Water-blown polyurethane-polyisocyanurate foams based on bio-polyols with wood fibers

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Abstract: In this paper rigid polyurethane-polyisocyanurate (PUR-PIR) foam and wood fiber composites were synthesized using two types of bio-polyols. The PUR-PIR systems were modified with 3 and 6 wt % of wood fibers. The influence of the content of wood fibers on the cellular structure was examined with scanning electron microscopy (SEM). Thermal and mechanical properties of the composites were characterized with thermogravimetric analysis, thermal conductivity, compressive strength, and Young modulus measurements. The influence of wood fibers on flammability of PUR-PIR foams was analyzed by oxygen index and cone calorimeter tests. For the most of foams, introduction of wood fibers did not affect the change in compressive strength. Introduction of wood fibers increased the temperature at which thermal degradation began, as well as the temperature at which occurs 5, 25 and 50 % weight loss. The studies have shown that the oxygen index of the obtained PUR-PIR foams insignificantly decreases with increasing wood fibers content.

Keywords: rigid polyurethane-polyisocyanurate foams, bio-polyol, wood fibers, mechanical properties, thermal properties, flammability.

Spieniane wodą pianki poliuretanowo-poliizocyjanurowe otrzymane z bio-polioli i modyfikowane włóknami drzewnymi

Streszczenie: Z użyciem dwóch rodzajów biopolioli i włókien drzewnych (w ilości 3 i 6 % mas.) otrzymano kompozyty sztywnych pianek poliuretanowo-poliizocyjanurowych (PUR-PIR). Zmiany struktury komórkowej pianek w zależności od zawartości włókien drzewnych badano za pomocą skaningowej mikroskopii elektronowej (SEM). Właściwości termiczne i mechaniczne kompozytów charakteryzowano wykonując analizę termograwimetryczną oraz wyznaczając przewodnictwo cieplne, wytrzymałość na ściskanie oraz moduł Younga. Analizując wskaźnik tlenowy i szybkość wydzielania ciepła wyznaczaną za pomocą kalorymetru stożkowego określano wpływ zawartości włókien drzewnych na palność kompozytów. Stwierdzono, że w przypadku większości materiałów dodatek włókien drzewnych nie wpływa istotnie na zmiany wytrzymałości na ściskanie, powoduje natomiast wzrost temperatury, przy której następuje 5, 25 oraz 50-proc. ubytek masy badanej próbki oraz nieznaczne zmniejszenie wartości wskaźnika tlenowego.

Słowa kluczowe: sztywne pianki poliuretanowo-poliizocyjanurowe, bio-poliol, włókna drzewne, właściwości mechaniczne, właściwości termiczne, palność.

Vegetable oils are an abundant source of raw materials for polyurethane-polyisocyanurate (PUR-PIR) material production. Several methods of polyols synthesis are suitable for sustainable production. In recent years this topic has been widely studied by many research teams [1—3]. The following two methods of polyols synthesis can be also applied [4, 5]:

— oil epoxidation and oxirane ring opening with diethylene glycol,

— fatty acid triglyceride ester bond transesterification with triethanolamine.

Polyols developed from rapeseed oil have competitive properties to petrochemical materials. Their production costs and stability of characteristics is also on par with conventional materials due to well-developed rapeseed oil production technology [6].

A natural way to reduce the price and increase renewable material content in developed PUR-PIR materials is addition of biomass based fillers. Yuan *et al.* [7] studied influence of the addition of wood flour on the properties of rigid polyurethane foams. Their investigations showed that incorporation of 5 % of wood flour to the polyurethane matrix improved the compressive modulus by about 19 %. The modification of PUR foams with

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wood flour resulted also in a reduction of tensile and flexural properties, however also in an improvement of thermal stability of the foams [7]. Wood fibers are interesting filler for this purpose because they are wood processing by-product, which means they are a cheap raw material [8]. An addition of wood fibers would be justifiable if the properties of obtained materials are not worsened. There are studies that show that it is possible to increase physical and mechanical properties of PUR materials with the addition of solid micro fillers. The best results were obtained with various nanofillers [9—11]. However various biomass based fibers also have positive influence on PUR-PIR foams properties [12—14]. Due to the presence of functional groups on the surface of wood fibers it is expected that there will be good adhesion between polymer and fibers surfaces even with a possible covalent bond [15].

The main application of rigid PUR-PIR foams is thermal insulation. The different isocyanate indices are used to tailor material for specific uses. PUR foams usually are used as thermal insulation in the appliance industry as well as in civil engineering solutions [16, 17]. When specific applications require reduced flammability of porous materials, the rigid PIR foams are applied [18, 19]. The rapeseed oil-based polyols are suitable for rigid PUR foams as well as rigid PIR foams. For both types of foams the main characteristics is thermal conductivity coefficient (λ) that should be in the range between 20 and 24 mW/(m · K) [20].

There are several flammability determination methods and each of them is designed for specific fire scenario. One of most commonly used methods of material reaction to heat flux is the test with cone calorimeter. This method allows easily comparing different material behavior, heat and smoke release in fire disaster scenario [21]. Limited oxygen index describes minimum oxygen content in atmosphere for sustained burning of a material sample. This gives the idea about how easy it is to ignite a material [22].

The goal of this study was to develop heat insulating materials on the base of rigid PUR-PIR foams, containing bio-polyols from rapeseed oil that would have competitive properties in the current market. To increase renewable material content and reduce price of final product wood fibers as filler were also used.

EXPERIMENTAL PART

Materials

Two different rapeseed oil-based polyols were used. The first one, denoted as EP, was prepared in the Department of Chemistry and Technology of Polymers in Cracow University of Technology. It was characterized by the hydroxyl number of 256 mg KOH/g and by the water content of 0.47 wt %. The second polyol, denoted as TE, was prepared in the Latvian State Institute of Wood Chemistry. It was characterized by hydroxyl number of 365 mg KOH/g and the water content of 0.07 wt %. Bio-polyols EP and TE were obtained on the base of rapeseed oils, products of Kruszwica SA and SIA "Iecavnieks & Co", respectively. EP bio-polyol was synthesized using epoxidation with oxirane rings opening. 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). TE polyol was synthesized by transesterification of rapeseed oil with triethanolamine (TEOA) in molar ratio of 1:2.9.

Polyetherol with the trade name Lupranol 3422 having a hydroxyl number about 490 mg KOH/g and the water content of 0.10 wt % was supplied by BASF. Polymeric methylene diphenyldiisocyanate (PMDI) containing 31.5 wt % of free isocyanate groups was supplied by Minova Ekochem S.A. Pentamethyldiethylenetriamine (Polycat 5) produced by Air Products and Chemicals and potassium acetate produced by Performance Chemicals were used as catalysts. A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc., was used as a stabilizer of the composite structure. Applied flame retardant tris(3-chloropropyl)phosphate (TCPP) was produced by Lanxess.

Carbon dioxide generated in the reaction of water with isocyanate groups was used as a chemical blowing agent.

The PUR-PIR systems were modified with wood fibers that were manufactured by LaSole. The average values of length and diameter of fibers, shown in SEM image (Fig. 1), were 286 μm and 8 μm, respectively.

Preparation of the PUR-PIR foams

The PUR-PIR porous composites were obtained by mixing two components (A and B). The component A was prepared using two types of rapeseed oil-based polyols, petrochemical polyol, flame retardant, water, catalysts and surfactant. The chemical compositions of component A is shown in Table 1.

Table 1. The chemical compositions of component A

Raw material	Foams with EP bio-polyol	Foams with TE bio-polyol
Lupranol 3422	30.0	30.0
TCPP	30.0	30.0
Polycat 5	1.5	1.5
Potassium acetate	1.0—2.0	1.0—2.0
L6915	1.5	1.5
Water	4.0—6.0	3.2—5.0

Such mixtures (component A) were modified by the addition of wood fibers. The fiber concentrations were 3 or 6 wt % relative to the total weight of PUR-PIR components. The amount of introduced fibers was limited due to the increasing viscosity of component A. The pre-selected amounts of fibers were added to the polyol premix and stirred to obtain a homogeneous mixture. In the next stage component B (PMDI) was added to component A and after stirring the mixture for 7 s it was poured into a mold. The isocyanate indices were 150 (group ratio NCO:OH = 1.5:1) and 250 (group ratio NCO:OH = 2.5:1) for prepared PUR-PIR formulations.

The composites were marked by symbols of contained type of bio-polyol, isocyanate index and fibers content given in wt %. For example, symbol EP-150/W3 means foam with isocyanate index of 150, prepared using EP polyol and 3 wt % of fibers.

Methods of testing

The following properties of the foams were measured in accordance with ISO Standard tests:

— ISO 845:2010 apparent density (kg/m^3);

— ISO 844:2014-11 compressive strength 10 % (kPa);

— ISO 4590:2005 closed cells content (%).

The mechanical properties of the foams were estimated in two directions, parallel and perpendicular to the foam rise.

The oxygen index was determined according to ISO 4589-2:2006.

The behavior of rigid PUR-PIR foams and their composites with wood fibers under heat flux of 35 kW/m^2 was tested using FTT Dual Cone Calorimeter (Fire Testing Technology Ltd.). Tests were performed according to ISO 5660-1:2002 standard.

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the structural features of the sample foams.

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

The thermal conductivity factors were determined using a Laser Comp heat flow instrument Fox 200. The measurements were made at an average temperature of 10 °C (temperature of the cold plate 0 °C and the warm plate 20 °C).

The thermal stability was tested by thermogravimetric analysis using a Mettler Toledo TGA/SDTA 851e apparatus under nitrogen flow and at the heating rate of 10 °C/min from the room temperature to 1000 °C.

RESULTS AND DISCUSSION

Rigid PUR-PIR foams are materials characterized by the lowest thermal conductivity among commercially available insulation materials. Restricted use of rigid PUR-PIR foams is caused by their high price. In order to reduce the cost of insulation, naturally cheap fillers can be introduced into polyurethane matrix. In order to obtain materials containing natural and cheap fillers, but with a reduced flammability, attempts to modify the matrix of PUR-PIR with bio-polyols EP and TE as well as wood fibers were made.

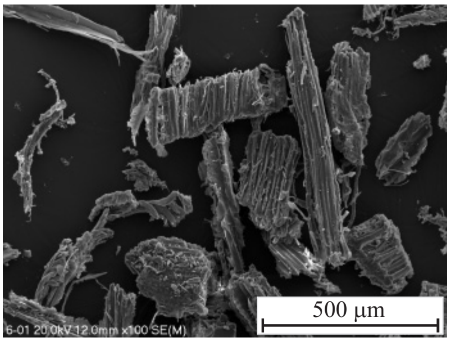

Fig. 1. SEM images of wood fibers

Twelve foams with similar apparent densities were obtained to compare selected properties of investigated materials. As it is shown in Fig. 2 no significant changes in the apparent density after the addition of wood fibers were noticed for most samples studied. However, in the case of six foams with isocyanate index 250, the maximum difference in apparent density reached nearly 20 %. The exception here comprises EP-250 system, in which changes in apparent density are associated with problems concerning the synthesis of the foam because of the high viscosity of the polyol premix.

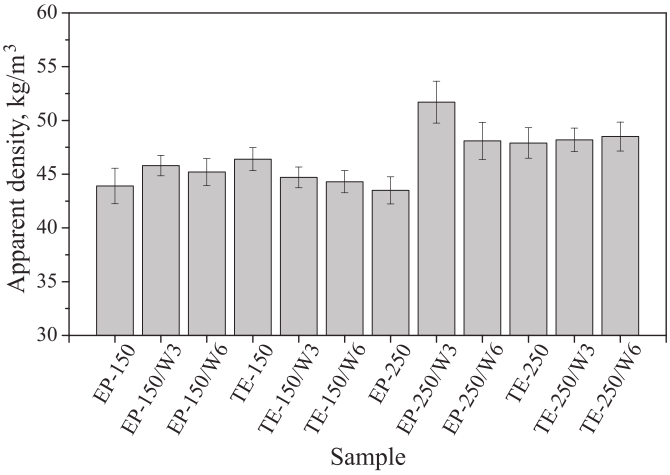

Fig. 2 Apparent density of prepared PUR-PIR foams modified with wood fibers

Thermal conductivity is one of most important properties of rigid foams being applied as heat insulating materials. The results of thermal conductivity and content of closed cells (having considerable influence on foam heat insulating property) as an effect of the used

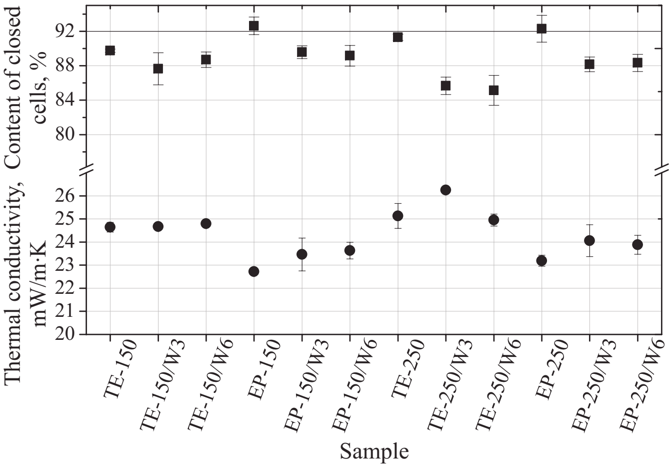

Fig. 3. Thermal conductivity and content of closed cells in rigid PUR-PIR foams modified with wood fibers

wood filler are shown in Fig. 3. The largest closed cell contents were characteristic for materials modified with EP bio-polyol. Higher content of closed cells contributes to smaller coefficients of thermal conductivity which is confirmed by the obtained results. Changes in the thermal conductivity coefficient are small and are within the scope of 1 mW/(m · K), compared to the λ value of the reference materials (without filler).

The effect of the wood filler content on compression strength of prepared samples is shown in Fig. 4. These figures show respectively the influence of the wood fibers on the values of the compressive strength at 10 % deformation of foams with isocyanate index 150 and 250. In both cases, the compression directions were parallel (pa) and perpendicular (pe) to the direction of foams rise.

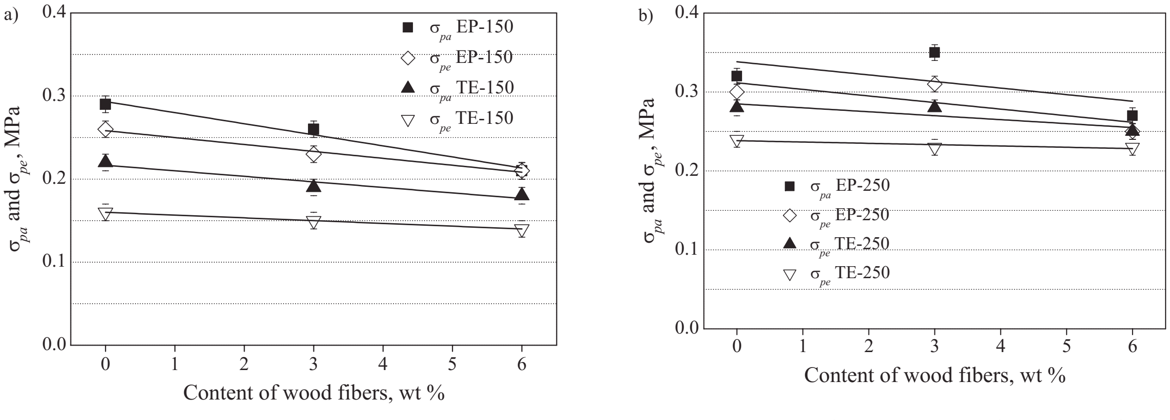

Fig. 4. Compressive strength in parallel direction (σ_{pa}) and in perpendicular direction (σ_{pe}) of rigid PUR-PIR foams modified with wood fibers; isocyanate index: a) 150, b) 250

The modification of foam formulation using TE bio-polyol with wood fibers did not significantly affect the compressive strength of rigid PUR-PIR foams synthesized with an isocyanate index of 150. However, in the case of systems with EP bio-polyol, a significant deterioration in compressive strength of the foams in the direction parallel to the direction of foam rise was noticed. It is important that in the case of deterioration in the compressive strength in perpendicular direction to the direction of foam rise (wherein the foam is characterized by smaller values of the mechanical properties) the changes are not considerable after the addition of wood filler. For rigid PUR-PIR foams prepared with isocyanate index 250 and modified with wood fibers, the increase in the compressive strength in the direction parallel to the direction of foam rise was achieved after introduction of 3 wt % of this filler. However, it is probably caused by a higher apparent density of the modified foam.

In the case of the PUR-PIR system EP-250, introduction of the wood fibers resulted in the increase of compressive strength in both directions, parallel and perpendicular to the direction of foam rise, although this improvement can be explained by an increase in apparent density of the foams (Fig. 2). For the foams based on TE bio-polyol, which were characterized by the comparable apparent densities, no significant changes were noticed after the addition of wood fibers. It is also a preferred result, because the increase of the renewable raw material content does not impair the mechanical strength of foams.

The effect of application of wood fillers on the mechanical properties of modified foams, are reflected by the data of normalized compressive strength (σ_n) which were calculated taking into account average apparent density of PUR-PIR foams, according to equation [22]:

$$\sigma_n = \sigma_i \left(\frac{\rho_{average}}{\rho_i} \right)^{2.1} \quad (1)$$

where: σ_i — the experimental raw strength of given foam, determined from the stress-strain curve, ρ_i — the apparent density of the same foam, $\rho_{average}$ — the average apparent density calculated on the base of compared foams densities.

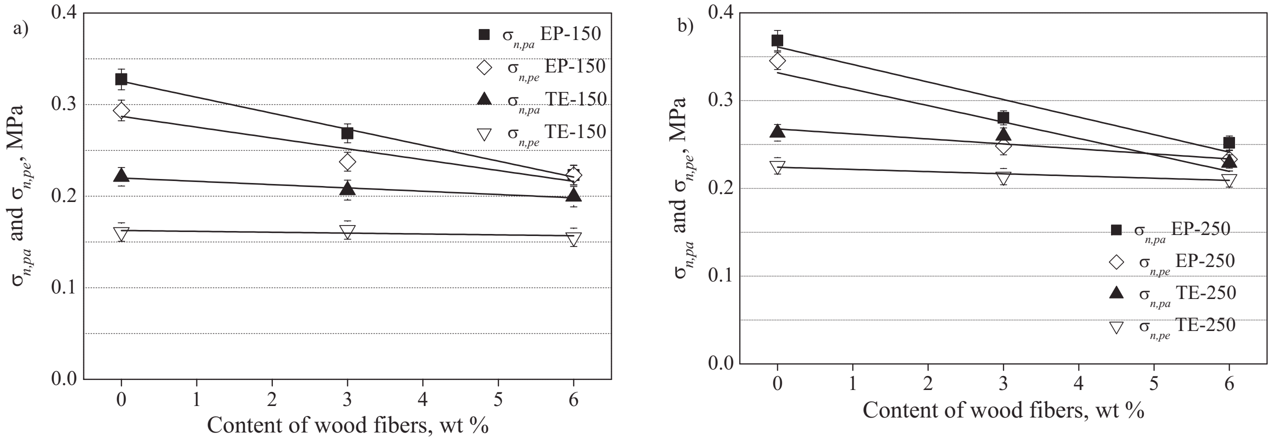

Fig. 5. Normalized compressive strength in parallel direction ($\sigma_{n,pa}$) and in perpendicular direction ($\sigma_{n,pe}$) of rigid PUR-PIR foams modified with wood fibers; isocyanate index: a) 150, b) 250 (data, taking into account apparent density of foams, normalized according to [22])

The dependencies of σ_n for prepared foams on the content of wood fibers are shown in Fig. 5. The analysis of these results proved that the modification of foam formulation using TE bio-polyol with wood fibers did not significantly affect σ_n of rigid PUR-PIR foams synthesized with both 150 and 250 values of isocyanate index. In the case of systems with EP bio-polyol, a significant deterioration in σ_n of the foams was noticed, although the mechanical properties of PUR-PIR foams with bio-polyol EP after deterioration being an effect of wood fibers additions, are more beneficial as in the case of foamed composites with TE bio-polyol.

Higher σ_n of the material with bio-polyol EP may be associated with a more regular cell structure as compared to the foams with the TE bio-polyol, which were shown in Fig. 6.

The effect of wood fibers on Young modulus of rigid PUR-PIR foams with isocyanate indices of 150 and 250 is shown in Fig. 7. In the case of rigidity modulus similar trends as in the case of compressive strength of the investigated PUR-PIR foams were observed. The foams con-

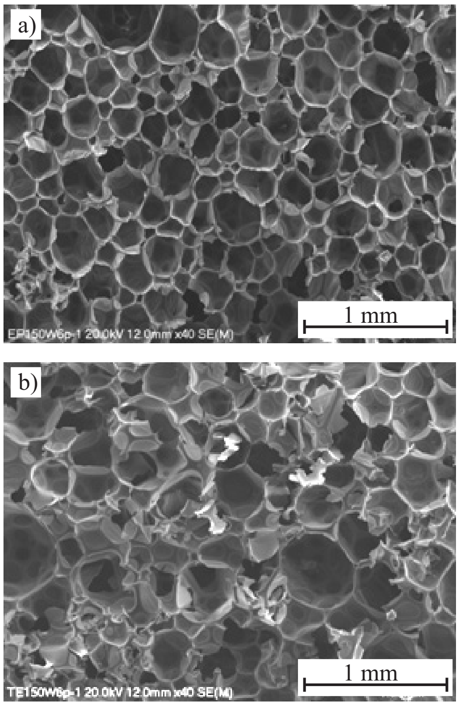

Fig. 6. Cellular structure of exemplary rigid PUR-PIR foams modified with wood fibers and bio-polyols: a) EP-150/W6, b) TE-150/W6

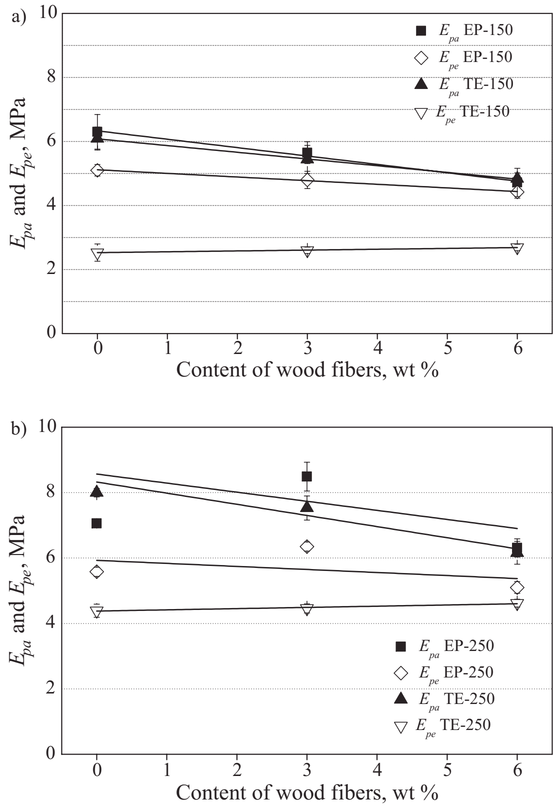

Fig. 7. Young's modulus in parallel direction (E_{pa}) and in perpendicular direction (E_{pe}) of rigid PUR-PIR foams modified with wood fibers; isocyanate index: a) 150, b) 250

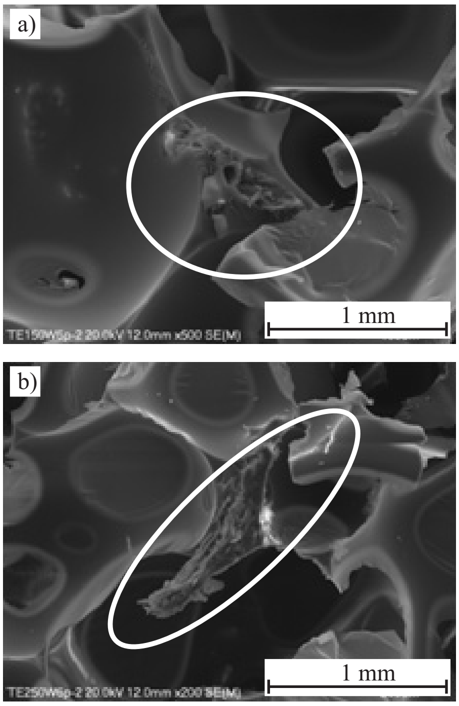

Fig. 8. Examples of wood fiber built in the PUR-PIR matrix shown in SEM images for samples: a) TE-150/W6, b) TE-250/W6

taining 3 wt % of wood fibers have a higher modulus of rigidity as compared to the unmodified material. The mechanical properties of foams can be influenced by location of fibers in foam matrix. If the fibers are placed in the struts between cells this may lead to an improvement of mechanical properties. The sample images showing the locations of wood fibers in different parts of PUR-PIR foams are presented in Figs. 8a (in a strut) and 8b (in a wall). An increase in the filler amount caused that fibers have tendency to be located in thin cell walls. It results, *i.e.* in piercing the walls by the fibers (Fig. 8b). The similar effect as shown in Fig. 8b was observed by Khazabi *et al.* [24] as an effect of increasing the amount of wood fibers in the PUR matrix. They have synthesized rigid polyurethane foam with an isocyanate index of 120 and with the participation of bio-polyol obtained from soybean oil.

In the case of Young modulus data, the similar normalizing analysis as for compressive strength was carried out according to the same method [23] but another formula describing normalized Young modulus (E_n) was used:

$$E_n = E_i\left(\frac{\rho_{average}}{\rho_i}\right)^{1.7} \tag{2}$$

where: E_i — the experimental raw modulus determined from the modulus-strain curve.

The effect of wood fibers content on E_n is shown in Fig. 9. Such analysis allowed to find the different tendency of modulus changing when there are compared normalized values of Young modulus for the foams with TE bio-polyol in parallel and perpendicular directions. The increase of wood fillers in these foams causes the decrease of E_n measured parallel to the foams rise direction but improve this parameter in the perpendicular direction. The lowering of differences in values of E_n measured parallel and perpendicularly to the foams rise direction can be an effect of more isotropic structure of foams with increased content of wood fibers.

Table 2. Thermal properties of selected PUR-PIR foam

Name of sample	T_{onset} °C	$T_{5\,\%}$ °C	$T_{25\,\%}$ °C	$T_{50\,\%}$ °C	Residue (800 °C), %
TE-250	223	260	220	345	28.2
TE-250/W3	234	263	349	567	20.7
EP-250	232	269	232	341	26.6
EP-250/W3	240	277	343	442	24.3

The results of thermal stability investigation of prepared foams are listed in Table 2. The addition of wood

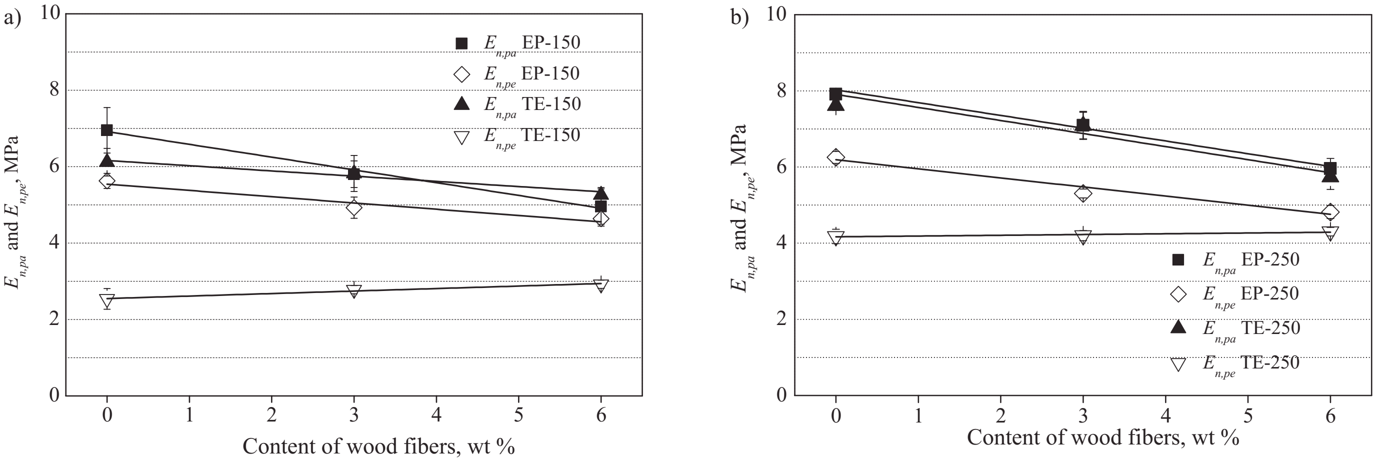

Fig. 9. Normalized Young's modulus in parallel direction ($E_{n,pa}$) and in perpendicular direction ($E_{n,pe}$) of rigid PUR-PIR foams modified with wood fibers; isocyanate index: a) 150, b) 250 (data, taking into account apparent density of foams, normalized according to [23])

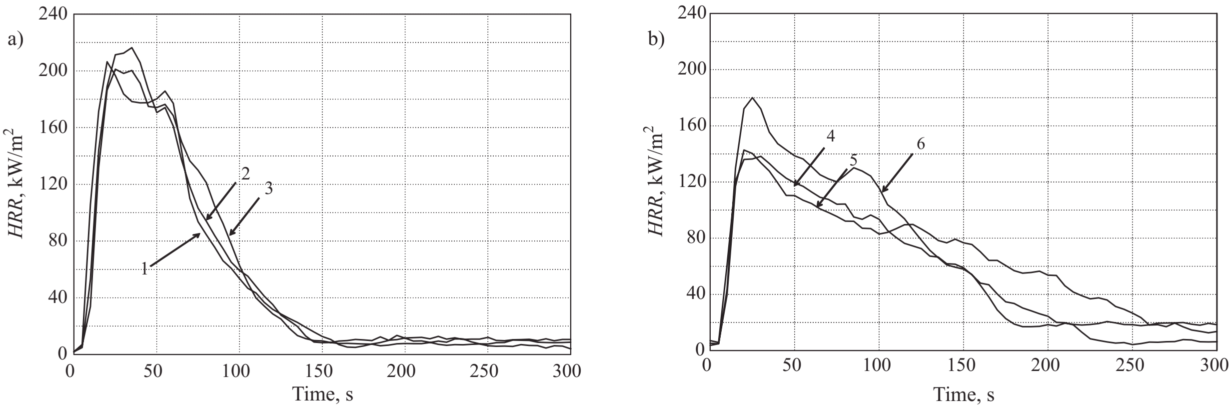

Fig. 10. The change of heat release rate (*HRR*) during the combustion of rigid PUR-PIR foams modified with wood fibers; isocyanate index: a) 150 (EP-150 — curve 1, EP-150/W3 — curve 2, EP-150/W6 — curve 3), b) 250 (EP-250 — curve 4, EP-250/W6 — curve 5, EP-250/W6 — curve 6)

fibers to PUR-PIR systems increased thermal stability of the obtained foams. The temperature at which there was 5 % of weight loss ($T_{5\,\%}$) increased in comparison to non-filled sample, by 8 and 3 °C, respectively for EP-250/W3 and TE-250/W3 materials. The largest changes occurred for temperatures at which the weight loss was 25 and 50 % ($T_{25\,\%}$ and $T_{50\,\%}$, respectively). For example, in the case of EP-250/W3 material $T_{50\,\%}$ has increased by about 100 °C, and in the case of TE-250/W3 by about 200 °C.

The addition of flammable plant filler into the matrix may have an impact on the heat release rate (*HRR*) and other characteristics associated with the flammability of foam materials. The *HRR* curves for investigated PUR-PIR foams are presented in Fig. 10. It can be concluded that the modification of foams with wood fibers did not affect significantly the maximum value of *HRR*.

During the combustion of foams only in the case of EP-250/W6 foam, the maximum of *HRR* increased by about 30 % comparing to the unmodified material (Fig. 10b).

The effect of modification of PUR-PIR systems (with isocyanate index 250) by wood fibers on the oxygen index of prepared foams is shown in Fig. 11. The introduction of wood fibers to the foams caused a decrease in their oxygen index what was expected, but the values of this parameter are still higher than 21 %. Such oxygen index value allows to confirm that the foams are slow-burning in the atmospheric air.

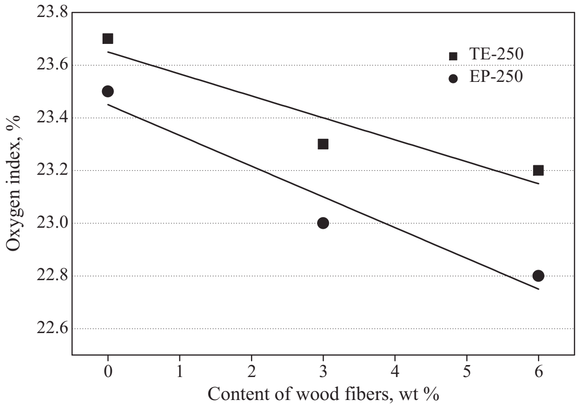

Fig. 11. The oxygen index of selected foamed materials modified with wood fibers

CONCLUSIONS

Wood fibers can be a good filler for PUR-PIR foams. However, their use in the polyol premix is limited due the viscosity of such mixtures, which can considerably increase. The application of wood fibers in PUR-PIR foam formulations allowed to increase the content of renewable components in final materials from about 22 to 27 wt %.

The increase of wood fillers content in PUR-PIR formulations caused that more of them is located in the cell walls causing an increase of open cell content in these foams. The content of closed cells in such porous composites depends also on the type of used bio-polyol. The foams prepared with EP bio-polyol synthesized by epoxidation and oxirane ring opening had the highest content of closed cells and the structure of these materials was more regular in comparison to foams with TE bio-polyol synthesized by oil transesterification.

A beneficial effect of EP bio-polyol together with wood fibers was also noticed in the case of mechanical properties of such foams in comparison to the materials prepared using bio-polyol TE. However, the increase of wood fibers in PUR-PIR formulations causes the decrease of difference in mechanical properties of the foams with EP and TE bio-polyols. The application of wood fibers in the amount of up to 6 wt % in PUR-PIR foams does not significantly affect their coefficient of thermal conductivity and considerably improve their thermal stability.

The introducing of wood fibers caused the worsening of flame retardancy of modified foams. However, it is possible to obtain low density PUR-PIR foams that are slow-burning in the atmospheric air.

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