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Characterisation of ureaurethane elastomers containing tall oil based polyols

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ABSTRACT

In the present work, ureaurethane elastomers (EPUUs) were obtained by a one-step method with various isocyanate indices (I_{NCO}) from tall oil (TO) polyols used as a chain extender. The aim of this work was to evaluate the impact of TO polyols on the thermal and mechanical properties of the manufactured EPUUs with regard to their industrial applicability. The temperatures of the glass transition and accompanying heat effects were analyzed by differential scanning calorimetry (DSC). The chemical structure and degree of phase separation related to the value of hydrogen bonds were determined by infrared spectroscopy (FTIR). The thermal degradation was investigated by the combined analysis of TGA/FTIR. The performance as a fire retardant and evaluation of the flammability of EPUUs were tested with a cone calorimeter (CC) and by the limiting oxygen index (LOI). The mechanical properties were tested by dynamic mechanical thermal analysis (DMTA), static tensile strength studies and wear resistance. As concluded from the study, the use of TO-based polyols as a chain extender affects the chemical structure of EPUUs and, consequently, changes the number of hydrogen bonds and degree of phase separation (DPS). Therefore, an introduction of the TO polyols resulted in an improvement of the thermal and mechanical properties of EPUUs. Furthermore, the heat release rate of the developed materials was up-to three times lower in comparison to the reference material.

1. Introduction

Ureaurethane elastomers (EPUUs) are polymers obtained from polyester or polyether diols, isocyanates and a chain extenders. The chains in the EPUU matrix have segmented structures consisting of flexible and rigid parts known as soft segments (SS) and hard segments (HS), respectively. The HS are obtained in the formation of urethane or urea groups from the reaction of isocyanate with the chain extender, and the SS are obtained from the reaction of isocyanate and polyol. The structure of EPUUs depends on the molecular weight of the soft segments (Aran-Ais et al., 2005), the nature of chain extender (Eceiza et al., 2008), the content of hard segments and method of synthesis. The segmented structure of EPUUs is the main reason for their excellent properties: good resistance to abrasion and to oils, to grease and to weather conditions. Therefore, they are used in many technical applications like furniture, medical devices and footwear industry, coatings, adhesives, sealants and as automotive parts (Chattopadhyay and Raju, 2007).

Significant problems like climate change and environmental degradation are associated with increased energy consumption (Yumurtaci and Kecebas, 2011). Therefore, a recent attention directed towards sustainable solutions has promoted research activities aiming to substitute petrochemical materials with renewable feedstock (Prasanth et al., 2016). The use of renewable materials will allow for a decrease in the energy input required for polymer production and processing, creating a more sustainable solution for common materials (Corre et al., 2016).

In the production of polyurethanes (PUR), natural oil polyols can be used to replace petrochemical materials (Gaidukova et al., 2017). The following vegetable oils are the most common raw materials for natural oil polyol synthesis: soy bean oil, rapeseed oil, castor oil and sunflower oil (Auguścik et al., 2016). These polyols can lead not only to the reduction of petrochemical raw materials consumption in the synthesis of PUR but also to the improvement of some product characteristics, like a higher hydrophobicity of the polymer matrix (Kirpluks et al., 2013; Cabulis et al., 2012). Polyols for the production of polyurethane have also been synthesized from wood biomass extracts – tall oil (TO), which is a by-product of cellulose processing. These extracts have an influence on many properties of wood such as strength, density, flammability and many others (Demirbas, 2011). The chemical composition of tall oil is a

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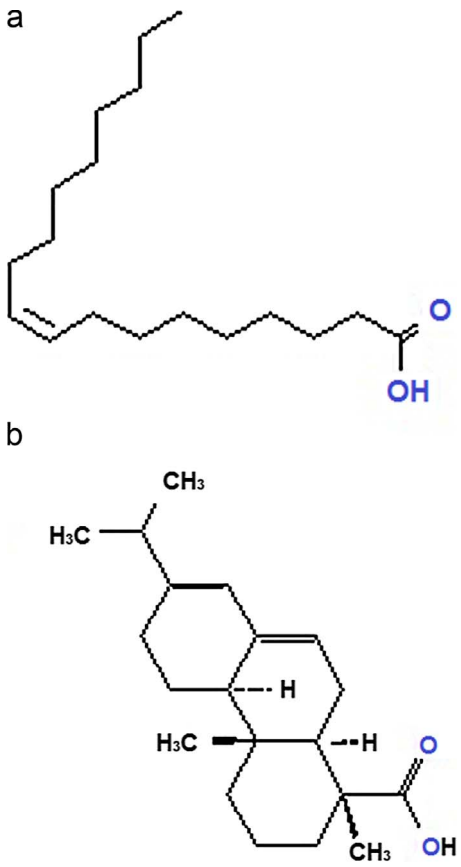

Fig. 1. Basic structure of TO components: a) rosin acids and b) fatty acids.

mixture of various fatty and rosin acids. The use of tall oil as an EPUU component requires proper chemical modification in order to introduce hydroxyl groups to their structure, which can be achieved by esterification of carboxyl groups with polyfunctional alcohols (Cabulis et al., 2012, Kirpluks et al., 2014).

This work describes the synthesis of EPUUs from a forest biomass product, TO, as a renewable and relatively cheap raw material. Crude TO is a by-product in pulp processing of resinous soft woods by means of a sulfate process and contains a broad range of various extracts (Temiz et al., 2008). TO is a mixture of various fatty acids and rosin acids: 40–50% rosin acids ($C_{20}H_{30}O_2$) (Fig. 1a), 30–40% fatty acids ($C_{18}H_{34}O_2$) (Fig. 1b) and up to 10% of neutral or unsaponifiable material (Altiparmak et al., 2007). According to some studies, the elemental composition of the crude TO is 79% carbon, 11% oxygen and 10% hydrogen (Sharma and Bakhshi, 1991).

Tall oil fatty acids, as well as vegetable oils, are used rather extensively in the production of polyurethane foams (Prociak et al., 2017), and adhesives and coatings (Yakushin et al., 2013). However, no sufficient data on the production of ureaurethane elastomers with tall oil based polyols have been reported yet. The limited number of publications concerning the application properties and synthesis of the ureaurethane elastomers produced using tall oil based polyols results in the low commercial availability of these products. Therefore, the current modifications of commercial products are mainly limited to design changes resulting in a variety of shapes and colors of the products and the packaging (Zieleniewska et al., 2016). In this regard, the introduction of new ecological products manufactured using tall oil based polyols would significantly improve their competitiveness on the market.

The subject of this work are ureaurethane elastomers (EPUUs) made with tall oil (TO)-based polyols as a chain extender. EPUUs were produced with various isocyanate indices (I_{NCO}) using MDI isocyanate and

Table 1
Characteristic of TO products used in this study (www.forchem.com/tall_ oil_products).

Characteristics	FOR2	FOR20
Acid value, mg KOH/g	197	190
Free fatty acids, %	97	76
Free rosin acids, %	**1.8**	**20**
Viscosity at 20° C, mPaS	30	70

The bold values are the informations about rosin acid content in tall oils use to produce polyols (PTO02 and PTO20). PTO02 polyol have 2% of rosin acid content, and PTO20 – 20% of rosin acid content.

ester polyol poly(ethylene adipate) (PEA). For the EPUUs production, polyols obtained by the esterification of TO with triethanolamine (TEA) were used. Their thermal and flammability properties were compared with traditional polyurethane elastomers (EPUs) using ethylene glycol (EG) as a chain extender.

In our previous work (Pietrzak et al., 2014), materials obtained from TO polyols with diethanolamine (DEA) were discussed.

2. Materials and methods

2.1. Materials

Two distilled TOs were obtained from Forchem Oy Company – (Rauma, Finland). TO polyols were synthesized by esterification with a polyfunctional amine – Triethanolamine (TEA) 99.2% (Huntsman, The Netherlands), which was used as purchased. Two different TO polyols (PTO02 and PTO20) were synthesized from distilled TO with different rosin acid contents, with functionality 2.25. TO products used to produce ureaurethane elastomers are characterized in Table 1.

Aromatic polyester poly(ethylene adipate) (PEA) with the trade name Polios 60/20, having a molar mass of 1906 g/mol, was supplied by Purinova, Bydgoszcz, Poland. Ethylene glycol (EG), having a molar mass of 62.07 g/mol, was supplied by Chempur, Piekary Slaskie, Poland. 4,4′-diphenylmethane diisocyanate (MDI) was supplied by Sigma-Aldrich Co., Poznan, Poland.

2.1.1. Polyol synthesis

Esterification of TO with TEA (molar ratios 1: 1.33 M). The reaction was carried out in a three neck, 1.0 L, thermo resistant glass, reaction flask submerged in a silicone oil bath. The reaction flask was equipped with a mechanical stirrer, a thermometer, a cooler and an argon inlet tube. 550 g of TO was added to the reaction flask and heated to 175 ± 5 °C. Then, during the next 15 min, 236 g of preheated (to 70 °C) TEA was added. The esterification reaction was carried out for 4–5 h. The reaction was finished when the acid value of the mixture reached 5 mg KOH/g. To use the obtained polyol for the production of EPU materials, it is necessary to separate water from the polyol. For this purpose, vacuum distillation at 0.267 bar was performed for 1.5 h. The basic reaction scheme of TO esterification with TEA is shown in Fig. 2.

By this method of esterification, two different polyols were synthesised from TO, as mentioned in Table 1. The first TO (PTO02) had a hydroxyl value of 337.3 mgKOH/g and 0.2% water content. The second TO (PTO20) had a hydroxyl value of 346.2 mgKOH/g and 0.16% water content.

2.2. Preparation of EPUs and EPUUs

EPUs with EG and EPUUs with TO polyols were synthesized using a two-stage method in a duralumin reactor with a mechanical stirrer. The molar ratio of the used substrates PEA:MDI:EG (or PTO) was equal to 1:1.5:0.5 and two different I_{NCO}: 1.05 and 1.18 were used. The use of TO polyol as chain extender resulted in the formation of urea bonds, which is the result of the reaction between isocyanate and water present in the TO polyols. The scheme of the reaction with TO polyol is