An Investigation on Possibilities for the sustainable development of Polyurethane waste recycling processes

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Submitted by

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JULY-2022



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BONAFIDE CERTIFICATE

I hereby certify that this project report " An Investigation on Possibilities for the sustainable development of Polyurethane waste recycling processes " is the bonafide work of Vibhu Sharma (18021011192) who carried out the project work under my supervision.

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ABSTRACT

The adoption of a responsible approach towards natural resources is rapidly gaining in significance in today's business environment. Social and societal responsibility are becoming a yardstick via which corporate success is measured. At the same time, however, companies are faced with rising raw material prices and increasing cost pressures. Growing water and land pollution, the potential for raw material depletion, and plastics' resilience to physical and chemical forces all contribute to the significance of synthetic polymer waste recycling, recovery, and ecologically appropriate disposal methods. Liquid isocyanate and liquid polyol resin components are frequently combined to produce polyurethanes, which are incredibly complex chemically. Polyurethanes are used in an exceptionally wide number of industrial applications, including carpet underlay, mattresses, furniture cushions, and the automobile industry. The processing of PU waste can be advantageous economically and environmentally thanks to a variety of tested and used processes, the two most significant of which are regrinding and glycolysis. Through these technologies, polyurethane rigid foams and composites can be recycled in a new, efficient, and cost-efficient way. The intrinsic energy value of polyurethanes may be recovered using current technology, which also cuts down on the need of fossil fuels.

TABLE OF CONTENTS

Ti	tle	Page no.
Bo	onafide Certificate	2
Aŗ	oproval Sheet	3
St	udent Declaration	4
A(CKNOWLEDGEMENT	5
At	ostract	6
Ta	ble of Contents	7
1.	Introduction	10
2.	Literature Review	12
3.	Polyurethanes	14
4.	PU wastes	15
5.	Polyurethane Waste Management	17
	5.1 Landfilling	18
	5.2 Mechanical Recycling	19
	5.2.1. Mechanical Reprocessing with Adhesives	19
	5.2.2. Mechanical Reprocessing without Adhesives	20
	5.3 Chemical and Feedstock Recycling	21
	5.3.1. Hydrolysis	21
	5.3.2. Hydroglycolysis	22
	5.3.3. Aminolysis / Ammonolysis	22

	5.3.4. Phosphorolysis	23
	5.3.5. Glycolysis	24
	5.3.6. Gasification	24
	5.3.7. Pyrolysis	25
	5.3.8. Hydrogenation	25
	5.4 Energy Recovery	27
	5.5 Biological Degradation	28
	5.5.1. Fungal Degradation	29
	5.5.2. Bacterial Degradation	29
	5.5.3. Enzymatic Degradation	29
	5.5.4. Polyurethane Modification	30
6.	Conclusion	31
7.	Potential or Upcoming Trends	32
8.	References	33

List of Figures and Tables

Figure	Title	Page no.
1.	Market share of different types of polyurethane.	12
	Products	
2.	Graphical abstract of recycling of polyurethane	13
	in Europe	
3.	Polyurethane synthesis reaction	14
4.	Different PU foam samples. PFW, Polyurethane	15
	Foam waste Mechanical grinding	

5.	Ladder of Lansink	17
6.	Polyurethane Hydrolysis	21
7.	Polyurethane aminolysis	22
8.	Polyurethane phosphorolysis	23
Tables	Title Pag	
1.	Advantages of polyurethanes against chosen	10
	Materials	
2.	Comparison of chemical polyurethane recycling	26
	Methods	

An Investigation on Possibilities for the sustainable development of Polyurethane waste recycling processes

1. INTRODUCTION

Early in the nineteenth century, synthetic polymers were first produced. Polyurethanes (PU) are the sixth most commonly used polymer in the world, accounting for roughly 8% of all produced plastics. PUs can be divided into two broad categories: foams and CASEs (Coatings, Adhesives, Sealants, Elastomers). Additionally, there are two varieties of foam: Flexible (used in beds and car seats) and Rigid (applied in building isolation and commercial refrigerators). Because of their adaptability and openness to alteration, polyurethane foams can now replace a number of previously utilised materials, both synthetic (PVC, rubber and polystyrene) and natural (leather). Because older polymers like polystyrene have greater production costs than polyurethanes, such actions may be required. When compared to conventional coatings that use solvents, some of them, such as aqueous polyurethane coatings, can have much lower risk of harmful volatile organic compound leakage. The obtained materials can occasionally be distinguished by noticeably improved mechanical properties (greater durability than PVC), higher resistance to solvents like water (they are the only raw materials that can be used in submarine coatings), oils and organic solvents, improved adhesives or electrical properties. The table below lists the key benefits of PU over rubber, metal, and plastic.

Rubber	Metal	Plastic
High abrasion resistance	Lightweight	High impact resistance
High cut and tear resistance	Noise reduction	Elastic memory
Superior load bearing	Abrasion resistance	Abrasion resistance
Thick section molding	Less expensive fabrication	Noise reduction
Colorability	Corrosion resistance	Variable coefficient of friction
Oil resistance	Resilience	Resilience
Ozone resistance	Impact resistance	Thick section molding
Radiation resistance	Flexibility	Lower cost tooling
Broader hardness range	Easily moldable	Low temperature resistance
Castable nature	Non-conductive	Cold flow resistance
Low pressure tooling	Non-sparking	Radiation resistance

Table 1. Advantages of polyurethanes against chosen materials.

However, the booming production of polyurethanes, which are primarily used in goods that degrade over time (like clothing or footwear) or that replaced with newer or better ones (like automobiles, furniture, or sporting goods), results in the buildup of post-consumer waste. Landfilling is still the most popular method of processing polyurethane waste due to PU's low vulnerability to physical, chemical, and biological elements as well as some of the combustion products' toxicity. However, due to the depletion of global fossil fuel reserves, such as petroleum, and the shrinking amount of landfill space, polyurethane waste processing has recently become more significant on a global scale.

This study is a review of the literature on the processing of polyurethane waste, with a focus on biological, mechanical, chemical, energy-recovery, and landfilling approaches. Additionally, it analyses potential uses for certain techniques.

2. LITERATURE REVIEW

AS AN INDUSTRY, SUSTAINABILITY HAS TO BE APPROACHED IN A RIGHT WAY: EUROPE

In 2015, the market for polyurethane in Europe was estimated to be worth \$15.42 billion. Over the projection period, strict restrictions in the region relating to energy efficiency and carbon emission reduction are expected to be the main driving factor. Construction environment is predicted to increase across the UK, Germany, Poland, and Sweden, driving the sector in Europe. A 7% rise over 2013's investment brought the total construction spending in the European Union to EUR 1.37 trillion in 2014.

According to ISOPA, the European Diisocyanate & Polyol Producers Association, buildings currently waste a significant portion of the energy that is supplied to them, warming the planet rather than people's houses. Due to its exceptional insulating qualities, polyurethane significantly aids in resource and energy conservation in buildings. Its inherent qualities of durability and abrasion resistance provide the items a long lifespan.

As shown in figure 1, the market for final polyurethane products in EMEA (Europe, Middle East, and Africa) is virtually evenly split between flexible foams (36%), rigid foams (32%) and CASE (32%).

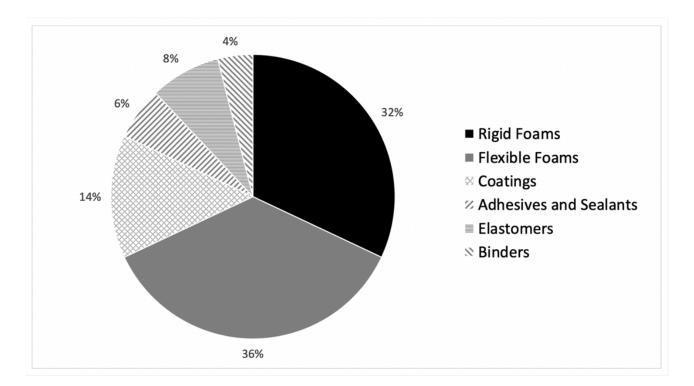


Figure 1. Market share of different types of polyurethane products.

A total of 6.47 million tonnes of polyurethane goods were produced in EMEA in 2017. Western Europe is where most of this production is located (more than 3.6 million tonnes in 2017). However, Eastern Europe showed the largest rise, mostly as a result of Turkey and Poland's rapid expansion.

However due to the depletion of global fossil fuel reserves, such as petroleum, and the shrinking amount of landfill space, polyurethane waste processing has recently become more significant on a global scale.

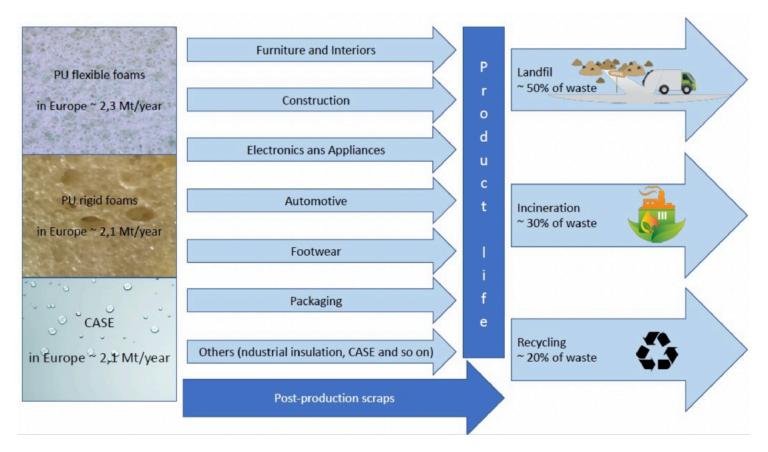


Figure 2. Graphical abstract of recycling of Polyurethane in Europe.

Legislative developments, such as European Commission's revision of Directive 1999/31/EC regarding landfilling, are also significant. Only 25% of municipal waste compared to prior year may be dumped in the landfill under the updated legislation after 1 January, 2015, and this quantity may not exceed 5% starting in 1 January 2030. Additionally, there should be a large increase in the rate of recycling and incineration.

3. POLYURETHANES

An extraordinarily wide range of commercial uses use polyurethanes. The class of polymeric compounds known as polyurethane is distinct from other polymers in a number of respects. They can all be used to create paints, liquid coatings, elastomers, insulators, electric fibres, foams, interior skins, and other things. Today's polyurethane-based foams are simply improved versions of inventions made by Dr. Otto Bayer and his colleagues, a German scientist. The Diisocyanate Polyaddition technique, invented by these researchers, led to the creation of the PU industry in 1937. PU is produced by reacting diisocyanate with polyester diol.

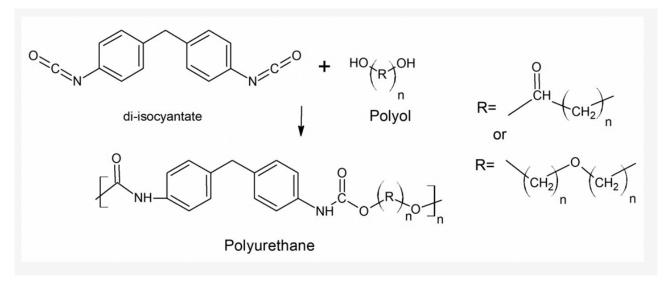


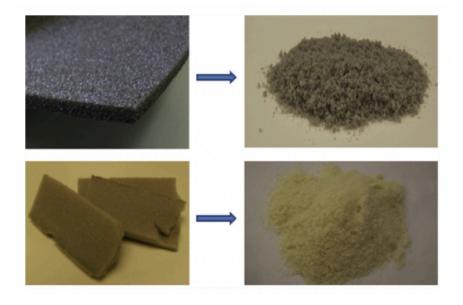
Figure 3. Polyurethane synthesis reaction.

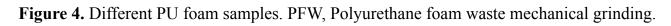
In addition to the two primary raw components, a range of additives are utilised, including foaming agents, fillers, and flame retardants. Methylene chloride and carbon dioxide, which are produced when isocyanates and water react, are used as foaming agents.

Urea bonds, which are produced by the reaction of water molecules with an isocyanate group after the reaction of freshly synthesised amine with another isocyanate group, are present in substantial amounts in the waterblown PU foams. The existence of alternate rigid (isocyanates) and flexible (Polyol) segments in polyurethanes is a significant characteristic. This enables their use as resilient components of furniture and mattresses, long lasting coatings, portable, strong building materials and attractive faux leather.

4. PU WASTES

Waste PU can be recycled using on of the three main materials: combined Chemolysis, chemical recycling (chemical degradation), or physical recycling. Physical recycling of used PU foam is easy, economical, practical, and environmentally friendly. Chemical and mechanical recycling are the two most significant methods or recycling PU foam trash. PU foam can be recycled most effectively by triturating polymer foams and incorporating them into new materials. Without chemical deterioration, mechanical recycling includes ways to recycle and reuse PU.





The trash is reduced by mechanical recycling into powders and small particles with a diameter of only a few millimetres. These wastes are frequently used by the industry to create new PU compounds as a diluent for polyols or as an inert filler. However, chemical recycling also includes biodegradation, thermochemical reactions, aminolysis, hydrolysis, and glycolysis. Numerous glycolysis reagents and catalysts, which are often found to be expressed under varied conditions, are used to degrade PU. The goal of this type of recycling is to recover the original raw materials, particularly to manufacture high-quality recovered Polyol monomers to include into a new polymer of the same type.

The process of microorganisms breaking down polymeric chains into smaller molecules is known as biodegradation. The chemical structure, molecular orientation, crystallinity, and cross-linking density of polymeric materials all affect how quickly they break down naturally. Hydrolysis or oxidation reactions with chemical or biochemical origins that involve natural or artificial sources can speed up this process. In addition to the fact that a wide variety of micro-organisms can biodegrade the medium, several publications suggested that the degradation product predominantly consists of ester linkages that are sensitive to hydrolysis and polyols.

Depending on the specific type of polyurethane being recycled, the various types of polyurethane waste products-which might be made up of old recycled parts or production waste-are often converted to a more useable form, like flakes, powder, or pellets. With regrinding and glycolysis being by far the most significant, the numerous recycling processes for material and chemical recycling of PU materials have significantly improved the overall perception surrounding the recyclability of polyurethanes in recent years. Through these technologies, polyurethane rigid foams and composites can be recycled in a new, efficient, and cost-efficient way. Regrind technology has been used to successfully recycle polyurethane foam used in vehicle seating. Glycolysis of polyurethanes can be economically acceptable, but still requires more development in order to tolerate more contamination in the post-consumer material. Current technologies can recover the inherent energy value of polyurethanes and reduce fossil fuel consumption. Energy recovery is considered the only suitable disposal method for recovered material for which no markets exist or can be created. Increasing waste-to-energy and other thermal processing activities involving gasification, pyrolysis and two-stage combustion has contributed for the disposal of significant amounts of scrap PU without many difficulties. It is concluded that many of the plastic feedstock recycling processes appear to be technically feasible and robust enough to warrant further development in the future.

5. POLYURETHANE WASTE MANAGEMENT

A growing amount of polyurethane trash is produced each year as a result of its numerous applications and economic success. End-of-life (EOL) and post-consumer (PC) items, as well as leftover scraps from the production of polyurethanes, are included in this waste. The latter can account for upto 10% of manufactured PUs and is result of flaws in the production and processing processes. EOL and PC waste, however is considerably bigger issue since it is frequently polluted or distorted, making it less likely to be recycled.

The "Ladder of Lansink", which establishes a generally agreed hierarchy of waste management techniques, often governs solid waste management. In terms of trash legislation and policy, this hierarchy establishes a priority order. However, it is necessary for technical, economic, or environmental reasons, it acknowledges the potential of skipping some processes.

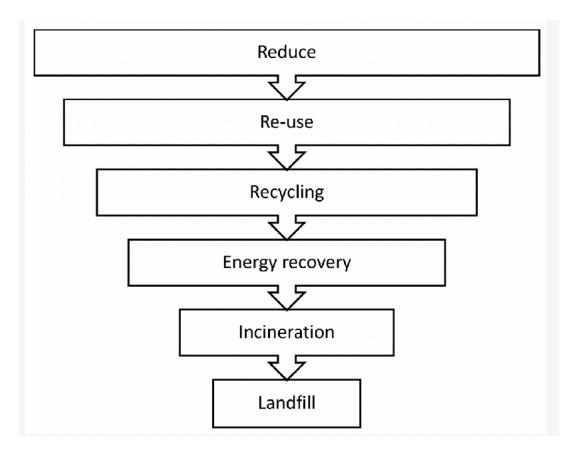


Figure 5. Ladder of Lansink.

5.1 LANDFILLING

The manufacture of polyurethane foams accounts for the largest portion of the issue. The most typical method for processing polyurethane waste is still landfill. The percentage of PUs disposed of in this manner is close to 50% of garbage (combined post consumer or post production ones).

They have big volumes due to their low apparent density. Additionally, a lot of air confined inside foam cells can fuel deep-seated fires with oxygen and thwart efforts to douse flames. Toxic vapours produced from the combustion of polyurethane are another risk associated with landfill fires. Recycling is a fantastic alternative to landfills, but despite significant efforts by producers and governing bodies, it still isn't the main way that PUs dispose of their trash.

Enhanced waste management and Enhanced Landfill concepts Landfilling will now be reclassified as a balanced process by mining. The landfill should not be viewed as a permanent solution, but rather as a temporary location to store wastes while they wait to be valued and processed further. Materials that have been kept can be used as a stock for new products (Waste-to-Product) or as an energy source, depending on their condition and the technologies that are available (Waste-to-Energy).

5.2 MECHANICAL RECYCLING

Recycling PUs is made most simple and straightforward by mechanical processing. The transformation of solid waste into flakes, grains, or powder is involved. They can be utilised as a substrate in other processes (Secondary Mechanical Recycling and Feedstock Recycling) or directly as stuffing for items like pillows, toys, etc. (Primary Mechanical Recycling).

By cutting, tearing, or grinding, fragmentation can be achieved. Two-roll mill processing is uses to create fine powders (with particles smaller than 100-125 microns). Acquired powders may be included as fillers in freshly produced polyurethanes. The biggest drawback of this method is the PU foam's viscosity. Additionally, this method is not particularly cost-effective, and the acquired goods are of poor quality, which severely restricts the number of potential markets for sales. Precision knife cutting is used to create powders with a greater diameter (less than 250 microns). Pellet mills are used to create granules. The polyurethane is forced through the metal plate's holes by two or more metal rollers. Depending upon the use of adhesives, shredded foams can be utilised as a feedstock for one of two types of reprocessing. Because of their contamination or the inclusion of additional elements, post-consumer waste products cannot serve as the raw material for mechanical recycling.

5.2.1. Mechanical Reprocessing with Adhesives

Re-bonding is the process of joining several polyurethane foam pellets or scraps using the adhesive, which is typically made of a polyurethane compound. The diameter of used particles is a few millimetres. The product produced by this technique have a higher density than the raw ingredients. They possess qualities that are challenging to obtain using conventional PUF production techniques. The resulting materials are employed as sports matting and floor coverings due to their flexibility and durability. Approximately 90% of the market for flooring underlay is generated each year through re-bonding techniques.

With the addition of adhesives (often polymeric isocyanate), adhesive pressing processes pellets at a high temperature and pressure (30-200 bar

and 100-200 c). This method enables the creation of shaped items like car mats and tyre covers. By using this technique, polyurethane construction panels exhibit good moisture resistance and excellent insulating qualities. The biggest drawback of this approach is the widespread use of flame retardants in foam, which significantly limits the supply of raw materials accessible and necessitates waste segregation. Additionally, their high density restricts available markets.

5.2.2. Mechanical Reprocessing Without Adhesives

One of the procedures that does not require binders is hot compression moulding. Under conditions of high pressure and temperature (180c and 350 bar), polyurethane foam that has been finely milled condenses. The primary application of this technique is the processing of bumper-related stiff polyurethane foam waste. Gained goods are rigid and threedimensional (ready-for-application parts like pump and motor covers), and when fibreglass is added during moulding process, they can be used as dashboards, door panels, etc. In comparison to materials filled with minerals, materials formed with polyurethanes as fillers during compression moulding of various resins (such as polyester resin mix) exhibit enhanced flexibility and impact toughness. Problematic recycling of painted parts and challenges in creating the smaller particles required for moulded items are two significant drawbacks of these materials.

The fabrication of electrical covers, computer and telecom equipment enclosures uses the reaction injection moulding (RIM) method. In this procedure, Polyol and isocyanate are mixed together before being injected into the mould that has already been created. The intended shape of polyurethane is created as result of the chemical reaction. It can be uniform or foamed, and fibreglass (RRIM) or a structural composite can be used to reinforce it (SRIM). RIM is applicable to batches of mixed polyurethane and to combinations of that material with other plastics (usually thermoplasts). After being regrinded into a fine powder, rigid PU foam waste can also be used as a core.

5.3 CHEMICAL & FEEDSTOCK RECYCLING

A type of polymer reprocessing known as feedstock recycling, often known as tertiary, involves the chemical breakdown of polymer chains into smaller molecules. Hydrolysis, glycolysis, Aminolysis, gasification, and other processes are among them. The ability to reversibly polymerise, enabling the recovery of building blocks, is a crucial characteristic of polyurethanes.

Chemical recycling is substantially more difficult than mechanical recycling when prices, applied temperates and additional substrates are taken into account. It enables the breakdown of polymers into a variety of raw materials that can be used as a stock material for new PU synthesis or as resources for operations unrelated to the manufacturing and processing of polyurethane.

5.3.1. Hydrolysis

The first chemical technique to recycle polyurethane waste, particularly flexible foams, was hydrolysis. Waste polyurethane reacts with water, either liquid or in the form of steam, to produce this reaction. Polyols, amine intermediates, and carbon dioxide are among the byproducts.



Figure 6. Polyurethane Hydrolysis

Its ability to be applied to both production leftovers and post-consumer wastes is its greatest benefits. The procedure is carried out at a high temperature (above 150-320c) and in anaerobic environment. The resultant Polyols can be utilised as fuel or as additions to the original Polyol when making polyurethane.

Furthermore, the recovery of the initial isocyanates is made possibly by amine intermediates following phosgene treatment. The polyurethanes used to make the insert can be created by reacting the Polyols and isocyanates that result from hydrolysis. The main drawback of hydrolysis is that it consumes a lot of energy in the reactor, either to heat the batch or to apply high pressure, making it unprofitable. Because of this, hydrolysis has yet to be implemented on a commercial basis.

5.3.2. Hydroglycolysis

The process of hydroglycolysis, which uses less rigorous operating conditions to mix water and glycols, is an improvement over hydrolysis. At a temperature of 200c, the process continues with lithium hydroxide acting as a catalyst. It is not frequently utilised because of the expensive nature of the process; nonetheless, one of its greatest advantages is the high tolerance to contamination and heterogeneity of the used polyurethane feedstock. For the manufacture of polyurethane foams, the resultant Polyols may make up to 50% of a mixture with virgin starting material.

5.3.3. Aminolysis / Ammonolysis

Anibolysis is a transesterification reaction where the ester group from urethane is exchanged for the amine group from ammonia or amine. Polyurethane-containing materials are mechanically ground or dissolved in an appropriate solvent, such as cyclic ether or a chlorinated hydrocarbon solvent with nitrogen. They are then put through aminolysis with a substance that has at least one -NH₂ group.



Figure 7. Polyurethane aminolysis

This reaction often uses catalysts like sodium hydroxide, aluminium hydroxide, and sodium methoxide and has a temperature range of 80 to

190c. Bi- or polyfunctional amines and alcohols can be produced depending on the diamine or amine alcohol utilised. They can be used to create polyurethanes, polyesters, polycarbonates, melamine resins, epoxy resins, and other materials. Additionally, two or more of the resulting functional phenols can be used to recover the matching isocyanates.

5.3.4. Phosphorolysis

The wastes are turned into a liquid product during the processing of polyurethanes with esters of phosphoric and phosphonic acids as result of the reaction between the urethane group and the ester alkoxy group. Through this method, a mixture of oligouretanes containing phosphorous was obtained. It can be used to create novel polyurethanes with enhanced UV resistance, adhesive qualities, and flame retardancy (like commercial goods with larger levels of flame retardants). The method's drawback is that the input materials cannot be recovered, meaning that the input materials cannot be recovered, meaning that they cannot be recycled back into it but are instead transferred to others forms of production. Additionally, phosphorolysis has not been used on a large scale technically, and there have been no updates on this subject since 2013.

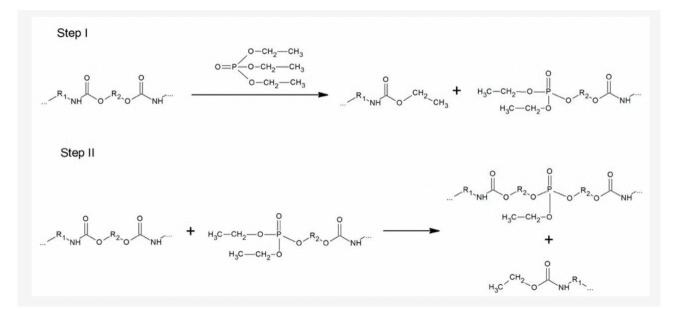


Figure 8. Polyurethane Phosphorolysis

5.3.5. Glycolysis

The most used chemical recycling process for rigid and flexible polyurethane at the moment is glycolysis. It is based on a transesterification reaction in which an ester group containing a carbonyl carbon from a urethane bond is replaced by a hydroxyl group from glycol. This reaction creates Polyols whose properties can be somewhat regulated and may resemble those of the starting material. They can be utilised to make polyurethanes.

The glycolysis process is divided into two primary directions. With the first, Polyols may be recovered and used to make flexible polyurethane foam. Second, rigid and flexible Polyols are produced by so-called split-phase glycolysis (SPG). The foundation of SPG is the distinct processing of the top and bottom layers during glycolysis of diethylene glycol (DEG). The lower layer is treated with propylene oxide to create rigid polyols, and the upper layer, which primarily consists of flexible polyols, is washed with DEG.

The biggest restriction on glycolysis is the requirement for separate disposal of spent waste because to the different process conditions for flexible and stiff foams. Due to great sensitivity of the reaction to the presence of contaminants that may typically present in consumer trash, this approach is also substantially more successful when used on postproduction waste.

5.3.6. Gasification

The partial oxidation of carbonate minerals during gasification is a highly exothermic reaction. Ash and "syngas", a combination primarily composed of carbon monoxide and hydrogen, are its principal byproducts. This is quite exothermic. The lack of the requirement for waste separation is one of the most important benefits of gasification. Additionally, the procedure may also involve the usage of polyurethanes blended with other basic materials. The potential use of syngas as an energy source and a raw material for the synthesis of methanol, ammonia, carbohydrates, acetic acid, etc., however, has a significant impact on how economically viable this process is.

Additionally, the process is made simpler by using atmospheric air as the reaction medium, however molecular nitrogen tends to lower the amount of energy produced during gasification. Nitrogen dioxide and deadly hydrogen cyanide are produced in substantial amounts during gasification procedures, according to study. This emission can be somewhat decreased by the inclusion of a suitable catalyst. Additionally, oxygen helps to lessen the amount of waste produced by subsequent reactions to nitrogen molecules found in ashes.

5.3.7. Pyrolysis

Pyrolysis is the heat breakdown of lengthy polymeric chains into less complicated molecules at high pressure and anaerobic conditions. Oil, gas, and ash are primary products that provide value for a variety of businesses. The degradation of the Polyol component and isocyanate part takes place in at least two phases. Over 50% of the polymer mass is lost in the first stage, which runs at temperature between 100 and 300c. Beginning at 300-800c, the second stage of decomposition begins. Less than 3% of the initial polyurethane is left as ash following pyrolysis. Their findings support the two-stage degradation of these polymers, showing that the urethane link breaks down in the first step to produce isocyanates and that the second step involves the breakdown of the ethereal Polyol to produce ashes resembling those produced during fire. The fact that pyrolysis produces such little waste and allows for the use of the end products in other petrochemical processes is without a doubt a benefit. Unfortunately, due to the inability to calculate the ratio of individual products and the challenge of finding products with the appropriate qualities, this is not always feasible. Because of its high calorific content, the resultant gas is occasionally used in gas engines to generate heat and power.

5.3.8. Hydrogenation

Pyrolysis and gasification are processes that are comparable to hydrogenation. Gas and oil are formed as a result of it. The use of high-

pressure hydrogen rather than inert gas is the key distinction between this method and pyrolysis. The composition of the acquired oil and gas and the cost of converting them into functional products, which may be then used as energy materials and substrates in chemical processes, must be addressed for this approach to be effective, just as with the prior procedure.

Only glycolysis and gasification of the chemical processes for recycling polyurethane have been put into practise on a significant scale; the others are still in the research phase. And the only process that results in the recovery of raw materials is glycolysis.

Treatment	Input	Output	Large Scale Application
Hydrolysis	EOL products production scraps	polyols, amine intermediates	No
Hydroglycolysis	EOL products, production scraps	polyols	No
Aminolysis	only foams	bi- or polyfunctional amines and alcohols	No
Phosphorolysis	production scraps	phosphorus containing oligouretanes	No
Glycolysis	only foams, segregated for rigid and flexible	polyols	Yes
Gasification	EOL products, production scraps	syngas	Yes
Pyrolysis	EOL products, production scraps	oil, gas, ash	No
Hydrogenation	EOL products, production scraps	gas, oil	No

EOL-End of life.

Table 2. Comparison of chemical polyurethane recycling methods.

5.4 ENERGY RECOVERY

Due to the significant increase in raw material recovery, energy recovery is only used for polyurethanes that cannot be processed by any recycling method. Materials destroyed during combustion and incineration cannot be restored. The ability to use polyurethanes that are contaminated, foamed with Freon, or permanently bonded to wood, leather, or cloth is the process' key benefit. Additionally, up to 99% of the volume of the garbage that is landfilled is reduced by burning and incineration.

This approach is not perfect, particularly as more and more polyurethane foams are made with flame retardants to promote user safety. Energy recovery is made difficult or even impossible by these additions. Additionally, PU foams can emit carcinogens and poisonous substances such as carbon monoxide, hydrogen cyanide, and nitrogen oxides when exposed to high temperatures. Under aerobic conditions, polyurethanes exhibit significantly higher toxicity during heat decomposition. While the amount of nitrogen oxide released under aerobic conditions can increase up to 2.5 times, standards are maintained at higher temperatures when pyrolysis occurs and only barely surpasses the threshold at 550c. Isocyanates, which are highly hazardous chemicals, may also be present in the gases produced by combustion. They can irritate skin, eyes and respiratory system when exposed to them. The last one can be so potent that exposure at merely 0.02 ppm can cause what is known as "isocyanate asthma". Pneumothorax can occur at higher doses.

5.5 BIOLOGICAL DEGRADATION

The breakdown of organic materials by living things or their enzymes is referred to as biodegradation. As a result, polymer chains are condensed and some of their components are removed. That causes its molecular weight to decrease, and under the right circumstances, it might even cause the deteriorated material to completely mineralise. Large polymers, however, typically require the cooperation of a number of different organisms to degrade completely. There may be several stages to it, including the decomposition of the polymer into monomers, their reduction to simpler compounds, and their eventual decomposition into carbon dioxide, water, and methane (under aerobic conditions).

Both aerobic and anaerobic conditions can result in the breakdown of organic molecules. Polymer breakdown with oxygen occurs in a natural setting, without oxygen in landfills, and mixed- nature degradation is possible in compost and soil. Micro-organisms that are already present in the landfill or compost can degrade it, or a carefully chosen consortia of microorganisms or enzymatic combination can be added.

Since it doesn't require high temperatures or tricky reagents, biodegradation is typically more environmental friendly than chemical degradation. Additionally, it can be used to degrade post-consumer waste.

Although improving the degradability of polyurethanes is crucial, doing so does not address the issue of already present environmental damage. The three types are bacterial biodegradation, enzymatic biodegradation, and fungal biodegradation. Polyurethanes made of polyester are substantially more prone to biological deterioration than those made of polyether. Research using fungus strains produces more encouraging outcomes for polyether ones. This disparity can be ascribed to mycelium accessing material pores and mechanically cracking more resistant polyether urethanes, which are typically used in foams. On the other hand, bacteria are used in the majority of PU coating degradation studies. The ability of bacteria to build biofilm on the smooth coated surface may be the cause of it.

Varied PU's unique characteristics, such as crystallinity, molecular orientation, or cross-linking, which control which chemical bonds are accessible for enzymatic degradation, lead to different patterns of degradation of various polyurethane samples. Due to their improved accessibility, amorphous portions of polyurethanes are more prone to deterioration than crystalline parts. Sadly, despite encouraging results, polyurethane biodegradation is still in its early stages. The lengthy period needed to receive results could be the primary cause of this problem.

5.5.1. Fungal Biodegradation

In laboratory-tested species, it is well established that fungus are the microorganisms that mostly cause PU degradation. There are only few filamentous fungi that can break down polyurethane that are beneficial to yeasts. This disparity may be caused by abiotic impacts of microbial deterioration. Growing filaments pierce the substance, increasing the pore size and perhaps causing material fracture. All types of polyurethanes, including polyester, polyether, thermoplastic PU, foams, and coatings, have been found to degrade by the action of fungi.

5.5.2. Bacterial Degradation

Although fungi are responsible for the majority of encouraging findings, some studies suggest that bacteria may also be potential degraders of polyurethane.

5.5.3. Enzymatic Degradation

The possibility of regulated bond cleavage, which results in the formation of building blocks that can be added back into the production process or used as a substrate in the creation of various materials, is the fundamental advantage of enzymatic degradation over microbial degradation. The key challenge with this strategy is that each type of PU must be approached separately due to the wide variety of raw ingredients utilised in polyurethane synthesis. In addition, because polyurethanes are rarely found in nature, there are very few enzymes that can break down these polymers. PU-degrading enzymes include oxidiseductases and hydrolases like esterases, ureases, proteases, and elastase, depending on the substances utilised in synthesis together with isocyanate.

5.5.4. Polyurethane Modification

It would appear that only polymers with degradable flexible chain might be disposed of in this way as the majority of findings indicate that the availability of urethane bonds for enzymes is limited. However, the necessity for energy-intensive, high-tech processing methods for the synthesis of polyurethanes comprising petroleum based polyols and the growing environmental problem led to a need for materials made from renewable and biodegradable resources. The tremendous potential of polyols and isocyanates derived from vegetable oils such as soybean oil, rapeseed oil, castor oil, jatropha oil, cardanol oil, and palm oil is indicated by numerous studies. Bio-polyols made from lignocellulosic biomass that have been liquified in polyhydric alcohols are another option for petroleum based Polyol replacement.

Due to the reduction of refractory waste and potential use of softer reaction conditions, biodegradable additives or replacements make polyurethane much more environment friendly. Due to the effect of additions and substitutions on a wide range of qualities, a lot of testing is necessary for any novel biodegradable material. Additionally, improvements in some of the traits may coexist with negative changes in others.

6. CONCLUSION

There are many methods for handling polyurethane waste, however they could all use some refinement. The most common method for getting rid of polyurethane trash right now is to out it in a landfill, however this method has many negative environmental, land-use, and economic consequences. Recycling by means of machines is another common technique. Although it is reasonably priced, it has a number of drawbacks. Additionally, it produces goods that are far more affordable than the original polyurethane product. High temperatures and harsh reagents are necessary for chemical and feedstock recycling, although only one of those procedures is now used on a wider scale. Although there is still a long way to go before biological degradation may be used on a large scale technology, it requires a moderate temperature and doesn't require any hazardous chemicals. Notably, the most promising method is biodegradation because there are so many options and changes accessible. Additionally, creating degradable polymers from correctly modified building blocks during the PU synthesis might be thought of as a viable alternative to the accumulation of polyurethane waste.

7. POTENTIAL OR UPCOMING TRENDS

The structure of PU foams can be flexible, semirigid, or rigid and they can be created in a wide range of densities. When making foams, a variety of blowing agents, additives, surfactants, catalysts, etc. are used. Since PU, which includes foam, is one of the most significant groups of materials now available, recycling PU is both economically and environmentally advantageous. Despite the many options for PU foam recycling that are currently accessible, such as landfills, chemical breakdown, physical breakdown, etc., none of these options have been financially viable as a business model. Additionally, none of these processes are capable of generating high-quality, recyclable raw materials that may be used to create new goods without compromising the characteristics of the end product or foam. This is important from an environmental perspective.

Recycling of PU foams must have a high conversion yield and high product quality procedure in order to be considered a practical and profitable way to handle foam waste. For large enterprises to show interest, the process must be cost-effective and environmentally beneficial, providing high-quality raw materials for further processing.

Recycling is proving to be more important than ever in light of rising environmental consciousness and the depletion of natural resources. Recycling with a high conversion rate and excellent quality will not only slow down the rate of environmental degradation but also aid in creating a sustainable future.

8. REFERENCES

- 1. PlasticsEurope Association of Plastics Manufacturers Plastics—The Facts 2019 An analysis of European Plastics Production, Demand and Waste Data.
- 2. Agrawal, A., Kaur, R. and Walia, R.S. (2017) PU Foam Derived from Renewable Sources: Perspective on Properties Enhancement: An Overview. European Polymer Journal, 95, 255-274.
- 3. Cregut, M., Bedas, M., Durand, M.-J. and Thouand, G. (2013) New Insights into Polyurethane Biodegradation and Realistic Prospects for the Development of a Sustainable Waste Recycling Process. Biotechnology Advances, 31, 1634-1647.
- 4. Molero, C., de Lucas, A., Romero, F. and Rodríguez, J.F. (2008) Influence of the Use of Recycled Polyols Obtained by Glycolysis on the Preparation and Physical Properties of Flexible Polyurethane. Journal of Applied Polymer Science, 109, 617-626.
- 5. PlasticsEurope Association of Plastics Manufacturers Plastics—The Facts 2019 An analysis of European Plastics Production, Demand and Waste Data.
- 6. Akindoyo, J.O.; Beg, M.D.H.; Ghazali, S.; Islam, M.R.; Jeyaratnam, N.; Yuvaraj, A.R. Polyurethane types, synthesis and applications-a review. RSC Adv. 2016, 6, 114453–114482.
- Bhargava, S.; Kubota, M.; Lewis, R.D.; Advani, S.G.; Prasad, A.K.; Deitzel, J.M. Ultraviolet, water, and thermal ageing studies of a waterborne polyurethane elastomer-based high reflectivity coating. Prog. Org. Coat. 2015, 79, 75–82.
- 8. Howard, G.T. Biodegradation of polyurethane: A review. Int. Biodeterior. Biodegrad. 2002, 49, 245–252.
- 9. Morton-Jones, D.H.; Ellis, J.W. Polymer Products, Design, Materials and Processing; Chapman and Hall Ltd.: London, UK, 1986; ISBN 9789401083201.

- 10. Europeean Commission. Green Paper on a European Strategy on Plastic Waste in the Environment; Europeean Commission: Brussels, Belgium, 2013.
- 11. Simón, D.; Borreguero, A.M.; de Lucas, A.; Rodríguez, J.F. Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability. Waste Manag. 2018, 76, 147–171.
- 12. Austin, A.; Hicks, D. A review of the global PU industry 2016 and outlook for 2017. PU Mag. 2017, 14, 4–16.
- Gamerith, C.; Herrero Acero, E.; Pellis, A.; Ortner, A.; Vielnascher, R.; Luschnig, D.; Zartl, B.; Haernvall, K.; Zitzenbacher, S.; Strohmeier, G.; et al. Improving enzymatic polyurethane hydrolysis by tuning enzyme sorption. Polym. Degrad. Stab. 2016, 132, 69–77.
- 14. Garrido, M.A.; Font, R. Pyrolysis and combustion study of flexible polyurethane foam. J. Anal. Appl. Pyrolysis 2015, 113, 202–215.
- 15. Cregut, M.; Bedas, M.; Durand, M.J.; Thouand, G. New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process. Biotechnol. Adv. 2013, 31, 1634–3647.
- 16. Datta, J.; Kopczyńska, P.; Simón, D.; Rodríguez, J.F. Thermo-Chemical Decomposition Study of Polyurethane Elastomer through Glycerolysis Route with Using Crude and Refined Glycerine as a Transesterification Agent. J. Polym. Environ. 2018, 26, 166–174.
- 17. Bukowski, A. and Gretkiewicz, J. (1982) Polyurethane Synthesis Reactions in Asphalts. Journal of Applied Polymer Science, 27, 1197-1204.
- Yang, W., Dong, Q., et al. (2012) Recycling and Disposal Methods for Polyurethane Foam Wastes. Procedia Environmental Sciences, 16, 167-175.
- 19. Braslaw, J. and Gerlock, J.L. (1984) Polyurethane Waste Recycling. 2. Polyol Recovery and Purification. Industrial & Engineering Chemistry Process Design and Development, 23, 552-557.

- 20. Gadhave, R., Srivastava, S., Mahanwar, P. and Gadekar, P. (2019) Lignin: Renewable Raw Material for Adhesive. Open Journal of Polymer Chemistry, 9, 27-38.
- 21. Ulrich, H., Odinak, A., Tucker, B. and Sayigh, A.A.R. (1978) Recycling of Polyurethane and Polyisocyanurate Foam. Polymer Engineering & Science, 18, 844-888.
- 22. John, L., Gerlock, J.B. and Albright, J. (1982) Process for Polyol Recovery from Polyurethane Foam Comprising Alcohol and Steam Hydrolysis. US Patent No. 4316992.
- 23. Asahi, N., Sakai, K., Kumagai, N., Nakanishi, T., Hata, K., Katoh, S. and Moriyoshi, T. (2004) Methanolysis Investigation of Commercially Available Polyurethane Foam. Polymer Degradation and Stability, 86, 147-151.
- 24. Benes, H., Hajek, M., Horak, Z. and Krulis, Z. (2010) Method of Recycling Waste Polyurethane Foams. US Patent No. EP2183311A2.
- 25. Takamoto, T.; Shirasaka, H.; Uyama, H.; Kobayashi, S. Lipasecatatyzed hydrolytic degradation of polyurethane in organic solvent. *Chem. Lett.* **2001**, 492–493.
- 26. Ratner, B.D.; Gladhill, K.W.; Horbett, T.A. Analysis of in vitro enzymatic and oxidative degradation of polyurethanes. *J. Biomed. Mater. Res.* **1988**, *22*, 509–527.
- 27. Phua, S.K.; Castillo, E.; Anderson, J.M.; Hiltner, A. Biodegradation of a polyurethane in vitro. *J. Biomed. Mater. Res.* **1987**, *21*, 231–246.
- Magnin, A.; Pollet, E.; Perrin, R.; Ullmann, C.; Persillon, C.; Phalip, V.; Avérous, L. Enzymatic recycling of thermoplastic polyurethanes: Synergistic effect of an esterase and an amidase and recovery of building blocks. *Waste Manag.* 2019, 85, 141–150.
- 29. Shah, A.A.; Hasan, F.; Akhter, J.I.; Hameed, A.; Ahmed, S. Degradation of polyurethane by novel bacterial consortium isolated from soil. *Ann. Microbiol.* **2008**, *58*, 381–386.

- 30. Howard, G.T.; Vicknair, J.; Mackie, R.I. Sensitive plate assay for screening and detection of bacterial polyurethanase activity. *Lett. Appl. Microbiol.* **2001**, *32*, 211–214.
- 31. Peng, Y.H.; Shih, Y.H.; Lai, Y.C.; Liu, Y.Z.; Liu, Y.T.; Lin, N.C. Degradation of polyurethane by bacterium isolated from soil and assessment of polyurethanolytic activity of a *Pseudomonas putida* strain. *Environ. Sci. Pollut. Res.* **2014**, *21*.
- 32. Zevenhoven, R. Treatment and disposal of polyurethane wastes: Options for recovery and recycling. In *Energy Eng. Environ. Prot. Publ. Espoo 2004. Rep. TKK-ENY-19*; Helsinki University of Technology: Helsinki, Finland, 2004.
- 33. Sheratte, M.B. Process for Converting the Decomposition Products of Polyurethane and Novel Compositions Thereby Obtained. U.S. Patent 4,110,266, 29 August 1978.
- 34. Malewska, E.; Bąk, S.; Kurańska, M.; Prociak, A. The effect of various rapeseed oil-based polyols on selected properties of flexible polyurethane foams. *Polimery* **2016**, *61*, 799–806.
- 35. Jašo, V.; Glenn, G.; Klamczynski, A.; Petrović, Z.S. Biodegradability study of polylactic acid/ thermoplastic polyurethane blends. *Polym. Test.* **2015**, *47*, 1–3.