Wheat straw lignin as filler for rigid polyurethane foams on the basis of tall oil amide[*)]

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Abstract: Rigid polyurethane (PUR) foams with the apparent density in the range of 45—60 kg/m^3 were produced from tall oil polyol (TOP) and organosolv wheat straw lignin as filler. PUR foams were filled with lignin in the amount of 0—6.3 wt %. Mechanical properties, dimensional stability, water absorption and thermal conductivity of prepared foams were investigated. The use of lignin increased the content of renewable materials in the end product, reaching together with TOP the value of 23.6 wt %. The viscosity of polyol system and foaming process parameters (cream time, gel time, tack-free time and full rise time) were determined. The viscosity of polyol system rose exponentially when concentration of lignin in the PUR foam was increased. The maximum value of compressive strength (0.35 MPa parallel to the foaming direction) was reached in the PUR sample where the concentration of lignin in foam was 1.2 wt %. It was concluded that wheat straw lignin can be used as a filler to obtain rigid PUR foams having the characteristics of thermal insulation material.

Keywords: rigid polyurethane foams, tall oil, polyol, lignin.

Lignina ze słomy pszenicznej jako napełniacz stosowany do sztywnych pianek poliuretanowych na bazie amidów oleju talowego

Streszczenie: Stosując poliol z oleju talowego (TOP) oraz ligninę ze słomy pszenicznej jako napełniacz otrzymano sztywne pianki poliuretanowe (PUR) o gęstości pozornej 45—60 kg/m^3. Wyznaczono właściwości mechaniczne, stabilność wymiarową, chłonność wody oraz współczynnik przewodzenia ciepła przygotowanych materiałów w zależności od zawartości ligniny (0—6,3 % mas.). Wprowadzenie ligniny spowodowało zwiększenie udziału surowców odnawialnych w końcowym produkcie, które razem z TOP osiągają 23,6 % mas. W ramach pracy wyznaczono lepkość przedmieszki poliolowej oraz parametry technologiczne procesu spieniania (czas startu, czas żelowania, czas wzrostu, oraz czas suchego lica). Lepkość przedmieszki poliolowej wzrastała wykładniczo wraz ze zwiększaniem zawartości ligniny. Największą wytrzymałość na ściskanie (0,35 MPa w kierunku równoległym do wzrostu pianki) otrzymano w przypadku pianki PUR o zawartości ligniny 1,2 % mas. Stwierdzono, że lignina ze słomy pszenicznej może być użyta jako napełniacz w procesie otrzymywania sztywnych pianek PUR mających cechy materiałów termoizolacyjnych.

Słowa kluczowe: sztywne pianki poliuretanowe, olej talowy, poliol, lignina.

Nowadays it is important to find new ways to replace petro-chemical products with renewable raw materials because of environmental and economic concerns. Polyols used in polyurethane (PUR) production can be obtained from different natural oils and different natural fillers could be used to improve characteristics of PUR, reduce production costs and to enhance the renewable content in the material.

Lignin, a product of bio-refining, can be characterized as an amorphous heterogenic polymer with high amount of aromatic units in its structure. The common property of lignin is the content of three types of hydroxyl groups (aliphatic, phenolic, carboxylic), capable of chemical interaction with isocyanates, and/or physical interaction by hydrogen bonds with structural units of PUR [1]. Due to the hydroxyl functionality, lignin can be used as reactive filler in the production of PUR. The use of lignin can improve the mechanical characteristics and thermal stability of PUR in certain cases [2]. However the structural heterogeneity, functional composition and solubility of lignin vary depending on the methods of its isolation and the plant source. Correspondingly, the properties of PUR foams containing lignin depend on the lignin type (Kraft lignin, Klason lignin, organosolv etc.) used. Due to the

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[**)] Author for correspondence; e-mail: aiga.paberza@gmail.com development of new generation of biomass processing, the examination of novel lignin products for creation of lignin-containing PUR remains actual up to now.

A novel type of organosolv lignin marketed under the trade name biolignin^{TM} extracted from wheat straw in organic acid media using biomass refinery technology developed by Compagnie Industrielle de la Matière végétale (CIMV, France) was used for preparation of lignin-containing PUR in this study [3]. The disadvantage of biolignin^{TM}, in its application as a macro monomer in PUR, is the weak solubility in polyols and in organic solvents.

The properties of PUR containing lignin depend on the method of lignin incorporation. The possible synthetic routes for lignin incorporation into PUR materials are following:

— as an additive filler in the form of powder,

— as a hydroxyl functional reactive filler in the form of powder [4—5],

— as a hydroxyl functional monomer in a liquid form obtained by chemical modification, for example by alkoxylation of lignin [2, 3—5].

The aim of this study was to test the possibility to use chemically non-modified biolignin^{TM} as filler in rigid PUR foams and to evaluate the influence of lignin on the properties of PUR foams. The compositions of rigid PUR foams were based on tall oil polyol (TOP) to increase the content of renewable materials in the end product. The influence of lignin as filler on physical and mechanical properties, dimensional stability, water absorption properties and thermal conductivity were investigated and were evaluated according to European standard for thermal insulating products for buildings (EN 14315-1). It was assumed that lignin acts only as additive filler.

EXPERIMENTAL

Materials

Tall oil polyol (TOP, OH = 269 mg KOH/g; H_2O = 0.2 wt %) was synthesized from tall oil and diethanolamine by amidization reaction. More detailed description of TOP synthesis is given in our previous work by Cabulis et al. [7]. Lupranol 3422 (OH = 490 mg KOH/g) from BASF is higher functional polyether polyol based on sorbitol and was used to increase the average functionality of polyol mixture. Glycerine (OH = 1824 mg KOH/g) from Sigma-Aldrich was used as an additional crosslinking agent.

The catalysts used were NIAX Catalyst E-A-1 from Momentive Performance Materials and 30 % solution of potassium acetate in diethylene glycol from Performance Chemicals Handels GmbH. NIAX Catalyst E-A-1 is an amine catalyst. Potassium acetate promotes reaction of isocyanate trimerization.

Surfactant NIAX Silicone L6915 from Momentive Performance Materials was used as an additive to provide closed foam structures.

Distilled water was used as a blowing agent.

Polymeric diphenylmethane diisocyanate — IsoPMDI 92140 (PMDI) from BASF was used as an isocyanate component (w_{NCO} = 31.5 %).

Biolignin (H_2O = 10 wt %) was ground with laboratory disintegrator DESI-11 (rotors rotation rate 10000 rpm). The ground lignin was dried for 24 h at 40 °C and p = 30 mbar. After drying the moisture content of 2 wt % was reached.

Sample preparation

The substrates for rigid PUR foams preparation is composed of PMDI and other ingredients, which was named polyol system. The composition of polyol systems used in this work are presented in Table 1. We developed two series of PUR compositions. Because lignin additive affects PUR foams apparent density, series 1 was prepared in order to investigate density and determine the amount of a foaming agent which will provide appropriate density of all foams. Therefore in series 1 only the amount of lignin differs, but in series 2 the samples with lignin contents of 7.5, 15 and 22.5 parts by weight (pbw) were repeated with adjusted amount of the blowing agent (series 2) to obtain samples with unified apparent density.

Table 1. The composition of the mixtures, named polyol systems, that were added to PMDI in two series of prepared samples

Component	Content of component in polyol system, pbw								
	series 1						series 2		
	1-1	1-2	1-3	1-4	1-5	1-6	2-1	2-2	2-3
TOP	75.0						75.0		
Lupranol 3422	20.0						20.0		
Glycerol	5.0						5.0		
Lignin	0	1.88	3.75	7.5	15.0	22.5	7.5	15.0	22.5
Water	2.0						2.5	3.5	3.5
Catalyst EA-1	0.5						0.5		
Potassium acetate	0.5						0.5		
L6915	1.5						1.5		

The amount of necessary PMDI was calculated according to equation:

$$m_{PMDI} = \frac{II}{w_{NCO}} \cdot \left(\sum \frac{OH_n \cdot m_n}{1336} + 4.67 \cdot m_{H_2O} \right) \tag{1}$$

II — isocyanate index (II = 155), m_{PMDI} — mass of PMDI, w_{NCO} — content of NCO groups of PMDI (w_{NCO} = 31.5 %), m_n — mass of each polyol, OH_n — hydroxyl value of each polyol (in mg KOH/g), m_{H_2O} — summary mass of water in polyol system.

In our experiments lignin was assumed to act as non-reactive filler. Therefore the hydroxyl group content of lignin was not taken into calculation of the necessary amount of PMDI needed.

Polyol systems were made as follows — polyol composition ingredients (TOP, cross linkage reagents, catalysts, surfactant, blowing agent) were mixed together in plastic cup for 3 minutes at the speed of 2000 rpm. Afterwards the necessary amount of the ground and dried lignin was added and mixed for 4 minutes at the speed of 2000 rpm. High speed mechanical stirrer IKA RW 20.n was used for mixing.

To prepare PUR samples the necessary amount of PMDI was added to polyol component and the whole system was mixed for 15 s at the speed of 2000 rpm. The parameters of foaming process (cream time, gel time, tack-free time and full rise time) were determined. Larger samples of PUR foams were prepared using 20 × 30 × 10 cm mold. The height of these foams was 8—10 cm. The obtained samples were conditioned for 24 h at the room temperature. PUR samples for testing were cut out afterwards.

Methods of testing

Scanning electron microscope SEM Tescan TS 5136 MM was used to test the size of lignin particles. A&D moisture analyser MX-50 was used for in lignin determination of water content. Viscosity was tested for polyol systems kept for 5 days at two temperatures: room temperature and 50 °C. Temperature 50 °C was chosen to evaluate the influence of storage temperature to polyols viscosity. Higher temperature is not favorable for tall oil polyol storage. After conditioning the viscosity of polyol systems was tested with the rotation viscometer Haake Viscotester 6L/R Plus at 20 °C.

The tests of rigid PUR foam compression were performed on testing machine Zwick/Roell Z100 (LVS EN ISO 844:2009 standard, percent of compression 10 %). The measurements of closed cell content and apparent density were done according to the standards ISO 4590:2003 and ISO 845:2009, respectively. Water absorption was tested according to ISO 2896:2001 standard by immersing PUR samples in water for 7 days. The dimensional stability was established according to ISO 2796:1986 standard. The dimensional stability was determined for two sets of parameters: 28 days at 80 °C, ambient relative humidity (*RH*) and 28 days at 70 °C, *RH* = 97 %. The thermal conductivity in the range between 10 and 30 °C was tested with Linseis HFM (Heat Flow Meter) 200. Because the series 1 was made to determine necessary water amount needed in series 2 samples, only the apparent density was tested for series 1. All previously mentioned tests were carried out for samples with unified density.

RESULTS AND DISCUSSION

Characterization of lignin

Lignin disintegration was carried out to enlarge the active surface area and to reach uniform refinement of lignin. The size of lignin particles before and after grinding was determined using SEM images presented in Fig. 1. Before disintegration the size of lignin particles was higher than 50 μm but after disintegration it was between 1 and 20 μm. After drying the moisture content of 2 wt % was reached.

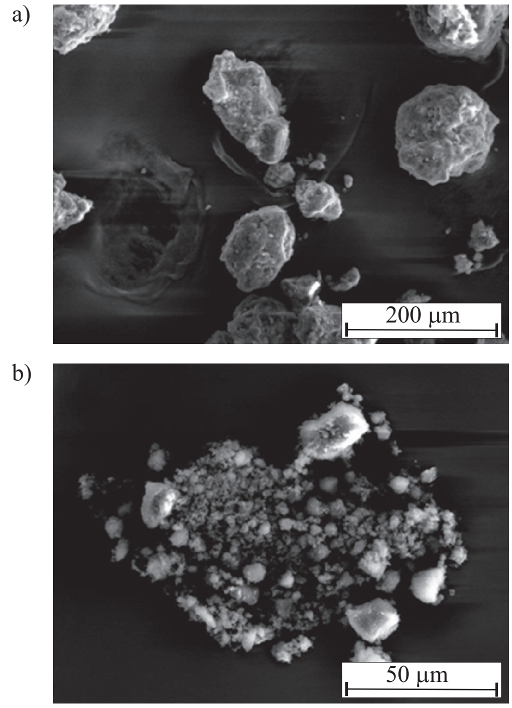

Fig. 1. SEM images of lignin: a) before disintegration, b) after disintegration

Viscosity of polyol systems

The viscosity of polyol systems is an important parameter that determines the possibility and efficiency of mixing (which affects the quality and uniformity of foam). Viscosity is also an important parameter to deter-

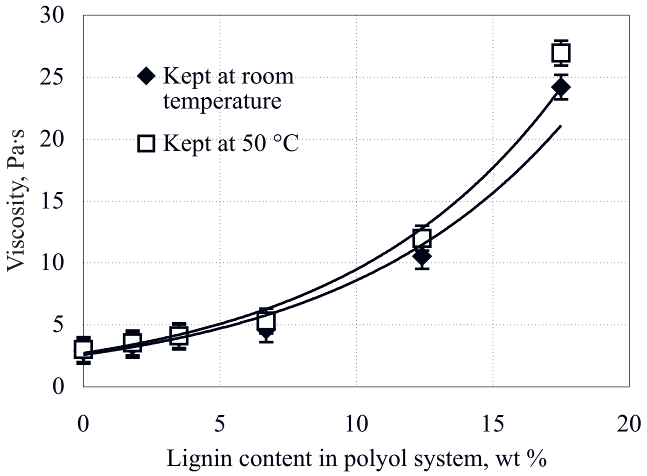

Fig. 2. Viscosity at 20 °C of polyol systems with different lignin content

mine the possibilities of polyol to be used in industrial production as well. The viscosity of polyols can be affected by its storage temperature. The viscosities of prepared polyol systems versus lignin contents are presented in Fig. 2. The viscosities of the mixture kept at the room temperature exponentially rises from 3.0 ± 0.1 to 24.2 ± 0.2 Pa · s when the concentration of lignin in polyol system increases from 0 to 17.5 wt %, respectively. The viscosity of mixtures kept at 50 °C was slightly higher than viscosity of samples kept at the room temperature. It could indicate the engorgement of lignin particles in polyol system as the result of physical and chemical interaction of polyols with functional groups of lignin located on the outer surface of lignin particles. The increase of viscosity during storage is caused by swelling of lignin particles in polyol.

Rigid PUR samples characterization

Apparent density is an important property of rigid PUR foams because it strongly affects other properties of foams such as dimensional stability and compressive strength. Usually technical requirements for rigid PUR foams depend on apparent density. Figure 3 shows the effect of lignin concentration on apparent density of PUR foams prepared using both series of polyol systems. The density of series 1 samples increased from 45 to 60 kg/m^3. The quantity of blowing agent (water) was adjusted to obtain series 2 rigid PUR foams with density of 49.5 ± 1.8 kg/m^3. The changes of water content were taken into account when the necessary amount of PMDI was calculated. II was the same (II = 155) for all samples.

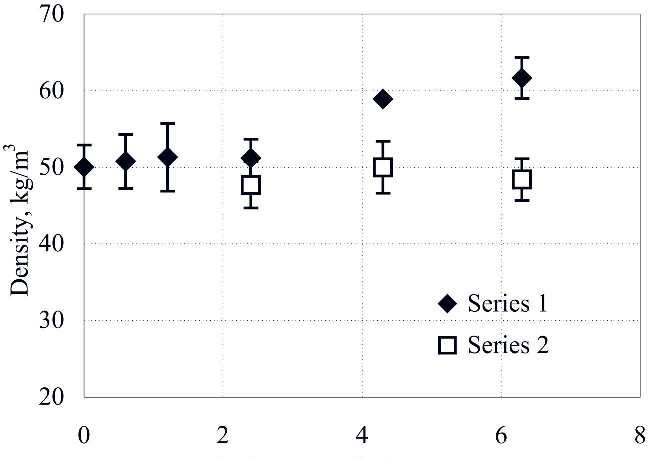

Fig. 3. The apparent density of PUR foams with different lignin content: series 1 and series 2

The closed cell content varied between 92 and 96 vol. %. Obtained rigid PUR foams were classified as CCC4 class for closed cell content (according to EN 14315-1).

Table 2 presents the foaming process parameters describing its kinetics.

T a b l e 2. Parameters of foaming process for samples with unified apparent density

Symbol of polyol system	Concentration of lignin in foam, wt %	Cream time, s	Gel time, s	Tack--free, s	Full rise, s
1-1	0	19	55	86	135
1-2	0.6	20	59	93	150
1-3	1.2	20	65	98	148
2-1	2.4	23	73	115	150
2-2	4.3	23	110	185	215
2-3	6.3	37	170	315	328

The increase of lignin content slows down the foaming rise as evidenced by the rise of cream, string, tack-free and full rise time. It is a result of the acidity of lignin (w_{COOH} = 1.71 ± 0.16 wt %) and increased viscosity (Fig. 2).

In Fig. 4 the compressive strength values of prepared samples are shown as a function of lignin concentration.

Compressive strength parallel to the foaming direction slightly increases in samples where the concentration of lignin in foam is up to 1.2 wt %. The maximum value of compressive strength (0.35 MPa parallel to foaming direction) is reached for PUR sample where the concentration of lignin in foam is 1.2 wt %. It complies with the CS(10\Y)300 level for compressive strength (according to EN 14315-1). The compressive strength decreases to 0.28 MPa when concentration of lignin is higher than 2.4 wt %. It complies with the level CS(10\Y)200 (according to EN 14315-1).

The thermal conductivities for samples with unified apparent density are listed in Table 3. The thermal con-

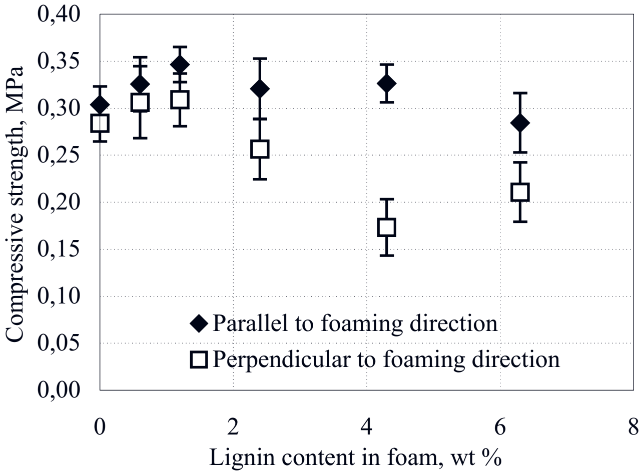

Fig. 4. Compressive strength of PUR foams with different lignin content for samples with unified apparent density

ductivity decreases from 0.0352 to 0.0298 W/m · K with increasing lignin content in PUR foam from 0 to 6.3 wt %.

Table 3. Thermal conductivity for samples with unified apparent density

Symbol of polyol system	Lignin content in foam, wt %	Thermal conductivity, W/m · K
1-1	0	0.0352 ± 0.0008
2-1	2.4	0.0324 ± 0.0011
2-3	6.3	0.0298 ± 0.0002

Table 4. Water absorption and dimensional stability for samples with unified apparent density

Symbol of polyol system	Concentration of lignin in foam wt %	Water absorption vol. %	Dimensional stability	
			volume change (80 °C, ambient *RH*), %	volume change (70 °C, *RH* = 97 %), %
1-1	0	1.86 ± 0.40	0.6 ± 0.4	1.0 ± 0.5
1-2	0.6	1.67 ± 0.18	0.1 ± 0.4	-0.7 ± 0.5
1-3	1.2	2.24 ± 0.12	-0.8 ± 0.4	0.1 ± 0.5
2-1	2.4	2.25 ± 0.27	-0.4 ± 0.4	0.3 ± 0.5
2-2	4.3	1.87 ± 0.21	-0.4 ± 0.4	0.0 ± 0.5
2-3	6.3	1.97 ± 0.15	-0.6 ± 0.4	0.1 ± 0.5

For samples with unified apparent density the water adsorption and dimensional stability were determined and were collected in Table 4. Water absorption after 7 days is 2.1 ± 0.2 vol. % (Table 4). Absorption of water is not affected when lignin is added. Volume changes of PUR samples are no more than 1.5 % for all samples (Table 4). It complies with the level 3 for dimensional stability under the specified temperature and humidity conditions (according to EN 14315-1).

CONCLUSIONS

It was concluded that it is possible to use chemically non-modified biolignin™ as filler in rigid PUR foams. The rigid PUR foam composition was developed where total concentration of lignin in PUR foam reached 6.3 wt %. The viscosity of the polyol component system too much when more than 6.3 wt % of lignin was added. Increasing viscosity decreased the efficiency of component mixing and slowed down the time of foam rise. Lignin did not impact water absorption and dimensional stability indicators in PUR materials. The maximum value of compressive strength (0.35 MPa parallel to the foaming direction) is reached in PUR foam sample where the content of lignin in foam is 1.2 wt %. Increasing concentration of lignin in rigid PUR foam improved thermal insulation properties (thermal conductivity decreased).These rigid PUR foam compositions can be used for further research as thermal insulation material using renewable raw materials. In this case flame retardants should be added. It was possible to obtain rigid PUR foams with the renewable raw materials in the amount of 23.6 wt % due to the use of TOP and lignin.

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