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Material Properties

Statistical evaluation of the effect of formulation on the properties of crude glycerol polyurethane foams

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ABSTRACT

In our pursuit of developing ecofriendly materials, the effect of the main components of the formulation used for the preparation of polyurethane foams (PUFs) derived from unrefined crude glycerol (CG) has been systematically studied. A series of PUFs has been prepared using formulations with judicious variations of the percentage of each component. The physical properties of the resulting PUFs were measured and the data collected were statically treated using a four-way functional ANOVA method. From the ANOVA results, the paramount importance that the blowing agent and the surfactant have on the regulation of density and thermal conductivity of PUFs was recognized. Regarding the mechanical properties, the isocyanate content presented a dominant influence on the increase of Young's modulus, toughness and compressive stress of PUFs.

1. Introduction

Polyurethanes (PUs) are versatile engineering materials which find a wide range of applications because their properties can be readily tailored by the type and composition of their components [1]. PU is the general name for a polymer having urethane linkages in their chain structure resulting from the reaction between NCO groups of an isocyanate and the OH groups of a polyol [2]. The foaming reaction where water is frequently used as blowing agent occurs in parallel to the polymer reaction. The foaming results from its reaction with isocyanate groups, which spontaneously releases carbon dioxide, thus generating bubbles [3]. In that sense, the isocyanate and polyol, as well as catalysts, surfactants and blowing agents are used to regulate the morphology of the cell structures and the mechanical properties of the foams.

Rigid PUFs have been widely used as thermal insulation materials, because the air trapped within the cellular structure develops passive heat absorption capacity. The low thermal conductivity, high mechanical and chemical stability at high and low temperatures are some of their advantages [4]. In turn, it is well established that the mechanical response and thermal properties of these materials depend on their architecture, the cell wall thickness, the size distribution and the shape of the cells, among others [4,5]. Nevertheless, whatever their application, optimization of their formulation is needed, as well as the understanding of the relationship between the microstructure and the mechanical and thermal properties.

Like other polymers, PUs rely on petroleum feedstocks, and the increasing concern over environmental issues as well as the supply of petroleum have motivated the development of PUs from renewable raw materials [1,6–8]. Liquefied lignin [9], cork [10,11], coffee grounds [12,13], starch [14], soybean straw [15], sugar beet pulp [16] or date seeds [17] have been used as substituents or at least partial substituents of petroleum feedstocks in the synthesis of PUFs, and the results obtained demonstrated that the ensuing foams had comparable foaming kinetics, density, cellular morphology and thermal conductivity to those obtained using petroleum derived polyols. Another potential renewable resource that can be used as polyol is crude glycerol (CG), which is a byproduct of biodiesel production [18]. The successful replacement of petrochemicals polyols by CG in PUF production has the potential to reduce their cost and environmental impact. The production of PUFs from CG might also contribute to alleviating the current CG glut and contribute to the sustainability of the PUFs industry.

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Although the variability of the composition of such raw material could be a constraint, we have recently demonstrated that it is not the case [18]. In fact, adjustments in formulations of PUFs can modulate the properties of the resulting materials.

In the present work, CG was directly used without any pre-treatment or purification step as the polyol component in the production of PUFs, and different formulations were used to statistically evaluate the influence of the different relative percentages of the components on the properties of the ensuing foams. To the best of our knowledge this is the first report on the optimization of the PUFs formulation derived from CG where the effect on the properties of the resulting PUFs was statistically evaluated. The statistical method used was performed by a four-way functional ANOVA, which allows testing the different foam properties according to the quantity of reactants used. The quantity of each reactant are the factors, the properties of the ensuing foams are the dependent variables and the statistical significance level of the model (p-value) used was 0.050.

2. Experimental

2.1. Materials

The foams studied were produced by reaction of CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. The CG sample was kindly supplied by Bioportdiesel and is composed of 84% of glycerol and 16% of fatty acids and methyl esters with a water content of 1.6 ± 0.01, *AV* of 23.1 ± 0.2 mg_{KOH}/g and OH_{number} of 399.0 ± 4.7 mg_{KOH}/g. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% (weight percent free isocyanate content), functionality of 2.7, viscosity of 190 mPa s (at 25 °C) and an isocyanate equivalent of 135 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane with a density of 1.045–1.065 g/cm^3 (at 25 °C) was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine with a density of 0.84 g/cm^3 (at 25 °C), was used as catalyst and supplied by Air Products. Distilled water was used as blowing agent.

2.2. Characterization of crude glycerol

The determination of the water content was carried out using a KF 756 Coulometer for Karl Fisher titration, based on ISO 14897:2002. The sample was analyzed using Hydranal (Hydranal Coulomat AG, Sigma) as reagent. The analysis was performed in triplicate and the results averaged.

The acid value (*AV*) was determined based on ISO 2114:2000. Approximately 2 g of CG were dispersed in 50 mL of ethanol in a 100 mL Erlenmeyer flask. Titrations were conducted using 0.1 N NaOH solution and the end point determined by a digital pH meter (HI 2211 pH/ORP–Hanna Instruments), equipped with a HI 1043B probe. The number of milligrams of KOH required to neutralize the acid of one gram of sample was calculated using Eq. (1).

$$AV = (A - B) \times 56.1 \times N/W \quad (1)$$

where *A* is the volume of NaOH solution required for titration of the sample (mL); *B* is the volume of NaOH solution required for titration of the blank (mL); *N* is the normality of the NaOH solution; and *W* is the weight of the sample (g).

The hydroxyl number (OH_{number}) was determined based on ISO 14900:2001 in which the esterification process is catalyzed by imidazole. Titrations were conducted using 0.5 N NaOH solution and the end point determined by a digital pH meter. The OH_{number} was corrected taking into account *AV* and calculated according to Eq. (2).

$$OH_{number} = ((A - B) \times 56.1 \times N/W) + AV \quad (2)$$

where *A* is the volume of NaOH solution required for the titration of the sample (mL); *B* is the volume of NaOH solution required for the titration of the blank (mL); *N* is the normality of the NaOH solution; *W* is the weight of the sample (g); and *AV* is the acidity of the sample (mg_{KOH}/g_{CG}).

2.3. Production of PUFs

Different amounts of surfactant, catalyst and blowing agent were added to CG and placed in a polypropylene cup. The mixture was homogenized using an IKA Ost Basic mixer with rotating blades for *ca*. 10 s at 700 rpm. Different amounts of isocyanate were added to these mixtures and mixing continued. The foams were obtained by free expansion in the cup mold at room temperature. Table 1 lists the amount of each reactant based on 100 parts by mass of CG.

2.4. Characterization of PUFs

PUFs specimens (10 × 10 × 10 mm^3) were cut and weighed to determine the density by dividing the weight of the specimens by the calculated volume. The values presented correspond to the average density determined for 10 specimens of each foam.

A KD2 Pro (Decagon Devices) was used to measure the thermal conductivity of the PUFs by introducing the thermal conductivity sensor into the foams.

SEM analyses were performed in a SU-70 (Hitachi) scanning electron microscope at an accelerating voltage of 15.0 kV after vacuum-coating with gold to avoid electrostatic charging during examination.

An Instron 5966 universal mechanical test machine was used to measure the compressive strength of the foams, according to the ISO 844:2014. Before analysis, PUFs specimens (10 × 10 × 10 mm^3) were conditioned at 21 °C and 41% relative humidity, for 24 h. Samples were then placed between the two parallel plates and compressed at 10 mm/min up to 30% deformation.

3. Results and discussion

In order to get a better understanding of the influence of the different components and respective relative percentages on the

Table 1
PUFs formulations.

Sample code[a]	Polyol	Isocyanate	Catalyst	Surfactant	Blowing Agent
PUF-130-6-6-5	100	130	6	6	5
PUF-160-6-6-5	100	160	6	6	5
PUF-130-8-6-5	100	130	8	6	5
PUF-160-8-6-5	100	160	8	6	5
PUF-130-6-9-5	100	130	6	9	5
PUF-160-6-9-5	100	160	6	9	5
PUF-130-8-9-5	100	130	8	9	5
PUF-160-8-9-5	100	160	8	9	5
PUF-130-6-6-7	100	130	6	6	7
PUF-160-6-6-7	100	160	6	6	7
PUF-130-8-6-7	100	130	8	6	7
PUF-160-8-6-7	100	160	8	6	7
PUF-130-6-9-7	100	130	6	9	7
PUF-160-6-9-7	100	160	6	9	7
PUF-130-8-9-7	100	130	8	9	7
PUF-160-8-9-7	100	160	8	9	7

[a] Sample Code (PUF-A-B-C-D): A - wt% of isocyanate; B – wt% of catalyst; C – wt% of surfactant; D – wt% of blowing agent.