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Research Paper

# Rapeseed-based polyols and paper production waste sludge in polyurethane foam: Physical properties and their prediction models

Agnė Kairytė[a,*], Saulius Vaitkus[a], Sigitas Vėjelis[a], Giedrius Girskas[b], Giedrius Balčiūnas[a]

[a] Vilnius Gediminas Technical University, Scientific Institute of Thermal Insulation, Laboratory of Thermal Insulating Materials, Linkmenu st.28, LT, 08217, Vilnius, Lithuania

[b] Vilnius Gediminas Technical University, Scientific Institute of Thermal Insulation, Laboratory of Building Products Technology, Linkmenu st. 28, LT, 08217, Vilnius, Lithuania

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ABSTRACT

Intervention into the present building industry is the main strategy of the European Commission in order to achieve one of its planned aims regarding the reduction of greenhouse gas emissions up to 20% up by 2020 and up to 80% by 2050. Therefore, it is necessary to develop not only energetically efficient but also more environmentally friendly materials. This work presents bio-based propylene glycol and paper waste sludge particles modified polyurethane foams, their physical properties and their prediction models. The conducted research has revealed that paper waste sludge particles negatively affect dimensional changes. In order to eliminate the negative impact of paper waste sludge, bio-based propylene glycol is used. The obtained results have shown that this raw material allows development of dimensionally and structurally stable polyurethane foams used as a thermal insulating layer having the following properties: density in the range of 40–50 kg/m$^3$, compressive strength in the range of 193–243 kPa, thermal conductivity in the range of 0.0349–0.0359 W/(m·K), long-term water absorption in the range of 6–11 vol.% and water vapour transmission factor in the range of 26.2–40.9. On the basis of the results, prediction models are suggested for the most important physical properties of propylene glycol and paper production waste sludge particles modified polyurethane foams.

## 1. Introduction

Intervention into the present building industry is the main strategy of the European Commission in order to achieve one of its planned aims regarding the reduction of greenhouse gas emissions up to 20% by 2020 and up to 80% by 2050 (General Assembly, 2015). Therefore, increasing requirements for the energy efficiency of buildings that covers not only the improvement of thermal insulating properties of materials but also production and installation costs forces the building materials sector to seek not only energetically but also more environmentally friendly materials.

Polyurethane foam is a versatile material, and petroleum-based polyols used for the production of foam may be replaced by polyols from biomass (e.g., rapeseed, castor, soy, hemp and sunflower oils) (Özveren and Seydibeyoğlu, 2017; Ng et al., 2017; Rojas et al., 2017; Li et al., 2017a,b). Polyols intended for the production of rigid polyurethane foams must conform to the following requirements: functionality > 3, molecular weight < 1200 g/mol and hydroxyl value varying from 350 mg KOH/g to 600 mg KOH/g. If these requirements are conformed, polyols will become a cheap and environmentally friendly alternative to traditional petroleum-based polyols (Zieleniewska et al., 2015; Luong et al., 2016). However, in the case of non-conformity, such polyols determine polyurethane foams having high initial shrinkage and sensitivity to higher temperature and moisture conditions (Girotti, 2013; Zarzyka, 2014).

For the improvement of properties of polyols and the final products obtained, low molecular weight glycols may be incorporated. In terms of bio-based products, there are only a few published research works concerning the application of environmentally friendly chain extenders for the production of polyurethane foams. Rashmi et al., 2013 have used corn sugar to synthesise 1,3-propanediol, which has low molecular weight (76 g/mol) and functionality equal to 2. Moreover, Datta and Głowińska, 2014 have used the hydroxylation method to obtain 1,2- and 1,3-propanediols from rapeseed glycerine (RPG). The use of bio-glycols in polyurethane synthesis has had a significant impact on their properties; therefore, the investigations on structure-property dependencies in various polyurethane products are currently of great interest among various researchers (Septevani et al., 2017; Serrano et al.,

* Corresponding author.
*E-mail addresses:* agne.kairyte@vgtu.lt (A. Kairytė), saulius.vaitkus@vgtu.lt (S. Vaitkus), sigitas.vejelis@vgtu.lt (S. Vėjelis), giedrius.girskas@vgtu.lt (G. Girskas), giedrius.balciunas@vgtu.lt (G. Balčiūnas).

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2017; Sung and Kim, 2017).

Conversely, the use of renewable resources, especially industrial waste systems, is a perfect alternative for the production of thermal insulating materials and their composites (Hejna et al., 2016; Zhang et al., 2013; Estravís et al., 2016; Formela et al., 2017), which basically contributes to one of the sustainable development aims – reduction and reuse of waste. Therefore, the intensive efforts on how accumulating paper production waste sludge (PPWS) arising from the wastewater treatment process can be used in the same or other industrial areas in order to obtain products characterised by the same or even better properties (Joshi et al., 2017; Fang et al., 2017). It has been noticed by Bajpai (2015) that thermally treated PPWS is extremely porous; therefore, it could positively affect the main property of thermal insulating materials – thermal conductivity. However, according to our best knowledge, there is no information on the application of this waste for the improvement of thermal insulating materials properties. Still, some studies have been carried out to investigate the impact of the main components in PPWS particles on polyurethane foams. Sá e Sant'Anna et al., (2008) have tested the impact of calcium carbonate ($CaCO_3$) on polyurethane foams. The obtained results have shown that increasing the amount of 100–250 μm-sized particles from 1 wt.% to 30 wt.% reduces the capacity of even distribution due to immoderate particle size variation, and the particles tend to agglomerate because of uneven distribution of the attractive forces between the filler and polymer matrix. It has also been determined that too high an amount of $CaCO_3$ increases hysteresis and worsens the quality of the final product. Agarry et al., 2015 have used fractioned $CaCO_3$ particles (0.06 μm, 0.5 μm, 3.5 μm, 10 μm, 20 μm and 841 μm) as filler, which varied in amount from 5 wt.% to 40 wt.%. It has been determined that the use of a high amount of filler determines poor distribution of particles and formation of agglomerates, which enables the occurrence of stress concentration. Latinwo et al., 2010 have noticed that polyurethane foam without $CaCO_3$ filler was characterised by an uneven structure and larger cells. The formation of which is determined by homogeneous nucleation requiring higher activation energy, whereas the use of filler enables the formation of gases between the particle and polymer matrix. These gases allow the formation of microbubbles, which reduce the activation energy required for cell formation in the polyurethane foam structure.

With respect to sustainability, the use of renewable resource-based polyols and inorganic as well as organic waste systems for the production of polyurethane foams or their composites is presently relevant. In order to use such products in the building industry, it is important to conduct additional scientific research allowing the determination of possibilities to obtain dimensionally and structurally stable products that are environmentally friendly and conform to energy efficiency principles. Therefore, the aim of this research is to develop and test dimensionally stable RPG and PPWS particles modified polyurethane foams and describe the models that could be used for the prediction of its main physical properties.

## 2. Materials and methods

### 2.1. Materials

The basis of the polyurethane foam was rapeseed oil-based polyester polyol from JSC IMD Technologies, Lithuania with a hydroxyl value of 323 mg KOH/g, functionality of 2.7 and water content of 0.25%. RPG was used as a chain extender obtained from ADM Industrials, Germany with a hydroxyl value of 1474 mg KOH/g, functionality of 2 and water content of 0.13%. Distilled water was used as blowing agent. 4,4'–diphenylmethane diisocianate (Lupranate M20S) (BASF, Germany) was used as a polyurethane foam hardener with average functionality of 2.7 and amount of reactive groups at 31.5%. PPWS obtained from the wastewater treatment process was collected from Grigiškės Ltd., Lithuania. Its quantitative and qualitative composition was (wt.%): $SiO_2$ (5.8–6.0), $Al_2O_3$ (4.6–4.8), CaO (48.5–49.5), MgO (0.4–0.5), $Fe_2O_3$ (0.5–0.6), $Na_2O$ (0.03–0.04), $K_2O$ (0.14–0.15), $SO_3$ (0.17–0.20), $P_2O_5$ (0.05–0.06), organic matter (21.1–24.3) (mainly composed of cellulose, hemicellulose and lignin (wood and paper fibres) as well as polyethylene (wrapping paper)) and other compounds (13.9–18.7; Cl, MnO, NiO, CuO, ZnO, Br, $Rb_2O$, SrO, BaO, $Nb_2O_5$ and $Cr_2O_3$).

The main properties were thermal conductivity (0.084 ± 0.0015 W/(m·K)), bulk density (0.48 ± 0.044 g/cm$^3$), water content (1.5 ± 0.162%) and particle size (0.04–629 μm). Titanate coupling agent (TCA) K44 (Capatue Chemicals, China) was used for the modification of PPWS particles. Catalysts Lupragen N101 (BASF, Germany) and Lupragen DMI (BASF, Germany) were used in order to balance blowing and gelling reactions. For the formation of cellular structure, surfactant Tegostab B 1048 (Evonik, Germany) was used.

### 2.2. Research methods of PPWS

Structural research of coupled and non-coupled PPWS particles was carried out using a scanning electron microscope (JEOL JSM-7600F) with a resolution of 1.5 nm and magnification from 25 times to 1 million times. Before the research, particles were coated with a thin gold layer under a vacuum environment using the QUORUM Q150R ES. For the verification of successful coating, energy dispersive spectrography was additionally used. Local chemical composition was determined in accordance with induced characteristic X-ray spectrums. The amount of organic matter in PPWS particles was determined based on EN 13820 requirements by drying at 105 ± 5 °C and burning at 500 ± 10 °C. The granulomeric composition of PPWS was evaluated using the Cilas 1090 LD apparatus. Water content was analysed with A&D MX-50. For the determination of bulk density, the standard method described in EN 1097–3 was implemented. Thermal conductivity of particles was determined based on the requirements of EN 12667 using a heat flow meter (FOX 304) with active specimen edge protection. Thermal conductivity was measured at an average temperature of 10 °C when the difference between upper and lower plates was 20 °C (temperature of the cold plate was 0 °C and that of the hot plate was 20 °C).

### 2.3. Preparation of RPG and PPWS particles modified polyurethane foams

PPWS was dried at 70 ± 5 °C for 24 h. Dried stone-shaped PPWS was crushed, milled and sieved through 0.63 mm-size sieve. The solution of isopropyl alcohol and 1 wt.% of TCA was poured into well-agitated PPWS particles and mixed for 30 min. Then, the obtained mixture was dried at 100 ± 5 °C for 48 h and at ambient temperature for an additional 24 h.

The selected proper amounts of raw materials for the preparation of RPG and PPWS particles modified polyurethane foams are presented in Table 1.

For the production of polyurethane foams, 10%, 15% and 20% of bio-polyols were replaced by RPG. First, RPG was mixed with polyols, catalysts and surfactant for 1 min at 1800 revolutions per minute (rpm). Then, the required amount of water and titanate coupled PPWS particles were added. The obtained component A was additionally mixed for 1 min at 1800 rpm. Further, a scaled amount of component B was added to component A and mixed for another 10 s. The obtained mixture was poured into a 400 × 400 × 100 mm-sized mould and foamed at 23 ± 2 °C. Samples were kept for 24 h before being demoulded and cut into the right sizes. Before the test, specimens were maintained at 23 ± 5 °C and 50 ± 5% relative humidity for 24 h.

### 2.4. Research methods of RPG and PPWS particles modified polyurethane foams

For the balance of blowing and gelling reactions, cream, string gel and tack free times as well as the height of specimens were determined according to ASTM D7487 using the standard cup test method. In order