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Linseed oil as a natural modifier of rigid polyurethane foams

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ABSTRACT

Fast growing awareness of environmental and economic problems associated with global climate warming and anticipated future depletion of petroleum resources is driving the fast growing demand for new sustainable biomaterials. A scale of new developments of versatile materials made from abundant and inexpensive natural sources is growing worldwide. Following a wide volume of research studies focused on application of bio-based components for production of plastic foams, composites, coatings, sealants or adhesives, this paper reports the development of a novel type of rigid polyurethane foams (RPUFs), containing linseed oil (LO) as a natural modifier of the rigid polyurethane foams. The use of natural bio-oils for polyurethane composites, broadens the range of functional properties and reduces the costs of production. The bio-composites are more ecofriendly and creates the opportunity to utilize linseed oil, a raw material available in many countries in large quantities. Our research shows that polyurethane foams containing linseed oil demonstrate variety of favorable properties, including the improvement of mechanical strength characteristics. The aim of this work was to determine the influence of the linseed oil on the foam morphology and their physical properties. Our major goal was to optimize the foam formulation, including the content of linseed oil in the reaction mixture.

1. Introduction

Polyurethanes (PUs) were invented by Otto Bayer in the 1930s. They are block copolymers, having urethane moiety (−NHCO−O−) as a common group (Chian and Gan, 1998). The PUs are generally prepared through the exothermic reaction between compounds with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (diisocyanates or polymeric isocyanates) (Fig. 1) (Chen et al., 2014). The structure and properties of PU materials are directly connected with the type of used isocyanates and polyols.

The wide range of raw materials as well as the variety of building blocks has led to almost unlimited formulation possibilities for PU materials (Xu et al., 2014). The great versatility in PU synthesis makes it possible to selectively alter the properties of PUs and tailor them to a wide range of purposes such as elastomers, coatings, adhesives, sealants, fibers or binders (Cinelli et al., 2013; Petrovic, 2008; Xu et al., 2014). PUs have grown to be one of the most diverse and widely used plastics with an increasing global market. One of the most important commercial products made of PU materials is represented by rigid polyurethane foams (RPUFs). RPUFs are highly crosslinked, three-dimensional polymers with most-often a closed-cell structure. Their physical and mechanical properties can be selectively modified through alterations of the PU foam chemical formulations. Thanks to the fact that RPUFs exhibit very good thermal insulation and mechanical characteristics, high resistance to weather conditions, low moisture permeability, and relatively low apparent density (Tan et al., 2011), they are commonly used in a variety of industries such as automotive, furniture, construction, packaging and manufacturing (Nikje et al., 2015; Beltrán and Boyacá, 2011). In buildings, they are usually applied as insulating materials for pipelines and lightweight construction components e.g. parts of door and window frames, furniture or home and commercial refrigeration equipment (Chian and Gan, 1998). The global RPUF market is expected to reach 619 billion dollars by 2020 in construction applications, such as in residential and commercial roofs, panels, and in appliance applications (Engels et al., 2013; Zieleniewska et al., 2015).

One of the biggest problems associated with a large-scale production of RPUFs is their dependence on petroleum-derived precursors. Since environmental aspects have a strong influence on the development of polymer materials, one of the main challenges is to develop bio-based renewable sources, which would reduce the demand for non-

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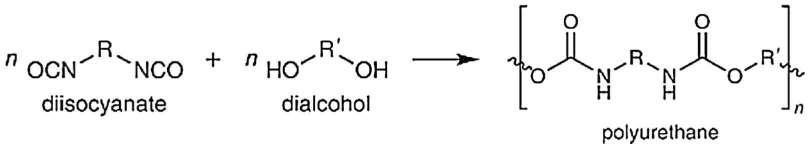

Fig. 1. Reaction of PU synthesis.

renewable petrochemicals and limit the emission of carbon dioxide (Babb, 2011). In this regard, a growing tendency to modify RPUFs with additives obtained from renewable, bio-based sources has been observed (Hatakeyama, 2002; Kurimoto et al., 2001, 2000). Among the renewable sources, vegetable oils are one of the cheapest, most abundant and annually renewable natural materials, which can be applied in an increasing number of industrial applications (Sharma and Kundu, 2006; Seniha Güner et al., 2006; Lebarbé et al., 2012).

Vegetable oils consist of triglicerides of a long-chain fatty acid which can be saturated (stearic or palmitic acids) or unsaturated with the double bonds located at the 9th, 12th and 15th carbons (oleic, linoleic, linolenic, ricinoleic acids) (Lligadas et al., 2010). The aliphatic chain of plant oils presents many reactive sites, which can be chemically modified in order to achieve products that are useful for the polymer industry (Desroches et al., 2012a). Currently, plant oils are mainly used as a renewable feedstock in the preparation of polyols, which can be used as raw materials in the preparation of bio-based PU foams (Hu and Li, 2014). The most common vegetable oils used for the production of polyols depends on the geographical location of the production plants, e.g. in Europe – rapeseed and sunflower oils, in Asia – palm and coconut oils, in North America – soybean oil (Yeganeh and Mehdizadeh, 2004). Numerous publications have appeared in the last few years that reflect the extensive use of plant oils in PU technology. Most of these publications focus on applying bio-polyol as a substitute for petrochemical polyols (Zatorski et al., 2008; Veronese et al., 2011). For example, Veronese et al. (Veronese et al., 2011) synthesized RPUFs based on 100% modified soybean or castor oil polyols. Foams with apparent density of 50 ± 1 kg/m^3 and compression strength of 200 kPa were obtained. Ionescu et al. (Ionescu et al., 2012) reported the synthesis of a series of biobased Mannich polyols starting from cardanol through the oxazolidine group. The foams prepared had low density (32 kg/m^3) and had good compressive strength (190 kPa) as well as flame retardancy. RPUFs have been prepared using soybean oil by Tan et al. (Tan et al., 2011). These foams exhibit comparable to conventional petroleum-based foams foaming kinetics, density, cellular morphology, and thermal conductivity. Compressive strength of the soy-based RPUFs were superior to those of petroleum-based foams. RPUFs were prepared from palm oil by Septevani et al. (Septevani et al., 2015). Mechanical and thermal properties as well as dimensional stability of RPUFs with up to 30% palm based polyol gave comparable or better properties to polyether polyol based foams.

Up to date, there are no publications with researches carried out to verify the improvement the physical and mechanical properties of RPUFs with addition of plant oil. This modification of the polymer matrix can lead to a better adsorption of the heat released during the polymerization reaction, acceptable density as well as mechanical properties of obtained PU foams. Considering the fact that linseed oil contains long, aliphatic chains in the molecule (Fig. 2), they can be also successfully applied as a modifier in the synthesis of RPUFs.

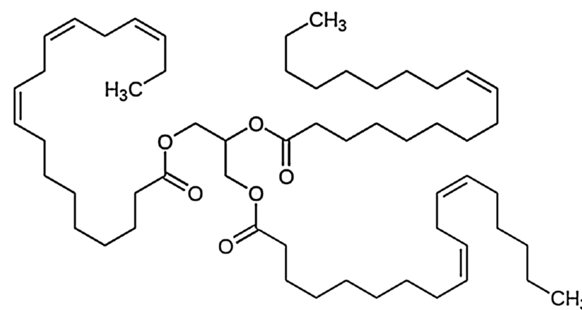

Fig. 2. Representative triglyceride found in a linseed oil, a trimester (triglyceride) derived of linoleic acid, alpha-linolenic acid and oleic acid.

2. Experimental

The aim of this work was to determine the influence of the linseed oil (LO) on the foam morphology and physical properties. The major goal was to optimize the foam formulation, including the adequate content of LO in the reaction mixture. The formulations were modified with an addition of LO in concentrations of 5, 10 and 15% in relation to the total polyols mass. The final PU foams were characterized by analytical (Fourier Transform Infrared Spectroscopy, FTIR; Differential Scanning Calorimetry, DSC; Thermogravimetry, TGA), morphological (optical microscopy) and mechanical techniques (three point bending test and compression test). Additionally, the apparent density, dimensional stability, contact angle, water absorption and flammability were determined for the synthesized materials.

2.1. Materials

- The PU system (*Izopianol 30/10/C* and *Purocyn B*) supplied by Purinova Sp. z o.o. was used as a two component system to produce RPUFs. *Izopianol 30/10/C* is a fully formulated mixture which contains polyester polyol (hydroxyl number ca. 240–260 mgKOH/g, functionality of 2), catalyst (Diethanoloamine), flame retardant (Tris(2-chloro-1-methylethyl)phosphate) and chain extender (1,2-propanediol) (Purinova, Producer information). A commercial isocyanate, polymeric diphenylmethane 4, 4′ diisocyanate (*Purocyn B*, Purinova Sp. z o.o.) containing 31 wt.% of free isocyanate groups was used. Both components were mixed in a ratio of 100:160 (ratio of OH:NCO groups, according to the information provided by the supplier). Carbon dioxide generated in the reaction of water and isocyanate groups was used as a blowing agent. Components of the system and their characteristic are presented in Table 1.
- Commercially available linseed oil (producer: Ol'vita, Poland) was used as a modifier of RPUFs. According to the data sheet provided by the supplier, the moisture content of commercial vegetable oil is lower than 0.2% (Ol'vita, Producer information). Composition in fatty acids (saturated and unsaturated) for linseed oil provided by the producer is shown in Table 1.

Table 1
RPUF composition (Ol'vita, 2018 Producer information; Purinova, 2016 Producer information).

Mixture	Component	Content [Mass%]
Izopianol 30/10/C	Tris(2-chloro-1-methylethyl)phosphate	≤ 22
	Diethanoloamine	< 3,6
	1,2-propanediol	< 2
Purocyn B	4,4′-Diphenylmethane diisocyanate	100
Linseed oil	Palmitic acid	≤ 7
	Stearic acid	≤ 6
	Oleic acid	≤ 18
	Linoleic acid	≤ 17
	Linolenic acid	≤ 53