


The role of recyclates in the polyurethane industry: Environmental and economic aspects

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Abstract

The main objective of this article was to provide an overview of the polyurethane industry and waste treatment methods to identify the best method for polyurethane (PUR) reprocessing (recycling). To understand the need for recycling, existing knowledge will be referenced. Many literature studies discuss the role of recyclates in the polyurethane industry. According to these, the best available options to recapture value, for example, from raw materials, are polyurethane recycling and energy recovery.

The research material was created via the glycolysis of polyurethane foam scrap. The experiments in this work include the glycolysis of polyurethane foam with a complex discussion of materials (polyurethane foam, glycols, catalysts, and properties of the obtained recyclate).

Based on the research, analyses, and tests carried out related to glycolysis, the most appropriate conditions to recover polyols from scrap were the following reaction conditions: temperature 170–190°C; pH – basic; and atmosphere (air), which was the same for all samples. A total of 14 samples were tested. Two samples GL:12 [6:1] and GL 13 [8:1] were further investigated. The numbers presented in brackets [6:1] mean that a ratio of 180 g of polyurethane foam and 30 g 1-3-propyleneglycol was used. The outstanding properties of glycolysate samples called GL:12 [6:1] and GL 13 [8:1] were achieved thanks to the ranges of the basic parameters (dosage time, time after dosage). The sample GL:12 [6:1] – dosage time 20 min and time after dosage 15 min and the GL 13 [8:1] sample – dosage time 22 min and time after dosage 15 min. The apparatus used for glycolysis included: reactor +heater, stirrer, feeder, reflux condenser, thermocouple, and temperature regulator.

By analyzing the obtained results, it can be concluded that the most promising polyurethane waste management process is glycolysis.

Introduction

Due to the current demand for multi-use and long-lasting materials, we can observe dynamic progress in the production of polymeric materials. Determining the role of recycled polymeric materials in environmental protection has become one of the most important subjects of recent studies. The wide range of unique properties (lightweight,

durable, flexible, versatile, and strong) have resulted in their use in nearly all branches of industry – from packing to the wings of airplanes.

Polymeric materials meet the challenge of creating a final product that has a desirable form, high quality, high performance, and is affordable. As we can see, polymeric materials possess very high usability and can enhance our quality of life; however, the amount of polymeric waste in developing

countries increases as the quantity of consumed polymeric materials increases (Zevenhoven, 2004).

Unfortunately, the natural environment is not equipped to deal with reusing these types of materials. To conserve natural resources and reduce environmental impacts, the management of post-consumer plastic products is an urgent task due to the non-biodegradable and non-renewable nature of these materials. What is more outstanding, their physicochemical properties make them resistant to many different factors. During production and their life-cycle, some of their advantages complicate their further processing, which may cause many polymeric scraps from different industries to be discarded, which exhausts landfill spaces. The origins of plastic wastes are presented in Figure 1 (Eunomia, 2017).

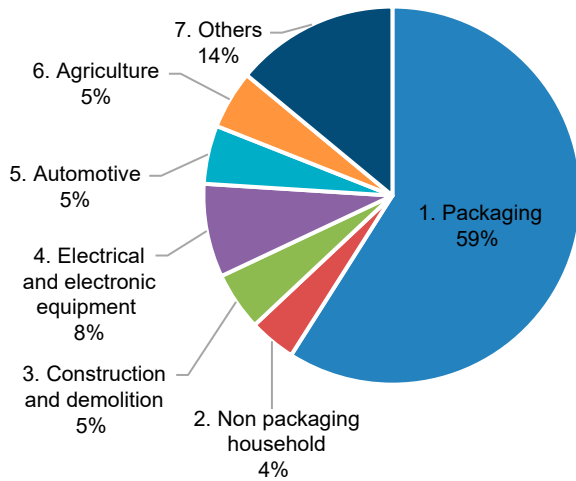


Figure 1. EU plastic waste generation (Eunomia, 2017; European Parliament, 2018)

Plastics have countless industrial and consumer applications. According to Figure 1, plastics are used in key sectors, such as packaging, agriculture, construction, automotive, and electrical equipment.

In Poland, the current plastic usage exceeds 1 mln tons per year, which indicates how important

proper waste management is (Goleń, 2017). There are three ways of solid waste management: incineration, landfilling, and recycling. Thus, this research aims to identify the best method of polyurethane (PUR) reprocessing (recycling).

A more reasonable and environmentally friendly strategy of solid waste management, rather than landfilling and incineration, is recycling and recovery.

In addition to benefiting the environment by reducing the amount of scrap discarded to landfills and discouraging people from illegally dumping plastics, recycling is also valued for the recovery of raw materials from waste matter. Polyurethanes play an important role in sustainable development, which means that they “satisfy people’s current needs without compromising the needs of future generations” (United Nations, 1978).

Due to the properties that have been previously mentioned, polymeric materials can undergo recycling and energy recovery, which directly contributes to conserving resources, reducing waste, minimizing pollutant emissions, safety, energy efficiency, fuel savings, and lowering production costs (which makes the obtained product affordable).

The recycling of polymeric materials is an environmentally friendly waste management policy. The chemical recycling of polyurethane foam is of great environmental importance, and the obtained product also has favorable economic aspects – the obtained repolyol is cheaper than standard polyol (Sołtysiński et al., 2018).

Literature review of the options for the waste management of plastics

Many years of studies, testing, and research have shown that there is a huge demand for different methods to recycle and recover polyurethanes that are simultaneously environmentally friendly and economically useful. The reuse of polyurethanes can

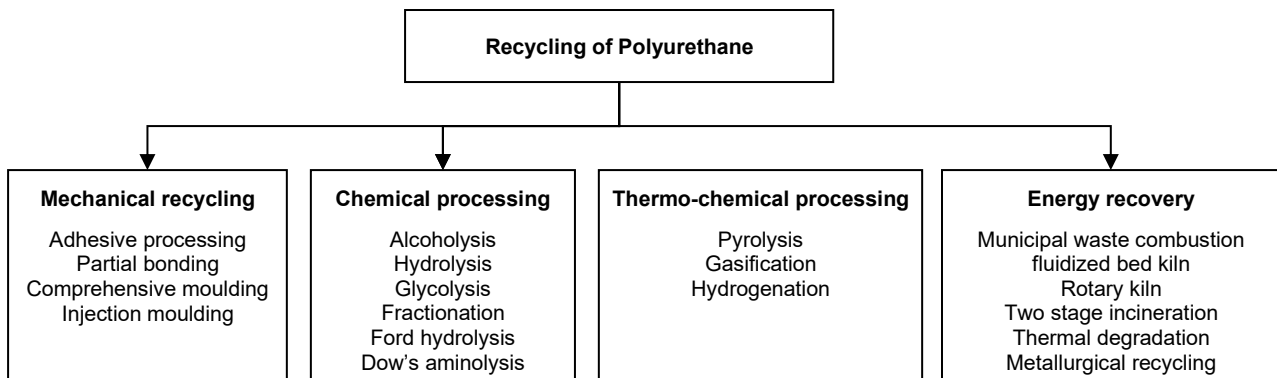


Figure 2 Recycling of polyurethane (Weigand, 1996)

be performed by few different methods (as shown in Figure 2): material recycling, chemical recycling (feedstock), and energetic recycling called, which is also called energy recovery (Rittmeyer et al., 1994; CLG, 2008).

However, to choose the most suitable solution, some criteria should be taken into consideration: location and existing permits, waste market, possible effects, future application of recyclate, available treatment techniques, and market capability to assimilate recyclate. The various recycling technologies are presented in Figure 2 (Mahmood Zia, Nawaz Bhatti & Ahmad Bhatti, 2007).

Materials and methods

The aim of this study was to determine the best of polyurethane recycling strategy. To accomplish this goal, first, a discussion of available options for polyurethane recycling is needed. Below, possible methods to recover polyols from scrap are presented.

Mechanical recycling

Mechanical recycling, also called physical recycling, is the recycling of polyurethane particles. Recycling is carried out under a high pressure, high heat, and, in some cases, high shear stress. The rebonding of flexible foam binds 90% particles with 10% polyurethane binders and is carried out under pressure and heat (CLG, 2008).

During particle bonding from 30 to 70%, polyurethanes are bound and then serve as a base for different kinds of components.

The compression molding process recombines 100% of polyurethane particles under such factors as heat, high pressure, and shear stress (Scheirs, 1998).

In powdering at the 20% load level, polyurethane powder can be transformed into a new PU product.

The simplest way to reuse polyurethane foams is by grinding and applying them as a filler in the packaging of sensitive goods. Powdered material can be introduced as an extender to thermoplastic materials. Soft, reground foams may also undergo moulding under pressure without a bonding agent. Previously-pressed powdered polyurethane foams with bonding agents can also be pressed with an auxiliary agent such as carbon fibre (ISOPA, 2001).

Chemical recycling

Chemolysis (depolymerization) is a recycling process in which high-molecular-weight polyurethanes,

a polyaddition material, and condensed polymers are broken down into smaller building blocks. The obtained chemical materials can be reused to make new polyurethanes with properties of the raw materials. Another important conclusion about chemolysis is that the obtained recycling product has nearly the same functionality and properties as the precursor and, thus, can be used in the same applications. The described recycling process can involve the alternation to energy recovery, feedstock recovery, and mechanical recycling. The main aim of chemical recycling is to obtain liquid degradation components from polyurethanes that are functional, to obtain a new material for the production of new polyurethanes (Campbell & Meluch, 1976).

The most commonly used reagents in chemolysis, whose function is to break urethane bonds are: water, amines, and glycols. The most favorable conditions for chemolysis are when a homogenous waste stream with a known content can be used. In the case of mixed waste streams, the best possible solution is gasification, which involves heating a plastic, followed by combining it with air/O₂. The product of the reaction is CO+H₂ (syngas), which can be used in the industry (refinery) to produce ammonia, oxo-alcohol, and methanol. The chemical recycling methods of polyurethanes are presented in the ISOPA Fact Sheet 2001 (Figure 3).

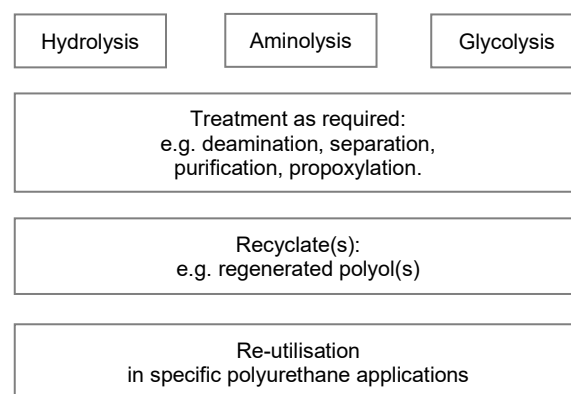


Figure 3. Chemolysis (ISOPA, 2001)

Hydrolysis can be briefly described as the process in which a polyurethane foam reacts with water at a high temperature and pressure. This produces two groups of chemicals: diamines (hydrolysis products of diisocyanates) and polyether polyols. These components are then separated depending on the further destination (reprocessing or re-sing). Polyols can serve as fuels, whereas amines can be used to make polyurethane raw materials (Mahoney, Weiner & Ferris, 1974).

During aminolysis, a polyurethane foam reacts with amines such as dibutylamine, ethanolamine, and lactam adducts, at high temperatures and under pressure. The aminolysis process is under investigation.

Glycolysis is a process in which a polyurethane foam is chemically mixed with diols above 200°C to cleave covalent bonds. It is a process where cross-linked, high-molecular-weight solid polyurethanes are broken down into lower-molecular-weight liquid products. Split-phase glycolysis separates the product into two phases. These include a the top layer, which is a flexible foam polyol which, after purification, can be used alone to make the same flexible foam again. The second phase is the bottom layer, which, after post-treatment with propylene oxide, can be converted into a high-quality rigid polyol (Scheirs, 1998).

Feedstock recycling

The feedstock material such as post-consumer and post-industrial waste plastics are used in the petrochemical and chemical industries. In order to obtain the highest efficiency and due to economic purposes, it must be performed on a 100,000 tones scale. The main advantage of this process is the recovery of value from large amounts of mixed plastic scrap.

Feedstock recycling gets its name due to the process in which scrap waste is processed to recover valuable chemicals like oil and gas from waste and “feeding” them once more into the petrochemical industry. During this process, plastic waste is heated and melted down into liquid and gaseous hydrocarbons from which oil and gas can be recovered. The product can be used further as a feedstock in chemical and petrochemical technologies. The most commonly used methods to recycle large quantities of plastics (feedstock) for the petrochemical industry (e.g., oil refineries) are the reduction of iron ore, pyrolysis, hydrogenation, and synthesis of gas.

Energy recovery

This process is said to be the most ecological, cost-effective, and technically effective way to reduce the amount of polyurethane scrap material that would otherwise be deposited in landfills. Additionally, the recovery of fossil fuels from polymers during the incineration of plastic waste material with or without other scrap causes no carbon dioxide

emissions that are harmful to the natural environment. When describing energy recovery, a few other advantages of this recycling strategy should not be forgotten (Scheirs, 1998).

Since polymers can undergo combustion, the amount of organic waste stored in landfills has significantly decreased. The value of energy extracted from plastic scrap (net caloric value of polyurethanes is in the range of 24 to 30 MJ/kg) is similar to the energy potential of coal; thus, plastic wastes can serve as a source of energy for heating and electricity for households and industrial power stations (Rittmeyer et al., 1994).

All these polyurethane recycling emissions have one thing in common: from an ecological viewpoint, the main aim of recycling and recovery is to process polyurethanes as long as possible and treat landfilling as a last resort.

Research material and methodology

Polyurethane foam, solvent (glycol): DEG (diethyleneglycol), PPG (polypropylene glycol), and catalysts: KAc (potassium acetate) and NaOH (sodium hydroxide). The foam used for glycolysis was a scrap of ether foam from a production line. The material originated from the production that is why it was important to avoid mechanical impurities. The color of the foam was oatmeal. The filler content was 3–8%. The disintegration was carried out using 6–10 mm diameter. To perform glycolysis of the polyurethane foam scrap, the production used NaOH (sodium hydroxide) and KAc (potassium acetate) as catalysts, and glycols, DEG (diethyleneglycol) and PPG (polypropylene glycol), were used. To obtain the best possible properties of the recycle, the glycolysis conditions were as follows. To start the dosage of material (PU), the temperature must reach 170°C because at a lower temperature (165°C) the reaction is not efficient. After introducing the estimated amount of polyurethane foam scrap, the temperature reached 190°C, and this process was carried out. The average dosage time can vary from 20 to 65 minutes depending on the skills of the operator. The apparatus used for glycolysis included a reactor + heater, stirrer, feeder, reflux condenser, thermocouple, and temperature regulator.

Table 1 shows the glycolysis process using low-molecular-weight glycol, DEG (diethyleneglycol), in the presence of KAc (potassium hydroxide) as the catalyst. Sodium methanolate, sodium phenolate, sodium phosphate, or potassium acetate are also common catalysts used in glycolysis. The

Table 1. Synthesis (the author's study based on thesis)

Sample No.	Reaction temperature [°C] 1. During dosage 2. End temperature	Reaction time (dosage + finishing) [min]	Glycol and amount [g]	Catalyst and amount [g]	Amount of PUR [g]
1	1. 130 2. 190	65 + 20	DEG – 25	KAC – 1	200
2	1. 130 2. 190	65 + 40	DEG – 25	KAC – 1	200
3	1. 130 2. 190	65 + 60	DEG – 25	KAC – 1	200

Table 2. Synthesis (the author's study based on thesis)

Sample No.	Reaction temperature [°C]	Reaction time (dosage + finishing) [min]	Glycol and amount [g]	Catalyst and amount [g]	Amount of PUR [g]
1	3. 180 4. 190	50 + 10	PPG – 100	KAc – 4	200
2	3. 130 4. 190	10 + 15	PPG – 50	KAc – 0.2	100

Table 3. Synthesis (the author's study based on thesis)

Sample No.	Reaction temperature [°C]	Reaction time (dosage + finishing) [min]	Glycol and amount [g]	Catalyst and amount [g]	Amount of PUR [g]
1	5. 200	15 + 15	PPG – 150	KAc – 0.6	150

Table 4. Synthesis (the author's study based on thesis)

Sample No.	Reaction temperature [°C] during dosage	Reaction time (dosage + finishing) [min]	Glycol and amount [g]	Catalyst and amount [g]	Amount of PUR [g]	Ratio
1	180	15 + 15	PPG – 50	NaOH – 0.2	100	1/2
2	180	19 + 3	PPG – 30	NaOH – 0.12	120	1/4
3	180	12 + 15	PPG – 30	NaOH – 0.12	120	1/6
4	180	17 + 15	PPG – 20	NaOH – 0.08	160	1/8
5	180	18 + 15	PPG – 20	NaOH – 0.08	200	1/10

Table 5. Synthesis (the author's study based on thesis)

Sample No.	Reaction temperature [°C] during dosage	Reaction time (dosage + finishing) [min]	Glycol and amount [g]	Catalyst and amount [g]	Amount of PUR [g]	Ratio
1	180	14 + 15	1.3 PPG – 70	NaOH – 0.28	140	1/2
2	180	18 + 15	1.3 PPG – 40	NaOH – 0.16	160	1/4
3	180	19 + 15	1.3 PPG – 30	NaOH – 0.12	180	1/6
4	175	22 + 15	1.3 PPG – 30	NaOH – 0.08	180	1/8
5	180	24 + 15	PPG – 20	NaOH – 0.08	200	1/10

above-mentioned compounds are often chosen for this process due to their satisfactory hydroxyl number in the range 271–452 mg KOH/g or 609–947 mg KOH/g (Wu, Chang & Li, 2002).

The glycolysis of PUR foam using PPG with KAc (potassium hydroxide) as a catalyst is presented in detail in Table 2. Temperatures of 130–190°C and various molar ratios were used. A higher temperature (200°C) was used with extended reaction times, and the details are presented in Table 3.

The glycolysis of PUR foam with PPG in the presence of NaOH as a catalyst is described in detail in Tables 4 and 5. The temperatures of 175–180°C, various molar ratios of glycol: PUR, different catalyst contents, and various reaction times are shown.

Results and discussion

Waste polyurethane foam was subjected to glycolysis using DEG and PPG. The process was

conducted in an apparatus used for glycolysis. The studies were carried out for the author's thesis (Bielenia, 2007).

PUR glycolysis can be carried out under various glycol: PUR mass ratios (Table 6, 7). The best for many reasons were the recyclates: GL 10 [2:1], GL 11 [4:1], GL 12 [6:1], GL 13 [8:1], and GL 14 [10:1]. The compositions of the reactionary mixture are presented in Table 6. The molar ratio of [NCO]:[OH] groups in each synthesis were constant and ranged from 0.08 to 0.28.

Table 6. Recyclates – composition of reactionary mixture (part 1) (the author's study based on thesis)

Sample name	Polyurethane foam [PUR] Mass [g]	1-3 propylene-glycol [PG]	Sodium hydroxide [NaOH]
GL 10 [2:1]	140	70	0.28
GL 11 [4:1]	160	40	0.16
GL 12 [6:1]	180	30	0.12
GL 13 [8:1]	180	20	0.08
GL 14 [10:1]	200	20	0.08

Table 7. Recyclates – composition of reactionary mixture (part 2) (the author's study based on thesis)

Sample name	Temperature [°C]	Dosage time [min]	Time after dosage [min]	pH	Atmosphere
GL 10 [2:1]	170–190	14	15	Base	Air
GL 11 [4:1]	170–190	18	15	Base	Air
GL 12 [6:1]	170–190	20	15	Base	Air
GL 13 [8:1]	170–190	22	15	Base	Air
GL 14 [10:1]	170–190	24	15	Base	Air

Different GL: PUR mass ratios were used in a series of experiments, namely 2:1, 4:1, 6:1, 8:1, and 1:10 (Figure 5). Table 7 presents some physicochemical properties of the glycosylates formed under conditions with different initial reactant ratios. The glycosylates were formed under different initial reactant ratios and dosage speed/dosage times (Figure 4). The results presented in the experimental part of this article unveiled the conditions to obtain the product that was most suitable for synthesizing cast urethane elastomers.

The main purpose of glycolysis (chemical reaction) is to determine which terms result in obtaining the highest quality of recovered polyols from scrap and simultaneously solving the problem of disposal. Glycolysis was used to recycle the raw materials of the polyurethane foam. The degradation of the scrap foam that occurred during glycolysis using glycols and catalyst and under glycolysis conditions resulted

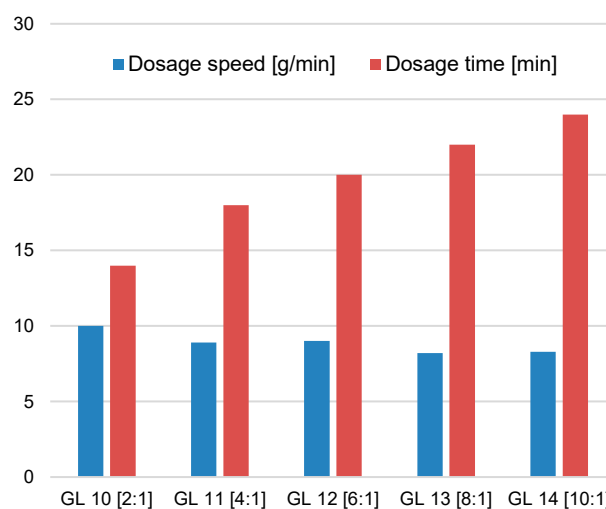


Figure 4. Representation of dosage speed/dosage time (the author's study based on thesis)

in the recovery of polyols as oligourethanoeterols. After analyzing the results of the performed experiment, the most appropriate intermediates for the synthesis of cast elastomers were applied via glycolysis of the samples GL 12 PG/PUR 1/6 and GL 13 PG/PUR 1/8. These recyclates possess good properties (density, viscosity, hydroxylic number, etc.).

Conclusions

The research results presented in this article confirmed that the degradation of the scrap foam that occurred during the glycolysis of glycols produced the highest-quality recovered polyols. In recent years, the volume of production and consumption of polyurethanes has increased significantly. Due to their advantages, they have become the most popular materials in the furniture, automotive, and construction industries. The consumption of polyurethanes increases 5–6% annually. Traditional methods to utilize wastes, such as combustion, exert unfavorable impacts on the environment because they produce pollutants such as nitrogen oxide, carbon dioxide, hydrocyanic acid, and urea, which may contaminate the water and air. Rapid and effective strategies of recycling and energy recovery are required. While gathering materials and information for this article, the author discovered that polyurethane recycling is important. The mass of landfilled wastes is several times greater than the mass of recycled waste material. The most environmentally friendly, cost-effective, and efficient ways were regrinding, powdering, adhesion pressing, rebonding, and energy recovery. The most helpful process of feedstock recycling to solve the problem of polyurethane waste was glycolysis. Promisingly, this process produced high-quality

polyols that may serve as the raw material for many applications. Additionally, amongst available chemical methods for polyurethane recycling, glycolysis has found applications on a large scale, whilst others remain in the research phase. According to the author, the results presented in this thesis may contribute to the development of science and find applications in economic practice. In Poland, the recovery of crosslinked polymeric materials (PUR) under heating is currently carried out only on the laboratory scale, but industrial implementation is expected in the coming years. From both a scientific and a practical business perspective, the recycling of polyurethane foam is important. The main goal of chemical recycling methods, in this case hydrolysis, is to obtain a product with properties that are suitable for reuse, and, at the same time, to manage polyurethane waste.

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