

KINETIC STUDY OF THE GLYCOLYSIS OF FLEXIBLE POLYURETHANE WASTES USING STANNOUS OCTOATE AS CATALYST

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Abstract

Polyurethanes represent one of the most important groups of plastics, and so the increasing quantity of wastes makes their recycling an urgent task. Among the processes suitable, glycolysis, and specially glycolysis in two phases is the one that allows better quality products. It has been demonstrated that stannous octoate is the catalyst that provides the fastest decomposition rate and allows to obtain a polyol with similar characteristic to fresh polyol. In this work a study of the main reaction parameters has been carried out. The optimal catalyst concentration and the ratio of glycolysis agent (DEG) to the treated PU foam have been determined.

Keywords: Polyol; Polyurethane; Recovery; Glycolysis; Octoate

1. Introduction

Polyurethanes (PU) have been used in diverse areas and are one of the most important groups of plastics because of their versatility. Flexible PU foams are the most important group among PU specialties. They are widely used in furniture, mattresses and automotive seats. As a direct consequence of their commercial success an increasing quantity of wastes is disposed by landfilling. By this reason its recycling is now an urgent task. Two-phase glycolysis has been demonstrated to be the method to obtain the best quality products. The glycolysis of PU's is a chemical recycling process based on the exchange reaction of polyols and glycols in the urethane bond. The process allows the breaking down of the PU matrix [1] and the release of the polyol. One of the most decisive aspects is the catalyst choice. This reaction has been traditionally catalyzed by alkanolamines, titanium compounds, or acetates. Later the employment of catalysts based on potassium and calcium octoates opened up a new way to catalyze the glycolysis of polyurethanes. Recently stannous octoate have showed proper catalytic activity with an enhanced quality of the recovered polyols and faster decomposition rates. In this work the optimal stannous octoate concentration and the ratio of glycolysis agent (DEG) to the treated PU foam have been determined.

2. Materials and Methods

Industrial samples of flexible PU foam based on polyether polyol [poly(propylene oxide-block-ethylene oxide) $M_w=3500$, functionality with respect to OH groups:3, 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 (potassium 2-ethylhexanoate 46,4 % by weight in decyl alcohol (isomers mixture), from NUSA, Spain).

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 feeding rate selected was 5 g min⁻¹. The zero time for the reaction was taken when all the foam was fed (aprox during 1 h). Temperature was maintained constant during the feeding and the reaction. Experiments were carried out in the temperature interval 179-189°C.

The reaction mixture was periodically sampled and analyzed. Gel permeation chromatography (GPC) was used to determine the molecular weight distribution as well as the concentration of polyol in the products. Measurements were performed using Tetrahydrofurane (THF) as eluent and poly(ethylene glycol) standards.

3. Results and Discussion

As reported in a previous work, the transesterification of urethanes with the hydroxyl groups of glycols proceeds very slowly in the absence of a catalyst [2]. This fact has been marked in the literature [3] for this kind of interchange reactions in condensation polymers. For this reason the choice of catalyst for the process is an important factor affecting the properties of the recovered products and the time taken to reach the complete degradation of the PU chain. In literature the catalysts used in PU glycolysis include Lewis acids and bases such as amines, hydroxides, and alkoxides [4]. Recently, the performance evaluation of new catalysts based on alkaline-earth octoates has been carried out. In a previous report stannous octoate had been demonstrated to be the catalyst with the fastest decomposition rate [5]. In addition, this catalyst provides a polyol with a purity greater than those obtained using other catalysts previously employed for this kind of reaction. The use of stannous octoate as transesterification catalyst for the PU glycolysis has provided a novel way to enhance the polyol recovery. In this work some of the main reaction parameters have been studied.

3.1. Catalyst concentration

Degradation reactions of the PU foams were carried out in the same conditions, just varying the amount of catalyst added. In Fig.1 the evolution of polyol concentration in the upper phase with the reaction time is depicted as a function of the catalyst amount used.

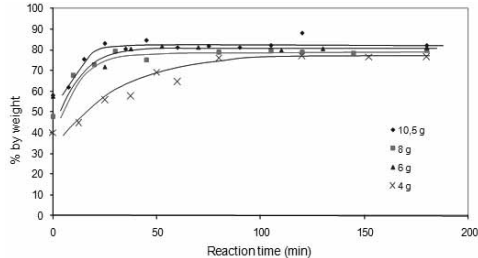


Fig.1. Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different catalyst concentrations, in the presence of DEG as glycolyzing agent. $T_R=189^\circ\text{C}$; $W_{\text{glycol ag}}/W_{\text{PU}}=1.5$

As can be seen, there is an amount of catalyst (6 g) from which to up the reaction rate remain more or less constant. That is, the addition of more catalyst does not improve the reaction rate, approaching zero order behavior [6]. For this reason the use of 6 g (catalyst concentration in the glycolysis agent=1.3 %) of stannous octoate would be the best choice.

3.2. Mass ratio of glycolysis agent

In a two-phase glycolysis of PU, the amount of glycol added is much larger than the stoichiometric quantity required to produce the transesterification. The excess is used not only to displace the equilibrium to the glycol substitution, but also to promote the phase splitting which allows the obtaining of a polyol-rich phase. However, a too large excess of glycol would imply huge volume equipment requirements and larger amounts of bottom phase that has to be recycled by distillation. In order to determine the optimal amount of glycol a series of degradation experiments were carried out. In these reactions all the parameters were kept constant just varying the mass ratio of glycolysis agent to PU foam. Fig.2. shows polyol concentration history in the upper phase.

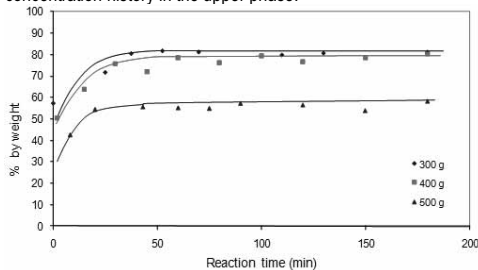


Fig.2. Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different ratios of glycolysis agent (DEG) to the treated foam. $T_R=189^\circ\text{C}$; Catalyst concentration in the glycolysis agent=1.3%.

It can be observed that a mass ratio of glycolysis agent to PU foam of 0.9:1 (500 g of PU foam) provides a low polyol content in the upper phase. Mass ratios 1.125:1 (400 g of PU foam) and 1.5:1 (300 g PU foam) let to obtain a similar polyol. The only difference is the reaction time. Reaction time with the mass ratio 1.125:1 is only ten minutes more than ratio 1.5:1. This means that glycolysis reactions must be carried out at a mass ratio glycolysis agent to PU foam of 1.125:1.

3.3. Influence of temperature

The beginning of thermal degradation of PU compounds and their derivatives is around 120-250 °C. This range is strongly influenced by the physical characteristic of the PU. With the aim of minimizing depolymerisation reactions the maximum glycolysis temperature for the study was set at 189°C that was determined to be the optimal temperature in a previous report [7]. Fig.3. represents the evolution of polyol concentration in the upper phase with reaction time.

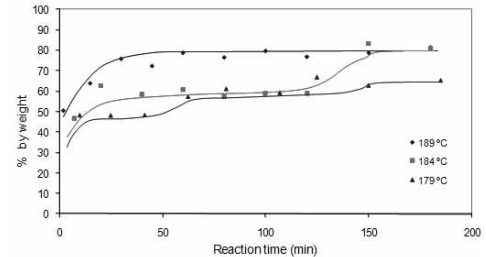


Fig.3. Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams at different temperatures. Catalyst concentration in the glycolysis agent=1.3%; $W_{\text{glycol ag}}/W_{\text{PU}}=1.5$.

Reactions carried out at 179°C and 184°C provides a slow recovery process, as demonstrated by the low percentage of polyol in the upper phase. It has been demonstrated that a slight decrease in the temperature affects strongly to decomposition rate. Take into account this fact, the optimal reaction temperature would be 189°C.

4. Conclusions

Stannous octoate shows a proper performance as catalyst in the glycolysis of PU wastes. As it had been reported in a previous report, an increase in the reaction temperature and catalyst concentration enhances the degradation rate. It has been proved that the optimal conditions to carry out the glycolysis reaction are the following ones: Catalyst concentration in the glycolysis agent =1.3 %; Mass ratio of glycolysis agent to PU foam=1.125:1; Reaction temperature=189°C.

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