



Glycolysis of flexible polyurethane wastes containing polymeric polyols



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ABSTRACT

Nowadays polymer recycling processes are an urgent task due to the huge quantity of wastes that are generated. Polyurethane is the 6th polymer most used all over the world with a production of approximately 12 million tons per year. Flexible foams represent about the half of polyurethane total production and among them conventional polyurethane flexible foams mean the 80%. This type of foams are synthesized or using only a flexible polyether polyol or a mix of a flexible polyether polyol with a polymeric polyol. A series of works about the glycolysis of flexible foams synthesized only with flexible polyether polyol have been carried out by our research group. In this work, for the first time in literature, a detailed study of the glycolysis of flexible polyurethane foams containing polymeric polyol has been accomplished. It has been demonstrated that is possible to carry out the glycolysis of these foams using similar reactions conditions determined for the glycolysis of conventional flexible polyurethane foams synthesized only with flexible polyether polyol. Furthermore, after a proper treatment process of the recovered polyol, flexible polyurethane foams have been synthesized using mixtures of raw polyol with the recovered one.

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1. Introduction

Due to the increase of the plastic market, polymer recycling processes are one of the most prolific investigation topics at the present time. Polyurethane (PU) is placed the 6th in the plastic world market with a production of approximately 12 million tons in 2010 [1]. It is well known that the PU group is synthesized by a reaction between a polyol and an isocyanate. Depending of the kind of the employed polyol and isocyanate, foams with different properties or the denominated CASEs (Coatings, Adhesives, Sealants, Elastomers) can be obtained. Furthermore, foams can be flexible, such as the ones used in mattresses and automotive seats [2] or rigid which are employed in buildings insulation [3–5] and commercial refrigeration [6]. On the other hand, CASEs are used in sporty shoes, electronic products and in shipbuilding industry. Flexible foams represent about the 45% of the total polyurethane production what means about 5.4 million tons per year [7] and therefore their recycling is an urgent task. Flexible foams can be classified into three different groups: conventional foams, which represent about the 80% of the total production, viscoelastic foams, corresponding with the 15% of the production and High Resilience

(HR) foams, which means the 5%. Conventional foams are synthesized or using only a flexible polyether polyol (uncommon) or a mixture of a flexible polyether polyol with a polymeric one. Our research group has developed a glycolysis process of conventional flexible PU foams to recover the raw polyol [8–11]. The process is a split phase glycolysis, where the upper phase is mainly constituted by the recovered polyol, partially unpurified, and the bottom one by the excess of glycol employed in the transesterification reaction and by the glycolysis byproducts such as carbamates and aromatic amines [12]. There are many publications related to conventional flexible polyurethane foams containing only flexible polyether polyols [13–19]. Nevertheless there is no reports about works performed with blends of flexible polyether polyols with polymeric ones, even though these foams containing a flexible polyether polyol and a polymeric one are the PU ones most produced all over the world, what justified the interest of this research work. Polymeric polyols are an acrylonitrile – styrene copolymer (SAN) dispersion in a flexible polyether polyol. The monomers of this polyol are soluble in the solvent (flexible polyether polyol) while the copolymer is insoluble. This research has demonstrated the feasibility of the glycolysis process of flexible PU foams containing polymeric polyol. It has been proven that the recovered polyol can partially replace the raw one for the foams synthesis after a proper purification process.

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2. Experimental

2.1. Materials

Industrial samples of flexible PU foams based on polyether polyol [poly(propylene oxide-block-ethylene oxide) with molecular weight (M_w) of 3500, functionality with respect to OH groups of 3 and polydispersity (PD) of 1.06], on polymeric polyol [functionality with respect to OH groups of 3] and toluene diisocyanate (TDI) were scrapped with an arbitrary diameter ranging from 5 to 25 mm. Two different types of flexible PU foam have been employed: 25HD (provided by Interplasp) with a proportion of 60 pph of flexible polyether polyol (M_w of 3500) and 40 pph of polymeric polyol and 28S (supplied by Interplasp) with a composition of 90 pph of flexible polyether polyol (M_w of 3500) and 10 pph of polymeric polyol. These foams were prepared in the presence of a cell regulator (surfactant), crosslinking agent, catalyst, colouring agent, mineral loads and water as a foaming agent. The ratio of glycolysis agent to PU foam was 1.5:1 by weight, with diethylene glycol (DEG) (from Panreac, Spain) as glycolysis agent. Stannous octoate was used as catalyst (from Sigma–Aldrich).

The glycolysis reactions were carried out in a jacketed 1 L flask equipped with stirrer and refluxing condenser under nitrogen atmosphere to avoid oxidation. The glycolysis agent was placed in the flask and when the temperature reached the desired value (190 °C), the required quantity of scrap foam was added by means of a continuous feeder during an hour, according to its dissolution. The zero time for the reaction was taken when all the foam was fed. Temperature was maintained constant during the feeding and the reaction.

The extraction process to purify the polyol phase was carried out using demineralised water as solvent, acidified with hydrochloric acid (37%, from Panreac, Spain) to obtain a solution with pHs between 4 and 5. The purification process was also carried out in a jacketed 1 L flask equipped with stirrer and refluxing condenser under nitrogen atmosphere to avoid oxidation. Once the extraction temperature was achieved, the sample was agitated at 300 rpm during 10 min. Next, it was centrifuged for 10 min at 3000 rpm in a Jouan MR 1812 centrifuge to ensure phase separation. Furthermore, water was removed from the refined recovered polyol by means of a furnace working at 100 °C.

The foaming assays were carried out using blends of polyether polyol [poly(propylene oxide-block-ethylene oxide) molecular weight (M_w of 3500), functionality with respect to OH groups of 3, polydispersity (PD = 1.06)] with the recovered one. TDI 80:20 (supplied by Merck) was employed as isocyanate and stannous octoate (from Sigma–Aldrich) was used as chain extension catalyst. Water was used as blowing agent. The amine catalysts Tegoamin 33 and Niax A-1 (Tegoamin BDE) were supplied by Goldschmidt. Niax silicone L-620 LV was provided by Osi Specialities.

2.2. Characterization techniques

At given times intervals aliquots were sampled, cooled and centrifuged to ensure the total separation of phases. They were dissolved in tetrahydrofuran (THF from Panreac, Spain) at a concentration of 10 mg ml⁻¹ and then filtered (pore size 0.45 μm). Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution (MWD) as well as concentration of polyol in the products. The percentage of recovered polyol was calculated as a function of the chromatogram areas. The correspondence between the chromatogram areas and the polyol, sub-products and glycol concentrations are determined by previous calibration with different solutions of raw polyols and DEG of known concentration. This method allows to calculate the polyol

concentration in the upper phase with an accuracy of ±0.04% by weight. Measurements were performed with a Viscotek GPCmax VE-2001 TDA 302 Detectors, equipped with two columns (Waters Styragel HR2 and Styragel HR0.5) using THF as eluent at 40 °C (flow: 1 mL min⁻¹) and a refractive index detector. Poly(ethylene glycol) standards (from Waters, USA) were used for MWD calibration. The glycolysis products were separated and their properties analysed. Hydroxyl number and acidity were determined by standard titration methods (ASTMD-4274-88 [20] and ASTMD-4662-93 [21], respectively). Viscosity was measured by a rotational Brookfield LVTDV-II viscometer. Each experimental analysis (OH number, acidity and viscosity) was repeated at least twice and the average value has been given.

All chemicals used in these analyses were of the quality required in the standards. Chemical structures of the glycolyzate products were studied by Fourier Transform Infrared Spectroscopy using a Perkin Elmer 16PCFT-IR spectrometer; droplet samples were impregnated on KBr discs.

Refined recovered polyol was also analysed by means of GPC in order to know polyol, by-products and DEG concentration in the final product.

3. Results and discussion

3.1. Feasibility study of the glycolysis process of flexible PU foams containing polymeric polyol

Glycolysis reactions were carried out in the optimal conditions previously determined for conventional flexible PU foams synthesized only with a flexible polyether polyol [22].

Fig. 1 shows the GPC chromatograms of an upper phase (UP) and a bottom phase (BP) sample at 40 min of the 25HD foam glycolysis in comparison with GPC chromatograms of flexible polyether polyol, polymeric polyol and diethylene glycol (DEG).

In Fig. 1 the Peak I of the upper phase of the 25HD foam glycolysis corresponds with a molecular weight of 27,050 g/mol and

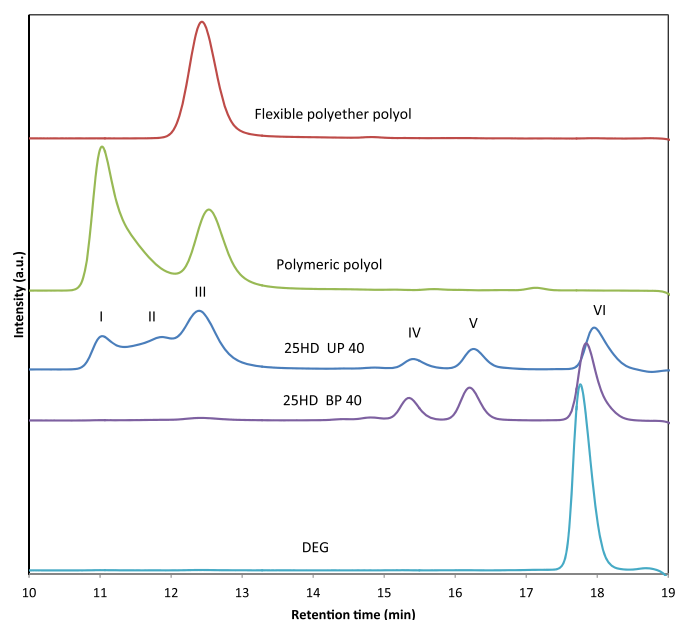


Fig. 1. GPC chromatograms of an upper phase (UP) and a bottom phase (BP) sample at 40 min of the 25HD foam glycolysis obtained with diethylene glycol and stannous octoate in the glycolysis agent in comparison with GPC chromatograms of flexible polyether polyol, polymeric polyol and diethylene glycol (DEG). Peak I = SAN; Peak II = urethane oligomers; Peak III = recovered polyether polyol; Peaks IV and V = reaction by-products; Peak VI = glycolysis agent.

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