Chemical recovery of flexible polyurethane foam wastes

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Abstract

The development of a chemical process for the recovery of polyols from flexible polyurethane foam wastes with enough quality to be reutilized in foaming has been a major challenge for scientists during recent years. In that way the objective of chemical recycling of PU wastes is the recovery of its major constituent, the polyol, in an environmental friendly way that is performed with the lowest cost and without hazardous residues production. The glycolysis of PU wastes in the presence of a large excess of glycolitic agent allows one to obtain a polyol rich upper phase and a bottom phase containing mainly glycol and isocyanate derivatives. Different metal octoates derived from cycloaliphatic carboxylic acids can be used as the catalyst with suitable catalytic activity. The optimization of process conditions has demonstrated that there is a narrow window of process conditions (relation between phases, temperature, catalyst, etc) in which the split phase glycolysis can be carried out. The recovered polyols have to be subjected to purification by aqueous liquid-liquid extraction before refoaming in a conventional formulation mixed with fresh ones in a large range of proportions. The excess of glycolyzing agent in the bottom phase has to be returned to the cycle by vacuum distillation. The vacuum residue containing the isocyanate derivatives can be applied as an initiator in the synthesis of rigid polyols, allowing the complete use of the glycolyzates from PU recycling.
Keywords: glycolysis, PU wastes, octoates, plastic recycling.

1 Introduction

Since polyurethanes (PU) were discovered in 1937, it has turned out to be one of the most important groups of plastics. They are produced by the reaction of an

isocyanate and a multifunctional alcohol, called polyol. Although there is a wide variety of polyols, polyether polyols are the most common product used. The variety of polyols and additives used in polyurethane manufacture yields a whole family of polyurethane specialities to be applied in multiple products. Among them, flexible foams are the most important group, reaching 29% of the total PU production [1]. However, as a direct consequence of their commercial success, an increasing quantity of wastes is disposed of in landfills, involving environmental problems. One technological option for waste disposal of PU foam, other than landfilling, is recycling.

Physical recycling processes, such as melt-processing methods, are successfully applied to thermoplastics, but in the case of PU most of them are not suitable due to their crosslinked structure [2]. Only rebonding has been developed for carpet underlay. An alternative way to recycle includes chemical treatment to convert the PU back into its starting raw materials, especially polyols.

Hydrolysis, treatment with esters of phosphoric acid, aminolysis with low weight alkanolamines and glycolysis have been described as suitable procedures to break down the polyurethane chain [3-9]. 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.

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 this kind of PU. 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 polyol from the PU and the bottom layer by the excess of glycolysis agent [10].

The purpose of this research project was the development of a chemical process for the recovery of polyols from wastes of flexible PU foams. To make this, a two-phase glycolysis process was selected. Using a two-phase glycolysis, better quality products can be achieved from flexible PU foams, enabled by the higher molecular weight of polyols used in this kind of PUs. 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.

2   Preliminary approach

Firstly, previous assays were carried out to establish an experimental procedure and to check the viability of the process for the industrial flexible PU foam wastes selected. In these experiments, diethylene glycol was used as glycolysis agent and diethanolamine as catalyst, as described in the literature for the treatment of other kind of PU´s [11, 12]. It was observed reaction products splitting, where the upper layer was mainly formed by the recovered polyol from the PU and the bottom layer by the excess of glycolysis agent and the reaction by-products. As a result of these experiments, a basic approach of the reaction mechanism was established.

The choice of glycol and catalyst was an important factor affecting properties of the recovered products and time required to reach the complete degradation of the foam. Therefore, in order to know their effect on the process, a study of the glycolysis reactions in the presence of different low weight glycols and catalysts was fulfilled: monoethylene glycol (MEG), diethylene glycol (DEG), monopropylene glycol (MPG), dipropylene glycol (DPG) as glycols and diethanolamine and titanium n-butoxide as catalysts. In the study were also included two new compounds that had not been previously described in such applications: potassium octoate and calcium octoate.

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 [13, 14].

As can be seen in Figure 1 whatever the catalyst used, DEG provided the highest polyol content in the upper phase, as well as the faster degradation process.

All the catalysts assayed showed appropriate activity in comparison with the noncatalyzed process, allowing the complete recovery of the polyol. Potassium and calcium octoates have been found advantageous to catalyze the process [15]. They provided reaction times and polyol concentration in the upper phase comparable to those obtained with DEA, the most active of the catalysts previously reported. Additionally, the amount of octoate added represented only the 15% of the DEA used.
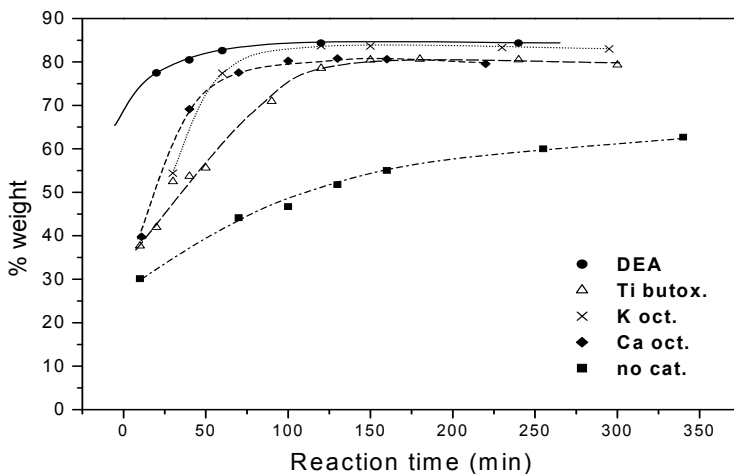

Figure 1:   Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different catalysts in the presence of DEG as a glycolysis agent. Tr = 198ºC; $W_{glycol\ ag.}$ / W_{foam} = 1.5 (from [15]).

3 The octoates performance

Because octoates showed a proper performance as catalysts in the glycolysis, a detailed study on the activity of octoate metal salts was carried out.

The analysis of the influence of catalyst concentration revealed that an increase in their amount helped the PU decomposition. However, this increase is less noticeable as the catalyst concentration raises [16]. As example, in figure 2 can be appreciated that as greater is the amount of catalyst lower is the concentration in polyol of the upper phase.

It means that a catalyst concentration increase entails a negative effect on the recovered polyol purity. The bigger the catalyst concentration, the more polluted the polyol is due to the surfactant ability of metal octoates.

It was also established that the temperatures suitable for glycolysis operation are included in a narrow interval. Temperatures lower than 170ºC provides too slow degradation rates, whereas values higher than 200ºC promote secondary reactions of decarboxylation. In this interval, an increase in the reaction temperature speeds the degradation up markedly. There is also oxidation of reaction products related to this rise, as well as a steady increase in the polyol pollution.

The influence of the mass ratio glycolysis agent to treated foam was also examined because it affects not only the operation but also is related to economic factors. A minimum glycol to foam ratio of 0.75 is required to achieve phase
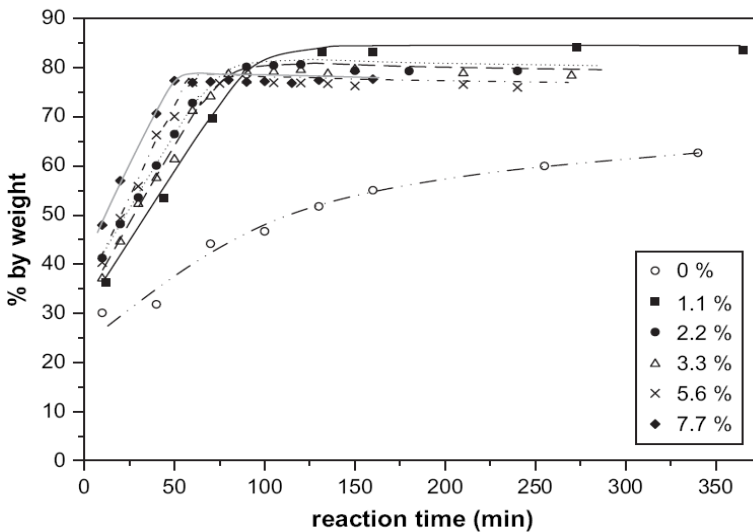

Figure 2: Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different catalyst concentrations, in the presence of DEG as a glycolyzing agent. $T_R=190ºC$; $W_{glycol\ ag.}/W_{PU}=1.5$ (from [16]).

splitting and proper mixing of the initial mixture. It was also observed that a large excess of glycol enhanced the prompt dissolution of the foam and the overall operation, in addition to the improvement of the polyol phase purity. As an increment of the foam:glycol ratio larger than 1:1,5 did not produce a significant improvement of the process, that proportion was selected as the optimal value to carry out the process.

4   The importance of the type of salt

As previously the application of metal octoate salts as catalyst for PU degradation has not been described, it was necessary to know if the anionic or the metallic part of the molecule is the main responsible of the catalytic activity and their influence on the process. In addition, the results obtained in this study of reactivity allowed us to propose a chemical mechanism for the process.

Potassium benzoate and potassium acetate were assayed against octoate to study the influence of the type of chain linked to the carboxylic group. It was not observed any relevant change in the characteristics of the products obtained or in the degradation kinetics. All the catalysts showed a weak basic character, being the transesterification driven by this basicity. The polyol concentration history in the upper phase with different transition metals is shown in Figure 3.

For each cation studied, the octoate salts exhibited different catalytic activities according to the cation hardness and coordination ability [17, 18].

Taking into account several theories applied to polyester transesterification [19, 20], it can be postulated that the glycolysis of polyurethanes in the presence
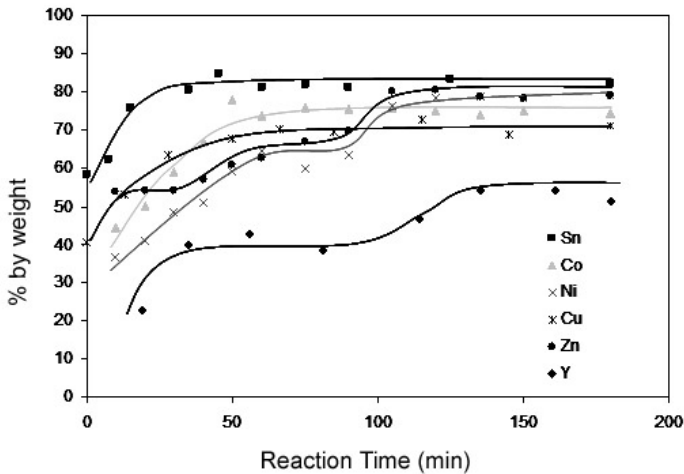

Figure 3:   Evolution of polyol content in the upper phase during the glycolysis reaction of PU foams for different transition metal octoates as catalysts in the presence of DEG as a glycolyzing agent. $T^a_R = 190°C$; $W_{glycol\ ag.}/W_{PU} = 1.5$; $C_{cation} = 6 \cdot 10^{-2}$ m.

of transition metal carboxylates is not only a result of a simple addition of an alkoxide, but there could be also an intermediate formed by a coordination complex of the metallic species with the carbonyl group of the urethane, specially favorable in the case of the stannous salt.

Depending on the catalyst type (alkaline, alkaline-earth or transition metal salt) it would be promoted the alkoxide formation, or the coordination for the insertion. Lithium and stannous octoates were the most active catalysts in good agreement with their greater hardness and ability of coordination, respectively.

5 The purification and conditioning of the phases for further reuse

The biphasic glycolysis process, despite providing a purer product in the upper phase than other methods, requires a further purification of both phases. The upper rich polyol phase has to be cleaned of low molecular weight glycols in order to be applied like a commercial polyol and the large excess of glycol in bottom phase has to be vacuum distilled in other to be reused obtaining a toxic hazardous residue from the isocynate part of PU formulation.

Liquid-liquid extraction, namely a washing with water, is a suitable solution for the purification of the rich in polyol upper phase. Low weight polyhydroxy compounds such as the glycol used show high affinity towards water, making
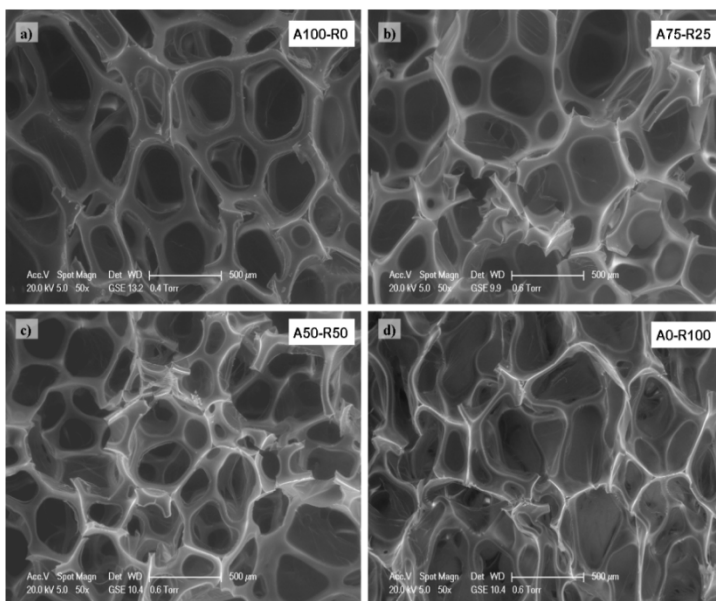

Figure 4:   Microphotographs of the PU foam framework for different percentages of recovered polyol replacing the raw standard polyol. a) Fully fresh polyol, d) fully recovered polyol (from [22]).

water extraction a suitable alternative for the purification. The use of a slight acid pH an medium temperature enhance the efectibity of the washing of the polyol phase [21].

This change of properties can be easily understood if one has a look on the foam cells microstructure. As it can be seen in the SEM microphotograph in Figure 4 the cell structure becomes more imperfect as the amount of recovered polyol employed in the recipe increased

The foaming assays performed with the polyols obtained by glycolysis demonstrated that with the exception of using only recovered polyol to get the foam, the rising profiles of the foams formulated with recovered polyol were close to that obtained with fresh polyol. Nevertheless other physical properties of the foam such as resilience, compresion strenght, tensile strength and the elongation suffer a slight reduction when recycled polyol is used.
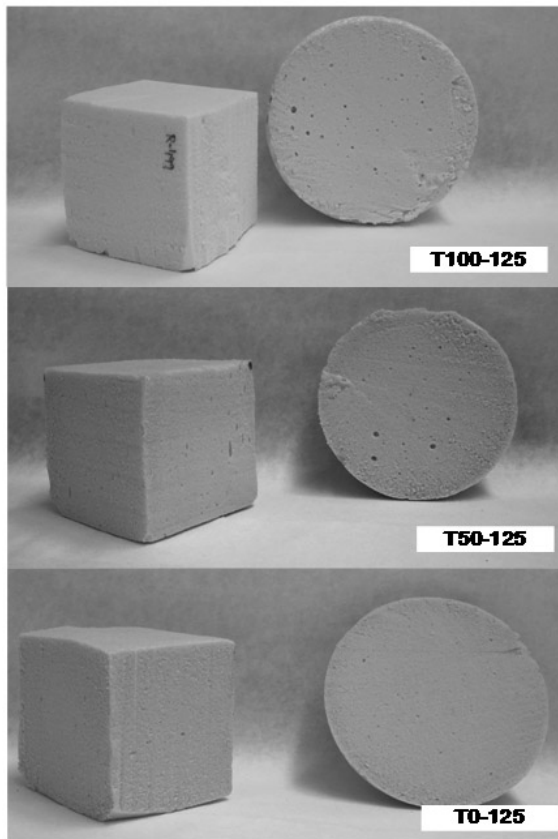

Figure 5:   Foams synthesized with polyols prepared using the residue from the glycolyzed isocyanate part of PUs obtained after distillation of the bottom phase.

Replacements of fresh polyol up to 50% by weight in the formulation did not give rise to changes in the physical properties of foams. Bigger percentages allowed the foaming, but it would be required a change in the formulation in order to keep constant the mentioned properties of interest related to comfort applications of the PU foams [22].

The glycolysis bottom phase is a side product of the recycling process. That implies an environmental and economic problem which should be solved. In order to give value to these by-products, it has to be recovered by means of distillation under reduced pressure. Thus, most of the glycol is returned in the glycolysis.

The bottom residue after distillation contains active hydrogens due to remaining glycol, aromatic amines, transreaction carbamates and other by-products. These functional groups make it suitable to be used as initiator of anionic polymerization for the synthesis of polyether polyols. The residue was characterized, and according to its properties, can be used as initiator like in a commercial grade of rigid polyol based on toluenediamine (TDA). Subsequently the polyols obtained were successfully foamed in a TDA-polyol based formulation [23]. Rigid foams of a nice quality were obtained using the bottom phase residue as can be seem in figure 5.

According to the studies on the further treatment of both phases, an integrated process for the glycolysis was proposed and protected under patent [24, 25]. It allows the recovery of a quality poliol avoiding economic and environmental problems related to by-products generation.

6   Conclusions

By means of a two-phase glycolysis process, quality recovered polyols can be obtained from flexible PU foams. The research work developed in the mentioned field has allowed the development of an integrated process for two-phase glycolysis of flexible polyurethane foam wastes. The process has been scaled up until pilot scale yielding identical quality products and recovery levels of raw materials than at lab scale. The upper phase was constituted by the recovered polyols and the bottom one by the reaction by-products. The recovered polyols have been subjected to purification by aqueous liquid-liquid extraction. From the residual phase obtained, the excess of glycolyzing agent has been recovered by distillation for reuse in the glycolysis. The vacuum residue has been applied in rigid polyol synthesis, allowing the complete use of glycolyzates from PU´s and the purified polyol polyol phase can be refoamed mixed wish fresh polyol to give high quality PU foams.

Acknowledgements

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