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Effect of the addition of tall oil-based polyols on the thermal and mechanical properties of ureaurethane elastomers

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ABSTRACT

As part of this work, the test results for ureaurethane elastomers (PUURs) manufactured with the use of tall oil (TO)-based polyols with a rosin acid content ranging from 2 to 20% are presented. The goal of this study was to verify the thermal and mechanical properties of bio-based PUURs. The physicomechanical properties of PUURs were tested along with the strength (static tensile test) and thermal properties: thermogravimetry (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). A structural analysis of the materials was also carried out via Fourier transform infrared (FTIR) spectroscopy. The replacement of the chain extender with tall oil-based polyols resulted in materials with different properties, different chemical constitutions and different thermal decomposition patterns. PUURs with TO polyols had a higher thermal resistance, and this resistance increased for higher isocyanate numbers (I_{NCO}). The thermal decomposition of the tested PUURs with TO polyols increased with the increase in the rosin acid content. The mechanical properties of the PUURs show that changing the chain extender with the TO polyols causes an increase in the storage modulus.

1. Introduction

In recent years, there has been an increasing demand for natural products in industrial applications for waste disposal, environmental issues and the depletion of non-renewable resources [1,2]. Renewable resources can partially (or to some extent totally) replace petro-chemical-based polymers through the design of bio-based polymers that can compete with or surpass the existing petrochemical-based materials with respect to cost [3,4]. The synthesis of polymers from renewable resources has been investigated by leading research teams from different countries [5,6].

Among the large group of polymers, the most distinguished are polyurethanes (PURs). The cause of the high demand for these materials is their excellent properties, such as good resistance to abrasion and to oils, to grease and to weather conditions. PURs are used for many applications such as flexible foams in upholstered furniture, rigid foams used as insulation in walls, roofs and appliances, thermoplastic polyurethanes used in medical devices and footwear industries, and as coatings, adhesives, sealants and elastomers used on floors and automotive parts [7]. The properties of different types of PURs are dependent on molecular weight, degree of crosslinking, intermolecular forces, crystallinity and the content of the hard segments [8]. These properties depend on the mixing of three primary substrates: polyisocyanates, polyhydroxyl-containing polymers (polyester polyol or polyether) and chain extenders (diol or diamine) [9]. Currently, the PUR industry is highly dependent on oil because its two main raw materials, polyols and isocyanates, consist largely of petroleum. Because of global warming and the oil crisis, alternative substrates that are renewable and of plant origin are being sought [10]. For this reason, efforts have been made to find solutions permitting the combination of PUR with renewable components [11]. For this purpose, different plant oils such as soy bean oil, rape seed oil, castor oil and sunflower oil are usually used [12]. This combination of PUR with renewable elements may lead not only to the reduction of the use of petrochemical materials but also to the improvement of some characteristics, such as the higher hydrophobicity of the polymer matrix [13–19]. In the field of PUR, natural oil polyols have emerged as a hot topic in recent years as a result of the growing interest within the global sustainability movement [20].

The forest biomass represents an abundant, renewable and low cost resource that may represent an alternative to petrochemical resources. The production and use of the forest biomass are greenhouse gas neutral, while the expansion of plantation forestry

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has a positive benefit to greenhouse gas reduction through increasing the acreage devoted to forests as a carbon absorber. For this project, tall oil (TO) was chosen as a renewable raw material. TO is a by-product of cellulose production; therefore, TO is a relatively cheap resource. TO, in comparison to the aforementioned oils, has a significant advantage because it is not a product of agriculture and does not have to compete with food production.

TO is a by-product of the paper industry, where TO is recovered from the black liquor resulting from the kraft pulping of coniferous woods [21]. The chemical composition of TO depends on the age and the species of pine as well as the geographic location of the coniferous trees and oil production process. Tall oil rosin or other liquids are composed of a mixture of fatty acids, rosin acids and unsaponifiable matter (e.g., sterols, waxes, and hydrocarbons) in a ratio of 5:4:1 [22]. Crude TO contains 40–50% rosin acids, 30–40% fatty acids and 10% neutral material [23].

In the present work, for PUR production, polyols obtained by the amidisation of TO with DEA were used. TO is a mixture of different fatty acids (C_{12}–C_{22}) and rosin acids (C_{20}). Common samples are given: (a) fatty acid – oleic acid ($C_{18}H_{34}O_2$); (b) rosin acid – abietic acid ($C_{20}H_{30}O_2$) Fig. 1.

TO is widely used in industrial applications, such as in nylon, glue, and iron-steel, and is also used as an additive in the production of diesel fuel. TO has mainly been used in the production of diesel. However, because of the high rate of the development of the polymer industry, especially PURs, TO is now used in this industry. In the 1960s, there were already patents relating to the use of tall oil in the production of PURs [24] and polyurethane foams [25,26]. A patent for the dissolution of PURs and polyureas with TO had also been filed [27].

The subject of this study was to perform syntheses of biomaterial ureaurethane elastomers (PUURs) based on petrochemical polyol with a tall oil (TO)-based polyol as a chain extender. These PUURs were compared with PURs with ethylene glycol (EG) as chain extender. The syntheses were conducted with two different isocyanate indexes (I_{NCO}) and by using MDI as the diisocyanate. For the production of PUUR materials, three different polyols from TO were used, and the rosin acid content in TO ranged from 2 to 20%. The polyols were obtained by an amidization method with diethanolamine (DEA) [28,29]. The results presented in this paper were obtained in collaboration with the Latvian State Institute of Wood Chemistry and Warsaw University of Technology.

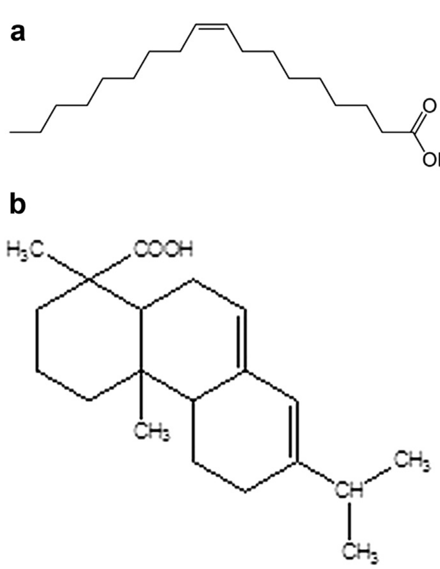

Fig. 1. Basic composition of TO.

2. Experimental

2.1. Materials

The following components were used to produce PUR and PUUR: poly(ethylene adipate) (PEA); Polios 60/20, with an average molar mass of 1906 g/mol, from Purinova, Bydgoszcz, Poland; and 4,4′-diphenylmethane diisocyanate (MDI), 4,4′-MDI, from Sigma Aldrich Co., Poznan, Poland. As an extender, EG, with an average molar mass of 62.07 g/mol, from Chempur, Piekary Slaskie, Poland and TO were used. For polyol synthesis, a TO with a different rosin acid content was used. Forchem Oy Company – (Rauma, Finland) distils crude TO into products with a different rosin acid content. For this project, different grades of TO were used (2%; 10%; 20% rosin acid content in the TO). The properties of the TO used are shown in Table 1. Diethanolamine (DEA) 99.2% (Huntsman, The Netherlands) was used as purchased.

2.2. Polyol synthesis

Amidization of TO with DEA (molar ratio 1:1.15 M). The reaction was carried out in a three-neck 1.0 L thermo-resistant glass reaction flask submerged in a silicone bath. The reaction flask was equipped with a mechanical stirrer, a thermometer, a cooler and an argon inlet tube. TO was heated to 140 ± 5 °C and after 15 min, DEA preheated to 70 °C, was added. The reaction of amidization was carried out for 4–5 h. This time of polyol synthesis has been selected based on previous work. At 4 h of synthesis samples of polyol were taken and acid value was tested. When acid value reached below 5 mgKOH/g the synthesis was stopped and vacuum distillation of water started at 266.6 hPa and was carried out for 1.5 h. To use the obtained polyol for production of PUR materials it is necessary to separate water from polyol. The basic reaction scheme is shown in Fig. 2.

For this project, three different polyols were synthesised from TO products. The polyol sample names are shown in Table 2 as well as the TO type used, the hydroxyl value (IOH) and the moisture content of the polyol that was obtained.

2.3. Preparation of PURs and PUURs

PURs and PUURs were produced using a two-stage method with two different I_{NCO} (1.05 and 1.18), with a constant molar ratio of PAE:MDI:EG (or TO) equal to 1:1.5:0.5. The theoretical content of the hard segments (HSs) is calculated stoichiometrically and in materials with an isocyanate index of 1.05 amounted to approximately from 18% to 21% HSs, while for materials made with an isocyanate index of 1.18, the HS equalled approximately from 19% to 23%.

Table 1
Characteristics for TO products used in this project [30].

Characteristics	FOR2	FOR10	FOR20
Acid value, mgKOH/g	197	194	190
Cloud point, °C	−1	2	5
Colour Gardner, photometer	4	4.5	4.5
Density at 20 °C, kg/m^3	904	920	930
Flash point, closed cup, °C	205	200	200
Free fatty acids, %	97	87	76
Free rosin acids, %	**1.8**	**10**	**20**
Pour point, °C	–	−7	−5
Unsaponifiables, %	1,3	3	3
Viscosity at 20 °C, mPaS	30	50	70
CAS Number	61790-12-3	8002-26-4	8002-26-4

The bold values are the informations about rosin acid content in tall oils use to produce polyols (TO02, TO10 and TO20). TO02 polyol have 2% of rosin acid content, TO10 – 10% and TO20 – 20% of rosin acid content.