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Open cell semi-rigid polyurethane foams synthesized using palm oil-based bio-polyol

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ABSTRACT

Semi-rigid polyurethane foams were successfully prepared by blending up to 70 wt.% of a palm oil-based bio-polyol with a petrochemical polyether polyol. Due to the high viscosity of the bio-polyol derived from palm oil, polyol premixes were heated before mixing with an isocyanate component. Despite this, a slowdown in the foaming and gelling reactions was detected as the content of the palm oil-based bio-polyol in the formulation increased. The thermal conductivity of the modified foams was higher than that of the reference one, even when they exhibited a lower apparent density. In addition, their mechanical and dynamic mechanical properties decreased as the palm oil-based polyol content in the final foams increased. These effects are attributed to the foams' cellular structure since the closed cell content decreased as the amount of the petrochemical polyol replaced by the bio-polyol increased. However, the water absorption decreased as the bio-polyol concentration in the polyurethane formulation increased and the modified foams exhibited excellent dimensional stability Taking into account potential applications of polyurethane systems, the formulation containing 30 wt.% of the bio-polyol could be used in the preparation of a new generation open cell semi-rigid foams permeable to moisture and with higher content of biomass-derived constituents.

1. Introduction

The synthesis of polymers based on natural components is one of the most important fields in the current research and development for the environmental protection (Tanaka et al., 2008; Cateto et al., 2011; Oliveira et al., 2015). Studies on polyurethanes (PURs) based on components from natural resources have a great potential in contributing to the development of this area (Calvo-Correas et al., 2016). PURs are obtained through the reaction of polyols and isocyanates. Nowadays, commercial isocyanates and polyols for the synthesis of PUR foams are mostly derived from petroleum. However, a trend to use components based on renewable resources is observed in research works (Zhou et al., 2015). Among such raw materials, mostly petrochemical polyols are partially or even fully replaced by bio-polyols, especially those derived from natural oils, starch, sugar and lignin (Yao et al., 1996; Cateto et al., 2009; Hakim et al., 2011; Seydibeyoglu et al., 2013; D'Souza et al., 2014; Paberza et al., 2014; Bernardini et al., 2015; Arshanitsa et al., 2016). Thus, there have been many reports on synthesizing PUR foams using bio-based polyols from various vegetable oils such as palm (Tanaka et al., 2008; Pawlik and Prociak, 2012; Zeimaran et al., 2013), soy (Campanella et al., 2009), linseed (Calvo-Correas et al., 2015), rapeseed (Prociak and Rojek, 2012; Kirpluks et al., 2013; Kurańska et al., 2015a,b), tung (Mosiewicki et al., 2008; Soto et al., 2016) and castor oil (Mosiewicki et al., 2009; Gomez-Fernandez et al., 2016). Palm oil is one of the most important vegetable oils due to its price and production efficiency in comparison to any other commercial oils. The production of crude palm oil in Malaysia was approximately 19.22 million tonnes in 2014 (Arniza et al., 2015).

Palm oil-based bio-polyols can be obtained by an introduction of hydroxyl groups into the positions of double bonds or ester bonds. Several methods, such as epoxidation followed by opening of oxirane rings using various compounds with active hydrogen atoms, hydroformylation, ozonolyzis and hydrogenation, transesterification and transamidization, can be used in their synthesis. These different methods of converting natural oils into bio-polyols allow obtaining hydroxyl derivatives characterized by various chemical structures. The structure of polyols has a significant influence on the final properties of PUR foams, which also depend on the foaming process conditions (Arbenz et al., 2016).

Kurańska and Prociak (2016) analyzed the foaming process of water-blown PUR foams with different contents of rapeseed

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oil-based polyols. They concluded that a replacement of a petrochemical polyol with a rapeseed oil-based polyol had a significant effect on the foaming process by reducing the reactivity of the PUR system. The foaming process was analyzed using a FOAMAT® system, a device that allows analyzing the dielectric polarization of reaction mixtures (among others), which reflects the conversion degree of functional groups during the PUR formation. A modification of the reference PUR system based on a petrochemical polyol by replacing the petrochemical polyol with rapeseed oil-based hydroxyl derivatives resulted in a smaller decrease in the dielectric polarization which reflects slower gelling and foaming reactions.

Bio-polyols can be used for a preparation of different types of PUR materials including flexible and rigid foams. An addition of natural raw materials can change both the physical and chemical properties of PUR foams and result in a more ordered cellular structure of the modified foams than in the case of the reference material, as was reported in several papers (Pawlik and Prociak, 2012; Prociak et al., 2012).

Bio-polyols used to obtain flexible foams usually have a hydroxyl number in the range of 50–200 mgKOH/g (Campanella et al., 2009; Prociak and Rojek, 2012; Zhang and Kessler, 2015). Flexible foams obtained with palm oil-based bio-polyols have a generally higher apparent density than the reference foams. Moreover, it turned out that the mechanical properties of the materials modified had been improved. The foams with an addition of 15% of the bio-polyol had almost twice the tensile strength and three times higher compressive stress at 40% strain in comparison to the petrochemical foams. The foams' resilience increased with an increasing bio-polyol addition (Pawlik and Prociak, 2012; Prociak et al., 2012). The cellular structure of the foams was also influenced when a rapeseed oil-based bio-polyol was used as the replacement of a petrochemical polyol resulting in smaller cell sizes as the amount of the bio-polyol increased. In this case, it was also observed that the mechanical properties of the foams prepared depended on the concentration of the rapeseed oil-based polyol: the introduction of the rapeseed oil-based polyol to the PUR formulation increased the apparent density (as in the case of the palm oil-based bio-polyol), but reduced the hardness and resilience of the final foams. What is more, the foams modified with the rapeseed oil-based bio-polyol had a higher value of support factor in comparison to the reference foam (Malewska et al., 2015; Prociak et al., 2015).

Bio-polyols used to obtain rigid PUR foams usually have a hydroxyl number in the range of 250–400 mgKOH/g (Lee et al., 2007; Kurańska et al., 2015a,b; Zieleniewska et al., 2015). Such foams obtained with bio-polyols have properties similar to commercial materials and can be used, for example, as heat insulating materials. A replacement of a petrochemical polyol with rapeseed oil derivatives is possible even up to 80 wt.% and their use can have a beneficial influence on the heat insulating properties of such bio-foams, as reported in several papers (Kurańska et al., 2013; Arniza et al., 2015).

Most often, rigid PUR foams are characterized by closed cell structures. Such materials have excellent thermal insulating properties due to a gas (blowing agent) enclosed in their structures. Such PUR foams have the highest resistance to heat flow among commercially available thermal insulating materials. The chemical structure of PUR materials provides effective air barrier, low moisture vapour permeability and resistance to water.

Nowadays, an increase in the people's interest in the application of rigid and semi-rigid PUR foams with an open cell structure as heat insulating building materials is noticeable. This type of materials is permeable to moisture, has a lower apparent density and as a consequence is cheaper. However, their thermal conductivity is higher in comparison to closed cell foams.

Table 1
Formulations of semi-rigid foams modified with palm oil polyol.

Component	REF	PP10	PP30	PP50	PP70	PP100
Component A						
RF 551	100	90	70	50	30	0
PP102	0	10	30	50	70	100
Water	4.5	4.5	4.5	4.5	4.5	4.5
Polycat 9	1.8	1.8	1.8	1.8	1.8	1.8
L6915	1.5	1.5	1.5	1.5	1.5	1.5
Component B						
p-MDI	188.4	179.9	162.5	145.6	128.7	103.3

In the scientific literature, open cell semi-rigid and rigid PUR foams are described very rarely. Therefore, an application of bio-based components in PUR systems for the production of open cell semi-rigid foams should be interesting.

In this paper, a palm oil-based polyol was obtained and characterized in order to be further used to modify a PUR formulation to produce semi-rigid foams. Both the foaming process and selected properties of the PUR foams modified are discussed.

2. Experimental

2.1. Materials and methods

A petrochemical polyether polyol Rokopol RF-551 with a hydroxyl value of 449 mgKOH/g was supplied by PCC Rokita SA.

A palm oil-based bio-polyol was prepared in the Department of Chemistry and Technology of Polymers in Cracow University of Technology. The bio-polyol was synthesized by the epoxidation of palm oil at 60 °C using performic acid generated in situ by the reaction of hydrogen peroxide (H_2O_2) with a formic acid followed by ring opening with H_2O in the presence of a concentrated sulfuric acid as a catalyst. Water was used stoichiometrically to the epoxide groups and the second step of the reaction (oxirane ring opening) was carried out at 80 °C. This is a well-established economical route to produce bio-polyols in which double bonds are converted into oxirane moieties, which next are converted into hydroxyl groups by the ring opening reaction using suitable reagents to give a polyol (Pillai et al., 2016). The reaction parameters (solvent type, time and temperature) were optimized in order to produce the most economical and functional bio-polyol. The resulting bio-polyol was marked as PP102.

Polymeric methylene diphenyldiisocyanate (PMDI), containing 31.5 wt.% of free isocyanate groups, was supplied by Minova Ekochem S.A. Polycat 9, an amine based compound produced by Air Products, was used as a catalyst. A silicone surfactant with the trade name Niax Silicone L-6915 produced by Momentive Performance Materials Inc. was used as a stabilizer of the foam structure. Distilled water was used as a "green" chemical blowing agent.

2.2. Foam synthesis

Semi-rigid PUR foams with different contents of the PP102 bio-polyol and petrochemical polyol were prepared using a one-step method. The different mass shares of the synthetic polyol were replaced by their bio-polyol equivalents. The formulations are shown in Table 1.

The polyols, amine catalyst, surfactant and water (named "component A") were mechanically stirred for 15 s to ensure their complete homogenization. After that, PMDI (component B) was added to the polyol premix at a NCO/OH molar ratio of 1.1:1.0 (the contributions of the polyols and water were taken into account in the OH calculation) and the whole mixture was mechanically stirred for 5 s and then immediately poured into a plastic container (25 cm × 25 cm × 10 cm).