Glycolysis of Advanced Polyurethanes Composites containing Thermoregulating Microcapsules

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Abstract

Rigid PU foams are properly recycled by a single-phase glycolysis process employing crude glycerol as transesterification agent. A high pure recovered polyol (71% of purity) was obtained using a mass ratio of PU scraps to crude glycerol of 1 to 1, a reaction temperature of 190ºC and stannous octoate as catalyst in a 1.3wt% concentration. PU foam composites containing thermoregulating microcapsules constituted by a paraffin core (Rubitherm®RT27) and a polymer shell material (LDPE and EVA) were glycolyzed, allowing to recover the microcapsules components and the polyol separately. This way, both components of the composite are recovered and can be reused in the manufacturing of new products; demonstrating for first time the viability of the chemical recycling of this kind of composites. Besides, the developed process was successfully applied for foams containing different proportions between the hard and soft segments, demonstrating its robustness. Finally, the recovered polyols were successfully employed to replace a raw rigid polyether polyol in the synthesis of new rigid PU foams. The most important physical and mechanical properties (density, maximum compressive strength and Young modulus) were maintained constant for the incorporation up to a 25 wt% of recovered polyol coming from conventional rigid PU foam scraps and up to a 37.5 wt% with the recovered polyol from rigid PU foam containing thermoregulating microcapsules. Regarding the effective thermal conductivity, it remained constant, even with 100 wt% of recovered polyol from PU scraps with thermoregulating microcapsules.

Key words: polyurethane, chemical recycling, polyol, rigid foam, PCMs

1. Introduction

Polyurethane (PU) is one of the most relevant families of polymers with a global production of 17.565 millions tons per year [1]. PU synthesis main reaction consists 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]. PU covers a wide range of products, from foams (flexible or rigid) to the denominated CASEs (Coatings, Adhesives, Sealants and Elastomers). PU specialties are demanded in a huge number of application fields such as bedding industry [3], automotive sector [3], footwear [4], ergonomy [4], commercial refrigeration [5], buildings isolation [6-8] and so on. As a consequence of the commercial success of PU, an increasing quantity of non biodegradable PU waste is being generated all over the world and, therefore, finding a solution to this environmental problem is a crucial task.

In addition to these facts, the global tendency in the polyurethane market is the development of advanced products with superior performance in one or more characteristics than the marketed traditional ones. One of the PU specialties that is attracting more and more attention from managers and enterprises all over the world are the rigid PU foams containing phase change materials (PCMs) embedded in their structure for thermoregulating (energy saving) purposes in building applications [9]. The formation of these innovative products generally consists in the incorporation of microcapsules containing PCMs into the recipe of the PU during its foaming process, obtaining this way a composite material [9]. These composites provide improved thermal isolation properties compared to those of standard rigid polyurethane foams and are undergoing an exponential development [9]. Thus, it is an essential issue to look for solutions for the recycling of their waste at the end of their lifetime in order to ensure the applicability of these composites in a sustainable way. The recycling of this kind of advanced PU materials should take into consideration the presence and the destiny of these microcapsules.

Traditionally, landfill was the most used alternative at the end of a PU product life. However, as a direct result of the current enforcement of the environmental legislations, polymer recycling processes are attracting the attention from the research and the industrial world, causing an important increase in the research of polymer waste treatment [2].

In the concrete case of PU recycling, due to PU crosslinking structure and thermostable nature, chemical recycling processes are the best ones to be used. Among them, glycolysis is the one that provides the better results in terms of recovered product quality and mild reaction conditions [2]. Glycolysis process is based in 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].

In literature, the glycolysis studies are well reported including a wide range of polyurethane specialties, flexible foams [10-31] and rigid ones [32-38] and also the denominated CASES [10, 14, 39-44]. Moreover, glycolysis processes have been also developed for reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) polyurethanes [45-48].

Nevertheless, glycolysis processes of PU thermoregulating composites materials have not been yet reported in literature. Therefore, this paper focus its attention in the extension of the glycolysis process to rigid PU foams containing a microencapsulated phase change material. The final aim is to get, on one hand, a recovered rigid polyether polyol, susceptible of replacing partially a raw rigid polyether polyol in the synthesis of new PU products with suitable properties (mechanical, structural, thermal) to be employed in the PU industry, and; on the other hand, the phase change material. For this, the glycolysis process conditions optimized in a previous work [29] will be applied but studying different ratios of PU to glycolysis agent in order to maximize the recovery of polyol.

2. Experimental

2.1. Materials

a) Glycolysis

Residual scraps with an arbitrary diameter ranging from 5 to 25 mm from a conventional rigid PU foam and from a rigid PU foam containing thermoregulating microcapsules were treated.

Table 1 shows the formulation of both foams.

The quantity of the microcapsules added is calculated by means of Equation 1 [49]:

$$\text{g PCM} = \frac{g_{reference} \cdot wt\%\ PCM}{100 - \text{wt\% PCM}} \qquad [1]$$

where wt%PCM is the mass percentage of thermoregulating microcapsules (since they contain PCMs), g PCM is the mass of microcapsules to be added in the final foam recipe and $g_{\text{reference}}$ is the amount of the rest of the foam components. Microcapsules consisted of a paraffin core and a polymeric shell from low density polyethylene (LDPE) and ethylvinylacetate (EVA). Microcapsules average particle size was 10 µm with a latent heat of 98.14 J/g [49].

Both recipes are based on a rigid polyether polyol [poly(propylene oxide-block-ethylene oxide), with functionality 4.5, M_n 555 g/mol and OH number 455 mg KOH/g] and on polymeric methylene diphenyl diisocyanate (PMDI).

The mass ratio PMDI to rigid polyether polyol of the two recycled foams is different (1.57 for conventional rigid PU foam and 1 for the PU foam containing PCMs), with the aim of checking if the developed glycolysis process could be successfully applied to foams with different hard segments (PDMI) to soft segments (rigid polyether polyol) proportions.

Crude glycerol with a purity of 80 % (provided by Biocombustibles de Cuenca S.A.) was used as glycolysis agent. Stannous octoate (from Sigma-Aldrich) was used as catalyst.

b) Polyurethane synthesis

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, viscosity= 5250 cp and humidity=0.1 %). Different percentages of the rigid polyol are replaced with the recovered polyols obtained from the glycolysis of the PU containing microencapsulated PCMs. PMDI was supplied by Poliuretanos Aismar, S.A (NCO content=31%). 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 (190ºC), 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}. Three different ratios of PU foam to glycolysis agent (W_{PU}:$W_{g.a}$) were tested, varying from 1:1.5 to 1:0.5 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.Rigid polyurethane foams synthesis

The new rigid PU foams were synthesized by weighting and mixing the desired masses of the raw rigid polyol and the recovered ones (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 during 24 h.

2.4. Characterization techniques

At given times intervals, aliquots were sampled from the reactor, cooled and centrifuged to ensure the total separation of phases in the case of split-phase glycolysis reactions. Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution (MWD) as well as concentration of polyol in the products. 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 ºC (flow:1 mL min^{-1}) and a refractive index detector. Poly(ethylene glycol) standards (from Waters, USA) were used for MWD calibration. The percentage of recovered polyol was calculated as a function of the chromatogram areas. The samples were dissolved in tetrahydrofuran (THF from Panreac, Spain) at a concentration of 10 mg ml^{-1} and then filtered (pore size 0.45 μm). The correspondence between the chromatogram areas and the polyol, subproducts and glycerol concentrations are determined by previous calibration with different solutions of raw rigid polyether polyol 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. Hydroxyl numbers of the recovered polyols 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 of the recovered polyols 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. Viscosity was measured by a rotational Brookfield LVTDV-II viscometer. Thermogravimetric analysis were obtained by using the TA instruments SDT Q600 Simultaneous DSC-TGA from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.5. Foams characterization

2.5.1. Apparent density

Foams apparent density was measured according to ISO 845 standard. The density tests were conducted on rectangular shape foam samples with the dimensions of 50 mm × 50 mm × 25 mm which were cut using a hot wire device. Then, the specimens were weighed and their dimensions were measured.

2.5.2. Compression test

Compressive properties of foams were analyzed according to standard ASTM D1621 for rigid cellular plastics. Uniaxial compression tests were performed using a MTS 370.02 testing instrument. The compression tests were carried out at a cross-head speed of 2.5 mm/min. The tested foam specimens were prism of 5.1x5.1x2.6 cm and each analysis was repeated 3 times. From these test results, the Young's modulus (E) is determined as the slope value of the initial part of the compression curves, while the maximum compressive strength (σ_{max}) is determined as the point in which the plateau region starts or, in absence of plateau, in the inflection point of the curve.

2.5.3. Foam morphology

The synthesized rigid PU foams were analyzed by SEM in order to study the influence of the amount of the recovered polyols in the cell structure. This study was performed for recovered polyols from the conventional rigid PU foam scraps and from rigid PU foams containing PCMs.

2.5.4. Effective conductivity

The thermal behavior of the synthesized rigid foams has been studied using a homemade equipment described and proved in previous works [50-51]. The experimental device is shown in Fig. 1. Tests were carried out applying a thermostatic bath set-point step change from 18 to 40 ± 0.1 ºC while temperatures at different foam sample locations and the inlet and outlet heat fluxes were registered with time. The foams samples dimensions were of 3 x 6 x 10 cm^3. Six thermocouples of K-type were located across the probe thickness: two in the external sample surface (T_{up}), two in the middle (T_{middle}) and the other two on the aluminum cell (T_{down}). The heat fluxes were measured by using heat flow sensors PU22T for monitoring the inlet (Q_{in}) and outlet ($Q_{out\ i}$) heat fluxes on line (Fig. 1b). The temperature of the thermostatic fluid inside the insulated aluminum cell without foam sample is considered as the indoor temperature.

Using these signals, it is possible to quantify the effective thermal conductivity at the final steady state (κ) by means of Equation 2, where Q_{in} is approximately equal to $Q_{out\,2}$.

$$\kappa = \frac{Q_{in} \cdot \chi_f}{(T_{down} - T_{up})} \qquad [2]$$

where Q_{in} is the inlet heat flux at the final steady state condition (W/m^2) and χ_f (m) is the foam thickness.

3. Results and discussion

3.1. Glycolysis process of conventional rigid PU foams

Several glycolysis reactions with conventional rigid PU foams scraps were performed by using the optimal conditions obtained in previous works for flexible PU foams and employing crude glycerol (waste from the biodiesel production) as decomposing agent [29].

Figure 2 shows the GPC chromatograms of the upper and the bottom phase (UP and BP, respectively) at 60 min of the conventional rigid foam glycolysis reaction together with the chromatograms of the raw rigid polyether polyol and with the crude glycerol one. It can be appreciated that Peak I corresponds to urethane oligomers, while peaks II, III and IV are assigned to the rigid polyether polyol due to the coincidence in retention times with the raw rigid polyether polyol chromatogram. Peak V represents the glycolysis byproducts, mainly low weight carbamates ending in hydroxyl groups and aromatic amines [26] similar to MDA. The commented byproducts are generated in several secondary reactions that take place at the same time that the main glycolysis reaction. Some of these reactions are 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 [2]. According to the area of peak V, observed in Figure 2, byproducts concentrations are quite low in the glycolysis upper phase. Finally, Peak VI corresponds with the employed transesterification agent, crude glycerol, according to the coincidence in the retention time with the GPC chromatogram of the crude glycerol.

It can be appreciated that crude glycerol concentration represents a remarkable percentage by weight in the upper phase (≈ 20 wt%). This is so due to the low molecular weight of the recovered polyol; since, the lower the molecular weight of a polyol, the higher its dielectric constant and, in consequence, its affinity with the crude glycerol, which is a polar component with high dielectric constant (ε=42.5). For the same reason, polyol losses can be observed in the bottom phase chromatogram shown in Figure 2. However, in spite of the important polyol solubilisation, crude glycerol (Peak VI) is the predominant component of the bottom phase.

Besides, the evolution of the glycolysis reaction was studied by taking samples at different times and quantifying the concentration of the glycolysis products in the upper phase, by the integration of their respective areas in the GPC chromatograms using the methodology explained in a previous paper [28].

Figure 3 shows the concentration of recovered rigid polyether polyol and oligomers in the upper phase during the glycolysis reaction. It can be observed an increase in the recovered polyol content and a reduction in the oligomers concentration with the reaction advance. This is explained by the progressive urethane groups degradation due to the action of the transesterification agent. It must be noted that the maximum polyol content is achieved at 150 min (73 wt%) when the PU oligomers have been completely degraded and converted into recovered polyol, indicating the end of the glycolysis reaction. In the case of the glycolysis of flexible PU foams [25-30] a residual content of oligomers was always maintained in the final product, probably due to the higher molecular weight of the flexible polyether polyols in comparison to the rigid ones.

The rest of components concentrations in the upper phase and the composition of the bottom phase at the end of the reaction time were also analysed. According to these analyses, reaction byproducts represented just about a 9 wt% and 4 wt% in the upper and bottom phases, respectively. Regarding crude glycerol, its concentration in the upper phase is slightly reduced with the reaction advancement, achieving a minimum value of

18 wt%; since the higher the reaction time, the greater the differences in polarity between crude glycerol and the glycolysis upper phase (polyol phase). Despite of this improvement in the polyol purity, it is far from the purity of the polyols recovered from flexible foams with the same conditions [29, 30]. Besides, it is crucial to note that a remarkable quantity of recovered polyol (28 wt%) is solubilized in the bottom phase, although it is mainly formed by crude glycerol (68 wt%). This represents a relevant polyol loss, provoking a significant reduction in the net quantity of recovered polyol.

Hence, the feasibility of the glycolysis of conventional rigid PU foams using crude glycerol and the same glycolysis reaction conditions previously optimized for flexible PU foams in previous works [25-30] has been demonstrated but with a significant loss of the rigid polyol in the bottom phase. In order to solve this drawback, it was considered to carry out an optimization of the mass ratio between the PU foam scraps and the crude glycerol.

3.2. Influence of the mass ratio of conventional rigid PU foam scraps to glycolysis agent

With the aim of avoiding the polyol losses in the bottom phase, the mass ratio of PU foam scraps to glycolysis agent (W_{PU}:$W_{g.a}$) was modified, using ratios of 1:1 and 1:0.5. The glycolysis agent proportion is reduced in order to eliminate the excess of glycolysis agent necessary for the split-phase process and obtain a single-phase product with a recovered polyol content similar to the one obtained in the upper phase of the split-phase glycolysis process. The experiments were carried out maintaining constant the reaction temperature (190ºC) and the catalyst concentration in the glycolysis agent (1.3 wt%).

The first W_{PU}:$W_{g.a}$ studied was 1:0.5. As expected, the glycolysis reaction ran as a single-phase process due to the reduction of the glycolysis agent from 1:1.5 to 1:0.5. Figure 4 shows the GPC chromatograms of the single-phase product obtained at different reaction times for the W_{PU}:$W_{g.a}$ = 1:0.5.

As can be seen in Figure 4, the higher the reaction time, the lower the intensity of oligomers peak (peak I). However, it is important to note that at 150 min of reaction time the content of oligomers in the glycolysis product is quite remarkable; since for this low ratio (W_{PU}:$W_{g.a}$ = 1:0.5), non-dissolved PU portions were found in the glycerol, providing a low quality product and problems related to agitation. For solving this problem, the W_{PU}:$W_{g.a}$ was increased to a value of 1:1. The GPC chromatograms of samples of the glycolysis with a mas ratio 1:1 can be seen in the supplementary information (Figure S1).

Figure 5 shows the concentration of recovered rigid polyether polyol and oligomers in the single-phase product during the glycolysis reaction performed with a mass ratio 1:1. It can be observed that from 110 min of reaction time the recovered polyol content remains constant and the oligomers are completely degraded, indicating the end of the transesterification reaction. Thus, for a mass ratio of 1:1, the single-phase glycolysis process runs successfully. The quantitative study shows a recovered polyol content of 71 wt% in the obtained product. Besides, the contents of byproducts and crude glycerol were calculated, obtaining a value of 9 wt% and 20 wt%, respectively.

It is important to note that the composition of the single-phase product obtained for the W_{PU}:$W_{g.a}$ = 1:1 is very similar to the one obtained in the upper phase of the split-phase glycolysis achieved with W_{PU}:$W_{g.a}$ = 1:1.5. At the same time, the ratio 1:1 presents two advantages since it reduces significantly the employed quantity of crude glycerol, improving the process economy, and the net amount of recovered polyol in the single-phase product is much greater than the one achieved in the upper phase of the split-phase glycolysis process. Taking all this into consideration, the selected mass ratio to carry out the glycolysis of conventional rigid PU foam was 1:1.

Then, the recovered polyol from conventional PU foam scraps employing a mass ratio 1:1 was characterized, determining the average molecular weight in number (Mn), the hydroxyl number (OH) and the functionality (f). These properties are the main parameters that must be evaluated for the selection of a polyol as raw material for the synthesis of rigid PU foams.

The average molecular weight in number was determined from the content (wt%) of the different compounds obtained from the areas integration of the GPC chromatograms and from the molecular weight of each individual compound obtained with poly(ethylene glycol) standards used for MWD calibration. The obtained value was 460.11 g/mol. The data for obtaining this value can be seen in the supplementary information (Table S1).

Regarding the hydroxyl number of the recovered polyol, it was determined by a standard titration method (ASTMD-4274-88) and the obtained value was 850 mg KOH/g.

Finally, taking into consideration the average molecular weight in number and the hydroxyl number, functionality can be calculated by means of equation 3 [52]:

$$OH_{number} = \frac{56100 \cdot f}{Mn} \qquad [3]$$

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}.

Substituting the data in equation 3, the functionality of the recovered polyol from conventional rigid PU foam waste was 6.97.

It is well known that for getting a successful PU rigid foam, the polyols used must present molecular weights in the range 300-700, high functionality (3-8) and high hydroxyl value

(250-1000 mg KOH/g) [53]. Hence, all the properties of the recovered polyol from conventional rigid PU foam scraps are in the typical range of the raw rigid polyether polyols, demonstrating the high quality of the single-phase recovered product and, hence, the suitability of the glycolysis process employed.

3.3. Recycling of rigid PU foam scraps containing thermoregulating microcapsules

Once developed a successful single-phase glycolysis process for conventional rigid PU foams, the next efforts were focused in trying to extend this process to rigid PU foams containing thermoregulating microcapsules, due to the great acceptation that are receiving these composites materials for the thermal energy storage capacity in buildings and industrial sector. The recipe employed to synthesize the composites was shown in Table 1. The mass ratio PMDI : rigid polyether polyol assayed in the composite recipe was lower than the one employed for the manufacture of the conventional foam (see Table 1), with the goal of determining if the glycolysis process can be applied with independence of the proportion hard segments (PDMI):soft segments (rigid polyether polyol) in the original rigid PU foam to be recycled.

Therefore, several glycolysis reactions were carried out employing the conditions described in the previous section, obtaining two phases clearly separated: one corresponding to the microcapsules components (the PCM and the polymeric shell) and another phase mainly constituted by the recovered rigid polyol, indicating that the developed glycolysis process can be successfully applied for the recycling of this kind of composites. Additionally, it has been also corroborated that the glycolysis process under the selected conditions takes place favourably, regardless the mass ratio PMDI: rigid polyether polyol employed in the manufacture of the PU foam, demonstrating the robustness of the developed glycolysis process.

The obtention of the separated phases is a consequence of the different polarity between them. The recovered polyol is of polar nature while the microcapsules components are all of them non-polar compounds. The physical aspect of both phases can be appreciated in Figure S2 of the supplementary information.

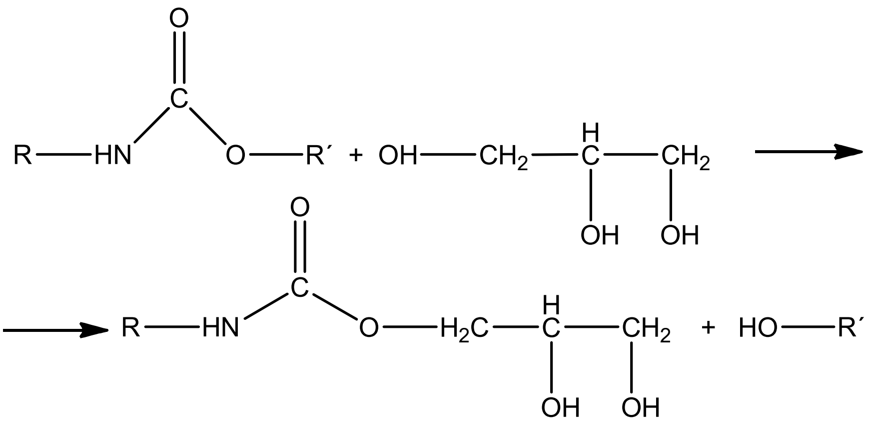
Moreover, the mass proportion between phases is in agreement with the composition of the rigid PU foam containing PCMs (Table 1). In Table 1, the weight percentage of microcapsules (non-polar phase) in the PU foam is indicated to be 30 wt%, which taking into consideration the employed W_{PU}:$W_{g.a}$ (1:1) would imply a 15 wt% of non-polar phase (microcapsules phase) in the glycolysis product. However, in the final product this weight percentage was slightly lower (13 wt%), as a consequence of the degradation of the paraffin with the temperature, as must be noted in the TGA thermogram of RT27 paraffin depicted in Figure 6. In this Figure, it can be observed that at the glycolysis reaction temperature, approximately a 1-2 wt% of the paraffin has been degraded, explaining the reduction in the content of microcapsules phase in the final product.

Moreover, Figure 6 also corroborates the presence of the polymeric shell in the microcapsules phase. In fact, according to the TGA thermograms comparison, the paraffin content in the microcapsules phase is approximately 50 wt%, whereas the other 50 wt% of this non-polar phase corresponds to the polymers that constituted the microcapsules shell, LDPE and EVA. This result is in agreement with the paraffin content of the thermoregulating microcapsules (49.32 wt%) synthesized in a previous work by the research group [54].

Besides, once the glycolysis product reaches the room temperature, the microcapsules phase becomes solid and can be easily separated from the recovered rigid polyether polyol and reused. The employed microcapsules were synthesized by a spray drying technique in which the paraffin and the polymers are dissolved together in a solvent and them sprayed and drying in a drying chamber where the microcapsules are formed [54]. Thus, the microcapsules phase can be dissolved and reused in the spraying drying process for the synthesis of new microencapsulated PCM.

On the other hand, the recovered polyol was also characterized with the aim of checking if its properties were in the range of commercial rigid polyether polyols and could replace a raw one in a further foaming process.

Hydroxyl number was determined by means of a standard titration method (ASTMD-4274-88) and the value obtained was 812 mg KOH/g, which is in the range of commercial rigid polyether polyols (250-1000 mg KOH/g). The reduction of the hydroxyl number in comparison with the one obtained for the recovered polyol from conventional rigid PU foam scraps (850 mg KOH/g) can be explained attending to the proportion between the hard and soft segments of the original foams recycled (Table 1). The rigid foam containing PCMs was synthesized employing a lower quantity of polymeric methylene diphenyl diisocyanate (PMDI) and, thus, with higher content of raw rigid polyether polyol, whose hydroxyl number (455 mg KOH/g) is lower than the one of crude glycerol (1827 mg KOH/g). Moreover, the lower the isocyanate content, the lower the quantity of byproducts with high hydroxyl number and low molecular weight, such as low weight carbamates coming from the isocyanate part of the glycolyzed foam (Scheme 1), reducing of this way the hydroxyl number of the recovered polyol.



(1)

Next, the viscosity was measured obtaining a value of 13000 cp, which is higher than the one of the raw rigid polyether polyol (5250 cp) and lower than the viscosity value determined for the recovered polyol from conventional rigid PU foam scraps in the previous section. This reduction in the viscosity value can be explained again attending to the decrease of the isocyanate content in the foam recipes (see Table 1), since there would be a lower content of hard segments.

Hence, it has been demonstrated that is possible to carry out the glycolysis of rigid PU foam scraps containing thermoregulating microcapsules employing the same reaction conditions that for conventional rigid PU foam scraps, obtaining a product with two phases, both of which can be reused as raw materials: a phase composed by the thermoregulating microcapsules components and a recovered polyol. Moreover, it has been also demonstrated that the developed glycolysis process can be applied for rigid PU foams with different proportion between the hard and soft segments (PDMI and rigid polyether polyol, respectively) in their formulation.

3.4. Synthesis and characterization of the synthesized rigid PU foams with the recovered polyols

The final goal of any chemical recycling process is to obtain products that can be useful as reagent materials in the chemical and petrochemical industry. Concretely, in the glycolysis of PU foams, the aim is to be able to get a recovered polyol with suitable properties to be used as replacement of a raw one. The three main parameters of a polyol regarding the foaming process are hydroxyl number, functionality and average number molecular weight. Table 2 summarizes the values of these properties for both of the recovered polyols of this work in comparison to those typical for commercial raw rigid polyether polyols.

As commented before, the three variables of both recovered polyols are in the typical range of commercial rigid polyether polyols. The observed differences between them regarding the M_n and the hydroxyl value can be explained attending to the different proportion polyol/isocyanate employed in the synthesis of the original rigid PU foams, as explained in the previous section.

Additionally, water content was measured by means of Karl-Fischer method using an automatic titrator, achieving a value of 0.1 %, which is typical for rigid polyether polyols. Thus, the recovered polyols can be used directly for the synthesis of new PU foams. Several rigid PU foams were synthesized substituting different percentages of the raw rigid polyether polyol (P) by the recovered polyols (R) ranging from 0 to 100%. The amount of isocyanate needed was calculated following the procedure detailed in a previous article [28] for a isocyanate index of 106, taking into consideration the hydroxyl number values of the recovered polyols. For the case of the recovered polyol from conventional rigid PU foam scraps, four rigid PU foams were synthesized with replacements between 0 and 37.5 wt%. On the other hand, with the recovered polyol from rigid PU foam scraps containing thermoregulating microcapsules, seven rigid PU foams were synthesized, since its lower viscosity allowed replacements up to 100 wt%.

Table 3 and Table 4 show in detail the foam recipes of the different synthesized foams using the recovered polyol from conventional rigid PU foam scraps and from rigid PU foams containing PCMs, respectively.

Figure 7 shows the rigid PU foams internal aspect. It can be observed that all the foams, but the one of PU foam with a 37.5 wt% of recovered polyol from conventional rigid PU foam, exhibited regular structure without internal defects, demonstrating the high quality of the recovered polyols obtained from the glycolysis process. The imperfect aspect of the PU foam with a 37.5 wt% of recovered polyol from conventional rigid PU foam can be attributed to the high viscosity of the recovered polyol, which affects in a great extension to the final PU foam structure.

On the other hand, in order to ensure that the PU foams synthesized using the recovered polyols can be employed in the same applications that those made just from the raw polyol, their apparent density, maximum compressive strength, Young modulus and thermal conductivity were analysed, since these properties are the most important ones for rigid PU foams.

i) Apparent density

Figure 8 shows the apparent density values of the rigid PU foams synthesized with the recovered polyols. It can be observed that the rigid PU foam synthesized employing exclusively the commercial rigid polyether polyol presents a density of approximately 70 kg/m^3. In the case of the recovered polyol from conventional PU foam scraps, the density values remain constant around 70 kg/m^3 up to a 25% of polyol replacement. However, for higher contents of recovered polyol, the density experiments a considerably rise, achieving values of approximately 100 kg/m^3 for a 37.5 wt% of recovered polyol.

Introducing recovered polyol in the foaming formulation implies to reduce the molecular weight of the polyols mixture (M_n raw polyol = 555 g/mol; M_n recovered polyol from conventional rigid PU foams = 460.11 g/mol), giving as a result a density increase. This behaviour was previously reported by several authors [19, 31, 55].

Regarding the PU foams synthesized with the recovered polyol from rigid PU foam scraps containing thermoregulating microcapsules, it can be observed in Figure 8 that the density values remain constant regardless the recovered polyol content. This can be explained attending to the higher molecular weight of this recovered polyol in comparison to the recovered polyol from conventional rigid PU foam scraps and to its lower viscosity.

ii) Compression test

In Figure 9 are depicted the maximum compressive strength and the Young modulus values of the rigid PU foams synthesized with the recovered polyols. It can be observed that both mechanical properties follow the same tendency, as could be expected taking into account that both parameters are directly related by means of equation 4.

$$\sigma = E \cdot \varepsilon \qquad [4]$$

where σ is the maximum compressive strength, E is the Young modulus and ε is the deformation.

According to the results shown in Figure 11, the replacement of the raw rigid polyol by the recovered polyol from conventional PU foam scraps up to a 25 wt% did not affect to the maximum compressive strength nor the Young modulus. Nevertheless, for higher percentages of polyol replacement, both properties diminish, since the incorporation of a higher content of recovered polyol into the formulation causes an increase of the presence of short chain segments that provokes a worsening in the compressive properties.

On the other hand, Figure 9 shows that in the case of the rigid PU foams synthesized with the recovered polyol from rigid PU foam scraps containing thermoregulating microcapsules, the studied compressive properties did not experiment a significant variation up to a 50% of polyol replacement. This can be explained attending to the higher molecular weight of the recovered polyol from rigid scraps containing PCMs, which is more similar to that of the raw rigid polyether polyol one, admitting a higher recovered polyol content to be introduced in the formulation without worsening the compressive properties of the rigid PU foams synthesized. However, a massive increase in the recovered polyol content implies a drastically reduction in the compression strength and Young modulus values as a result of the short chain segments present in any recovered polyol [31] up to a values of 207 kPa and 6.636 MPa, respectively. Nevertheless, for many rigid polyurethane foam applications, a compressive strength value of 100 kPa [56] and a Young modulus between 7-19 MPa [57] are sufficient. In some insulation applications, for example in flat roofing, flooring, ceilings or perimeter insulation, high pressure loadings can occur and it is important to maintain the good compressive strength values.

iii) PU foams structural characterization

With the aim of elucidating if there is some kind of relation between the mechanical properties of the foams and the PU foams cell structure, SEM analyses were carried out.

Figure 10 shows the microphotographs obtained by SEM with magnification x100 of the rigid foams synthesized by means of employing different proportions of recovered polyols. It can be observed that, in general, the PU foams preserve the polyhedral cell structure. Nevertheless, the synthesized PU foam with a 37.5 wt% of recovered polyol from conventional rigid PU foam scraps does not present this typical structure, probably due to the high viscosity of the recovered polyol, which affects in a great extension to the final PU foam framework and, consequently, to the mechanical properties previously commented. Moreover, it must be noted, in a general way, a reduction in the cell size with the content of recovered polyol, independently on the kind of recovered polyol employed for synthesizing the rigid foams. This fact can be explained attending to the polyol mixture viscosity and to the CO_2 expandability [58]. The higher the viscosity of the polyol mixture (what means higher content of recovered polyol), the more restricted the CO_2 to be expanded, giving as a result a decreasing in the PU foam cell size [31, 58, 59].

It is important to take into consideration that the same base recipe has been applied for the manufacture of all the rigid PU foams synthesized in this research, only modifying the isocyanate quantity according to the polyol mixture hydroxyl number. Nevertheless, the rest of the components proportions (water, surfactant, amine catalysts) have not been modified in order to facilitate the employment of the recovered polyols to a further industrial production of rigid PU foams with the less possible changes. However, with slight customized modifications to the foaming recipe, properties more similar to the ones of the foam synthesized exclusively with the commercial polyol could be achieved, even with high content of recovered polyol in the foam formulation.

iv) PU foams thermal characterization.

Some of the main applications of the rigid PU foams are the isolation in buildings and refrigerated trucks. Hence, a proper thermal conductivity (k) is essential to ensure the applicability of the foams created from recovered polyols and will be evaluated.

Figure 11 shows the effective thermal conductivity values for the rigid PU foams synthesized with the recovered polyols. It can be observed that up to replacements of 25 wt%, the effective k remains practically constant in a value around 0.04 W/m·K. The typical effective conductivity range of commercial rigid PU foams is from 0.025 to 0.04 W/m·K [60], demonstrating that the rigid foams synthesized employing the recovered polyol from conventional rigid PU scraps could be successfully applied in the isolation sector up to this content. However, greater proportions (37.5 wt%) worsen the isolation properties, probably as a consequence of the wider struts and broken cells that could be observed in SEM image of the Figure 13a, which provoke CO_2 leakages and as a result a deterioration in the isolation properties.

On the other hand, Figure 11 also shows the effective conductivity for rigid PU foams synthesized with the recovered polyol from rigid PU scraps containing thermoregulating microcapsules. It must be noted that, regardless the quantity of recovered polyol, the effective conductivity remains constant, even with 100 wt% of recovered polyol.

Therefore, it can be concluded that rigid PU foams with proper isolation performance can be synthesized employing recovered polyols from rigid PU foams, independently on the presence of PCMs embedded in the original rigid PU foams structure.

4. Conclusions

Rigid PU foams can be properly recycled by a single-phase glycolysis process employing crude glycerol as transesterification agent. This process allows to achieve a high pure recovered poyol (71 wt% of polyol) when using a mass ratio of PU scraps to crude glycerol of 1:1, a reaction temperature of 190ºC and a stannous octoate as catalyst in a 1.3 wt% concentration.

The same process conditions can be applied to recycle PU foam composites containing thermoregulating microcapsules constituted by a paraffin core and a polymer shell material, allowing to recover the microcapsules components and the polyol separately.

This way, both components of the composite are recovered and can be reused in the manufacturing of new products.

Besides, the developed process can be successfully applied for foams containing different proportions between the hard and soft segments, demonstrating its robustness.

Both recovered polyols obtained from the glycolysis of conventional rigid PU foam scraps and from rigid PU foams containing thermoregulating microcapsules were characterized, and taking into consideration their properties (OH number, molecular weight, functionality), they were applied as partial, or even total, replacement of a commercial raw rigid polyether polyol in the synthesis of new rigid PU foams. In general, the manufactured foams exhibited regular structure without internal defects, independently on the recovered polyol employed and on the recovered polyol content, with the only exception of the PU foam synthesized with a 37.5 wt% of recovered polyol from conventional PU foam scraps. Moreover, in a general way, the main physical and mechanical properties (density, maximum compressive strength, Young modulus) were maintained constant with the incorporation up to a 25 wt% of recovered polyol coming from conventional rigid PU foam scraps and up to a 37.5 wt% with the recovered polyol from rigid PU foam containing thermoregulating microcapsules. Regarding the effective thermal conductivity, which is the main thermal property for isolation applications, when the recovered polyol from PU scraps with PCMs was employed, it remained constant, even for a 100 wt% of recovered polyol. Thus, the suitability of the developed glycolysis process for the recovery of polyol from rigid PU foams and from PU foams composites with PCMs, the high quality of the recovered product and its applicability in isolation applications have been demonstrated.

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TABLES

Table 1. Rigid PU foams formulation.

	Conventional rigid PU foam	**Rigid PU foam with 30 wt% of PCMs**
Reagent	**pph**	**pph**
Rigid polyether polyol	100	100
H_2O	2.5	2.5
Tegoamin BDE	2.5	2.5
Tegostab B8404	1.5	1.5
PMDI	157.13	100
PCMs		88.5

Table 2. Recovered polyols properties in comparison to the ones of commercial rigid polyether polyols.

Chemical	**Mn (g/mol)**	**OH_{number} (mg KOH/g)**	**Functionality**
Raw rigid polyether polyols	300-700	250-1000	3-8
Recovered polyol from conventional rigid PU scraps	460.11	850	6.97
Recovered polyol from rigid PU scraps containing PCMs	481.55[a]	812	6.97[b]

[a] M_n was calculated from equation 3.

[b] The same functionality value was considered as an approximation for both polyols due to the great similarity between them in terms of functionality.

Table 3. Foaming experiments carried out with the recovered polyol from conventional rigid PU foam scraps (reagents contents in pph of polyol).

	P100-R0	**P87.5-R12.5**	**P75-R25**	**P62.5-R37.5**
Raw rigid polyether polyol OH=455 mgKOH/g	100	87.5	75	62.5
Recovered polyol OH=850 mgKOH/g	0	12.5	25	37.5
Polyol mixture hydroxyl number (mgKOH/g)	455	504.38	553.75	603.13
Tegostab B8404	1.5			
Water	2.5			
Tegoamin BDE	2.5			
PMDI	157.13	169.69	182.25	194.81

Table 4. Foaming experiments carried out with the recovered polyol from rigid PU foam scraps containing PCMs (reagents contents in pph of polyol).

	P100-R0	**P87.5-R12.5**	**P75-R25**	**P62.5-R37.5**	**P50-R50**	**P25-R75**	**P0-R100**
Raw rigid polyether polyol OH=455 mgKOH/g	100	87.5	75	62.5	50	25	0
Recovered polyol OH=812 mgKOH/g	0	12.5	25	37.5	50	75	100
Polyol mixture hydroxyl number (mgKOH/g)	455	499.63	544.25	588.89	633.5	722.75	812
Tegostab B8404	1.5						
Water	2.5						
Tegoamin BDE	2.5						
PMDI	157.13	168.48	179.84	191.19	202.54	225.25	247.95

FIGURES

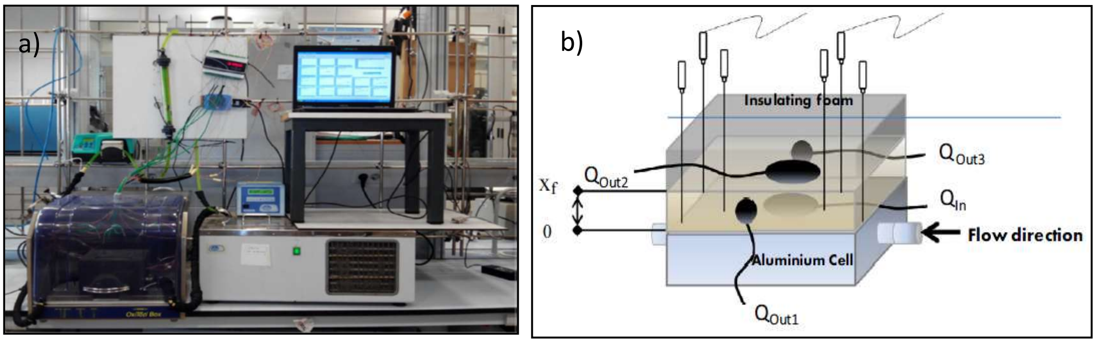


Figure 1. Experimental device for the materials thermal behavior tests: (a) photo; (b) sketch of the heat flux sensor position.

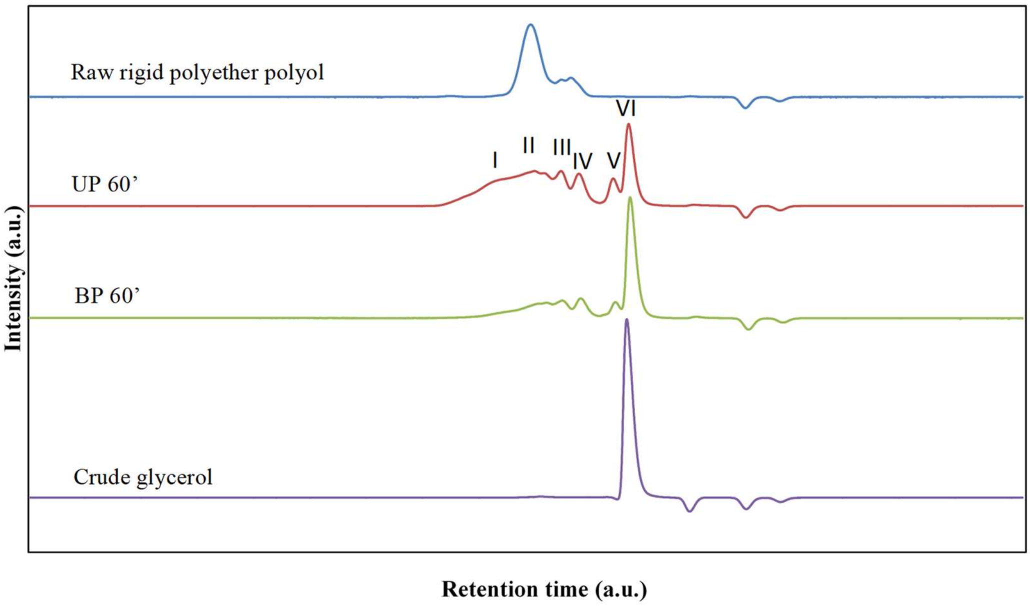


Figure 2. GPC chromatograms of the upper phase (UP) and the bottom phase (BP) at 60 min of the conventional rigid PU foam glycolysis reaction obtained with crude glycerol in comparison with GPC chromatograms of raw rigid polyether polyol and of crude glycerol. W_{PU}:$W_{g.a}$ = 1:1.5. Peak I= oligomers; Peaks II, III and IV=rigid polyether polyol; Peak V=reaction by-products; Peak VI= Crude glycerol.

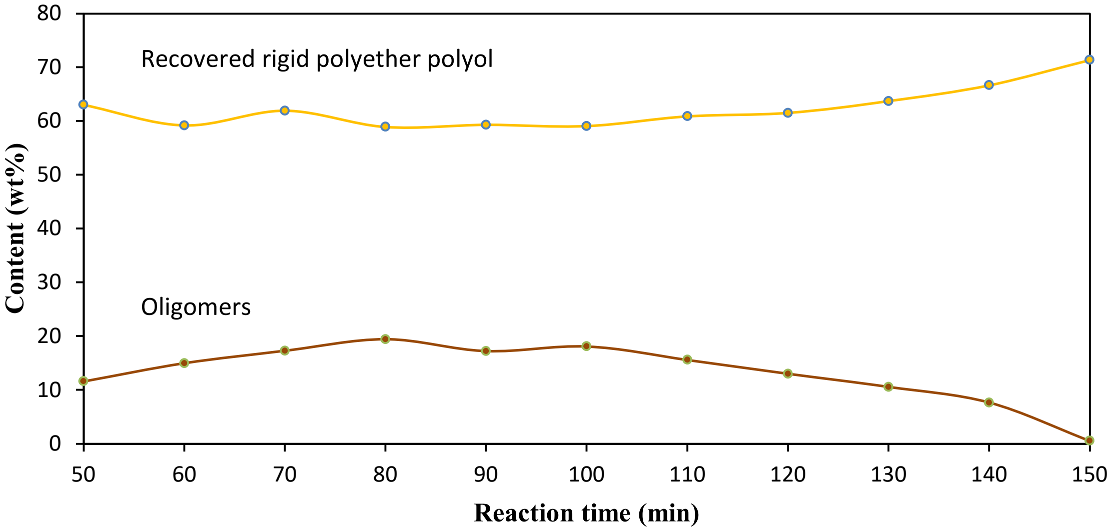


Figure 3. Evolution of recovered rigid polyether polyol and oligomers content in the glycerolysis upper phase during the chemolysis reaction of the conventional rigid PU foam. W_{PU}:$W_{g.a}$ = 1:1.5; Catalyst concentration in the glycolysis agent 1.3 %; T_r = 190ºC.

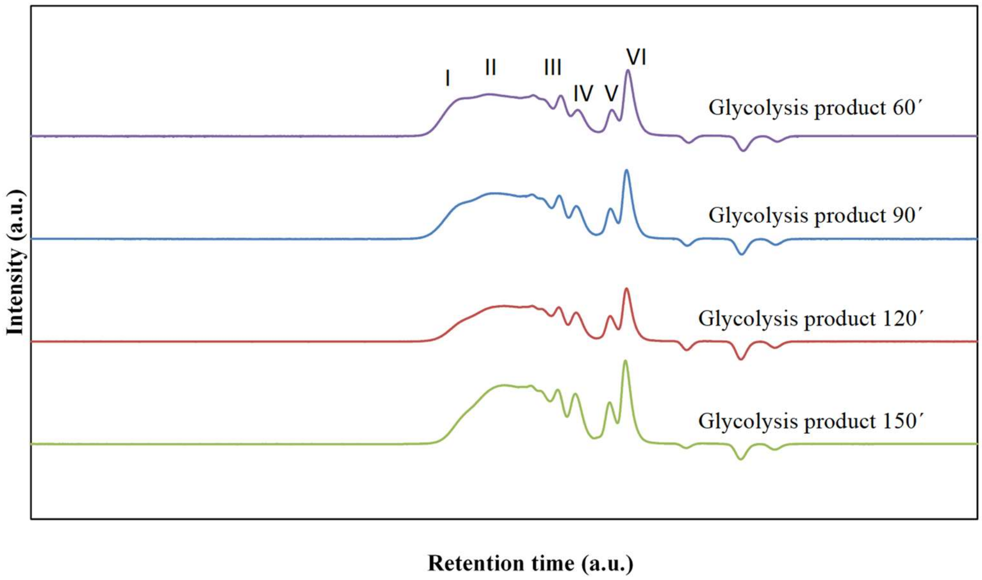


Figure 4. GPC chromatograms of the glycolysis product at different reaction times using crude glycerol and stannous octoate in the glycolysis agent W_{PU}:$W_{g.a}$ = 1:0.5; Catalyst concentration in the glycolysis agent 1.3 %; T_r = 190ºC. Peak I= urethane oligomers; Peaks II, III and IV=rigid polyether polyol; Peak V=reaction by-products; Peak VI= Crude glycerol.

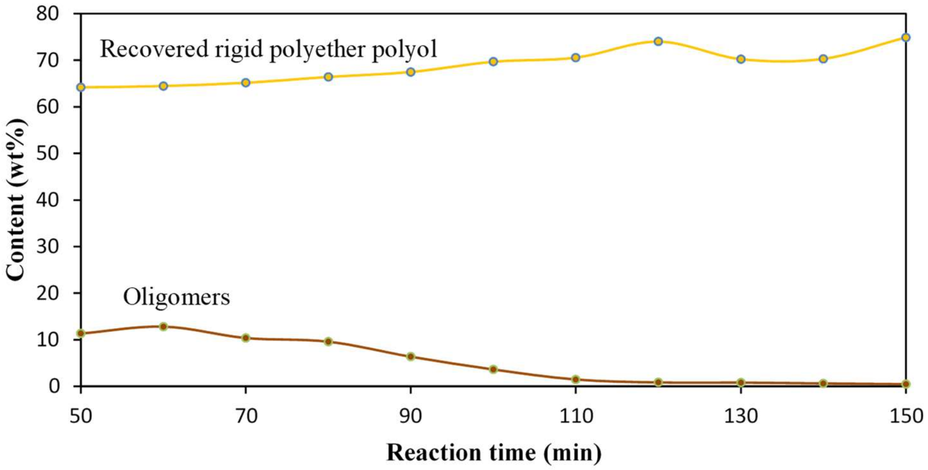


Figure 5. Evolution of recovered rigid polyether polyol and oligomers content in the glycerolysis single-phase during the chemolysis reaction of the conventional rigid PU foam. W_{PU}:$W_{g.a}$ = 1:1; Catalyst concentration in the glycolysis agent 1.3 %; T_r = 190ºC.

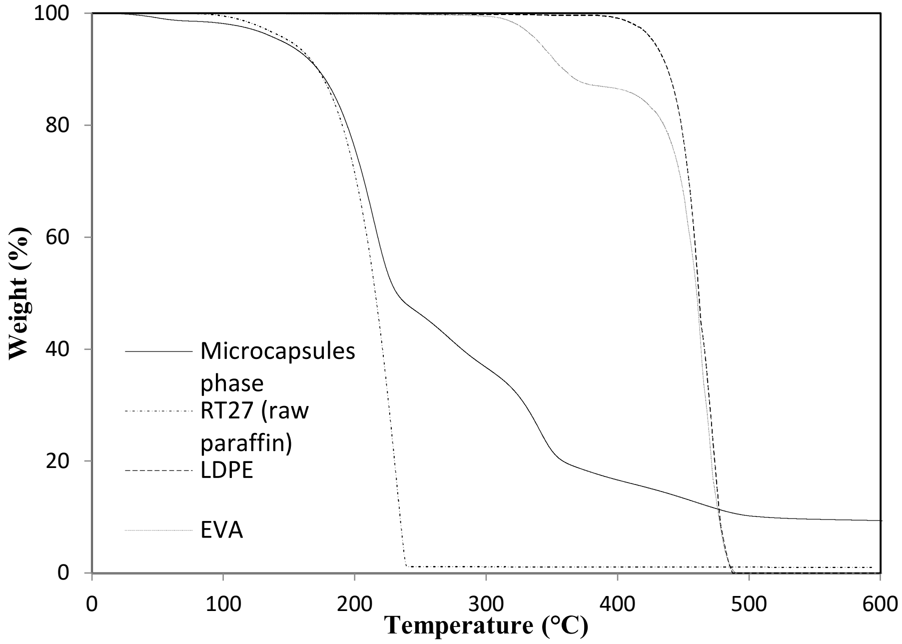
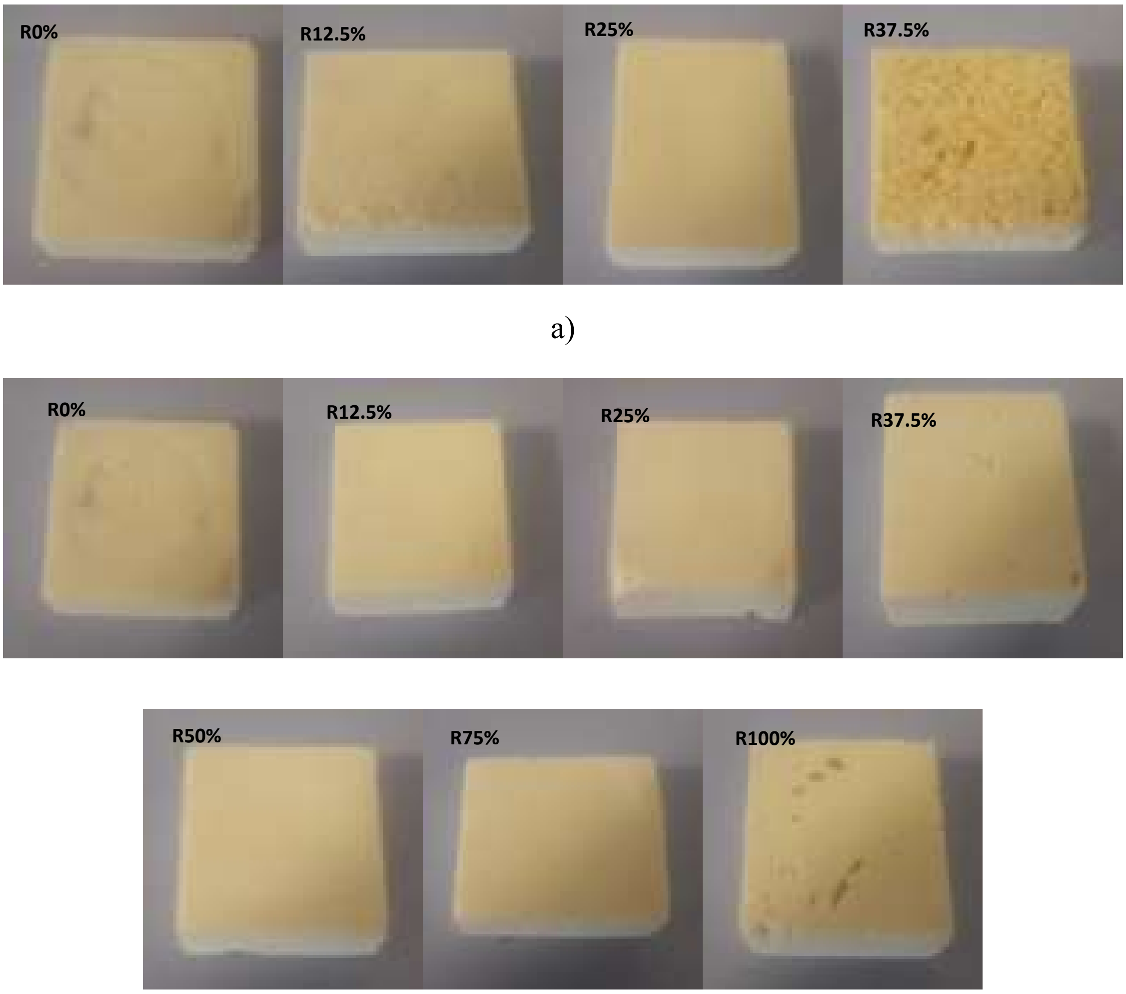


Figure 6. TGA thermogram of the microcapsules phase in comparison with the ones of RT27, LDPE and EVA.



a)

b)

Figure 7. Internal appearance of the rigid PU foams synthesized with different proportions of the recovered polyols a) from conventional rigid PU foam scraps b) from rigid PU foam scraps containing PCMs.

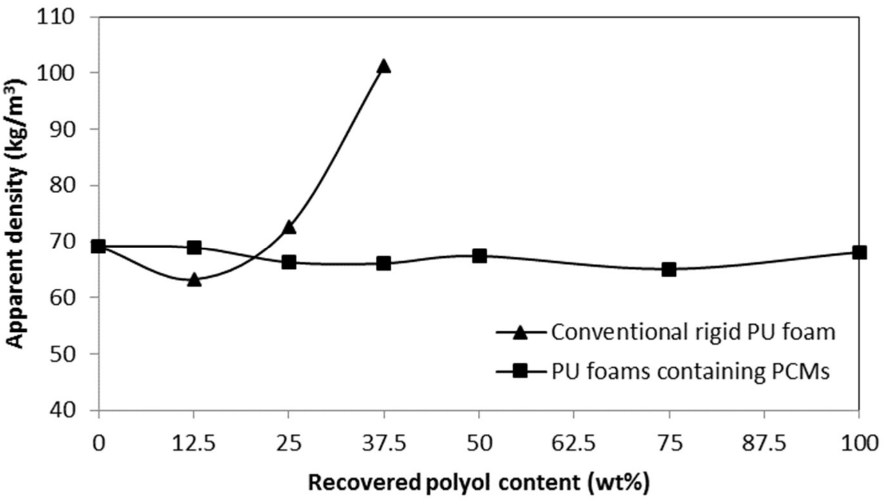
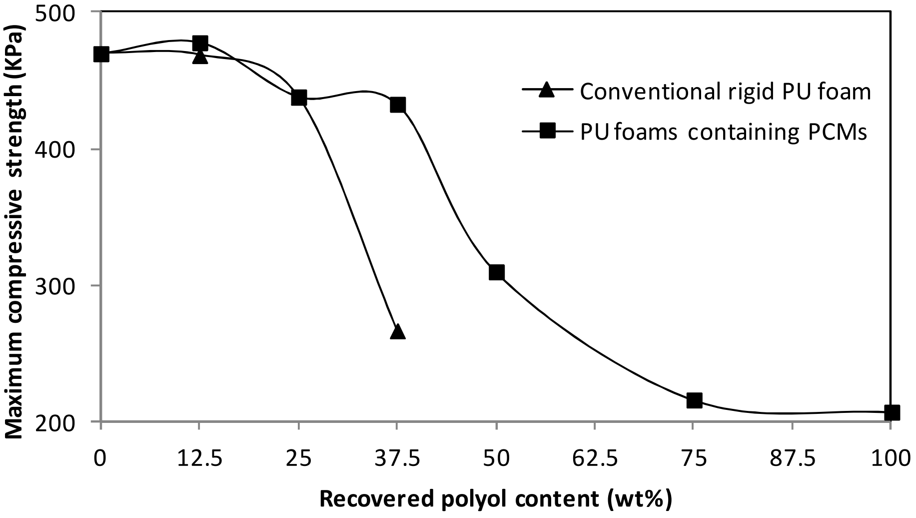
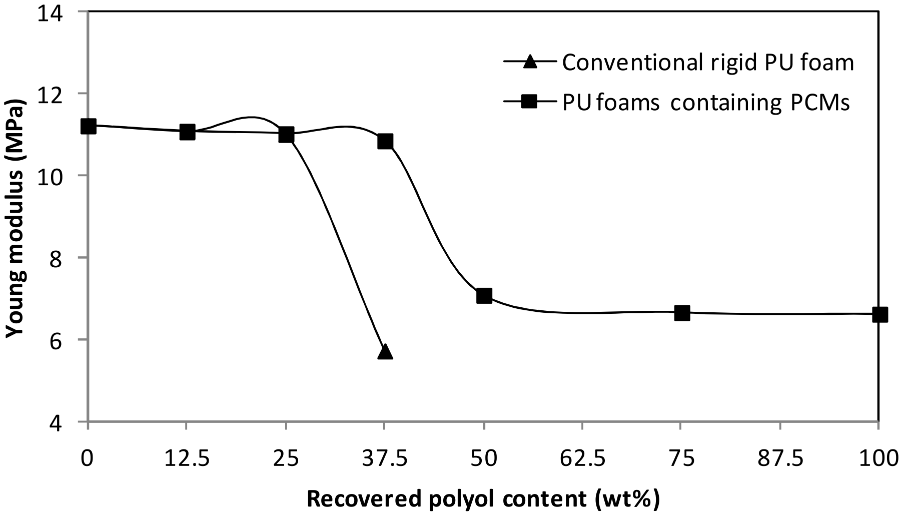


Figure 8. Dependence of foams apparent density as a function of the recovered polyol percentage replacing the raw rigid polyol. Recovered polyol from: conventional rigid PU foams ▲ and from rigid PU foams containing PCMs ■.

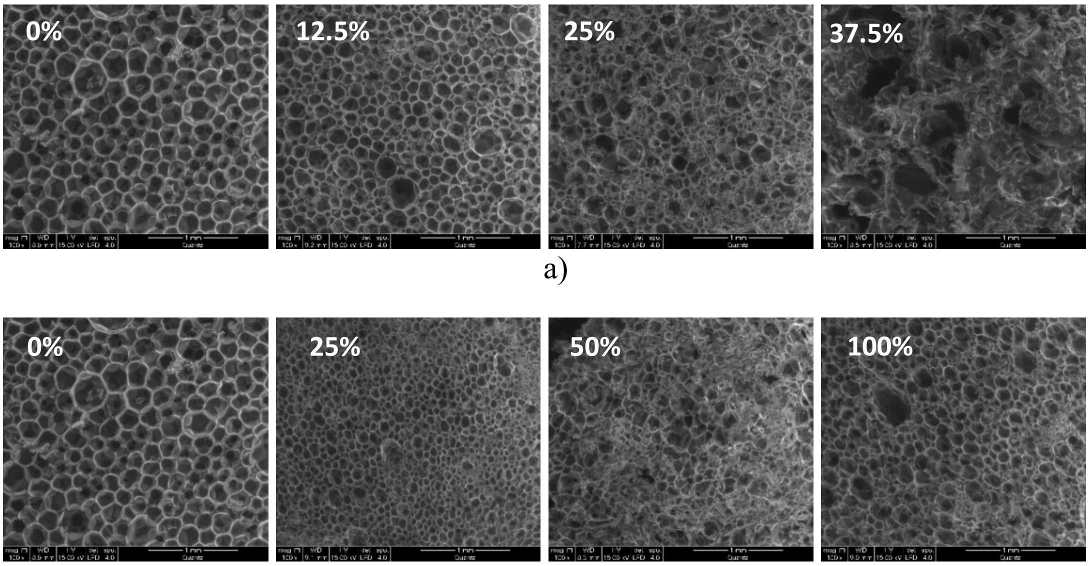


a)



b)

Figure 9. Maximum compressive strength (a) and Young modulus (b) depending on the recovered polyol percentage replacing the raw rigid polyol. Recovered polyol from: conventional rigid PU foams ▲, rigid PU foams containing PCMs ■.



a)

b)

Figure 10. SEM micrographs with magnification x100 of the PU foam framework for different percentages of recovered polyols. Recovered polyol from: conventional rigid PU foams a) and from rigid PU foams containing PCMs b).

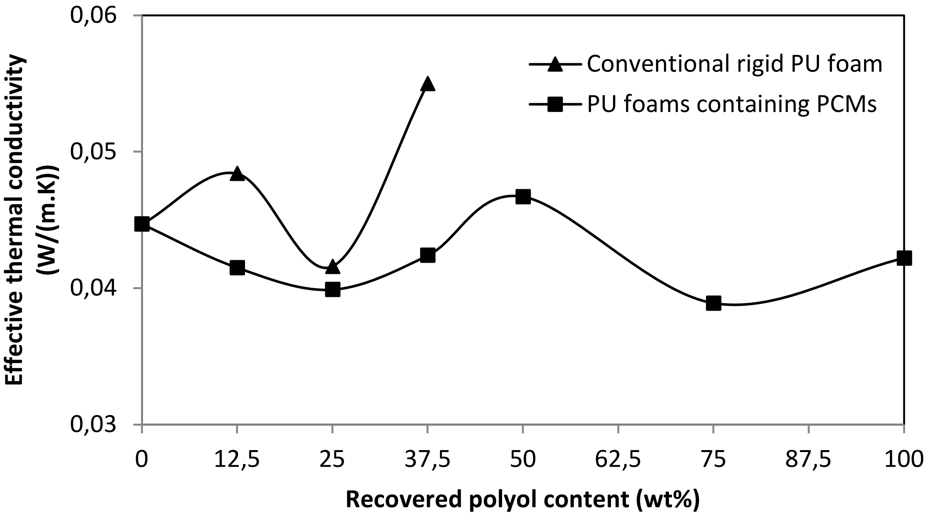


Figure 11. Effective thermal conductivity as a function of the recovered polyol percentage replacing the raw rigid polyol. Recovered polyol from: conventional rigid PU foams ▲ and from rigid PU foams containing PCMs ■.