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Polyurethane rigid foams obtained from polyols containing bio-based and recycled components and functional additives

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ABSTRACT

We report the preparation of polyurethane (PU) rigid foams from bio-based and recycled components. Rapeseed oil (RO) and recycled polyethylene terephthalate (rPET) were used to synthesize PU polyols. Fifty-five percent of the content of the proposed PU polyols originates from renewable or recycled material. Glycerol (GL) and adipic acid (ADA) were added to improve the final properties of the foams. The GL/ADA content was varied from 1 to 6 wt.%. The hydroxyl value, acid value, water content, and viscosity of the synthesized polyols were measured. Using compression tests on PU rigid foams, we found that for some GL/ADA contents the rigidity increased almost 3-fold; whereas the strength increased almost 2-fold. The water absorption of the foams was below 3 wt.%. Optical microscopy of foam cross-sections revealed a mean cell sizes of 330 μm for PU with GL/ADA, and 420 μm for PU supplemented with GL/ADA and RO. FTIR measurements revealed enhanced hydrogen bond networking due to the incorporation of GL/ADA fragments and RO long aliphatic blocks in the PU chain backbone.

1. Introduction

Polyurethane (PU) is a high consumption commodity polymer. The PU polymer family includes elastomers, thermoplastics, thermosets, and one- or two-component curable compositions. PUs have a broad range of applications, including in solid rubbers (Prisacariu, 2011), rigid and soft foams (Ashida, 2006), fibers and coatings (Szycher, 2012), and adhesives and sealants (Sonnenschein, 2014). PUs are characterized by a urethane group (—NH—(C═O)—O—) in their backbone but can also contain aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, and isocyanurate groups (Szycher, 2012).

Initially, the crude oil is utilized to produce the raw ingredients for PU synthesis (Ionescu, 2005; Sonnenschein, 2014). Recently, natural raw components for PU fabrications have attracted considerable interest because of green chemistry and environmental concerns (Babb, 2012; Bobade et al., 2016). Vegetable oils can be chosen as bio-based and renewable feedstock to produce polyol components for manufacturing PU materials (Li et al., 2015; Petrovic, 2008). The hydroxylated derivatives of the soybean (Orgilés-Calpena et al., 2014), coconut (Chethana et al., 2014), rapeseed (Kurańska and Prociak, 2016), sunflower (Omrani et al., 2016), palm (Pillai et al., 2016a), and castor (Kurańska et al., 2017) oils can be used for the synthesis of PU materials. For example, rapeseed oil (RO) is an abundant and inexpensive renewable natural compound (Islam et al., 2014; Meier et al., 2007). RO does not contain hydroxyl groups and cannot react with the isocyanate components, but can be easily chemically converted to a polyol. The main chemical modification routes for RO are ozonolysis (De Souza et al., 2012), epoxidation (Zhang et al., 2014), hydroformylation (Petrović et al., 2012), esterification (Valero and Gonzalez, 2012), and amidization (Kirpluks et al., 2013) reactions. All the functionalization methods mentioned above involve the formation of the polyol suitable for PU foam preparation (Lligadas et al., 2010; Pfister et al., 2011). The molecular weight (MW) and hydroxyl groups (OH value) present in the final polyol product depend on the applied modification method. Generally, the MW and OH values are in the range of 500–4000 g/mol and 50–300 mg KOH/g, correspondingly. Kurańska and Prociak (2016) and Kurańska et al. (2015, 2017) report that RO can be utilized as an excellent starting material to synthesize oligomeric polyols for the fabrication of flexible and PU rigid foams.

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Generally, butanediol (Ren et al., 2016), ε-caprolactone (Hou et al., 2016), and glycerol (Lee and Lee, 2016) are also proposed as chain extenders to modify the functionality and molecular structure of the polyol and network structure of PU materials.

The next trend for the production of PU, which is mostly driven by ecological sustainability concerns, relates to the utilization of recycled polymer materials (Kopczyńska et al., 2016; Sinha et al., 2010). Much study has been aimed at the recycling of linear polyesters, such as polyethylene terephthalate (PET) waste (Duldner et al., 2016; Patel et al., 2005). PET is the commodity plastic widely used to produce various consumer products (e.g., bottles, films, and fiber materials). PET is conventionally produced by the polycondensation reaction of terephthalic acid and ethylene glycol (Thomas and Visakh, 2011). Two principal strategies have been applied to recycle the PET waste—mechanical and chemical routes (Dutt and Soni, 2013).

The mechanical recycling of post-consumer PET waste is performed by the melt extrusion and reactive extrusion processing of the recycled polymer into bottles, packaging films, and fibers (Welle, 2011). The chemical recycling of PET is the depolymerization process to the monomer and oligomer substances, which is achieved by the thermal treatment of the plastic flakes in the solution (Karayannidis and Achilias, 2007). A large variety of solvents (organic solvents, glycols, ionic liquids, supercritical liquids, etc.), chemicals (alcohols, carbonic acids, anhydrides, etc.), and catalysts (metal–organic compounds, phase transfer compounds, hydrotalcites, metal oxides, etc.) are successfully utilized for that purpose (Geyer et al., 2016; Karayannidis and Achilias, 2007; Khoonkari et al., 2015; Sinha et al., 2010). The main reported chemical reactions to depolymerize the PET are glycolysis, methanolysis, hydrolysis, and aminolysis (Sinha et al., 2010). It is also reported that the depolymerization process of PET can be rigorously intensified with the assistance of ultrasonic and microwave treatment (Zeltins et al., 2016). Miscellaneous PET depolymerization products have been developed, including unsaturated polyester resins, alkyd resins, and polyols for polyurethane foams and coatings (Güçlü and Orbay, 2009; Patel et al., 2005; Viksne et al., 2000; Vitkauskiene et al., 2011a).

Depolymerization products of PET can be successfully utilized in the production of aromatic polyester polyols, which may be used for manufacturing PU foams (Kirpluks et al., 2016). Kirpluks et al. (2016) reported that the presence of aromatic blocks in the backbone structure of the polyol could enhance the final mechanical and thermal properties of PU foams. Unfortunately, the aromatic polyester polyols generated the by PET recycling process have limited compatibility with physical foaming agents because of the presence of hydrofluorocarbons and a tendency to crystallize. It has been proposed that the compatibility of such aromatic polyester polyols could be improved by the addition of ε-caprolactone, butanediol, polyglycols, glycerol, and adipic acid additives, which modify the branching and functionality of the molecular backbone of the aromatic polyester polyols (Kathalewar et al., 2013; Vitkauskiene et al., 2011b). The positive effects of castor and palm oils on the structure of the aromatic polyester polyols have been reported (Cakić et al., 2015; Pillai et al., 2016b). Thus, the final thermal and physical–mechanical properties of the PU materials can be improved (Sonnenschein, 2014).

Here we report new formulations of aromatic polyester polyols, which were synthesized from building blocks of RO and depolymerized PET oligomer, and their use in the manufacturing of rigid PU foams for thermal insulation applications. The synthesis of PU bio-based polyols was carried out in three steps: (1) the transesterification of RO with triethanolamine (TEA); (2) the industrial PET waste depolymerization by the transesterification reaction with diethylene glycol (DEG) in the presence of various concentrations of functional additives glycerol (GL) and adipic acid (ADA); and (3) synthesis of the final PU polyol by the transesterification of the above-mentioned intermediary components. On average, the polyols blends that were processed into the PU rigid insulation foams consisted of 55% renewable and recycled components. The structure and mechanical properties of the processed PU rigid foams were investigated.

2. Material and methods

2.1. Raw materials

All raw components were used without any additional treatments. PET flakes of clear grade were obtained from PET Baltija, Latvia. RO (specifications: iodine value (IV) = 117 I_2 mg/100 g sample; acid value = 2.1 mg KOH/g; saponification value = 192 mg KOH/g sample) was supplied by Iecavnieks & Co., Latvia. RO consists of unsaturated fatty acids, including oleic (56%), linoleic (26%), and linolenic acids (10%), as well as saturated fatty acids [palmitic (4%) and stearic acids (2%), and other fatty acids (2%)] (Kirpluks et al., 2013). Triethanolamine (TEA) (99.5%) was from BASF, Germany, and zinc acetate dehydrate (ZnAc) (≥98%) and diethylene glycol (DEG) (99%) from Sigma Aldrich, Germany, and were used without any further purifications for the synthesis of PU polyols. Polyether polyols Lupranol 3422 (BASF, Germany; OH value = 490 mg KOH/g), polymeric diphenylmethane diisocyanate IsoPMDI 92140 (pMDI) (BASF, Germany; NCO group content = 31.5%), foaming agent Solkane 365/227 (Solvay, Belgium; Pentafluorobutane/Heptafluoropropane 87/13), and other reagents, such as the catalyst dimethylaminopropyldipropanolamine PC CAT NP-10 (Performance Chemicals Handels, Germany), silicone surfactant NIAX Silicone L6915 (Momentive Performance Materials, Germany), and flame retardant trichloropropylphosphate (Lanxess, Germany) were used without further purification for preparation of PU rigid foams.

2.2. Polyol synthesis

These synthesis reactions were carried out in a three-neck 1.0 L reaction flask equipped with a mechanical stirrer, a thermometer, a condenser, and an argon inlet. The aromatic polyester polyols were synthesized from PET. The glycolysis reaction of PET waste was performed by slowly heating the PET flakes (1 M) with DEG (2 M) at 190 °C in the presence of ZnAc catalyst (Vitkauskiene et al., 2011a); the blend was heated to 240–250 °C for 3 h; then, GL/ADA functional additives were introduced into the reaction blend.

The vegetable oil based polyol was synthesized by the transesterification reaction of RO (1 M) with TEA (2.9 M) according to Fig. 1. A more detailed description of the of bio-based polyol (RO/TEA polyol) synthesis is given in our previous works (Fridrihsone et al., 2013; Kirpluks et al., 2016; Kurańska et al., 2015; Stirna et al., 2013). RO/TEA polyol contains saturated and unsaturated fatty acid chain blocks with alkyl chain lengths of C_{16}–C_{18}. The reaction was carried out at 170 °C for 1 h in the presence of a catalyst (0.15 wt.% of ZnAc). The end of the reaction was tested by the solubility of the obtained product in ethanol at the volume ratio (resin:ethanol = 1:1). The obtained polyol was characterized with viscosity 160 mPa s, hydroxyl value 363 mg KOH/g, acid value 2.5 mg KOH/g, number-average molecular weight 323 g/mol, number-average functionality 2.3, and 0.12% water content. These polyols are suitable for PU rigid foam production (Kurańska et al., 2015; Stirna et al., 2006).

The obtained aromatic polyester GL/ADA polyols were further transesterified with bio-based RO/TEA polyol by the weight ratio 1:1 at 180° C for 1 h. The final polyol formulations contained 14 different combinations of GL/ADA and GL/ADA-RO concentration