating materials due to their low coefficient of thermal conductivity, and good physical-mechanical properties [3]. Traditional rigid PUR foams are synthesized by the reaction of polyols and diisocyanates. Both components are derived mainly from petroleum resources which are diminishing rapidly. The current research has been focused on developing polyols synthesis from renewable raw materials [4, 5]. Several methods and their modifications have been reported for converting natural oils (e.g. soybean, rapeseed, palm) into polyols [613]. Other natural renewable products, such as natural fibers, are also used in the modification of rigid PUR foams [14–16]. In previous work, Prociak et al. analyzed the influence of rapeseed oil-based polyol and flax fibers on properties of rigid PUR foams. They have found the possibility to increase the amount of biodegradable raw materials in the formulation of rigid PUR foams without deteriorating their physical-mechanical properties [17]. Yuan et al. modified PUR foams with wood flours to improve their properties and to reduce the cost of foams production. The introduction of wood flour improved the compressive property of PUR foams, whereas its tensile and flexural properties were reduced. The thermal stability of the PUR foams was improved with the addition of wood flour [18].

Another important concern is thermal stability of PUR foams. An improvement of foams, thermal stability can be achieved through introduction, into the PUR matrix, of isocyanurate rings, which are more stable from thermodynamic point of view than urethane bonds [19].

This paper describes the influence of the flax fiber on the properties of rigid PUR-PIR foams based on bio-polyols obtained from rapeseed oil.

2. Experimental part

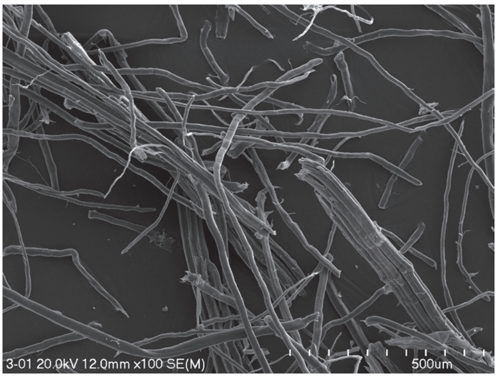

Fig. 1. SEM microphotograph of flax fibers

The polyurethane-polyisocyanurate (PUR-PIR) foams were obtained by mixing two components (A and B). The chemical compositions of component A consisted of a bio-polyol, petrochemical polyol (Lupranol 3422), catalysts (Polycat 5 and potassium acetate 30%), surfactant (L-6915) and chemical blowing agent (water). This formulation was modified with flax fibers (3 and 6 wt.%). Natural fibers, before adding to the polyol premix, were fractionated, and then dried to constant weight. The maximum length of flax fibers was 0.5 mm. The amount of introduced fibers was limited due to the increasing of component A viscosity. The SEM microphotography of flax fibers was shown in Fig. 1.

In prepared foams 70 wt.% of petrochemical polyol was replaced by rapeseed oil-based polyol (RP). A two-step process was used for the preparation of RP. In the first step, unsaturated fatty acids in triglycerides reacted with acetate peroxyacid to form epoxidized oil. Through the epoxidation, the double bonds of the triglycerides were transformed into oxirane rings. In the second step, the epoxidized oil was converted into a polyol using diethylene glycol (DEG). RP has been prepared in the Department of Chemistry and Technology of Polymers. The isocyanate indices were 150 and 250. The rigid PUR-PIR foams were marked with respect to isocyanate index and content of flax fibres (e.g. RP150/F3, RP250/F3). The foams were obtained using the one-shot and free rise method. Foams were prepared in two different moulds that allowed free rise of reaction mixture in vertical and horizontal directions respectively.

The foams were conditioned at 22°C and in 50% relative humidity for 24 hours, before being cut for analysis. 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. The apparent density of PUR-PIR foams was determined according to ISO 845. Thermal conductivity factors – λ values (mW/m·K) were estimated using Laser Comp Heat Flow Instrument Fox 200. The average temperature of measurements was 10°C (the temperature of cold plate was 0°C and of warm plate 20°C). Closed cells content (%) was determined according to ISO 4590. Compressive strength was measured according to ISO 826 and compressive force was applied at the speed of 2 mm/s. Compressive strength has been investigated in two directions: parallel (z) and perpendicular (x) to the direction of the foam rise. Thermal stability was studied by means of thermogravimetric analysis under nitrogen flow and the heating rate of 10°C/min from room temperature to 1000°C. During this test, the following parameters were determined: thermal degradation onset temperature (T_{onset}), the temperature at which thermal degradation reached 25 and 50% by weight of the sample ($T_{25\%}$, $T_{50\%}$). The behavior of rigid PUR-PIR foams under heat flux of 35 kW/m^2 during 300 s was tested using FTT Dual Cone Calorimeter (Fire Testing Technology Ltd., UK). Tests were done according to ISO 5660-1 standard. During the experiments, the time required to initiate the reaction of combustion and such parameters as average heat rate release (HRR), total heat release (THR), and total smoke released (TSR) were measured. The oxygen index (LOI) was determined according to ISO 4589-2.

3. Results and discussion

The basic physical-mechanical properties of PUR-PIR foams are shown in Table 1. The largest change in the apparent density of the foams was observed in the case of foam with isocyanate index of 250 and flax fibers in the amount of 6 wt.%. Changing the foams apparent density may be associated with high viscosity of the polyol premix.

The introduction of flax fiber into PUR-PIR matrix had beneficial effect on the mechanical properties of foams with isocyanate index of 250. Such effect can be associated with the size of foam cells. Rigid PUR-PIR foams obtained with isocyanate index of 250 were characterized by bigger cells in comparison to cells of foams with isocyanate index of 150 (Fig. 2).

Table 1

Physical-mechanical properties of rigid PUR-PIR foams prepared in vertical mould

Symbol	Apparent density, [kg/m^3]	Compressive strength [MPa]		Young' modulus [MPa]	
		z	*x*	*z*	*x*
RP150	43.9	0.32	0.23	5.89	3.94
RP150/F3	42.0	0.26	0.19	5.49	3.89
RP150/F6	39.5	0.21	0.14	4.69	3.24
RP250	43.5	0.26	0.24	6.02	4.36
RP250/F3	43.2	0.28	0.24	6.65	4.79
RP250/F6	48.2	0.30	0.25	6.05	5.00

z, *x* – parallel and perpendicular respectively to foam rise direction.

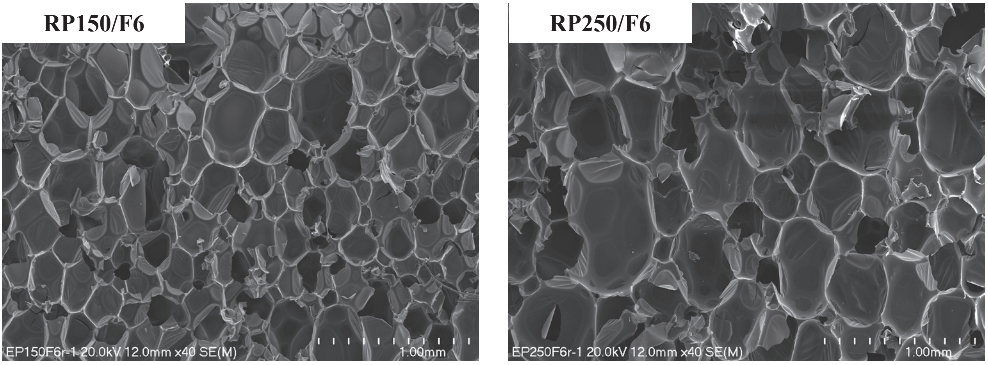

Fig. 2. SEM microphotographs of selected PUR-PIR foams

Larger cell size allows for the incorporation of filler in the cell wall, while in the case of smaller cells, the filler can break down the foam cells (Fig. 3).

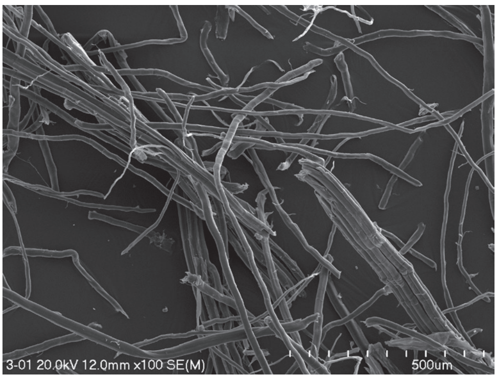

Fig. 3. SEM microphotographs of foams modified with flax fiber

Materials obtained in horizontal mould had higher apparent density than foams shown in Table 2.

Table 2

Selected properties of rigid PUR-PIR foams obtained in horizontal mould

Symbol	Apparent density [kg/m^3]	Content of closed cells [%]	Coefficient of thermal conductivity [mW/m·K]
RP150	49.6	96.5	22.72
RP150/F3	49.0	97.3	23.66
RP150/F6	54.0	94.9	24.00
RP250	48.7	91.9	23.19
RP250/F3	54.3	93.8	23.80
RP250/F6	67.5	94.8	25.12

It is caused by the fact that the apparent density of the materials obtained in the horizontal mould was determined with the so-called "peel" where the concentration of the material occurs. All of the foams are characterized by high content of closed cells, which is very important in the case of heat insulating materials. The incorporation of flax fibers to PUR-PIR matrix caused a slight increase of the thermal conductivity coefficient, what is an effect of foams apparent density increase.

Rigid foams are used in the construction industry. Therefore, it is important to analyze the influence of filler on the flammability of obtained materials (Table 3).

Table 3

Influence of flax fibres on flammability of rigid PUR-PIR foams

	Time to ignition [s]	Total heat release [MJ/m^2]	Heat release rate peak [kW/m^2]	Total smoke release [m^2/m^2]	Oxygen index [%]
RP150	2	15.68	206.5	654.1	22.4
RP150/F3	4	14.75	211.6	705.2	22.0
RP150/F6	3	15.08	215.3	689.7	21.8
RP250	3	16.90	138.3	545.6	23.5
RP250/F3	6	16.34	135.0	433.4	23.2
RP250/F6	4	18.66	152.7	613.0	23.0

In the case of the cone calorimetry test method, there was no significant correlation depending on amount of the flax fiber in PUR-PIR matrix. The oxygen index slightly decreased with an increasing amount of flax fibers.

It is important that the flax fiber has not significantly increased the flammability of obtained materials, as it was also confirmed by the rate of heat release during combustion of the sample (Fig. 4).

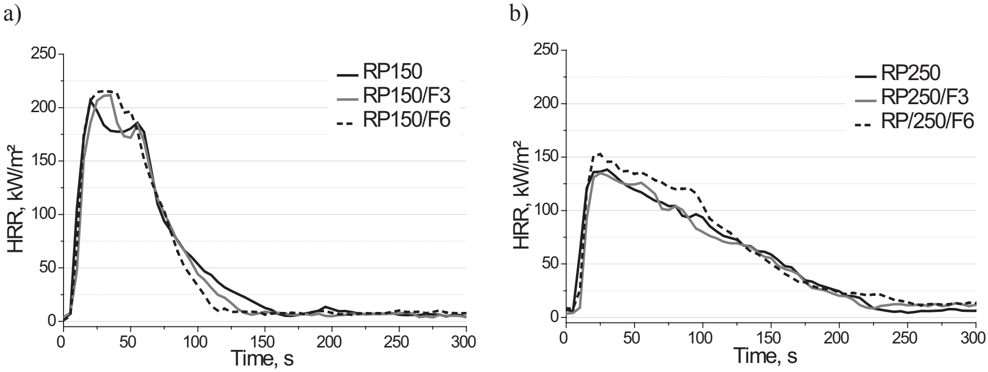

Fig. 4. Influence of flax fibers on heat rate release of rigid PUR-PIR foams with isocyanate index 150 (a) and 250 (b)

The introduction of fiber does not significantly affect the course of thermal degradation, which can be seen on the thermograms (Fig. 5).

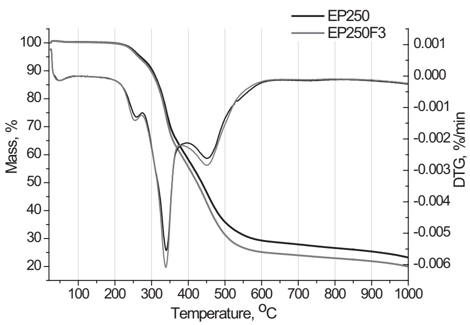

Fig. 5. Thermograms TG and DTG rigid PUR-PIR foams modified and unmodified with flax fibers with isocyanate index 250

Determined from the thermograms, the temperature at which 5 and 25% weight loss occur leads to the conclusion that flax fibers increase thermal stability of the foams (Table 4).

The mechanism of thermal degradation of PURs is a very complex process. The isocyanurate linkage has higher thermal stability than that of the urethane linkage (urethane dissociates at approx. 200°C as opposed to 350°C for polyisocyanurates). Polymers based on isocyanate provide thermal stability in the following order: isocyanurate (350°C) > urea (250°C) > urethane (200°C) > biuret (135–140°C) > allophanate (106°C) [20, 21].

Table 4

Thermal properties of selected samples

Symbol	T_{onset}	$T_{25\%}$ [°C]	$T_{50\%}$ [°C]	Residue [%]
RP250	232	232	341	23.2
RP250/F3	230	337	423	20.0

4. Conclusions

The study has shown that polyol from rapeseed oil and flax fibers are raw materials, which can be successfully used in the synthesis of rigid polyurethane-polyisocyanurate foams. The replacement of petrochemical polyol with the amount of 70 wt.% of rapeseed oil-based polyols and the addition of flax fibers to foams with isocyanate index of 250 allows to increase the compressive strength. The addition of flax fibers slightly increases thermal conductivity, which is the effect of apparent density increase. On the other side the addition of flax fibers improves thermal stability of rigid polyurethane-polyisocyanurate foams.

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