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Flexible polyurethane foams based on 100% renewably sourced polyols

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ABSTRACT

Since polyol is one of the major components in polyurethane foam synthesis, introducing renewably sourced polyols in the foam formulation leads to materials with high renewable carbon content. A series of flexible polyurethane foams with variations in polyol composition were synthesized with castor oil based Lupranol Balance® 50 polyether polyol and corn based polytrimethylene ether glycol mixtures. Water was used as the unique and eco-friendly blowing agent. The effect of the relative amount of each polyol on the structure and properties was analyzed by optical microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, tensile and compressive tests, dynamic mechanical analysis and atomic force microscopy. The average molecular weight and hydroxyl number of the polyol components showed to influence the foaming reaction and hence the structure and properties of the polyurethane foam. The newly developed peak force quantitative nano-mechanics technique was used to map the elastic modulus values of foam cell struts and it seemed to be adequate to assess the purity of the different phases.

1. Introduction

Flexible polyurethane foams have been widely used in many applications such as mattresses, seating and car industry and they are gaining great interest in areas such as biomedicine, intelligent materials and nanocomposites (Hodlur and Rabinal, 2014; Kang et al., 2013; Liu et al., 2013; Singhal et al., 2014). Nowadays, there is a growing concern about environmental issues in material synthesis. This reason together with crude price fluctuations have encouraged scientific community to develop materials, including polyurethanes, based on renewable resources which do not depend on petroleum based raw materials (Rashmi et al., 2013). Regarding renewable-based resources, vegetable oils have received special attention as raw materials for polyol synthesis (Ionescu et al., 2012; Narine et al., 2007; Palanisamy et al., 2011; Sharma et al., 2014). Helling and Rusell (2009) carried out a life cycle assessment analysis for vegetable oil based polyols and demonstrated that a reduction of 33–64% on fossil resources consumption as well as a lowering on greenhouse gas emissions could be achievable by using soy or castor oil.

Foam synthesis involves two main reactions: blowing and gelling. Blowing reaction arises from the reaction of an isocyanate group with water and yields urea and carbon dioxide, which expands the air bubbles entrapped inside the reactive mixture. Gelling reaction implies an isocyanate group and a hydroxyl group to form a urethane linkage. The microstructure is accepted to be composed by both physical and chemical crosslinks. Physical crosslinks arise when urea groups of sufficient size and concentration establish hydrogen bonding interactions with other urea groups and phase separate from soft segments into hard domains (Dounis and Wilkes, 1997). Chemical crosslinks are the result of the urethane reaction, whereby a covalent network is formed between polyurea oligomers and polyol soft segments through urethane bonds. The microstructure and morphology depend on several factors such as the competition between the two main reactions, mobility of urea groups, the level of crosslinks arised from the reaction between the diisocyanate and polyol and the specific interactions between polyol and polyurea segments (Heintz et al., 2005; Li et al., 2002).

Determining the mechanical properties on the micro-and nanoscale is a matter of interest in materials property analysis. Nanoindentation techniques are widely used to assess local mechanical properties. However, this method is time consuming and presents various uncertainties when determining the local

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elastic modulus (Miller et al., 2008; Varam et al., 2014). When working with soft materials such as polymers, the high deformations produced in the material and the importance of adhesive forces are important challenges when using nanoindentation analysis (Gupta et al., 2007; Kohn and Ebenstein, 2013; VanLandingham et al., 2011). Peak force quantitative nano-mechanics is a new technique that allows the mapping of mechanical properties by using a scanning probe microscope at a similar scanning speed to tapping mode. With difference to tapping mode atomic force microscopy, the controlled variable is the maximum force (peak force) applied to the surface and it is maintained constant during the scan. Force vs separation curves are obtained and information about adhesion force, elastic modulus, deformation and dissipation can be extracted (Adamcik et al., 2011). The reduced elastic modulus can be determined by using the Derjaguin–Muller–Toporov (DMT) model shown in Eq. (1) (Derjaguin et al., 1975).

$$F_{\text{interaction}} = \frac{4}{3}E^* \sqrt{R(d-d_0)^3} \quad (1)$$

where $F_{\text{interaction}}$ is the tip-sample force, E^* is the reduced elastic modulus, R is the tip radius and $d - d_0$ is sample deformation.

The reduced modulus is related to the sample modulus by Eq. (2).

$$E^* = \left[\frac{1-\upsilon_s^2}{E_s} + \frac{1-\upsilon_{\text{tip}}^2}{E_{\text{tip}}}\right]^{-1} \quad (2)$$

where E^* is the reduced elastic modulus, υ_s and υ_{tip} are the Poisson's ratios of sample and tip respectively and E_s and E_{tip} are the elastic modulus of sample and tip respectively. Considering that E_{tip} is much higher, sample Young's modulus (E_s) can be calculated if υ_s is known (Pittenger et al., 2012).

The aim of this work was to synthesize flexible polyurethane foams using bio-derived polyols and to analyze the effect of variations in polyol composition over foam morphology and properties. Synthesis was carried out in a single step process and foams were cured in an open mold. Characterization was realized by optical microscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal conductivity measurements, tapping mode atomic force microscopy (TM-AFM), peak force quantitative nanomechanics atomic force microscopy (PFQNM-AFM), mechanical testing and dynamic mechanical analysis (DMA).

2. Experimental

2.1. Raw materials and synthesis

A series of flexible polyurethane foams with variations in polyol mixture composition were synthesized with castor oil based Lupranol Balance® 50 polyether polyol, kindly supplied by BASF, and polytrimethylene ether glycol (PO3G) obtained from corn sucrose (Ugarte et al., 2014). Amine catalyst Tegoamin® B75 and tin catalyst Kosmos® 29, together with surfactant Tegostab® B-4900 (all three from Evonik) and distilled water as blowing agent, were used in the B-side of the formulation. Toluene diisocyanate (TDI), generously supplied by Bayer, was used as diisocyanate in the A-side of the formulation. Hydroxyl number of Lupranol Balance® 50 and PO3G were determined by titration according to ASTM D 4274-05. All reactants were used as received. Polyols main properties are summarized in Table 1.

Foams were synthesized at room temperature by reacting A-side with B-side in a two-step reaction. Polyol or polyols mixture, catalysts, water and surfactant were mixed at 2000 rpm for 2 min. Then, the fixed amount of TDI was incorporated and mixing continued for 10 s at the same speed. The mixture was then quickly poured into an open mold to left the foam rise freely. Foams were cured at room temperature for at least 24 h before characterization. Isocyanate index was maintained constant (I.I. = 120) in all foams. Maximum PO3G substitution was 20%. With higher substitution values, foaming and gelling reactions were not well balanced with the fixed catalysts quantities and the obtained foams were not acceptable.

Foam designation and formulations are indicated in Table 2.

Table 1
Main properties of the polyols.

Property	Lupranol Balance® 50	PO3G
OH number (mg KOH g^{-1})	49.7	79.4
Functionality	2.7	2
Number average molecular weight (g mol^{-1})	3048	1413

2.2. Characterization techniques

2.2.1. Cell size and density

Core density of samples was determined according to ASTM D-3574-11, test A. Four measurements were made for each sample. Cell size of foams was analyzed by a Nikon Eclipse E 600 optical microscope. Twenty-five measurements of cell average diameter were made on each sample, using a 50× magnification lens.

2.2.2. Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the functional groups of the synthesized polyurethane foams. Measurements were performed with a Nicolet Nexus FTIR spectrometer equipped with a MKII Golden Gate accessory, Specac, with diamond crystal as ATR element at a nominal incidence angle of 45° with a ZnSe lens. Single-beam spectra of the samples were obtained after averaging 64 scans in the range from 4000 to 800 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were obtained in the transmittance mode.

2.2.3. Thermogravimetric analysis

Analysis was performed on a TGA/SDTA 851 Metler Toledo equipment to evaluate thermal stability of polyurethane foams. Samples were heated from room temperature to 650 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. For comparison purposes, a foam with the same formulation to PF-100 but based on a petrochemical polyether polyol supplied by Repsol and named PF-PC, was also analyzed. It had an equivalent molecular weight of 1167 g eq^{-1} and a hydroxyl number of 48 mg KOH g^{-1}. The formulation of PF-PC was adjusted in order to have similar cell size and density characteristics to PF-100 foam.

2.2.4. Thermal conductivity

Thermal conductivity measurements were carried out in a PVT 100 Haake equipment with a 556-1082 sensor model at 35 °C. Cylindrical-shaped foam samples with a diameter of 9 mm were

Table 2
Designation and formulation of synthesized polyurethane foams (PF). All formulations are based on 100 parts by weight of polyol (php).

Component	PF100	PF95	PF90	PF85	PF80
Lupranol Balance®50	100	95	90	85	80
PO3G	–	5	10	15	20
Water	3.5	3.5	3.5	3.5	3.5
Tegoamin®B75	0.3	0.3	0.3	0.3	0.3
Kosmos® 29	0.4	0.4	0.4	0.4	0.4
Tegostab® B-4900	1.1	1.1	1.1	1.1	1.1
TDI (g)	49.3	49.6	50.0	50.3	50.6