



## DIMENSIONALLY STABLE WATER-BLOWN POLYURETHANE FOAM EXTENDED WITH BIO-BASED PROPYLENE GLYCOL AND MODIFIED WITH PAPER WASTE SLUDGE

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**Abstract.** Paper waste sludge (PWS) is the main and the greatest by-product in paper production process, and its elimination as well as destruction is a primary environmental problem. This research explores the feasibility of such wastes to be used in polyurethane foam composites. It is well known that using water as a sole blowing agent has major drawbacks such as long demould time, shrinkage, high diffusion rate of carbon dioxide and etc.; therefore, the bio-based propylene glycol (RPG) is used in order to solve such problems. The addition of 20 parts by weight (pbw) of RPG eliminates the primary shrinkage of the foam composites when PWS is used in the amount varying from 5% to 20%, and improves the dimensional stability at 70 °C and 90% relative humidity conditions. The addition of titanate coupling agent modified PWS particles increases the compressive strength of the final composites from ~26% to ~53%, from ~17% to ~31% and from ~3% to ~23% for, respectively, 10 pbw, 15 pbw and 20 pbw RPG extended foam composites.

**Keywords:** polyurethane, paper waste sludge, composites, bio-based materials, propylene glycol, shrinkage, strength, dimensional stability.

### Introduction

The negative impact on the environment may be reduced by using renewable resources which have a great potential in replacing traditional polymers produced from petroleum feedstocks (Belgacem, Gandini 2008; Alagi *et al.* 2016). Vegetable-based oils are renewable resource which may be used as a primary material for the development of products which are characterised by various structural and functional variations. Abundance, accessibility and relatively low cost make vegetable oils an attractive raw material in the plastics' industry. These oils and fatty acids obtained thereof are considered as the most important renewable raw materials in chemical industry and production of eco-

logical-functional polymers and polymeric materials (Miao *et al.* 2014; Alam *et al.* 2014; Pillai *et al.* 2016).

For the production of vegetable oil-based polyols, conversion of C = C double bonds or ester groups into hydroxyl groups is necessary. Such methods are analysed using various oils, e.g. palm (Pawlik, Prociak 2011), soy (Gu, Sain 2013), rapeseed (Kurańska *et al.* 2015), castor (Wik *et al.* 2011) and even molasses (Hatakeyama *et al.* 2011), corn, potato starches and wheat (David *et al.* 2009). In order to replace petroleum-based polyols with polyols from vegetable oils, they must conform certain requirements raised for polyols used in the production of polyurethane foams, i.e. they

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must have corresponding functionality ( $>3$ ), molecular weight ( $<1200$  g/mol) and hydroxyl value varying from 350 mg KOH/g to 600 mg KOH/g (Pawar *et al.* 2016). Whereas polyurethane foams from vegetable oil-based polyester polyols are characterised by excessive shrinkage after production and poor dimensional stability when water is used as a blowing agent (European Commission 2013), scientists use fillers, chain extenders or cross-linking agents in order to overcome such problems.

Pollution prevention in paper production industry is a worldwide aspiration (Directive 2008/98/EC). One of the main aims of European Commissions and Directives is to transform European Union countries into “recycling community” which is capable of reducing the accumulation of wastes and using them in different processes. Paper waste sludge (PWS) is the main and the greatest by-product in paper production process (approx. 35% of the produced paper (Frías *et al.* 2015)), and its elimination and destruction is primary environmental problem. Gluth *et al.* (2014) have determined that the main components in PWS are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  from kaolinite and  $\text{CaO}$  from calcium carbonate. Scientists Sá e Sant’Anna *et al.* (2008) have conducted a research on the impact of the main PWS component – calcium carbonate on the properties of flexible polyurethane foam. The obtained results have shown that increasing the amount of  $\text{CaCO}_3$  (particles size of (100–250)  $\mu\text{m}$ ) from 1 wt.% to 30 wt.%, uniform distribution worsens due to overmuch variation in particles’ size, particles are tend to agglomerate owing to non-uniform distribution of attraction forces between the filler and polymer matrix. It is as well determined that immoderate amount of calcium carbonate increases the hysteresis and worsens the quality of the final product. For the production of flexible polyurethane foams, authors Agarry *et al.* (2015) have used fractioned calcium carbonate particles (0.06  $\mu\text{m}$ , 0.5  $\mu\text{m}$ , 3.5  $\mu\text{m}$ , 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , 841  $\mu\text{m}$ ) as filler with the varying amounts from 5 wt.% to 40 wt.%. They have determined that increasing amount of filler reduces tensile strength by  $\sim 75\%$  independently from the size of particles. Too much filler determines poor dispersion of particles and the formation of agglomerates what causes the stress concentration in polymeric matrix. The similar tendency of reducing tensile strength for flexible polyurethane foams reinforced with  $\text{CaCO}_3$  has been observed by Usman *et al.* (2012). Therefore,

the application of some coupling agents and chain extenders such as titanates and propylene glycol from rapeseed glycerine (RPG) has been studied in order to overcome poor dispersion, non-uniformity of properties as well as excessive shrinkage after production and under the higher temperature and relative humidity conditions of reinforced and filled polyurethane foam composites.

The aim of this study is to choose the proper amount of water according to the requirements applied to factory made rigid polyurethane foams, and reduce the shrinkage by using chain extension with RPG and obtain PWS filled polyurethane foam composite characterised by sufficient dimensional stability and mechanical properties.

## 1. Experimental

### 1.1. Materials and methods

Polyester polyol synthesised from rapeseed oil by chemo-enzymatic route using lipase Novozym 435 (LLC IMD Technologies, Lithuania) is implemented. It has hydroxyl value of 323 mg KOH/g. For the research of shrinkage and dimensional stability, RPG (Dow, Germany) is used as co-polyol in the production of polyurethane foam. 4,4'-diphenylmethane diisocyanate Lupranat M20S (BASF, Germany) with the functionality of 2.7 and reactive groups' content of 31.5% is used as a hardener. In order to adjust the characteristic foaming times, blowing and gelling catalysts Lupragen N101 (BASF, Germany) and Lupragen DMI (BASF, Germany) are applied. Water is used as an ecological alternative for traditional blowing agents. Surfactant Tegostab B 1048 (Evonik, Germany) is used in order to obtain uniform structure. For the promotion of adhesion between polymer matrix and PWS particles, titanate coupling agent TCA-K44 (Capatue Chemical, China) is added. PWS particles are obtained from JSC Grigiskes, Lithuania. They are a mix wastes from hygienic and packing paper, honeycomb filler, corrugated cardboards as well as packages, and they form in the waste water cleaning equipment.

International standard ASTM D7487: 2016 is used in order to test polyurethane foams for cream, gel and tack-free times by cup test method. Length and width of specimens are determined according to EN 12085:2013, density – based on EN 1602 (2013) requirements. Compressive stress at 10% deformation or

compressive strength up to 10% deformation (further compressive strength) and tensile strength are determined for specimens with the size of (50×50×50) mm in accordance with the requirements of EN 826:2013 and EN 1607:2013, respectively, using universal testing machine H10KS Hounsfield. The direction of loading during compression and tension is perpendicular to the foaming direction. Before the tensile strength determination, specimens have been glued to (100×50) mm sized metal plates and conditioned for 24 h at (23±5) °C temperature and (50±5)% relative air humidity conditions. In order to obtain average value of compressive and tensile strengths, 10 specimens from each sample are tested. Primary shrinkage is evaluated for specimens having the size of (400×400×50) mm after 0.5 h and 1 day after production by measuring length and width at the same position. The numerical value of shrinkage is calculated according to Eq. (1):

$$\Delta\varepsilon = \frac{b_1 - b_2}{b_1} \cdot 100, \quad (1)$$

where:  $\Delta\varepsilon$  – shrinkage in the direction of length, width or thickness, %;  $b_1$  – length, width and thickness after 0.5 h after production, mm;  $b_2$  – length, width and thickness after 1 day after production, mm. For the evaluation of average shrinkage, three specimens of each sample are tested. Dimensional stability test is carried out according to EN 1604:2013. Specimens have been held at (70±2) °C temperature and (90±5)% relative humidity conditions for 48 h in climatic chamber Feutron 3522/51. For each sample, three specimens with the size of (100×100×50) mm are tested. In order to evaluate the impact of PWS on polyurethane foam composites' structure, scanning electron microscope (SEM) JEOL JSM-7600F with the resolution of 1.5 nm and magnification capability from 25 to 1000000 times is implemented. Before the test, specimens are coated with thin layer of gold under vacuum using apparatus QUORUM Q150R ES. For the calculation of percentage amount of closed cells, standard EN ISO 4590 (2 method) is used for three specimens from each composition. The size of specimens is of (100×30×30) mm. Quantitative analysis of PWS is carried out using X-ray fluorescence spectroscopy method with Axios mAX. Particles have been compressed into 37 mm diameter tablets. Moisture content of PWS particles is determined with analyser A&D MX-50. Three 10 g weighting specimens are used to obtain average value.

## 1.2. Preparation of RPG extended and PWS modified polyurethane foam composites

For the selection of proper amount of water, following amounts of water, pbw: 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0 are used. Compositions of polyurethane foam and its composites are presented in Table 1 and Table 2.

Table 1. Composition of polyurethane foams modified with different amounts of water

Material	Amount of the materials, pbw
Component A	
Polyol	100
Distilled water <sup>a</sup>	1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0
Lupragen N101	1.8
Lupragen DMI	1.2
Tegostab B 1048	2
Component B	
Isocyanate	Isocyanate index <sup>b</sup> 125

Notes: <sup>a</sup>Different amount of water is evaluated into calculation of isocyanate required to react with all hydroxyl groups; <sup>b</sup>isocyanate index is the ratio of equivalent and theoretical isocyanate amounts multiplied by 100.

Table 2. Composition of polyurethane foam composites extended with RPG and modified with PWS

Material	Amount of RPG <sup>a</sup> , pbw		
	10	15	20
Component A			
Polyol	90	85	80
Distilled water	3	3	3
Lupragen N101	1.8	1.8	1.8
Lupragen DMI	1.2	1.2	1.2
Tegostab B 1048	2	2	2
PWS/TCA K-44 (1%)	0; 5; 10; 15; 20 wt.%		
Component B			
Isocyanate	Isocyanate index 125		
Re-calculated amount of water taking into account moisture in RPG <sup>b</sup>	2.76	2.77	2.77

Notes: <sup>a</sup>Hydroxyl value of RPG is taken into account when calculating the required amount of isocyanate; <sup>b</sup> Overall moisture content in polyol and RPG is recalculated for the amount of water needed to foam the specimens.

For the production of polyurethane foams with different amounts of water, polyol, catalysts and surfactant have been mixed for 1 min at a speed of 1800 rpm. The obtained mixture has been divided into 10 equal portions. Into each of 10 parts, required amount

of water has been poured. The final mixture of the materials is so called Component A, and it has been mixed for another 1 min before the pouring a Component B – isocyanate.

For the production of polyurethane foam composites, 10 pbw, 15 pbw and 20 pbw of polyol is replaced by RPG. It has been mixed with polyol, catalysts, surfactant for 1 min at a speed of 1800 rpm. The obtained mixture has been divided into 3 equal portions. Into each of them, the required amount of water and titanate modified PWS particles are poured. The obtained Component A has been mixed for 1 min at the same speed. Further, scaled amount of Component B is added. The obtained mixture has been mixed for another 10 s and poured into (400×400×100) mm sized mould where it has been allowed to freely expand at (23±5) °C temperature. The obtained samples have been stored for 24 h, demoulded and cut into proper size specimens. Before the tests, specimens have been conditioned for 24 h at (23±5) °C temperature and (50±5)% relative air humidity conditions.

## 2. Results and discussion

### 2.1. Characterisation of PWS particles

PWS particles are characterised by high moisture content (39%), organic matter (wood (Fig. 1a), cellulose fibers, lignin and in some cases organic binder) and

mineral loading (Fig. 1b) consisting of calcium carbonate (CaCO<sub>3</sub>), kaolinite, talc, dolomite (Kairytė et al. 2016), however, chemical composition and physical properties vary depending on the quality of the paper, technology of waste water cleaning and fresh water usage specifics (Zule et al. 2007).

Milled and sieved through 0.63 mm sized sieve PWS particles have been exposed at 70 °C temperature for 24 h. The moisture content of dried particles is determined to be 1.5%. Conducted quantitative analysis (Table 3) shows that the most of PWS particles consist of CaCO<sub>3</sub> which in paper production industry is used as whiteness, stiffness and smoothness promoter.

It is previously determined (Kairytė et al. 2016) that the size of PWS particles varies from 0.4 µm to 629 µm. Additionally to the results of quantitative chemical analysis made by X-ray fluorescence in Table 3, there are (21.1 –24.3)% of organic matter, i.e. cellulose, hemicellulose, lignin.

### 2.2. Selection of water amount for the preparation of polyurethane foam composites

For the production of polyurethane foam composites, the amount of water is determined according to the results of dimensional stability at 70 °C temperature and 90% relative humidity conditions (further dimensional stability), shrinkage after 1 day after production (further shrinkage) and apparent density. The conducted

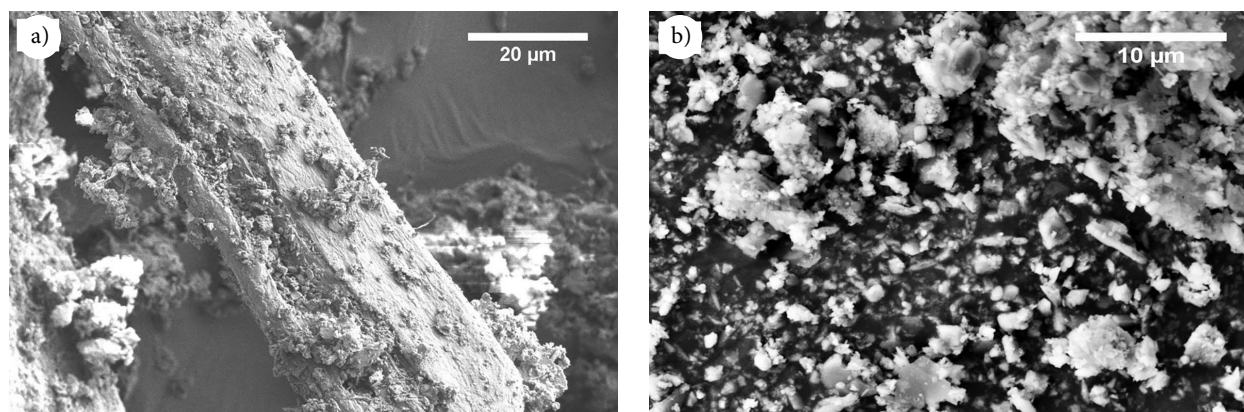


Fig. 1. SEM images of PWS particles: a) organic matter (magnification of ×2000); b) inorganic matter (magnification of ×3000)

Table 3. Quantitative chemical composition of PWS particles

Amount, wt.%									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Other <sup>a</sup>
5.8–6.0	4.6–4.8	48.5–49.5	0.4–0.5	0.5–0.6	0.03–0.04	0.14–0.15	0.17–0.20	0.05–0.06	13.9–18.7

Note: <sup>a</sup>Cl, MnO, NiO, CuO, ZnO, Br, Rb<sub>2</sub>O, SrO, BaO, Nb<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>.

research has shown that apparent density of polyurethane foam depends on the amount of water. Figure 2 shows the dependence of apparent density on the amount of water in Component A from 1.0 pbw to 6.0 pbw in step of 0.5 pbw.

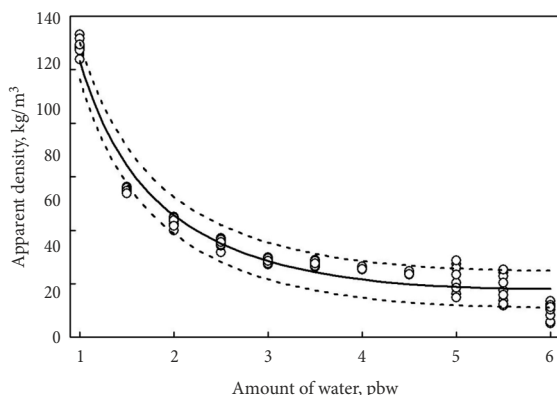


Fig. 2. The dependence of polyurethane foam's apparent density on the amount of water:  $\circ$  – experimental data; (—) – regression line (Eq. 2); (-----) – prediction line

In order to evaluate the relationship between these two factors, mathematical-statistical analysis is conducted. It allows quantitative evaluation of the change in apparent density which depends on the change in the amount of water. Average values of polyurethane foam's apparent density may be described by regression equation (Eq. (2)) with the standard deviation of  $S_{\bar{\rho} \rightarrow m} = 5.32 \text{ kg/m}^3$  when  $n = 110$ .

$$\bar{\rho} = -1.861 + 3.252 \cdot m + \frac{122.9}{m}, \quad (2)$$

where:  $\bar{\rho}$  – an average value of apparent density,  $\text{kg/m}^3$ ;  $m$  – the amount of water in Component A, pbw. Pre-

dicted two-tailed confidence interval of the results is  $\rho_{pred.} = \bar{\rho} \pm \delta$  with the possibility of  $P = 0.95$  and Student's criterion  $t_{0.05} = 1.66$  when  $\alpha = 0.05$  (Fig. 2 the dotted line). The obtained determination coefficient  $R^2 = 0.958$  shows that polyurethane foam's apparent density by 95.8% depends on the amount of water and the rest 4.2% on other, e.g. technological factors.

Increasing the amount of water from 1.0 pbw to 6.0 pbw, apparent density has averagely reduced from  $128.7 \text{ kg/m}^3$  to  $30.1 \text{ kg/m}^3$ , i.e. by approx. 76.6%. Whereas  $\text{CO}_2$  gases form during the water and isocyanate reaction, increasing the amount of water increases the concentration of  $\text{CO}_2$  gases in air bubbles formed during the mixing. It determines greater foaming capability, thus foams are characterised by lower apparent density. The research of Thirumal *et al.* (2008) has shown that similar tendency of the change in apparent density when water amount is increased from 0 pbw to 3.0 pbw is observed. The density has averagely reduced from  $116 \text{ kg/m}^3$  to  $42 \text{ kg/m}^3$ , i.e. by approx. 63.8%. Comparing the results with other authors at water amounts varying from 1.0 pbw to 3.0 pbw, the average reduction in apparent density is, respectively, 53.3% and 62.3%. The difference arises due to the use of different raw materials. It is as well observed from Figure 1 that scattering of apparent density results for polyurethane foams when the amount of water varies from 5.0 pbw to 6.0 pbw is sufficiently high. It may be attributed to non-homogeneity of the final product.

The additional research of dimensional stability and shrinkage has been conducted (Fig. 3). It may be observed that the increase in the amount of water from

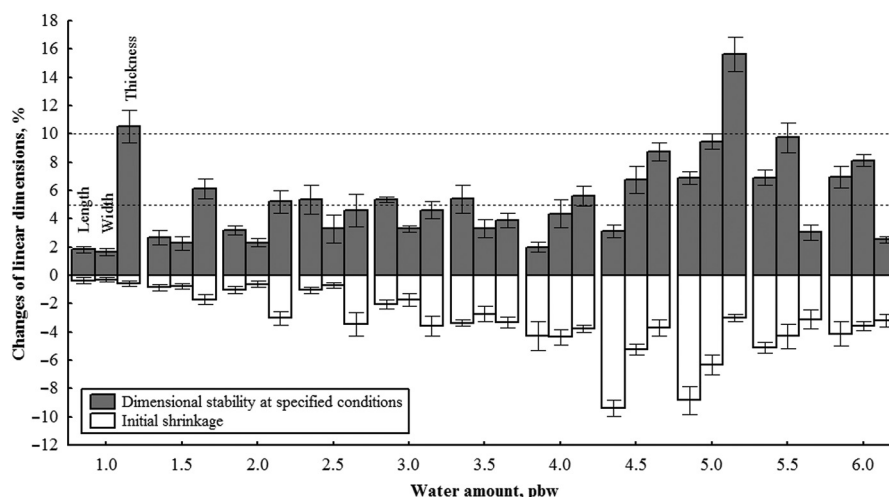


Fig. 3. The dependence of the change in polyurethane foam's linear dimensions on the amount of water: (-----) – maximum allowable changes in dimensions in the directions of length, width and thickness according to EN 13165:2012+A2:2016

1.0 pbw to 6.0 pbw increases the shrinkage. It means that the structure of the final product is not sufficiently stiff for the assurance of equilibrium in pressure difference between cellular structure and the surrounding environment. The intensity of these shrinkages depends on the amount of water used in the forming mixture as well as the nature of cellular structure (closed cell or open cell). The increase in the amount of water determines the polyurethane foams' structure characterised by larger closed cells as well as thinner cells' walls, and it means that the diffusion of CO<sub>2</sub> gases through thinner walls is more intense, thus increasing the shrinkage of the final product (Xiaobin *et al.* 2008).

All materials more or less expand and shrink under the changing temperatures. Figure 3 presents the results which may be divided into the three main zones: from 1.0 pbw to 3.0 pbw, from 3.5 pbw to 5.0 pbw and from 5.5 pbw to 6.0 pbw. Conducted research on shrinkage shows the increase in the change of dimensions where the amount of water varies from 1.0 pbw to 3.0 pbw. Polyurethane foams with the greatest apparent density have stiff cellular structure which is characterised by thicker walls. It constrains the penetration of CO<sub>2</sub> gases into the surrounding environment what determines low shrinkage. However, the rest gases located in the cells of the product exposed to higher temperature and humidity diffuses out ruining the structure what influences the negative dimensional changes during the dimensional stability test, i.e. 0.4% from shrinkage test and additional 10.6% in the thickness direction from dimensional stability test when the amount of water during production is of 1.0 pbw.

Contrary tendency is observed for products where the amount of water varies from 3.5 pbw to 5.0 pbw. It is explained by decrease in the amount of water needed to foam products with lower apparent density. As a consequence, cell walls in the structure become thinner, the rate of CO<sub>2</sub> gases diffusion and their induced dimensional changes after production and during the dimensional stability test intensify. The reduction in the change of linear dimensions may be observed in the interval from 5.5 pbw to 6.0 pbw. In case of lower amount of water, e.g. 5.0 pbw and less, isocyanate amount in the forming mixture is sufficiently low in order to assure the compatibility, uniform mixing and proper reaction start time between these two components (Table 4).

Further increase in the amount of water increases the amount of isocyanate. This material is hydrophobic, consequently, increasing amount of it and water, does not assure the sufficient compatibility what is showed by delayed cream time. It means that the reaction rate of polymer formation is slower than the blowing rate. When the gel reaction finishes, polymeric carcass is not sufficiently firm in order to withstand the further growth of cells; therefore, partial destruction of cells is observed what results in an increase of open cell content. CO<sub>2</sub> gases diffuse out of the product structure without ruining it due to partially open cell structure. Hereby, shrinkage and dimensional changes under higher temperature and humidity conditions are reduced. Evaluation of the obtained results for apparent density, shrinkage and dimensional stability indicates that the most suitable amount of water is 3.0 pbw.

Table 4. Characteristic foaming times and structural parameters of polyurethane foams

Amount of water, pbw	Parameter				
	Cream time, s	Gel time, s	Tack-free time, s	Cell size, mm	Closed cell content, %
1.0	27±2	91±2	190±4	0.125±0.03	90.2±3.2
1.5	28±1	98±3	198±2	0.130±0.04	89.3±2.8
2.0	31±3	98±1	200±3	0.132±0.05	89.0±4.1
2.5	35±3	99±2	210±4	0.145±0.03	89.1±3.6
3.0	37±4	102±4	215±3	0.152±0.02	88.0±4.7
3.5	40±3	114±4	231±1	0.201±0.04	87.4±2.6
4.0	44±2	118±2	235±2	0.264±0.03	88.2±1.8
4.5	49±2	124±3	239±3	0.320±0.06	88.6±4.0
5.0	51±4	131±3	254±2	0.476±0.05	87.4±3.7
5.5	51±4	134±3	261±2	0.558±0.06	74.2±2.4
6.0	53±2	139±2	268±3	0.720±0.06	70.5±2.1

### 2.3. Characterisation of RPG extended and PWS modified polyurethane foam composites

The determined proper amount of water which is 3.0 pbw, is used for the following research of mechanical properties and shrinkage of PWS filled and RPG extended polyurethane foam composites. Density is one of the most important parameters which determines the all mechanical properties of almost all materials and its values depending on the amount of PWS are presented in Table 5. It can be clearly seen that increasing amount of PWS increases the density of the obtained polyurethane foam composites. As it has been determined by the previous research of authors (Kairytė *et al.* 2016), the bulk density of PWS particles is 480 kg/m<sup>3</sup>; therefore, the increase in an apparent density at the amount of 20 wt.% of PWS is ~78% for 10-RPG composites, ~15% for 15-RPG composites and ~21% for 20-RPG composites comparing to the neat polyurethane foam. A typical effect of the addition of inorganic particles to the reaction mixture is an increase in viscosity. The filler can induce a decrease in the reactivity of the components in the system, affecting the foam expansion, thus increasing the density of the cellular materials.

It is well known that the compressive strength is mainly influenced by the density of material, and Table 5 shows the numerical values of the mentioned parameter as well as tensile strength. Increasing com-

pressive strength indicates greater bonding between PWS particles and polymeric matrix, thus anticipating better stress transfer from matrix to the filler. Compressive strength of PWS filled polyurethane foam composites at a maximum concentration of PWS has increased by ~53% for 10-RPG composites, by ~31% for 15-RPG composites and by ~23% compared to the neat polyurethane foam. The increase tendency of compressive strength reduces with the increase of RPG from 10 pbw to 20 pbw, and this could be attributed to the fact that RPG makes resultant foams more friable, thus reducing the interfacial adhesion between PWS particles and polymer. This can be observed as well from the results of tensile strength. 10 pbw of propylene glycol in polyol mixture does not affect the tensile strength of resultant composites; therefore, the increase of tensile strength values may be seen at PWS amount varying from 5 wt.% to 15 wt.%. The improved mechanical performance may be attributed to the efficient homogeneity of thermoplastic polymer matrix, reinforcing effect and sufficient dispersion of particles as well as matrix which inhibited the agglomeration and allowed uniform distribution of stress (Nandi *et al.* 2013) due to modification of PWS particles with 1% of coupling agent, however, 20 wt.% of PWS reduced the mentioned parameter due to increased viscosity of the mixture and enlarged capability of PWS particles to agglomerate what can be seen from Figure 4.

Table 5. Apparent density and mechanical properties of RPG extended and PWS filled polyurethane foam composites

Amount of PWS, wt. %	Apparent density, kg/m <sup>3</sup>	Compressive strength, kPa	Tensile strength, kPa
10-RPG			
0	37.7±5.5	177.7±13.4	191.2±11.5
5	41.7±1.2	224.3±14.1	245.7±8.72
10	44.5±6.9	228.0±16.1	368.3±9.23
15	54.2±1.5	248.3±14.1	375.3±10.5
20	67.4±3.2	271.4±14.9	253.8±13.4
15-RPG			
0	42.1±1.6	184.7±17.7	260.3±17.8
5	42.2±2.4	215.6±9.74	235.2±9.14
10	43.4±2.9	237.3±12.2	231.8±11.0
15	45.6±2.6	241.3±7.80	219.3±15.7
20	48.3±3.0	242.5±18.3	197.2±13.6
20-RPG			
0	41.3±1.1	186.9±15.1	295.1±8.12
5	42.1±1.1	193.3±13.5	285.3±12.9
10	42.9±2.1	197.0±15.3	253.5±12.3
15	44.9±1.7	207.0±14.5	241.0±16.7
20	50.0±3.5	229.4±13.3	236.9±15.2

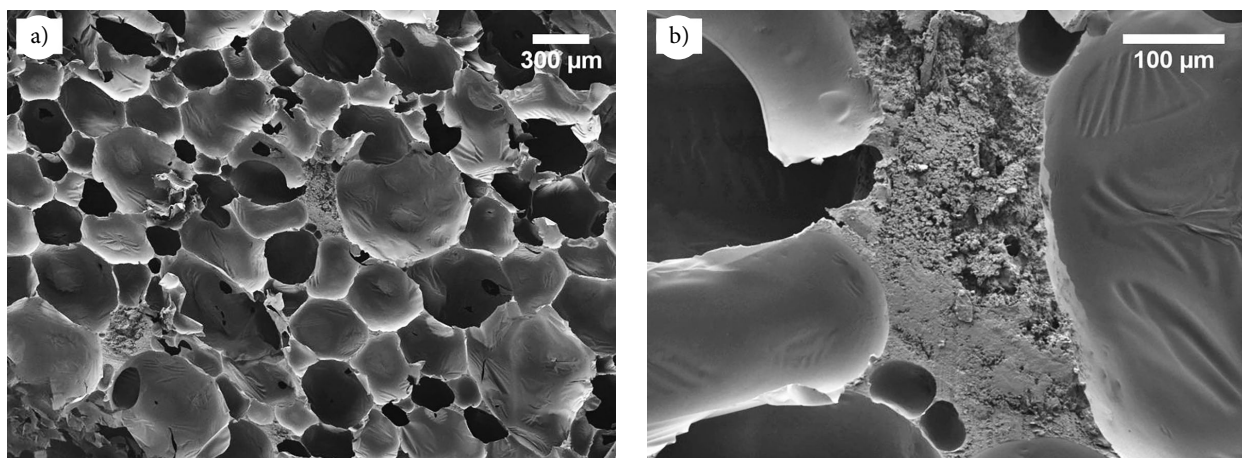


Fig. 4. Microstructure of 10 pbw of RPG extended and 20 wt.% of PWS filled polyurethane foam composite parallel to the foaming direction: a) at  $\times 35$  magnification; b) agglomerate of PWS particles at  $\times 200$  magnification

Further increase in RPG from 15 pbw to 20 pbw worsens the tensile strength of PWS filled composites by  $\sim 24\%$  for 15 pbw of RPG extended composites and by  $\sim 20\%$  for 20 pbw of RPG extended composites compared to the neat polyurethane foam.

The agglomerates, as it is observed from Fig. 4a, are not distributed evenly throughout all microstructure; they are heterogeneous and have rough granulometry. The similar results have been obtained by authors (Sá e Sant'Anna *et al.* 2008) for composites filled with coupling agents unmodified particles.

There is only few information on such properties as dimensional stability of polyurethane foams or their composites. In order to assure the reliability of such properties for polyurethane foams from polyols obtained using natural oils, scientist use higher functionality having petroleum polyols (Kurańska *et al.* 2016), however, it is now of great importance to increase the bio-based matter in polymer systems. The modification of polyurethane foams with RPG with the varying amounts from 10 pbw to 20 pbw is basically conducted in order to reduce the excessive shrinkage of the filled polyurethane foam composites. Figure 5 presents the results of the shrinkage after 1 day after production and dimensional stability at higher temperature and humidity conditions.

It is clear that the increase in RPG reduces the shrinkage and expansion of the obtained composites. As it is seen from Figure 5a, the expansion in length and width directions after dimensional stability at higher temperature and humidity conditions test may be observed for foams with 10 pbw of RPG compared to 15 pbw and 20 pbw of RPG extended foam com-

posites. Basically, the difference between the levels of expansion may be explained by the higher content of closed cells (Table 6).

The strictest requirements of product standard EN 13165:2012+A2:2016 indicate dimensional changes of 1% for length and width as well as 4% for thickness. Taking into consideration the standard deviation and the two-tailed prediction of the results, the requirements are fulfilled by composites extended with 20 pbw of RPG. Furthermore, polyurethane foam composites extended with 10 pbw and more gives products without shrinkage, and it is controlled by urethane hard segments content which increases with the increase in the amount of RPG. The above results also indicate that the addition of low molecular weight RPG into higher molecular weight having rapeseed polyol allow obtaining foams with more stable structure at higher temperature and humidity conditions.

## Conclusions

Regarding the dimensional stability, primary shrinkage after 1 day after production and density, the most suitable amount of water is 3 pbw. This is the marginal value of the amount of water when the maximum change does not exceed the limits, respectively  $\leq 5\%$  in the directions of length and width as well as  $\leq 10\%$  in the direction of thickness according to the requirements of EN 13165 for factory made rigid polyurethane foams, and density ( $48.5 \text{ kg/m}^3$ ) is proper to use such foams for thermal insulating purposes in building envelopes. Such amount of water has been used for the production of RPG extended and PWS particles filled polyurethane foam composites. The obtained results have



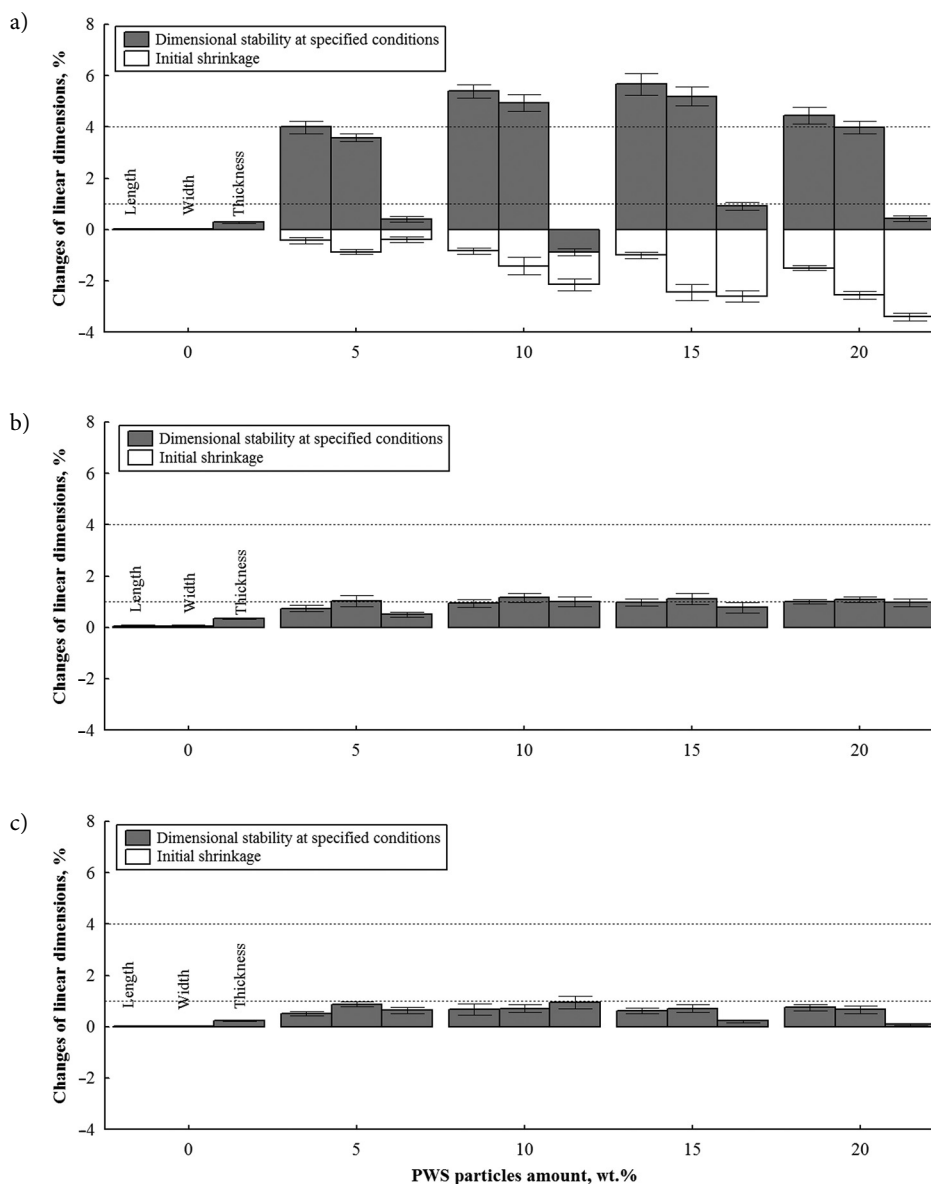


Fig. 5. Shrinkage and dimensional stability of PWS filled polyurethane foam composites modified with a) 10 pbw; b) 15 pbw and c) 20 pbw of RPG. (-----) – minimum allowable changes in dimensions in the directions of length, width and thickness according to EN 13165:2012+A2:2016

Table 6. Closed cell content of RPG extended and PWS filled polyurethane foam composites

Parameter	Amount of RPG, pbw	Amount of PWS, wt.%				
		0	5	10	15	20
Closed cell content, vol. %	10	64.4±4.7	79.1±3.6	80.9±1.2	84.3±2.2	92.3±4.8
	15	31.3±2.4	77.0±4.2	78.9±3.7	80.4±2.4	82.6±4.0
	20	18.5±2.4	77.2±2.8	78.5±2.3	79.1±4.2	80.5±3.8

shown that 20 pbw of RPG allow obtaining composites with the sufficient dimensional stability and no shrinkage. The addition of titanate coupling agent modified PWS particles from 5 wt.% to 20 wt.%, increases the compressive strength of the final composites from ~26% to ~53%, from ~17% to ~31% and from ~3%

to ~23% for, respectively, 10 pbw, 15 pbw and 20 pbw RPG extended foam composites. It is shown that PWS amount of up to 20 wt.% as well as 15 pbw and 20 pbw of RPG can be used in order to obtain dimensionally stable water blown thermal insulation for building envelopes in the form of slab stocks.

## Disclosure statement

Authors declare that they do not have any competing financial, professional, or personal interests from other parties.

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