



# Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol



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## ABSTRACT

In the last years, high resilience polyurethane foams (HR foams) production has experienced an intensive growth as a consequence of their wide application field, causing an important increment of the generated waste. HR foams containing PU dispersions polyols are the last tendency in the HR foam industry, due to the improvement of the flame retardant properties and the emissions reduction of volatile compounds in comparison to the traditional graft polymeric HR polyols. In this work the extension of the glycolysis process to the recycling of this kind of foams has been carried out. Diethylene glycol (DEG), glycerol 99% PS and crude glycerol, coming from the biodiesel production, have been assayed as glycolysis agents. All of these glycolysis agents provided a split phase product with an upper phase mainly constituted by a traditional HR polyol and a bottom phase consisting of the excess of glycolysis agent and several reaction byproducts. However, the polyol content in the final product has been greater with the employment of glycerol. Moreover, flexible and rigid foams have been synthesized by using the recycled polyols or the glycolysis bottom phase, respectively. This way, it is achieved a global and sustainable recycling process for the valorization of two waste substances: the HR PU foam and the crude glycerol.

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## 1. Introduction

Nowadays, polymer recycling processes attract the attention from the research and industrial worlds as a direct result of the enforcement of the environmental legislations. Some years ago, landfill was the most used alternative at the end of a product life. However, the massive enforcement of the environmental laws has provoked an increase in the research of their waste treatment. Polyurethane (PU) is one of the most important kinds of polymers with a global production of 17.565 millions tons [1], which makes its recycling an urgent task. PU is synthesized by means of the reaction between a polyol, which contains active hydrogen groups, and an isocyanate; giving as a result a substituted carbamic acid ester or urethane. The mechanism of this reaction is a nucleophilic addition of the polyalcohol oxygen to the carbon of the isocyanate group, by six-centred ring as reaction intermediate [2]. The diversity of polyols and isocyanates allows the synthesis of numerous different compounds covering a huge range of

application, generating different kinds of residues that must be recycled to agree the environmental legislation. The PU can be classified mainly in foams and in the denominated CASEs (Coatings, Adhesives, Sealants and Elastomers). Furthermore, foams can be divided in flexible, such as the ones used in mattresses and automotive seats [3], and rigid, commonly applied in buildings isolation [4–6] and commercial refrigeration [7]. Regarding the CASEs uses, they can be found as part of sporty shoes, athletics tracks, electronic products and ships structures.

Physical recycling processes are useless for the majority of the polyurethane specialities due to their thermostable nature and, as a consequence, chemical recycling processes are the best ones to be used. The most interesting and extended chemical recycling process for PU is glycolysis. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of the glycol [2].

Glycolysis processes have been described for a great variety of polyurethane products, including flexible foams [8–26] and rigid ones [27–32] and also the denominated CASEs [8,33–35]. Glycolysis processes of reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) polyurethanes have been also reported [36–39].

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Nevertheless, glycolysis processes of high resilience flexible PU foams have not been yet reported in literature. In recent years, there has been a significant increase in the manufacture of HR foams in Europe and, as expected, HR foams are now attracting the attention of many foam manufacturers in North America and Asia [40]. In the last years, high resilience foam production has begun to increase sharply as a consequence of the wide application field that presents this kind of foams. HR foams are involved in flexible PU foams with high performance properties for superior comfort, support and durability. HR foams present a better support factor (which is the main function a foam can provide), higher fatigue resistance and larger durability compared to conventional foam and for this reason its popularity is increasing continuously, providing an important increment of the generated waste. HR foams are produced by long-chain polyether polyols with higher molecular weight (4000–6000 g/mol) and a higher proportion of ethylene oxide than in the case of conventional foams [41]. Besides, in their synthesis is very common the employment of HR polymeric polyols instead of traditional HR polyols, with the aim of improving the mechanical properties of the final foam.

The last tendency in the synthesis of HR foams consists on the employment of polymeric polyols containing disperse particles of polyurethane (polyisocyanate polyaddition polyol, PIPA polyols [42]) in a traditional HR polyol with the aim of improving the mechanical properties of the final HR foam. This kind of polymeric polyol does not contain any monomers as styrene and acrylonitrile, improving this way the flame retardant properties of the HR foam synthesized and reducing the emissions of residual VOCs (volatile organic compound) up to a 75%. Fig. 1 shows the emissions reduction achieved by means of using HR PIPA polyols in comparison to the traditional graft HR polyols for a HR foam with a density of 60 kg/m<sup>3</sup> [43].

In another study, residual VOC tests carried out to LGA standard with the employment of a PIPA polyol based foam of 60 kg/m<sup>3</sup> density showed that the total emissions were of 95 ppm after 3 days and of 25 ppm after 7 days [40], while for a similar styrene/acrylonitrile copolymer polyol (graft polyol) were 220 ppm after 3 days and 100 ppm after 7 days.

Additionally, PIPA polyols present excellent resilience (>65–73% higher than normal HR), impressive support factor, also known as compression modulus (up to 3.3, comparable to latex and about 20–25% higher than conventional HR foams), superior “hand feel” (similar to latex), superior long term physical properties when compared to the usual HR systems available from the market and lower odour as a result of the elimination of styrene and acrylonitrile.

Taking into consideration all the commented technical and environmental advantages that provide PIPA polyols to the synthesis of HR flexible PU foams, it is estimated that their level of production will increase sharply in the following years all over the world [40].

Hence, the principal goal of this paper is to extend the glycolysis process, developed for conventional and viscoelastic flexible foams, to PIPA polyols based HR foams with the same conditions and cleavage agents, in order to put in value the foam waste without needing a selective collection or a previous separation step. Furthermore, the other main goal is to demonstrate the great benefits (scientific, environmental and economic) of the employment of crude glycerol, coming from the biodiesel production, in the glycolysis process of flexible HR PU foam waste. Finally, the suitability of both of the recovered phases for new foams synthesis has been demonstrated.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Glycolysis

Residual scraps with an arbitrary diameter ranging from 5 to 25 mm from the HR flexible PU foam named 35HR (provided by INTERPLASP) were treated. This HR foam presents an isocyanate index of 104 and is based on a PIPA HR polyether polyol [poly(propylene oxide-block-ethylene oxide), with functionality 3, a base polyol of M<sub>n</sub> 4850 g/mol and OH number = 35 mg KOH/g] and on toluene diisocyanate (TDI). Besides, it was originally prepared incorporating in the recipe a cell regulator (surfactant), a cross-linking agent, catalyst, colouring agent, mineral loads and water (foaming agent). Diethylene glycol (DEG) (from Panreac, Spain), Glycerol 99% PS (from Panreac, Spain) and crude glycerol with a purity of 80% (provided by Biocombustibles de Cuenca S.A.) were used as glycolysis agents. Stannous octoate (from Sigma-Aldrich) was used as catalyst.

#### 2.1.2. Polyurethane synthesis

The flexible foaming assays were carried out using mixtures of the recovered polyols with polyether polyol poly(propylene oxide-block-ethylene oxide), M<sub>n</sub> of 3500, functionality with respect to OH groups of 3, polydispersity (PD) = 1.06. 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 Tegoamin BDE were supplied by Goldschmidt. Nix silicone L-620 LV was provided by Osi Specialities.

Rigid PU foams based on polymeric methylene diphenyl diisocyanate (PMDI) were prepared using a raw rigid polyol (M<sub>n</sub> = 555 g/mol, OH = 455 mg KOH/g, acidity = 0.15 mg KOH/g and humidity = 0.1%) and replacing it partially with the bottom phases that have been obtained in the glycolysis of HR foam. PMDI was supplied by Poliuretanos Aismar, S.A. The catalyst used was Tegoamin BDE and the surfactant was Tegostab B8404, both supplied by Evonik Degussa International AG. Deionized water was used as a blowing agent.

### 2.2. Glycolysis

The glycolysis reactions were carried out, during 150 min after the conclusion of the feeding time, 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 optimal feeding rate selected was 5 g min<sup>-1</sup>. The ratio of glycolysis agent to PU foam was 1.5:1 by weight and 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 catalyst concentration in the glycolysis agent was kept constant at 1.3 wt%.

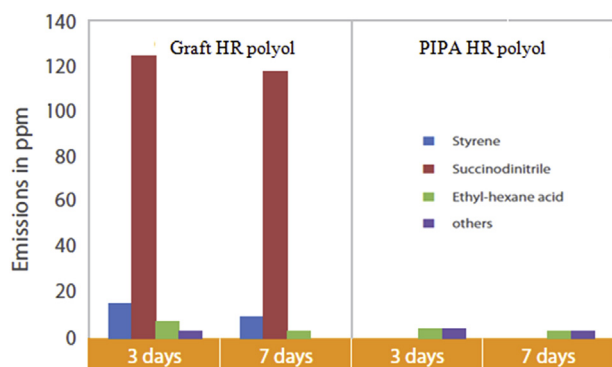


Fig. 1. VOCs emissions comparison [43].

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