



The influence of crude glycerol and castor oil-based polyol on the structure and performance of rigid polyurethane-polyisocyanurate foams



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ABSTRACT

In this work, biopolyol obtained from two types of industrial crops' processing products: crude glycerol and castor oil was used for preparation of rigid polyurethane-polyisocyanurate foams. Bio-based polyol was obtained via crude glycerol polymerization and further condensation of resulting polyglycerol with castor oil. Rigid polyurethane-polyisocyanurate foams were prepared at partial substitution (0–70 wt.%) of petrochemical polyol with synthesized bio-based polyol. Influence of the biopolyol content on the chemical and cellular structure, insulation properties, static and dynamic mechanical properties, thermal degradation and fire behavior of foams was investigated. Incorporation of crude glycerol-based polyol into formulation of rigid polyurethane-polyisocyanurate foams had beneficial impact on the structure of material reducing average cell size from 372 to 275 μm and increasing closed cell content from 94.0 to 95.7%. Such changes resulted in 7% decrease of thermal conductivity coefficient to 21.8 mW/(mK). Mechanical performance of foams was enhanced by partial substitution of petrochemical polyol with synthesized biopolyol. Compressive strength of modified foam was more than 90% higher than for reference sample. The modifications of foams caused changes in thermal degradation pathway, nevertheless thermal stability of the reference foam was maintained. Incorporation of crude glycerol-based polyol into foams' formulation decreased maximum value of heat release rate by 3.5%, increased char residue after combustion by 24% and reduced emission of toxic carbon monoxide during burning of foam by 35%.

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1. Introduction

Various legislation regulations, such as European Union directives or Provisions of the Kyoto Protocol intend to reduce the greenhouse gases emission (Hoekman et al., 2012). Quite simple and obvious way to inhibit the excessive emission of CO₂ is the use of energy and raw materials from renewable resources. Nowadays, polyurethane (PU) industry is strongly depending on the petroleum, since majority of components used in PU manufacturing is petroleum-based (Allauddin et al., 2016). Nevertheless, petroleum is non-renewable raw material, whose availability will be limited and price will be growing in the future. Having this

in mind, researchers became focused on environmentally friendly efforts, and intensive development of technologies based on ecological materials has started (Arshanitsa et al., 2016; Kairyte and Vejelis, 2015; Tong et al., 2015). Various sources have been investigated as raw materials for biopolyols production, mainly vegetable oils, such as rapeseed, sunflower, palm, coconut, linseed or soybean oils (Amir Uddin and Azad, 2012; Kurańska and Prociak, 2016; Kurańska et al., 2016; Scholz and da Silva, 2008; Zieleniewska et al., 2015). However, these oils are successfully used in food industry and their broader incorporation into PU industry might have unfavorable influence on the price of different food products. That is why scientific and industrial circles have been lately focused on the application (in PU manufacturing) of various by-products from processing of crops and other renewable materials, like the most popular crude glycerol originated from production of biodiesel, which generally is a product of industrial processing of rapeseed oil.

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For each ton of produced biodiesel, around 100 kg of glycerol is obtained (Choi, 2008). Estimating current European production of biodiesel as exceeding 9.5 million tonnes, almost 1 million tonnes of crude glycerol is generated annually in Europe (Puri et al., 2012; Ragauskas et al., 2006). Such glycerol, however, contains various impurities – water, soaps, fatty acids and their esters, methanol and catalyst of transesterification, mainly KOH (Thompson and He, 2006). Detailed composition of crude glycerol depends on the type of used raw materials, applied catalyst and post-reaction processes, such as acidification or demethylation. Incorporation of crude glycerol into PU industry does not require complicated and often expensive purification processes, in contrary to the utilization of glycerol in food, pharmaceutical or cosmetics industry (Yazdani and Gonzalez, 2007). Crude glycerol can be applied in PU manufacturing in various ways, which can be divided into two groups: direct and indirect. Indirect approaches include use of compounds obtained from crude glycerol, such as propanediol and butanediol resulting from microbial conversion (Petrov and Petrova, 2010; Szymanowska-Powałowska, 2014) or glycerol carbonate from glycerol carboxylation or glycerolysis of urea (Casiello et al., 2014; Ezhova et al., 2012; Jagadeeswaraiah et al., 2014; Nguyen and Demirel, 2013). Direct methods include using of biopolyols produced through lignocellulose biomass liquefaction (Cheng et al., 2014; Hu and Li, 2014; Hu et al., 2012) or by polymerization of crude glycerol (Nik Siti et al., 2013). Obviously, simpler and economically more beneficial are direct approaches.

Polymerization process of glycerol can be performed using different types of catalysts (preferably base catalysts) and resulting polyglycerol may be successfully used in preparation of polymeric materials (Salehpour and Dubé, 2012). Various complicated catalysts have been used in glycerol polymerization, such as zeolites (Melero et al., 2012), mesoporous materials (Clacens et al., 2000) or ion-exchange resins (Klepáčová et al., 2005), however the most popular are the simpler ones, metal hydroxides (Salehpour and Dubé, 2011). Microwave irradiation was also applied at polymerization of crude glycerol in order to eliminate the use of catalysts (Nik Siti et al., 2013). Also conditions of the process have noticeable effect on final properties of polyglycerols. Lower reaction temperatures and low pH values result in the formation of cyclic isomers, while at elevated temperatures side reactions show unfavorable influence on color and smell of final products.

Polyglycerols, because of their branched structure can be considered as very interesting substrates for synthesis of highly cross-linked PU materials, such as rigid PU foams (Li et al., 2014).

Ionescu and Petrovic (2010) synthesized polyether polyols based on polyglycerol. First step of the process was polycondensation of pure glycerol in the presence of potassium methoxide or potassium hydroxide. Later, polyglycerols were subjected to propoxylation in order to prepare high functionality polyether polyols. Resulting biopolyols were used in manufacturing of rigid PU foams, which showed good physical and mechanical properties, especially very good dimensional stability and low friability.

Luo et al. (2013) analyzed the influence of process parameters (time and temperature of reaction) and the content of catalyst (sulfuric acid) on the properties of biopolyols produced from crude glycerol. Polyol prepared under preferential conditions (200 °C, 90 min, 3 wt.% of sulfuric acid) was characterized by hydroxyl value of around 480 mg KOH/g, acid number lower than 5 mg KOH/g and viscosity about 25 Pa.s. Subsequently, authors used obtained biopolyols to prepare PU foams, which showed comparable properties to petroleum-based materials – apparent density of 43 kg/m³ and compressive strength of 185 kPa.

In previous work (Piszczyk et al., 2014b) we used two types of commercially available polyglycerols from Eco Innova, named Pole and PGK. Substitution of 35 and 70 wt.% of commercial Rokopol RF551 by polyglycerols resulted in the increase of apparent den-

Table 1

Properties of polyols used for the production of rigid polyurethane-polyisocyanurate foams.

Property	Polyol		
	CG	Lupranol 3300	Lupranol 3422
Density, g/cm ³	1.18	1.05	1.09
Hydroxyl number, mg KOH/g	460	400	490
Viscosity, mPa s	840	373	22750
Water content, wt.%	0.207	0.368	0.301

sity and simultaneous enhancement of mechanical performance of polyurethane foams. Moreover, incorporation of 35 wt.% of polyglycerols did not affect the cellular structure and thermal properties of foams, hardly any changes in cell size, closed cell content and thermal conductivity coefficient were observed.

Majority of the research works focused on the incorporation of bio-based polyols into PU foams. Nevertheless, it seems more interesting to develop formulations for rigid polyurethane-polyisocyanurate (PU-PIR) foams, which are nowadays substituting conventional PU foams, due to their superior thermal properties and fire resistance. Manufacturing of PU-PIR foams requires adjustment of recipe comparing to unmodified polyurethane foams, therefore proper examination of crude glycerol-based polyols is required.

In this work the potential of biopolyol prepared from industrial crops' processing products: crude glycerol (by-product from production of biodiesel, prepared from rapeseed or soybean) and castor oil (obtained from ricinus) in the manufacturing of rigid PU-PIR foams is evaluated. In the light of above mentioned studies, we aimed to examine the possibility of partial substitution of petrochemical based polyol with biopolyol and the influence of its share in polyol mixture (0–70 wt.%) on the chemical (FTIR studies) and cellular (SEM analysis, determination of closed cell content) structure, mechanical (compression tests, dynamic mechanical analysis) and thermal (thermogravimetric analysis, thermal conductivity coefficient measurement) properties and fire behavior of resulting rigid foams.

2. Experimental

2.1. Materials

Bio-based polyol was synthesized from crude glycerol and castor oil. Crude glycerol was acquired from Bio-Chem Sp. z o.o. (Poland), while castor oil was acquired from Pro-Lab (Poland). 85% aqueous solution of orthophosphoric acid was used as a catalyst and 50% aqueous solution of sulfuric (VI) acid was used to neutralize reaction products. Both acids were obtained from POCH S.A. (Poland).

Rigid PU-PIR foams were prepared from previously obtained bio-based polyol, later noted as CG (like crude glycerol) and commercially available polyols from BASF company, Lupranol 3300 (trifunctional polyether based on glycerol) and Lupranol 3422 (high functional polyether based on sorbitol). Two different petrochemical polyols were applied in order to exploit their advantages – low viscosity, hence easier processability of Lupranol 3300 and higher functionality of Lupranol 3422 resulting in enhancement of foams' crosslink density (Andersons et al., 2015; Kirpluks et al., 2014). Basing on the viscosity of CG biopolyol it was used as a substitute of Lupranol 3300 in combination with high-functionality Lupranol 3422. The properties of the aforementioned polyols are presented in Table 1.

Isocyanate used in the reaction was polymeric 4,4'-methylene diphenyl diisocyanate (pMDI) characterized by a 31.5% content of NCO groups (BASF). The average functionality of pMDI was c.a. 2.8.

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