



Bio-based polyurethane foams toward applications beyond thermal insulation



Nuno V. Gama^a, Belinda Soares^a, Carmen S.R. Freire^a, Rui Silva^b, Carlos P. Neto^a, Ana Barros-Timmons^{a,*}, Artur Ferreira^{a,c}

^a CICECO, Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, Campus Santiago, 3810-193 Aveiro, Portugal

^b Sapeç-Química SA, Zona Industrial de Ovar – Lote 18, 3880 Ovar, Portugal

^c Escola Superior de Tecnologia e Gestão de Águeda, Rua Comandante Pinho e Freitas, nº 28, 3750-127 Águeda, Portugal

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ABSTRACT

In this work the preparation of viscoelastic bio-based polyurethane foams (PUFs) using polyols obtained via acid liquefaction of coffee grounds wastes has been optimized. In a first stage, the effect of different ratios of isocyanate content to hydroxyl number (0.6, 0.7 and 0.8) and of three distinct percentages of catalyst (3%, 5% and 7%) on the extent of the polymerization reaction was studied by infrared spectroscopy. Next, different percentages of surfactant (14%, 16% and 18%) and blowing agent (12%, 14% and 16%) were used to assess their effect on the density, thermal conductivity and mechanical properties of the foams, including their recovery time. The mechanical properties of the ensuing foams proved to be very interesting due to their viscoelastic behavior. PUFs were also characterized by scanning electron microscopy (SEM) revealing a typical cellular structure and by thermogravimetric analysis (TGA) which proved that these materials are thermally stable up to 190 °C. These results suggest other potential applications for these materials beyond heat insulation in areas where damping properties can be an added value.

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1. Introduction

Polyurethane foams (PUFs) are a class of lightweight porous materials with enormous interest because of their specific properties and potential application in several fields [1]. PUFs can be classified into two major categories: flexible and rigid foams. In some classifications PUFs are subdivided in semi-rigid and semi-flexible foams [1]. Moreover, some flexible foams can also be classified as viscoelastic when they show a delayed recovery. In fact, other expressions like, visco-hyperelastic, memory, slow recovery, controlled recovery or low resilience foams are also used [2–4]. Besides applications in thermal insulation, the range of applications of viscoelastic PUFs includes acoustic absorbing materials for noise and vibration control due to their great potential for the damping of mechanical vibrations [5]. Therefore, they are often used to reduce vibrations and harshness and consequently increase comfort [6]. For these reasons, viscoelastic PUFs are commonly used in seats in automobile and aircraft industries. Furthermore, depending on their viscoelastic properties PUFs may also be used as panels in buildings for heat [7], sound [8] and vibration [9]

insulation consisting in a significant contribution to energy management, as well as helping to reduce noise pollution. Yet, the use of these porous materials to hamper vibrations requires specific viscoelastic characteristics when they are bound onto the vibrating structure [10].

Currently, the polyurethane (PU) industry is still heavily petroleum-dependent because its two major feedstocks, polyols and isocyanates derive entirely from it. However, due to the uncertainty about the cost of petroleum in the future, as well as the need to move toward more environmentally friendly feedstocks, many recent efforts have been focused on replacing all or a portion of the conventional petroleum-based polyols by counterparts obtained from renewable resources. In fact, many non-petroleum resources, as well as different processes of production of non-petroleum derived polyols have been used in PUs production. Processes such as oxypropylation [11] or acid liquefaction [12] of several biomass residues, as well as the modification of vegetable oils following different strategies [13] have been used to produce renewable polyols for the PUs industry. The acid liquefaction of biomass resources, like starch [14], soybean [15], alginic acid [16], palm [17], sugar-cane bagasse [18], lignin [19], cork [20] or coffee grounds [21], to obtain products which can be used as the polyol component in the production of PUFs is a particular

* Corresponding author.

E-mail address: anabarros@ua.pt (A. Barros-Timmons).

interesting strategy. This is due to the fact that it does not involve the use of a large amount of harmful solvents or reagents nor pressure thus, it presents a relatively low environment impact. However, the majority of these studies are generally associated with the production of rigid PUFs as a result of the functionality of the ensuing polyols.

Due to their unique taste and flavor, coffee brews are among the most consumed beverages in the world and have grown steadily in commercial importance during the last 150 years. With an annual worldwide production of approximately 120 million tons, large quantities of residues are generated [22]. The spent coffee grounds, the solid residues obtained from the treatment of coffee powder with hot water to prepare instant coffee, are the main industrial residues with a worldwide annual generation of 6 million tons [22]. Considering the huge amount of coffee residues produced all over the world, its reutilization and valorization is of major relevance [23]. The composition of coffee grounds may vary from species to species, but they are typically rich in polysaccharides (34–53%, w/w) [22,24], which make them suitable for liquefaction into bio-based polyols [21] to be used in PUFs formulations.

In the present study liquefied coffee grounds were used as the polyol component for the production of viscoelastic bio-based PUFs. To the best of our knowledge this is the first report on the production of PUFs with a distinct viscoelastic behavior from that of typical rigid foams produced using bio-based polyols. The formulation used in the production of PUFs was first optimized and the resulting foams were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), density and thermal conductivity measurements, compressive tests, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

Spent coffee grounds, typically consisting of hemicelluloses (37 wt%), lignin (25 wt%), extractives (15 wt%), cellulose (9 wt%) and ashes (1–2 wt%), used in this study were kindly provided by NESTLÉ S.A. (Portugal). The material with initial moisture content of 80 wt% was air dried (moisture content achieved 10 wt%), milled in a Retsch cross beater mill SK1 (Haan, Germany), sieved and the 18–60 mesh fraction was selected for the liquefaction experiments. This fraction was oven dried at 105 ± 2 °C for 24 h (moisture content around 1–2 wt%) before the liquefaction step. Polyethylene glycol (PEG, 99% purity and average molecular weight of 400), supplied by Merck, and glycerol (99.5% purity), purchased from Sigma–Aldrich, were used as solvents in the liquefaction process. Sulfuric acid (H_2SO_4 , 95–97% purity) supplied by Fluka was used as catalyst. The resulting polyol presented an hydroxyl number (*OH number*) of 287.2 mg_{KOH}/g , an average molecular weight (*Mn*) of 575.0 g/mol, an acid value (*AC*) of 9.8 mg_{KOH}/g and a water content of 2.0% (w/w), and was used to produce PUFs by the reaction with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. The polymeric isocyanate Voranate M229 MDI (methylene diphenyl diisocyanate) with an average molecular weight of 340–380 g/mol, a NCO content of 31.1% (weight percent of free isocyanate groups), a functionality of 2.7, a viscosity of 190 mPa s (at 25 °C) and an isocyanate equivalent of 135 was kindly supplied by Dow Chemicals. A mixture of Tegostab B8404 (70% w/w) and Dabco DC3043 (30% w/w) was used as surfactant. Tegostab B8404, supplied by Evonik, is a polyether-modified polysiloxane with a density of 1.045–1.065 g/cm^3 (at 25 °C), while Dabco DC3043, supplied by Air Products, and is a silicone glycol copolymer with a density of 0.98 g/cm^3 (at 21 °C).

Dichloromethane was supplied by Fluka and used as blowing agent, while Polycat 34, supplied by Air Products, is a tertiary amine with a density of 0.84 g/cm^3 (at 25 °C) and was used as catalyst. All the solvents used were of analytical grade and were used as received.

2.2. Liquefaction of coffee grounds

Coffee grounds were used to produce the polyol via acid liquefaction reaction in a 300 cm^3 stainless steel vessel (PARR, model 4566), equipped with an independent controller (PARR, model 4842), stirring (200 rpm), heating resistance (1000 W), internal water cooling system and temperature sensor, following the procedure reported by Soares et al. [21]. The dried coffee grounds powder, solvent mixture (PEG/glycerol, 90/10 wt/wt) and sulfuric acid (4 wt%) were reacted at atmospheric pressure and moderate temperature (160 °C) during 80 min. The liquefaction solvents/coffee grounds powder ratio used was 3/1 (wt/wt).

2.3. Characterization of coffee grounds derived polyol

2.3.1. Acid Value and hydroxyl number

The *AC* and *OH number* of the polyol were determined according to the procedures described in our previous report [21].

2.3.2. Average molecular weight

The number average molecular weight (*Mn*) of polyol was measured using a K-7000 Vapor Pressure Osmometer (Knauer) calibrated using four standard solutions of benzil in acetone, at 40 °C, in the concentrations range of 4.5883 g/L up to 20.6790 g/L.

2.3.3. Water content

The determination of the water content was carried out using a KF 756 Coulometer for Karl Fisher titration, according ASTM D6304-07. The samples of polyols were analyzed using Hydranal (Hydranal Coulomat AG, Sigma) as reagent. The analyses were performed in triplicate and the results averaged.

2.4. First step – optimization of isocyanate/polyol ratio and catalyst content

For the optimization of isocyanate/polyol molar ratio ($R_{NCO/OH}$) and percentage of catalyst ($\%_{cat}$), the coffee grounds derived polyol was mixed with the isocyanate in the presence of the catalyst. Polyol and different amounts of isocyanate and catalyst were placed in polypropylene cups and the mixtures were homogenized using an IKA Ost Basic mixer with rotating blades, during ca. 10 s at 700 rpm. The resulting products were analyzed by FTIR and the area of the isocyanate peak (≈ 2250 cm^{-1}) measured to monitor the extent of reaction.

According to Kapps and Buschkamp [25] the $R_{NCO/OH}$ used in the PUFs production was determined using Eq. (1).

$$R_{NCO/OH} = \frac{m_{iso} \times \frac{\%_{NCO}}{M_{NCO}}}{m_{polyol} \times \frac{OH_{number} + AC}{M_{KOH}} + m_{H_2O} \times Eq_{H_2O}} \quad (1)$$

where $R_{NCO/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH mole of the polyol, m_{iso} is the mass (g) of isocyanate, $\%_{NCO}$ is the quantity of NCO groups in the isocyanate (31.1%), M_{NCO} is the molecular weight of NCO group (0.042 g/mmol), m_{polyol} is the mass (g) of the polyol, OH_{number} and *AC* are the hydroxyl number and the acid value of polyol, respectively (mg_{KOH}/g) and M_{KOH} is the molecular weight of KOH (56.1 $mg/mmol$). Finally, m_{H_2O} is the mass of water present in the polyol while Eq_{H_2O} is the equivalent of OH groups present in the water (111 $mmol/g$).

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