

Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol

D. Simón, A. de Lucas, J.F. Rodríguez, A. M. Borreguero*

Chemical Engineering Department, University of Castilla-La Mancha, Institute of Chemical and Environmental Technology, ITQUIMA, Avda. Camilo José Cela s/n, 13004, Ciudad Real, Spain.

*Corresponding author. Tel: +34-926-295300 ext. 6353; fax: +34-926-295318. E-mail address: Anamaria.Borreguero@uclm.es

Abstract

In the last years, high resilience polyurethane foams (HR foams) production has experienced an intensive growth as a consequence of their wide application field, causing an important increment of the generated waste. HR foams containing PU dispersions polyols are the last tendency in the HR foam industry, due to the improvement of the flame retardant properties and the emissions reduction of volatile compounds in comparison to the traditional graft polymeric HR polyols. In this work the extension of the glycolysis process to the recycling of this kind of foams has been carried. Diethylene glycol (DEG), glycerol 99% PS and crude glycerol, coming from the biodiesel production, have been assayed as glycolysis agents. All of these glycolysis agents provided a split phase product with an upper phase mainly constituted by a traditional HR polyol and a bottom phase consisting of the excess of glycolysis agent and several reaction byproducts. However, the polyol content in the final product has been greater with the employment of glycerol. Moreover, flexible and rigid foams have been synthesized by using the recycled polyols or the glycolysis bottom phase, respectively. This way, it is achieved a global and sustainable recycling process for the valorization of two waste substances: the HR PU foam and the crude glycerol.

Key words: *polyurethane, high resilience, glycolysis, dispersion polyol, crude glycerol*

1. Introduction

Nowadays, polymer recycling processes attract the attention from the research and industrial worlds as a direct result of the enforcement of the environmental legislations. Some years ago, landfill was the most used alternative at the end of a product life. However, the massive enforcement of the environmental laws has provoked an increase in the research of their waste treatment. Polyurethane (PU) is one of the most important kinds of polymers with a global production of 17.565 millions tons [1], which makes its recycling an urgent task. PU is synthesized by means of the reaction between a polyol, which contains active hydrogen groups, and an isocyanate; giving as a result a substituted carbamic acid ester or urethane. The mechanism of this reaction is a nucleophilic addition of the polyalcohol oxygen to the carbon of the isocyanate group, by six-centred ring as reaction intermediate [2]. The diversity of polyols and isocyanates allows the synthesis of numerous different compounds covering a huge range of application, generating different kinds of residues that must be recycled to agree the environmental legislation. The PU can be classified mainly in foams and in the denominated CASEs (Coatings, Adhesives, Sealants and Elastomers). Furthermore, foams can be divided in flexible, such as the ones used in mattresses and automotive seats [3], and rigid, commonly applied in buildings isolation [4-6] and commercial refrigeration [7]. Regarding the CASEs uses, they can be found as part of sporty shoes, athletics tracks, electronic products and ships structures.

Physical recycling processes are useless for the majority of the polyurethane specialties due to their thermostable nature and, as a consequence, chemical recycling processes are the best ones to be used. The most interesting and extended chemical recycling process for PU is glycolysis. 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 [2].

Glycolysis processes have been described for a great variety of polyurethane products, including flexible foams [8-26] and rigid ones [27-32] and also the denominated CASES [8, 33-35]. Glycolysis

processes of reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) polyurethanes have been also reported [36-39].

Nevertheless, glycolysis processes of high resilience flexible PU foams have not been yet reported in literature. In recent years, there has been a significant increase in the manufacture of HR foams in Europe and, as expected, HR foams are now attracting the attention of many foam manufacturers in North America and Asia [40]. In the last years, high resilience foam production has begun to increase sharply as a consequence of the wide application field that presents this kind of foams. HR foams are involved in flexible PU foams with high performance properties for superior comfort, support and durability. HR foams present a better support factor (which is the main function a foam can provide), higher fatigue resistance and larger durability compared to conventional foam and for this reason its popularity is increasing continuously, providing an important increment of the generated waste. HR foams are produced by long-chain polyether polyols with higher molecular weight (4,000–6,000 g/mol) and a higher proportion of ethylene oxide than in the case of conventional foams [41]. Besides, in their synthesis is very common the employment of HR polymeric polyols instead of traditional HR polyols, with the aim of improving the mechanical properties of the final foam.

The last tendency in the synthesis of HR foams consists on the employment of polymeric polyols containing disperse particles of polyurethane (polyisocyanate polyaddition polyol, PIPA polyols [42]) in a traditional HR polyol with the aim of improving the mechanical properties of the final HR foam. This kind of polymeric polyol does not contain any monomers as styrene and acrylonitrile, improving this way the flame retardant properties of the HR foam synthesized and reducing the emissions of residual VOCs (volatile organic compound) up to a 75%. Figure 1 shows the emissions reduction achieved by means of using HR PIPA polyols in comparison to the traditional graft HR polyols for a HR foam with a density of 60 kg/m³ [43].

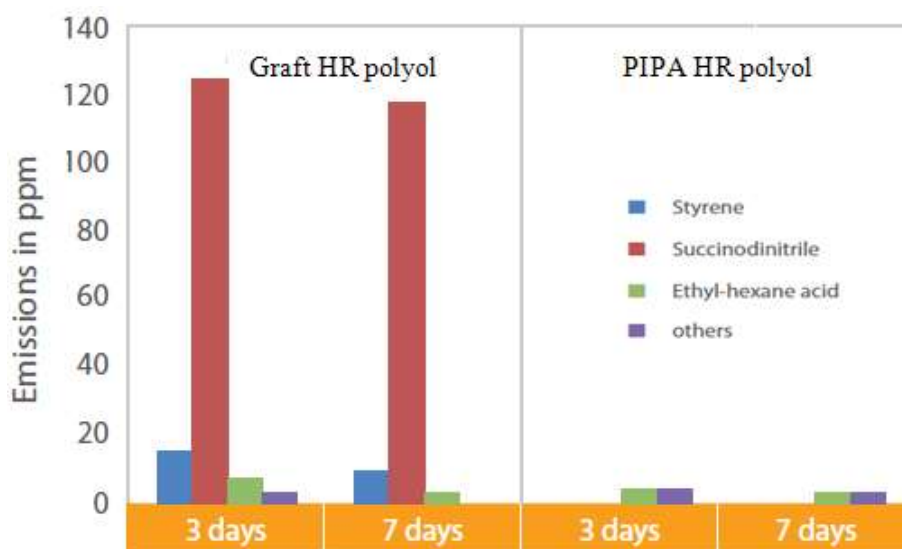


Figure 1. VOCs emissions comparison [43].

In another study, residual VOC tests carried out to LGA standard with the employment of a PIPA polyol based foam of 60 kg/m³ density showed that the total emissions were of 95 ppm after 3 days and of 25 ppm after 7 days [40], while for a similar styrene/acrylonitrile copolymer polyol (graft polyol) were 220 ppm after 3 days and 100 ppm after 7 days.

Additionally, PIPA polyols present excellent resilience (> 65 – 73% higher than normal HR), impressive support factor, also known as compression modulus (up to 3.3, comparable to latex and about 20 to 25% higher than conventional HR foams), superior “hand feel” (similar to latex), superior long term physical properties when compared to the usual HR systems available from the market and lower odour as a result of the elimination of styrene and acrylonitrile.

Taking into consideration all the commented technical and environmental advantages that provide PIPA polyols to the synthesis of HR flexible PU foams, it is estimated that their level of production will increase sharply in the following years all over the world [40].

Hence, the principal goal of this paper is to extend the glycolysis process, developed for conventional and viscoelastic flexible foams, to PIPA polyols based HR foams with the same conditions and cleavage agents, in order to put in value the foam waste without needing a selective collection or a previous separation step. Furthermore, the other main goal is to demonstrate the great benefits

(scientific, environmental and economic) of the employment of crude glycerol, coming from the biodiesel production, in the glycolysis process of flexible HR PU foam waste. Finally, the suitability of both of the recovered phases for new foams synthesis has been demonstrated.

2. Experimental

2.1. Materials

a) Glycolysis

Residual scraps with an arbitrary diameter ranging from 5 to 25 mm from the HR flexible PU foam named 35HR (provided by INTERPLASP) were treated. This HR foam presents an isocyanate index of 104 and is based on a PIPA HR polyether polyol [poly(propylene oxide-block-ethylene oxide), with functionality 3, a base polyol of M_n 4850 g/mol and OH number=35 mg KOH/g] and on toluene diisocyanate (TDI). Besides, it was originally prepared incorporating in the recipe a cell regulator (surfactant), a crosslinking agent, catalyst, colouring agent, mineral loads and water (foaming agent). Diethylene glycol (DEG) (from Panreac, Spain), Glycerol 99% PS (from Panreac, Spain) and crude glycerol with a purity of 80 % (provided by Biocombustibles de Cuenca S.A.) were used as glycolysis agents. Stannous octoate (from Sigma-Aldrich) was used as catalyst.

b) Polyurethane synthesis

The flexible foaming assays were carried out using mixtures of the recovered polyols with polyether polyol poly(propylene oxide-block-ethylene oxide), M_n of 3500, functionality with respect to OH groups of 3, polydispersity (PD) =1.06. TDI 80:20 (supplied by Merck) was employed as isocyanate and stannous octoate (from Sigma-Aldrich) was used as chain extension catalyst. Water was used as blowing agent. The amine catalysts Tegoamin 33 and Tegoamin BDE were supplied by Goldschmidt. Niaux silicone L-620 LV was provided by Osi Specialities.

Rigid PU foams based on polymeric methylene diphenyl diisocyanate (PMDI) were prepared using a raw rigid polyol (M_n =555 g/mol, OH=455 mg KOH/g, acidity=0.15 mg KOH/g and humidity=0.1

%) and replacing it partially with the bottom phases that have been obtained in the glycolysis of HR foam. PMDI was supplied by Poliuretanos Aismar, S.A. The catalyst used was Tegoamin BDE and the surfactant was Tegostab B8404, both supplied by Evonik Degussa International AG. Deionized water was used as a blowing agent.

2.2. Glycolysis

The glycolysis reactions were carried out, during 150 min after the conclusion of the feeding time, 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), the required quantity of scrap foam was added by means of a continuous feeder during an hour, according to its dissolution. The optimal feeding rate selected was 5 g min⁻¹. The ratio of glycolysis agent to PU foam was 1.5:1 by weight and the zero time for the reaction was taken when all the foam was fed. Temperature was maintained constant during the feeding and the reaction. The catalyst concentration in the glycolysis agent was kept constant at 1.3 wt%.

2.3. Extraction process

The extraction process to purify the polyol phase was carried out using demineralised water as solvent, acidified with hydrochloric acid (37%, from Panreac, Spain) to obtain a solution with pHs between 4 and 5 in the case of the degradation reaction carried out with DEG. The purification process was also carried out in a jacketed 1 L flask equipped with stirrer and refluxing condenser under nitrogen atmosphere to avoid oxidation. Once the extraction temperature was achieved, the sample was agitated at 300 rpm during 10 minutes. Next, it was centrifuged for 10 min at 3000 rpm in a Jouan MR 1812 centrifuge to ensure phase separation. Furthermore, water was removed from the refined recovered polyol by means of a furnace working at 100°C.

2.4. Polyurethane foam synthesis

a) Flexible foams

The foaming experiments were carried out according to the evaluation method in free expansion foaming of conventional slabstock foams. A formulation recipe for flexible foams was employed based on a polyol of Mn 3500 in which the virgin polyol was totally or partially replaced for recovered polyol. Flexible foams were cured at 100°C during 15 min.

b) Rigid foams

The rigid PU foams were synthesized by weighting and mixing the desired masses of raw rigid polyol and glycolysis bottom phases (polyol mixture), silicone, water and amine catalyst. Then, the adequate quantity of isocyanate (PMDI) was added to the mixture and the resulting solution was stirred for just 5 s until the moment at which the foam started to grow up. Finally, the obtained foams were cured at room temperature.

2.5. Characterization techniques

At given times intervals, aliquots were sampled from the reactor, cooled and centrifuged to ensure the total separation of phases. They were dissolved in tetrahydrofuran (THF from Panreac, Spain) at a concentration of 10 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. The percentage of recovered polyol was calculated as a function of the chromatogram areas. The correspondence between the chromatogram areas and the polyol, subproducts and glycerol concentrations are determined by previous calibration with different solutions of raw PIPA HR polyol, diethylene glycol, glycerol 99% and crude glycerol of known concentrations. This method allows to calculate the polyol concentration in the upper phase with an accuracy of ±0.04 % by weight. Measurements were performed with a Viscotek GPCmax VE- 2001 TDA 302 Detectors, equipped with two columns (Waters Styragel HR2 and Styragel HR0.5) using THF as eluent at 40 °C (flow:1 mL min⁻¹) and a refractive index detector. Poly(ethylene glycol) standards (from Waters, USA) were used for MWD calibration. The glycolysis products were separated and their properties analysed. Hydroxyl numbers of the recovered polyols and of the bottom

phases were determined by a standard titration method (ASTMD-4274-88). Each experimental analysis was repeated at least twice and the average value has been given.

All chemicals used in this analyse were of the quality required in the standards.

Water content measures for the recovered polyols from HR flexible PU foam scraps were determined by Karl-Fischer method using an automatic titrator Titrino KF. Hydranal Composite 5 (Fluka, Germany) and methanol according Karl Fischer (Panreac, Spain) were used as reagents. These measures were repeated three times and the average value was recorded.

Chemical structures of the glycolyzate products were studied by Fourier Transform Infrared Spectroscopy using a Perkin Elmer 16PCFT-IR spectrometer; droplet samples were impregnated on KBr discs.

3. Results and discussion

3.1. Feasibility study of the glycolysis process of HR flexible PU foams

Taking into account the optimal conditions obtained in previous papers for conventional flexible PU foams regardless the presence of polymeric polyol [22, 24] and for viscoelastic flexible PU foams [25, 26], several glycolysis reactions with the HR foam 35HR were performed. These reactions were carried out employing diethylene glycol (DEG), glycerol 99% PS and crude glycerol (waste from the biodiesel production) as decomposing agents.

Figure 2 shows the GPC chromatograms of upper and bottom phases (UP and BP, respectively) samples at 100 min of the 35HR foam glycolysis reactions and those of the raw PIPA HR polyol and of the transesterification agents.

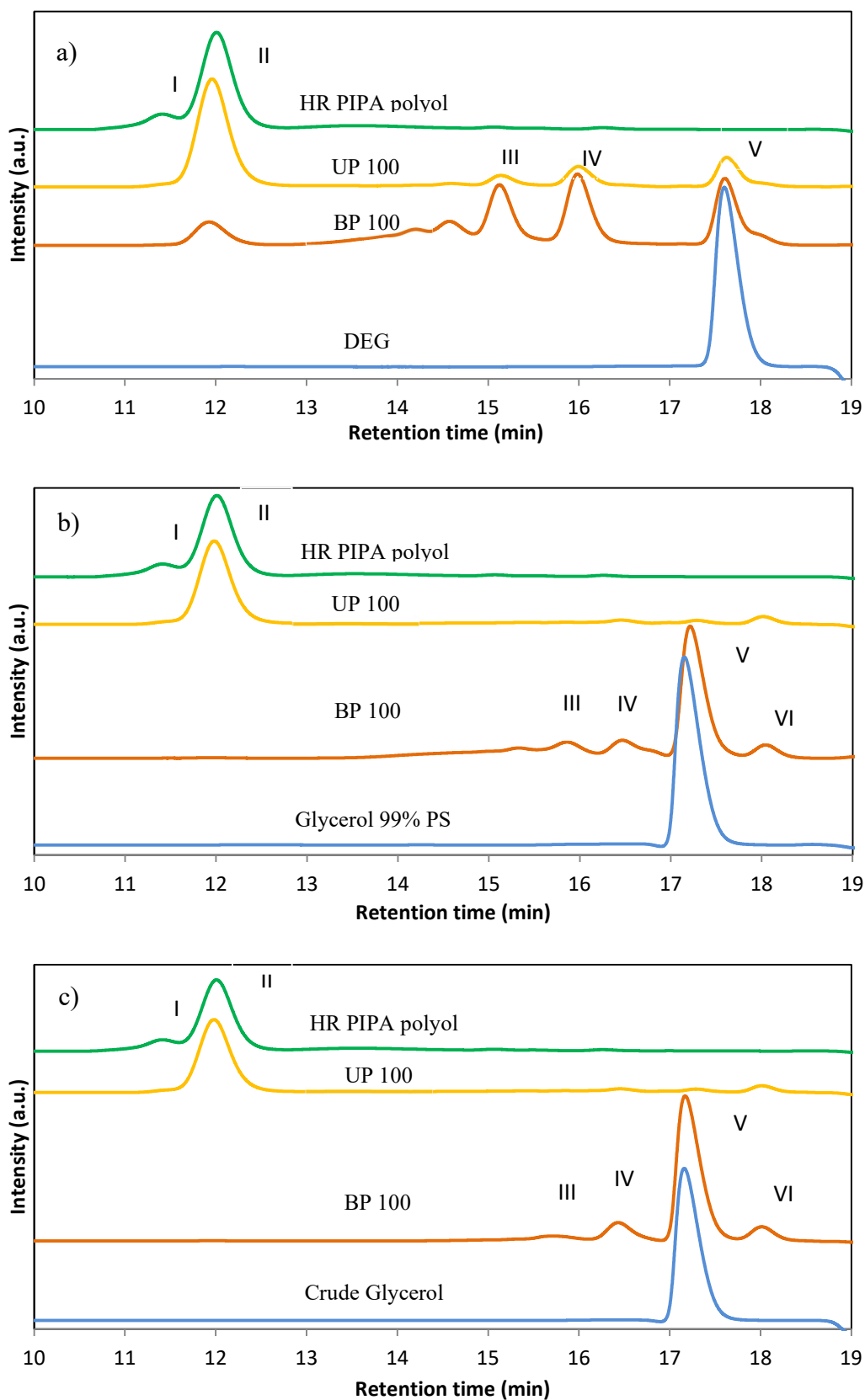
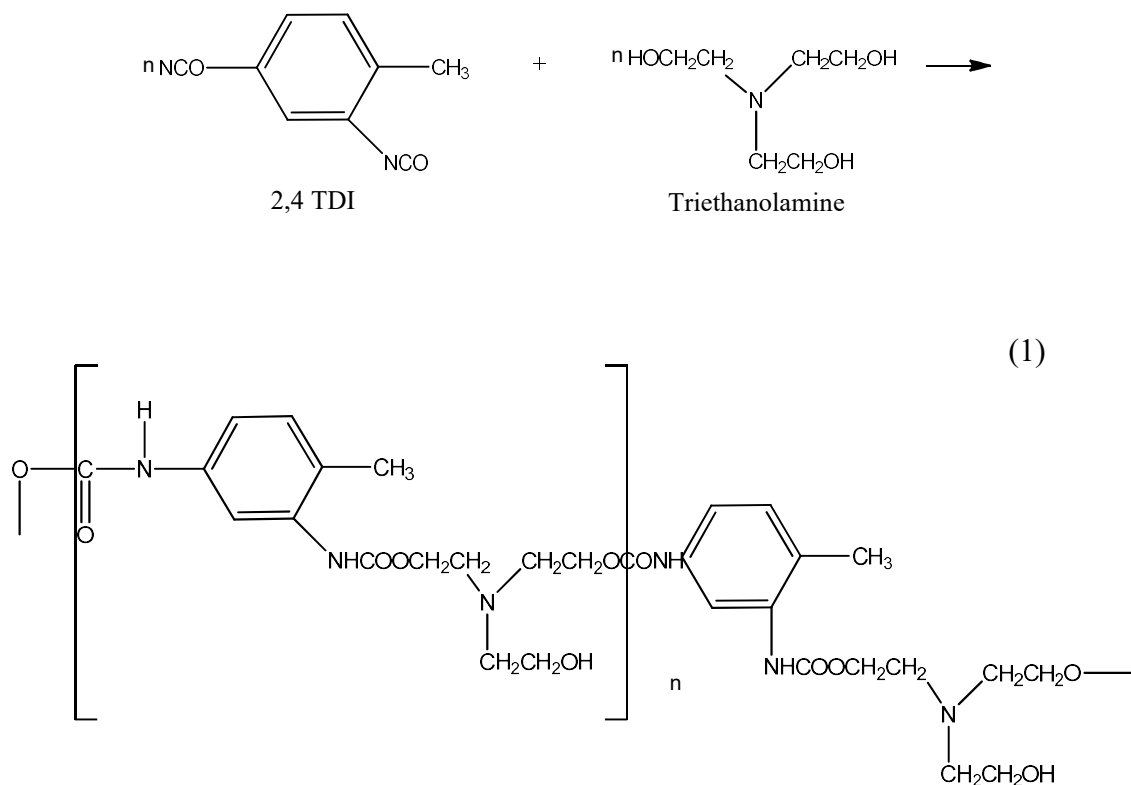


Figure 2. GPC chromatograms of upper phase (UP) and bottom phase (BP) samples at 100 min of the 35HR foam glycolysis reaction obtained with: a) diethylene glycol, b) glycerol 99% PS and c) crude glycerol in comparison with GPC chromatograms of raw PIPA HR polyol and of the raw transesterification agents. Peak I= dispersed PU particles; Peak II=HR base polyol; Peaks III, IV and VI =reaction by-products; Peak V= Transesterification agent.

It can be observed that PIPA HR polyol is constituted by two different peaks. The first one, at a retention time of 11.40 min, corresponds to PU particles that are dispersed in the PIPA polyol, whereas the second peak is assigned to the HR base polyol (retention time 12 min; $M_n=4850$ g/mol). With the aim of understanding the showed chromatogram of the PIPA HR polyol it is crucial to take into consideration that polyisocyanate polyaddition (PIPA) polymer polyols consists of PU particles finely dispersed in liquid polyether polyol obtained *in situ*. The polyether polyols used most frequently for their synthesis are propylene oxide (PO) homopolymers or random propylene oxide - ethylene oxide (PO-EO) copolymers (MW of 3000-3600 daltons) or PO-EO block copolymers with terminal poly[EO] block (MW of 4700-5000 daltons), as it is the case of the 35 HR foam assayed. The formation of PU particles takes place due to the TDI reaction with an alkanolamine (most used route) or a diol in the liquid polyether polyol. The most common alkanolamines are triethanolamine and diethanolamine, whereas the diisocyanates used are TDI and low functionality MDI [42]. PU particles are created as shown in formula 1:



The reactivity of the hydroxyl groups from triethanolamine and from liquid polyether with the diisocyanate is quite similar. Therefore, with the goal of accelerating the reaction of diisocyanate with the primary hydroxyl groups of triethanolamine and ensuring the PU particles formation, catalysts such as dibutyl tin dilaurate or stannous octoate are added [42].

Peaks III, IV and VI of Figure 2 correspond with several glycolysis byproducts, mainly low weight carbamates ending in hydroxyl groups and aromatic amines similar to TDA [23]. These byproducts appear due to secondary reactions such as the glycolysis reaction of the urea groups contained in the PU foam waste, the hydrolysis reaction of PU and the reactions of thermal degradation of PU [25]. Finally, Peak V is assigned to the transesterification agent employed, a) DEG, b) glycerol PS 99% or c) crude glycerol, according to the coincidence in the retention time with the GPC chromatogram of the raw glycol/glycerols.

Regardless the transesterification agent used, Fig. 2 shows that the byproducts concentrations and the one of the decomposing agent are low in the glycolysis upper phase, due to these species present a polarity more similar to the glycolysis agent than to the base HR polyol, which constitutes primarily the chemolysis upper phase. Thus, glycolysis bottom phases are mainly formed by high dielectric constant compounds, such as the reaction byproducts and the transesterification agents.

It is worthy to point out that, glycerol (pure or crude) allows to obtain a cleanest upper phases, with insignificant concentration of byproducts and glycolysis agent. This behavior can be explained considering the higher dielectric constant of the glycerol ($\epsilon = 42.5$) in comparison to the DEG one ($\epsilon = 31.69$), generating of this way a higher affinity of these non-desirable products for the glycolysis bottom phase. This result agrees with the previous results obtained by the research group for the glycolysis of viscoelastic PU foams [26]. Moreover, DEG reaction GPC chromatograms show that the HR recovered polyol represents an important percentage of the glycolysis bottom phase in this reaction (10.6 % by weight), causing a significant decrease in the reaction yield. At this point it is important to take into consideration that HR polyols present a higher proportion of ethylene oxide in

their structure than conventional or viscoelastic polyols [41]. Polyols made only with propylene oxide are terminated with secondary hydroxyl groups and are less reactive than polyols capped with ethylene oxide, which contain a higher percentage of primary hydroxyl groups. Therefore, the increase of the ethylene oxide proportion implies an increasing in the molecule polarity. This is the reason why HR base polyol is partially soluble in the glycolysis bottom phase (even despite of its high average molecular weight) when DEG is the cleavage agent selected, as can be appreciated in Figure 2. However, the higher dielectric constant (higher polarity) of the glycerol avoids the solubilization of the HR base polyol in the bottom phase, remaining entirely in the upper phase and increasing the glycolysis yield.

In summary, crude glycerol avoids the solubilization of HR base polyol in the glycolysis bottom phase and provides an upper phase practically free of byproducts and cleavage agent, demonstrating that can be applied as a novel, very effective and environmental friendly transesterification reactive in the glycolysis process of flexible HR PU foams. It has also the advantage of being the residue of another process and, hence, it has a null or low price, improving the economic feasibility and interest of the process.

Furthermore, it has been demonstrated that is possible to recycle flexible HR PU foams using the same glycolysis reaction conditions previously optimized for conventional flexible PU foams [22, 24] and for viscoelastic ones [25, 26]; avoiding the necessity of a selective collection or a previous separation step.

3.2. Evolution of the glycolysis products in the upper phase during the transesterification reaction of HR PU foam scraps

The evolution of the glycolysis products in the upper phase was studied by means of the areas integration of the GPC chromatograms using the same methodology that was widely explained in a previous paper [25].

The concentration evolution of the PU dispersed particles, the HR base polyol ($M_n=4850$ g/mol) and the cleavage agent during the glycolysis reactions of the HR foam with the different transesterification agents are depicted in Figure 3.

In Figures 3a) and 3b), it can be observed that the higher the reaction time, the lower the dispersed PU particles concentration while the higher the HR base polyol one, respectively. This is a consequence of the progressive urethane groups degradation by the action of the chemolysis agent.

Moreover, Figure 3c) shows that the cleavage agent concentration, regardless the agent considered, is reduced with the reaction evolution since the higher the reaction time, the greater their differences in polarity with the glycolysis upper phase (polyol phase) and they pass to the bottom phase. Furthermore, it can be observed that the results obtained with glycerol 99% PS and with crude glycerol are really similar, demonstrating that the glycerol purity does not affect to the chemolysis process. This fact was also demonstrated in a previous paper by the research group for viscoelastic foams [26].

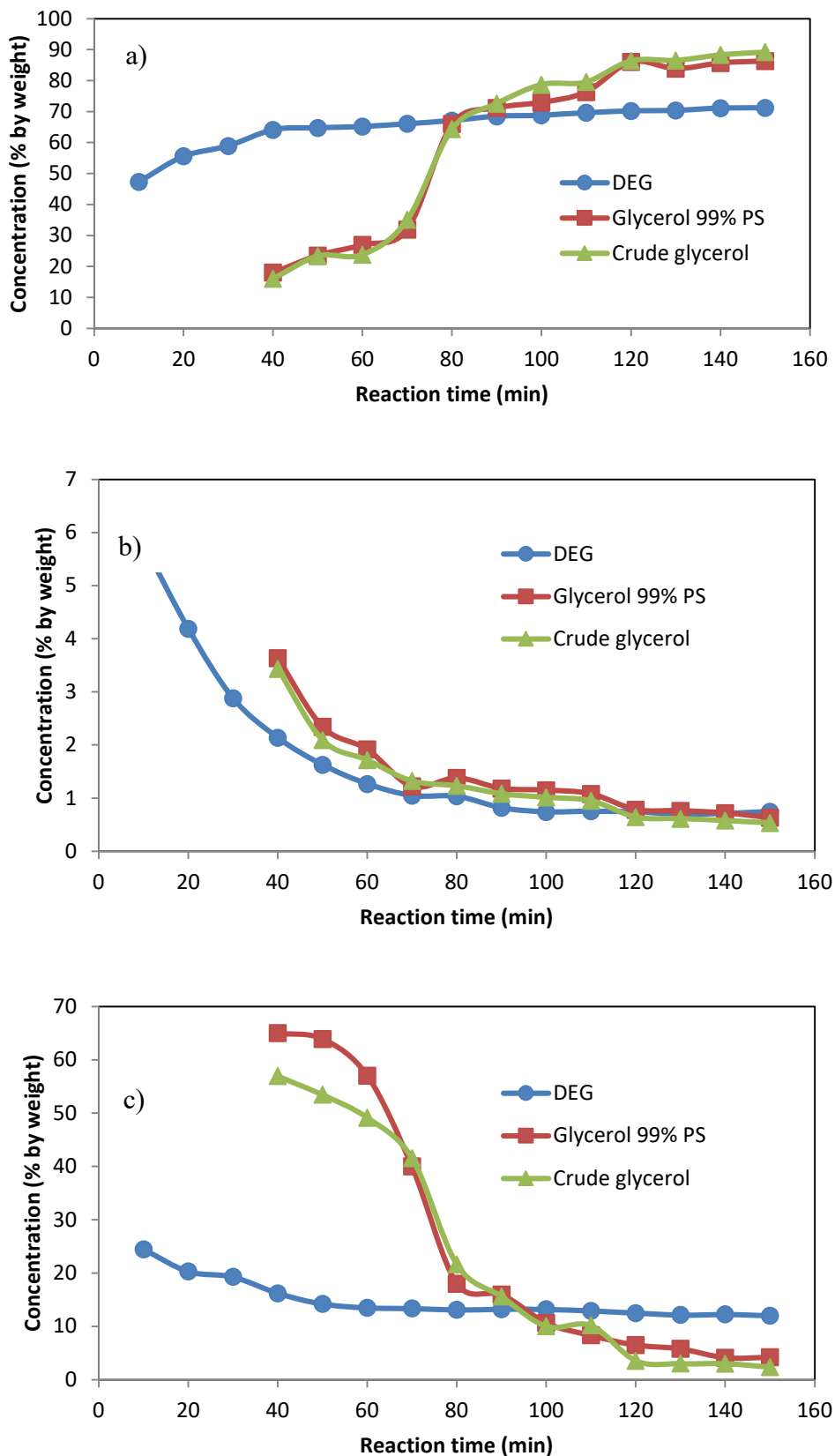


Figure 3. Evolution of a) dispersed PU particles, b) HR recovered polyol and c) Transesterification agent content in the glycolysis/glycerolysis upper phase during the chemolysis reaction of the HR foam 35HR. $W_{PU}:W_{g,a} = 1:1.5$; Catalyst concentration in the glycolysis agent 1.3 %; $T_r = 190^\circ\text{C}$.

It is important to note in Figure 3b) that when glycerols were used as cleavage agents, the split phase did not happen until 40 min of reaction time probably due to the higher viscosity of glycerol ($\mu_{20^{\circ}\text{C}}=1500$ cp) in comparison to the one of DEG ($\mu_{20^{\circ}\text{C}}=35.7$ cp). This fact increases in a great extension the reaction media viscosity at the beginning of the chemolysis process and as a consequence worsens the contact between the PU scraps and the transesterification agent, provoking a slower degradation process for the first reaction times.

However when the recovered polyol content reaches the 35 wt% this condition changes and the degradation rate increases being finally even better than that of the DEG. Moreover, as it was observed and commented in Figure 2, DEG provides an important solubilization of the HR recovered polyol in the bottom phase, at any reaction time considered, as a result of the DEG lower dielectric constant in comparison to the one of the glycerol. Furthermore, as it is shown in Table 1 and was previously observed in Figure 2, byproducts and cleavage agent concentration are considerably lower in the reaction carried out with crude glycerol than in the reaction developed with DEG. Hence, as a result of the lower byproducts and cleavage agent concentration and of the total insolubilization of the HR recovered polyol in the glycerol phase, crude glycerol provides a glycolysis upper phase with a substantial higher concentration of HR recovered polyol (89.26 % by weight) than in the degradation reaction carried out with DEG (71.25 % by weight).

Table 1. Glycolysis products concentration comparison in the glycolysis upper phase depending of the glycolysis agent used.

	% by weight					
UPPER PHASE 150min	Dispersed PU particles (Peak I)	HR recovered polyol (Peak II)	Byproduct 1 (Peak III)	Byproduct 2 (Peak IV)	Glycolysis Agent (Peak V)	Byproduct 3 (Peak VI)
Diethylene glycol	0.75	71.25	6.11	9.71	12.18	-
Glycerol 99% PS	0.63	86.41	0	4.18	3.02	5.76
Crude glycerol	0.54	89.26	0	3.31	2.40	4.49

3.3. Polyol phase purification

It is well known that glycolysis process generates a series of by-products that mainly consist on low weight carbamates and amines compounds; which, as commented before, are the result of secondary reactions such as the glycolysis reaction of the urea groups contained in the PU foam waste, the hydrolysis reaction of PU and the reactions of thermal degradation of PU [25].

These by-products and the glycol/glycerol used as transesterification agent are in a relative low concentration in the upper phase of the split-phase glycolysis. It has been found in the previous section that the concentration of these undesirable products in the polyol phase (upper phase) depends of the cleavage agent polarity.

In Figure 2 were shown the GPC chromatograms of the upper phases obtained with DEG, glycerol 99% PS and crude glycerol.

It can be observed that the upper phases obtained from the glycolysis reactions carried out with glycerol as transesterification agent (glycerol 99% PS or crude glycerol), present a significative lower proportion of undesirable products (by-products and cleavage agent). On contrary, upper phase obtained by means of employing DEG as reactive agent shows an important pollution of these non

desirable compounds in the polyol phase (upper phase), provoking a reduction in the net content of HR recovered polyol and, therefore, a decrease in the chemolysis reaction yield. Hence, it is mandatory to carry out a purification process of the polyol phase obtained with DEG since these undesirable products cause a huge increase in the hydroxyl number (OH) as a consequence of their higher hydroxyl number. The removal of the byproducts allows to achieve an hydroxyl number similar to those of raw flexible polyols and facilitate the further foaming process.

The hydroxyl number of the upper phase obtained with DEG was determinate by a standard titration method (ASTMD-4274-88) and the value obtained was 270 mg KOH/g. Moreover, with the aim of checking this datum, it was also calculated from the GPC results, with the integration of the chromatogram areas and the molecular weights obtained by means of poly(ethylene glycol) standards, as it was previously developed in a paper of this series [25]. Table 2 shows the commented calculation of the hydroxyl number.

Table 2. Hydroxyl number calculation by means of GPC of the 35HR foam glycolysis upper phase obtained with diethylene glycol.

UPPER PHASE 150 min	% by weight	f	M _n	OH* (mg KOH g ⁻¹)	Proportional OH **
Dispersed PU particles (Peak I)	0.75	3	10849	15.51	0.12
HR recovered polyol (Peak II)	71.25	3	4850	34.70	24.72
Byproduct 1 (Peak III)	6.11	3.2	392	457.96	27.98
Byproduct 2 (Peak IV)	9.71	3.2	203	884.33	85.87
DEG (Peak V)	12.18	2	106	1058.49	128.92
					OH = Σ = 267.62 mg KOH g ⁻¹

$$*OH = \frac{56100 \times f}{M_n}$$

$$** \text{ Proportional OH} = \frac{OH^* \times \% \text{ by weight}}{100}$$

It can be appreciated that the value obtained by means of the GPC method (267.62 mg KOH/g) is practically identical to the one determined with the standard titration method (270 mg KOH/g), with a percent error of only 0.88%. Furthermore, it must be noted that this error percent is almost the same that was obtained in a previous paper for the glycolysis of viscoelastic flexible PU foam waste (relative error: 0.89% [25]), showing the hydroxyl number GPC based calculation as a novel and robust characterization method, very useful when the dark colour of the recovered polyols makes difficult the titration of the standard method.

However, the hydroxyl number obtained is not similar enough to the hydroxyl number of base HR flexible polyether polyol (35 mg KOH/g) of the PIPA HR polyol since the byproducts and DEG hydroxyl numbers (DEG: 1057 mgKOH/g) are much higher than the HR base polyol one. Thus, a purification process is crucial to ensure a recovered polyol suitable for further foaming process. Considering the similarity of the glycolysis by-products, regardless the PU foam waste, the polyol phase purification process was carried out using the optimal conditions determined in a previous paper [24].

Figure 4 shows the GPC chromatogram of the 35HR foam glycolysis upper phase obtained with DEG in comparison with the refined and the extract ones for different extraction steps. It can be observed that the byproducts and DEG concentration is progressively reduced with the purification steps, passing from 28 wt% to 19.28 wt% in three extractions; causing an increase in the net polyol proportion, reaching a 79.37 wt%. Moreover, as it can be observed in Fig. 4b, the purification process does not produce polyol losses in the extract phases, showing that the selected solvent pH is the correct one due to the polyol nucleophilic oxigens have not been protonated and for this reason polyol free extracts have been obtained.

With the goal of checking the efficiency of the purification process, the hydroxyl number of the purified HR recovered polyol (Refined 3) was measured by a standard titration method (ASTMD-4274-88) and the value obtained was 42 mg KOH/g. Therefore, the extraction process is able to reduce

the hydroxyl number from 270 mg KOH/g to 42 mg KOH/g, confirming the great performance of the purification process.

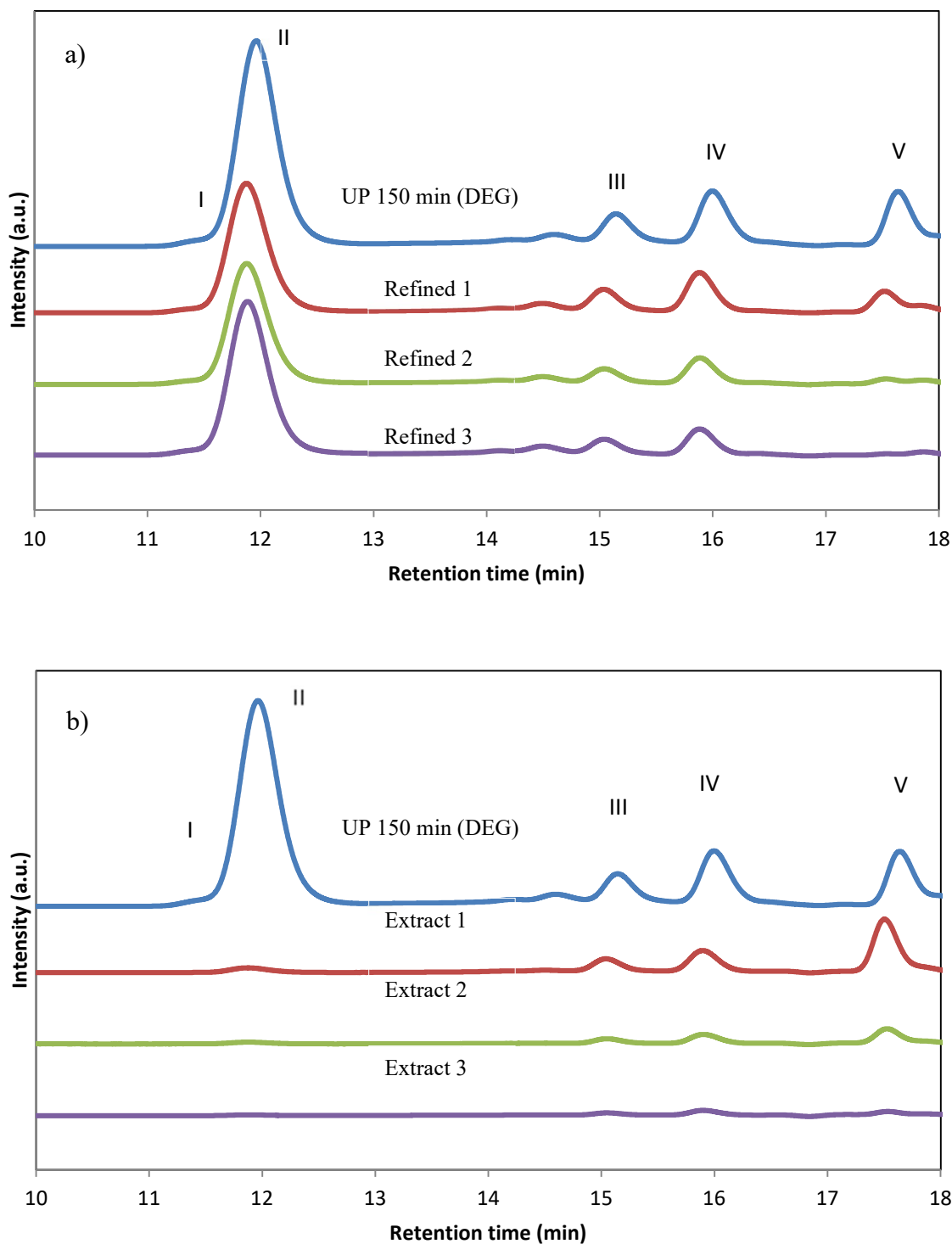


Figure 4. GPC chromatogram of 35HR foam glycolysis upper phase obtained with diethylene glycol and stannous octoate as the glycolysis agent ($W_{PU}:W_{g.a} = 1:1.5$; Catalyst concentration in the glycolysis agent = 1.3 %; $T_r = 190^\circ\text{C}$) in comparison with the refined ones (a) and the extract ones (b). Peak I= dispersed PU particles; Peak II=HR base polyol; Peaks III, IV= reaction by-products; Peak V= Transesterification agent (DEG).

Moreover, as it is shown in Table 3, purified upper phase hydroxyl number was also determined by means of the GPC results, calculating an average molecular weight and functionality of the purified HR recovered polyol, following the method previously developed for viscoelastic flexible PU foams [25, 26] and taking into consideration that the hydroxyl number can be calculated by means of equation 2 [42]:

$$OH_{number} = \frac{56100 \cdot f}{M_n} \quad (2)$$

where f represents the functionality of the compound, M_n is the number average molecular weight and 56100 is the molecular weight of KOH in mg mol^{-1} .

Table 3. Hydroxyl number calculation by means of GPC of the purified recovered HR polyol coming from the glycolysis reaction of the 35HR foam with diethylene glycol.

Refined 3	% by weight	f	M_n	Proportional M_n^*	Proportional f^{**}	OH (mg KOH g^{-1})
Dispersed PU particles (Peak I)	1.35	3	10849	146.46	0.041	$OH_{number} = \frac{56100 \cdot f}{M_n}$
HR recovered polyol (Peak II)	79.37	3	4850	3849.45	2.381	
Byproduct 1 (Peak III)	5.46	3.2	392	21.40	0.175	
Byproduct 2 (Peak IV)	10.09	3.2	203	20.48	0.323	
DEG (Peak V)	3.73	2	106	3.95	0.075	
				$M_n = \Sigma = 4041.75$	$f = \Sigma = 2.994$	OH _{number} = 41.55 mg KOH g^{-1}

* Proportional $M_n = \frac{M_n \times \% \text{ by weight}}{100}$

* Proportional $f = \frac{f \times \% \text{ by weight}}{100}$

In Table 3, it can be appreciated that the hydroxyl number obtained by means of the GPC chromatograms (41.55 mg KOH/g) is really similar to the titrator value (42 mg KOH/g) with an error of 1.07 %, value that is similar to the percent error obtained from the calculation of the purified upper phase hydroxyl number of viscoelastic flexible PU foam waste (1.43% [25]), remarking the trustworthiness of the obtained results.

On the other hand, as it was previously commented and observed in Figure 2, glycolysis upper phases coming from glycerol (99% PS or crude) present an almost negligible concentration of undesirable products. As a consequence, it was not considered to carry out any further treatment to the obtained upper phases, reducing the operative costs of the HR polyol recovery process.

Therefore, upper phases hydroxyl numbers coming from the chemolysis process carried out with glycerol were measured by a standard titration method (ASTMD-4274-88), obtaining a value of 40.2 mg KOH/g and 39 mg KOH/g for the upper phases obtained with glycerol 99% PS and crude glycerol, respectively. These results were corroborated by means of the GPC based hydroxyl number calculation methodology developed by the research group, obtaining values of 39.65 mg KOH/g and 38.46 mg KOH/g for the polyols recovered by using glycerol 99% PS (Table 4) and crude glycerol (Table 5), respectively. Hydroxyl number for the upper phase obtained with glycerol 99% PS presents a percent error of 1.37 % and the percent error of the upper phase coming from the glycolysis process with crude glycerol is 1.38 %. It can be observed that the percent errors are in the previously commented range, indicating again the reliability of the GPC based calculation.

Hence, crude glycerol is able to provide a glycolysis upper phase with a hydroxyl number (39 mg KOH/g) really similar to the one of the PIPA HR base polyol (35 mg KOH/g) without further purification treatment. In addition, crude glycerol not only provides a higher content of polyol in the upper phase (89.26 wt%), even after of purifying the upper phase obtained with DEG (79.37 wt%), but also avoids HR recovered polyol solubilization in the bottom phase, as a consequence of its higher dielectric constant.

Table 4. Hydroxyl number calculation by means of GPC of the 35HR foam glycolysis upper phase obtained with glycerol 99% PS.

UPPER PHASE 150 min	% by weight	f	M _n	Proportional M _n *	Proportional f**	OH (mg KOH g ⁻¹)
Dispersed PU particles (Peak I)	0.63	3	10849	68.35	0.019	$OH_{number} = \frac{56100 \cdot f}{Mn}$
HR recovered polyol (Peak II)	86.41	3	4850	4190.89	2.592	
Byproduct 1 (Peak III)	0	3.2	233	0	0	
Byproduct 2 (Peak IV)	4.18	3.2	142	5.94	0.134	
Glycerol 99% PS (Peak V)	3.02	3	92	2.78	0.091	
Byproduct 3 (Peak VI)	5.76	3.2	80	4.61	0.184	
				M _n = Σ = 4272.56	f = Σ = 3.020	OH _{number} = 39.65 mg KOH g ⁻¹

* Proportional $M_n = \frac{M_n \times \% \text{ by weight}}{100}$

* Proportional $f = \frac{f \times \% \text{ by weight}}{100}$

Table 5. Hydroxyl number calculation by means of GPC of the 35HR foam glycolysis upper phase obtained with crude glycerol

UPPER PHASE 150 min	% by weight	f	M _n	Proportional M _n *	Proportional f**	OH (mg KOH g ⁻¹)
Dispersed PU particles (Peak I)	0.54	3	10849	58.58	0.016	$OH_{number} = \frac{56100 \cdot f}{Mn}$
HR recovered polyol (Peak II)	89.26	3	4850	4329.11	2.678	
Byproduct 1 (Peak III)	0	3.2	233	0	0	
Byproduct 2 (Peak IV)	3.31	3.2	142	4.70	0.106	
Crude glycerol (Peak V)	2.40	3	92	2.21	0.072	
Byproduct 3 (Peak VI)	4.49	3.2	80	3.59	0.144	
				M _n = Σ = 4398.19	f = Σ = 3.016	OH _{number} = 38.46 mg KOH g ⁻¹

$$* \text{ Proportional } M_n = \frac{M_n \times \% \text{ by weight}}{100}$$

$$* \text{ Proportional } f = \frac{f \times \% \text{ by weight}}{100}$$

Moreover, with the goal of checking the high quality of the recovered polyols, several FTIR analyses were carried out. The IR spectra of the glycolysis upper phases, of the glycolysis bottom phases and the spectrum of the raw PIPA HR polyol are depicted in Figure 5.

It must be noted the great similarity of the raw polyol with the recovered ones, regardless the glycolysis agent employed. However, it is crucial to remind that in the case of using glycerol it is not necessary a further purification process, what implies an important additional operative advantage.

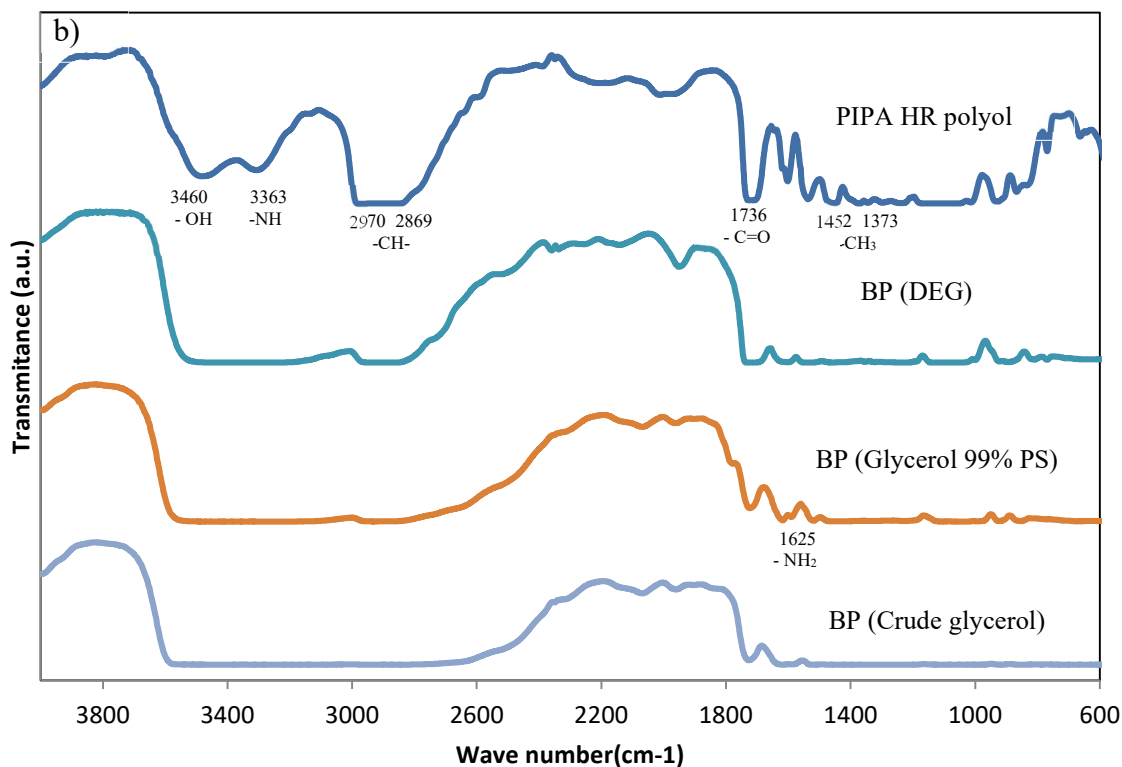
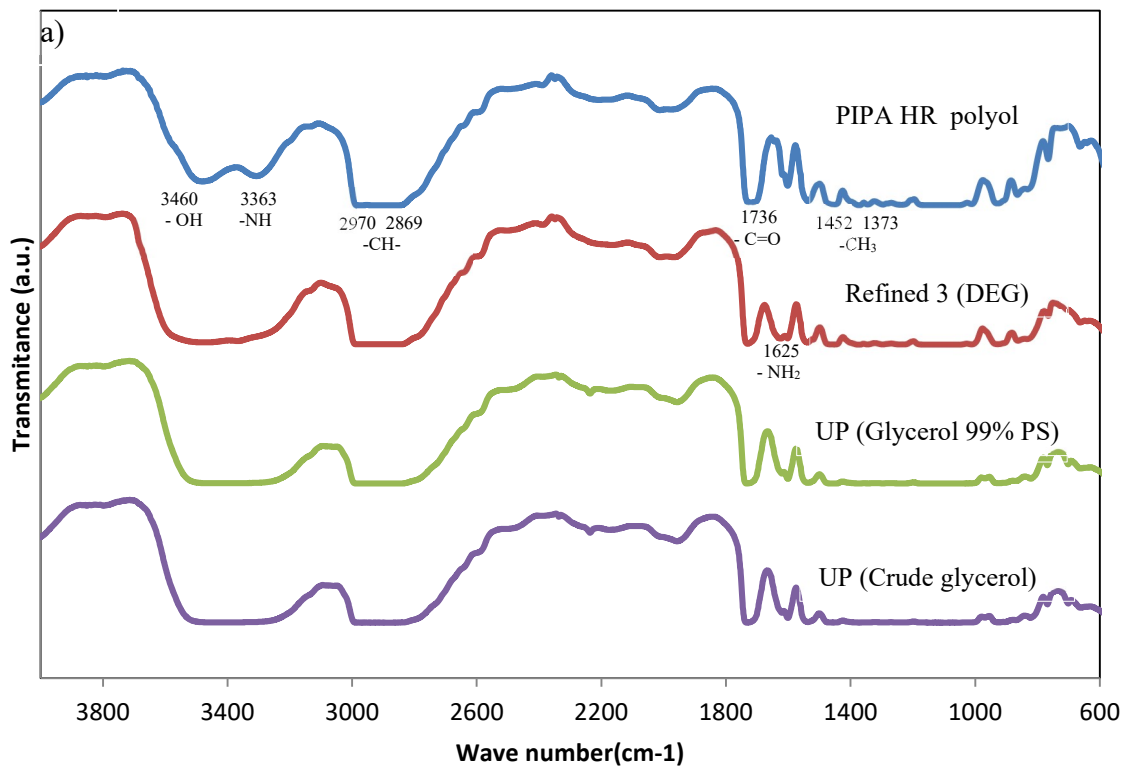


Figure 5. Comparison of the FTIR spectrum of the raw PIPA HR polyol with the glycolysis upper phases spectra a) and with the glycolysis bottom phases ones b).

Raw PIPA HR polyol spectrum presents the characteristic functional groups of a traditional HR flexible polyether polyol, with an absorption band assigned to stretching vibrations of the hydroxyl groups at 3460 cm^{-1} , the absorption bands corresponding to the stretching vibrations of CH bonds of the aliphatic carbons of the polyol chain in the spectral region $2800\text{-}3000\text{ cm}^{-1}$ and the characteristic signal of the bending vibrations of methylene groups in the polyol chain in 1373 and 1452 cm^{-1} . However, raw PIPA HR polyol spectrum presents two additional peaks in comparison with a traditional HR polyether polyol as a consequence of the PU particles embedded in the HR polyol structure. The first additional signal appears at 3363 cm^{-1} and corresponds to the stretching vibrations of -NH bond coming from urethane bond and the second one can be appreciated at 1736 cm^{-1} and it is assigned to the stretching vibrations of the C=O bond of the PU embedded particles.

It is quite interesting to note that the solid fraction of PIPA polymer polyols has an appreciable concentration of hydroxyl groups (see formula 1) and, as an immediate consequence, the PIPA polyols present a higher hydroxyl number than the initial polyols used as liquid medium for reaction. In the case of the foam assayed in this study, the raw PIPA HR polyol presents a hydroxyl number of 50 mg KOH/g [40], whereas the hydroxyl number of the base HR polyol, according to equation 1, its functionality (3) and its average number molecular weight (M_n 4850 g/mol), has a value of 34.7 mg KOH/g . This hydroxyl number agrees with that of the base HR polyol showed in the Materials and Methods section (35 mg KOH/g).

Upper phases spectra show a great similarity with the raw PIPA HR polyol. The main difference is that the band corresponding to the stretching vibrations of -NH bond of urethane bond (3363 cm^{-1}) is not present anymore as a consequence of the chemolysis of the embedded PU particles. Furthermore, in the case of the upper phases spectra, the band at 1736 cm^{-1} is assigned to stretching vibrations of the C=O bond produced by the transesterification carbamates (glycolysis by-product) and not by the PU embedded particles. Moreover, a new signal at 1625 cm^{-1} can be also observed in the recovered

polyols, regardless the cleavage agent employed. This signal is assigned to primary amine groups (glycolysis by-product) as a consequence of the bending vibrations of N-H bond.

With respect to the glycolysis bottom phases spectra, it must be noted that the band assigned to stretching vibrations of -OH groups (3460 cm^{-1}) presents a much greater intensity as a consequence of the huge hydroxyl numbers of the cleavage agents ($\text{OH}_{\text{DEG}}= 1057\text{ mgKOH/g}$ and $\text{OH}_{\text{Glycerol}}=1800\text{ mgKOH/g}$) in comparison with the hydroxyl number of the raw PIPA HR polyol (50 mg KOH/g).

3.4. Valorization of the products obtained in the glycolysis process

3.4.1. Synthesis of flexible PU foams with the glycolysis upper phase.

The main aim of the work was the recovery of the HR foam raw materials for its use in further foam synthesis. In order to check the suitability of the recovered polyols for this purpose, it is crucial to attend to their hydroxyl number value ($\text{OH}_{\text{number}}$), functionality (f) and average number molecular weight (M_n), which constitute the main aspects involving the PU foaming process. It is necessary to take into account that, as it was commented in the previous point, DEG glycolysis polyol phase required a further purification process in order to achieve a recovered polyol with suitable properties to be foamed.

In a general way, polyols for synthesis of flexible PU foams present molecular weights in the range 2000-6000, low functionality (2-3) and low hydroxyl value (28-160 mg KOH/g). Concretely, high resilience (HR) foams are produced by long-chain polyether polyols with higher molecular weight (4,000–6,000 g/mol) than those for conventional and viscoelastic foams and with a higher proportion of ethylene oxide [41].

At this point, it is important to remind that the foam glycolyzed in this paper, 35HR foam, was synthesized by means of employing a base HR flexible polyether polyol with a molecular weight of 4850 g/mol, functionality 3 and a hydroxyl number value of 35 mg KOH/g.

Tables 3, 4 and 5 shows the values of these three parameters for the polyols recovered with DEG, glycerol 99% PS and crude glycerol, respectively.

Table 6. Foaming experiments carried out with the HR recovered polyols obtained in the glycolysis of flexible HR PU foam scraps.

CHEMICAL		P100-R _{HR} 0	P87.5-R _{HR} 12.5	P75-R _{HR} 25
<i>Raw polyol M_n 3500 (OH=48 mgKOH/g)</i>		100	87.5	75
<i>Water</i>		4.60	4.60	4.60
<i>Tegoamin 33</i>		0.10	0.10	.10
<i>Niax A-1</i>		0.05	0.05	0.05
<i>Silicone L-620 LV</i>		1.40	1.40	1.40
<i>Sn Octoate</i>		0.20	0.20	0.20
<i>Recover polyol</i>	<i>DEG (OH=41.55 mgKOH/g)</i>	0	12.5	25
	<i>Glycerol 99% PS (OH=39.65 mgKOH/g)</i>	0	12.5	25
	<i>Crude glycerol (OH=38.46 mgKOH/g)</i>	0	12.5	25
<i>TDI (80 : 20)</i>	<i>DEG (OH=41.55 mgKOH/g)</i>	54.58	54.45	54.32
	<i>Glycerol 99% PS (OH=39.65 mgKOH/g)</i>	54.58	54.41	54.24
	<i>Crude glycerol (OH=38.46 mgKOH/g)</i>	54.58	54.39	54.19
<i>Isocyanate index</i>		105	105	105

It must be noted that, regardless the cleavage agent used, molecular weight, functionality and hydroxyl number of the HR recovered polyols are similar to the ones of the raw flexible HR base polyol, indicating a successful glycolysis process. However, it is relevant to point out that the recovered polyols obtained by means of glycerols present more similar values to the virgin polyol than in the case of employing DEG. Moreover, it is crucial to remark that these upper phases coming from the chemolysis reactions with glycerol did not require a further purification process, demonstrating the superior performance of glycerol as a glycolysis agent of flexible HR foams. Additionally, water content was determined by Karl-Fischer method using an automatic titrator, obtaining values of 0.1 % for the three recovered polyols, value that is in the range of commercial HR flexible polyether polyols.

Considering the hydroxyl numbers of the HR recovered polyols and its water content, it was calculated several formulations recipes by means of using the same base recipe developed in previous reports by the research group [24-26].

In order to check the foaming behavior of the HR recovered polyols, several flexible PU foams with proportions of HR recovered polyols from 0 to 25% with respect to the total polyol quantity were synthesized by means of mixing them with a raw flexible polyether polyol.

Table 6 shows the foaming formulation recipes calculated for the HR recovered polyols obtained of the glycolysis process with DEG, glycerol 99% PS and crude glycerol as cleavage agents.

Figures 6a, 6b and 6c show the physical appearance of the flexible PU foams obtained with the HR recovered polyols. Foams synthesized with the HR recovered polyols present a great homogeneity, with regular structure and without remarkable internal defects.

Hence, crude glycerol, coming from the biodiesel production, has provided a high quality HR recovered polyol, avoiding the necessity of a further upper phase purification process, and allowing the valorization of two residues, HR polyurethane foam scraps and crude glycerol.



a)



b)



c)

Figure 6. Internal structure of the flexible foams synthesized with different proportions of the recovered polyols and cleavage agents: a) DEG, b) Glycerol 99% PS and c) Crude glycerol.

3.4.2. Synthesis of rigid PU foams with the glycolysis bottom phase

Glycolysis bottom phase mainly consists of the reaction by-products and the excess of cleavage agent. These compounds are considered undesirable products in the glycolysis upper phase since their presence would mean a contamination of the recovered polyol and would increase its hydroxyl number.

On the other hand, it is important to keep in mind that the bottom phase is the most abundant one since it is necessary to add a glycol excess in the chemolysis process in order to displace the transesterification equilibrium to the polyol release. Therefore, giving value to glycolysis bottom phase is a crucial goal.

The components of this bottom phase contain labile protons receptive of interacting with the isocyanate group as a consequence of the high reactivity of the isocyanate group in the presence of this kind of protons [2]. Thus, it is probable that they can be used for the synthesis of polyurethanes. In order to explore this possibility, hydroxyl numbers of the glycolysis bottom phases were measured by a standard titration method (ASTMD-4274-88). The hydroxyl numbers obtained were 602 mg KOH/g, 781 mg KOH/g and 785 mg KOH/g for the bottom phases obtained from the glycolysis reactions with DEG, glycerol 99%PS and crude glycerol, respectively. It must be noted that hydroxyl number values for glycerol based bottom phases are higher than the hydroxyl value of the bottom phase coming from DEG as a consequence of the higher hydroxyl number of the glycerol. Furthermore, the concentration of cleavage agent in the bottom phase obtained with DEG is lower than in the case of employing glycerol, as can be observed in Figure 2. This can be explained by the lower dielectric constant of DEG compared to the glycerol one.

Since the hydroxyl number values obtained are in the typical range of raw rigid polyether polyols (250-1000 mg KOH/g [2]), independently on the transesterification agent used, these bottom phases were used as a raw rigid polyol replacement in the synthesis of new rigid PU foams.

Several rigid PU foams were synthesized with different percentage of bottom phases ranging from 0 to 100% and a raw rigid polyether polyol. The amount of isocyanate needed was calculated following the procedure detailed in a previous article of this series [25].

Table 7 shows the recipes of the manufactured rigid foams. It must be noted that the higher the content of bottom phase, the higher the required amount of PMDI as a consequence of the increase in the hydroxyl number of the polyol mixture, since the isocyanate index must be kept in 106.

Table 7. Foaming experiments carried out with the bottom phases obtained in the glycolysis of flexible HR PU foam scraps.

CHEMICAL		P100- BP0	P75- BP25	P50- BP50	P25- BP75	P0- BP100
<i>Raw polyol M_n 555 (OH=455 mgKOH/g)</i>		100	75	50	25	0
<i>Tegostab B-8404</i>		1.5	1.5	1.5	1.5	1.5
<i>Water</i>		2.5	2.5	2.5	2.5	2.5
<i>Tegoamin BDE</i>		2.5	2.5	2.5	2.5	2.5
<i>Bottom phase</i>	<i>DEG (OH=602 mgKOH/g)</i>	0	25	50	75	100
	<i>Glycerol 99% PS (OH=781 mgKOH/g)</i>	0	25	50	75	100
	<i>Crude glycerol (OH=785 mgKOH/g)</i>	0	25	50	75	100
<i>PMDI</i>	<i>DEG (OH=602 mgKOH/g)</i>	157.13	166.48	175.83	185.18	194.53
	<i>Glycerol 99% PS (OH=781 mgKOH/g)</i>	157.13	177.86	198.60	219.33	240.06
	<i>Crude glycerol (OH=785 mgKOH/g)</i>	157.13	178.12	199.11	220.09	241.08
<i>Isocyanate index</i>		106	106	106	106	106

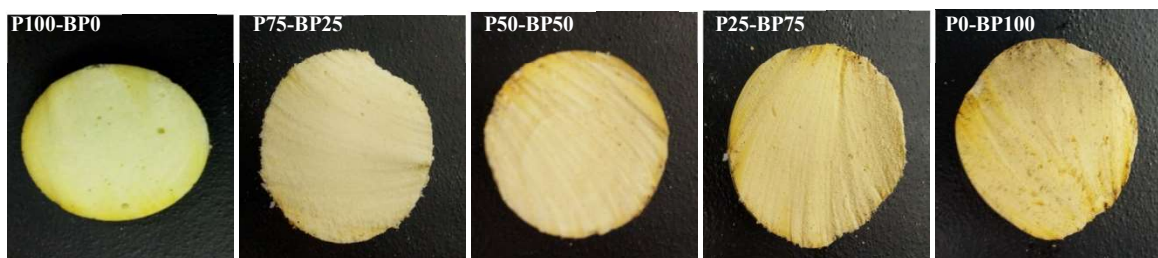
Figure 7 shows the internal structure of the rigid foams synthesized with different contents of the glycolysis bottom phases.



a)



b)



c)

Figure 7. Internal structure of the rigid foams synthesized with different proportions of the glycolysis bottom phases and cleavage agents: a) DEG, b) Glycerol 99% PS and c) Crude glycerol.

Regardless the cleavage agent employed, rigid foams presented a great homogeneity and did not show any structural fault. Moreover, it was observed a rise in the foaming process rate when the content of glycolysis bottom phase was increased in the recipe as a consequence of the amines contained in the bottom phases since the isocyanates reaction with amines at room temperature is faster than the reaction with alcohols [2]. The amines also provide a high reticulation grade in the PU structure as a result of polyurea domains in the polymer structure.

This behavior was also appreciated in previous reports [25, 26], demonstrating the great similarity in the composition of the bottom phases obtained from the glycolysis process, with independence of the kind of PU waste recycled.

Hence, it has been demonstrated that the glycolysis bottom phases coming from the glycolysis of HR flexible PU foam scraps containing polyurethane dispersion polyol are susceptible of being applied as a raw rigid polyether polyol replacement in the synthesis of new rigid PU foams with a high crosslinking grade.

4. Conclusions

The feasibility of the glycolysis process of HR flexible PU foam waste by means of employing the reaction conditions optimized in previous works for conventional flexible PU foam scraps and for viscoelastic ones has been demonstrated for the first time in literature. Besides, different cleavage agents (DEG, glycerol 99% PS and crude glycerol) have been assayed. The HR foam chosen to carry out the report was a PIPA HR polyol based one, which represents the last innovation tendency in the polymeric polyols industry. As a result of the chemolysis reactions two phases were obtained. The upper phases were mainly constituted by the PIPA HR base polyol, whereas the bottom phases consisted of several glycolysis byproducts and the excess of the transesterification agents. Crude glycerol provided an upper phase with a lower concentration of byproducts and glycolysis agent and, as a result, with a higher proportion of the HR recovered polyol which present similar hydroxyl

number than raw polyols without need of purification. Therefore, the use of glycerol increases the polyol recovery yield in comparison with the performance showed by the DEG. This is so, thanks to the higher dielectric constant of the glycerol. Additionally, for the same reason, crude glycerol avoided the solubilisation of the HR recovered polyol in the bottom phase. Furthermore, even after carrying out a purification process of the upper phase obtained from the DEG as cleavage agent, the upper phase obtained from the glycolysis reaction developed with crude glycerol (byproduct of the biodiesel production) presented a higher concentration of the HR recovered polyol, indicating the crude glycerol as the best alternative from a technical, environmental and economical point of view to carry out the degradation process of HR flexible PU foam waste. Finally, flexible and rigid PU foams were successfully synthesized, regardless the cleavage agent employed, by using the glycolysis upper phases (refined product in the case of the reaction with DEG) and the bottom ones, respectively.

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