

PRELIMINARY STUDY OF THE RECYCLING OF POLYURETHANES BY GLYCOLYSIS TO OBTAIN NEW RECYCLED FOAMS

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Abstract

A preliminary study of the main parameters affecting the reaction and properties of the recovered polyol has been carried out using reference and waste polyurethane samples. The glycolysis experiments were performed under atmospheric pressure in a glass stirred tank reactor at a constant temperature. Diethylene glycol and diethanolamine were used as solvent and catalyst respectively. Gel permeation chromatography was used to determine the presence of polyol in the products and chemical structure of glycolysate products were studied by FTIR. The application of the recovered polyol was evaluated by foaming tests to study the replacement ratio of the commercial polyol by recycled polyol. Replacement ratios up to 30% of the commercial polyol by the recycled one have been achieved.

Keywords: Waste Polyurethane, Glycolysis, Feedstock Recycling, Polyol

1. Introduction

Polyurethanes (PU) comprise a major engineering plastic material family with an annual production capacity world wide of nearly 12 million tonne (2007) [1]. Despite their spreading in different applications their recycling rate is low. Polyurethanes constitute a group of polymers with versatile properties and a wide range of commercial products. Polyurethane foams, are used for many engineering applications, such as thermal insulation in construction, cushions, acoustic and comfort applications in automotive and so on.

The general purpose of the polyurethane feedstock recycling is to recover constituent polyol, a valuable raw material. One of the alternatives for the recycling of polyurethane foams includes their chemical treatment by glycolysis to convert the PU back to polyols [2]. In this study, the split-phase glycolysis of flexible polyurethanes, from cushions and comfort applications was investigated to define the suitable treatment for this flexible PU waste.

2. Materials and Methods

Industrial samples of flexible PU foam and 4,4'-methylene bis-(phenylisocyanate) (MDI) were scrapped with a diameter ranging from 8-15 mm. The scrap foams were reacted with diethylene glycol (DEG) as a glycolysis agent (PS, from Panreac, Spain) and diethanolamine (DEA) (PS, from Panreac, Spain) as a catalyst [3]. The mass ratio of glycolysis agent (DEA+DEG) to PU foam was 1.5:1.0 and 1:6 between catalyst and glycol (DEA:DEG) [3].

The glycolysis reactions were carried out under atmospheric pressure in a glass stirred tank reactor at a constant temperature, 195°C. When the temperature of DEG and DEA mixture reached the specified value, the scrap flexible PU foam was fed. The temperature was kept at 195°C during the feeding. At given intervals, aliquots were sampled and cooled to room temperature. The samples were dissolved in tetrahydrofuran (HPLC, from Labscan, Ireland) and then filtered (pore size 0.45 µm). GPC was used to study the evolution of the reaction and FTIR spectroscopy was used to study the chemical structures of the glycolysate products [4].

3. Results and Discussion

The degradation process of the flexible PU foam resulted in the yield of two liquid phases. The upper one, which mainly contains the polyol, was pale yellow while the other, essentially DEA and DEG, was brown.

3.1 Study of the polyol content

The study of the polyol content of the glycolysate products was made by following two different strategies. In the first set of experiments, the zero time for the reaction was taken when all the foam was fed, 50 g. Then aliquots were sampled at given intervals and subsequently analyzed by GPC to study the presence of the polyol in the upper layer (Figure 1). Peak I is assigned to the original polyol in agreement with the GPC profile of the commercial polyol. On the other hand, peaks II and III are related to un-reacted DEG and DEA, respectively.

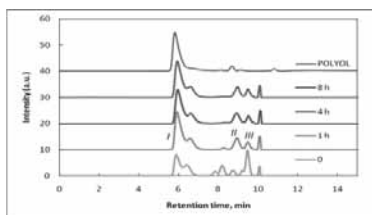


Figure 1. GPC record of upper liquid layer of products after PU glycolysis with DEG and DEA

In the second set of experiments, aliquots were sampled during the feeding process. Polyurethane foam was fed discontinuously in batches of 5 g. Then, when the 5 g of PU were totally dissolved the aliquots were sampled. The increasing intensity of the polyol signal during the addition of PU foam could mean that the dissolution process can be considered as a reaction process because the polyol is appearing in the liquid phase proportionally to polyurethane addition.

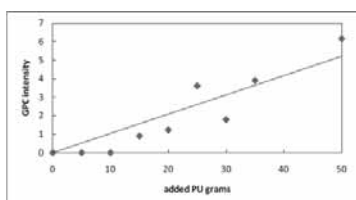


Figure 2. Maximum intensity of the Peak I (polyol) during the feeding

In Figure 2 are shown the FTIR spectra of the starting polyol used in the synthesis of the polyurethane foams and the one recovered from the upper phase. The IR spectral examination confirms the GPC results; the chemical structure of the recovered product is quite similar to the virgin one.

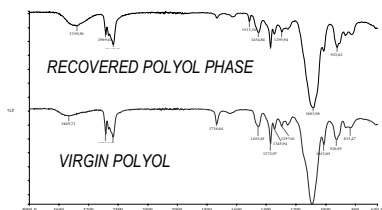


Figure 3. Comparison of FTIR spectra of the polyol and recovered product

3.2 Application of the product in the formulation of new PU foams

Foaming assays were made to study the application of the upper layer obtained in the glycolysis of flexible PU foam. The foaming formulations were modified replacing original polyol by the recovered product but other products like foaming agents and catalyst were not added in this study. In Figure 3 commercial PU foam,

foam with the 33% of replacement and foam with 50% of replacement are shown respectively.



Figure 3. Foaming assays with partial replacement of the commercial polyol by recovered polyol 33% (centre) and 50% (right)

4. Conclusions

A simplified evaluation of the recycling of polyurethanes by glycolysis has been attempted in order to understand how the process must be carried out in order to recover a polyol which could be used for new formulations of flexible polyurethanes.

GPC profiles show that a polyol containing phase is achieved. According to Figure 1, the dissolution process of the PU must be studied to complete the study of the reaction and the kinetic. The replacement of commercial polyol by recovered products without adding any other substances in the foaming process, decreases the quality of the final product but show potential to foam. Foaming assay has to be completed with the optimization of the process by adding foaming agents, surfactants and catalyst and a further characterization of the obtained foams.

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