

Glycolysis of flexible polyurethane wastes using stannous octoate as the catalyst: Study on the influence of reaction parameters

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ABSTRACT

The general purpose of polyurethane chemical recycling is to recover constituent polyol. Among the suitable processes, glycolysis, and specially glycolysis in two-phases is the one that allows recovering the polyol with the highest quality in comparison to single-phase processes. Recently stannous octoate has been stated as the catalyst that provides the fastest decomposition rate and the one that allows obtaining a recovered polyol with similar characteristics to fresh polyol. In this work a study of the main reaction parameters has been carried out. Optimal catalyst concentration, ratio of glycolysis agent to treated PU foam and optimal reaction temperature have been determined.

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1. Introduction

Polyurethanes (PU) have been used in diverse areas and are one of the most important groups of plastics because of their versatility. Polyols are essential components in the manufacture of polyurethanes. By modifying molecular weight and functionality, polyols provide a diverse range of PU materials. The most important group among PU specialities are the flexible foams, reaching the 29% of the total production. They are widely used in furniture, mattresses and automotive seats [1]. As a direct consequence of their commercial success an increasing quantity of wastes is disposed by landfilling. Such wastes comprise not only post-consumer products but also scrap from slabstock manufacturing, which can reach the 10% of the total foam production. Recycling is an alternative approach to landfilling. On the one hand there are physical processes. These kinds of processes do not modify polymer internal structure. In physical processes, chemical wastes are mechanically turned into flakes, granules or powder to be used in new materials production [2]. Physical processes such as melt-processing methods are successfully applied to thermoplastic, but in the case of PU foams these kinds of processes are not suitable due to PU foam crosslinked structure. Only rebonding has been

developed for carpet underlay [3]. By this reason PU foam wastes must be treated using chemical recycling processes. Chemical recycling involves chemical processes and/or thermal processes in which polymers are decomposed in basic hydrocarboned units known as monomers that can be used as synthesis materials in chemical and petrochemical industry. Chemical processes implying product degradation, like pyrolysis or oxidative degradation [4,5] have been described in literature. Hydrolysis, treatment with esters of phosphoric acid, aminolysis with low weight alkanolamines and glycolysis have been stated as suitable processes to break down the PU chain by transesterification [6–11]. However, most of these processes produce a liquid mixture of compounds with hydroxyl active groups, which can be used only in blending with raw materials to obtain low quality products.

All over the years, our research group has investigated in the development of a chemical process for the recovery of polyols from wastes of flexible PU foams. The selected process is a two-phase glycolysis. As it has been commented before, single-phase processes produce a liquid mixture of products containing the recovered polyol and other hydroxyl active groups [12–18]. Nevertheless, better quality products can be achieved from flexible polyurethane foams using a two-phase glycolysis, enabled by the higher molecular weight of polyols used in these kinds of polyurethanes. By means of an excess of glycolysis agent, much larger than the stoichiometric quantity, the reaction product splits in two-phases, where the upper layer is mainly formed by the recovered

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polyol from the PU and the bottom layer by the excess of glycolysis agent and reaction by-products [19]. This process is based on the transesterification of urethane bonds by the reaction of hydroxyl end groups of glycols, releasing the polyol to the reaction mixture.

A very important variable in glycolysis process is the choice of glycol. The time required to reach the complete conversion, the chemical properties of the polyol phase and its purity depend on it. In order to know its effect on the process, a study of the glycolysis reactions in the presence of different low weight glycols was fulfilled: monoethylene glycol (MEG), diethylene glycol (DEG), monopropylene glycol (MPG), dipropylene glycol (DPG) were studied as possible glycols to be used in the two-phase glycolysis process. Glycols containing primary hydroxyl groups, more polar than the secondary ones, led to less polluted polyols. Propylenic glycols increased mutual solubility of phases, and even prevented the phase splitting when DPG, a branched glycol, was used. Whatever the catalyst used, DEG showed the best performance providing the highest polyol content in the upper phase, as well as the faster degradation process [19].

Another important factor affecting properties of the recovered products and time required to reach the complete degradation of the foam is the choice of catalyst. With the aim of determining the optimum catalyst to carry out the glycolysis process several ones were proved. Potassium octoate showed to be a very effective catalyst of the PU glycolysis process and the conditions for its usage were optimized. One established a standard reaction condition, the activities of several octoates were compared in order to establish the reaction mechanism [20–22]. In general, all the catalysts assayed showed appropriate activity after 2 h, allowing the complete recovery of the polyol. Among them, stannous octoate employed in standard conditions, yielded the highest quality of recovered polyol in the shortest reaction time [21,22]. The activity of stannous octoate in comparison with the other catalysts assayed was so high that a new study for the optimization of the conditions for using stannous octoate in the PU degradation process is necessary. In this work, as an extension of previous studies, optimal stannous octoate concentration, ratio of glycolysis agent (DEG + Stannous octoate) to treated PU foam and optimal reaction temperature have been determined.

2. Experimental

2.1. Materials

Industrial samples of flexible PU foam based on polyether polyol [poly(propylene oxide-block-ethylene oxide) molecular weight ($M_w = 3500$), functionality with respect to OH groups:3,

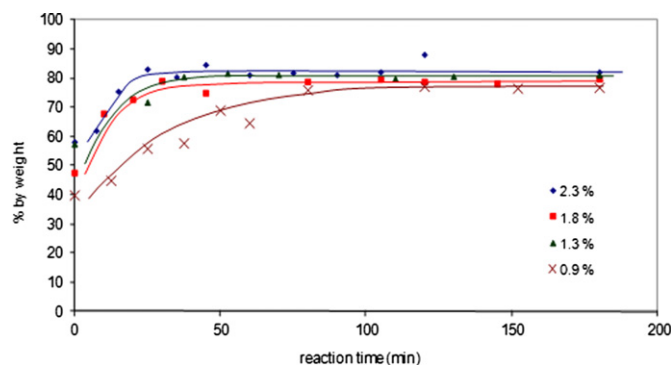


Fig. 1. Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different catalyst concentrations, in the presence of DEG as glycolyzing agent. $T_R = 189^\circ\text{C}$; $W_{\text{glycol ag.}}/W_{\text{PU}} = 1.5$.

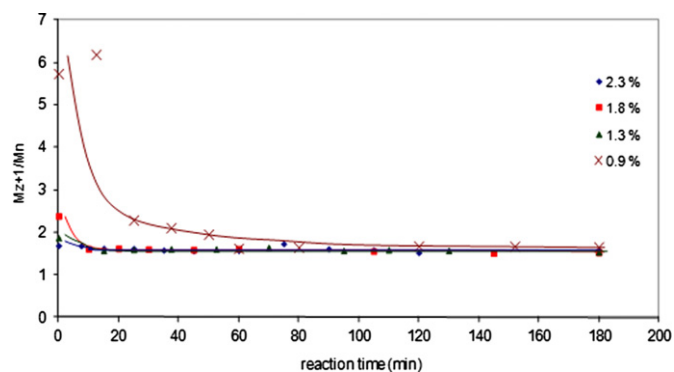


Fig. 2. Evolution of glycolysis products in the upper phase during the glycolysis reaction of PU foams for different catalyst concentrations, in the presence of DEG as glycolyzing agent. $T_R = 189^\circ\text{C}$; $W_{\text{glycol ag.}}/W_{\text{PU}} = 1.5$. Changes in M_{z+1}/M_n with time.

polydispersity (PD = 1,06)] and toluene diisocyanate (TDI) were scrapped with an arbitrary diameter ranging from 5 to 25 mm. These foams had been prepared in the presence of a cell regulator (surfactant), crosslinking agent, catalyst, colouring agent, mineral loads and water as a foaming agent. The scrap foam was reacted in several mass ratios, with diethylene glycol (DEG) (PS from Panreac, Spain) as glycolysis agent. The ratios of glycolysis agent to PU foam ranged from 0.9 to 1.5 by weight. 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 raised the desired level, the required quantity of scrap foam was added during an hour by means of a continuous feeder, 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. Experiments were carried out in the temperature interval 179–189 °C.

2.2. Characterization techniques

At given time 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 1.5 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

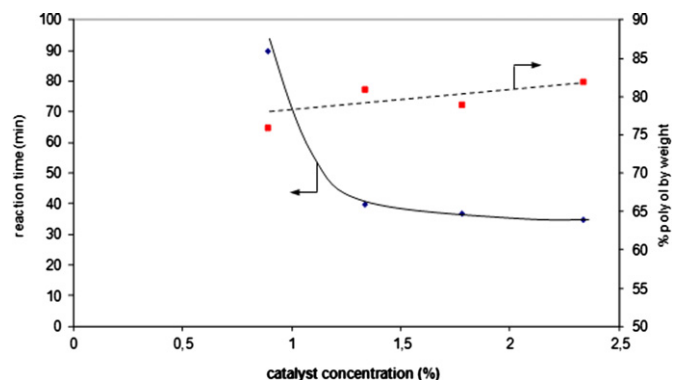


Fig. 3. Influence of the catalyst concentration on the time to reach the maximum polyol recovery and on the final polyol concentration in the upper phase. $T_R = 189^\circ\text{C}$; $W_{\text{glycol ag.}}/W_{\text{PU}} = 1.5$.

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