

Flexible polyurethane foams synthesized employing recovered polyols from glycolysis: physical and structural properties

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ABSTRACT

Polyurethane (PU) is one of the most important polymers with a global production of 17.565 million tons, which makes its recycling an urgent task. Besides, the main goal of PU recycling is to recover constituent polyol as a valuable raw material that allows to obtain new PU with suitable properties. Split-phase glycolysis can be considered the most interesting PU recycling process since provides high quality recovered products in terms of polyol purity.

The aim of this work was to evaluate several recovered polyols as replacement of the raw flexible polyether polyol in the synthesis of new flexible PU foams. These recovered polyols come from the split-phase glycolysis of different types of polyurethane foams and employing as cleavage agents diethylene glycol (DEG) or crude glycerol (biodiesel byproduct). The influence of the foam waste type and of the cleavage agent on the foams properties was analyzed. The recovered polyols were evaluated by performing several foaming tests according to the method of free expansion foaming of conventional flexible foam. Synthesized flexible foams containing different proportions of recovered polyols were characterized by means of SEM, density and tensile properties; obtaining similar and sometimes even better values compared to the foams manufactured from commercial polyols.

Key words: *polyurethanes, recycling, foam, properties and characterization*

1. INTRODUCTION

Polyurethane is the 6th most manufactured polymer all over the world with a production of approximately 17.565 million tons per year [1]. As a result of its commercial success, a large amount of waste is generated and its treatment is an environmental challenge. Some decades ago, landfilling was the solution to the problem. However the large biodegradation period of the polyurethanes (> 10 years) [2] and the new environmental laws, do essential to develop environmental sustainable recycling processes.

Physical recycling processes do not modify polymer internal structure, rather that, the polymer waste is mechanically processed into flakes, granules or powder to be used in new materials production. These physical processes can be successfully employed with thermoplastic polymers but they are useless for the majority of the polyurethane specialties due to their thermostable nature. On the other hand, chemical recycling processes allow to obtain basic hydrocarbon units that can be used as synthesis materials in chemical and petrochemical industry, achieving high value-added products [3]. Since chemical processes are suitable to treat thermostable polymers, these processes are the optimal ones to be used in the PU recycling. Among them, glycolysis is the most extended chemical recycling process for PU. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of the glycol [4].

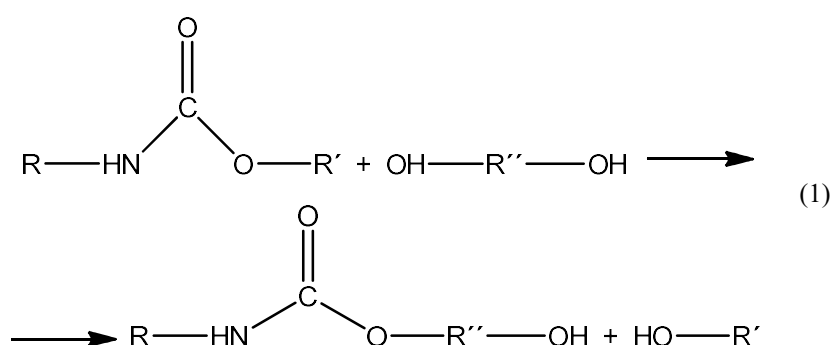
Glycolysis processes have been widely described in literature for almost every polyurethane specialty, including flexible foams [5-24] and rigid ones [25-30] and also the denominated CASES (Coatings, Adhesives, Sealants and Elastomers) [5, 31-33]. Glycolysis processes of reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) polyurethanes have been also reported [34-37].

Among the glycolysis processes, split-phase glycolysis appears to be more efficient to obtain high quality recovered products than single phase processes in terms of recovered polyol content.

Performing the degradation reaction with a large glycol excess, the reaction product splits in two phases: the upper layer is mainly formed by the recovered polyol and the bottom layer by the excess of glycolysis agent and reaction by-products.

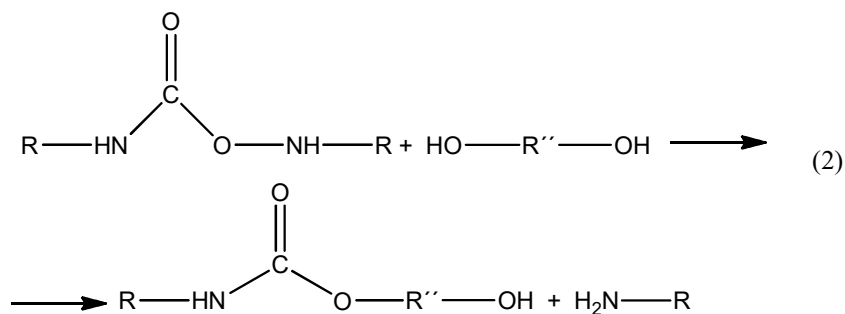
In previous works [14–24], an integrated process for the recovery of polyols from flexible PU foams (conventional, viscoelastic and high resilience foams) by means of two-phase glycolysis has been developed. As explained in these works, diethylene glycol (DEG) and crude glycerol (a biodiesel production by-product) have shown a suitable behaviour to be employed as cleavage agents while stannous octoate was a good catalyst which allows the obtention of high-quality polyols in fast reaction times. However, in spite of the promising properties that presented the recovered polyols (OH number, functionality, molecular weight, water content) it is a crucial task to study the foaming behavior and the mechanical and structural properties of the flexible foams synthesized by means of recovered polyols in order to determine the feasibility of the replacement of virgin polyol by the recovered ones in the synthesis of new polyurethane foams, since in the glycolysis process occurs a wide reactions sequence that could affect the further foaming process of the recovered polyols.

The main reaction that takes place is shown in Scheme 1.

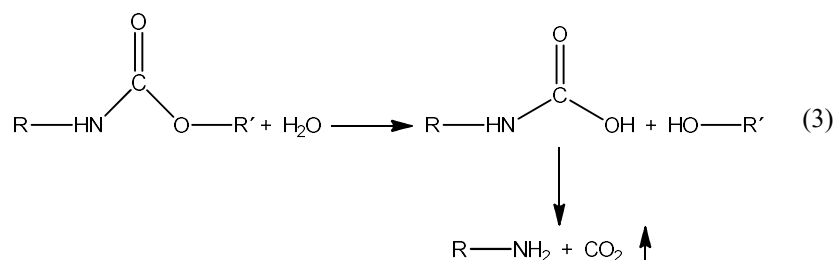


It consists of a transesterification reaction, in which the ester group joined to the carbonylic carbon of the urethane is interchanged by the hydroxyl group of a glycol.

However, polyurethane structure is not only formed by urethane units, but it is also compounded by other functional groups such as urea. These urea groups appear due to the amines formed in the gas formation reaction of the polyurethane synthesis. In a following step the amines may react with free isocyanate giving as a result a substituted urea. Urea groups are also susceptible of the glycolysis process giving as a result a low weight carbamate and an aromatic amine, as shown in Scheme 2.

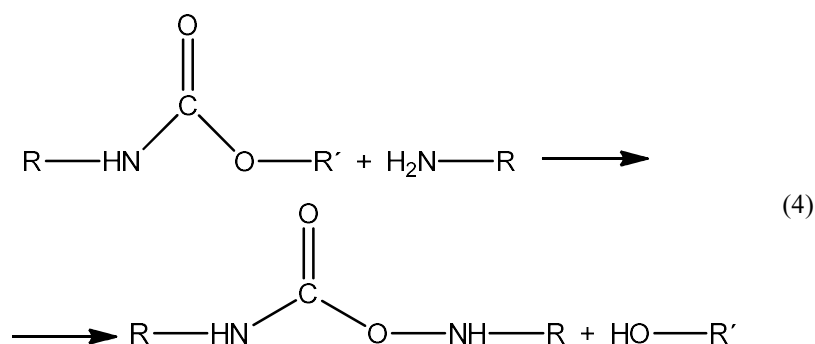


Furthermore, the urethane group may react with water giving as a result a hydrolysis reaction that would be a competitive reaction for the glycolysis one (Scheme 3).

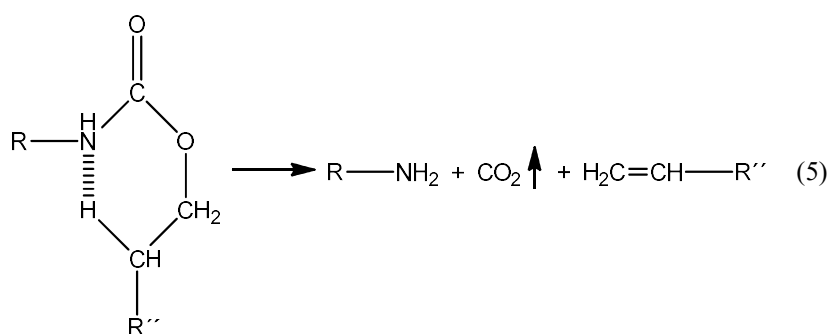


As can be observed, this reaction leads to the formation of a polyol and an unstable carbamic acid that at the reaction temperatures decarboxiles and leads to the formation of a secondary amine while carbon dioxide is evolved.

What is more, the urethane group may react with amines (generated by reactions 2 and 3) to form urea (Scheme 4). However, glycolysis is the main reaction since glycol is much more abundant than amines in the reaction system.



Finally, at the reaction temperatures urethane may be degraded in a thermal way giving as a result carbon dioxide, amines and unsaturated compounds (Scheme 5).



As it can be seen from schemes 1 to 5, several side reactions take place simultaneously to the glycolysis reaction of PU group, and may provoke final PU products with properties out of commercial specifications if recovered polyols from glycolysis are employed to synthesize them.

The aim of this work was to investigate PU foams containing different recovered polyols proportions to define their potential of raw polyol replacement, based on the mechanical and structural properties of the obtained foams. Besides, as commented before, recovered polyols come from the split-phase glycolysis of different types of polyurethane foams and employing as cleavage agents diethylene glycol (DEG) or crude glycerol, in order to evaluate also the influence of the foam waste type and of the cleavage agent on the final foams properties.

2. EXPERIMENTAL

2.1. Materials

The recovered polyether polyols for foaming assays were obtained from the glycolysis of three samples of residual flexible PU foams (TSUGFB, 25HD and V-50 190). The glycolysis process and polyol purification was described in previous works [21-23]. TSUGFB is a conventional PU foam based on polyether polyol [poly(propylene oxide)- block (ethylene oxide), molecular weight (M_n) 3500, functionality with respect to OH groups (f) of 3] and toluene diisocyanate; 25HD is a polymeric conventional PU foam (provided by Interplasp) with a proportion of 60 pph of flexible polyether polyol [poly(propylene oxide)- block (ethylene oxide), M_n 3500, functionality with respect to OH groups of 3] and 40 pph of polymeric polyol; and V-50 190 is a viscoelastic PU foam (provided by Interplasp) based on a viscoelastic polyol founded on polyether polyol [poly(propylene oxide)-block-ethylene oxide), functionality with respect to OH groups of 3] and toluene diisocyanate (TDI).

Table 1 shows the properties of the recovered polyols obtained in previous works [21-23].

Table 1. Properties of the recovered polyols.

Polyol type	Recycled foam	Foam type	Cleavage agent	Mn (g/mol)	OH number (mg KOH/g)	f
<i>Flexible polyether</i> M_n 3500	TSUGFB	Conventional	Crude glycerol	3309	51	≈ 3
<i>Flexible polyether</i> M_n 3500 + <i>Graft polyether</i>	25HD	Polymeric conventional	DEG	-	60	≈ 3
<i>Viscoelastic polyether</i>	V-50 190	Viscoelastic		2556	65	≈ 3
<i>Viscoelastic polyether</i>	V-50 190		Crude glycerol	2007	84	≈ 3

The flexible foams were prepared using mixtures of the recovered polyols from the glycolysis of the three different foams with virgin 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. Niax silicone L-620 LV was provided by Osi Specialities.

2.2. Polyurethane foam synthesis

The foaming experiments were carried out according to the evaluation method in free rise of conventional slabstock foams. Formulations (Table 2) for flexible foams in parts per hundred (pph) of polyol were employed based on a trifunctional polyether polyol of M_n 3500 in which the virgin polyol was partially replaced by recovered polyol. Flexible foams were cured at 100°C during 15 min.

The base recipe is shown in Table 2.

Table 2. Foaming recipes.

CHEMICAL	P100-R0	P87.5-R12.5	P75-R25	P50-R50
<i>Raw polyol M_n 3500 (OH=48) (pph)</i>	100	87.5	75	50
<i>Purified glycolysis upper phase (pph)</i>	0	12.5	25	50
<i>Water (pph)</i>	4.60			
<i>Tegoamin 33 (pph)</i>	0.10			
<i>Niax A-1 (pph)</i>	0.05			
<i>Silicone L-620 LV (pph)</i>	1.40			
<i>Sn Octoate (pph)</i>	0.20			
<i>Isocyanate index</i>	105			

2.3. Foams characterization

2.3.1. Apparent density

Foams density was measured according to **ISO 845** standard. The density testings 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.

2.3.2. Compression set

The compression set 50% (remaining deformation 50%) was measured according to **ISO 1856/A** standard. The remaining deformation of 50% measures the permanent changes of the thickness that take place in a test probe under compression of 50% at a specified humidity and temperature conditions during 22 h and it is expressed in percent compared to the initial thickness. The compression testings were conducted on prismatic foam samples with the dimensions of 50 mm × 50 mm × 25 mm which were cut using a hot wire device.

2.3.3. Tensile strength and elongation

The tensile strength and the elongation were measured according to **ISO 1798** standard. The test determines the tensile strength at which the test probe failure occurs. The elongation is defined as the percentage of the initial length that the test tube increases in that moment. The tensile tests were performed on test probes type 1A which were cut using a hot wire device. The tests were carried out using an Electromechanical Universal Testing Machine (MTS Criterion C43), with a load cell of 1 kN and crosshead speed of 500 mm/min.

For the physical and mechanical tests, four samples were tested and the average value of the data and their standard deviations are shown in the results section.

2.3.4. Foam morphology, Cell size and Cell size distribution

Prepared flexible PU foams were analyzed by *SEM* in order to access the cell structure when different amounts of recovered polyols, from different kinds of flexible PU foams waste and

obtained using distinct cleavage agents, were added to the foaming formulation. Quanta 250 (FEI Company) was the apparatus employed for scanning electron microscopy analyses.

Foam cell size distribution and the average cell size were determined by the Motic Image Plus program by measuring more than 70 cells. The standard deviations of these data are also calculated.

3. RESULTS AND DISCUSSION

3.1. PU foams physical characterization.

3.1.1. Apparent density

Figures 1a) and 1b) show the density values and their standard deviation of the PU foams synthesized with the recovered polyols employing DEG and crude glycerol as cleavage agents, respectively.

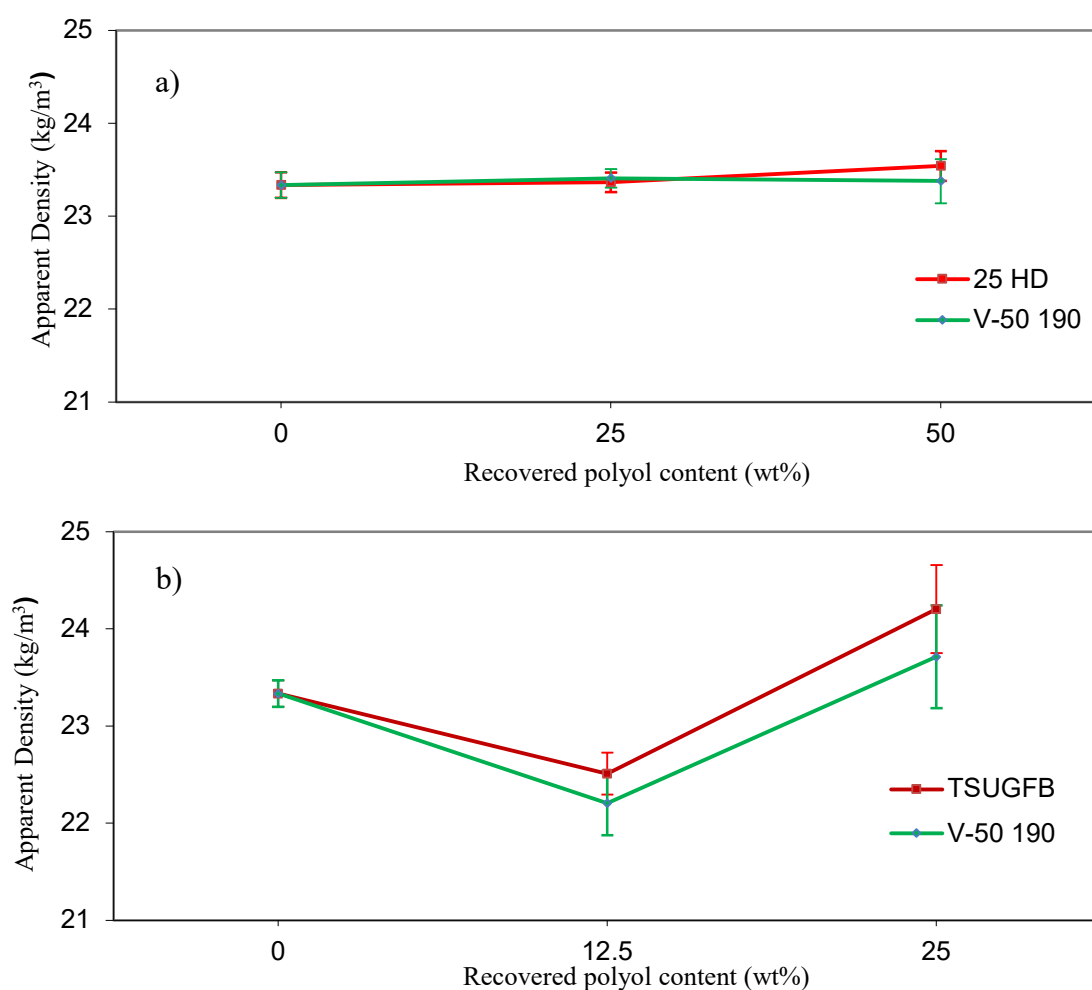


Fig. 1. Dependence of foams apparent density as a function of the recovered polyol percentage replacing the raw standard polyol. Cleavage agent: DEG a) and crude glycerol b).

Figure 1 shows that the density of the foam obtained with the raw polyol is approximately 23 kg/m³. It can be observed that the foams obtained with the recovered polyols, regardless the PU foam recycled and the cleavage agent employed, presented density values similar to the one of the foam achieved by means of the raw polyol. It must be noted that the inclusion of small percentages of recovered polyols obtained with crude glycerol in the foaming recipes provoked a slight reduction in the foam density, whereas higher percentages lead on to slightly greater density values due to introducing recovered polyols implies to reduce the molecular weight of the polyol mixture, giving as a result a density increase. This behaviour was previously reported by other authors such as Sendijarevic [38] and Molero [39].

Besides, it was observed a great homogeneity in the foams synthesized, since the maximum standard deviation had a value of 0.53 kg/m³ with a maximum coefficient of variation of 2.23%.

3.1.2. Compression set

In Figures 2a) and 2b) are depicted the remaining deformation 50% values and their corresponding standard deviation of the PU foams synthesized with the recovered polyols, employing DEG and crude glycerol as cleavage agents, respectively.

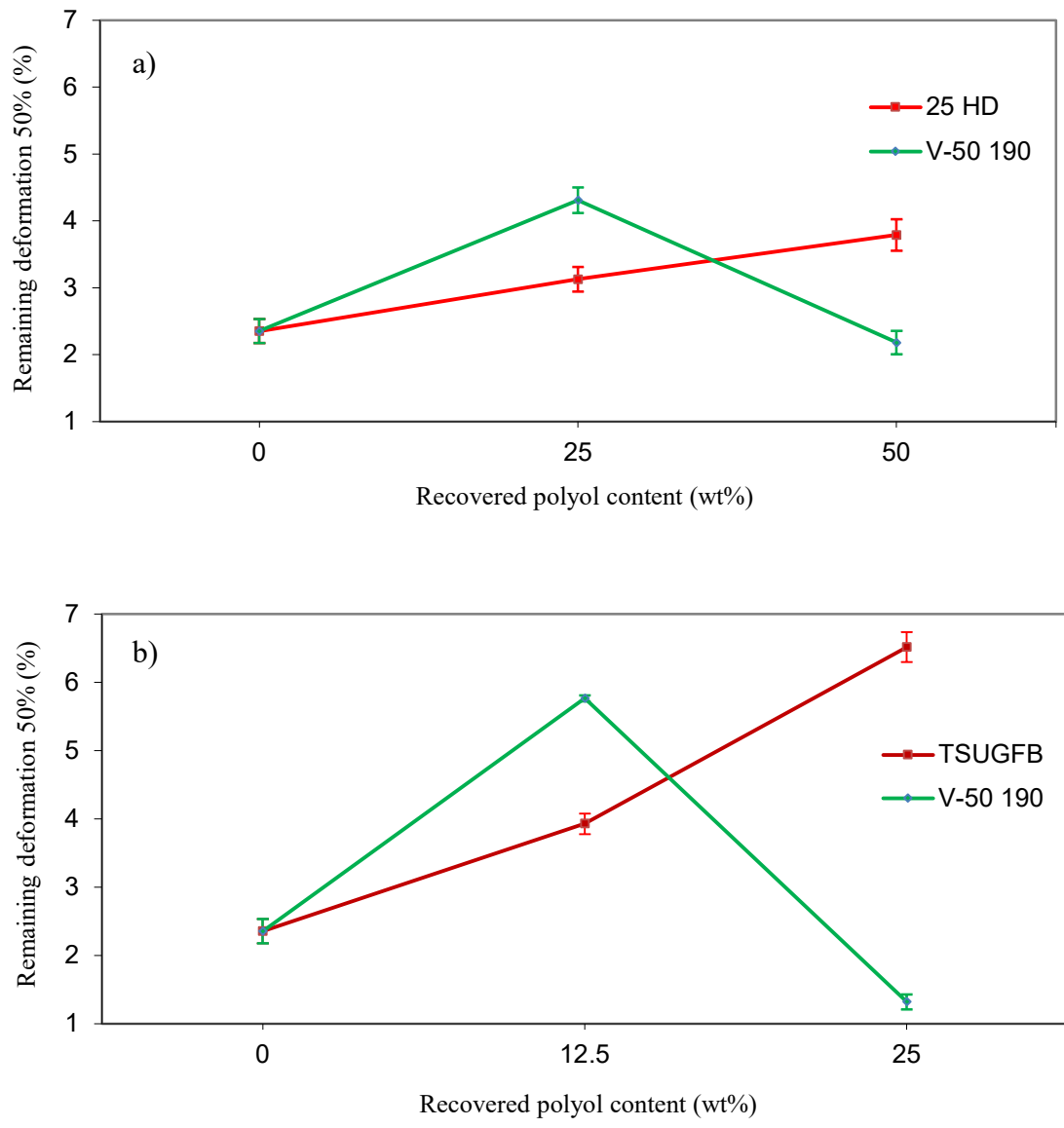


Fig. 2. Remaining foams deformation 50% as a function of the recovered polyol percentage replacing the raw standard polyol. Cleavage agent: DEG a) and crude glycerol b).

In Figure 2, it must be noted that in the case of PU foams synthesized employing recovered polyols coming from conventional foams (TSUGFB and 25HD), the higher the polyol content, the higher the remaining deformation 50%, regardless the cleavage agent used. It can be explained attending to short chain segments present in the recovered polyols, such as the byproducts and the excess of chemolysis agent [21].

On the other hand, PU foams synthesized employing recovered polyols coming from viscoelastic foam V-50 190, showed two different behaviors depending on the quantity of recovered polyol

introduced in the formulation, regardless the cleavage agent considered. At low recovered polyol percentages, the influence of the short chain segments in the recovered polyol is more noticeable than the viscoelastic polyol effect provoking an increase in the remaining deformation of the PU foams. Nevertheless, higher percentages of recovered polyol lead to lower remaining deformation values than even in the case of the PU foam synthesized with the conventional raw polyol as the only polyol component in the recipe. At higher percentages of recovered polyol, the effect of the viscoelastic polyol (low remaining deformation) is more influential than the effect of the short chain segment in the recovered viscoelastic polyol. Moreover, it is crucial to remark that in the case of the recovered polyol obtained with crude glycerol, the “viscoelastic effect” appears at a lower recovered polyol percentage (25%) than in the case of employing DEG due to crude glycerol let to obtain a polyol more similar to the raw viscoelastic one and as a consequence with a better remaining deformation performing than DEG [22, 23]. Thus, an increase of the recovered polyols content from viscoelastic foam in the foaming recipe, provokes flexible PU foams with better compression set behaviour, regardless the cleavage agent used, from the moment in which the viscoelastic behaviour is predominant over the influence of the short chain segments in the recovered polyol.

Moreover, the statistical study of the results showed really good reproducibility of the tests since the standard deviation and the coefficient of variation presented very low values, with maximum standard deviation and coefficient of variation of 0.22% and 8.24%, respectively.

3.1.3. Tensile strength and elongation

Figure 3 shows the tensile strength and the standard deviation of the flexible PU foams synthesized employing DEG (a) or crude glycerol (b) as glycolysis agent.

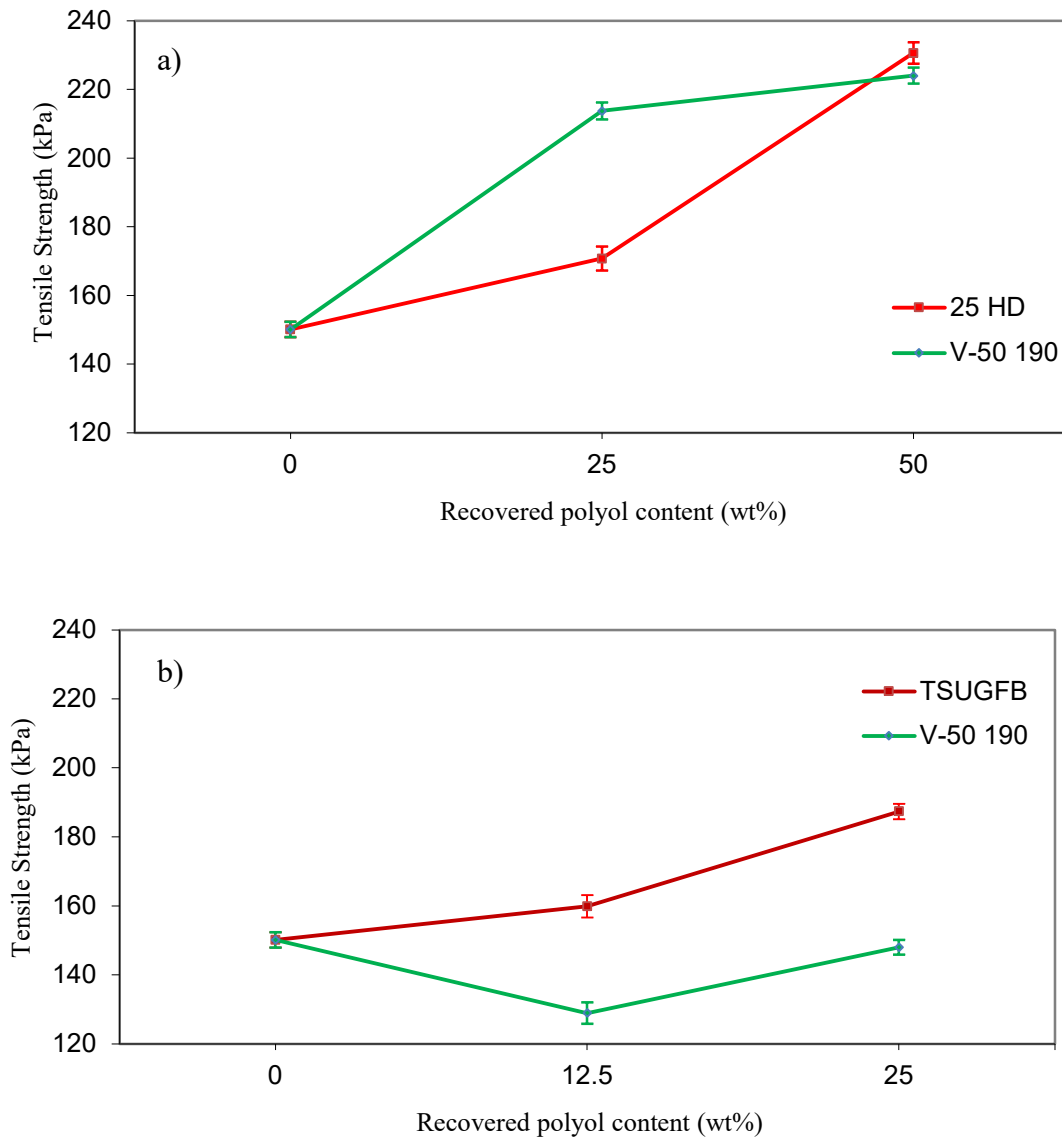


Fig. 3. Tensile strength of foams as a function of the recovered polyol percentage replacing the raw standard polyol. Cleavage agent: DEG a) and crude glycerol b).

As reported by other authors [40], it can be observed in Figure 3 that an increase in the recovered polyol content causes an improvement in the tensile properties of the PU foams probably due to the higher crosslinking and higher urea formation. In fact, it can be observed that the foams synthesized with glycolyzates obtained employing DEG as cleavage agent show the highest values of tensile strength since these recovered polyols present the highest proportion of compounds that increase the crosslinking and the urea domains in the PU structure (glycolysis agent excess and byproducts) [21-23].

The statistical study of these data confirmed the obtained results reliability since the low standard deviations achieved (lower than 3.4 kPa) showed that all the density values of the different foams were clustered closely around the mean. Besides, the coefficient of variation were all lower than 2.5%.

On the other hand, Figures 4a and 4b show the elongation and the standard deviation of the PU foams synthesized with the recovered polyols from glycolysis employing DEG and crude glycerol as cleavage agents, respectively.

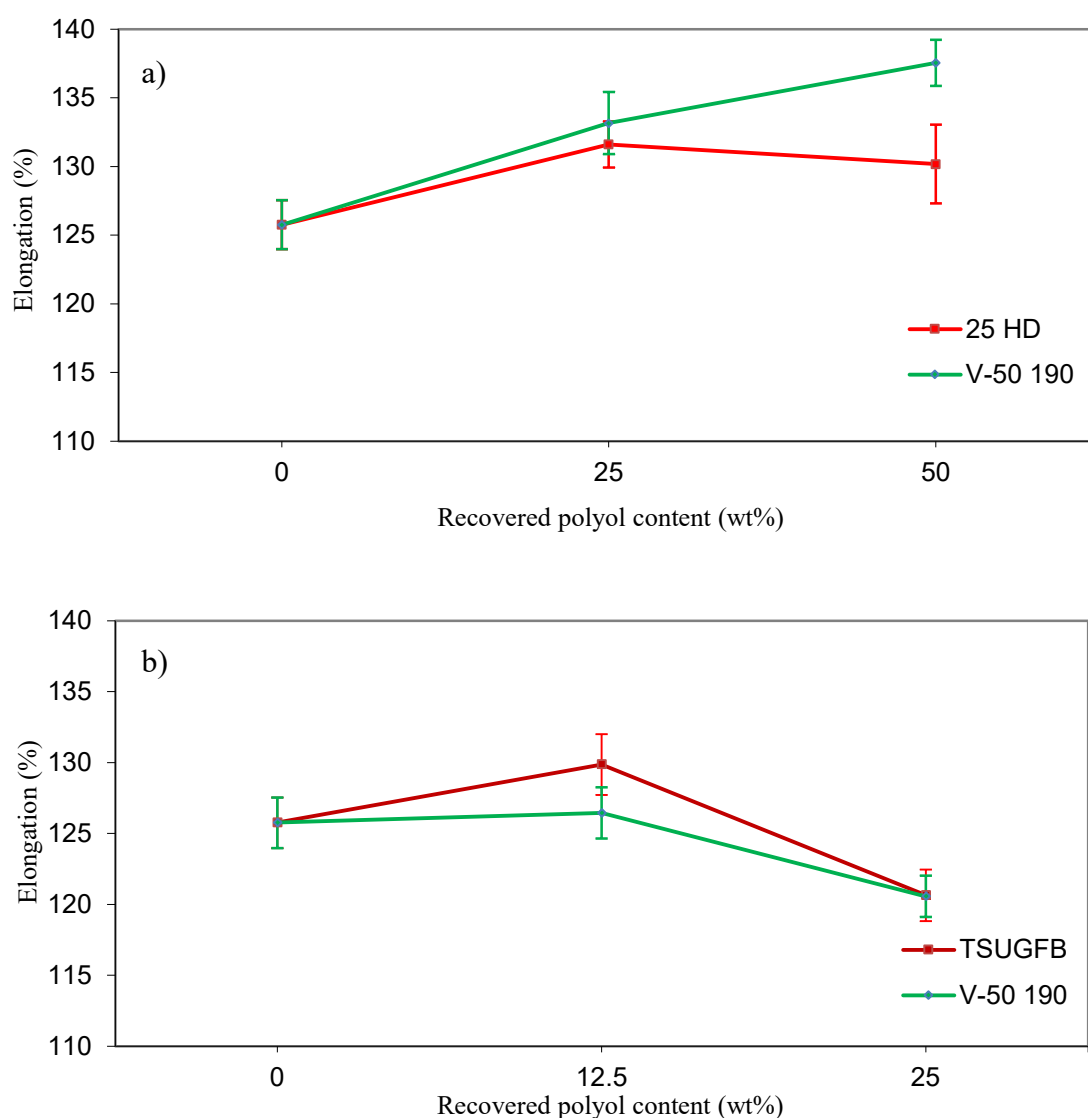


Fig. 4. Foams elongation as a function of the recovered polyol percentage replacing the raw standard polyol. Cleavage agent: DEG a) and crude glycerol b).

As can be observed in Figure 4, elongation values remain in the range 120 – 140 %, regardless the recycled PU foam, the cleavage agent employed and the percentage of recovered polyol introduced in the formulation, confirming the high quality of the recovered polyols obtained by means of the split phase glycolysis process. Therefore, it has not been reported a worsening in the tensile properties of the final PU foams as stated by other authors when glycolyzates from single phase glycolysis were employed for the synthesis of new PU specialties [41, 42]. For this property, the maximum values of the standard deviation and coefficient of variation were 2.87 and 2.20, respectively; showing again a good reproducibility of the foam performance.

3.2. Foam morphology, Cell size and Cell size distribution

Figure 5 shows the microphotographs obtained by SEM with magnification x100 of the foams synthesized by means of employing different proportions of recovered polyols from several kinds of PU foams waste obtained using DEG and crude glycerol as cleavage agents.

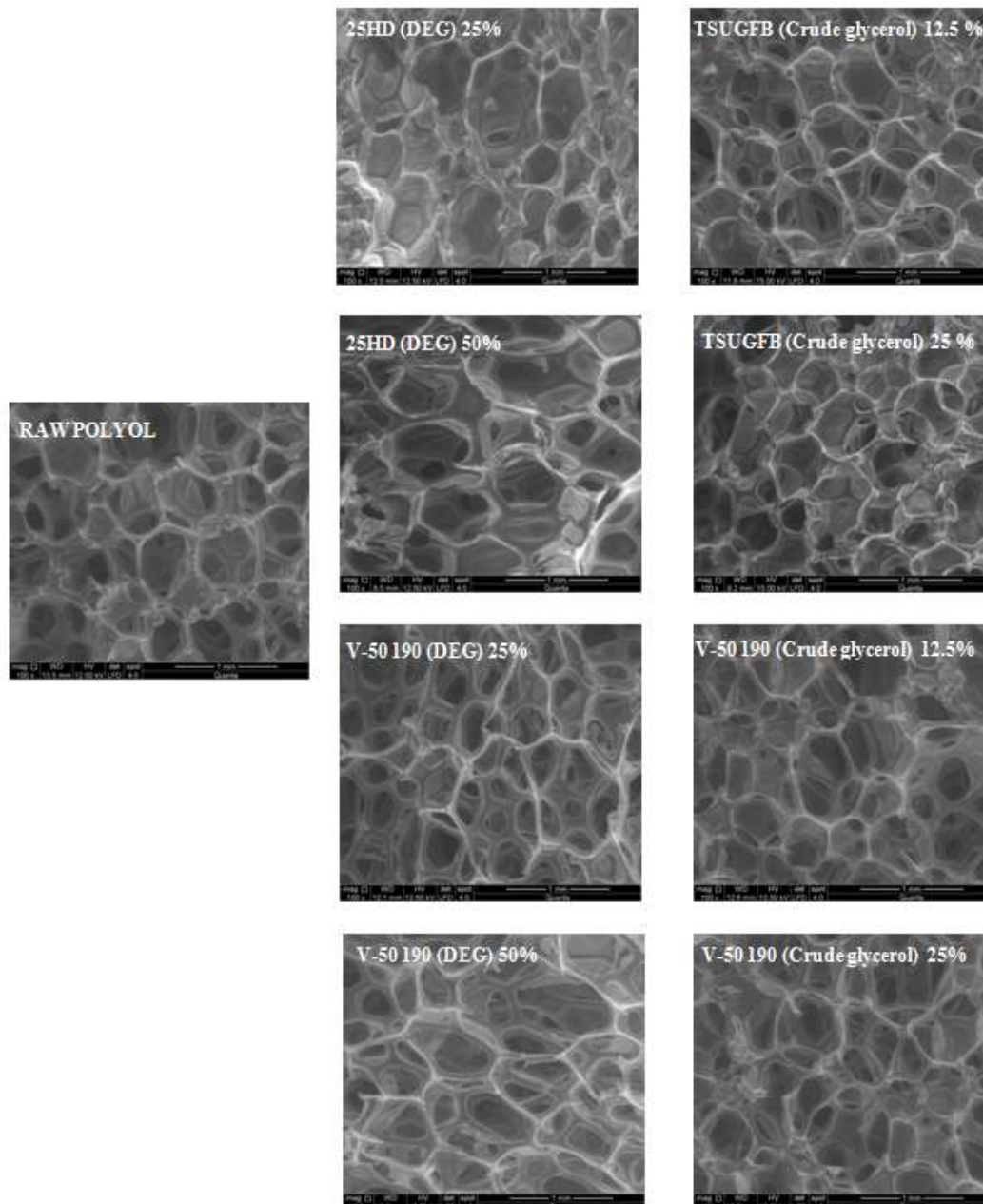


Fig. 5. SEM micrographs with magnification x100 of the PU foam framework for different percentages of recovered polyols, coming from different types of PU foams waste and employing as cleavage agents DEG or crude glycerol.

In a general way, it can be observed that the foams preserve the polyhedral cell structure independently on the content of recovered polyol and on the cleavage agent. However, crude glycerol promotes the reduction of the cell size, while when using DEG cell size increases with the amount of recovered product, regardless the kind of PU foam recycled. This can be explained attending to the different viscosities of glycerol (1412 cp at 20 °C [43]) and DEG (35.7 cp at 20°C

[44]) since foam cell size is a function of the mixture viscosity and of the CO₂ expandability [40]. In fact, the higher the viscosity of the polyol mixture, the more restricted the CO₂ to be expanded, giving as a result a decreasing in the PU foam cell size [40, 45]. Figure 6 shows the cell-size distribution of all synthesized foams.

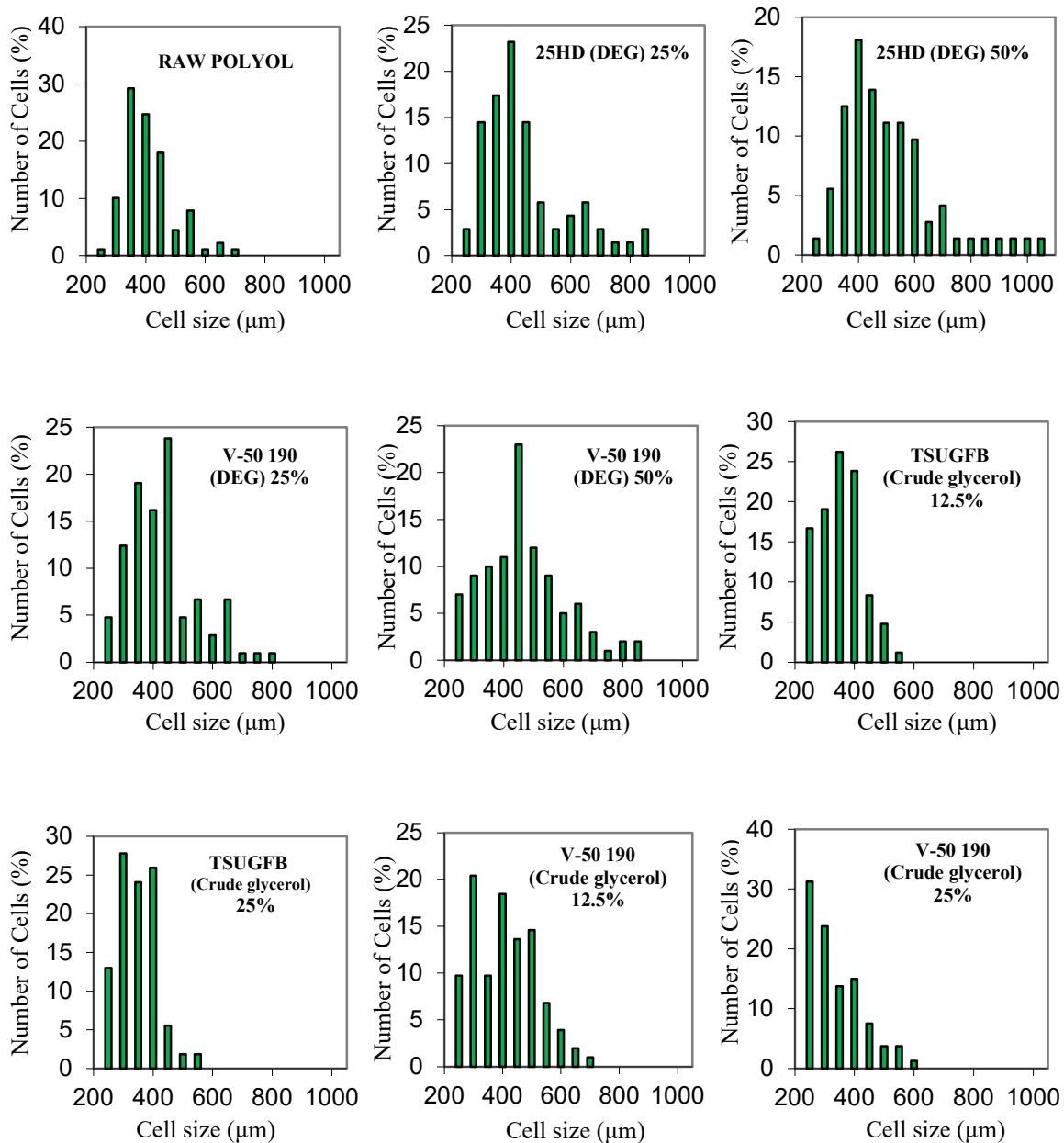


Fig. 6. Cell size distribution of the PU foams for different percentages of recovered polyols, coming from different types of PU foams waste and employing as cleavage agents DEG or crude glycerol.

From the cell size distribution depicted in Figure 6, it is possible to obtain the average cell size and the standard deviation of the PU foams cells, as can be appreciated in Figure 7.

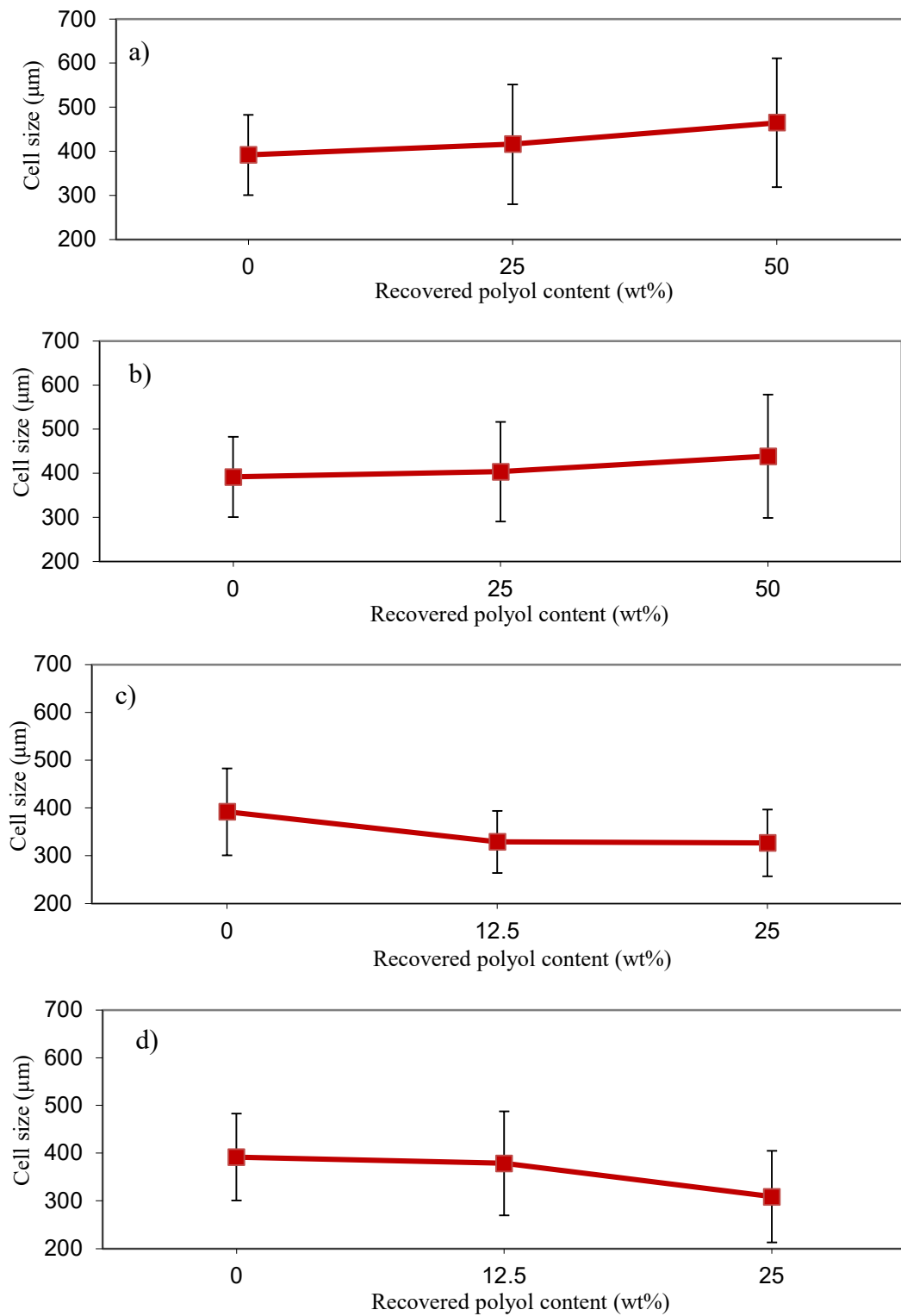


Fig. 7. Average cell size and standard deviation of the synthesized foams as a function of the recovered polyol percentage replacing the raw standard polyol. a) 25 HD (DEG), b) V-50 190 (DEG), c) TSUGFB (Crude glycerol) and d) V-50 190 (Crude glycerol).

Figure 7 confirms that the higher the quantity of the recovered polyols obtained from crude glycerol as cleavage agent, the lower the cell size of the final PU foams synthesized. On the other hand, it has been also verified that increasing the quantity of the recovered polyols obtained with DEG lead on to higher cell sizes. Moreover, it can be also appreciated in a general way in Figure 7 that the higher the recovered polyol content employing DEG as cleavage agent, regardless the PU foam recycled, the higher the standard deviation. However, it must be noted that recovered polyols from crude glycerol as cleavage agent provides lower standard deviation values in the cells of the synthesized foams than recovered polyols from DEG. In fact, in the case of the foam TSUGFB, the standard deviation values are even lower than the one obtained for the synthesized foam with the virgin polyether polyol.

Furthermore, it is also remarkable to note in Figure 7 that the recovered polyol from the conventional flexible PU foam containing polymeric polyol (foam 25HD) is the one that provides the highest average cell sizes. It can be explained attending to the presence of copolymer particles of SAN (styrene-acrylonitrile) in that recovered polyol [21]. These copolymer particles aid in cell opening at the end of the rise process, causing an increase in the average cell size [46, 47] and acting as a reinforcement that improves the hardness and the load bearing properties of the resulting filled flexible PU foams.

It is important to take into account that all the flexible PU foams synthesized in this research have been achieved by means of employing the same formulation, changing only the isocyanate quantity depending of the polyol mixture hydroxyl number. However, water content, surfactant, amine catalysts and chain extension catalyst concentrations have been maintained constant with the aim of adapting the recovered polyols to a further industrial production of flexible PU foams. Nevertheless, in order to keep perfectly constant all the structural and physical properties of the foams it could be performed a slight modification in the foaming recipe at high percentages of recovered polyol.

4. CONCLUSIONS

SEM micrographs and physical properties (density, compression set, tensile strength and elongation at break) have confirmed that it is possible to obtain flexible PU foams with physical and structural properties similar to those of a PU foam obtained with a raw flexible polyether polyol by means of employing recovered polyols.

In fact, some properties have experienced an improvement in comparison with the raw polyol based foam, depending of the PU foam recycled and the cleavage agent employed. Apparent density and elongation values have been nearly maintained constant, regardless the type of PU foam recycled and the cleavage agent employed. Recovered polyols from viscoelastic foam have yielded flexible PU foams with better compression set behaviour, regardless the cleavage agent used. Moreover, an increase in the recovered polyol content has succeeded an improvement in the tensile properties of the PU foams synthesized, regardless the cleavage agent employed and the kind of PU foam recycled, due to the higher crosslinking and higher urea formation that provoke in the new PU foams the recovered polyols from the split-phase glycolysis process.

Regarding the cell sizes of the obtained foams, crude glycerol let to obtain flexible foams with lower average cell size and recovered polyol from polymeric conventional foam has led to new flexible PU foams with higher average cell size.

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GRAPHICAL ABSTRACT

