NOI METODE DE PRODUCERE A SPUMELOR POLIURETANICE FLEXIBILE, CU IMPACT POZITIV ASUPRA MEDIULUI

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

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Table of Content

1. Literature overview

1.1. Importance of the subject

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 [4]. 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.

Various applications of flexible PU foams, such as bedding and furniture, involve a conversion process in complex forms leading to large amounts of foam waste,

1

which could result in up to 20% trim foam. There are also huge amounts of old furniture and mattresses selectively collected in specialized centers, allowing these PU waste foams to be used as a potential new feedstock. In the best case, the entire amount of flexible PU foam waste could be converted back into the life cycle.

Although a large portion of polyurethane foam waste is already reused, an important part still contributes to the waste disposed of in landfills. Polyurethane flexible foam waste can be reused using typical methods such ad thermochemical, or physical, and the most important chemical methods. Physical recycling methods such as rebinding, adhesive pressing, regrinding, injection molding or compress molding are well established, while the main methods that implies chemical degradation of polyurethane foams are: acidolysis, hydrolysis, glycolysis [7] are mostly in the development stage, as will be presented.

Taking in consideration the high quantities of polyurethane foam waste suitable in a large amount to be recovered and the global effort to reduce fossil consumption, there is a clear demand to identify new methods or improve the efficiency of existing methods. Waste prevention is the first principle of Green Chemistry (Figure 1). Recycling represents a vital area of Green Polymer Chemistry, and the present developments are driven by environmental concerns, sustainability, and efforts to reduce the dependence on petroleum-based materials [8]. An efficient design of PU degradation makes PU waste suitable for recycling and fits into Principle 10 of Green Chemistry. Therefore, recycling PU foam waste will contribute to a greener chemical manufacturing industry and a cleaner environment. A recent review summarized the main scientific and technological achievements to create polyurethanes that cause less pollution to the environment, making their synthesis and use reliable with the principles of Green Chemistry and sustainable economy [9].

Figure 1.1 *The principles of green chemistry, highlighting the importance of reuse, reduction, and recycling [10]*

1.2. Circular economy and waste management

The European Commission has adopted the concept of circular economy, one of the main blocks of the European Green Deal, as the new agenda of Europe for sustainable growth. This action plan announced several initiatives throughout the life cycle of products, endorsing circular economy processes, promoting sustainable consumption, and ensuring that the available resources used will be kept in the EU economy for as long as possible [11].

This Circular Economy Action Plan provides a future-oriented agenda for achieving a cleaner and more competitive Europe in cooperation with the main economic actors, consumers, citizens, and civil society organizations. It aims to accelerate the transformational change required by the European Green Deal. This plan will ensure that the regulatory framework is streamlined and adapted for a sustainable future, maximizing the new opportunities arising from the transition, and at the same time minimizing the possible worries on people and businesses [11].

The plan presents a set of interrelated initiatives to establish a strong product policy framework that will make sustainable products, services, and business models capable of transforming consumption patterns. This product policy framework will be progressively implemented, while key product value chains will be addressed as a matter of priority. Additional measures are planned to reduce waste and guarantee that the EU has a functional internal market for secondary raw materials of high-quality. The capacity of the European Union in order to responsible manage all waste-related concerns will also be strengthened [11].

As concerns PU flexible foams, they currently face one of the biggest difficulties in recycling or finding outlets. In 2019, approximately 45% of the polyurethane foam waste that resulted from end-of-life products such as mattresses or furniture was landfilled. Another 33% of the foam waste was incinerated and therefore at least the caloric value was recovered. Mechanical recycling by conversion to other finished products is estimated to be in the range of 22%. In January 2019, the European Union set very ambitious goals for end-of-life mattresses and furniture, to reuse or recycle 55% of end-of-life products by 2025, together with a target reduction of landfill products to 10% by 2030 [12]. Mattresses and furniture represent a huge potential source of recycled PU, but they are complex products that comprise

4

many different materials alongside PU. Within the EU, 30 million mattresses are discarded on average every year. Most of these go into landfills or are incinerated [57]. If they were piled up, they would be approximately 680 times the height of Everest. The EU generates about 200 kT/year of polyurethane waste solely from end-of-life mattresses. In fact, the volume of scrap resulting from the manufacture of mattresses and upholstered furniture is larger. Bed, furniture, and mattress makers generate about 310 kT/ year of trim foam, all of which is mechanically recycled. Really large volumes are in end-of-life furniture upholstery. Europe processors generate around 660 kT/year of this, about 50% being incinerated and 50% landfilled. Additionally, the automotive sector produces about 130 kT/year of PU foam scrap, which is mechanically recycled, incinerated, or landfilled. In total, the waste of PU foam in the EU that requires processing amounts to 1.3 mT/year [13].

A conjugated effort will be required for the recycling of old foam to solve this problem. Although the role of technology is essential, a consortium of companies and organizations must also be involved to support the circular economy, since circular chains are much more complex compared to linear value chains [13].

Figure 1.2 Mattress collection center [13]

Figure 1.3 Recycle point of old mattresses in The Netherlands *[14]*

1.2.1 RePURpose initiative

A wide diversity of products use polyurethanes, from insulation materials and mattresses to components in wind turbines and aircraft or medical devices. Currently, there are only a few methods for recycling polyurethane, despite the high value of this material compared to other plastics. Moreover, they provide a recycled product in which the original properties of polyurethane are not completely retrieved, meaning that the current management of end-of-life PU products cannot be considered sustainable.

RePURpose [15] is one of the most important projects at European scale, targeting innovative technologies for the recycling of PU. The technologies developed in this project, funded by the Innovation Fund Denmark, will cover recycling through innovative granular methods (ReUSE) and recycling via chemical restoration of the monomers, the original building blocks of the material (ReCYCLE).
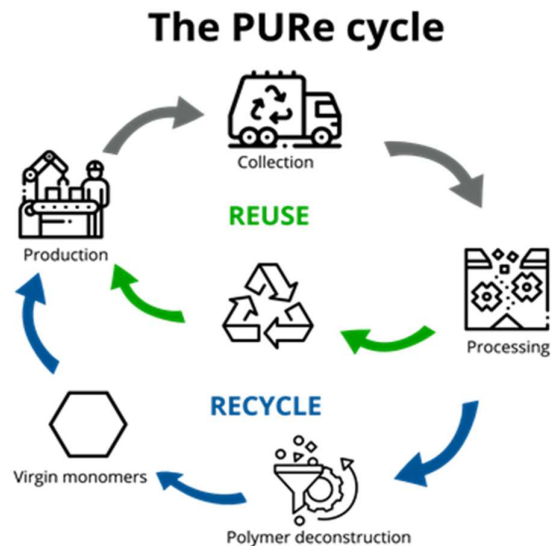
Figure 1.4 *Life cycle of polyurethane waste [15]*

ReUSE addresses the recycling of production waste that occurs at the individual manufacturer of PUR products. Production waste is a pure, homogeneous, and well-defined flow of material of the same high value as the finished products. If the production waste can be traced back into production, it will create value instead of leaving the production plant as waste. The goal of ReUSE is to develop a simple method and an associated process plant, based on a new granular technology that allows waste from production to be included in the production of new products. At the end of the project, the partners in the project are expected to install ReUSE process plant prototypes [15].

ReCYCLE addresses the recycling of PU products that come back from consumers and focuses on developing innovative and mild chemical reaction conditions that can degrade PU. The products of this degradation process will consist mainly of the original building blocks of polyols and isocyanates. Thus, ReCYCLE will be able to supply virgin material to the PUR value chain, material that can be made into any new high-value product [15].

7

1.3. Production process and raw materials for flexible polyurethane foams

Most flexible polyurethane foam is made using a continuous process known as the slabstock process, as opposed to discontinuous processes such as molding. In the slabstock process, the liquid raw materials are continuously metered in a mixing chamber. The still liquid but reacting mass is continuously dispensed on a moving conveyor where a major part of the reaction and expansion takes place.
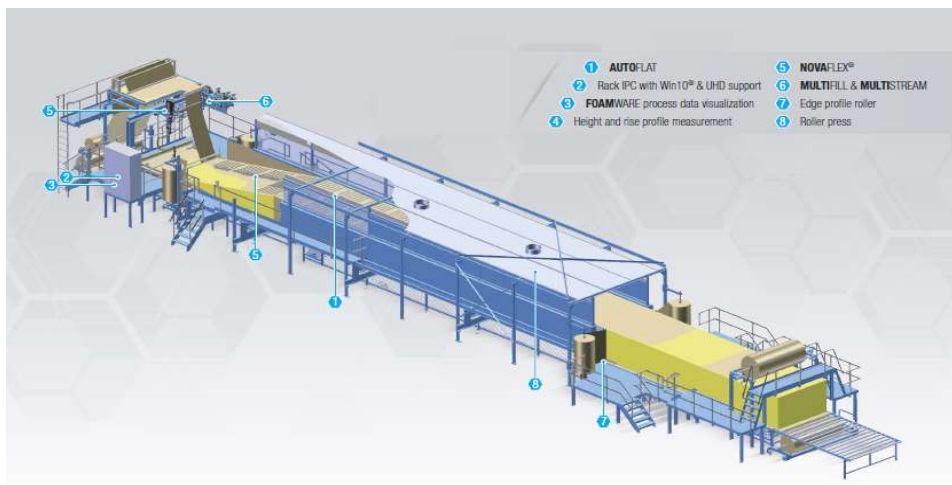
Figure 1.5 *Typical slabstock process for the production of flexible polyurethane foam at Hennecke Polyurethane Technology (Germany)* [16]

Figure 1.6 *Polyurethane slabstock foam block, 60 m long, 2 m wide, and 1.2 m high* [17]

Continuous blocks are cut into sections, stored, and finally cut to the size and shape of the finished item. The main uses of these foams are in mattresses, furniture, automotive seating, carpet underlay, textile padding, etc. The slabstock technique is

8

not restricted to the manufacture of flexible foam, as some rigid foam is also made using this method.

A slabstock production unit generally consists of storage tanks for the raw materials (optionally smaller day tanks), individual metering units (pumps, flow meters) for every raw material or stream (the auxiliary components are usually metered into the main polyol stream via a manifold; the contents of this manifold are metered into the mixing head; toluene diisocyanate (TDI) and the tin catalyst are metered directly into the mixing head), heat exchangers (at least for the major streams) to ensure constant temperature, a mixing chamber (mixing head) with stirrer for continuous and homogeneous mixing of the individual components; air feed (nucleating air) to control cell structure, metered into TDI, polyol or directly into the mixing head. Furthermore, a back pressure valve for additional control of the cell structure; a dispensing device (hose, trough); a continuous bottom conveyor with lining (polyethylene or paper); side support for the rising liquid (either stationary walls or continuous side conveyors), also with lining extraction facilities (exhaust fans) to remove toxic vapors (the combination of bottom conveyor, sides, and the top enclosure necessary for gas extraction is called the tunnel). Toward the end of the production line, a vertical cut-off saw is also available to cut the foam block. For curing, foam block storage facilities racks or floor space is available. Handling equipment such as overhead cranes and forklift trucks is used to transport the foam blocks.

Within the overall framework of flexible slabstock foam there are different categories, each characterized by certain properties of the end product, which are in turn provided by the type of raw materials used.

CONVENTIONAL SLABSTOCK : This type of foam is used for seating and bedding: It uses conventional polyether polyols, TDI, and water. Flame-retarded foams and filled foams are usually included in this category.

HIGH RESILIENCE (HR) SLABSTOCK: again, seating and bedding foams are produced, but with superior comfort characteristics, similar to those of foam rubber. Reactive (capped) polyols, TDI, water, and crosslinkers are the main reactants.

VISCOELASTIC (SLOW RECOVERY) FOAM – uses both TDI and methylene diphenyl diisocyanate (MDI). The key feature is that the foam is lazy and slow with high damping characteristics.

ESTER POLYURETHANE SLABSTOCK FOAMS : These foams found utility for sound deadening, textile applications or automotive, predominantly using the process called flame lamination, packaging , air or water filters, etc. As the name implies, the polyols in use are polyester polyols, together with TDI and water. These types of polyurethane foam have significantly low comfort characteristics and is more prone to hydrolytically decomposition than ether or High resilience foam. Ester foam is therefore not used for seating or bedding.

1.3.1. Basics of polyurethane synthesis

Polyurethanes are produced by the reaction of isocyanate groups present in polyisocyanates with hydroxyl groups present in polyols. Polyurethane foam production, the reaction of polyisocyanates with polyols, is carried out in the presence of several additives: surfactants, catalysts, cross-linking agents, water, blowing agents, and other additives.

1. R—N=C=O + HO—R^1 ⟶ R—N—C=O
                                                         H   O—R^1

    Isocyanate   +   Alcohol ⟶   Urethane

2. R—N=C=O + H_2O ⟶ R—N—C=O ⟶ R—NH_2 + CO_2
                                              H   O—H

    Isocyanate + Water ⟶   Carbamate   ⟶ Amine + Carbon Dioxide
                                         (unstable)

3. R—N=C=O + H_2N—R ⟶ R—N—C=O
                                               H   N—H
                                                       R

    Isocyanate + Amine ⟶   Urea
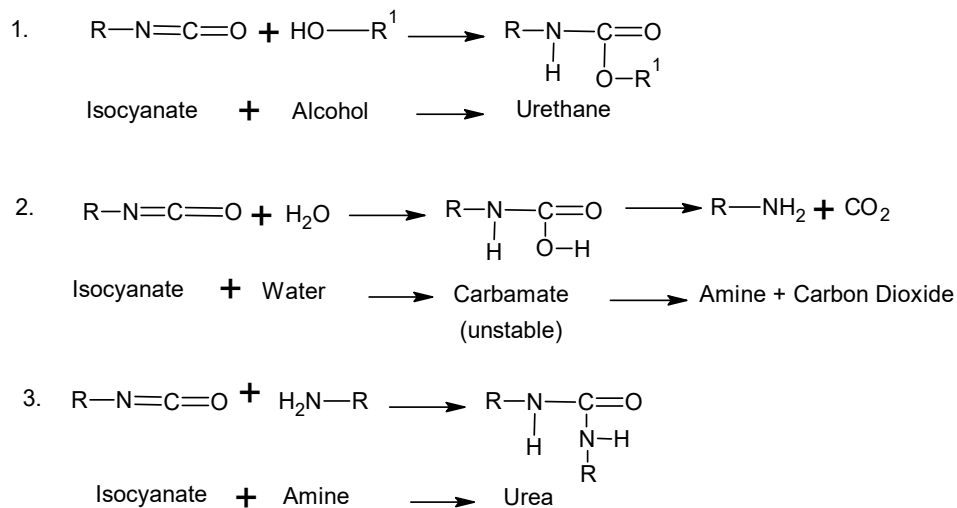
Figure 1.7 Main reactions involved in polyurethane foam synthesis. Reaction 1 represents the schematic polyaddition of isocyanate and polyol, while reaction 2 represents the reaction of isocyanate and water, generating CO_2 for foam expansion.

The carbon dioxide from the isocyanate / water reaction acts as a blowing agent for foam formation. These reactions are exothermic (ca. 20 kcal/mole). In the

polyurethane foam core, due to the exothermic reaction, a temperature of up to 160°C can be achieved. A temperature higher than 160°C must be critically monitored, as the risk of autoignition increases. At a higher level of water use, the exothermic reaction can be controlled with auxiliary blowing agents such as methylene chloride. The boiling point of methylene chloride is 39.7°C. Therefore, during the foaming process, specifically at the beginning of the reaction, methylene chloride absorbs a part of the heat generated by the system, to enable the process of material to change from liquid to gas form. As a result, the overall exothermic process of the foaming reaction is controlled. Moreover, methylene chloride acts as an expanding agent, and the overall density of the PU foam decreases.

Two secondary reactions can also take place; the active hydrogen in the urethane or urea molecule can further react with the isocyanate, forming allophanate and biuret, respectively. A typical conventional polyether foam formulation is presented in Table 1.1.

Table 1.1 *General polyurethane foam formulation for conventional foam* [18]

Foam Formulation	Parts by weight (Pbw)
Polyether polyol	100
Water	1 - 5
Silicone surfactants	0.5 - 3
Amine Catalysts	0.05 - 1.0
Tin Catalyst	0.0 – 0.5
Physically blowing agents	0 - 40
Other additives	Variation
Physically blowing agents	0 - 40
Isocyanates Index*	70 - 120

* as specified in Section 1.3.2.1

11

1.3.2. Polyols

A polyether polyol is the polymeric reaction product of an organic oxide and an initiator containing two or more active hydrogen atoms. In the presence of a base catalyst, the active hydrogen compound initiates the ring opening reaction and successive insertion of oxypropylene units, which is continued until the desired molecular weight is obtained. If the initiator has two active hydrogens, a diol is obtained [19].

Glycerine   Propylene Oxide   A Triol
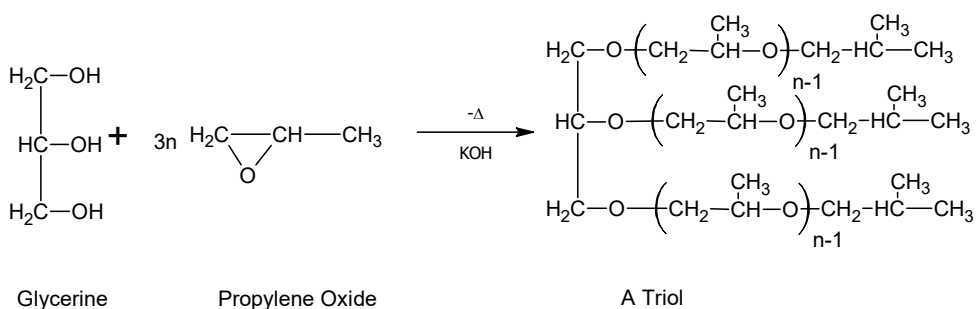
Figure 1.8 *Reaction scheme of polyether polyol synthesis by propoxylation of glycerin with propylene oxide in the presence of KOH* [19]

1.3.2.1. Main polyol types

POLYETHER POLYOL: made from a polyfunctional starter molecule (in most cases, glycerin), reacted with propylene oxide (PO) or PO plus ethylene oxide (EO). Typical molecular weights are between 3000 and 6000 (see definition of OH value).

CONVENTIONAL POLYOL: such a polyether polyol terminated with PO and hence with secondary hydroxyl groups.

CAPPED (REACTIVE) POLYOL: a polyether polyol terminated with EO, hence, with a high percentage of primary hydroxyl groups (Figure 1.9). EO capping is never 100% effective; typical values for capped polyols are 50-90%.

12
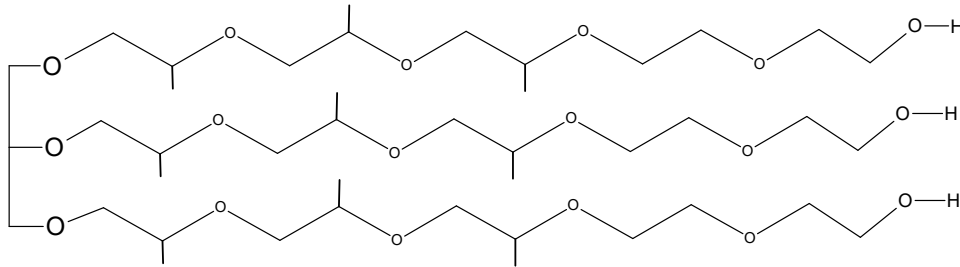
Figure 1.9 *Schematic chemical structure of a polyether polyol starting from glycerol and ending in ethylene oxide*

POLYESTER POLYOL : made from difunctional acids (mainly adipic acid) and diols (diethylene glycol), optionally with some higher functionality alcohol, via a condensation reaction.

POLYMER POLYOL (GRAFT POLYOL) : a conventional polyol containing copolymerized acrylonitrile/styrene chains. This copolymerization is carried out in the finished polyether polyol by peroxide catalysis. Some copolymer is grafted onto the polyether chains. Used for high-load bearing foams (the copolymer acts as a filler). It is characterized by its copolymer content and high viscosity. Current polymer polyols contain up to 50% copolymer.

1.3.2.2. Polyol functionality and hydroxyl value

FUNCTIONALITY : the average number of functions (reactive sites, hydroxyl groups) in a polyol, e.g., a glycerin-starting polyol, has a theoretical functionality of 3. In practice, the functionality is lower because of the water present in glycerin, PO, and EO, and because of the isomerization of PO to allyl alcohol (which further reacts with PO and EO to form long-chain monohydroxy alcohols).

HYDROXYL VALUE (OH VALUE) : number characterizing the equivalent weight of a polyol. The metric is used to calculate the amount of isocyanate needed to react with this polyol. The OH value is calculated using the following formula (56.1 is the molecular weight of KOH used for titration):

$$OH - VALUE = \frac{56100 \text{ x functionality}}{\text{molecular weight}} = \frac{56100}{\text{equivalent weight}}$$

Figure 1.10 *Formula for calculating hydroxyl values for polyols*

13

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1.3.2.3. Polyols based on natural oils for a reduced carbon footprint

Polyols used in the production of polyurethanes are typically petrochemical in origin, often called virgin polyols, being generally derived from propylene oxide, ethylene oxide, and various starters such as propylene glycol, glycerin, sucrose, and sorbitol. Polyether polyols are the most common polyols used in polyurethane production. For flexible foams, polyester or polyether polyols with molecular weights of about 500 to 10,000 are generally used. For example, a patent [20] discloses a foam-forming composition comprising a polyether polyol, an organic polyisocyanate, a catalyst, water, dissolved pressurized inert gas serving as a blowing agent and a silicone surfactant with two different sets of polyether pendent groups, wherein the second set has an ethylene oxide content <70 %, leading to a fine cell structure foam. Another patent [21] discloses similar foam-forming compositions in which a surfactant with a total ethylene oxide content of the surfactant structure of less than 37% by weight is applied. These types of polyols contribute to the depletion of petroleum-derived oil, a non-renewable resource [22]. Thus, in recent years, other polyols have been sought for use in making foams. Vegetable oil-based polyols have penetrated a variety of polyurethane applications. Growing consumer demand for "greener" products and the depletion of nonrenewable resources have created increasing demand for polyurethane foams produced with renewable content. Derived from renewable resources, vegetable oil-based polyols, also known as "natural oil-based polyols", present an alternative to petroleum-based feedstock. As both polyol suppliers and polyurethane foam producers have recognized this opportunity, natural oil-based polyols are increasingly used in a broad range of polyurethane foams, in combination with petroleum-based polyols. Natural oil-based polyols (NOP) currently used in polyurethane foams are usually based on at least one vegetable oil, including but not limited to soybean, castor, sunflower, canola, linseed, cottonseed, tung, palm, poppy seed, corn, and peanut. In one respect, NOP can generally be classified as hydroxylated vegetable oils or alkoxylated vegetable oils, depending on the extent and nature of the chemical modifications to which the vegetable oils are subjected [23].

Polyether carbonate polyols have also been proposed as an alternative polyol to petroleum-based polyols. Polyether carbonate polyols are made by copolymerizing a starter molecule (propylene glycol, glycerin, sucrose, and sorbitol) with carbon

dioxide and an alkylene oxide, resulting in polyol with incorporated carbon dioxide content from 1 wt% to about 40 wt% [24]. The use of petroleum-based polyols in polyurethane foams is a well-established technology that has created products that meet strict industry requirements. However, the attempt to substitute them partially or completely with natural oil-based polyols or polyether carbonate polyols in the manufacturing of polyurethane foams has resulted in loss of product quality. This is especially true in the case of flexible polyurethane foams, where increasing incorporation of natural oil-based polyols or polyether carbonate polyol has a negative impact on the physical properties of the foam [22]. Specifically for the polyether carbonate polyols, the ingenious way to incorporate carbon dioxide into the molecular chain to the polymer up to 40 %, followed by the use of such a martial as feedstock for the creation of flexible polyurethane foam offers a unique way to physically use carbon dioxide from nature as raw material. This technology and any other technologies that aim to use carbon dioxide as feedstock in finished goods will have a positive impact on the environment, CO_2 balance, ultimately helping to combat potential climate change.

1.3.3. Isocyanates

TDI 80 : toluene diisocyanate, mixture of two isomers: 2,4-TDI / 2,6-TDI in a ratio of 80/20 (w/w). If the term TDI is used without a number, it usually means TDI 80 standard isocyanate for flexible slabstock foam characterized by NCO content (48.27 % wt.) and isomer ratio.

2,4 TDI   2,6 TDI
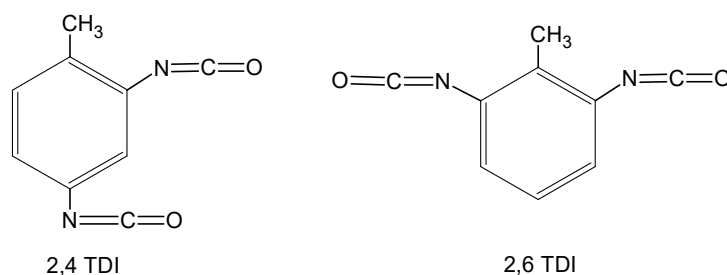
Figure 1.11 *Chemical structure of toluene diisocyanates (TDI). The 80% 2.4 TDI and 20% 2.6 TDI (TDI 80:20) are mostly used in flexible slab foam*

15

TDI 65: mixture of the same isomers in a ratio of 65/35. Used mostly in ester foams, some use in high load bearing foams (Europe). Characterized by the NCO content (48.27 % wt.) and the isomer ratio.

MDI: methylene diphenylene diisocyanate. Usually a mixture of oligomers (crude MDI). Used mostly in rigid foams. Some special MDI (a mixture of 4,4' and 4,2' isomers) is used in flexible applications (molding). The toxicity of MDI as such is equally high as that of TDI; MDI, however, has a much lower vapor pressure and is therefore less hazardous to handle. Characterized by NCO content (ca. 31% by weight for crude MDI, 33.6 % for pure MDI). The term functionality also applies to isocyanates. TDI and pure MDI have a functionality of 2; crude MDI ranges between 2.2 and 2.7).
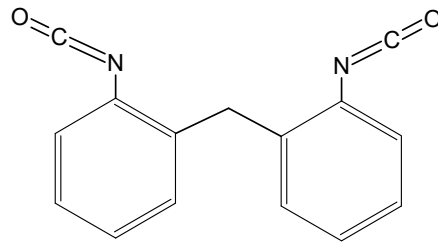
Figure 1.12 *Chemical structure of methylene diphenylene diisocyanate*

1.3.3.1. Isocyanate Index

ISOCYANATE INDEX, TDI INDEX: represents the percentage of isocyanate used relative to the stoichiometric amount required to fully react with all active hydrogen compounds (polyol, water). An Index value of 100 means exact stoichiometry, index 110 means 10% more isocyanate, index 95 means 5% less. The value of the Isocyanate Index influences the physical properties of the foam.

CALCULATION OF ISOCYANATE AMOUNTS: The basic assumption is that one equivalent of active hydrogen reacts with one equivalent of isocyanate. The actual parts of isocyanate used in a recipe are based on 100 parts of polyol (characterized by its OH-value), plus the desired parts of water (determined by the balance of foam properties). The amount of isocyanate (expressed as php, *per hundred parts of polyol*) is calculated with the following formula:

$$\text{php isocyanate} = \frac{4200 \text{ x index}}{\%\text{NCO x } 100} \text{ x } \frac{\text{OH} - \text{value}}{561} + \frac{\text{parts water}}{9}$$

Figure 1.13 *Formulation for calculating isocyanate amounts in the polyurethane formulations*

1.3.4. Silicone surfactants

Surfactants are essential additives during the polyurethane foam manufacturing process and have a significant impact on the physical properties of PU foam. Most conventional surfactant types are based on siloxane/polyether copolymers. Almost all flexible slabstock polyurethane foams are produced in the presence of silicone-based non-ionic surfactants. In general terms, surfactants perform several functions. Silicones are non-hydrolysable surfactants typically prepared from the reaction of polysiloxane fluid with an unsaturated polyglycol of the general form shown in Figure 14 [19].
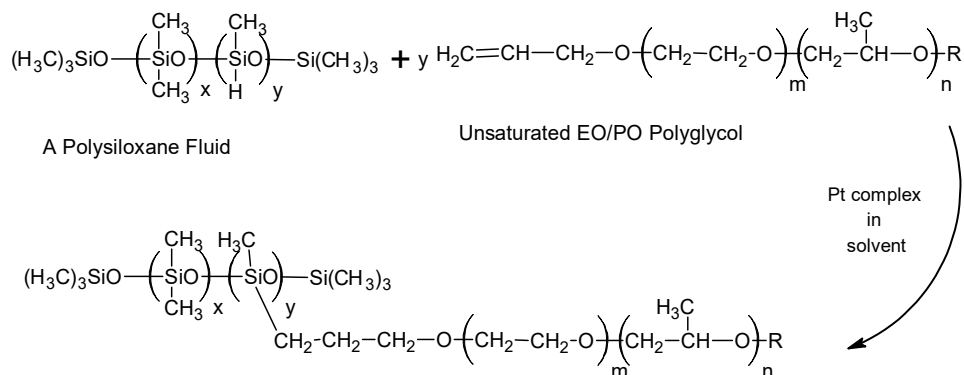
Figure 1.14 *Reaction scheme for the synthesis of non-hydrolysable silicone surfactants used in the production of polyurethane foams* [27].

The silicone surfactant role is to:

- Lower surface tension;
- Emulsify incompatible formulation ingredients;
- Promote the nucleation of bubbles during mixing;

17

• Stabilize the rising foam by reducing stress concentrations in the thinning cell-wall;

• Counteract the defoaming effect of any solids added to or formed.

Stabilization of cell walls can be considered the most important of these functions. In this way, the coalescence of rapidly growing cells can be prevented until those cells can attain, through polymerization, an adequate strength to become self-supporting. In the absence of this effect of the surfactant, a continued cell coalescence would result in total collapse of the foam. Another important role of the surfactants is controlling the precise timing and degree of cell opening. A more detailed discussion of surfactant effects is provided in Chapter 3. The selection of a surfactant or combination of surfactants for any foam system is a challenging task.

1.3.5. Catalysts

The chemistry of polyurethanes is based on reactions of isocyanates, compounds having one or more reactive isocyanate groups (-N=C=O), with active hydrogen-containing compounds. This isocyanate group can readily react with hydrogen atoms that are attached to atoms which are more electronegative than carbon. Among several compounds that fit this condition, those considered of primary interest for polyurethane-forming reactions are presented in Table 1.2 [19].

Table 1.2 *Active hydrogen compounds in order of decreasing reactivity with isocyanates* .

Active Hydrogen Compound	Typical structure	Relative rate of the uncatalyzed reaction at 25°C
Primary aliphatic amine	$R{-}NH_2$	100.000
Secondary aliphatic amine	$R{-}\underset{\underset{R}{|}}{NH}$	20.000-50.000
Primary aromatic amine	$Ar-NH_2$	200-300
Alcohols with primary hydroxyl group	$R{-}CH_2{-}OH$	100
Water	$H{-}OH$	100

Carboxylic acid	O ‖ R—C—OH	40
Alcohols with secondary hydroxyl group	R | R—CH—OH	30
Ureas	O ‖ R—NH—C—NH—R	15
Alcohols with tertiary hydroxyl group	R | R—C——OH | R	0.5
Urethane	O ‖ R—NH—C—O—R	0.3
Amide	O ‖ R—C—NH$_2$	0.1

1.3.5.1 Amine catalysts

Amines are the catalysts of choice using the production of flexible polyurethane slabstock foam. Generally, the polyurethan reaction requires two type s for catalyst, on one hand is the gelling reaction and at the same time the blowing reaction. Amine catalysts are generally helping the reaction between OH of polyols and the water, hence they tend to be more blowing catalysts, however small contribution will be also for the gelling reaction. The nitrogen atom is steric hindrance the main factors towards influencing the catalytic activity of various tertiary amines is based on the electronic effects of substituent groups , along with the nitrogen atom [19]. In specific formulations, the synergy of various tertiary amine based catalysts are utilized targeting to balance the gelling and blowing polyurethane foam reactions , leading to a better foaming process control and adequate polyurethane foam quality. Following parameters are critically important in the reaction process of polyurethane foams: cream times, the rise profile measured by the rate of rise, the gel time and cure of the exterior skin surface. This can be easily controlled by the appropriate selection of amine catalyst types and the overall concentration of these amines in the polyurethane final formulation. The selection of the right or wrong amines would also impact typical foam properties such density, foam porosity or hardness through influences on the main reactions, which are the polyaddition reaction, often called

19

primary reaction and allophanate and biuret, so called secondary foam reactions. Foam odor is an important characteristic when finished articles such as upholstered furniture, bedding or matrasses are produces. As a result of that some amines catalysts exhibit a residual odor that may stay in the polyurethane foam, which may also limit or even eliminate the use of them in the aforementioned finished applications . One can consider the use of higher volatility amine catalysts to produce the polyurethane foam. The advantage is that the odor will eventually be eliminated in large proportion of the amine during the foam process thanks to its low boiling point. The disadvantage of higher volatility, is that the amine may reduce the cure. High level of volatility in most cases leads in products with low flash point, significantly higher vapor pressures, thus considerably impacting the handling problems of that specific products, where additional precautions will have to be taken once such a product is handled. Several amine catalyst producers have introduced the amines containing a reactive group to help incorporate the molecule into the polymer matrix, hence the volatility of this product will not be impacted anymore. These amines care called low emission catalysts. Although very useful in more and more applications, generally the catalytic activity decreases as the polyurethane reaction progresses, due to the decrease concentration of amine during reaction process, as a result of their incorporation in the Polyurethane matrix [19]. Low emission amine catalysts with no impact towards catalytic activity loss has also been reported in the literature [25].

Below examples are typical requirements that imparts avery good catalytic activity for polyurethane foams:

- Strong nucleophilicity, enabling to attack the carbon of the isocyanate group

- Capability to easily form an active hydrogen amine complex

- Solubility in water and the ability to form stable hydrogen bonds

For flexible foams, the most popular amine catalysts are *bis*-[2-(*N*,*N*-dimethylamino)-ethyl]-ether and 1,4-diazabicyclo[2.2.2]octane (Figure 1.15).
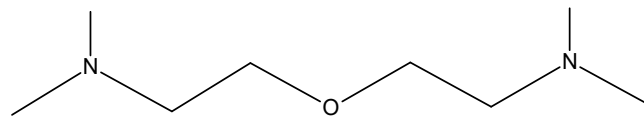
Bis-[2-(N,N-dimethylamino)-ethyl]-ether
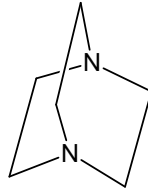
1,4-Diazabicyclo[2.2.2]octane

Figure 1.15 *Chemical structure of main amine catalysts for polyurethane foams*

The reaction mechanism of polyurethane foam formation catalyzed by a tertiary amine includes a reversible nucleophilic attack of the amine on the C-atom to form a complex, which is activated. Both the aromatic and carbonyl groups of aromatic isocyanates have electron-withdrawing effect considered to be moderate.
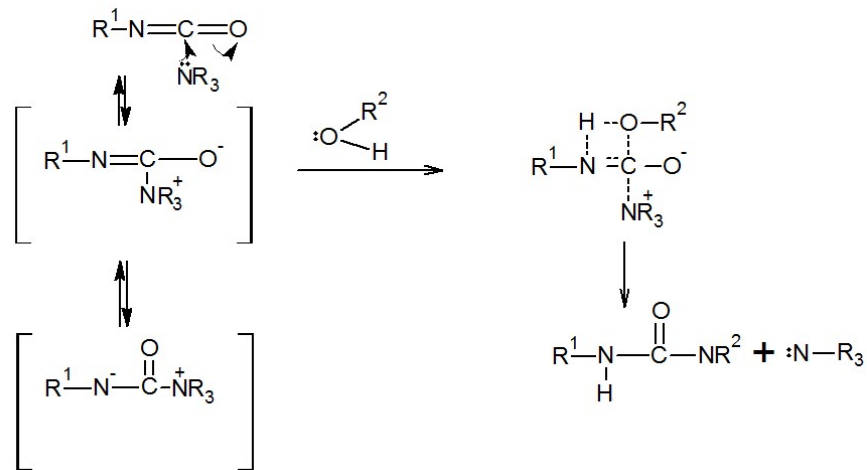
Figure 1.16 *Reaction mechanism of polyurethane foam formation in the presence of a tertiary amine, such as triethylene diamine* [19].

1.3.5.2 Organometallic catalysts

The organometallic catalysts are responsible for formation of polymers, including polyurethane foams, by promoting the gelation reaction between the polyol and isocyanate in order to produce this kind of material. Stannous compounds are the most commonly used metal catalysts, when compared to the many metals available in the marketplace. Stannous or tin based catalysts act as Lewis Acid and are typically considered to perform by interacting with the polyols and isocyanate specifically interacting with the presence of basic sites. Three mechanism steps were proposed. At first, the OH group of polyols will be activated, and this happens thanks to the formation of complex that includes stannous catalyst (in below figure "L" represents ligand substituent to the stannous catalyst uses in the process) and the results is a stannous alcohols adducts. The stannous alkoxide from the tin alcohol adduct may interact by reaction with the isocyanate leading to a carbamate. This further will react with another polyol to propagate the formation of polyurethane and regenerate the catalysis species for a new polyaddition process formation.
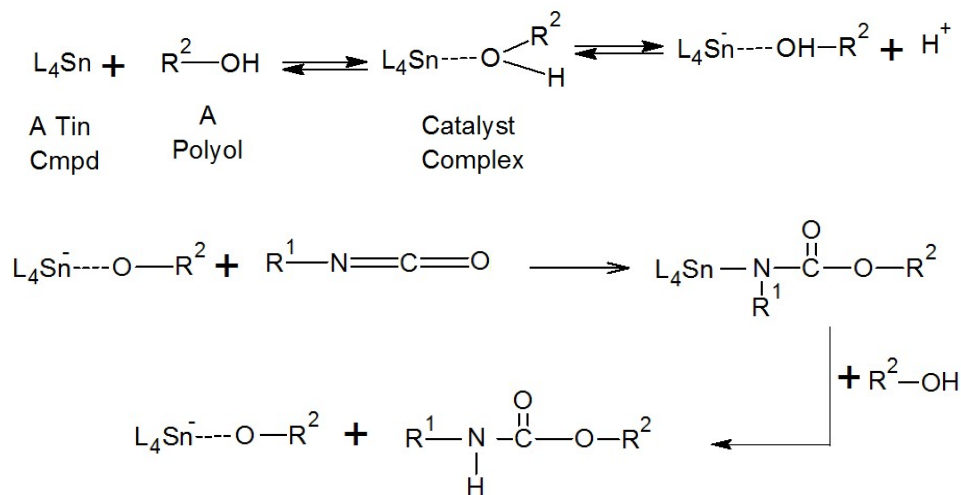
Figure 1.17 Reaction mechanism for polyurethane foams with organometallic catalysts [19]

Looking specifically to polyurethane slabstock foam, tin(II)2-ethyl hexoate (or stannous octoate) is the gelling catalyst of choice. The compound very effective gelling catalyst however is also very easily hydrolyzed and oxidized in the presence

of water and tertiary amine, hence special precaution in handling is required. Reactors used in the production has to be dedicated to stannous octoate only and may ensure a inert gas blanket at onto the material at all time. The correct use level or catalyst concentrations has to be determined for each individual polyurethane foam formulation.

1.3.6. Other additives

Fillers - compounds added to a to a polyurethane foam formulation to influence the weight, hardness, strength, price, or other properties of the final foam. Examples of fillers are barium sulfate, calcium carbonate, melamine, rebounded foam powder, and graphite powder. Rebounded foam powder is one of the methods to reintroduce polyurethane foam scrap back into the life cycle.

Softeners – special additives added in flexible PU foams to enable soft foam production. The application for such a foam can be considered pillows or backrests for couches, where the soft or eventually silky touch of the team is preferred.

Hardeners – additives with firmness enhancement for flexible PU foam.

Antistatic additives. Polyurethane foams have the capability to charge electrostatically. Applications such as packaging for electronic devices require more conductive materials. For flexible PU foams, special additives are incorporated in the formulation to avoid electrostatic charge of the foam.

Flame lamination additives are used as processing aids for special processes where a flexible polyurethane foam is exposed to a flame to generate a certain burn rate of the foam and consecutively sufficient amount of melted material that enables bonding with a substrate such as fabric, leather, PVC, or special textile film.

Flame retardant additives for foam application with certain flammability requirements. The addition of flame retardant additives is widely practiced. Examples of liquid flame retardant additives are tris(2-chlorisopropyl)phosphate (TCPP) and tris(1,3-dichlorisopropyl)phosphate (TDCP), while melamine, although it is a solid filler, can also play an important flame retardant role.

Color paste – mainly used for a quick differentiation of polyurethane foam quality during the production and conversion process.

1.4. Sources and recovery of flexible polyurethane foam waste

About 45% of the total PU production is flexible foam, classified into three categories, as conventional foams, viscoelastic foams, and high resilience foams. Conventional PU foams are produced as slabstocks, viscoelastic foams are generally used for mattresses and pillows, while high resilience foams are used mainly in the automotive industry [26].

Flexible PU foam is one of the most popular materials used in home furnishings, including furniture, bedding, and carpet underlay. As a cushioning material for upholstered furniture, flexible PU foam helps on making the furniture more durable, comfortable, and supportive [27]. Another essential application of polyurethane foams is in the automotive industry, in car seats, bumpers, interior "headline" ceiling sections, the car body, spoilers, doors, and windows. PU also helps the car manufacturers to reduce the weight of vehicles and save fuel, to increase the comfort and resistance to corrosion, as well as to improve insulation and sound absorption [27].

The production and conversion of flexible PU foam generates foam waste, often called trim foam. This can be classified into two different categories. The first is the foam waste generated during the production and conversion of the foam into finished articles, such as mattresses or sofas. For the synthesis of PU foam, the process is continuous, and the beginning of the production as well as the production stop generally leads to foam with defects. This generates roughly 2-3% of foam waste. For the conversion, the slabstock blocks that are usually 2 m wide, 1.2 m high and length typically between 1.5 and 2 m. These flexible PU blocks are cut in various geometries with special equipment to give the desired shape. Foam conversion leads to a loss of up to 20%.

The second category of foam waste is post-consumer foam, generated from end-of-life mattresses and furniture. By dismantling old mattresses and furniture, in its initial raw materials, wood, metal textile, polyester fabric, and polyurethane foam are generated. Among these, PU foam is found to be the most difficult to reuse or recycle in an optimum manner.

At a global production of 5 million tons of flexible PU slabstock foam, approximately 1 million tons of foam waste resulted only from the production process. Considering the cost of raw materials, the efforts of waste reduction, the national or European legislations of around zero waste generation, the high cost associated with the material disposal, there is a clear need to eliminate foam waste.

Although there is a large quantity of foam waste generated either during production conversion or available as post-consumer waste, a large part of this foam waste is reutilized, as rebounded foam, filled material for various articles such as pillows, sofas, and others [18]. These well-established methods in the industry allow a good part of the trim foam to be converted into finished products. However, there is still a significant part of unused PU foam waste that ultimately contributes as waste to the land field.

The recycling processes of plastic products were classified by the ASTM D5033-00 standard in the following categories [6]:

- *Primary recycling,* "the processing of scrap plastic product into a product with characteristics similar to those of the original product.
- *Secondary recycling*, "the processing of scrap plastic product into a product that has characteristics different from those of the original product."
- *Tertiary recycling,* "the production of basic chemicals or fuels from segregated plastic scrap or plastic material that is part of a municipal waste stream of other source."
- *Quaternary recycling,* "the useful retrieval of the energy content of scrap plastic by its use as a fuel to produce products such as steam, electricity and so forth."

Polyurethane foam waste may be recovered using various methods such as: thermochemical, physical, and chemical depolymerization procedures. The known physical type of recycling for polyurethanes includes processes involving primary and secondary recycling, where the internal structure of the polymer is not changed, but the polymer waste is turned into flakes, granules, powders, etc., able for utilization in new materials. Chemical recycling is basically tertiary recycling, allowing partial recovery of monomers, which can be used again in the manufacturing process [6]. Physical recycling instead including binding or adhesive pressing for polyurethane foam waste is most commonly used, while he most common methods that involves

chemical reaction to decompose a thermoset material such as polyurethaen foam are acidolysis, hydrolysis and glycolysis [28].

1.4.1. Mechanical Grinding

PU foam mechanical grinding technology exists under Gridflex technology, as a joint development of Metzeler Schaum GmbH, Bayer AG, and Hennecke GmbH [29]. Depending on the recipe, it can be used to add up to 30% polyurethane powder (based on the amount of polyol) to the polyol flow. Foam residues are crushed into loose flakes and ground into powder in a roller mill by shearing. Screened, larger particles are fed to the grinder until the appropriate fine grist fraction with grain sizes below 0.2 mm is reached. This regrind powder can be stored temporarily in storage containers [29].

Ugarte *et al.* reported combined mechanical grinded polyurethane material and glycolysis using different recycled PU sources: a thermoplastic PU series using a glycosylated polyol obtained from the glycolysis of elastomeric PU waste (chemical recycling) and a series of PU flexible foam loaded with PU dust waste created in the shaping of PU surf tables (mechanical recycling). The results showed that the incorporation of recycled components into the formulation improved mechanical properties in both the case of thermoplastic polyurethanes and polyurethane foams. The optimal amount of glycosylated polyol was found to be 15% over the total polyol weight for thermoplastic PUs. In the case of foams, a maximum of 20% PU dust over the polyol weight was incorporated [30]. However, flexible PU foams were not investigated by this procedure.

1.4.2. Rebounded foam

Bonded foam, or rebound, is a molded PU product made from pieces of shredded flexible polyurethane foam, which are held together using a binder. It is characterized by a relatively high density and excellent resilience. Therefore, rebounded foam is suitable for a wide range of applications which include vibration sound damping, flooring, cushioning, packaging, and carpet underlay. Currently, in western Europe up to 50,000 tons of rebound foam are processed each year, while new applications are also continuously developed [31].

A careful selection of the base material, particle size, compression ratio, type, and quantity of the binder means that the properties of rebounded foams can be varied over a wide range, leading to applications that previously could not be reached by the original foam material [31].

1.4.3. Thermomechanical recycling

When it comes to thermomechanical recycling, typically three methods are considered: gasification, pyrolysis and certainly the hydrogenation of the PU foam waste. The differences between the aforementioned processes are:

- Gasification takes place in an oxygen environment

- Pyrolysis takes place in an oxygen-free environment

- Hydrogenation takes place in the presence of hydrogen

Apart from that, the general principle of these three different established technologies is to turn the municipal solid waste into gas. The municipal waste often contains polyurethane foam and following these processes one can consider reusing them as raw material or as fuel. The big advantage is that separate collection is not needed.

A recent review summarized the actual knowledge on the thermochemical recycling methods of PU foams [32]. When pyrolysis is carried out, the highest TDI and polyol recovery yields were reported at low temperatures (150–200°C). At the same time, it was stated that pure feedstock cannot be produced in this way, further upgrading of condensate is needed, together with a thermal or alternative treatment of non-condensable resulting from the process [32].

Although technical viability was there, these projects have not been successful from an economical viewpoint. However, due to increasing pressure around sustainability this may eventually change in medium term. Several leading companies from the industry designed a large-scale plant in Netherlands, planned to produce synthetic gas from the general waste and the aim is to transformation the waste in two chemical steams ammonia and methanol. Also Energy Recovery Systems, a company from Saudi Emirates announced significant expansion by investing in the port of Antwerp. The plan is to build a huge plant to produce urea and ammonia from waste plastic [33].

1.4.4. Chemical recycling

Mechanical recycling is not considered the ideal solution for the recycling of PU foams because they are thermoset polymers with cross-linked structure. Therefore, chemical recycling has attracted increased interest, as it is based mainly on the degradation of the urethane bond, leaving the ether groups of polyether polyol unmodified [34]. Among mentioned technologies to address the chemical recycling of flexible polyurethane foam, the most common are acidolysis and glycolysis. They are differentiated predominantly by the materials used to react the polyurethane foam. Efforts to reduce fossil-based materials were initiated by Serrano *et al.,* to obtain biodegradable polyurethane foams [35]. Ravindra *et al.* described various chemolysis processes, including acidolysis, in their study [36]. Wenqing *et al.* studied the recyclability of rigid polyurethane foam [37].

Although several chemical methods for recovering polyurethane foam waste are described in the literature and numerous patents have been issued on this topic [38-47], the industrial production of recycled polyol has rarely been mentioned [48]. One of the least chemical recycling plant for polyurethane slabstock foam that is producing today in Europe is situated in Poland, at the company Dendro (currently IKANO).

Figure 1.18 *The repolyol plant at IKANO, in Poland [49]*

It is based on acidolysis technology, by which polyurethane slabstock foam is exposed in a presence of special polyol and a mixture of carboxylic acid to produce recycled polyols. However, the production process enables recycling of shredded

poyluethane foam from own production. Thus, the chemical composition can be predicted. Additionally, the multitude in the foam qualities limited. Once the recycled polyl has been produced from the shredded foam waste, this can be used up to 20% , replacing virgin polyol to produce to produce polyurethane foam[50].

However, chemical recovery of polyurethane foam is more demanding for post-consumer PU foams due to the variation in the foam qualities, the lack of information regarding chemical structures of these polyurethane foams. Research are being performed to implement chemical recycling as a viable technique and technology for the recycling post-consumer polyurethane foam. H&S Anlagentechnik (Germany has performed investigation at large scale using recycling of post-consumer flexible PU foam from old mattresses. Flexible slabstock polyurethane foam was chemically degraded using an acidolysis technology. The outcome was recovered polyether polyols that could be eventually re-used for the rigid foams production. Applications for these material can be considered insulation panel, even spray foam fro gap fillers. Another project with potential end application, using the same technology was approved back a few years ago (2016) was focusing on the reuse of recycled polyols for the production of adhesives. At glance the chemical process to recover thermoset material appears to be a promising for post-consumer polyurethane foam, it is expected that more research will be needed in order to establish a well implemented and sustainable large scale recovery of polyurethane foams, specifically from end of life type of waste [51].

Obviously, glycolysis or acidolysis recycling processes were successfully developed and are ready to use even at industry level, although hydrolysis was the first chemical method developed to recycle polyurethane waste [52] and could be competitive with the other methods [53]. Further chemical recycling processes such as aminolysis [54] and phosphorolysis [55] are still in an earlier stage of investigation. Li *et al.* recently reported a very promising ammonolysis process. The carbamate and urea bonds of the rigid waste PU foam were degraded using a mixture of urea / ethanol at 180°C for 10 h. It was observed that the C−C bonds and C−O−C of ether linkages as framework structure remained unbroken in the degradation process, while aromatic polyamines and polyether polyols were recovered as the main products [56]. Multistage chemical recycling can also be considered as a future possibility for the complete recovery of all monomers. Zahedifar *et al.* proposed a conventional

glycolysis to recover polyol and to obtain smaller carbamates at the same time, which are then separated and used for a further hydrolysis step to recover amines that can be reprocessed into isocyanates [57]. A hydroglycolysis process was patented already in 1982 by Ford Motor Company, claiming that it generates significantly fewer products, which makes purification of the polyols more feasible. PU foams are degraded in the presence of water, diethylene glycol and alkali metal hydroxides at 200°C. When NaOH is added as a catalyst to the reaction mixture, the side products of carbamate and urea are transformed into amines and alcohols by hydrolysis, and polyol separation can be performed easier [8;58].

Based on data from the available literature, chemical recycling can be considered more valuable than physical recycling, both from technical and environmental considerations.

1.4.4.1 Glycolysis

Glycolysis is the most widely investigated and used chemical recycling process for PU waste. It represents a transesterification reaction, in which the ester group of urethane is replaced by the hydroxyl group of a glycol (Figure 1.19) [6;59].
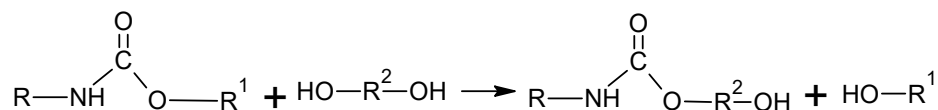
Figure 1.19 Reaction scheme of PU degradation by glycolysis [6].

Chemical recovery by glycolysis was mentioned for a wide variety of Polyurethane products. This includes CASE (Coating, Adhesives, Elastomers and Sealants), rigid polyurethane foam, flexible molded or slabstock polyurethane foam [6], and even flexible polyurethane foams with high resilience [60]. Datta *et al.* studied the use of various types of glycols starting from lower molecular weight and their impact towards structure of glycolyzed materials [61]. Another investigation worthily to mention was made by Prof. Datta from Gdansk and his group, as well. They focused on glycerol, a trifunctional material and a by-product of biodiesel manufacturing site, using it as main glycolysis agent for recycling of polyurethane from waste [62].

Th glycolysis process is strongly influenced by the nature and structure of the catalyst, which must be selected according to the type of PU foam, various types of catalysts have been investigated for PU glycolysis reactions [63], for example potassium hydroxide [64], potassium acetate [65], diethanolamine [66], di-n-butyl amine [67], potassium octoate [68], metal salts and Lewis acids [69], stannous octoate [26;70;71], or even ionic liquids such as 1-butyl-3-methylimidazole trichloromanganate [72].

Borda *et al.* performed the glycolysis of flexible polyurethane foams and elastomers with ethylene glycol, 1,2-propylene glycol, triethylene glycol, polyethylene glycol and diethanolamine, also proposing a reaction mechanism [37]. Shin *et al.* obtained a recycled polyol by glycolysis of waste rigid polyurethane foams scraps, but this recycled product needed further chemical modification by addition polymerization with propylene oxide, to deactivate the isocyanate-derived amine adducts [38]. Rigid polyurethane foams were also depolymerized using the glycolysis process. This carried out in the presence of microwaves as an energy source and basic catalysts, the most promising results have been identified when sodium hydroxide and potassium hydroxide was used [73]. Molero *et al.* used stannous octoate for all time first as a catalyst for o choice for the glycolysis process of flexible slabstock polyurethane waste, reporting higher yield of decomposition along with polyol purity, when compared to that obtained with various other catalysts reported in the literature [74]. The use of ionic liquids was another development that led to promising process in recycling polyurethane foam waste. This also included the investigation of these agents from renewable sources of the aforementioned ionic liquids [75].

The glycolysis process for a special family of flexible polyurethane foams, specifically based on polyester polyol, was not thoroughly studied, and this will be one of the original contributions of this work.

1.4.4.2 Acidolysis

Another method to depolymerize flexible foam waste more efficiently is acidolysis. Acidolysis is usually based on the cleavage of the polyurethane chain by a dicarboxylic acid, yielding a polyol and other oligomers (Figure 1.20).

31
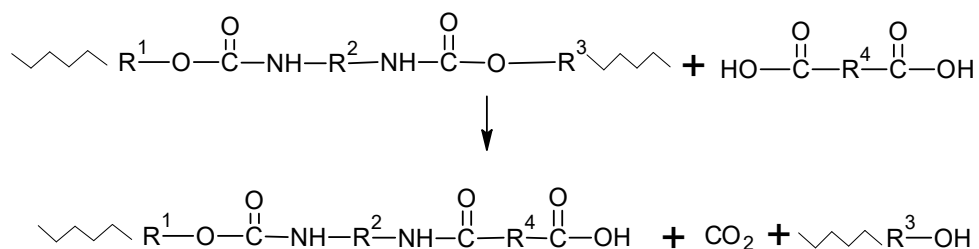
Figure 1.20 Reaction scheme of PU degradation by acidolysis. R1 and R3 correspond to polyol chains, while R2 corresponds to isocyanate chains in the original PU structure; R4 is the hydrocarbon chain of dicarboxylic acid [76].

Acidolysis reactions were reported using different types of inorganic and organic acids. By this procedure, the urethane group is decomposed, yielding together with the main polyol product a variety of other products such as amides, amine salts, and oligo ureas. An important advantage of acidolysis reactions is represented by the mild reaction conditions compared to other chemical recycling processes (about 60°C and atmospheric pressure, short reaction time) [36].

Although some companies are already using acidolysis as a chemical route, the main degradation mechanisms and chemical reactions involved in this type of recycling process have received less attention. Recently, a group from Portugal made a notable contribution to this topic. Gama *et al.* investigated the reaction path involved in the depolymerization of PU wastes of flexible foams with succinic acid. The process was monitored using Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and the amount of water formed during the reaction. The data obtained suggested that both thermal degradation and reactions between succinic acid and PU took place. The ensuing recycled polyols (RP) were used as a partial substitute for conventional polyol (up to 20% w/w) in the production of rigid foams that were extensively characterized [9]. In a more recent report, different types of PU waste foams (polyester, polyether, and viscoelastic) were depolymerized with succinic acid and the recovered polyols were characterized by OH number, acid value, and viscosity. A selected recycled polyol was used to produce PU coatings and its properties were compared with those manufactured with a conventional polyol [76].

A recent publication also emphasized the advantages of the acidolysis process, carried out with adipic acid without a medium or in a virgin polyol medium, in which

32

the residues of the hard segments of the PU foam are mostly insoluble, easing the isolation of the polyol product and its purification to remove the low-molecular-weight by-products. Using microwave heating, the reaction time was reduced to less than 1 h. Flexible PU foams were synthesized with up to 100% recycled polyol. The main problem was a side reaction that led to polyol chains terminated with carboxyl groups and increasing carboxyl functionality in the formulation of the PU foam resulted in a decrease in the average pore size, an increasingly closed cell morphology, a higher modulus and stress at 40% compression and a higher compression set. This means that this acidolysis process cannot still produce a recycled polyol which is perfectly equivalent to virgin polyol in terms of functionality and further research is needed [34].

The industrial production of recycled polyols by acidolysis is seldom mentioned. However, Soltysinski *et al.* reported the production of recycled polyol from polyurethane foam waste [77]. Research has been carried out to determine the possibility of reusing polyols produced in the chemical recycling process of PU foam technological waste and post-consumer mattresses for the production of mattress and thermal insulation panels. It was found that such PU waste can be converted into repolyol using processes similar to those currently used by the Dendro company (Poland). The mixture containing repolyols was used to produce rigid and flexible polyurethane-polyisocyanurate (PUR-PIR) foams. A mixture of polyols containing up to 50 wt. % of repolyols to be in the preparation of rigid or foams. The most suitable application was identified as rigid PU-PIR foam for thermal insulation. The rigid foams produced showed good performance in the foaming process, foam structure, and dimensional stability [77].

1.5. Outcome of the literature overview

Flexible polyurethane foams have developed extremely much in recent decades, reaching a very wide range of finished products, through different methods of synthesis and processing. Applications such as mattresses, upholstered furniture, the automotive industry and many more, cover this high consumer demand. Some of this waste is recovered through various procedures, such as mechanical recovery, involving the reuse of waste as fillers in various items, pillows, sofas, and other products. Discontinuous waste gluing procedures, followed by the use of finished products in selective applications (such as special mattresses) are also used.

Different ways of chemical recovery have been described in the literature [78-81]. Glycolysis of polyurethane waste was technically successful, but difficult to implement due to economic factors. The existing methods described above allow the recovery of only a certain part of the waste, leaving a significant amount of polyurethane foam in the form of raw waste, which would ultimately become industrial waste.

Considering the huge amount of flexible polyurethane foam available for recovery, the research accomplished in this thesis will aim to depolymerize industrial foam waste and try to reincorporate the product into flexible polyurethane foams through innovative methods, that will have a positive impact on the environment.

2. Original Contributions

2.1. Objectives of the thesis

Despite a sustained research effort, the methods of chemical recycling of PU foams still suffer from several drawbacks, mainly incomplete or nonselective degradation of urethane linkages, as partial cleavage of urea groups also occurs. Therefore, the current recycling methods are not able to produce high-quality virgin-like polyols that can be used for the manufacturing of new flexible PU foams exclusively from the recycled polyol, and the main target is to replace as much virgin polyol as possible with the recycled one, preserving the foam properties.

From an industrial point of view, it is obvious that glycolysis and acidolysis were developed allowing present or future large-scale production. Although several chemical methods are described in the literature for recovering polyurethane foam waste and numerous patents have been issued on this topic, the processes employing glycolysis have not yet been reported to operate on a large scale, mainly affected by economic or even quality reasons [5]. Glycolysis processes for flexible polyurethane foam have been thoroughly investigated, but incorporation of a large amount of recycled polyol back into low-density flexible polyurethane foams was accomplished only in limited quantities [8]. The significant costs of these processes along with several technology difficulties hindered, with some exceptions, a sustainable application at the large scale. The glycolysis process is usually followed by large number of separation steps until a polyol obtained, resulting in increased costs. Considering the large amount of material that is being landfill, polyurethane foam waste must be recovered in a sustainable manner. There is a clear need to identify and further investigate methods in this space.

The main objective of the present thesis was to find out new ways to increase the level of recycled polyol usage to produce flexible PU foam in low-density formulations, replacing fossil-based polyols. The results shall enable a much better understanding specifically considering the relationship between the use level of the recovered polyol and foam properties. The ultimate goal was to find the optimal conditions, and how we can afford a higher use level of recycled polyol in the flexible slabstock foam formulations, while maintaining or even improving key foam

35

properties. This woks should point out towards best integration of waste back into the life cycle of industrial-scale polyurethane foam production. An important milestone towards global industrial efforts in carbon footprint reduction and contribute to the goals of the circular economy.

Considering these targets of improving the life cycle of PU foam by reducing waste, utilizing increased amounts of recycled polyol, and producing PU with a reduced carbon footprint, three important objectives were addressed.

1. The first objective was to identify improved and economically efficient ways to recycle flexible polyurethane foams, by evaluating different glycolysis methods and reintegration of the recycled material in industrial PU foam formulations. Various glycolysis techniques of polyurethane foam waste were studied, such as the atmospheric pressure method, the autoclave method, or the high frequency method, evaluating the highest possible yield of recycled material. The glycolysis product was recycled using the same formulations as in the industrial process, targeting the replacement of the main raw material, polyether (or polyester) polyols. The study should allow for a better understanding of the relationship between recovered polyol use level and foam properties. The ultimate goal was to find the optimal conditions from the perspective of raw material recovery, allowing the best integration back into the life cycle of industrial-scale polyurethane foam production.

2. Incorporation of a large amount of industrially recycled polyol via the acidolysis process back into low-density flexible polyurethane foam, specifically based on the type of polyether polyol, was the second main objective of this work. Although this topic has not been thoroughly studied until now, it represents a major perspective for future PU recycle applications considering the purpose of greener PU manufacturing according to sustainability criteria. Furthermore, a method for increasing the recycled polyol content in low-density flexible PU foam formulations by utilization of a selective amine catalyst has not yet been reported in the literature and was also accomplished in this thesis.

3. Development of new silicone polyether surfactants for use in polyurethane foams. Such silicone surfactants having dimethyl siloxane backbones with attached alkyl and polyether pendant groups can provide improved properties for flexible PU foam compositions that use polyether carbonate polyols. The goal was to increase as

much as possible the polyether carbonate content of the polyol component by using a silicone polyether surfactant, providing stable flexible foams with appropriate properties.

All this research, with the aforementioned specific objectives, was designed as a contribution to global efforts to reduce carbon footprint, minimize plastic waste, and eventually contribute to circular economies efforts for this specific area.

2.2. 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. Using the atmospheric pressure method, it was found that the reaction time was longer to ensure complete synthesis of the polyurethane foam. The faster method was glycolysis using microwave, however the procedure is considered too costly. Hence, the most efficient method proved to be the autoclave, where the method allowed a higher incorporation of polyurethane foam waste, providing a higher yield for the glycolyzed product.

2.2.1. Comparative evaluation of the glycolysis methods

More specifically, three different glycolysis procedures have been investigated to select the method leading to the best result for the recovered polyurethane material, glycolysis at atmospheric pressure, in the autoclave, and using microwave heating. The main target was to investigate the influence of the glycolysis conditions on the decomposition ratio of the polyurethane foam waste and characterize the glycolyzed products based on main specification characteristics, such as viscosity, hydroxyl number and water content. Ultimately, the objective was to use the glycolyzed material back into the polyurethane foam formulations and compare the advantages

37

vs. shortcomings of each method. It is important to mention that all three glycolysis methods used the same type of foam waste, as well as the same batches of DEG and DEOA, respectively, enabling a minimization of potential variations. It was also important to evaluate which method enabled the best balance between the yield of the recovered polyol and the possible industrial implementation, specifically looking to the improvements in foam properties. Foam waste generated from polyester-based polyurethane foam was used for the glycolysis process.

Therefore, ester slabstock foams are used for textile applications (flame lamination), packaging, filters, etc. This type of foam has inferior comfort characteristics and is hydrolytically less stable than polyether-based polyurethane foam, therefore, it is not used for seating or bedding applications [82]. 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 [18].

Stepwise addition of the foam waste was necessary in the glycolysis procedure at atmospheric pressure because the foam waste absorbs the raw materials used for glycolysis, resulting in swelling of the foam that can impede mixing. To avoid that, a tenth of the foam waste was added every ten minutes. Under these conditions, the degradation of the polyurethane foam occurred acceptably, allowing a new portion of the PU foam waste to be added. However, mixing difficulties were observed after every addition stage, and in the last foam waste addition sequences the difficulties were even greater. On the contrary, the glycolysis using autoclave did not require stepwise addition and was not hindered by mixing difficulties, even allowing the utilization of higher PU waste/DEG ratios. The third method, the glycolysis using microwave equipment, allowed a much shorter time to complete the decomposition, but a potential industrial application would involve an increased equipment cost as well as high energy consumption.

Table 2.1 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 (Figure 30) 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 2.1 *Formulation and comparative results of the glycolysis types*

Glycolysis method	Atmospheric pressure	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

Figure 2.1 *Glycolyzed products obtained using (a) atmospheric pressure method, (b) autoclave, and (c) microwave*

The FTIR analysis of the glycolyzed products (Figure 2.1) shows the three synthesized products, glycolyzed at atmospheric pressure, in autoclave and with microwave. The FTIR spectrum allows the identification of various groups or molecules, and the overlapping of these graphs helps for direct comparison. The intensity of the absorption band at 3500-3000 cm^{-1} indicates the water content. It can be observed that fits with the values from Table 2.1, where EXP. 3G (in microwave) showed the highest water content. The vibrations of the ester groups were identified for each glycolyzed product between 2000 and 1500 cm^{-1} The most intense spectral bands are located in the 1500-700 cm^{-1} region, due to a mixture of various oligomers.

The main conclusion of these results is that, regardless of the glycolysis method, we can obtain a consistent product that ultimately can be used in the production of polyurethane flexible foam.
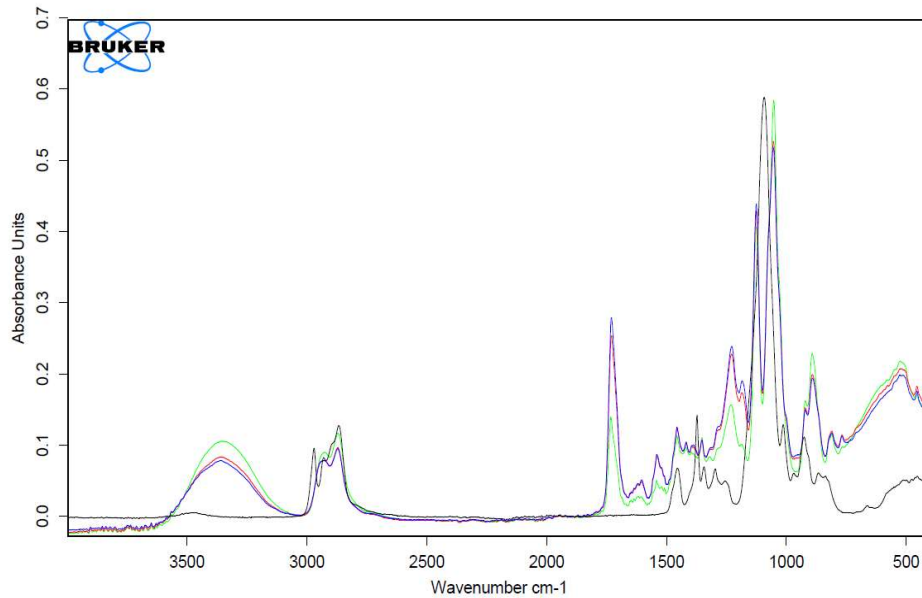
Figure 2.2 *FTIR analysis of the autoclave glycolysis products (Blue - EXP. 1G; Red - EXP. 2G; Green - EXP. 3G; Black - reference polyol)*

2.2.2. 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.

The polyester foam formulations presented in Table 2.2 are original developments achieved during this work. The objective was to develop laboratory-scale formulations sufficiently close to those used in current industrial practice, resulting in best foam performances for polyester-based slabstock foam production, such as fine cell structure, stable foam, and good foam porosity. At the same time, the developed formulation was sufficiently sensitive to allow identification of a possible shift in performances.

Table 2.2 *Formulation of the polyester foam used in this study*

Foam Formulation	Pbw*
Desmophen 2200B	100**
Recycled Polyol	vary
Water	4.90
Niax catalyst C-131 NPF	1.00
Niax catalyst DMP	0.15
Niax silicone L-537XF	1.50
TDI 80/20	51.00

*Pbw=parts by weight (used in industrial PU formulations);
**Desmophen 2200B quantity was recalculated for every synthesis,
in function of the added recycled polyol

Table 2.3 contains the results using the ester foam formulation of Table 2.2. The reference formulation was made using 100 parts virgin polyol. In the following experiments, 1% virgin polyol was replaced by recycled polyol obtained from glycolysis experiments EXP.1G to EXP.3G. Various properties have been analyzed in a back-to-back comparison relative to the reference foam. The rise time was similar between all different foams, indicating that there was no deviation when a recycled polyol was used. A second important parameter is the so-called "foam settling". This is a critical parameter that enables the detection of foam instability or over stabilization. The results of Table 2.3 indicate a minimal stability shift, regardless of the recycled polyol used.

Furthermore, foam properties were measured after 24 h allowing full curing of the polyurethane foams. The foam density of the reference foam was 25.1 kg/m^3. The addition of recycled polyol decreases the foam density with an average of 0.6 kg/m^3. It must be pointed out that a lower density foam, using the same total amount of raw materials would turn into a significant benefit, as in most cases the foam is sold per volume or per unit, hence a lower density foam would be advantageous.

Table 2.3 *Properties of the foams obtained using the ester formulation presented in Table 2.1, 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.

Compression sets (expressed as percent) represent the ratio between the initial thickness and the foam thickness after compression treatment. Lower compression sets of a polyurethane foam indicate better foam recovery. As shown in Table 2.3, the addition of recycled polyol slightly increased the compression sets.

Foam airflow is the parameter that indicates the close-cell versus open-cell content of the polymer. Low values usually indicate a high closed cell content, while higher values indicate the opposite. Flexible polyurethane foams are characterized by a lower level of close cell content, allowing good breathability. The results of Table 2.3 indicate slightly decreased airflow in case of the recycled polyols, compared to the reference.

Tensile strength is another important characteristic of polyurethane foam quality, representing the force needed to break the polyurethane foam sample. Therefore, a higher number indicates improved performance for this specific characteristic. In this case, 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 [83].

2.2.3. 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. Polyether foam formulations shown in Table 6 were also developed in-house. The raw materials differ from those of the ester foam; only the isocyanate and the recycled polyols were the same. The water content of 4.5 parts was selected for the polyether foam formulation, because it would lead to a density of 25 kg/m^3 or slightly lower, considered the average density for polyether foam formulations.

Table 2.4 *Formulation of the polyether foam used in this study*

Foam Formulation	Pbw
Voranol 3322	100**
Recycled Polyol	vary
Water	4.50
Niax catalyst B-18 (Niax catalyst A-1)	0.15
Niax Silicone L-595	1.00
Niax Stannous octoate	0.18
TDI 80/20	55.00

*Pbw=parts by weight (used in industrial PU formulations); **Voranol 3322 quantity was recalculated for every synthesis, in function of the added recycled polyol

Table 2.5 presents the properties of the foams obtained using the ether foam formulation described in Table 2.4. Similarly in the case of polyester-based PU foams, 1% recycled polyol from EXP. 1G to EXP. 3G was added, replacing virgin polyol. The same properties as for the ester-type formulation were assessed after 24 hours from foam production, using similar testing protocols.

The density of the reference foam was 23.2 kg/m^3. The addition of recycled polyol slightly drops the foam density with an average of 0.3 kg/m^3.

The reference foam exhibited a hardness value of 3.34 kPa, typical for this specific formulation. The addition of recycled polyol (EXP. 1G – 3G) enabled the manufacture of harder foam, without any influence on cell structure. Typically, an increase in foam hardness can be achieved with the use of special grafted polyols, the so-called styrene-acrylonitrile copolymer polyols, which by their nature and production process would add additional cost to foam [83]. Compared to the other recycled polyols, the highest hardness increase was observed when the glycolysis was performed in an autoclave.

Table 2.5 also 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

45

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 2.5 *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

2.2.4. 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

46

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. The next step was to investigate the possibility of increasing the amount of foam waste subjected to the glycolysis process using this method. The influence of the quantity of foam waste should allow for the best ratio between raw materials and polyurethane foam waste, the identification of critical processing edges, and the targeting of the highest possible amount of recycled foam.

2.2.4.1. 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 2.6.

Table 2.6 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

Obviously, the glycolysis product is of dark color compared to the virgin polyol as showed in Figure 2.3 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 2.3 *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)*

Using the autoclave method, the degradation of 1 part polyurethane waste was possible with only 1 part DEG, a much higher yield compared to the atmospheric pressure method. Since all glycolysis products showed appropriate properties for use in polyurethane foam formulations, they were investigated for the manufacturing of polyurethanes based on polyethers and polyesters, targeting the possible increase in recycled material.

2.2.4.2. Thermogravimetric analysis of autoclave glycolysis products

To study the thermal stability of the samples, TGA analysis was performed (Figure 2.4). Weight loss until 100°C was under 1% and is usually associated with the water content. These data are consistent with the water content of the samples in Table 8. 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%.
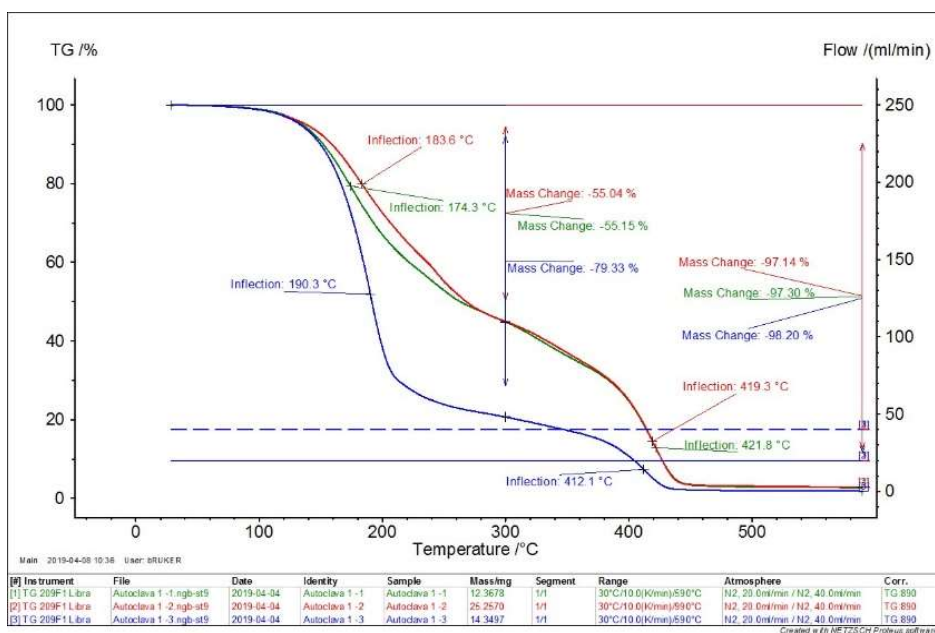
Figure 2.4 *TG curves of glycolysis products obtained by the autoclave method, at different PU waste/ DEG weight ratios; 1:3 (EXP 2G, blue line); 1:2 (EXP. 4G, red line), and 1:1 (EXP. 5G, green line)*

49

2.2.5. Influence of the amount of polyurethane foam waste and its level of use on the properties of ester foam

The purpose of this study was to determine the behavior of recycled polyol in relation to its use level and polyurethane foam waste content. Table 2.7 contains the properties of the ester foams obtained with recycled polyols replacing 1%, respectively 5% virgin polyol in the formulation.

Table 2.7 *Properties of ester foams obtained using the formulation indicated in Table 2.2, replacing 1%, respectively 5%, virgin polyol with recycled polyol*

Ester foam	Ref.	EXP. 2G	EXP. 4G	EXP. 5G	EXP. 2G	EXP. 4G	EXP. 5G
Desmophen 2200B (virgin polyol) (%)	*100.0*	*99.0*	*99.0*	*99.0*	*95.0*	*95.0*	*95.0*
Recycled polyol (%)	*0.0*	*1.0*	*1.0*	*1.0*	*5.0*	*5.0*	*5.0*
Foam physical properties							
Rise time (s)	119.0	118.0	117.0	117.0	113.0	111.0	112.0
Foam settling (%)	1.20	2.00	1.90	1.70	7.90	6.70	9.00
Density (kg/m3)	25.10	24.50	24.80	24.30	25.10	25.60	25.50
Hardness CFD-40% (kPa)	4.86	4.46	4.62	4.60	3.40	3.75	3.82
Compression set 22h 75% 70°C (%)	7.90	9.70	8.72	8.66	24.78	26.37	21.02
Initial air flow (l/min)	33.0	25.0	27.0	27.0	14.0	11.0	9.0
Tensile strength (kPa)	107.0	124.0	121.0	117.0	156.0	161.0	155.0
Cell structure (fine 1.... coarse 8)	5.0	4.0	4.0	4.0	3.0	3.0	3.0

Tendentially, at 1 part of recycled polyol a decrease in density with a softening effect, improved tensile strength, and smaller cell structure was observed for all recycled polyol compositions. The increase in recycled polyol to 5 pbw triggered a somewhat different behavior in the foam properties. The reactivity profile changed, leading to a slightly faster rise time, while the foam settling increased from a 1.2 % average to 7-9 % average. The combined effect between the decrease in rise time and the increase in foam settling indicates a destabilizing effect. Although at 1 part recycled polyols, improvements of most characteristics have been achieved, a too high level seems to affect the stability of the ester foam formulation. Compression sets are also affected by the increased level of recycled polyol, while tensile strength shows a strong improvement. The foam cell structure becomes finer with increasing the recycled polyol content.

Since each of the recycled polyols performed similarly, EXP 5G containing a higher foam waste content was preferred due to the better overall performance.

2.2.6. Influence of the quantity of polyurethane foam waste and its level of use on the properties of the ether foam

Table 2.8 presents the properties of the ether foams obtained with recycled polyols at 1 part, respectively 5 parts. At low level of recycled polyol use, improvements such as reduced foam density with increased hardness, as well as improved tensile strength were observed. However, the increase in recycled polyol to 5 parts triggers a different outcome than for ester foam evaluation. Unlike the ester foam, the addition of recycled polyol did not affect the reactivity profile or foam settling. Compression sets shift with the addition of higher recycled polyol, as in the previous example. Tensile strength also shows a strong improvement.

Table 2.8. *Properties of ether foams obtained using the formulation indicated in Table 2.4 replacing 1%, respectively 5%, virgin polyol with recycled polyol*

Ether foam	Reference	EXP. 2G	EXP. 4G	EXP. 5G	EXP. 2G	EXP. 4G	EXP. 5G
Voranol 3322 (virgin polyol) (%)	*100.0*	*99.0*	*99.0*	*99.0*	*95.0*	*95.0*	*95.0*
Recycled polyol (%)	*0.0*	*1.0*	*1.0*	*1.0*	*5.0*	*5.0*	*5.0*
Foam physical properties							
Rise time (s)	89.0	87.0	89.0	88.0	89.0	89.0	88.0
Foam settling (%)	0.60	0.80	0.60	0.80	0.50	0.70	0.80
Density (kg/m3)	23.13	22.84	22.99	22.96	21.58	21.36	21.60
Hardness CFD-40% (kPa)	3.34	3.44	3.41	3.48	3.22	3.43	3.34
Compression 22h 75% 70°C (%)	17.86	20.73	20.64	18.70	62.17	54.94	54.61
Initial air flow (l/min)	109.00	75.00	84.00	81.00	0.50	3.00	5.00
Tensile strength (kPa)	92.0	98.0	102.0	111.0	59.0	95.0	94.0
Cell structure (fine 1.... coarse 8)	2.0	2.0	2.0	2.0	3.0	3.0	3.0
Foam shrinkage	no	no	no	no	yes	no	no

One of the most affected characteristics is the foam airflow. Polyether polyurethane foams are characterized as high-foam openness materials if the intention is to be used in the bedding industry. The addition of 5 parts recycled polyol drops the airflow below 10 l/min. Such a polyurethane foam will be suitable for special applications such as sealed foam, which are characterized by very low air permeability. This is an outstanding feature that can normally be achieved only by using special raw materials. In addition to very low airflow, another requirement is to have a foam-free

52

shrinkage. The combined effects of very low airflow with free foam shrinkage were observed for the foams made with EXP. 4G and EXP. 5G, at a higher recycled PU waste content. The foam made with EXP. 2G enabled low airflow, too, but a strong foam shrinkage was observed. Considering the overall foam performances, specifically the foam shrinkage, EXP. 2G will likely be excluded for such an application, whereas EXP. 4G and EXP. 5G outperformed and could be considered candidates for sealed foam applications. It can be concluded that for such an application, a recycled polyol with a higher content of polyurethane foam waste is recommended. In our studies, recycled polyols with both 33.3 % (EXP 4G), or 50% (EXP 5G) polyurethane foam waste content performed well.

The reactivity profile represents the profile of foam expansion during polyurethane foam formation and the isocyanate reaction with water, which enables CO_2 formation for foam expansion. Time zero was considered when the addition of TDI in the formulation occurred. Throughout the 150 seconds the polymer formation, also called the polyurethane reaction, happens at the same phase with the foam expansion generated by the aforementioned reaction. The reaction kinetic is influenced by the catalyst package; hence a shift of reactivity towards the left will indicate a faster reaction. At the end of the foam expansion, the reactions are completed, and this can be illustrated through the rise profile with the flattening curve, which in figure 33 starts after roughly 90 seconds from the addition of TDI. One can say that the polyurethane reaction can be completed in 1.5 minutes, which is a typical reaction rate for the flexible slabstock polyurethane foam. In the continuous production, the conveyor speed for such a formulation is around 4 meter/minute, hence based on the reactivity profile, the pouring point and the end of rise have about 6 meter distance. This is a very important information, as the continuous machines have a segment system that allows the foam to grow upwards as well as downwards and optimize the profile of the large foam blocks. Therefore, the reactivity profile is a very important tool in order to control reactivity, identify a potential catalytic shift, and clearly observe foam height differences between the experiments. All of this information is assessed versus a reference formulation. In the case of foam height, if the reference foam has a foam height of 220mm, a substantially lower height for the tested formulation will indicate foam instability. Industrially such an unstable foam can lead to the risk of foam collapsing. To the contrary, if the foam height is significantly higher compared to the reference foam (more than 20 mm, as an

example), this will be characterized as an over-stabilized foam, highly likely with a foam porosity or foam airflow extremely low. In some cases the overstabilization combine with low airflow and lead to foam shrinkage.

In Figure 2.5 the reference formulation was compared with EXP 2G, EXP 4G, and EXP 5G used at 1% in the polyurethane formulation, replacing virgin polyol. The reactivity profile shows a similar foam rise. The foam height was slightly different, 220 mm for the reference foam and roughly 230-235mm for the foams made with EXP 2G, 4G, and 5G. This is a slight shift from the reference rise profile, however, within acceptable range.
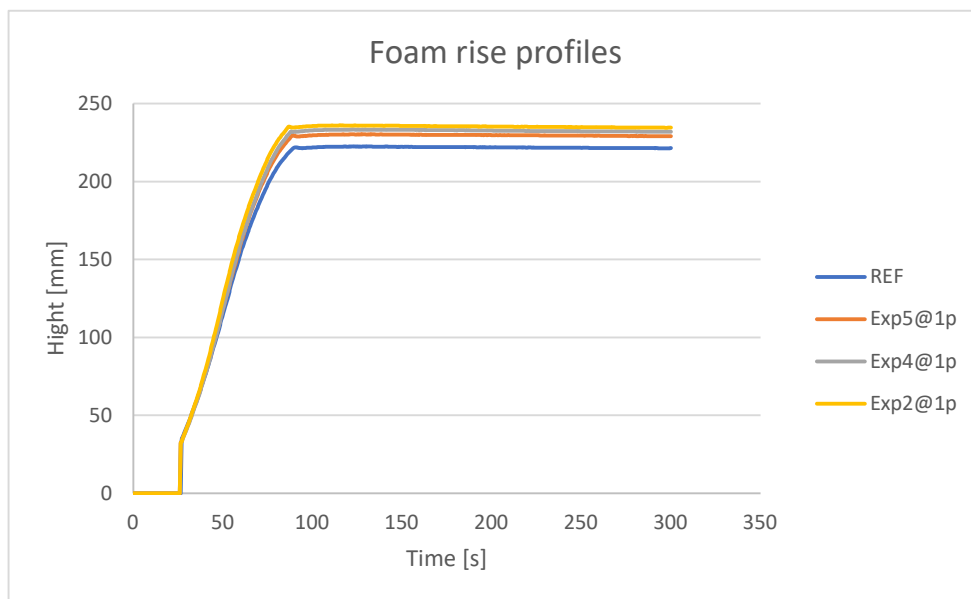
Figure 2.5 Rise profiles - ether foam evaluation at parts

In Figure 2.6, the reference formulation was compared to the same glycolyzed products, EXP 2G, EXP 4G and EXP 5G, but this time we increased the level of use to 5% in the polyurethane formulation, replacing virgin polyol. The reactivity profile for the first 50 seconds was similar for the reference and experimental foams. After that, a shift in reactivity was observed. The reference foam followed the typical reactivity, completing the reaction after around 90 seconds. All three experiments showed a shift towards slightly faster reactivity. EXP 4G and 5G , after 90 seconds of foam reaction the rise profile flattens. EXP 2G instead continued a steady increase in foam reactivity

observed between time 90 and 150 seconds. The continuation of foam rise profile is associated to inability of foam to allow the gas from the cell structures to be released, so it is expected that foam made with EXP 2G at 5G parts in the formulation will be totally closed cell structure.

The foam height in this experiment was very different, 220mm for the reference foam and roughly 250mm for the foams made with EXP 4G and 5G, while EXP 2G led to a very high foam, reaching 280mm. This is a very big change from the reference rise profile, and it is expected to trigger significant foam property changes.
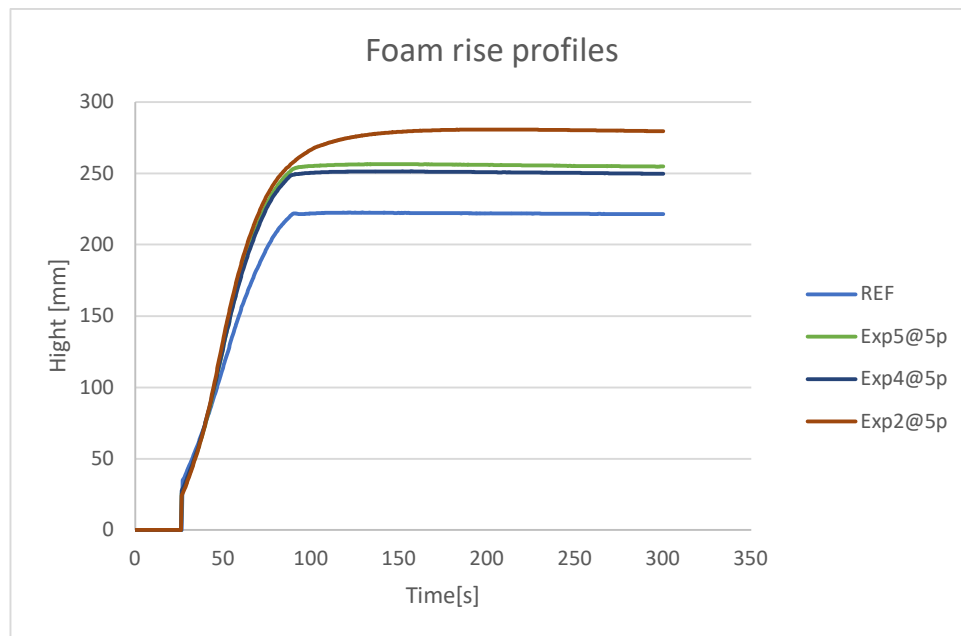
Figure 2.6 *Rise profiles - ether foam evaluation at 5 parts*

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

The results presented in the previous sections demonstrated that a small amount of recycled polyol can selectively improve the foam properties, both in ether foam and ester foam applications. At the same time, an increase in recycled polyol, specifically in ether foam formulation, could be suitable for low air-permeability foam

55

types. However, if the target application is comfort foams, it is a big challenge to increase the recycled polyol content without affecting the foam properties, especially the foam airflow. A potential technical solution that addresses this shortcoming could be optimization of the foam formulation, selecting the appropriate catalyst type and amount.
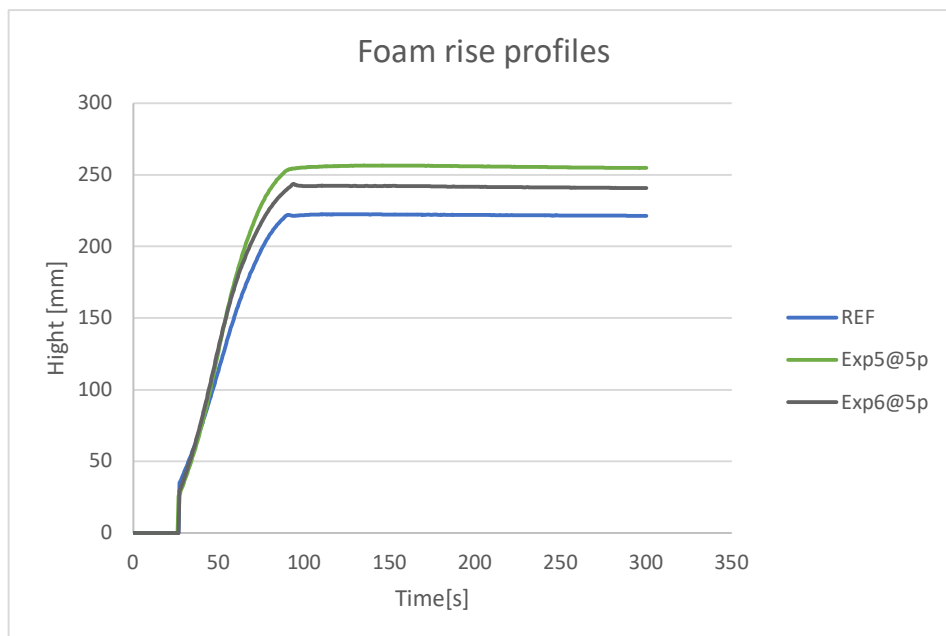

Figure 2.7 *Rise profiles - ether foam evaluation at 5 parts - Optimization of the ether foam formulation with recycled polyol by selection of the catalyst*

Figure 2.7 represents the foam rise profile of the reference foam made with 100 parts virgin polyol, compared to EXP 5G which used 5 parts recycled polyol replacing the same concentration of virgin polyol. The results were as expected; a roughly 40 mm difference in foam height was observed between the foams. The reference formulation has a typical reactivity profile, reaching a maximum foam height around 90 seconds. The foam height was around 220 mm. Unlike reference, EXP 5G at 5 parts of recycled polyol enabled a similar reactivity profile for approx. 90 seconds, but afterwards the rise profile started flattening and the foam height reached 260 m. Higher foam, combined with lower airflow of the foam, is a clear sign of overstabilization. Optimization of the formulation was carried out by improved selection of the amine catalyst along with proper adjustment of the stannous octoate

56

level (EXP 6G). To favor the blowing reaction and consecutively enable an increase in foam airflow, Niax Catalyst A-1 (NN-bis- dimethyamino ethyl ether) , known as a strong blowing catalyst, was tested instead of Niax Catalyst B-18 (triethylene diamine combined with bis dimethylamino ethyl ether). The optimum catalyst level was identified to be 50% less in amount. In addition, reduction of the Niax Stannous Octoate amount from 0.18% down to 0.12% was also identified as a solution for the optimum catalyst package. Table 2.9 presents the results of the foam property assessment.

Table 2.9 *Optimization of the process parameters for the ether foam formulation and properties of the foam obtained with 5 pbw recycled polyol*

Ether foam	Reference	EXP. 5G	EXP. 6G
Voranol 3322 (virgin polyol) (%)	*100.0*	*95.0*	*95.0*
Recycled polyol (%)	*0.0*	*5.00*	*5.00*
Niax Catalyst B-18 (%)	*0.15*	*0.15*	*-*
Niax Catalyst A-1 (%)	*-*	*-*	*0.075*
Niax Stannous octoate (%)	*0.18*	*0.18*	*0.12*
Foam physical properties			
Rise time (s)	89.80	88.40	94.10
Foam Settling (%)	0.60	0.80	1.30
Density (kg/m3)	23.13	21.60	22.66
Hardness CFD-40% (kPa)	3.34	3.34	2.74
Compression set 22h 75% 70°C (%)	17.89	54.60	22.70
Initial air flow (l/min)	109.0	5.0	113.0
Tensile strength (kPa)	33.0	27.0	14.0
Cell structure (fine 1.... coarse 8)	2.0	2.0	2.0

The reference foam based on 100 parts virgin polyol resulted in standard foam properties. The airflow value was 109 l/min, a typical value characterizing open polyurethane foam. Addition of 5 parts recycled polyol in EXP. 5G, replacing the virgin polyol, hugely dropped the airflow, to 5 l/min. These adjustments to the foam formulation allowed recovery of airflow characteristics similar to those of the reference foam. In conclusion, the right selection of raw materials and additives is the key issue to realize an increased level of recycled polyol use in polyurethane foam formulations. Taking this approach into account, further increase in recycled polyol could be possible, but a more in-depth evaluation was outside the scope of this study.

Figure 2.7 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 changes as described above. 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.
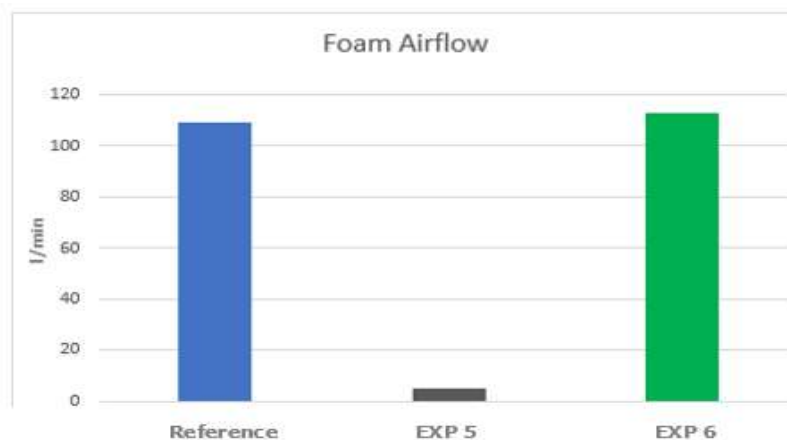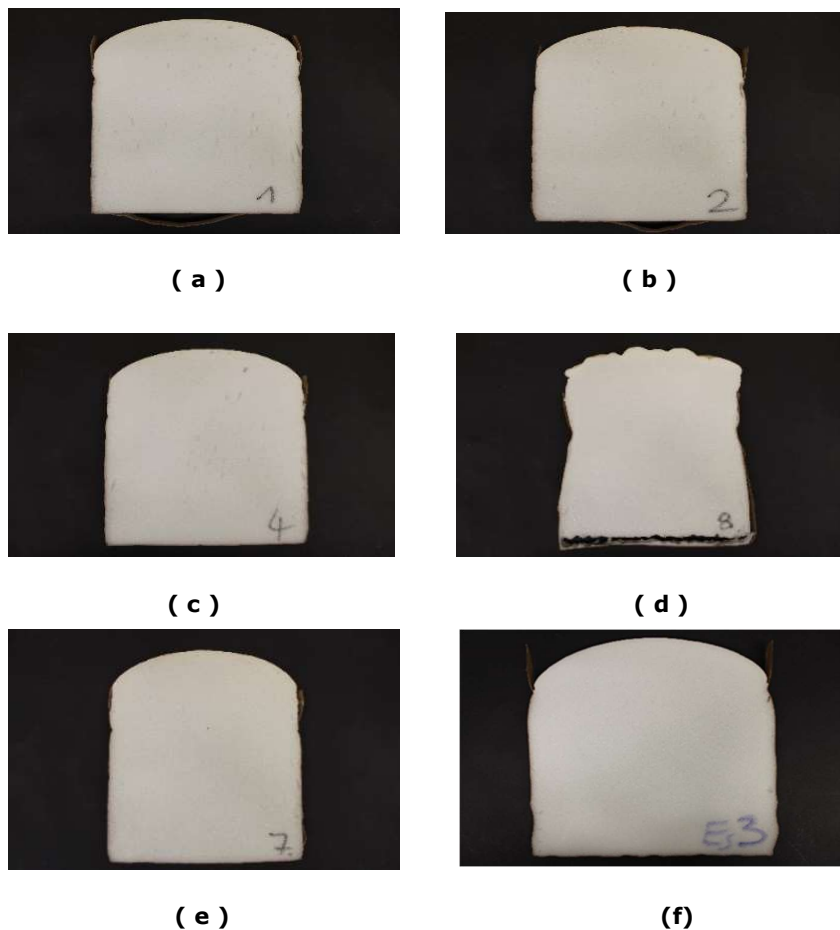

Figure 2.7. *Foam airflow of the reference polyether-based polyurethane foam (blue bar); polyether-based polyurethane foams obtained with 5% recycled polyol from 50% PU waste in EXP 5G (black bar); polyether-based polyurethane foams obtained with 5% recycle d polyol from 50% PU waste and optimized catalyst formulation in EXP 6G (green bar)*

58

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.

The dimensional stability of a polyurethane foam is critical. An optimum dimensional stability for a free-rise foam must be towards rectangular shape. The top of the foam generally takes a convex shape due to the free-rise profile. In continuous production, a top flat system is applied onto the foam block, and hence the convex shape of the top of the foam is fully converted into a perfect rectangular shape foam block. Figure 2.8 shows a vertical foam slice of various polyurethane foam formulations made for this evaluation. Foam 2.8a is the reference foam that dictates the expected shape of the block. All other vertical slices are very similar in foam geometry to the reference, except for foam 2.8d, made out of EXP 2G at 5G parts in the formulation. As already predicted at the rise profile assessment, where the foam showed much higher foam height (see Figure 2.7) this foam was very low in air permeability. The continuation of the rise profile from 90 to 150 seconds suggests the inability of polyurethane foam to allow the gas from the cell bubbles to be released. In general, gas loss is known to occur at the completion of the reaction. If this is not the case, the foam continues to rise. The exothermic reaction heats the CO_2 formed in the cell bubbles. When the foam starts to cool, the expanded CO_2 recovers its volume in relation to the achieved temperature. If the cell bubbles are closed, this phenomenon is known as foam shrinkage, very similar to the phenomenon represented in the picture 2.8d. Therefore, although there is a low air permeability, the dimensional stability of such foam is not acceptable. This foam was made with EXP 2G, which contains the lowest amount of foam waste. For an optimum formulation, a higher amount of foam waste to be recycled is preferred, since it allows use in special applications such as the aforementioned sealing foam.

59

(a)   **(b)**

(c)   **(d)**

(e)   **(f)**

Figure 2.8 *Images of reference polyether-based polyurethane foam (a); polyether-based polyurethane foams obtained with 5% recycled polyol from 25% PU waste EXP 2G (d), respectively, from 50% PU waste EXP 5G (e); polyether-based polyurethane foams obtained with 5% recycled pol-yol from 50% PU waste and optimized formulation EXP 6G (f)*

2.2.12. Partial conclusions

This work allowed for a detailed comparison of various glycolysis procedures, identifying the most optimum process. The recycled polyols can be used as raw material to replace virgin polyols in polyurethane foam formulations in both ester and ether applications. The preferred glycolysis method was considered to be the

autoclave method, allowing for increased level of foam waste use and improved overall properties. Utilization of recycled polyol at a low level resulted in improved foam density for ester and ether foams. The foam hardness effect was different, in ester foam the recycled polyol enabled the softening effect, while in ether foam it exhibited somewhat higher hardness. In both ester and ether foams, an improvement in tensile strength was observed. Generally, the increased level of recycled polyol use affects foam compression sets. In the case of ether polyurethane foam, a lower air-permeability foam can be achieved using a higher amount of recycled polyol. These foams could be used in special applications where low air permeability is the target.

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 amount of recycled polyol in the foam composition to increase to 5%. Although this amount is lower than reported in the literature by using purified recovered polyols [18], it has the important advantage of eliminating any separation step and recycling the whole glycolysis product. Based on these findings, further development of this strategy could target an even higher quantity of recycled polyols in polyurethane formulations with specified composition, identifying the best foaming conditions.

2.3. Laboratory-scale acidolysis of ether polyurethane foam waste

The first part of original contribution reported the depolymerization of a thermoset material of flexible polyester-type polyurethane foam using the glycolysis method. The analytical measurements demonstrated that this product has characteristics allowing it to partially replace the standard polyol. The reincorporation of this product back in the polyurethane foam formulation has also been studied. However, the main difficulty was to reproduce the same outcome when changing the type of 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.

2.3.1 Acidolysis in the autoclave using carboxylic acids from renewable sources

Autoclave was considered the most adequate method reported before in the glycolysis study. During the previous study only the polyester-based polyurethane foam was properly depolymerized by the glycolysis method. Changing the polyester type of foam waste to polyether foam waste and using the same method we were unable to accomplish the depolymerization at laboratory scale, even using autoclave method. Certainly, the ether groups abundantly present within the foam matrix are less prone for the glycolysis procedure. As a result, a new method has been explored, using the same autoclave equipment, and employing ether-type foam waste. It has been found out that the polyether foam waste can much easily be depolymerized in the presence of succinic acid and some additional ingredients, as reported in Table 2.10. Following this investigation, we consider that acidolysis in the autoclave is a suitable method to recover polyurethane foam waste, because the availability of this type of foam waste is significantly larger when compared to the ester foam waste.

Subsequently, 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. Ultimately, the objective was to move to industrially available polyol products recycled by acidolysis, test them in polyurethane foam formulations, and compare the advantages *vs*. shortcomings once the best method has been established. It is important to mention that all trials used the same type of foam waste based on mixture of foam with various densities. The most important issue was that the polyurethane foam waste was free of any ester foam waste material. The raw materials used in this investigation were Desmophen 2200 B from Covestro (a partly branched polyester based on adipic acid, diethylene glycol and trimethylol propane), diethylene glycol, and the specified acids used individually. The same batch of raw materials has been used for all tests, enabling the minimization of potential variations.

In this experimental setup, the polyurethane foam waste has been shredded in small pieces that would not exceed one centimeter length, width, or height. To do

so, a special shredder was used, enabling a uniform size of the shredded polyurethane foam. This time, because the quantity of shredded foam intended to use for acidolysis was significantly higher than for any previously investigated methods, the foam was exposed to a forced compression, enabling volume reduction of more than 10 times. This procedure allowed using 40% of foam waste in a significantly smaller autoclave. We enabled therefore a potential cost reduction of the autoclave due to volume reduction estimated to at least 6 times. Next step, once the shredded foam was added into the autoclave, a homogeneous mixture of diethylene glycol, acid, and Desmophen 2200B has been prepared. It is important to notice that without pre-mixing the three different raw materials we would not have been able to expose the shredded foam and the liquid to a uniform final mixture. This is mainly due to Desmophen 2200B, a high viscosity material, that reach up to 20000 cSt at room temperature. This autoclave process is free of any mixing protocol, supposing a simple addition of the liquid phase (a pre-mixture of diethylene glycol, acid, and Desmophen 2200B) to the solid phase (shredded ether polyurethane foam), followed by closing the autoclave to ensure a fully sealed system. The autoclave was placed in an oven at 180°C to accomplish the depolymerization phase. Once the reaction time has been completed, the system was let to cool down, and the material was collected in a glass recipient. The autoclave was cleaned and dried appropriately, and the next set of experiment, employing different acid was performed identically.

Table 2.10 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 (Figure 2.9) 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.

Another advantage of acidolysis compared to glycolysis is that it enables decomposition of the polyurethan foam waste even without the presence of a catalyst. Unlike glycolysis, where diethanolamine was used, here the depolymerization was made without addition of any catalyst.

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,

63

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 2.10, 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 2.10 *Formulation and comparative results of the laboratory-scale acidolysis using carboxylic acids from renewable sources*

Carboxylic acid type	Succinic acid	Lactic acid	Citric acid
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

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

The products obtained through acidolysis at laboratory scale (Figure 2.9), using the three selected carboxylic acids, were used as raw material for production of polyether-based flexible polyurethane foams. In all experiments, 10% of virgin polyol was replaced by the acidolysis product, and the impact of this recycled product on the physical properties of the new polyurethane foams was studied.

Figure 2.9 *Acidolysis products obtained by acidolysis in autoclave with various carboxylic acids, as described in Table 2.10*

The recycled polyol (as crude acidolysis product) was used in polyether-based foam applications, as partial replacement of virgin polyol. The polyether foam formulations shown in Table 2.11 were also developed in-house. A water content of 4.5 parts by weight was selected for the polyether foam formulation, because it would lead to a density of 25 kg/m^3 or slightly lower, this value being considered an average density for low density polyether foam formulations.

Table 2.11 *Formulation of the polyether foam used in this study*

Foam formulation	Pbw*
Voranol 3322	100**
Recycled polyol	vary
Water	4.50
Niax catalyst B-18 (Niax catalyst A-1)	0.15
Niax Silicone L-595	1.00
Niax Stannous octoate	0.18
TDI 80/20	55.00

*Pbw=parts by weight (used in industrial PU formulations);

**The Voranol 3322 quantity was recalculated for every synthesis, in function of the added recycled polyol

Table 2.12 presents the properties of the foams obtained using the ether foam formulation described in Table 2.11. 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 foam properties were assessed at 24 h following the foam production, using similar testing protocols as in the experiments presented in the previous chapters.

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 2.12, 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 [73]. As a result of this finding, we demonstrated the possibility of manufacturing a harder foam by using a recycled polyol obtained through acidolysis.

As mentioned, the foam properties were measured after 24 h, allowing a full curing of the polyurethane foams. 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 2.12 *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
Voranol 3322 (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 CFD-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 structure (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

67

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 (Table 2.12). At such and airflow level, the foam can be still processed in a safe manner, as being within the specifications; hence, the addition of recycled polyol did not to have real influence towards the foam airflow, which is a good sign concerning the quality of the recycled polyol obtained by acidolysis. In the previously studied glycolysis procedure, addition of only 1% of recycled polyol was possible without changing the foam properties, while at 5% signs of foam tightening were already observed. 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 airflow shift was smaller than in the case of the polyester foams with recycled polyol based on glycolysis in autoclave (as it was shown in Table 2.3, section 2.2.2).

The addition of acidolysis product from Exp. A and Exp. B did not shift the cell structure of the ether foams towards finer or coarser; hence, adding any of these products as a partial replacement of the virgin polyol had no impact on the cell structure, which is an expected and desired result. Contrary, when citric acid was used as acidolysis agent (Exp. C) the cell structure of that specific foam was ranked 4, meaning that the foam had significantly coarser cell structure compared with the reference or the other experiments. Moreover, in specific isolated parts of the foam, larger pinholes were noticed (images not shown), probably due to the uneven distribution of the recycled polyol based on citric acid in the reaction mixture. As mentioned in the previous chapter, visual observation of the polyol product revealed the presence of clumps after completing the acidolysis process for that experiment, indicating the presence of unreacted solid material (waste polyurethane foam). In the foaming process, these clumps created the undesired pinholes. Although citric acid was not as appropriate as succinic and lactic acid, it must be pointed out that these are the conclusions of a preliminary experiment, accomplished in non-optimized conditions. A more in-depth study also could reveal improved properties for the acidolysis product obtained with citric acid, and this will be one objective of future research.

68

In conclusion, the preferred acidolysis agents are succinic acid or lactic acid, as they lead to a product free of unreacted solids, in the same process conditions. Specifically, lactic acid is worth of interest, as it is obtained at industrial scale from natural sources (glucose, by fermentation) and is available at acceptable price. Therefore, the utilization of polyurethane foam waste along with lactic acid will increase the sustainability of the recycle process and could significantly reduce the carbon footprint, a huge advantage towards the circular economy objectives. Succinic acid is another platform chemical obtained from renewable sources which recently came in focus of research interest as a promising acidolysis agent [34]. Hence, a consistent increase of reports concerning the utilization of carboxylic acids from renewable sources in this direction is expected in the near future.

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. The next chapter presents original results achieved in this respect.

2.4 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, while thermogravimetric analysis and infrared spectroscopy were performed in comparison to the reference commercial polyol. 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,

69

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 [25].

2.4.1. Characterization of the recycled polyol

An important aim of this work was to investigate an industrially available recycled polyol, which could allow the overall efficiency of the PU waste reutilization. In this reason, the recycled polyol, supplied by an industrial partner, was characterized by dynamic viscosity, hydroxyl number, water content, and acid number, as well as by thermogravimetric analysis and infrared spectroscopy, compared with that of the petroleum-based reference polyol.

2.4.1.1. Physical properties of the polyols

Table 2.13 shows the typical physical properties of the recycled polyol (repolyol) obtained by an industrial acidolysis process, compared to the standard polyol.

Table 2.13 *Typical physical properties of repolyol and standard polyol*

| Property	Recycled polyol	Standard polyol
Color	Brown	Colorless
Water content (%)	0.05	0.05
Viscosity (cSt)	12500	550
Hydroxyl number (mg KOH/g)	46.90	48.00
Acid number (mg KOH/g)	0.22	0.05

70

The first noticeable difference is the color of the products, brown for the recycled polyol and colorless for the standard polyol. Hydroxyl number is an important parameter, as it indicates the total amount of isocyanate required to react with hydroxyl groups from polyols during the foaming process. The hydroxyl number was similar between the two polyols. A small difference from 48.0 to 46.9 can be easily adjusted to reflect the correct isocyanate content.

The water content of the polyol is important, specifically to properly define the water added in the foam formulation. The results show the same water content between the two polyols.

A large difference was noticed for the viscosity. A typical viscosity of 500- 600 cSt defines standard polyols, but the recycled polyol had a much higher viscosity, 12500 cSt. A material with such a high viscosity is difficult to process in the industrial application. However, people skilled in the art are familiar with polyols with even higher viscosity; hence, a metering system adaptation is required to enable its industrial use.

2.4.1.2 FTIR analysis

The FT-IR spectra of recycled polyol and reference polyol are presented in Figure 2.30. The spectra for both polyols exhibit characteristic peaks at 3300-3450 cm^{-1}, corresponding to the stretching vibration of the O-H and N-H groups. Peaks at 3000 – 2800 cm^{-1} correspond to alkyl C–H stretching vibration. The spectrum of recycled polyol presents at 1720 cm^{-1} the stretching C=O vibration of the COOH ending group from the acidolysis process, as also reported by Gama *et al.* [3].
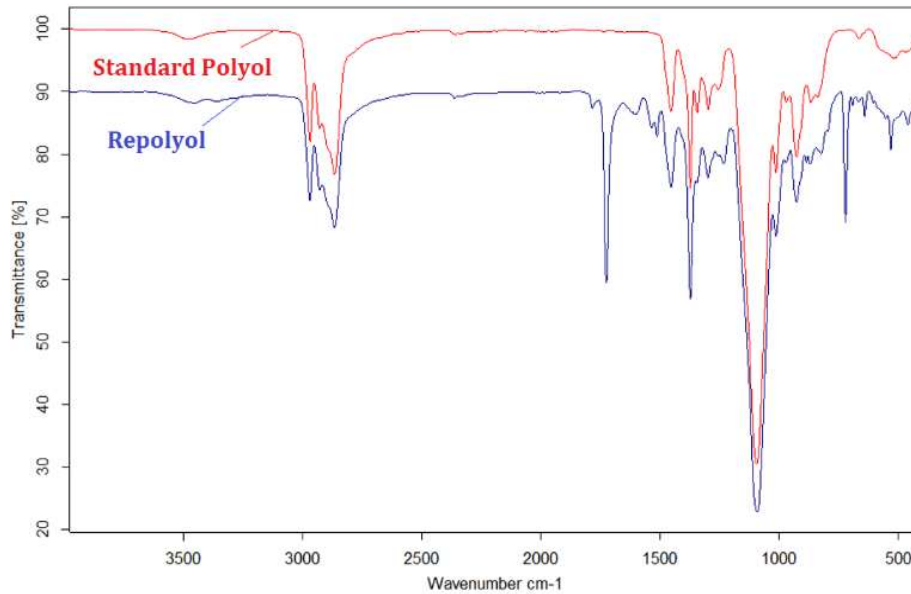
Figure 2.30 *FT-IR spectra of recycled polyol (blue line, lower spectrum) and reference polyol (red line, upper spectrum*)

2.4.1.3. Thermogravimetric analysis (TGA)

Figure 2.31a presents the TGA thermograms for recycled polyol and reference polyol. The samples present one degradation step behavior, between 260°C and 435°C. The onset temperature for the degradation process for the recycled polyol is 373.9°C, while for the standard polyol is 318°C. The mass loss at 120°C, which corresponds to the water content, is 0.05%, basically consistent with the water content reported in Table 2.13. The residual mass at 600°C is less than 3% for both polyols. The main degradation step takes place at a temperature about 50°C higher than in the case of the reference polyol, but this increased thermal stability has no adverse effect on the foam properties, as will be shown. The TGA thermograms for polyurethane (PU) obtained with standard polyol and recycled polyol are presented in Figure 39b. Both samples followed the same two-step degradation pattern under nitrogen atmosphere. The first degradation step has a maximum rate at 294°C and corresponds to the degradation of the urethane bonding within the foam, while the second degradation step has a maximum rate at 378°C and involves secondary degradation processes, such as the degradation of previously formed polyols [27].

(a)   (b)
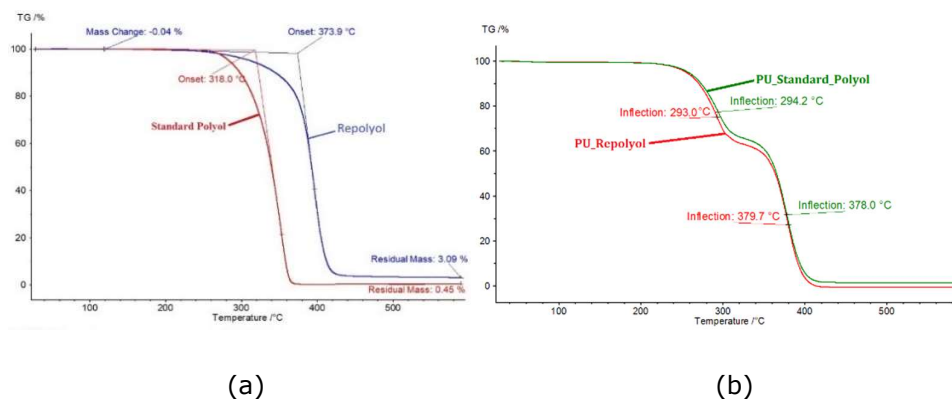
Figure 2.31 *TGA thermograms of (a) recycled polyol (blue line) and the reference polyol (red line) and (b) PU with recycled polyol (green line) and PU with standard polyol (red line)*

2.4.2. Optimized utilization of recycled polyol in flexible polyurethane foam formulations

In a previous work [18], 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.

The conventional polyether foam formulation was performed according to the experimental protocol presented in Table 2.14, where the formulation data was expressed as ranges from minimum to maximum level. To accurately highlight the formulation changes in the experiments carried out with recycled polyol, these changes are mentioned in the relevant tables in the original contribution part. The formulation ingredients with fixed amounts were kept unchanged for all experiments. In the recycling experiments, the reference polyol was gradually replaced by different

73

amounts of recycled polyol, while the standard tertiary amine catalyst package, consisting of Amine 1 and Amine 2 (the chemical structures are given in Figure 1.15), in a weight ratio of 1:3, was fully replaced by a reactive tertiary amine catalyst (Amine 3). The amounts of catalysts were predefined for each set of experiments, targeting a similar reactivity profile. Such a pre-definition of the amount of amine catalyst in polyurethane foam formulations is a common procedure employed by people skilled in the art. Therefore, the initial catalyst formulation presented in this work came from the usual practice and was not optimized. The novelty of this work is based on the positive effects identified by using Amine 3 in the foam formulation containing the highest recycled polyol content, as will be discussed.

Table 2.14 Basic formulation of the flexible polyether foam

Component	Pbw[a]
Reference polyol (Voranol 3322)	70 - 100
Recycled polyol	0 - 30
Water	4.50
Niax Silicone L-895	1.00
Niax Stannous Octoate	0.16
Amine catalyst(s)[b]	0.06 – 0.30
Isocyanate index[c] (TDI 80/20)	108

[a]pbw - parts by weight; [b]The amount of catalyst was optimized for each set of experiments, to enable similar reactivity profile; [c]The amount of isocyanate used in the reaction, in relation to the theoretical equivalent amount

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

The aim of this study was to develop laboratory-scale formulations very close to those used in current industrial practice, allowing the best performances for flexible polyether slabstock foam production, such as fine cell structure, stable foam, and good foam porosity. At the same time, the developed formulation was sufficiently sensitive to allow identification of a possible shift in performances.

74

Based on the formulation presented in Table 2.14, the results shown in Table 2.15 contain the properties of the foams obtained by gradual replacement of the reference polyol used in the manufacture of commercial PU foams with recycled polyol. EXP. 1A enabled 10 parts of recycled polyol, EXP. 2A used 20 parts, while 30 parts of recycled polyol were used in EXP. 3A. Various properties have been analyzed in a back-to-back comparison relative to the reference foam obtained with the virgin polyol. The rise time was almost similar for all foams, with no significant deviation when recycled polyol was used, except EXP. 3A when a 10 second longer rise time was observed. Foam settling was not visible for any of these experiments, indicating good foam stabilization.

Table 2.15 *Properties of foams obtained using the formulation presented in Table 2.14, gradually replacing standard polyol with recycled polyol*

Main formulation changes from Table 2.14	Reference	EXP. 1A	EXP. 2A	EXP. 3A
Standard polyol	*100.0*	*90.0*	*80.0*	*70.0*
Recycled polyol	*0.0*	*10.0*	*20.0*	*30.0*
Amine 1: Amine 2 at ratio 1:3	*0.06*	*0.06*	*0.06*	*0.06*
Physical properties of the foams				
Rise time (s)	102	100	100	111
Foam settling (%)	-	-	-	-
Density (kg/m^3)	22.60	22.50	22.50	23.20
Hardness CFD-40% (kPa)	3.26	4.06	4.15	5.17
SAG	2.45	2.49	2.69	3.77
Airflow (l/min)	123.00	91.00	20.00	1.00
Cell structure (fine 1.... coarse 8)	2	2	3	3

75

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.
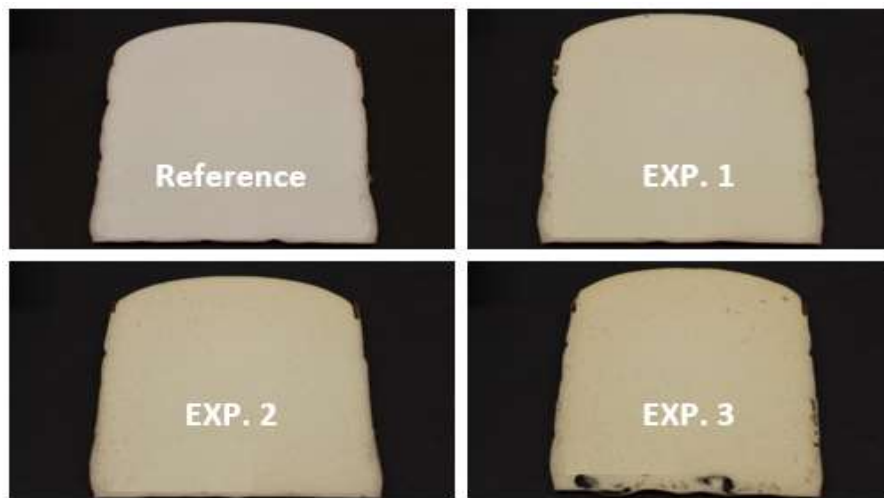
Figure 2.32. *Vertical foam slice with different standard polyol/ recycled polyol ratios, in formulation from Table 2.15*

Figure 2.32 shows images of vertical foam slices for the set of experiments performed in Table 2.15. The appearance of the flexible polyurethane foam is white for the reference foam, whereas a light brown foam color was observed for EXP 1A, 2A, and 3A. The color change is connected to the nature of recycled polyol and is widely accepted within the polyurethane industry. Moreover, foam surface discoloration is expected to occur over time, hence the reference foam will suffer a yellowing effect at the surface over a certain period of time. This experiment was, however, not part of the current work. The evaluation of cell structure is a visual observation and is reported in Table 2.15, where the smaller numbers were assigned for the finer cell structure. In this work, EXP. 1A indicated the same cell structure as the reference foam, while EXP. 2A and EXP. 3A indicates slightly larger cell structure. Furthermore, EXP. 3A indicated the appearance of bottom holes, a typical sign of over-stabilization [18].

2.4.2.2. 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. The mixture of the tertiary amines *bis*-[2-(N,N-dimethylamino)-ethyl]-ether (Amine 1) and 1,4-diazabicyclo[2.2.2]octane (Amine 2), at ratio of 1:3, is the most commonly practiced amine catalyst package in the flexible PU industry, being considered the standard amine catalysts. Table 2.16 presents the foam properties resulting from this approach. The formulation of 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 2.16, the foam properties generated for EXP. 4A and EXP. 5A are not satisfactory, specifically for the airflow parameter. As a possible solution for

77

elimination of this important drawback, a third tertiary amine, N,N'-bis[3-(dimethylamino)propyl]urea (Amine 3) was investigated as catalyst.

Table 2.16. *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 from Table 2.14	EXP. 3A	EXP. 4A	EXP. 5A	EXP. 6A
Standard 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 foam physical properties				
Rise time (s)	111	111	111	99
Foam settling (%)	-	-	-	-
Density (kg/m^3)	23.20	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

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

78

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.

Figure 2.33 shows the images of the vertical foam slices for the set of experiments performed in Table 2.16. A visual difference was the appearance of bottom holes for foams made according to EXP. 3A and EXP 4A, more pronounced for foam made with Amine 1 as sole catalyst, sign of overstabilization in the laboratory stage. The use of Amine 2 led to almost complete elimination of bottom holes, but the low airflow observed for this experiment makes it unsuitable for this formulation. Amine 3 instead resulted in a foam with free bottom holes, as well as high airflow, demonstrating a consistent improvement of foam properties, even at high recycled polyol loading in the formulation.

Figure 2.33 *Vertical foam slice with different amine catalysts in the formulation presented in Table 2.16*

2.4.2.3. Investigation of the cellular structure of the foams by SEM analysis

Figure 2.34 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.
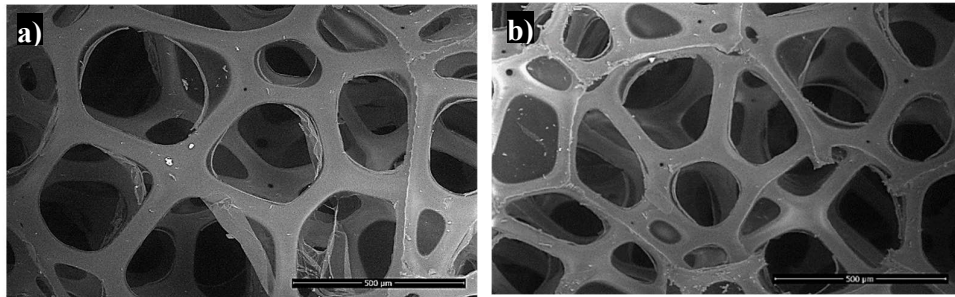
Figure 2.34 *SEM images with the cellular structures of PU foams obtained with reference polyol (a) and 30% recycled polyol, using the formulation of EXP. 6A (b)*

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, as shown for EXP. 1A (Table 2.15) and EXP. 6A (Table 2.16), respectively. 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.

2.4.3. Emission test assessment for the polyurethane foams obtained with recycled polyol

The utilization of flexible polyurethane foams can create concerns about consumer safety, particularly related to airborne pollutants such as volatile organic compounds (VOC), since these substances might be released from the materials used in the manufacturing of indoor products. The emission testing procedure used in this

80

study was the VDA-278 method [84]. For the VOC analysis, the foam sample was heated to 90°C for 30 minutes. The method described in this recommendation allows the analysis of substances in the boiling / elution range up to n-pentacosane (C25), the total value being determined as VOC. To determine the fogging value (FOG), a second sample is retained in the desorption tube after the VOC analysis and reheated at 120°C for 60 minutes. The FOG value represents the total substances with low volatility with a retention time starting from n-tetradecane (inclusive). It is calculated as the hexadecane equivalent. For this assay, compounds in the boiling range of n-alkanes C14 to C32 were determined and analyzed by GC-MS [85].

Table 2.17 shows the emission results for the reference foam and the foam made using Amine 3, a tertiary amine designed specifically to minimize or eliminate amine emissions from polyurethane foams [25].

Table 2.17 *Foam emission results using foams made with standard polyol at 100 parts (EXP. 1A) and standard polyol : recycled polyol 70:30 (EXP. 6A)*

Main Formulation Changes from Table 13	EXP. 1A	EXP. 6A
Standard Polyol	*100.0*	*70.0*
Recycled Polyol	*-*	*30.0*
Amine 1: Amine 2 at ratio 1:3	*0.06*	*-*
Amine 3	*-*	*0.30*
Stannous Octoate	*0.16*	*0.16*
Emission test VOC and FOG results (ppm)		
Total VOC	**102**	**41**
Catalyts package contribution	93	32
Total FOG	**194**	**187**
Catalyts package contribution	44	33

ppm – parts per million

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.

2.4.4. Partial conclusions

The industrially available recycled polyol can be used as raw material in low-density flexible polyurethane foam formulations, but only up to 10 pbw incorporation in the foam formulation can be achieved without formulation changes. The increase in recycled polyol in the formulation affects the physical properties of the foam, particularly the airflow. Enhancement of foam properties with a large amount of recycled polyol was achieved by replacing standard tertiary amine catalysts with a reactive tertiary amine catalyst, N,N'-*bis*[3-(dimethylamino)propyl]urea, identified in this study as the most efficient method to produce flexible polyurethane foams with recycled polyols. This amine catalyst enabled a threefold higher recycled polyol level compared to the standard catalyst package, without affecting the foam properties, allowing the production of a PU foam without defects and with optimum foam airflow. The environmental impact was also evaluated, demonstrating that the selected amine catalyst can also generate a reduction in the overall emission of volatile organic compounds.

The results of this 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 [25].

2.5. 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 the polymer structure, the low molecular weight polyether pendant groups have an ethylene oxide content of 70 weight percent of the alkylene oxide content or greater. It has been found that a foam forming composition comprising such surfactants can employ a substantial amount a polyether carbonate polyol as the polyol component. Using such surfactants allows for at least half and possibly all of the polyol in the composition to be a polyether carbonate polyol. These compositions can provide stable flexible foams with good properties.

The present technology provides a foam forming composition comprising a polyol comprising a polyether carbonate polyol; an organic polyisocyanate or polyisocyanate prepolymer; a catalyst for the production of polyurethane foams; a blowing agent; and a silicone surfactant. The silicone surfactant comprising a first set of polyether pendant groups having a first molecular weight, and a second set of polyether pendent groups having a second molecular weight, the second molecular weight being lower than the first molecular weight, wherein the second set of polyether pendant groups have an ethylene oxide content of 70 weight percent or greater of the alkylene oxide content of the polyether. In one embodiment, 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. In one embodiment of the foam forming composition of any previous embodiment, the second set of polyether

pendant groups have an ethylene oxide content of 100%. In one embodiment of the foam forming composition of any previous embodiment, the second set of polyether pendant groups have a blend average molecular weight of from 130 to 1000 grams/mole. In one embodiment of the foam forming composition of any previous embodiment, the second set of polyether pendant groups have a blend average molecular weight of from 400 to 600 grams/mole. In one embodiment of the foam forming composition, the silicone surfactant is of the general formula given in Figure 2.35:
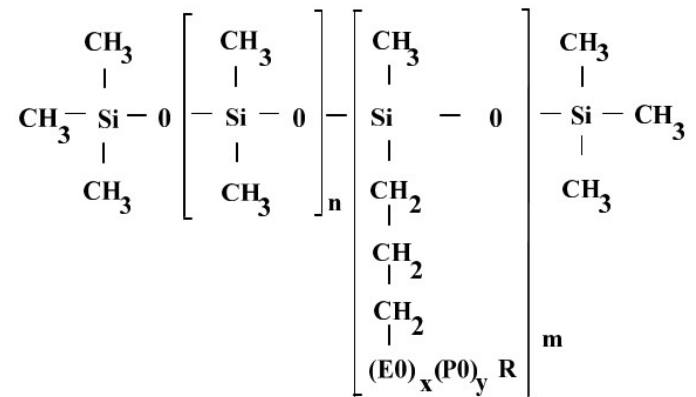

Figure 2.35 *Chemical structure of silicone surfactant based on polydimethyl siloxane and polyether's pendant copolymer*

In order to describe more in details the entire silicone polyether surfactant suture, the formula from Figure 2.36 has been established as innovative:

$$MD_xD'_yM$$
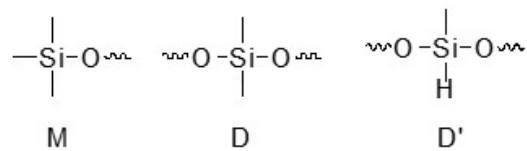
Figure 2.36 *Sequences of polydimethyl siloxane fluid used for the production of silicone polyether copolymers*

Figure 2.36 explains in detail a typical silanic fluid formula, and the constituents of that formula. In general, a polydimethyl siloxane fluid has a certain D' units associated to the functionality of that material. These type of components as described in figure 2.36 are also the intermediate to produce silicone polyether copolymers and are considered the hydrophobic part of that chemical. The hydrogen available for reaction (x units in the formula) as functionality is further reacted in the presence of a double bond polyalkylene oxide polyether.

$$CH_2 = CH_2 - (EO)_{40-100}(PO)_{40-100} - R$$
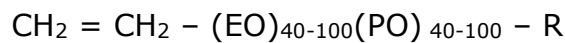
Figure 2.37 *General formula of a polyalkylene oxide polyether, where EO is ethylene oxide, PO is propylene oxide, and R alkoxy group*

Figure 2.37 is a chemical representation of an allyl started polyalkylene oxide polyether. For the production of a silicone polyether surfactant, typically requires one or more polyalkylene oxide polyethers. In this specific case, two polyalkylene oxide polyethers were used. For the simplicity, these two polyethers will enter under the nomenclature R1 and R2, where:

- R1 has a blend average molecular weight in the range of from 1500 to 6000 grams/mole; ethylene oxide (EO) is from 30 to 50 weight percent of the al-kylene oxide content of the polyether; and propylene oxide (PO) residues constitute 50 to 70 weight percent of the alkylene oxide content of the poly-ether.

- R2 has a blend average molecular weight in the range of from 130 to 1000 grams/mole; ethylene oxide (EO) content is from 70 to 100 weight percent of the alkylene oxide content of the polyether; and propylene oxide content is from 0 to 30 weight percent of the alkylene oxide content of the polyether;

In order to determine the nominal molecular weight for the different polyalkylene oxide polyethers R1 and R2 the so called blend average molecular weight was used. R1 has a blend average molecular weight in the range of from 3000 to 6000 grams/mole and ethylene oxide (EO) is from 20 to 60 weight percent of the alkylene oxide content of the polyether. R2 has a blend average molecular weight in the range of from 1100 to 2900 grams/mole and ethylene oxide is from 20 to 60 weight percent of the alkylene oxide content of the polyether. In the examples below we will use

85

other types of polyethers that vary average molecular weight in the range of from 130 to 1000 grams/mole, and ethylene oxide is from 70 to 100 weight percent of the alkylene oxide content of the polyether.

This kind of silicone polyether surfactants were used as stabilizers to produce polyurethane foam where the polyol comprises polyether carbonate polyol in an amount of 50 % or greater by weight of the polyol. The silicone polyether surfactant is present in an amount of 0.1 to 5 parts per hundred parts polyol. Details and examples of foam properties are further discussed in the next chapter.

2.5.1. Production of polyether-based flexible polyurethane foams. Comparison of various silicone polyether surfactant structures

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, as described in Table 2.18. It is important to mention that the maximum possible amount of polyether carbonate polyol was selected [22], to achieve the highest sensitivity of the polyurethane formulation.

Table 2.18 *Formulation of the polyether foam used in this study*

Foam Formulation	Pbw
Polyether Carbonate Polyol	100**
Water	4.50
Niax catalyst A-1	0.15
Silicones*	1.00
Niax Stannous octoate	0.20
TDI 80/20	55.00

*various silicones were used in the evaluation, with defined silicone chain length

Table 2.19 presents the properties of the foams obtained using the ether foam formulation described in Table 2.18. We directly went 100% use of polyether carbonate polyol instead of virgin polyol. The foam properties were measured

86

assessed after 24 hours from the foam production of the foam, using similar testing protocols. The density of the reference foam was 23.6 kg/m^3. The reference foam exhibited a 5.4 kPa hardness value, typical for this specific formulation. By changing with other silicone polyether surfactants, collapsing of the polyurethane foam was noticed. That means that these silicone structures, which are the typical structure used in the production of polyurethane foam with virgin polyol cannot act as a good foam stabilizer for this type of carbonate based polyol. Table 2.19 also shows that the addition of another silicone can also stabilize the polyurethane foam formulation leading to good foam properties, as exemplified in Ex. 5S.

Table 2.19 *Properties of the foams obtained using the ether formulation presented in Table 1, and changing only silicone polyether surfactants as for each experiment*

Silicone polyether surfactant EX. number	Ex. 1S	Ex. 2S	Ex. 3S	Ex. 4S	Ex. 5S
PE1 EO Content (%)	40.0	40.0	40.0	40.0	40
PE2 EO Content (%)	**100.0**	40.0	40.0	40.0	**75.0**
Foam physical properties					
Rise time (s)	98.00	-	-	-	98.00
Foam settling (%)	0.80	-	-	-	0.80
Density (kg/m^3)	23.6	-	-	-	23.6
Hardness CFD-40% (kPa)	5.40	-	-	-	5.40
SAG	2.2	-	-	-	2.2
Airflow (l/min)	27.0	-	-	-	27.0
Comments	Good foam	Collapsed foam	Collapsed foam	Collapsed foam	Good foam

A more detailed description of the silicone polyether surfactants from Table 2.19 and their structure property relation is presented below:

87

Silicone Polyether surfactant Ex 1S: Silicone polyether surfactant with two polyether substituents - 4000 MW polyether containing 40% ethylene oxide, and 550 MW polyether containing 100% ethylene oxide

Silicone Polyether surfactant Ex 2S: Silicone polyether surfactant with two polyether substituents - 4000 MW polyether containing 40% ethylene oxide, and 1500 MW polyether containing 40% ethylene oxide.

Silicone Polyether surfactant Ex 3S: Silicone polyether surfactant with two polyether substituents - 4000 MW polyether containing 40% ethylene oxide, and 1500 MW polyether containing 40% ethylene oxide.

Silicone Polyether surfactant Ex 4S: Silicone polyether surfactant with two polyether substituents - 4000 MW polyether containing 40% ethylene oxide, and 550 MW polyether containing 40% ethylene oxide.

Silicone Polyether surfactant Ex 5S: Silicone polyether surfactant with two polyether substituents - 4000 MW polyether containing 40% ethylene oxide, and 750 MW polyether containing 75% ethylene oxide

Examples 1S-5S are for foam formulations using a combination of 100% by weight polyether carbonate polyol. Ex. 1S and Ex. 5S uses the surfactant in accordance with the present technology. As shown, Ex. 1S and Ex. 5S are the only silicone polyether surfactants that provide foam stabilization and typical foam properties. It also provides good foam stabilization, as reflected by the higher final height values, and lower settling. Ex. 1S and Ex. 5S provided foam with adequate porosity values. By comparison, Ex 2S, Ex. 3S and Ex. 4S collapsed the foam, meaning that these silicone structures does not provide adequate foam stabilization to the polyurethane foam. It looks like that only the surfactants designed to have a larger ethylene oxide content in the second polyether pendant (e.g. Ex. 1S and Ex 5S), provided foam stabilization with adequate foam properties. The other surfactants that were tested did not provide adequate foam stabilization, resulting in foam collapse. Ex. 5S presents inventive compositions employing silicone surfactants having different ethylene oxide concentrations in the low molecular weight polyether pendent groups.

In conclusion, 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 Ex. 1S or Ex. 5S, 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 [22].

2.5.2. Partial conclusions

Polyether carbonate polyols are an important step towards reducing carbon footprint. However, many difficulties imped the utilization of such a raw material in a sustainable manner, employing standard silicone polyether copolymers. The breakthrough of the present technology, identified and reported through the recently granted patent [22], was the utilization of a special silicone polyether copolymer that contains the low molecular weight polyether pendant with high amount of ethylene oxide, 75% or even higher. According to this new patented technology, the silicone polyether copolymer enables up to 100 percent incorporation of polyether carbonate polyol for the production of flexible slabstock polyurethane formulation. At our best knowledge, it is the only available technology to afford such a high incorporation of polyols.

The new technology significantly helps reducing carbon dioxide emissions and through this innovative method, to "keep" the carbon dioxide in a mattress for many years. An aim of this technology is a forward looking platform, where according to the ideal scenario mattresses produced based on this process will reach their end of life and instead of landfill, back integration in the polyurethane life cycle will be enabled by either glycolysis or acidolysis, hence, closing the loop of circular economy.

3. Experimental

3.1. Glycolysis

Three different glycolysis procedures have been developed, glycolysis at atmospheric pressure, glycolysis in autoclave, and glycolysis using high-frequency (microwave) apparatus. All three methods used the same starting raw materials in the preparation of the glycolysis product, to minimize potential variations.

3.1.1. Raw materials used for glycolysis

Polyurethane foam waste. A flexible polyurethane foam waste based on polyester polyols was utilized for each experiment. This material, thanks to its strong flame bonding property on various substrates [71;82] and outstanding tensile and elongation properties possesses unique features in automotive as well as textile applications. Therefore, ester slabstock foams are used for textile applications (flame lamination), packaging, filters, etc. As the name implies, for the production of polyurethane foams, polyester polyols, together with TDI and water, are being used. This type of foam has inferior comfort characteristics and is hydrolytically less stable than ether or HR foam. Ester foam is therefore not used for seating or bedding [71]. The foam density is the main characteristic for polyurethane foams and varies from very low densities (15 kg/m^3) to high (80 kg/m^3) for these types of foams. For the scope of this study, average foam waste of 30-35 kg/m^3 was considered.

Figure 3.1. *Flexible polyurethane slabstock foam waste*

Glycolysis agent: Industrial diethylene glycol (DEG) from the company Sigma Aldrich was used for this study. Table 3.1 describes the product specification for DEG. The reason for choosing this material was linked to the hypothesis of good compatibility with the aforementioned foam waste, as well as the increase in the chances of high yield of the recovered products. 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 important to avoid eventual side reactions. For this reason, a maximum concentration of both MEG and TEG was kept below 0.5%. The water content is another important parameter. Foam waste, moisture, raw materials, or catalysts contribute to the total water content of the recovered material. The water content is not expected to have any negative influence, as water is the main chemical expanding agent used in the production of polyurethane foam. This is why a control of the water level in raw materials and the glycolyzed product has to be applied. For DEG, the water content is less than 0.5%.
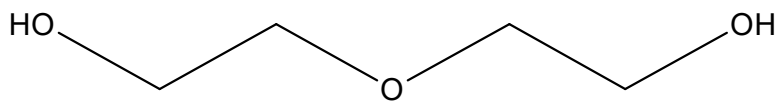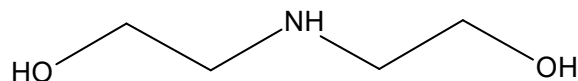

Figure 3.2. Chemical structure of diethylene glycol

Table 3.1 Product specification of diethylene glycol

Diethylene glycol (DEG)	Product specification
Diethylene glycol (DEG) content (%)	99 - 100
Monoethylene glycol(MEG) content (%)	<= 0.5
Triethylene glycol (TEG) content (%)	<= 0.5
Water (%)	<= 0.5
Density (g/cm3)	1.115 – 1.125

Catalysts – For the glycolysis study, diethanolamine (DEOA) (Sigma-Aldrich) has been used. Table 3.2 presents the product specification for DEOA. The general

91

use level of DEOA in the glycolysis process is rather low; hence, purity of the product should be kept as high as possible, to avoid undesired side reactions or eventual lack of depolymerization. The water content is also important, and it has been specified for DEG. The same rule should apply for DEOA as for DEG.

Figure 3.3 *Chemical structure of N,N-bis(2-hydroxyethyl)amine (diethanolamine)*

Table 3.2 *Product specification of diethanolamine*

| Diethanol amine (DEOA)	Product specification
Diethanol amine (DEOA) content (%)	99 - 100
Monoethanol amine (DEOA) content (%)	<= 0.5
Triethanol amine (DEOA) content (%)	<= 0.5
Water (%)	<= 0.15
Refractive index (NUM)	1.4770 – 1.4790

3.1.2. Glycolysis methods

Three glycolysis methods have been investigated, targeting the performance relationship versus various parameters, such as temperature, pressure, time, and the amount of polyurethane foam waste. It is important to mention that all three glycolysis methods used the same type of foam waste, as well as the same batches of DEG, respectively, DEOA. This selective approach to raw materials enables minimization of potential variations triggered by the raw materials. It is important to understand which methods provide the best balance between yield of the recovered polyol and the possible industrial implementation.

3.1.2.1. Glycolysis at atmospheric pressure

DEG and the DEOA catalyst were introduced into a 4 neck balloon, equipped with an agitator, distillation column, and nitrogen blanket (Figure 3.4). The oil heating bath was equipped with a temperature control system and a magnetic stirrer. The

92

material was gently stirred at 75 rpm, while the temperature of the bath increased. The bath temperature was pre-set for 180°C. The polyurethane foam waste was cut in small pieces that would not exceed 0.5 cm in size. Once the temperature reached 160°C, the first change of polyurethane foam waste was added through the fourth neck to the DEG/ DEOA mixture. The stepwise addition of the foam waste is necessary for this specific procedure. The reason is that the foam waste absorbs the raw materials used for glycolysis, and hence, to avoid blocking the agitator, stepwise addition was required. A rate of one-tenth of the foam waste was added every ten minutes until the entire foam waste was added to the mixture. Consecutively, the polyurethane foam degradation occurred, hence allowing a new charge of PU foam waste to be added, followed by the same material absorption into the freshly added foam waste, and that leads to mixing difficulties. Toward the last sequences of the foam waste addition step, difficulties of glycolysis were observed. The optimum ratio was identified as 1 part of polyurethane foam waste to 3 parts of DEG. The catalyst level was kept constant. The equipment used for this evaluation is a property of Momentive Performance Materials.
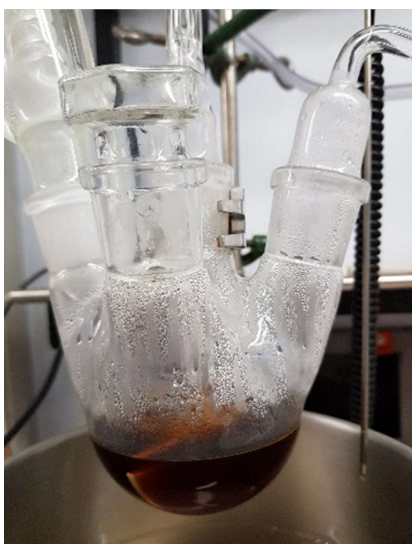
Figure 3.4 Glycolysis product obtained at atmospheric pressure

3.1.2.2. Glycolysis in autoclave

For this test, a standard metal autoclave, composed of the main autoclave body, a cap equipped with an adequate sealing system, and an eight screw system, was used. Unlike glycolysis at atmospheric pressure, in this case the stepwise addition of PU foam was not possible. Therefore, first, the total amount of PU foam waste was added into the autoclave, and a pressing system was used, allowing the whole PU quantity to be added, calling it one-shot process. DEG and DEOA were added to the PU foam waste. The autoclave was hermetically closed using its screw system. This press system process allowed a higher amount of PU foam waste to be added for glycolysis. The autoclave was placed in an oven and various temperatures from 160 ° C to 180 ° C were tested, for about two hours. The autoclave has definitely a bigger advantage versus atmospheric pressure glycolysis, allowing a higher use level of polyurethane foam waste to be glycolyzed in a one-shot process. The optimum was considered to be 1 part of PU foam waste with 1 parts of DEG, although later results will show that this method allows even 2 parts of PU foam waste to 1 part of DEG. The catalyst level was kept constant to 0.1%. as in the first example.

3.1.2.3. Glycolysis using a microwave equipment

This method is similar to the autoclave protocol, with the main difference that a microwave was used instead of a standard oven [43]. The glycolysis conditions were 190°C for 10 min, applying a 1:2 PU foam waste vs. DEG ratio. This method enables a much shorter time to complete the decomposition of PU foam, although a potential industrial application would eventually involve a huge equipment cost and energy consumption. Moreover, the 1:1 ratio of PU foam waste versus DEG was very difficult to obtain, due to the fact that there was not enough DEG to cover and interact with PU foam.

3.2. Flexible polyurethane ester foams obtained with the glycolyzed product

A polyurethane ester foam was made at the laboratory stage using the raw materials and methodologies described in the following subchapters.

3.2.1. Preparation of polyester-type polyurethane foams

For the experimental evaluation, a polyester foam formulation was selected and described in the original contribution part in Table 2.4. The recycled polyol behavior was evaluated under different foam conditions. A standard mixing station with variable rotation speed, equipped with a standard impeller has been used for foam preparation. The rise profile was recorded using a sonar sensor connected to the data acquisition software. The laboratory methodology for the preparation of the polyester foam started with the mixing of amine catalysts, water, and silicones until blend clarity. Separately, the polyols and TDI were weighed in a 1.5 L cup, slightly stirred until the mixture became clear, then mixed using the equipment described above for 8 sec. Subsequently, the amine premix was added to this mixture using a syringe, continuing to mix for another 8 sec. The resulted liquid foam was poured into a paper box having the dimensions 20x20x20 cm. The foam rise profile was recorded and the foams were cured in a forced air oven for 15 min, followed by cooling for 24 h [82]. The equipment described above, and the procedure thereof, are properties of Momentive Performance Materials.

3.2.2. Instrumental methods

3.2.2.1. FT-IR analysis

FT-IR spectra were recorded using Bruker Vertex 70 spectrometer equipped with Platinium ATR, Bruker Diamond Tip A225/Q.1., at room temperature (4.000-400 cm-1) with a nominal resolution of 4 cm-1 with 128 scans.

3.2.2.2. Thermogravimetric analysis (TGA)

TGA thermograms were recorded using TG 209 F1 Libra (NETZSCH-Gerätebau GmbH, Selb, Germany) thermo gravimetrical analyzer. The measurements were carried out in nitrogen atmosphere, in the temperature range 20–600°C, heating rate of 10°C/min. The data were processed with the Netzsch Proteus—Thermal Analysis program version 6.1.0. (NETZSCH-Geraetebau GmbH, Selb, Germany).

3.2.2.3. Scanning electron microscopy (SEM)

For the microstructural analysis the samples surfaces were characterized by scanning electron microscopy (SEM: Quanta FEG 250, FEI, The Netherlands) using back scattered electron detector (BSD).

3.2.3. Assessment of physical properties of the polyester foam

The physical properties of the foam were assessed using foam samples produced with the ester formulations presented in Table 2.4. Before physical property tests, all samples were conditioned at 23°C, 50% humidity and 1000 mbar atmospheric pressure. Foam density was measured in 10x10x5 cm foam samples according to DIN 53420. Compression force deflection (CFD) at 40%, expressed in kPa, was measured on 10x10x5 cm foam samples, according to the ISO3386 / 1 test method. Foam porosity or airflow, expressed in liters per minute (L/min), was measured on 5x5x2.5 cm foam samples according to the ISO7231 test method. Cell structure was characterized by visual observation, while cell size and distribution were assessed by cell count along a 1 inch axis, expressed in pore per inch (PPI), using BS 4443 part 1, method 4 [82].

3.2.4. Formulations and raw materials of the polyester foam

The polyester foam formulations used in this work were developed in house and are shown in Table 2.11. The reason for using a different level of recycled polyol use was to assess the behavior of the recovered material against virgin polyol for polyester foam applications. In terms of polyester foam formulation, the objective was to develop formulations sufficiently close to those used in industry today, resulting in best foam performances for polyester production, giving fine cell structure, stable foam, and good foam porosity. At the same time, the developed formulation was sensitive enough to allow the identification of possible performance shifts.

For this work, the following raw materials were used: a commercially available polyester polyol for the production of polyester polyurethane foams, Desmophen 2200B from Covestro, and toluene diisocyanate (TDI 80/20) from BAFS , available under the commercial name Lupranate T-80. The selected amine catalysts were Niax catalyst C-131NPF and Niax catalyst DMP gel catalyst, from Momentive Performance Materials. The silicon surfactant Niax L-537XF, also from Momentive Performance

Materials, was used. A similar foam formulation has been reported in the literature [82], except for the use of recycled polyol and additional small formulation adjustments. All raw materials, with the exception of recycled polyol, are commercially available.

Desmophen® **2200B** is a partly branched polyester polyol based on adipic acid, diethylene glycol, and trimethylol propane. At room temperature is a highly viscous, slightly yellowish liquid, used to manufacture flexible polyurethane slabstock foams [86].

Table 3.3 *Product specification of* Desmophen® 2200B [86]

Desmophen 2200B	Method	Unit	Values
Density 25°C	DIN 51757	g/cm^3	1.18
Appearance	PET-03-04		colorless to pale liquid
Specific heat capacity (Cp) at 25°C	DIN 51007	kJ/kg.K	1.85
Pour point	DIN ISO 3016	°C	-13.0
Flash point	DIN 51758	°C	> 200
TDI basic value			9.3
Thermal conductivity at 20°C	DIN 52612-1	W .m^{-1}. K^{-1}	0.19

Niax Catalyst C-131NPF from Momentive is a medium viscosity, low odor, water-soluble tertiary amine. Foams made with Niax catalyst C-131 exhibit significantly lower odor levels than those made with highly odorous conventional ester foam catalysts, such as N-ethyl morpholine (NEM), N-methyl morpholine or dimethylbenzylamine. The emission of amine vapors in the foam is substantially reduced when NEM is replaced with NiaxTM catalyst C-131. It exhibits the lowest possible odor in a high-performance tertiary amine ester catalyst. It has activity similar to that of NEM or other similar ester catalysts. Typically, 2.0 to 2.4 parts of Niax catalyst C-131 will replace approximately 2.0 parts of NEM. Provides excellent processing characteristics, producing a smooth consistent rise profile. Furthermore,

the NiaxTM catalyst C-131NPF may help compatibilized some of the difficult-to-handle additives used in ester foam processing [87].

Dimethyl piperazine (DMP), was supplied by Sigma-Aldrich.
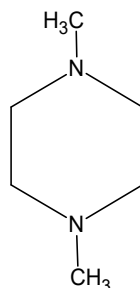
Figure 3.5 *Chemical structure of dimethyl piperazine*

Table 3.4 *Product specification of dimethyl piperazine*

Dimethyl piperazine (DMP)	Unit	Values
Density at 25°C	g/cm^3	0.84
Refractive Index	n20/D	1.4463
Boiling point	°C	131-132
Assay	%	98.0

Niax silicone L-537XF is an all-purpose silicone stabilizer for polyester formulations. It provides excellent stabilization of the fine cell structure and reduces the need for organic surfactants and emulsifiers. It is generally used for a wide range of polyester slabstock formulations [88]

3.3. Preparation of polyether-type polyurethane foams

For the experimental evaluation, a polyether foam formulation was selected (Table 2.11), and the behavior of recycled polyol was evaluated under different foam conditions. The equipment used for foam preparation was similar to the one described in ester foam preparation (section 3.2.2), while the foaming procedure differs. The

following procedure was used in the laboratory for the preparation of ether foam: polyols, silicone, and amine catalysts were weighted into a 2 L cup and stirred for one minute. Stannous octoate was added while the stirring was paused. The TDI was quickly added after restarting the stirring and continued to stir for 8 sec. Once the mixing process was completed, the liquid foam was poured into a 20x20x20 cm paper box. The foam rise profile was recorded, and the foams were cured in a forced air oven for 15 minutes then cooled for 24 h [82]. The equipment described above, and the procedure thereof is property of Momentive Performance Materials.

3.3.1. Assessment of the physical properties of polyether foam

Similar physical properties were assessed as for the polyester foam procedure. The physical properties of the foam were obtained using foam samples produced with the ether formulations in Table 2.11. Before physical property tests, all samples were conditioned at 23°C, 50% humidity and 1000 mbar atmospheric pressure. Foam density was measured in 10x10x5 cm foam samples according to DIN 53420. Compression force deflection (CFD) at 40%, expressed in kPa, was measured on 10x10x5 cm foam samples, according to the ISO3386 / 1 test method. Foam porosity or airflow, expressed in liters per minute (L/min), was measured on 5x5x2.5 cm foam samples according to the ISO7231 test method. Cell structure was characterized by visual observation, while cell size and distribution were assessed by cell count along a 1 inch axis, expressed in pore per inch (PPI), using BS 4443 part 1, method 4 [82].

3.3.2. Formulations and raw materials

The polyether foam formulations used in this work were developed in-house and are shown in Table 2.11. The raw material differs from ester foam; only the isocyanate and recycled polyols are raw materials part of the ester formulation presented in Table 2.4. The same target as previously mentioned for recycled polyol was used in this formulation to assess its behavior against virgin polyol this time in polyether foam applications. In terms of polyether foam formulation, a 4.5 part water formulation would lead to a density of 25kg/m^3 or slightly lower, the average density considered for polyether foam formulations.

For this work, the following raw materials were used: Voranol 3322 from Dow Chemicals. Isocyanate, toluene diisocyanate from BAFS, available under the commercial name Lupranate T-80, was used. The amino acids, Niax catalyst B-18,

and Niax stannous octoate were provided by Momentive Performance Materials. Silicone surfactant Niax Silicone L-595 from Momentive Performance Materials was used. All raw materials, with the exception of recycled polyol, are commercially available.

Voranol™ 3322 Polyol is a general purpose heteropolymer triol with nominal molecular weight of 3400, used in the manufacture of flexible slabstock polyurethane foams. It processes well on all types of foam machinery and can be used both with and without auxiliary blowing agents, producing a wide range of foam grades ranging from low to high density [89].

***Table 3.5** Voranol 3322 typical properties [89]*

Voranol 3322 - typical properties	Unit	Values
Density 25°C		1.02
Appearance		liquid, viscous
Hydroxyl number	mg KOH/g	45.5-49.5
Water max	%	0.08
Acid number, max	mg KOH/g	0.05
Color, max	APHA	30.00
Viscosity, 25°C	cSt	500-600
Flash point	°C	> 200

Niax catalyst A-1 is an amine catalyst for urethane foams, having a remarkable ability to facilitate chemical reactions on its own or as part of an amine catalyst system. Contains 70% bis (2-dimethylaminoethyl) ether, one of the most active catalysts currently used in the industry. Niax catalyst A-1 promotes the basic chemical reactions between polyol and isocyanate as well as water and isocyanate with high efficiency, and can improve the polyether foaming process of high-density unfilled foam, filled foam, high load-bearing flexible foam, low-density foam, and high-resilience molded foam.

100

Compared to the next most active amine catalyst, a mixture of triethylenediamines, Niax catalyst A-1 can enable a 10% higher specific rate constant in the chemical reaction between polyol and isocyanate. Moreover, Niax catalyst A-1 can enable a specific rate constant 50% greater than triethylenediamine in the chemical reaction between water and isocyanate.

The powerful effect of Niax catalyst A-1 on the reaction between water and isocyanate helps promote a controlled acceleration of the chemical reaction between polyol and isocyanate through small variations in the level of stannous octoate. This is an important feature in the production of commercial open-celled, split-free, flexible urethane foam. Another important feature of Niax catalyst A-1 is the ability to adjust the levels used over a broad range, to effectively control foam rise time and without sacrificing the operating range of stannous octoate [90].

Niax silicone L-595 is a high-performance silicone surfactant, proving as an excellent candidate for producing a wide variety of conventional slabstock foam. It typically demonstrates a broad process latitude in all grades of conventional flexible foam, including low-density foams that use a high loading of auxiliary blowing agents. It may also provide good stability for slabstock foam using a liquid CO_2 process [91].

Niax Stannous octoate is gel catalyst characterized by a fast gelling reaction, low use level, and relatively safe processing. The most important application of this catalyst is documented in the isocyanate and polyol reaction of manufacturing flexible polyurethane foams [92].

TDI/80/20, commercial name Lupranate T 80 A, is an isomer mixture of 80 % 2,4- and 20 % 2,6-toluene diisocyanate, obtained from the BASF company (Germany). Lupranate T 80 A must be protected from moisture. Oxygen and UV-light cause discoloration, which normally does not affect the processing of the material. The ideal storage temperature is between 20°C and 25°C. Under these conditions and if moisture and oxygen are excluded, Lupranate T 80 A can be stored for at least 12 month, but the storage tanks should be covered with nitrogen [93].

Storage at a higher temperature can lead to discoloration and to the formation of solids. These solids cannot be dissolved by heating. Storage for longer periods under + 15 °C can lead to crystallization. Crystallized material must be melted out by short-term heating in a hot air oven. The product temperature must not exceed 40°C.

101

Local overheating must be avoided, as Lupranate T 80 A will decompose with the formation of gas at temperatures above 250°C. Rolling of the drums in a hot air oven is the recommended method for dissolving the crystals. After melting out, the contents of the drum must be thoroughly mixed [93].

Table 3.6 Lupranate T-80 A typical properties [93]

Lupranate T-80 A properties	Method	Unit	Values
Appearance			Colorless liquid
Color number	DIN EN ISO 6271-2	HAZEN, APHA	10.00
Purity	EN ISO 14896	g/100 g	99.5
NCO-content	EN ISO 14896	g/100 g	48.2
2,4-Isomer	GC	g/100 g	80.5
Acidity, as HCI	ISO 14898	mg/kg	15.0
Hydrolysable chlorine	ISO 15028	mg/kg	40.0
Viscosity at 25 °C	DIN 51 550/53 018	mPa·s	3.0
Density at 25 °C	DIN 51 757	g/cm³	1.22

Labeling, transportation, storage, processing, waste treatment, and disposal of isocyanates must comply with national safety regulations.

3.4. Acidolysis of polyether-type polyurethane waste with carboxylic acids

The laboratory method involved shredding of the polyurethane foam waste in small pieces that would not exceed one cm length, width, or height. To do so, a special shredder was used, which allowed a uniform size of the shredded polyurethane foam. Next step, once the shredded foam was added to the autoclave, a homogeneous mixture of diethylene glycol, acid, and Desmophen 2200B has been prepared. Without premixing the three different raw materials we would not have been able to expose the shredded foam and the liquid to a uniform final mixture. The autoclave process is

free from any mixing protocol, a simplistic addition of the liquid phase on top of the solid phase, followed by closeting the autoclave with an 8-screw system, to ensure a fully sealed system. The autoclave was placed in an oven at predefined temperature of 180°C to carry out depolymerization. Once the time has been completed, we let the system to cool down, and the material was collected in a glass recipient. The autoclave was cleaned and dried appropriately, and the next set of experiments, employing different acid, was performed identically. All relevant results are reported in Table 2.10.

3.5. Polyether-type polyurethane foams obtained with repolyol from industrial acidolysis

The recycled polyol was obtained at industrial scale by an acidolysis process which uses flexible polyurethane foam waste supplied by IKANO (Poland).

3.5.1. Flexible polyurethane ether foam

The conventional polyether foam formulation was selected according to the experimental protocol presented in Table 25. The equipment used for foam preparation was a standard bench mixing station (manufactured by Pendraulik Maschinen und Apparate GmbH, Springe, Germany) with variable rotation speed, equipped with a standard impeller and rate of rise system (Format Messtechnik, Karlsruhe, Germany). The following raw materials were used for the preparation of polyurethane foam: standard polyol, under commercial name Voranol 3322, from Dow Chemicals (Midland, Michigan, U.S); recycled polyol obtained industrially by acidolysis process which uses flexible polyurethane foam waste, produced by the company IKANO Industries (Rogoźno, Poland); toluene diisocyanate, available under the commercial name Lupranate T-80, from BASF (Ludwigshafen, Germany); Silicone L-895 and Niax Stannous Octoate, supplied by Momentive Performance Materials (Leverkusen, Germany).

3.5.2. Amine catalysts

Three different amine catalyst were used: Bis-[2-(*N*,*N*-dimethylamino)-ethyl]-ether (Amine 1) and 1,4-Diazabicyclo[2.2.2]octane (Amine 2), were from Sigma Aldrich (Steinheim, Germany), while N,N'-Bis[3-(dimethylamino)propyl]urea

(Amine 3), available under the name Niax Catalyts EF-700, was supplied by Momentive Performance Materials (Leverkusen, Germany).
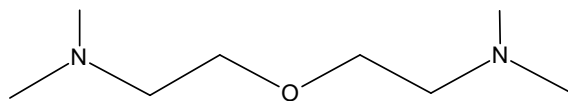
**Figure 3.6** *Bis-[2-(N,N-dimethylamino)-ethyl]-ether (Amine 1)*

Bis (2-dimethylaminoethyl) ether, is one of the most active catalysts currently used in the flexible foam industry. This catalyst can improve the polyether foaming process of high-density unfilled foam, filled foam, high-load-bearing flexible foam, low-density foam, and high-resilience molded foam. Typically, because of its high activity, the amine catalyst is diluted in glycols, for easier metering.

Compared to the next most active amine, a mixture of triethylenediamines, Niax catalyst A-1 [90] can enable a 10% higher specific rate constant in the chemical reaction between polyol and isocyanate. Moreover, the Niax catalyst A-1 can enable a specific rate constant that is 50% greater than triethylenediamine in the chemical reaction between water and isocyanate [92].
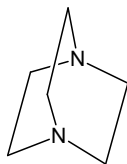
Figure 3.7 *1,4-Diazabicyclo[2.2.2]octane (Amine 2)*

Triethylene diamine, a tertiary amine compound, is used as a catalyst or cross-linker in the urea reaction as well as in the urethane reaction in the production of polyurethane foams, elastomers, and adhesives. TEDA has a strong catalyst effect for the reactions of alicyclic and aliphatic isocyanates, whereas it is less active in reactions of aromatic isocyanates.
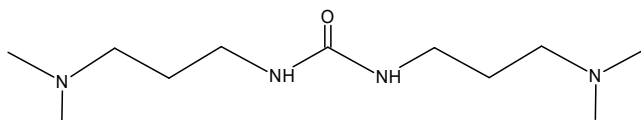
Figure 3.8 *N,N′-Bis[3-(dimethylamino)propyl]urea (Amine 3)*

104

N,N'-Bis[3-(dimethylamino)propyl]urea, commercial name Niax™ catalyst EF-700 [94], is a low odor tertiary amine used as an industrial catalyst by Momentive. The nonvolatile nature of this amine is the result of a molecular design and high molecular weight. As such, this amine is not expected to adversely affect typical foam physical properties. The first application considered for this catalyst was in automotive seat-molded foams, where interior fogging and emissions must be minimized. Can be also considered a possible candidate in flexible slabstock applications for conventional, volatile, blow-amine, when reduction of emissions is needed. It is an effective blow amine that can be used to control cream time during the manufacture of polyurethane flexible foams. The Niax™ catalyst EF-700 by Momentive is designed to minimize or eliminate amine emissions in automobile interiors.

3.5.3. Flexible polyether foam formulation

Table 3.7 *Formulation of the flexible polyether foam used in this study*

Foam Formulation	Pbw*
Standard Polyol	100 – 70
Recycled Polyol	0 – 30
Water	4.50
*Amine Catalysts**	*vary*
Niax Silicone L-895	1.00
Niax Stannous Octoate	0.15
Index TDI (TDI 80/20)	*108*

*Pbw=parts by weight or parts; **Catalyst amount was optimized for each set of experiments to allow for a similar reactivity profile

Niax Silicone L-895 is a high potency silicone with low emission properties for the production of flexible slabstock foam. As a high-performance stabilizer, this silicone is an excellent candidate for well-balanced processing, good foam porosity, fine cells, and superior density distribution.

3.5.4. Physical properties of the foam

Foam density was measured in 10x10x5 cm foam samples according to DIN 53420. Compression force deflection (CFD) at 40%, expressed in kilopascal (kPa), and SAG were measured using 10x10x5 cm foam samples, according to the ISO3386 / 1 test method. Foam airflow, expressed in litters per minute (l/min), was measured on 5x5x2.5 cm foam samples, according to the ISO7231 test method. The cell structure was characterized by visual observation [82].

Emission tests were performed according to the internationally accepted VDA-278 standard procedure for nonmetallic materials, largely used for testing emissions or high, medium, and low volatility compounds. VDA 278 measures the occurrence of volatile compounds within the test material: these analyzes are represented by the total VOC for compounds with high and medium volatility and the total FOG for compounds with low volatility [95].

3.6. Synthesis of silicone surfactants

Silicone surfactants have been produced using raw materials described in Figure 3.9. The silane fluid is described by the general formula MDxD'yM. The typical synthesis reacts D4 and M as well as D' [20]. The equilibration process between the aforementioned raw materials takes place at room temperature in the presence of catalyst, under continuous mixing.

Figure 3.9 *General reaction of the silicone surfactant*

The most commonly used catalyst is sulfuric acid, at approx. 1-2% in the formulation. The process takes about 12 h until full equilibration. Longer chains of silicones require higher equilibration times. After the equilibration step is completed, the catalyst is neutralized, and residual cyclic volatile siloxanes are removed using a vacuum system.

4. General conclusions and main achievements

The main objective of the thesis was to reduce the amount of polyurethane (PU) waste resulting from the synthesis and processing of this important category of plastic material and, ideally, to define protocols that can be applied at large scale. It is a topic of great global interest. Considering the huge amounts of waste generated and considering the new regulations in regard to waste, sustainability, and circular economy, it is essential that the polyurethane industry can find new ways to recover PU waste.

Chemical recovery can still be considered one of the less explored areas in the industrial-scale recovery of flexible polyurethane foam waste. Therefore, we identified unexplored ways to address the chemical recycling of flexible polyurethane slabstock foam and the possible benefits that these solutions can bring to the industry by implementing the technological pathways reported in this thesis. We achieved this goal following subsequent steps, which are described in detail in the thesis.

The first step was to obtain a detailed understanding of the existing scientific literature and patents in the field of chemolysis of flexible polyurethane foams. The objective in this step was to critically evaluate the different methods of chemolysis applied so far, in an attempt to quantify the results and identify innovative routes that can strengthen this technology at the industrial level.

Another step was the more elaborate analysis of the possibilities of chemolysis, looking for suitable methods to improve the synthesis yield, simplify the technology, and achieve the needed characteristics. A third and very important step was to optimally incorporate the resulting waste back into the polyurethane foam, trying to close the loop for this thermoset material. A diversity of specific polyurethane foams, from different types of waste, was studied; hence, we depolymerized waste polyurethane foams of both the ester type, using the glycolysis method and the ether type, using the acidolysis method.

The title of the research topic "New methods to produce flexible polyurethane foams with a positive impact on the environment" was chosen to highlight the environmental impact of recycling flexible polyurethane waste. In addition, new innovative solutions from the perspective of silicone polyether copolymers have been studied and included in an issued patent, to reveal further steps in reducing the carbon footprint by using special polycarbonate-polyols. This work allowed us to close the

107

loop in the production of flexible polyurethane foams by recovering foam waste, creating recyclable raw materials, and producing again a polyurethane foam block, as indicated in Figure 4.1.
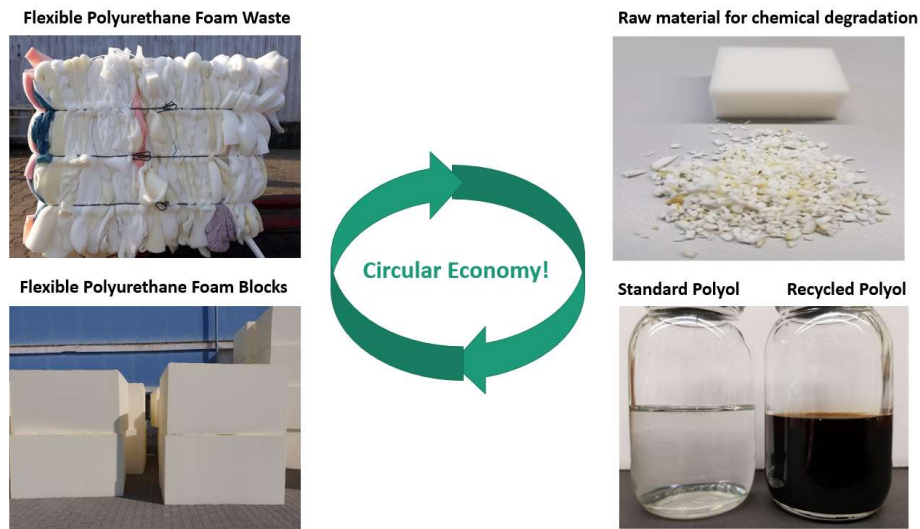
Figure 4.1 *Schematic description of recycled polyurethane foam waste in the circular economy concept*

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

109

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. Another important aim is to provide a forward-looking platform for the technologies mentioned in this original contribution. The future ideal scenario will be that finished articles, such as mattresses, will be produced based upon this technology, and once they reach end-of-life, instead of landfill, a sustainable back-integration in the polyurethane life cycle will be enabled by using either glycolysis or acidolysis degradation processes, as described in the original contribution. In addition, with special silicones, a more environmentally friendly production process can be enlightened, thus closing the loop of the circular economy. By doing so, we can provide sustainable chemical products for a sustainable planet, for us and for the next generations.

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Acknowledgements

List of publications

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