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Recovery of polyols from flexible polyurethane foam by “split-phase” glycolysis with new catalysts

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Abstract

Polyurethanes (PU) represent one of the most important groups of plastics, so the increasing quantity of wastes makes their recycling an urgent task. The general purpose of polyurethane chemical recycling is to recover constituent polyol, a valuable raw material. Among the suitable processes, glycolysis, specially in two phases, allows better quality products. In this study glycolysis reactions of flexible polyurethane foams were conducted in “split-phase” with different catalysts, in order to study their activity. Diethanolamine, titanium *n*-butoxide as well as octoate salts, which are novel compounds for this application, showed suitable catalytic activity. Reaction kinetics and glycolysis products were investigated. Times to reach complete conversion, chemical properties of the polyol phase and its purity depend on the catalyst employed. The novel catalysts developed have been probed to be a worthy and economic alternative to traditional catalysts.

Keywords: Polyol; Polyurethane; Recovery; Glycolysis; Catalysts

1. Introduction

In recent years, polyurethane (PU) materials have been developed strongly in the world, proving it to be one of the most versatile polymers. Since legislative measures for wastes involve increasing economical costs and public awareness of environmental issues has grown enormously, PU recycling is nowadays an urgent task. In the chemical recycling, the urethane bonds can be broken down releasing the polyols of the polymer chain by means of a suitable reagent. In the literature processes have been described based on hydrolysis and hydroglycolysis [1–4] or methanolysis [5] which can convert the PU into a liquid mixture of polyol and aromatic products. The reaction provides high conversion but leads to some drawbacks associated with purification costs and toxicity. PU has been also treated with esters of phosphoric acid [6] and low weight alkanolamines [7,8], although glycolysis seems more suitable to be applied on an industrial scale in order to obtain quality recovered products.

In the glycolysis processes, the polyurethane chain is degraded by successive transesterification reactions of the urethane bond with low molecular weight glycols with the aid of a catalyst. Several studies have been published dealing with glycolysis of polyurethanes [9–21], concerned mostly with formulation of glycolysis, properties of the products obtained from the recycled polyols and purification of the resulting products. Among other reaction variables, the choice of catalyst is an important factor affecting the properties of the recovered products, as well as the time to reach the complete degradation of the foam. Catalysts used in polyurethane glycolysis include bases like amines,

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hydroxides and alkoxides and Lewis acids as well [22], leading to different extension in secondary reactions.

Typical catalysts of hydrolysis such as alkaline hydroxides have been used in glycolysis processes [23], despite as reported by Simioni et al. [9] that hydrolysis reactions were promoted by potassium hydroxide, leading to higher contents of undesirable aromatic amines. Acetates of Pb, Zn, Mn, Ca, Co and Cd have been described as general catalysts in transesterification reactions [24], although in the case of transesterification of urethane bonds with glycols, only potassium acetate and sodium acetate are mentioned in the literature [10–12], leading to high amine values in the resulting products. As well as aminolysis agent, alkanolamines have been used as co-reagents. Borda et al. [13] studied the dependence of the reaction time on the ratio of diethanolamine to ethylene glycol, whereas Hayashi et al. [14] also included influence of monoethanolamine and triethanolamine. The increase in the amount of alkanolamine provides advantage for the decomposition reaction, although also increases the hydroxyl number and the amine number. In the last years unspecified organometallic catalysts have been used in glycolysis processes [15–17], specially in development of industrial-scale processes [25,26]. Among organometallic compounds, titanium *n*-butoxide has been reported [18,19] as selective catalyst for the urethane group transesterification.

Due to the presence of glycolysis agent, in most of the glycolysis processes above described polyols are recovered in a liquid mixture of products containing hydroxyl active groups. Nevertheless, better quality products can be achieved from flexible foams using a two-phase glycolysis, enabled by the higher molecular weight of polyols used in these kind of polyurethanes. By means of the use of excess amount of glycolysis agent, much more than the stoichiometric quantity, the reaction product splits in two phases, where the upper layer is mainly formed by the recovered polyol from the PU [20].

In this work, two-phase glycolysis reactions of flexible PU foams based in polyether polyols have been carried out with diethylene glycol (DEG) in presence of different catalysts, in order to study their influence on the process: diethanolamine, titanium *n*-butoxide and potassium and calcium octoates as novel compounds for such applications. DEG was selected to study catalyst influence and has since proved to be the most suitable low weight glycol to recover polyols from flexible polyurethane foams by split-phase glycolysis [20].

2. Experimental

2.1. Materials and methods

Industrial samples of flexible PU foam based on polyether polyol [poly(propylene oxide-block-ethylene oxide) $M \sim 3500$, functionality with respect to OH groups of tree] 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 a 1:1.5 mass ratio with diethylene glycol (DEG) (PS, from Panreac, Spain). As catalysts we used diethanolamine (DEA), titanium(IV) butoxide, potassium octoate and calcium octoate (Table 1).

The glycolysis reactions were carried out in a jacketed 1 dm^3 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 up to the desired level, the required quantity of scrap foam was added during an hour by means of a continuous feeder at a constant rate, according to its dissolution. This feeding rate selected was 5 $\mathrm{g\,min}^{-1}$. The zero time for the reaction was taken when all the foam was fed. Temperature was maintained at 189 °C during the feeding and the reaction.

2.2. Characterization

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 $\mathrm{mg\,mL}^{-1}$ 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. Measurements

Table 1
Properties of the catalysts used

Catalyst	Purity	Concentration (by weight)	Supplier
DEA	98.0%	Mass ratio to glycol 1:6	Panreac, Spain
Ti(IV) butoxide	98+%	0.34% in the glycolysis agent	Aldrich, USA
K octoate (potassium 2-ethylhexanoate)	46.4% in decyl alcohol (isomers mixture)	2.2% in the glycolysis agent	Nusa, Spain
Ca octoate (calcium 2-ethylhexanoate)	32.3% in T_b 200–220 °C petroleum distillate	2.2% in the glycolysis agent	Nusa, Spain