NEW METHODS TO PRODUCE FLEXIBLE POLYRETHANE FOAMS WITH POSITIVE IMPACT TOWARDS ENVIRONMENT - ABSTRACT

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The polyaddition reaction between an isocyanate and a diol, followed by the invention of polyurethane (PU) foams, was discovered in the early 1940s by Otto Bayer and his team, representing a major milestone in the development of industrial polymers. Since then, the production of flexible PU foams has increased exponentially, reaching a wide variety of qualities and applications. The main driving force of this amazing development was the aim to continuously increase the comfort and lifestyle of people all over the world. Consequently, several methods of producing PU foams have been designed, developed, and implemented [1,2]. Many end applications, such as bedding, mattresses, upholstery, automotive industry, are beneficiaries of this polymeric material with exceptional features.

The global polyurethane foam market is expected to grow at an annual rate of 7.5% between 2020 and 2025 [3], making it the sixth most widely used polymer in the world [5]. The global market for PU foam is expected to increase to $ 74.24 billion by 2021 [6]. In Europe, the production of PU slabstock foam has reached in 2018 a record of more than 1.2 million tons [3], while the global demand of polyurethane products was expected rising to 22 million tons in 2020 [4]. The main reasons for this spectacular development are the growing end-use industries, such as bedding and furniture, electronics, automotive, and building construction [3]. PU foams have their own special features such as comfort, insulation, resilience, or light weight, which were the main driving factors for the growth of their market. In particular, flexible slabstock PU foam covers about a third of the total global demand for PU foam. Polyether polyols, which are products based on petrochemistry, represent one of the main raw materials for flexible PU foam, meaning that the continuous expansion of the PU foam market leads to a linear increase in the consumption of fossil resources. Therefore, in accordance with the global effort to reduce the extraction of fossil-based resources, there is a strong need to find alternative solutions that can sustain future forecasts of the growth of the PU industry. Considering the huge amount of flexible polyurethane foam available for recovery, this thesis will aim to depolymerize industrial foam waste, and try to reincorporate waste into flexible polyurethane foams through new innovative methods, that later will have a positive impact on the environment.

This thesis is structured in 4 chapters:

The **first chapter** of the thesis presents a survey of the available literature, emphasizing the motivation for choosing this topic, as well as the fundamental aspects regarding the need to approach and develop these studies.

This chapter also presents the current state of research in the field of obtaining flexible

polyurethane foam in industrially, that included, production process and raw materials for flexible polyurethane foams, application and Sources of foam waste generation. Further, the ecovery of flexible polyurethane foam waste, via acidolysis method and glycolysis method was also highlighted in this chapter

The **second chapter** presents the original contributions of the doctoral thesis.

Glycolysis of ester polyurethane foam waste and reuse in industrial formulations

The recycling of waste generated from the production of polyurethane foam was investigated by the glycolysis method. So far, we have studied the glycolysis of polyurethanes by three specific laboratory methods, glycolysis at atmospheric pressure, glycolysis in the autoclave and in the microwave. The methods are similar in terms of process, but differences in the quality of the finished product were obtained. Raw materials, glycols, along with the shredded polyurethane foam waste, are subjected to synthesis at high temperatures (180 °C) for a defined period of time.

Comparative evaluation of the glycolysis methods

As regards the glycolysis agent, the reason for choosing diethylene glycol (DEG) was the good compatibility with the foam waste, increasing the chances toward high recovered product yields. The boiling point of DEG is 245°C, allowing glycolysis to be carried out at high temperature without loss of raw material. The purity of DEG is also important to avoid eventual side reactions [7].

Table 1 shows the results obtained by the three different glycolysis procedures. All three methods allowed the decomposition of the PU foam waste, resulting in a homogeneous brown liquid with typical characteristics, that could be recycled. EXP. 1G, EXP. 2G, and EXP. 3G were carried out using the same starting formulation, with 25% (weight) PU waste and 75% DEG. All methods led to stable recycled material. As discussed previously, the sequential addition of polyurethane foam waste slowed the whole process, leading to a long glycolysis time. The microwave glycolysis experiment (EXP. 3G) was a much faster process leading to recycled polyol with similar characteristics but is a more complex and high energy consumption procedure.

***Table 1** Formulation and comparative results of the glycolysis types*

Glycolysis method	**Atmospheric**	**Autoclave**	**Microwave**
Experiment number	EXP. 1G	EXP. 2G	EXP. 3G
PU Foam waste (%)	25.0	25.0	25.0
DEG (%)	75.0	75.0	75.0
DEOA (%)	0.5	0.5	0.5
Temperature (°C)	180-190	180.0	190.0
Reaction time (min)	120.0	120.0	10.0
Water content (%)	0.202	0.372	0.457
Viscosity (cSt)	179.0	172.0	167.0
Hydroxyl number (mg KOH/g)	823.0	869.0	784.0
Density (g/cm3)	1.12	1.14	1.17

Production of polyester-based flexible polyurethane foams using glycolyzed product as partial replacement of raw polyol

The glycolyzed products were used as raw material for production of both polyester-based and polyether-based flexible polyurethane foams. In all experiments, 1% virgin polyol was replaced by glycolysis products, and the impact of this recycled product on the physical properties of polyurethane foams was thoroughly studied.

Table 2 *Properties of the foams obtained using the ester formulation replacing 1 pbw virgin polyol (Desmophen 2200B) with recycled polyol*

Polyol used for the ester foam	**Reference**	**EXP.1G**	**EXP. 2G**	**EXP.3G**
Desmophen 2200B (virgin polyol) (%)	*100.0*	*99.0*	*99.0*	*99.0*
Recycled polyol (%)	*0.0*	*1.0*	*1.0*	*1.0*
Foam physical properties				
Rise time (s)	119.0	117.0	118.0	117.0
Foam settling (%)	1.20	2.10	2.00	1.50
Density (kg/m^3)	25.10	24.46	24.48	24.25
Hardness CFD-40% (kPa)	4.80	4.42	4.46	4.24
Compression set 22h 75% 70°C (%)	8.00	9.85	9.70	10.05
Airflow (l/min)	33.0	21.0	25.0	25.0
Tensile strength (kPa)	107.0	144.0	124.0	132.0
Cell structure (fine 1.... coarse 8)	5.0	4.0	4.0	4.0

The hardness of the reference foam was 4.8 kPa, representing a typical value for such a foam. The addition of recycled polyol resulted in somewhat softer foam using all three products from the glycolysis experiments. The loss of foam hardness is believed to be linked to a finer cell structure when recycled polyols are used. A finer cell structure is preferred in textile applications.

Foam airflow, the results of Table 1 indicate slightly decreased airflow in case of the recycled polyols, compared to the reference. Regarding tensile strength, all foams manufactured with recycled polyol indicated an improvement in this property.

Cell structure assessment is a subjective ranking of the size and uniformity of the foam cells. Lower numbers indicate finer and smaller cell sizes, while higher numbers indicate coarser and irregular cell sizes. The addition of recycled polyol improved the cell structure towards a finer level, as previously mentioned. A smaller cell size is preferred in textile and flame lamination foams [8].

Production of polyether-based flexible polyurethane foams using glycolyzed product as partial replacement of raw polyol

The recycled polyol was also used in polyether-based foam applications as a partial replacement of virgin polyol. Table 3 shows that the addition of recycled polyol does not appear to have a real influence on compression sets but leads to decreased foam airflow. In this case, the airflow shift was higher than in the case of the polyester foams with recycled polyol. Identical to the ester foams, the addition of recycled polyol improved the tensile strength. Unlike the ester foams, when the addition of recycled polyol shifted toward finer cell structure, in the case of ether foams adding any of the recycled polyols had no impact on the cell structure.

Table 3 *Properties of the foams obtained using the ether formulation presented in Table 2.4, replacing 1 pbw virgin polyol (Voranol 3322) with recycled polyol*

Ether foam	**Reference**	**EXP. 1G**	**EXP. 2G**	**EXP. 3G**
Voranol 3322 (virgin polyol) (%)	100.0	99.0	99.0	99.0
Recycled polyol (%)	0.0	1.0	1.0	1.0
Foam physical properties				
Rise time (s)	90.00	88.00	87.00	90.00
Foam settling (%)	0.60	0.70	0.80	0.80
Density (kg/m^3)	23.20	22.90	22.80	23.20
Hardness CFD-40% (kPa)	3.34	3.40	3.44	3.38
Compression 22h 75% 70°C (%)	17.86	14.40	17.70	17.50
Airflow (l/min)	109.0	76.0	75.0	73.0
Tensile strength (kPa)	92.0	99.0	98.0	98.0
Cell structure (fine 1.... coarse 8)	2.0	2.0	2.0	2.0

Detailed evaluation of the glycolysis of polyurethane foam waste using the autoclave method

The results presented in the previous sections designate autoclave glycolysis as the best among the three studied methods. Glycolysis at atmospheric pressure does not allow additional increase of the foam waste content, while glycolysis based on microwave is expected to be a high energy consumer. Therefore, the autoclave method was identified as the best performing in terms of glycolysis procedure and improved foam properties, in both polyester-based and polyether-based polyurethane foam formulations.

Influence of the amount of polyurethane foam waste

Various PU foam waste: DEG ratios, between 1:3 and 1:1, have been used in the autoclave glycolysis procedure. In all three experiments, a liquid glycolysis product was obtained, with the characteristics presented in Table 4.

Table 4 *Influence of the quantity of polyurethane foam waste on the characteristics of the recycled polyol, using autoclave glycolysis*

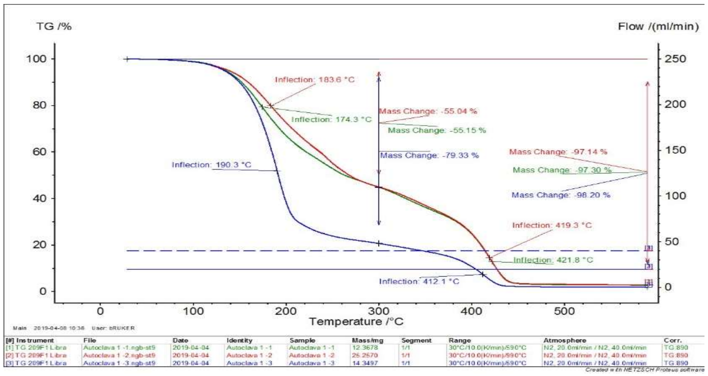
Glycolysis method	**Autoclave**	**Autoclave**	**Autoclave**
Experiment number	EXP. 2G	EXP. 4G	EXP. 5G
PU foam waste (%)	25.0	33.3	50.0
DEG (%)	75.0	66.7	50.0
DEOA (%)	0.5	0.5	0.5
Temperature (°C)	180.0	180.0	180.0
Time (min)	120.0	120.0	120.0
Characteristics of the recycled polyol			
Water content (%)	0.372	0.673	0.774
Viscosity (cSt)	172.0	1458.0	2502.0
Hydroxyl No. (mg KOH/g)	869.0	620.0	593.0
Density (g/cm^3)	1.14	1.15	1.15

The glycolysis product is of dark color compared to the virgin polyol as showed in Figure 1 for the product of EXP 5G. As expected, the increase in the amount of polyurethane foam waste material led to a higher viscosity. At 1:3 ratio the viscosity was rather low. With the increase of the foam waste content, the viscosity increase was significant while the hydroxyl number dropped, not necessarily respecting the linearity of the viscosity characteristics. It is important to note that a slight increase in water content was observed as a linear response to the increase of foam waste in the glycolysis mixture. Polyurethane foam waste can be considered as a carrier of water or moisture. It must also be noted that the water content is part of the polyurethane foam formulation, therefore, a recalculation of the added water will be necessary when using such recycled polyol. Alternatively, a drying procedure could be applied prior to glycolysis, with additional energy consumption for the overall procedure.

Figure 1 *Glycolysis product obtained from flexible PU foam waste and diethylene glycol in a 1:1 (w/w) ratio, in autoclave (image on right), compared to virgin polyol (image on left)*

Thermogravimetric analysis of autoclave glycolysis products

To study the thermal stability of the samples, TGA analysis was performed (Figure 2). Weight loss until 100°C was under 1% and is usually associated with the water content. The thermal decomposition of the samples occurred in two steps. The first step between 100°C and 240°C can be associated with the loss of small molecule compounds. EXP. 2G has the highest mass loss at 300°C (79,32%), consistent with the highest hydroxyl number (which denotes smaller molecules with lower boiling points) and the lowest viscosity. The samples from EXP. 4G and EXP. 5G have similar weight loss at 300°C and comparable hydroxyl number and viscosities. The second step is between 350°C and 460°C and is associated with the degradation of the glycolysis products. The final residue at 500°C was around 2%.



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] TG 209F1 Libra	Autoclava 1 -1.ngb-st9	2019-04-04	Autoclava 1 -1	Autoclava 1 -1	12.3678	1/1	30°C/10.0(K/min)/590°C	N2, 20.0ml/min / N2, 40.0ml/min	TG 890
[2] TG 209F1 Libra	Autoclava 1 -2.ngb-st9	2019-04-04	Autoclava 1 -2	Autoclava 1 -2	25.2570	1/1	30°C/10.0(K/min)/990°C	N2, 20.0ml/min / N2, 40.0ml/min	TG 890
[3] TG 209F1 Libra	Autoclava 1 -3.ngb-st9	2019-04-04	Autoclava 1 -3	Autoclava 1 -3	14.3497	1/1	30°C/10.0(K/min)/590°C	N2, 20.0ml/min / N2, 40.0ml/min	TG 890

Figure 2 *TG curves of glycolysis products obtained by the autoclave method, at different PU waste/ DEG weight ratios; 1:3 (EXP 2G, blue line); 1:2 (EXP. 4G, red line), and 1:1 (EXP. 5G, green line)*

Optimization of the ether foam formulation with recycled polyol by selecting the catalyst

Figure 3 shows the foam airflow of the three different polyurethane foams. The reference foam was made with 100 parts of virgin polyol. The second foam used 5 parts recycled polyol obtained under the conditions of EXP 5G, replacing the virgin polyol. The third foam (the green bar) foam used the same amount of recycled polyol, but was obtained under the conditions of EXP 6G, with catalytic package. An optimized foam airflow of roughly 100 l/min or slightly higher is optimal for comfort application. An airflow below 10 l/min or less is optimum for sealed type of foams, where the water permeability or air permeability must be as low as possible.

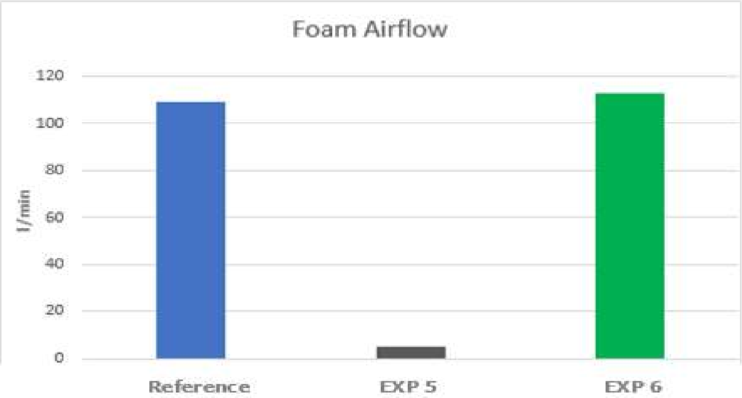


Figure 3 *Foam airflow of the reference polyether-based polyurethane foam (blue bar); polyether-based polyurethane foams obtained with 5% recycled polyol from 50% PU waste in EXP 5G (black bar); polyether-based polyurethane foams obtained with 5% recycle d polyol from 50% PU waste and optimized catalyst formulation in EXP 6G (green bar)*

This chart demonstrates that a glycolyzed product, such as EXP 5G, can be used in polyurethane foam under various conditions to provide specific features, such as sealed foam or even used in comfort application if appropriate catalytic changes are applied for the foam formulation.

Laboratory-scale acidolysis of ether polyurethane foam waste

Polyester polyurethane foam waste was possible to be recovered, while the recovery of the polyether based foam waste, which comprises most of the flexible polyurethane market, was unsuccessful through the mentioned glycolysis methods. Therefore, a new method has been investigated at laboratory scale, the acidolysis of ether polyurethane foam waste, using the same autoclave as in the glycolysis process.

Acidolysis in the autoclave using carboxylic acids from renewable sources

The utilization of other renewable carboxylic acids, lactic acid, and citric acid, has also been studied. The main target was to investigate the influence of the nature of the acid in the same reaction conditions and its impact the decomposition ratio of the polyurethane foam waste, as well as to characterize the acidolysis products based on the main specification characteristics, such as viscosity, hydroxyl number, and water content.

Table 5 shows the results obtained by using the mentioned renewable carboxylic acids, succinic, lactic, and citric. All three methods allowed the decomposition of the PU foam waste, resulting into a homogeneous brown liquid with typical characteristics, able to be recycled. EXP. A, EXP. B and EXP. C were accomplished using the same starting formulation, with 40% (weight) PU waste and 60% of diethylene glycol/acid/Desmophen 2200B mixture. All methods led to a stable recyclable material.

In this set of experiments, EXP. A with succinic acid gave the closest and best results in terms of depolymerization process and uniformity of the mixture. EXP. B, where acid lactic was used, also led to excellent results in terms of properties and aspect of the acidolysis product. The results of the preliminary experiment using citric acid, also presented in Table 5, were promising as well, however clumps of unreacted polyurethane foam has been noticed. Therefore, the investigations with this carboxylic acid need a more detailed approach, to optimize the process parameters.

Table 5 *Formulation and comparative results of the laboratory-scale acidolysis using carboxylic acids from renewable sources*

Carboxylic acid type	**Succinic**	**Lactic**	**Citric**
Experimental setup	EXP. A	EXP.B	EXP.C
PU foam waste (%)	40.0	40.0	40.0
Diethylene glycol (%)	15.0	15.0	15.0
Desmophen 2200B (%)	15.0	15.0	15.0
Acid (%)	30	30	30
Temperature (°C)	180	180.0	180.0
Reaction time (min)	240.0	240.0	240.0
Characteristics of the product			
Water content (%)	3.241	3.152	3.648
Viscosity (cSt)	12700	17000	22000
Hydroxyl number (mg KOH/g)	48.0	46.0	40
Density (g/cm3)	1.12	1.14	0.99

Production of polyether-based flexible polyurethane foams using the product of the laboratory acidolysis process

Table 6 presents the properties of the foams obtained using the ether foam formulation. In these experiments, directly a higher content of recycled polyol in the polyurethane formulation was preferred to a stepwise increase, by replacing 10% of virgin polyol with the acidolysis product.

The reference foam exhibited a 3.34 kPa hardness value, typical for this specific polyurethane formulation. The addition of acidolysis product (from EXP. A - C) enabled the manufacturing of harder foams, without any influence towards the cell structure. As shown in Table 6, the foam hardness revealed a significant increase with the addition of recycled polyol, more than 15% for all investigated carboxylic acids. This is a surprising positive effect on the foam property, as hardness increase can usually be achieved with special grafted polyols, such as styrene acrylonitrile ether polyols, which by their nature and production process would bring additional cost to the foam [9]. As a result of this finding, we demonstrated the possibility of manufacturing a harder foam by using a recycled polyol obtained through acidolysis.

The density of the reference foam was 23.2 kg/m^3. The use of recycled polyol slightly dropped the foam density with an average of 0.3 kg/m^3, although the foam made with the acidolysis product of EXP. C (using citric acid) showed a higher value, 23.2 kg/m^3, the same as in the case of reference foam. Because a standard deviation of 0.5 kg/m^3 can be considered acceptable at laboratory stage, it can be concluded that the addition of 10 pbw of recycled polyol did not significantly influence the foam density.

Table 6 *Properties of the foams obtained using the polyether-type polyurethane formulation presented in Table 2.11, replacing 10 pbw virgin polyol (Voranol 3322) with recycled polyol (acidolysis product)*

Ether foam	**Reference**	**EXP.A**	**EXP.B**	**EXP.C**
virgin polyol (%)	100.0	90.0	90.0	90.0
Recycled polyol (%)	0.0	10.0	10.0	10.0
Foam physical properties				
Rise time (s)	90.00	88.00	91.00	100.00
Foam settling (%)	0.60	0.70	0.80	0.80
Density (kg/m^3)	23.20	22.90	22.80	23.20
Hardness 40% (kPa)	3.34	4.00	4.00	4.21
SAG	2.51	2.55	2.53	2.32
Airflow (l/min)	119.0	98.0	102.0	100.0
Cell (fine 1.... coarse 8)	2.0	2.0	2.0	4.0

Another critical factor to define the foam quality is the foam airflow. This parameter describes the breathability of a polyurethane foam. A foam airflow of 100 l/min with a standard deviation of 20 l/min is considered optimal. The reference foam exhibited very high foam breathability, while the addition of 10 parts of recycled polyol as acidolysis product with succinic or lactic acid (EXP. A / EXP.B) dropped the value to roughly 100 l/min. Obviously, the acidolysis method allowed the use of ten times more recycled polyol without affecting the foam airflow, which is critical to foam recovery.

The results presented in this chapter can be considered innovative, enabling us to develop further investigation concerning the production and utilization of recycled polyols based on renewable carboxylic acids and polyurethane foam waste. Although a notable increase concerning the use of recycled polyol was already accomplished, the bottleneck is the still limited amount that can be reintroduced in the lifecycle of a polyurethane foam and hence in a finished article. Therefore, a major objective was to establish new ways of further increasing the amount of recycled polyol obtained at industrial scale.

Optimized incorporation of high amount of recycled polyol industrially produced by an acidolysis process

In this study, an industrially manufactured recycled polyol, obtained by depolymerization of flexible polyurethane foam waste using an acidolysis process, was characterized by dynamic viscosity, hydroxyl number, water content, and acid number. The recycled polyol was used to produce low density flexible polyurethane foams at 10 - 30 parts by weight (Pbw), replacing the reference polyol. The influence of increasing the amounts of recycled polyol on the properties of the polyurethane foam has been studied, and foam emission tests have also been performed to evaluate the environmental impact. Using 10 Pbw recycled polyol, no significant differences in physical properties were observed, but the increase of the amount of recycled polyol to 30 Pbw led to a dramatic decrease in foam air flow and very tight foam. To overcome this drawback, N,N'-*bis*[3-(dimethylamino)propyl]urea (Amine 3) was selected as tertiary amine catalyst, allowing the preservation of foam properties even at a high recycled polyol level. Foam emission data demonstrated that this optimized foam formulation also led to an important reduction in volatile organic compounds. These results were reported in a scientific publication [10].

Optimized utilization of recycled polyol in flexible polyurethane foam formulations

In a previous work [7], we demonstrated the possibility of recovering polyester-type foam waste by various glycolysis procedures and successfully reusing it without a purification step. Despite the important outcome of full reuse of the glycolysis product, the main shortcoming was the limitation to utmost 5% recycled polyol incorporated back into the flexible polyurethane foam. Therefore, in this work, a recycled polyol obtained at industrial scale via acidolysis was studied, to evaluate the influence of the recycled polyol in relation with its use level in low-density polyurethane formulations. Further, the possibilities of incorporating higher amounts of recycled polyol back into the polyurethane foam were investigated using a selective amine catalyst already applied in the production of flexible slabstock foam but not yet reported in connection with recycled polyols.

Influence of the amount of recycled polyol on the properties of the polyurethane foam

Foam properties were measured after 24 hours, allowing full curing of the polyurethane foams. The average density of the reference foam was 22.5 kg/m^3. A standard deviation of 0.5 kg/m^3 can be considered acceptable at the laboratory stage. The addition of 10 or 20 pbw of recycled polyol did not significantly influence the foam density. However, EXP. 3A showed a slightly higher density, 23.2 kg/m^3, still close to the accepted standard deviation. The foam hardness revealed a significant increase with the addition of recycled polyol. At 30 pbw of recycled polyol, the hardness was 60% higher compared to the reference. Another critical factor in defining the quality of the foam is the so-called foam airflow. This parameter describes the breathability of a polyurethane foam. A foam airflow of 100 L/min with a standard deviation of 20 L/min is considered optimal. The reference foam exhibited very high foam breathability, while the addition of 10 parts of recycled polyol (EXP. 1A) dropped the value to 90 L/min. The addition of recycled polyol to 20 pbw further decreased the airflow to 20 L/min, while 30 parts of recycled polyol (EXP. 3A) led to very high level of closed cell content, allowing only 1 L air per minute to penetrate through the cell walls. Such a low air permeability cannot be accepted in manufacturing practice. Therefore, further optimization of the process was required to accomplish the main goal of this investigation, the incorporation of higher amounts of recycled polyol without affecting the foam properties.

Optimization of polyurethane foam properties by replacing the catalyst

A higher amount of recycled polyol in the foam formulation negatively affected the foam airflow in this low-density foam formulation. We studied possible ways to further increase the level of recycled polyol use without negatively impacting foam airflow. For this study, three amine catalysts and their influence were studied, keeping the standard polyol : recycled polyol ratio at 70:30. Table 7 presents the foam properties resulting from this approach. EXP. 3A was known to give very low airflow (1 l/min). To better understand the influence of Amine 1 and Amine 2, two experiments were performed using the single catalyst approach, as shown in the results from EXP. 4A and EXP. 5A. In both these experiments, the same use level of 0.06 parts amine catalyst (Amine 1, respectively, Amine 2) was found as optimal. A higher use level was not possible to be tested at the laboratory stage in this formulation due to higher reactivity of these catalysts. As results from Table 7 the foam properties generated for EXP. 4A and EXP. 5A are not satisfactory, specifically for the airflow parameter. In contrast, Amine 3 was tested at a much higher level of use in the formulation (0.3 parts) and did not affect the reactivity of the whole polyurethane foam formulation. Surprisingly, Amine 3 enabled very high foam airflow (87 l/min), bringing this property within an acceptable range. The use of Amine 3, by replacing the typical amine catalysts Amine 1 and Amine 2 clearly affords a higher use level of 30 parts recycled polyol, as demonstrated in EXP. 6A, compared to the similar set of foam properties obtained in EXP. 2A, where only 10 parts of recycled polyol were possible to be used with the traditional catalyst package.

***Table** 7 Properties of the foams obtained using the formulation presented in Table 2.14, with different catalysts and a ratio of 70:30 standard polyol: recycled polyol*

Main formulation changes EXP	**3A**	**4A**	**5A**	**6A**
Virgin Polyol	*70,0*	*70,0*	*70,0*	*70,0*
Recycled Polyol	*30,0*	*30,0*	*30,0*	*30,0*
Amine 1: Amine 2 at ratio 1:3	*0,06*			
Amine 1		*0,06*		
Amine 2			*0,06*	
Amine 3				*0,30*
Results and physical poperties				
Rise time (s)	111	111	111	99
Foam settling (%)	-	-	-	-
Density (kg/m^3)	21,57	21,21	21,75	22,70
Hardness CFD-40% (kPa)	5,17	5,57	4,82	4,06
SAG	3,77	4,19	3,36	2,67
Airflow (l/min)	1,00	1,00	1,00	87,00
Cell structure (fine 1.... coarse 8)	3	3	3	2

Investigation of the cellular structure of the foams by SEM analysis

Figure 4 presents the SEM images showing the morphology and cellular structure of flexible PU foams obtained with the reference polyol (a) and with 30% recycled polyol (b) using Amine 3 as catalyst.

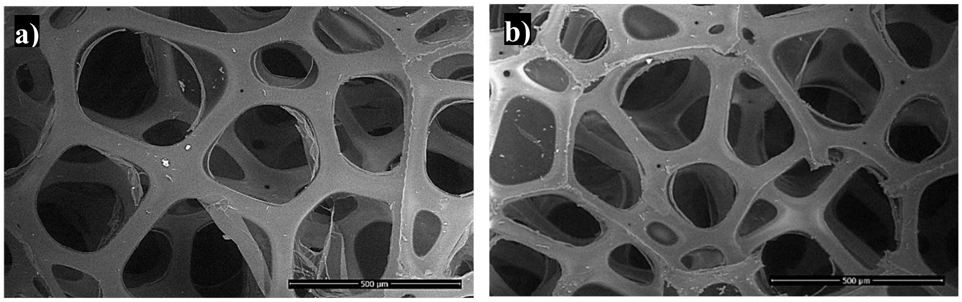


***Figure 4** SEM images with the cellular structures of PU foams obtained with reference polyol (a) and 30% recycled polyol, using the formulation of EXP. 6A (b)*

Obviously, the dimension of the cellular structure is very similar for both foam samples, which means that the morphological structure of the foam was not affected by the use of 30% recycled polyol. It can also be noticed that most of the cells are open. Airflow defines how many open cells are in the expanded foam. Due to the similar cellular morphology, the airflow values for the foam obtained with the reference and recycled polyol were similar. The dimensions of the cells for both foams obtained with standard and recycled polyol are between 300 – 400 µm. Furthermore, the thickness of the cell struts is very similar for both foams. These results confirm that up to 30% recycled polyol can be safely used in flexible PU foam formulations, under optimized formulation conditions

Emission test assessment for the polyurethane foams obtained with recycled polyol

The total VOC reference foam (EXP. 1A) was 102 ppm. The total volatile organic compound generated by the catalyst package used EXP. 1 (including Amine 1 and Amine 2, in 1:3 ratio) was 93 ppm. Foam made from recycled polyol and including Amine 3 using 30 parts recycled polyol (EXP. 6A) had a total VOC as low as 41 ppm. The differences between the catalyst package from EXP. 1A and EXP. 6A showed a VOC reduction of almost 200%, demonstrating that the use of Amine 3 enabled a significant improvement in terms of the environmental impact of the polyurethane foam.

Another important characteristic which was significantly improved was the contribution of the catalyst package to the VOC, as the catalyst package for EXP. 6A contributed with 32 ppm, compared to 93 ppm for EXP. 1A. As regards the total FOG values, they were also high under the conditions of EXP. 6A (almost double compared to the VOC values for the same foam), because the extraction was carried out at a higher temperature (120°C) compared to the VOC analysis (90°C). In this case, although the difference between the contribution from the catalyst package was not as great, a 25% reduction was still observed when using Amine 3

The results of the acidolyis work demonstrate that recycled polyols can be successfully incorporated into low-density flexible polyurethane foams by carefully tuning the formulation and selecting the appropriate tertiary amine catalyst [10].

New methods to produce flexible polyurethane foam waste with reduced carbon footprint

The present technology relates to innovative development of special silicone polyether surfactants for use in polyurethane foams. More particularly, the present work relates to silicone surfactants having dimethyl siloxane backbones with attached alkyl and polyether pendant groups that provide improved properties for flexible urethane foam compositions utilizing polyether carbonate polyols. The present technology employs a silicone based surfactant having high molecular weight and low molecular weight polyether pendant groups, where the low molecular weight polyether pendant groups have a high ethylene oxide content.

In order to determine the silicone polyether surfactant performance, a back to back comparison between silicones surfactants that contain higher amount of ethylene oxide and the standard silicone surfactants was made. A low density flexible polyurethane foam formulation was used. It is important to mention that the maximum possible amount of polyether carbonate polyol was selected, to achieve the highest sensitivity of the polyurethane formulation

The conclusion of this investigation was that the polyurethane foams that were stabilized by employing a surfactant with an ethylene oxide content of 100% in the low molecular weight polyether substituent, or a surfactant with an ethylene oxide content of 75% on the low molecular weight polyether substituent, are the preferred silicone polyether surfactants structures to stabilize polyether carbonate based polyols.

The results presented in this chapter are significantly encouraging and enable us to consider the use of polyether carbonate polyols as a fully replacement of petroleum based polyols. The only way to use 100 parts of polycarbonate base polyol in flexible polyurethane foam formulation based on our knowledge was by designing special silicone polyether surfactants. A silicone polyether surfactant functionalized with two different polyethers, as described in the main thesis, wherein the second set of polyether pendant groups have an ethylene oxide content of 70% to 100 weight percent of the alkylene oxide content of the polyether enabled the use of 100% polyether carbonate polyol. This breakthrough technology and innovation was recently patented [11].

The **third chapter** provides an overview of the materials, working and characterization methods, as well as the equipment used in order to carry out the experimental program.

The **fourth chapter** presents the final conclusions for each subchapter and the original contributions.

The following main points summarize our achievements and the original contribution of this work:

1. This research addressed the chemical recycling, more precisely the glycolysis and acidolysis of polyurethane foams. At the beginning, the possibilities of cleavage of the macromolecular chains were studied, with focus on the glycolysis method.
2. The optimization of the glycolysis procedure was carried out by designing the process conditions which provided the expected efficiency, leading to sufficient amounts of glycolyzed material which ultimately was appropriate for reuse in the production of flexible polyurethane foam.
3. Comparative evaluation of the glycolysis procedures indicated that the autoclave method was the fastest and most efficient, allowing advanced incorporation of the polyurethane foam waste and providing a higher yield of the glycolyzed product. The results demonstrated the viability of the method by recovering all the polyurethane waste.
4. The obtained products were analyzed using instrumental and analytical methods that allowed for appropriate physicochemical characterization. Thermal decomposition, hydroxyl index, acidity, water content, density, and viscosity of glycolysis products were studied.
5. The experimental results indicated that an increase in the amount of polyurethane waste leads to an increase in viscosity of the product, but this problem can be overcome in industrial practice. The hydroxyl index, together with other characteristics, demonstrated that the product was glycolyzed and the flexible polyurethane foam waste was converted into a suitable raw material for reintroduction into the polyurethane foam.
6. Incorporation of the glycolysis product back into the polyurethane foam was successfully achieved in both polyester-based and polyether-based polyurethane applications.
7. Improvements in the foam properties have been observed. Incorporation of glycolyzed material at a low level resulted in an improved foam density for ester and ether foams.
8. The foam hardness effect was different. In the ester foam, the recycled polyol enabled a softening effect, while in the ether foam resulted in somewhat higher hardness. In both ester and ether foams, an improvement in tensile strength was observed.
9. An increased level of recycled polyol negatively affected the foam compression sets. In the case of ether polyurethane foam, a lower air-permeability foam can be produced

using a higher amount of recycled polyol. These foams could be used in special applications where low air permeability is the target, such as in sealed applications.

10. Process optimization allowed for an increase of the amount of recycled polyol, enabling, at the same time, a higher airflow. The right selection of the formulation recipe with appropriate adjustments allowed the increase in the amount of recycled polyol in the foam composition to 5%. An important advantage was also the elimination of any separation step, allowing recycling of the entire glycolysis product.
11. Further development based on these results can target an even higher quantity of recycled polyols obtained through glycolysis in polyurethane formulations with specific compositions, identifying the best foaming conditions.
12. The acidolysis process was found to be more suitable for ether-type polyurethane foam waste, and the original contribution of this thesis refers to the acidolysis process at the laboratory stage, as well as to the improved use of an industrially produced recycled polyol.
13. Acidolysis experiments on a laboratory scale enabled the identification of succinic and lactic acids as appropriate for the recovery of polyether-type polyurethane foam waste using the autoclave process.
14. To the best of our knowledge, a catalyst-free acidolysis process in an autoclave for the recovery of flexible polyurethane foam waste using biobased carboxylic acids (particularly lactic and citric acid) is reported for the first time in this thesis.
15. A recycled polyol (repolyol), industrially produced by acidolysis, can be used as raw material in low-density flexible polyurethane foam formulations, but it can be incorporated only up to 10 weight parts into the foam formulation without formulation changes. A further increase in the repolyol content in the formulation affects the physical properties of the foam, particularly the airflow.
16. Another important achievement of this thesis is that a larger amount of recycled polyol can be reached by replacing standard tertiary amine catalysts used in the polyurethane industry with a reactive catalyst, N,N’-*bis*[3-(dimethylamino)propyl]urea. This catalyst enabled a three-fold higher recycled polyol level compared to the standard catalysts, without affecting the foam properties, allowing the production of a PU foam without defects and with optimum foam airflow.
17. The environmental impact of the use of this catalyst was also evaluated, demonstrating that N’-*bis*[3-(dimethylamino)propyl]urea can generate a reduction in the overall emission of volatile organic compounds.
18. Polyether carbonate polyols are an important step toward reducing the carbon footprint. However, it is difficult to use such a raw material in a sustainable manner in the polyurethane industry when using a standard silicone polyether copolymer.
19. It was found that by taking a typical silicone polyether copolymer structure and increasing the ethylene oxide content close to 100% in the short polyether chain of the silicone polyether copolymer, the incorporation of up to 100% polyether carbonate polyol will be enabled in the flexible slabstock polyurethane formulation. This innovative concept was confirmed by a patent recently issued in both Europe and the United States. To the best of our knowledge, this is the first technology to afford such a high incorporation of these kinds of polyols.

The results of this work demonstrated that recycled polyols can be successfully produced from polyurethane foam waste, and they can be efficiently incorporated back into flexible polyurethane foams. This is an important step towards global efforts to ensure that polyurethane foams could impart a positive environmental impact.

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