



Glycolysis of viscoelastic flexible polyurethane foam wastes



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ABSTRACT

Nowadays polymer recycling processes are one of the most published research topics due to the increasing importance that is achieving the environmental world. One of most important types of polymers are the polyurethanes and among them flexible foams are the most produced ones, posing about the half of polyurethane total production. Flexible foams can be classified as conventional, viscoelastic and High Resilience (HR) ones. In recent years, viscoelastic foams have had positive recognition and acceptance from consumers and, therefore, they have seen increased their applications in the world plastic market becoming of this way the PU sector that is undergoing a faster growing. As a consequence, viscoelastic foam wastes are experimenting an exponentially growing and therefore getting a proper solution is a crucial goal. In this work, for the first time in literature, the extension of the glycolysis process to flexible viscoelastic polyurethane foams scraps has been demonstrated based on the optimized conditions determined by the research group in previous papers for conventional flexible polyurethane foam wastes and consequently a glycolyzate susceptible of being foamed in a further step has been obtained. Furthermore, it has been stated that the glycolyzate, once the purification process has taken place, is really similar to the ones achieved in the glycolysis of conventional foams and for this reason the same foaming recipe has been successfully applied.

In consequence, one of the biggest challenges of the flexible PU foam glycolysis has been achieved since it has been demonstrated that the joint recycling treatment of conventional and viscoelastic PU foams blends, which mean approximately the 95% of the total flexible PU foam production, would be possible avoiding this way the necessity of a selective collection or a previous separation step of PU scraps.

Furthermore, it has been stated that the glycolysis bottom phase obtained from viscoelastic flexible PU foam scraps can be used to replace partially a raw rigid polyol in the synthesis of new rigid PU foams. Hence, a global valorization of the glycolysis phases has been achieved converting them in profitable substances.

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1. Introduction

Nowadays, polymer recycling processes are one of the most important research topics as a consequence of the enforcement of the environmental legislation. Several years ago, the final destiny of the most of the polymer wastes was the landfills. However, the present legislation has forced to look for new solutions for the wastes treatment. As a consequence, the investigation related to the polymer scraps treatment is a new and very promising field of research that has experimented an exponential growing in the last decade. Polyurethane (PU) is one of the most important polymers

all over the world with a production of approximately 12 million tons in 2010 [1] that placed PU the 6th in the plastic market. As a result of the high versatility of PU, a lot of different products can be synthesized and each product produces a different kind of residue that must be treated to obey the environmental laws. Glycolysis is the most widely used chemical recycling process for PU. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of the glycol. Glycolysis has been studied for a lot of polyurethane specialties, including flexible and rigid foams and also the denominated CASES (Coatings, Adhesives, Sealants, Elastomers). The glycolysis of elastomers based on polyether polyol and MDI has been described by several authors [2–4]. Besides, Datta and Haponiuk [5] studied the glycolysis of polyurethane coating wastes with mass ratios of scrap polyurethane coating to glycol

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ranging from 2:1 to 10:1, potassium acetate (KAc) and sodium hydroxide (NaOH) as catalysts and reaction temperatures from 190 to 240 °C. In addition to the glycolysis processes of CASES, glycolysis of foams has been also widely studied. Rigid PU foams glycolysis has been described in literature by several authors [6–10] with a range of temperatures between 170 and 200 °C and a ratio glycol:PU of 2:1 by weight. On the other hand, glycolysis processes of flexible PU foams have been also developed using different catalysts, glycols, temperatures and ratios glycol:PU [2,3,11–26]. Table 1 summarizes the main parameters involved in the glycolysis of the PU specialties. All the publications cited about PU flexible foams are related to glycolysis of conventional flexible PU foams synthesized only with a flexible polyether polyol. For this reason, in a previous report our investigation group carried out the extension of the glycolysis process to conventional flexible PU foams containing polymeric polyols [27]. However, in spite of the high number of publications about the glycolysis of flexible PU foams, there is no report about one of the most demanded PU specialties in these days, the viscoelastic flexible PU foams. Viscoelastic foams, also known as memory or temper foams, were first commercialized during the mid 60's as a result of NASA's AMES Research technology transfer program. The properties of these foams allowed to redistribute the G-Force suffered by astronauts during take-off and re-entry. However, it has not been until the last decade when the viscoelastic flexible PU foam market has begun to grow considerably and commercial products have been made widely available to consumers. The main advantage of this kind of foam is the pressure distribution performance. For this reason, viscoelastic foams are usually employed for mattresses and pillows, since they adjust themselves to accommodate the various pressure points, such as the shoulder and hips, which are body areas that press hardest into the bed during sleep. Due to its gradual recovery, viscoelastic foam also can be described as "slow recovery" foam. As a consequence of these viscoelastic foam's unique physical characteristics have promoted its popularity in the bedding and medical industries. Aside from bedding and medical purposes, viscoelastic material can be also used in a lot of different applications: standard household furniture, office furniture and vehicle seating applications. Furthermore it can be applied in sports equipment, power tools,

and footwear. Viscoelastic foam has also found utility in ergonomic applications such as neck, back and leg pads, as well as in arm and wrist rests for computers. Besides, it can act as shock protection within electronics equipment and has been used in specialty packaging, military and commercial aircraft seating and weaponry (for recoil suppression) [28]. The negative consequence of the viscoelastic flexible PU huge number of applications is the growing generation of non-biodegradable wastes and finding a solution to this problem is an urgent environmental goal. Therefore, the main aim of this report is to carry out the recycling process of viscoelastic flexible PU scraps by means of glycolysis with the final objective of achieving a glycolyzate susceptible of being foamed in a further step.

On the other hand, it is really important to take into consideration that flexible PU foam scraps arrive to the waste manager as a mixed waste collection. As a consequence, the development of a process to treat together the PU scraps with independence of the kind of PU foam would avoid the necessity of a selective separation step of PU scraps and would mean a great advance in the glycolysis world.

2. Experimental

2.1. Materials and methods

Industrial samples of the viscoelastic flexible PU foam V-50 190 (provided by Interplasp), based on a viscoelastic polyol founded on polyether polyol [poly(propylene oxide-block-ethylene oxide), functionality with respect to OH groups of 3] and toluene diisocyanate (TDI) were scrapped with an arbitrary diameter ranging from 5 to 25 mm. This foam was prepared in the presence of a cell regulator (surfactant), crosslinking agent, catalyst, colouring agent, mineral loads and water as a foaming agent. Diethylene glycol (DEG) (from Panreac, Spain) was used as glycolysis agent. 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 reached the desired value (190 °C),

Table 1
Global overview of the polyurethane glycolysis.

Polyurethane type	Catalyst	Glycol	Glycol:PU by weight	Temperature (°C)	References
Elastomer	EA	Monoethyleneglycol	2:1	160–190	[2–4]
	DEA	Monopropylene glycol			
	LiAc	Triethylene glycol			
		Poly(ethylene glycol)			
Coating	KAc	Diethylene glycol	1:2–1:10	190–240	[5]
	NaOH	Monoethyleneglycol			
Rigid foam	EA	Diethylene glycol	2:1	170–200	[6–10]
	DEA	Dipropylene glycol			
	BaO	Tetraethylene glycol			
	KOH				
	NaOH				
	Dibutyltindilaurate				
	NaAc				
	ZnAc ₂				
Flexible foam	KAc	Monoethyleneglycol	1:10–1.5:1	160–245	[2,3,11–26]
	DEA	Diethylene glycol			
	TiBut	Monopropylene glycol			
	LiOct	Dipropylene glycol			
	SnOct	Triethylene glycol			
		Poly(ethylene glycol)			
		Glycerine			
		Butane 1,4 diol			
		Pentane 1,5 diol			
		1,6-hexanediol			

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