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## Polyurethane Waste Reduction and Recycling: From Bench to Pilot Scales

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### Abstract

In this review, reports, patents and recently published papers and documents on polyurethane recycling, especially chemical recycling methods, are investigated in order to find an adequate method for waste reduction, protecting the environment and preventing waste land filling. The recycling of polyurethane has always posed unique challenges due to its wide variety of applications, from the industry to bio-based materials, namely, artificial organs. Mechanical regrinding is the oldest method in polyurethane waste recycling and the use of the regrind wastes as filler in the new formulations. Chemical recycling of polyurethanes by hydrolysis, aminolysis and glycolysis is for the most part considered economically uncompetitive compared to formulating with virgin raw materials. Also some thermochemical processes are utilized for PU recycling. Recycling has opened an effective and economic route for polyurethane waste treatment. Nonetheless, more research efforts are required in order to scale up the recycling methods.

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### Keywords

Polyurethane, recycling, physical, chemical, thermochemical

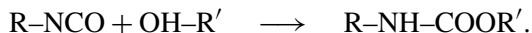
## 1. Introduction to Polyurethane

The German scientist Otto Bayer invented polyurethane (PU) in the 1930s, as part of his research on polymer fibers [1]. PU is formed by reacting a polyether or polyester polyol as a hydroxyl-containing monomer (a polymeric alcohol with more than two reactive hydroxyl groups per molecule), such as poly(propylene glycol) (PPG) or poly(tetramethylene glycol) (PTMG), with diisocyanate or a polymeric isocyanate, e.g., diphenylmethane diisocyanate (MDI) or toluene diisocyanate or (TDI), in the

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presence of suitable catalysts and additives, especially chain extenders, e.g., 1,4-butanediol [2, 3] as follows:



With a diverse range of high-performance properties, PUs are essential to a multitude of end-use applications. PU is one of the larger polymer product groups within the plastics family. Due to the broad versatility of the materials, it is around us in many products we use everyday. It can be found in liquid coatings and paints, tough elastomers such as roller blade wheels, rigid insulation for buildings, soft flexible foam in mattresses and automotive seats or as an integral skin in sports goods such as skis, surfboards and also automotive parts. Obviously, because of the large variety of isocyanates and polyols they would exhibit several organic chemical behaviors. Considering endless chemical processing routes of the reacting chemicals, numerous different materials may be synthesized which would fall under the definition PU. Besides these urethane linkages, the PU structure may be defined by ether-, urea-, amide-, etc., linkages. As a result, PU stands for a product range or plastics industry segment rather than for a single, well-defined polymer resin, for example, PVC, and the range of application of the different PU materials is extensive [4, 5]. A simple classification of PU-based products is given in Table 1.

The producers of PU are organized within the Isocyanate Producers Association (ISOPA) in Europe and API in North America. Total production volume of PU in Europe is more than 3 million tons per year. Rigid and flexible PU foams are highly produced and consumed in many industries. Nowadays the application ratio of rigid and flexible foam is in the order 1:3 [6]. Rigid and flexible PU foams are defined depending on whether the cell structure is ‘open’ or ‘closed’. In rigid PUF only a few percentage of cells are opened wall the bulk density of these products is about 30–35 kg/m<sup>3</sup>. The blowing agent gas contained in the cells results in a very low thermal conductivity, and the main use of rigid PUF is in insulating panels of refrigerators. Flexible PUFs have a virtually completely open cell structure with typical densities of 20–45 kg/m<sup>3</sup> and are, therefore, not useful as insulators. These foams are frequently used in production of seats, furniture, etc.

During the last decades, chlorofluorocarbons (CFCs) such as CFC-11 (CCl<sub>3</sub>F) were widely used since these are nontoxic, non-flammable, stable, cheap, effective,

**Table 1.**

Classification of PU-based products according to density and rigidity

| Density | Rigidity                 |                        |                             |
|---------|--------------------------|------------------------|-----------------------------|
|         | High                     | Medium                 | Low                         |
| High    | Glass fiber RIM-PUR      | Elastomer, TPU, RIM-PU |                             |
| Medium  | Rigid integral skin foam |                        | Flexible integral skin foam |
| Low     | Flexible foam            | Filling foam           | Rigid foam                  |

well soluble in isocyanate and polyols but not in the PU, and give excellent thermal insulation performance [1]. However, it should be noted that they are ozone depleting and are not environment-friendly. Low-boiling organic liquids have been found as useful agents in foam production, with the additional benefit, found when developing rigid PU foam, of improving the insulating properties of the foam. Producing PU foam is relatively straight forward and can be accomplished by adding water. This will result in the release of CO<sub>2</sub> gas, and larger amounts of urea  $-(NH-CO-NH)-$  linkages in the polymer chain [7]. Using water alone, however, would not result in satisfactory product quality or durability for most applications. In this review we consider polyol and polyisocyanate reactants as the ‘monomers’ which convert to PUs during chemical reactions.

## 2. Polyurethane Market and Consumption

Due to the variety in physical, chemical, thermal and mechanical properties, PUs have a broad range of applications, Some of the main applications are detailed below:

- Flexible PUF: automobile seating, furniture, carpets.
- Rigid PUF: refrigerator, insulation board.
- Elastomers: footwear, adhesives, medical.
- RIM: automobiles (bumpers, side panels).
- Other: carpets, casting, sealants [8].

Treatment of aged polymeric materials has been a problem all around the world, and trends indicate that the overall amount of solid waste that the human generate continues to increase. Nowadays, as PUs are used in so many every day applications and industrial uses, they enter the municipal solid waste stream, usually by way of discarded consumer and industrial products. These products frequently are durable goods with a long lifespan such as upholstered furniture, mattresses and automobile parts. By weight, approximately 1.3 million tons of waste PUs are generated each year in the USA alone. The largest market is for PUF (47% flexible and 28% rigid), followed by PU elastomers (8%). For the US this added up to around 1640 million ton in 1995. North America represents around 30–35% of the world total consumption, with the remainder in Western Europe (around 40%), the Far East (around 15%) and the rest of the world (around 10–15%) [9].

This variety of uses would result in a huge amount of consumption, causing some environmental problems (Table 2 and Fig. 1).

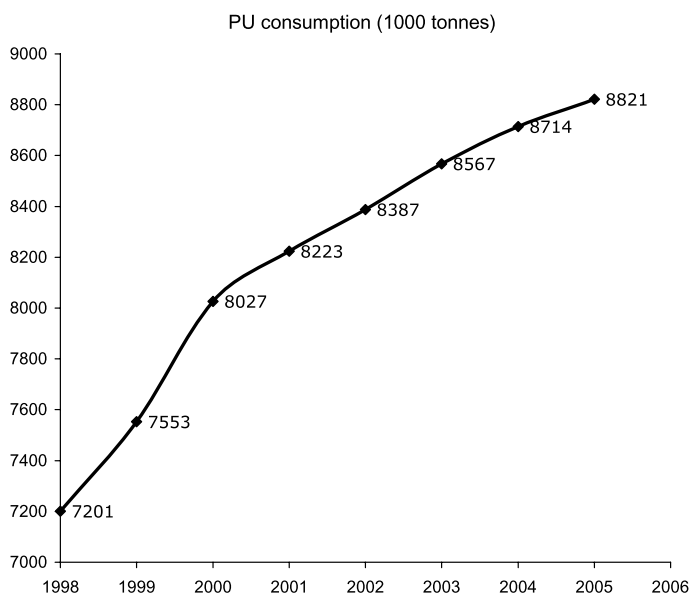
## 3. Physical Recycling

Physical recycling essentially consists of regrinding, rebinding, adhesive pressing, injection molding and compress molding. Grinding PU wastes into powders and

**Table 2.**  
PU consumption in the United States

| Application                  | Million pounds | %     |
|------------------------------|----------------|-------|
| Building and construction    | 1459           | 26.8  |
| Transportation               | 1298           | 23.8  |
| Furniture and bedding        | 1127           | 20.7  |
| Appliances                   | 278            | 5.1   |
| Packaging                    | 251            | 4.6   |
| Textiles, fibers and apparel | 181            | 3.3   |
| Machinery and foundry        | 178            | 3.3   |
| Electronics                  | 75             | 1.4   |
| Footwear                     | 39             | 0.7   |
| Other end-use markets for PU | 558            | 10.2  |
| Total PU production          | 5444           | 100.0 |

Source: *The Socio-Economic Impact of Polyurethanes in the United States* (February 2004), prepared by the American Chemistry Council.



**Figure 1.** Worldwide PU consumption 1998–2005 [8].

then re-using these powders in various ways constitutes a mechanical recycling approach. Wastes for this process can come from factory trim and scrap, as well as post-consumer products. The powdered PU is available as filler in production of PU foams or elastomers. When used as fillers, the powders are usually first added to the polyol component in a PU production process. Molded PU products, such as auto seat cushions can contain up to 20% regrind material without any deterioration in

properties or performance. Mechanical recyclers grind PU into powders with various milling and knife-cutting processes. To be used as fillers, PU particles should be less than 200  $\mu\text{m}$  in size, and preferably under 100  $\mu\text{m}$ . Shredded PUR foam wastes can be rebounded using heat, pressure and an adhesive binder. Rebinding is commonly used to make vibration sound dampening mats, flooring, sports mats, cushioning and carpet underlay. In a similar process, known as adhesive pressing, PU granules are coated with a binder and cured under heat and pressure. Contoured products are made from adhesive pressing; they include automotive floor mats and tire covers. RIM and reinforced-RIM parts can also be ground into small particles, which can be molded under high pressure and heat to form solid parts for the auto industry. These compression-molded solid parts, such as pump and motor housings, and catalytic converter shields, can contain up to 100% RIM regrind.

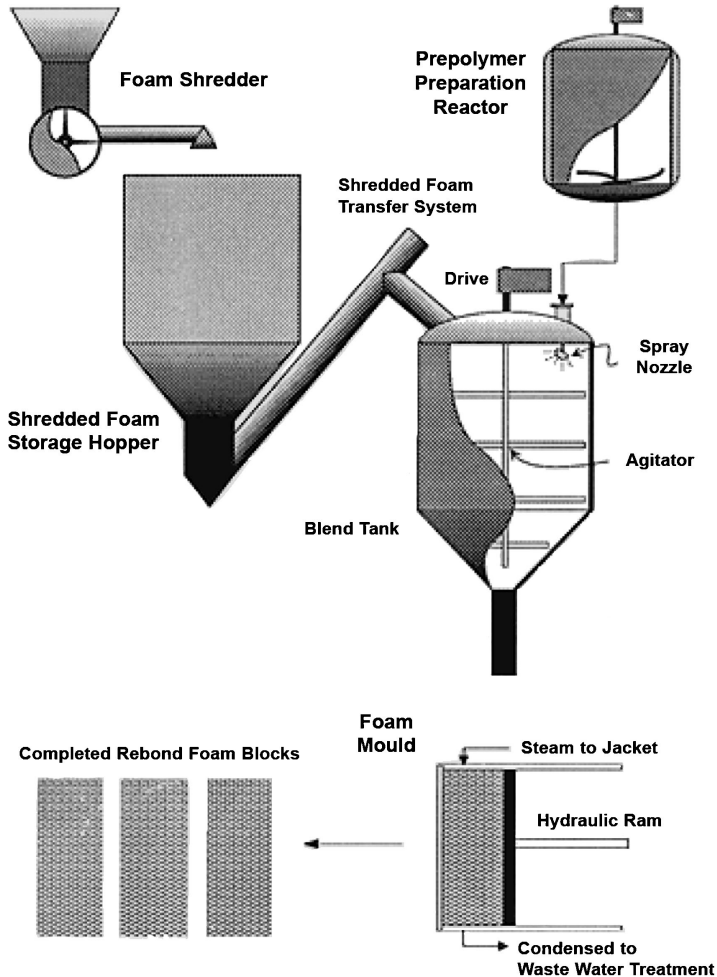
### 3.1. Rebinding

In the recycling process, the final product is molded PU from pieces of shredded flexible PU foam, held together with a binder. Its relative high density and excellent resilience make it suitable for applications including vibration sound dampening, flooring, sport mats, cushioning, packaging and carpet underlays [10, 11]. In fact, rebinding process has been in use for decades. Up to 50 000 ton of rebinding foam are processed each year in Western Europe and new applications are constantly being developed. PU foam scrap can be reprocessed by mixing scrap particles (size approx. 1 cm) with diisocyanate MDI followed by form-shaping at 100–200°C and 30–200 bar pressure. PU construction boards with excellent water and moisture resistance are obtained, or insulation panels for use in new refrigerators or freezers. PUF can likewise be recycled to blocks that find use in carpets, sports hall mats or furniture. The enormous amount of PUF foam recovered from scrapped vehicles may satisfy a large part (in the USA almost 50%) of the market of carpet underlay [12]. For PUR foam from scrapped buildings this recycling option is very important as well but is more complicated and often impossible due to the use of flame retardants in these materials [13]. Rebinding of PU foam can be carried out through batch or through continuous molding. The foam blocks are further processed to fabricate parts and articles, resulting in trim which in turn can be reused in the process. Rebinding is also applied in the molding to-final-shape technology which allows processors to optimize material use and cost.

The process flow is: collection  $\rightarrow$  sorting  $\rightarrow$  shredding  $\rightarrow$  coating with binder  $\rightarrow$  compressing shaping  $\rightarrow$  activation of adhesive binder  $\rightarrow$  curing of adhesive binder  $\rightarrow$  production of rebounded parts (Fig. 2).

The quality of the product of the rebinding process depends on several factors, such as types and grades of the foams used, particle size and uniformity of foam pieces, density required of the end product, quality of the binder, binder/foam ratio [11, 14].

Microcellular PUF is recycled by comminuting to particle sizes of 0.01–2 mm and addition to the poly-addition mixture for preparing PUs from polyisocyanates,



**Figure 2.** Typical rebinding equipment using batch molding (source: ISOPA).

substances reactive toward isocyanates and having active hydrogen and chain extenders or cross-linkers, catalysts, blowing agents and customary additives in an amount of from 0.1 to 40 wt%, based on the poly-addition mixture [15].

### 3.2. Regrinding

Regrind technology, sometimes also described as powdering, is a process to re-use ground PU waste as filler in PU foams or elastomers. It involves two steps: (i) grinding PU material into a fine powder and (ii) mixing powder with the polyol component to make new Pus.

The first step necessary for the potential recycling of PU involves a process required to reduce the particle size of the original PU product to a level that will allow the material to be reprocessed in a secondary manufacturing step. The optimum fi-

nal particle size is 50–200  $\mu\text{m}$ , depending on the application. The various types of PU waste products, consisting of either old recycled parts or production waste (e.g., trimmings, scrap parts, etc.), are converted to flake, powder or pellet, depending on the particular type of PU that is being recycled [16–18]. In most cases, this can be accomplished by either shredding or grinding the PU in order to provide the necessary media for recycling. This waste is usually a direct result of the trimming of the slab stock buns and the subsequent fabrication into the finished product. For molded foam operations, the waste is typically generated during the manufacturing process as a result of the flashing at the mold closing edges and the venting holes, which in extreme cases may amount to a total of 6% of material waste, depending on the size of the overall part. In the case of slab stock or flexible foam, up to 12% of cut-off waste is to be expected, depending on the particular manufacturing process [11, 19].

There are a number of ways to produce small particles. One option is the two-roll mill process. It consists of two rollers, rotating in opposite directions and at different speeds to create shear forces in the very narrow gap between them. Another grinding process, successfully used at pilot scale for flexible foams, is the pellet mill. It consists of two or more metal rollers, which press the PU foam through a metal plate with small holes (die). Other technologies, such the precision knife cutter, are also under evaluation for the grinding of flexible foams. A particular process combining cutting and mixing involves a high shear mixer installed in the polyol tank. The added benefit of this process is the prevention of any thermal degradation of the powder during size reduction. Glass-filled RIM parts require special grinding methods. The impact disc mill appears to be suitable as technique for pulverizing such very tough parts [20, 21].

At pilot scale, the high shear mixer appears to be suitable to provide the right mixing quality. The step to operational activity, however, requires adequate metering of the powder alongside the polyol. The metering unit of the entire PU machine needs to be suitable for the handling of filled polyols. Such technologies do exist. These were developed when glass filled RIM was first introduced into the market or when melamine powder was introduced into the flexible foam industry. The moisture content of the powder is critical and drying of the powder could be necessary before mixing [22].

One factor that limits the amount of scrapped PU foam that can be recycled by regrinding is the viscosity of the polyol-fine particle mixture that can be handled by the processing equipment. In practice this can be up to 15 wt% regrind when MDI polyol is used, and up to 25% with TDI [12]. The major problem of grinding processes for waste processing is that of economy: grinding scrap PU foam to a size below 100–125  $\mu\text{m}$  is no exception to that. Development work during the late 1990s reported by Stone *et al.* [23] has shown that two-roll milling can be economically viable alternative to cryogenic processes. This is demonstrated in a large commercial plant that produces around 450 kg/h fine powdered PU foam with an average particle size of 50  $\mu\text{m}$ . This powder can be used as filler in new PU foam, intro-



**Table 3.**

Comparison of the specifications of standard and recycled flexible car seat foams

| Property                 | Standard | Recycled |
|--------------------------|----------|----------|
| Powder content (%)       | –        | 15       |
| Indentation hardness (N) | 360      | 360      |
| Compression set (50%)    | 5.6      | 7.0      |
| Tensile strength (kPa)   | 152      | 144      |
| Elongation-at-break (%)  | 132      | 103      |

duced by mixing it into the polyol at a concentration of around 20 wt% of polyol. This keeps the viscosity of the powder-polyol slurry in the range 2000–5000 cP, below the practical limit of 20 000 cP where a transition from viscous fluid to paste was theoretically shown to occur, near a PU foam powder loading of 40–45 wt% of polyol.

PU foam in automotive seating has been successfully recycled using regrind technology. In laboratory tests, new molded foam seats have been made containing 15–20% recycled material and exhibiting excellent processing characteristics. Depending on foam type and filler loading, physical properties may be affected requiring an adjustment of material specifications (Table 3).

The investment cost of the first generation equipment has limited the operational potential of this technology to slab stock. Current development is directed to provide economic technologies to smaller operations. A typical scheme of the regrinding process is shown in Fig. 3.

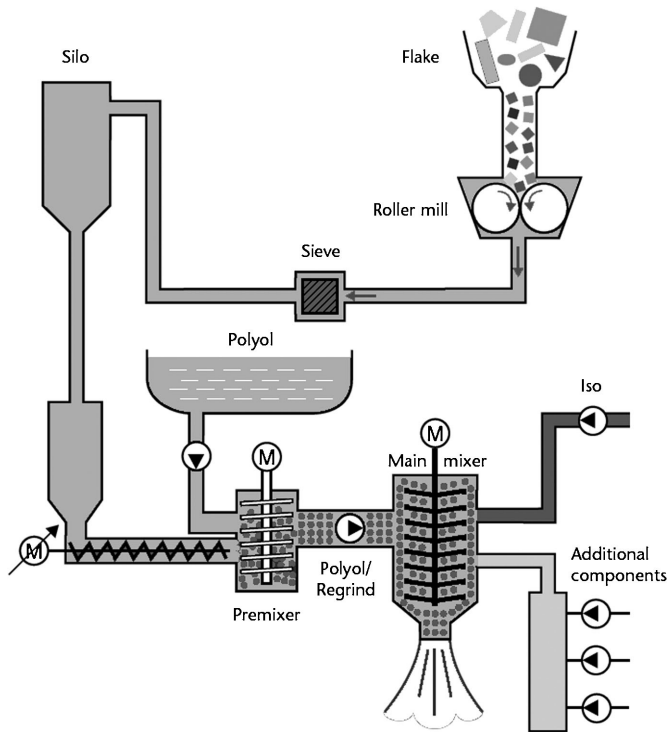
Bayer Corporation has invented a method for making energy-absorbing foam with PU fillers that produces energy-absorbing foam with properties that are comparable to foam made without fillers [11, 24].

### 3.3. Adhesive Pressing

This is a rapid and easy to perform route. In this recycling method the surface of PU particles is coated using an adhesive binder and bonded in a heated press. It has been suggested as the oldest method for flexible PU foam recycling. During the 1990s its market potential was about 10 000–20 000 ton per year in Western Europe and 50 000–60 000 ton per year in North America. In Europe, RIM particles are being recycled in under-floor heating pipes in buildings which have a very large recycling capacity, especially in Germany [13]. A typical process is to mix the PUF scrap particles with MDI which is followed by forming at 100–200°C and 30–200 bar pressure. The product of this method has been useful as insulation panels, carpets and furniture [12, 25].

### 3.4. Compression Molding and Injection Molding

This compression method involves molding PU particles at 180°C temperature and pressure of 350 bar in order to flow the particles together, without any binder. Com-

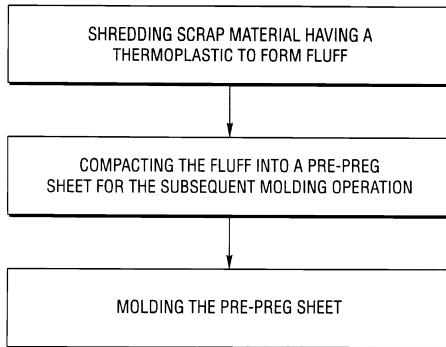


**Figure 3.** Typical regrinding process for PU recycling (source: ISOPA).

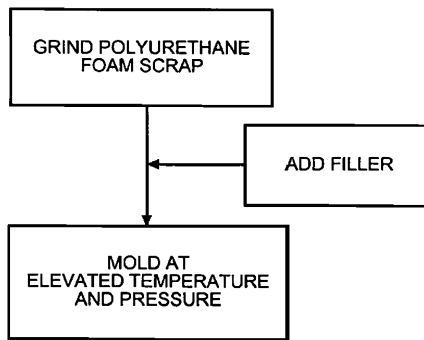
pression molded parts contain 100% recycled material. Compression molding, used primarily with reaction injection molded (RIM) PUs, is capable of producing high performance recycled products. RIM and reinforced RIM parts are ground into fine particles and subjected to high pressure and heat to generate a solid material that is ideal for many automotive applications. This method is successfully applied to RIM PU recycling into automotive parts [26].

Cross-linked PU recycling is also possible by injection molding. This method is also able to be performed on mixture of PU and other plastics. Presence of thermoplastics would help the process. The main advantages of this process are: improving the mechanical properties and surface shape of product while it can be any color [27, 28] (Fig. 4).

A method for recycling materials including a significant portion of PU foam includes forming the foam into a fluff of particle sized 0.25–1.0 inch, and most preferably 0.25–0.50 inch. The material is moved to a mold and molded at an elevated temperature and pressure. Preferably, the glass transition temperature of the foam is exceeded. Other filler materials may be mixed with the fluff material. This process would recycle scraps which include PU foam, greatly reducing the complexity of re-utilizing the scraps [29, 30] (Fig. 5).



**Figure 4.** Block diagram of recycling the thermoplastic containing PU wastes.



**Figure 5.** Block diagram of compress molding for PU recycling.

### 3.5. Energy Recovery (Combustion–Incineration)

Energy recovery is the only suitable disposal method for PU wastes with no markets and applications. Incinerations with energy recovery has an important role to play, viewed within then context of the growing range of recycling and re-use options for plastics, including PUs. With 86% of the world’s oil, coal and gas being burnt for energy, there is a strong case for partial substitution of the energy resources with waste plastics. Where it is identified as the most appropriate waste management option, modern technology can now ensure that the emissions from waste combustion plants are safely managed. This strongly applies to scrap with PU laminates to wood, leather or fabrics, or commingled materials. Also, flame-retardant materials make recovery and recycling very difficult. It offers the most valuable solution where other recovery options do not show environmental benefits and are economically more costly. Successful energy recovery schemes will largely depend on the economics of the collection system with facilities for separation and pre-treatment of the mixed plastics waste. Based on an effective logistics framework, energy recovery can become the most cost-effective recovery option. Although more needs to be done to establish the infrastructure throughout Europe, there is no doubt that incineration with energy recovery is key to the proper management of plastic waste,

including PUs. The relative cost of the various energy recovery options to society is similar for mono-combustion or for the use as co-fuel for cement kilns but here the cost of collection, sorting, pre-treatment and transport might add considerably to the overall cost [31–33].

Incineration of a PU foam results in a volume reduction of around 99% which has large implication to reducing the land filling of this material, at the same time destroying CFCs and other harmful foam blowing agents. The presence of flame retardants complicates things, and the effect of these compounds on combustion processes receives much attention nowadays [11, 34].

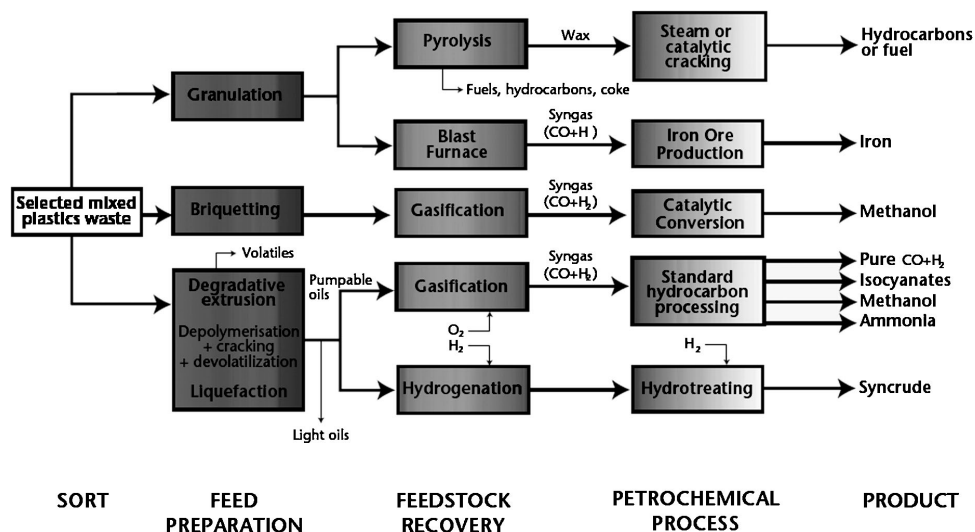
Aiming at reducing CO and NO emissions, first the effect of excess air has been studied at a combustion temperature of 900–1000°C. NO emissions have been found to increase with increasing primary air as well as with secondary air flow. The conversion of PU nitrogen to NO is about 5.7% and the conversion of PU carbon to CO is 0.55%. Further reduction of NO emissions would be obtained using re-circulation of flue gases to the primary air, which would also complete the burnout of traces of hydrocarbons, HCN and NH<sub>3</sub>. Two tests, involving 50 and 100% of the primary air by re-circulated flue gas at the same secondary air flow, show a further reduction of the CO and NO emissions by 15 and 45%, respectively [35]. The behavior of nitrogen from polymers and plastics in waste-derived fuels during combustion including PUF has also been investigated [36–38]. It was found that the emissions of NO + NO<sub>2</sub> during combustion in an entrained gas quartz tube reactor (750–950°C, O<sub>2</sub>/N<sub>2</sub> = 7 : 93) depended strongly on the amount of char produced from high-nitrogen fuels (PU foam, nylon, urea-formaldehyde glue, sewage sludge, etc.) and the nitrogen content of the fuels. At nitrogen content of 6.6 wt%, less than 10% of the PUF nitrogen is emitted as NO + NO<sub>2</sub>.

#### 4. Thermochemical Recycling

In the thermochemical recycling of PU products, it is tried to use the waste stream as a source of energy, fuel or some value monomers. A schematic flow diagram of all these methods is shown in Fig. 6.

##### 4.1. Pyrolysis

Pyrolysis is one of the recycling methods for PU wastes [35]. Pyrolysis uses a heated, oxygen-free environment to pyrolysis of plastics into gases and mixture of monomers [39, 40]. During the process, mass loss starts at about 250°C and levels off at a mass loss of 80% at 300°C, while the remaining 20% is decomposed until temperature reaches 500°C. Using differential scanning calorimetry (DSC) several exothermic peaks are observed in the process, the most important being at 250–300°C and others at the start (340°C) and end (490°C) of the second decomposition stage. A yellow smoke and viscous liquid are produced in the first stage, followed by slow decomposition of the liquid into gaseous products. Heating the PU samples at 300 K/s under a flow of nitrogen or air (850–1000°C), significant amounts of



**Figure 6.** Possible chemical products obtained through feedstock thermochemical recycling (source: ISOPA).

CO, CH<sub>4</sub>, HCN, NH<sub>3</sub> and NO are released in addition with probably some small amounts of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>. The measured amounts as fraction of PU foam carbon (for the CO and CH<sub>4</sub>) and nitrogen (for HCN, NH<sub>3</sub>, NO) have been found to be 26, 18, 34, 8 and 21% at 850°C and 24, 17, 64, 14 and 9% at 1000°C, respectively. The formation of CO and NO is explained through intermediates such as HNCOO. It is argued that first some PU nitrogen is released directly as NO, followed by a large release of HCN, which may be oxidized in the gas phase to NO as well. Pyrolysis of a PU adhesive is also a common process [41]. Decomposition of the PU to a mass loss of approx. 95% occurs between 230 and 380°C. RIM pyrolysis typically gives (at >450°C) 5–25 wt% char, 10–45 wt% liquids and >40 wt% gases. The liquid is red-colored viscous single-phase oil with a viscosity that increases with time. In order to increase the amount, quality and marketability of especially the liquid product, the use of activated carbon and PU chars in a secondary pyrolysis reaction step have been tested [42, 43].

#### 4.2. Gasification

This recycling method is useful for mixed waste streams, and consists of an exothermic process which would produce heat, ashes and gas (synthesis gas). The gas fraction contains the combustible gases H<sub>2</sub> and CO [6, 12, 44–46]. In this process, waste stream is heated and then combined with air/O<sub>2</sub>. This forms a CO + H synthesis gas, which can go into refinery processes for production of different chemicals, e.g., ammonia and alcohols. There is a pump required for liquid feedstock that is obtained by liquefaction; the process condition is: oxygen media at 1200–1500°C, 20–80 bar. In a few seconds it gives a 98–99% conversion into gases plus a slag.

The produced  $H_2$  and CO can be also used in polyether and isocyanates production, respectively.

### 4.3. Hydrogenation

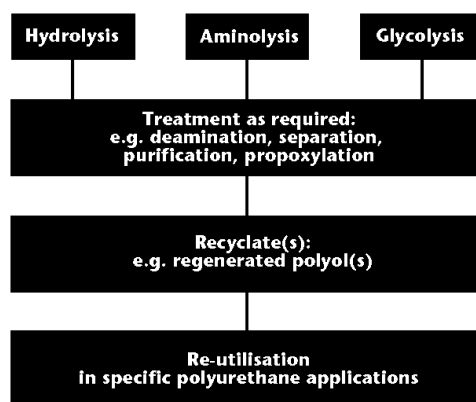
Hydrogenation is defined as a compromise between pyrolysis and gasification methods. The effect of heat and high-pressure  $H_2$  results in gaseous and liquid products [47]. Hydrogenation contains a step more than pyrolysis to produce even more pure gases and oils through a combination of heat, pressure and hydrogen. The viability of this method requires resolution of two important issues: the purity of gases and oils derived from pyrolysis and hydrogenation, and the associated costs to produce functional finished products. These can be used as fuel (partly used as energy source for the process) and chemical feedstock [48].

## 5. Chemical Recycling

The main goal in the chemical recycling is the recovering of monomers as the main products of urethane bonds breaking down under controlled reaction conditions. This goal can be achieved using main chemical recycling methods, namely, hydrolysis, aminolysis and glycolysis as the old methods and nowadays some modified processes (Fig. 7).

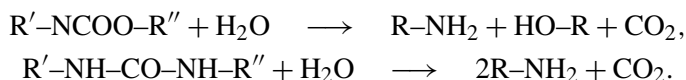
### 5.1. Hydrolysis

Recycling of PU wastes by hydrolysis started during the 1970s in the USA. Superheated steam at  $200^\circ\text{C}$  would convert PU foam from a two-phase liquid within around 15 min in an oxygen-free medium and under pressure. Hydrolysis is the reaction of PU with water, producing both polyols and amine-based products [12, 49, 50]. The recycled polyols can be used as a monomer in PU formation, and the amine intermediates can be re-used to produce other PU components, e.g., iso-



**Figure 7.** Chemical recycling methods for PU waste treatment (source: ISOPA).

cyanates [51–53]. The chemistry of a general hydrolysis process is:



As shown in the chemical formula, monomers are recovered as their previous forms (e.g., polyols) or as functional group interconversion (FGI) forms (e.g., amines as FGI forms of isocyanate functional groups). After recycling, the distilled and purified polyol can be used as a component in the new PU formulations [54]. Focusing later on the recovery and recycling of the polyol showed that superheated steam temperature should be around 288°C, producing a polyol that gave excellent new PU foam for seat cushions when mixed at 5% to virgin material. Too high temperature gives a decrease in useful polyol recovery, while polyol recovered at too low steam temperature produces unstable new PU foam due to unsuccessful recovering of the polyol [55]. In order to improve the hydrolysis process, PU hydrolysis suffers from unfavorable economics and lack of markets for the recycle products [12, 13].

Waste or scrap PU may be conveniently and economically converted to useful active-hydrogen-containing polyethers and polyamines by contacting the PU with water, strong base, and an activating agent such as a quaternary ammonium compound containing at least 15 carbon atoms or an organic sulfonate containing at least 7 carbon atoms. The activating agent acts as phase transfer catalyst (PTC) and helps to accelerate the rate of hydrolysis reactions and monomer recovering in high yields and high purities [56].

Recent studies nonetheless address the recovery of other products besides polyols, and the alkaline compounds that may accelerate the hydrolysis [57–59]. Kabushiki Kaisha and Takeda Chemical Industries in Japan have invented an apparatus for hydrolysis of polyisocyanate derivatives having at least one isocyanate group to be hydrolyzed into raw materials or derivatives thereof for the target compounds. The apparatus includes: a hydrolysis section for bringing only pressurized water in a liquid state at a temperature of 190–370°C into contact with the target compounds in the reactor and a post-processor for conducting such as dewatering, addition, distillation, separation, and liquid separation for a hydrolysis product discharged from the reactor [60].

The reaction of polyether-based PU foam with dry atmospheric pressure steam is also an approach to waste PU foam recovery. Complete reaction at 190–230°C yields high-quality polyol, isomeric toluenediamines and carbon dioxide as primary products. Kinetic analysis of toluenediamine yields versus time suggests the occurrence of a parallel first-order reaction scheme wherein urethane linkages react up to 50-times faster than urea linkages. The results derived from kinetic investigations indicate that urethane linkages are broken by direct hydrolysis, whereas urea linkages undergo thermal dissociation to parent isocyanate and amine [61, 62]. Hydrolysis of PUF and recovery of diamines and polyethers (or polyesters) from the hydrolysate would be carried out near atmospheric pressure and temperatures above about 185°C. The reaction zone would contain water vapor which comprises

increasing the rate of diamine production by inclusion of a minor, but effective amount of ammonia. Volatilized diamines are separated from the foam and preferably removed from the reaction zone, e.g., in an overhead stream, while polyethers (or polyesters) are recovered [63].

### 5.2. Aminolysis

Aminolysis is the reaction of PU waste with amines such as dibutylamine, ethanolamine, lactam or lactam adduct under pressure at elevated temperatures. In this process potassium and sodium hydroxide are the main catalysts. There are few studies in the field of amine treatment for PU recycling. Polyols, aromatic amines and carbamates are the main products. In order to improve the products ethylene or propylene oxide is reacted with it to convert the amines. Finally, the polyols are separated which can be used in new PUF formulation as virgin polyol. The results show significant changing in the new foam properties when the amine contaminants dose not separate from recycled polyol [64–66].

MDI-based flexible PUFs are recycled by alkanolamines without a catalyst at 150°C in order to recovering polyol monomers and amine-based compounds. The decomposition product is completely separated into two layers. The upper liquid layer is contaminated polyether polyol, and the lower liquid layer is methylene diphenyl amine (MDA) and alkanolamine derivatives [67].

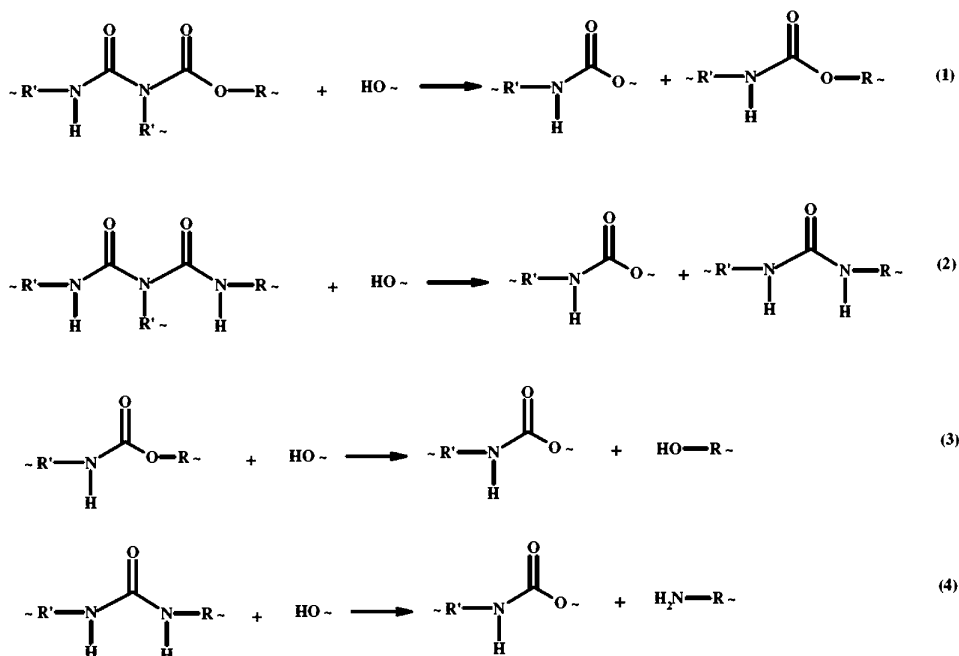
For successful recovery of value chemicals and liquid reactive compounds, the partial chemical recycling method of rigid PUF was reported. In this method the recycling process is completed in an extruder in a reheating process and using diethanolamine (DEA) as a decomposing agent. The product with stable viscosity is obtained by the reheating process at 175–200°C for 2 h, regardless of the extruding condition. An amine adduct, which is an intermediate, has been found to be the cause of instability of the discharged product from the extruder. At the initial stage of reheating, the intermediate would be decomposed, releasing toluenediamine, which promotes further decomposition of the discharged products [68].

In another research article, flexible PUF has been decomposed into a polyol mixture by an extruder with diethanolamine (DEA) as a decomposing agent. The resulting decomposed product could be used as an alternative virgin polyol in reclaiming PU. In the case of reclaiming elastomer by using the decomposed product without any purification, virgin polyol could be alternated by the decomposed product up to 80%. It is a great improvement compared with the reclamation to foam, whose percentage has been 5% maximum. Furthermore, the percentage could be improved up to 100% by purifying the decomposed product [69].

### 5.3. Glycolysis

Glycolysis is the most widely used chemical recycling method for PU wastes. This method was developed during 1980s [70–74]. Figures 8 and 9 show the schematic mechanism of the glycolysis process. The main aim of this process is the recovering





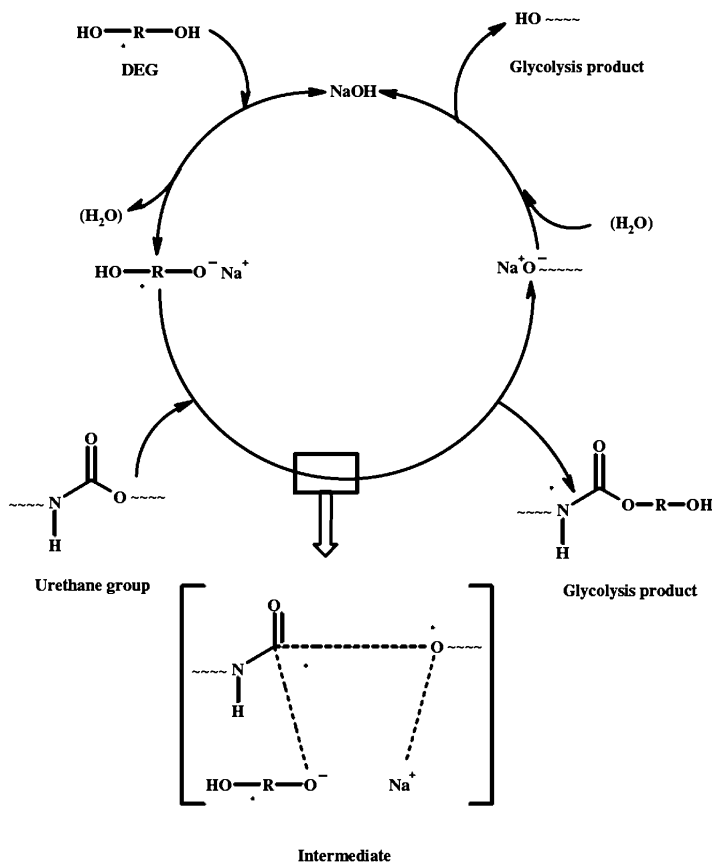
**Figure 8.** Glycolysis of urethane functional groups and their co-existing functional groups such as allophanate, biuret and urea.

of the valued monomers, namely, polyols from waste PU, for the production of new material.

Basically, glycolysis implies heating the PU scrap (grinded) up to 180–220°C in high-boiling-point glycols with a catalyst. Glycols act as destroying agents by attaching to the urethane functional groups which followed by breaking of bonds and liberation of the polyols and amines.

Various methods have been reported in chemical recycling and all of them have their own merits and drawbacks. The destroying agent is usually diethylene glycol (DEG) and co-reagent would be an amine, diethanol amine (DEA). A temperature below 180°C gives too low catalyst activity; a temperature above 220°C gives undesired side-reactions towards amines. One of the most important drawbacks in chemically used reagents is applying amine as co-reactant which causes some problems in using of end processed and recovered materials. Amines act as catalyst and enhance the reaction rate between polyol and polyisocyanate by increasing of the electrophilicity of isocyanate functional group and facilitate attaching of polyols and formation of PUs in too short and uncontrollable reaction conditions. It means that after treating of PU wastes by destroying agents containing amine, it need to lowering amine contents in the polyol portion in order to prevent undesired reactions and finding controllable reaction kinetic models.

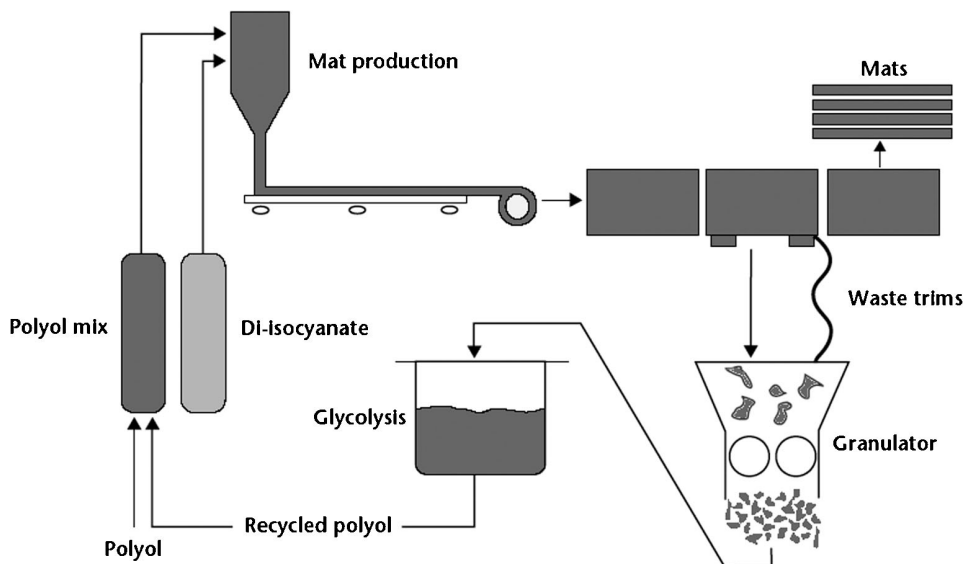
There are two approaches, wherein a single polyol is recovered or both flexible and rigid polyols components are recovered [12, 75–79]. A process for preparing a



**Figure 9.** Schematic mechanism of PUF glycolysis in the presence of a glycol as destroying agent and NaOH as the catalyst.

recyclate polyol obtained from glycolysis of PU comprises reacting scrap PU with a short-chain compound containing at least 2 OH groups in the presence of a catalyst and adding a cyclic carbonate. The process results in a recyclate polyol having a low primary aromatic amine content which may be used to produce cellular or non-cellular PUs, polyurea-PUs or polyisocyanurates [80]. As mentioned before, the main goal in recovering of the monomers is the reusing alone or in blend by virgin polyol in new PUF formulation. Nowadays and due to limitations in transporting and logistics, recycling and recovering of the polyols using a ‘foam to foam’ process omit the waste collections and solve transportation and logistics problems. Today, and in the chemicals market, many companies exhibit their recovered polyols from wastes alone and/or in blend with virgin one. In this review, we try to cover companies active in polyol chemical recycling using glycolysis technology and investigate the technologies in detail.

An industrially installed example of this process is the developed glycolysis process by Getzner Werkstoffe in Austria. Figure 10 shows the Getzner glycolysis concept.



**Figure 10.** The Getzner glycolysis concept (source: ISOPA).

A process for double-phase recovery of polyols was developed by ICI, referred to as the split-phase glycolysis process. In this process scrap PUF, preferably based on MDI, is reacted with DEG, producing two product phases in the reactor. The lighter layer contains the flexible polyol, the heavier layer contains the MDI derived compounds which are converted into a rigid polyol using propylene oxide. The recovered polyols can be used to produce new PUF [12, 81–93]. Reacting the glycolysis polyol product with an alkylene oxide in a mol ratio of  $<1$  mol of alkylene oxide per mol of active amine hydrogen atom in the glycolysis polyol product would yield a useful polyol [94]. It has been demonstrated that in the presence of MDI both of the split phases of the glycolysis mixture can be used as components of the urethane adhesive mixtures for bonding woods, metals, plastics, glass, ceramics, paper and leather [95]. In order to recycle the mixture of PUs and other plastics, the plastic waste is reacted with an alcohol mixture comprising at least one low-molecular-weight bi-functional alcohol and at least one polyether–polyol, and then the resultant glycolysis polyol is mechanically separated from the other plastic waste [96]. Nowadays many scientific groups investigate novel glycols, as well as new methodologies for chemical PU waste treatment and application of the recycled polyols in new foam formulations.

BASF has invested resources and technology to develop what are believed to be practical approaches to the chemical recycling of PU process and end-of-life waste. Initially, the well-established glycolysis technology developed at BASF Schwarzheide, Germany. BASF Corporation's Laboratory in Wyandotte, MI, USA has continued research and development in this area, concentrating on modifying the chemistry and process to suit our PU customers in North America. Their second-

generation chemistry has resulted in homogeneous recycled polyols with residual amine content of less than 0.1% in a one-pot process operating at ambient pressure and moderate temperatures [82].

Another process for the preparation of recyclate polyols invented by BASF is by reacting rigid PU foam with short-chain hydroxyl-containing compounds, which comprises adding epoxidized native fatty oils to the reaction mixture after glycolysis at a temperature range of 10–80°C below the glycolysis temperature [97].

The properties of the recyclate are generally dependent on the properties of the PU waste stream. A glycolysate from high density non-cellular rigid PU is possible to be made using the second generation technology, being reformulated into a variety of rigid and semi-rigid foams at up to 100% polyol loading while providing excellent mechanical and physical properties in the finished product. Examples include polyisocyanurate foam, insulation non-critical foam, structural foam, free energy absorbing foam, low density void filling foam, elastomeric coatings, rigid non-cellular PU and molded semi-flexible foam. Members of the European Diisocyanate and Polyol Producers Association (ISOPA) and independent researchers have optimized single-phase glycolysis. Split-phase glycolysis, where the product separates in two phases, has been developed up to pilot scale for MDI flexible foams. The viability of glycolysis appears to be in the area of recycling production waste as opposed to post consumer waste.

The glycolysis of water-blown PUF by ethylene glycol (EG) yields the polyol and a solution of ureas, carbamates and amines in the EG, while hexamethylenetetramine (HMTA) is added. HMTA suppresses the formation of solid phases in the products at a diaminotoluene (DAT) content below 100 ppm [98]. A research team in Taiwan has optimized the process conditions for glycolysis of PU from waste refrigerators/freezers, as to produce high-quality polyol recyclate [99–102]. In a stirred tank reactor at approx. 220°C (1 bar) a residence of 2 h is sufficient for 87–95% recovery yield with DEG reactant and potassium acetate as catalyst. A second study on PUF foams from ELVs has shown an optimal residence time of 90 min at the same temperature, pressure and catalyst. The recovered product polyols had then boiling points in the range of 245–260°C. For both studies initial PU scrap size has been 0.15–0.85 mm. Also recycled polyol from RIM PU scrap glycolysis has been used to replace up to 60% of the original for new PU RIM parts in Germany [13]. Nowadays, two step processes are going to be more convenient. In the first step of the process, PU-containing scrap is subjected to a glycolysis reaction to produce polyol products. In the second step, the polyol products are used as initiators in a reaction with alkylene oxide to produce oxyalkylated polyols for preparing PUs [86, 103].

Recovering of secondary polyols from polyadducts which contain non-glycolyzable constituents has been researched in Japan. In the process, a precomminuted polyadduct starting material is pretreated with glycols in a shear reactor at elevated temperature and pressure, for a relatively short time period, the non-glycolyzable constituent being further comminuted and dispersed and the polyadducts being

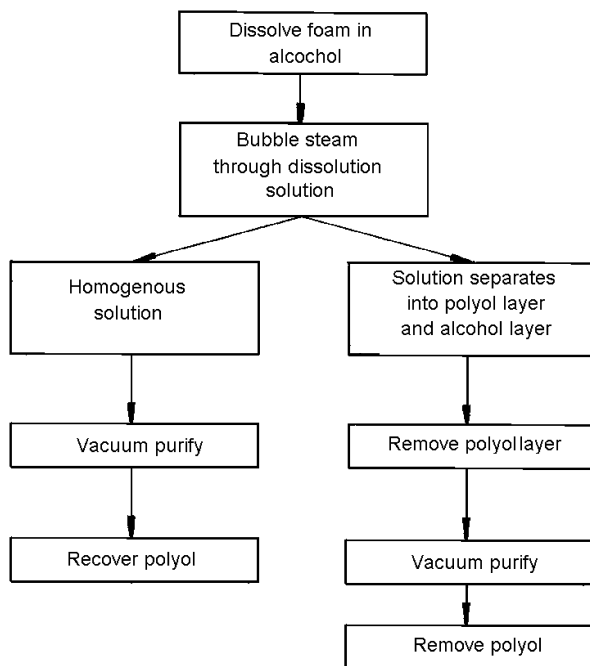
preglycolized. The pre-product thus obtained is broken down in subsequent stir reactors at a somewhat elevated temperature and for longer times, first without the further addition of glycol, and then with further addition of glycol. From the secondary polyol finally obtained, a plastic can be produced which can be further processed to make plastic components [104].

PU-based floorings, such as carpet, can be recycled by contacting with an organic polyol and heating it, so that the PU containing layer softens or partially liquefies, but can be re-solidified by contact with additional polyisocyanate [105, 106].

As the most economic process for PU recycling is the glycolysis process, there are many reports investigating the glycolysis of PU. These reports have discussed different aspects of catalyst effect in glycolysis, physical chemistry of glycolysis process, formulation of glycolysis product, etc. The glycolysis of flexible PU foam in various glycols has been investigated in US Patent No. 3,632,530. In this patent the temperature range employed in the dissolution reaction has been reported to be 170–185°C, using a tertiary amine as the catalyst, the glycol/PU scrap weight ratio is 3:1 [107]. Frulla and co-workers investigated the reaction conditions for the conversion of scrap rigid PUF to polyols. In their investigation, a combination of diethylene glycol and approximately 5% pbw diethanolamine was found to be especially useful in the recovery of scrap PUF [108]. Tucker and Ulrich have studied the glycolysis process for converting scraps flexible PUF to a homogenous mixture of polyols [109]. The recovered polyol is useful particularly in the preparation of rigid PUF. Kondo *et al.* provided the process for obtaining the polyol-containing homogenous liquid composition from rigid PUFs. The glycolysis of PUF was performed at 150–220°C in the presence of the mixture of aliphatic diol and a mono-alkanol amine. In this report the recovered polyol was useful in the preparation of rigid PUF [110]. Sheratte has reported a process for converting a depolymerized reaction product containing amines into polyols with using ethylene and propylene oxide at 120–140°C as capping agents [111]. In 1979, the glycolysis of thermoset PU elastomers was also examined [112]. Simioni and Bisello examined the glycolysis mechanism and the properties of glycolysis products of PUF scraps from industrial slab stock [113]. Simioni and co-workers investigated the glycolysis of PU elastomer waste mainly from shoe sole production. They have worked on different fields of PU recycling [114–116]. The interest in glycolysis method made it as the main aim of recycling researches during the last decade [73, 117–122].

#### 5.4. Other Chemical Recycling Methods

Hydroglycolysis is a complex method which is performed by adding water to a glycolysis process in which LiOH is used as the catalyst. Ford Motor Company has developed this process, it is claimed that this produces a simpler and more valuable product mixture. Although it is more expensive than conventional glycolysis as the purification of the polyol-rich product is more complicated. It has the advantage that complex mixtures of dirty and contaminated PU wastes can be processed as well, which otherwise would have to be land filled [123]. The recovered polyol may



**Figure 11.** Block diagram of hydroglycolysis recycling method.

replace up to 50% of virgin polyol material for PUF foams. The extraction of pure polyether triols from the products is accomplished using hexadecanes or similar boiling point hydrocarbons [124]. A schematic of the hydroglycolysis process is shown in Fig. 11 [125].

Another chemical recycling process is the reaction of waste PUF with alcohol under pressure and at an elevated temperature. This produces the original polyols together with urethane products. The various components are then separated in order to allow their reprocessing and reuse. This method uses a heated, oxygen-free environment to break down PU and plastics into gases, oils and solids. It seems difficult to scale up this process. A new recycling method has been introduced which is based on utilizing a polar and aprotic solvent, e.g., dimethylsulfoxide (DMSO), *n*-methyl pyrrolidone (NMP), dimethylformamide (DMF), acetonitrile, tetrahydrofuran (THF), hexamethylphosphoric acid triamide (HMPT) and mixtures thereof, for PU dissolution. PU waste is added to the solvent, and then a non-solvent is added to the PU solution to form a suspension of PU in the mixture. In the next step, the solvent is removed to form a suspension of PU in a non-solvent. Finally, the solution is filtered for further treatment.

## 6. Current and Future Developments

Increasing waste-to-energy and other thermal processing activities involving gasification, pyrolysis and two-stage combustion (removing problematic components in

the first stage) will also allow for the disposal of significant amounts of scrap PU without many difficulties. This may however be slowed down by lack of support for technology development: current trends focus very much on renewable energy (e.g., biomass), and more efficient fossil fuel-derived heat and power instead.

Recently, an elastic permeable pavement has been invented, which uses waste PU chips obtained from shoe soles, toys, refrigerators, vehicles and decrepit recycled PU resilient pavement to solve the smelling problem of waste tires, nurse resources and prevent environmental pollution, and to provide comfort and shock absorption in walking as well [126]. The addition of micronized PU powders obtained from waste flexible PUs to urea-formaldehyde resins and to phenol-formaldehyde resins improves markedly the performance of the panels prepared with these resins, namely plywood and particleboard [127]. Formulations of adhesives and film materials from PU waste would suggest a versatile resource-saving and environmentally sound procedure for the reuse of polyglycol adipate urethanes of dense and micro-cellular structure. The idea allows transformation of a polymer waste into a reclaim with a high level of service parameters [128].

Several methods for material and chemical recycling of PU materials have been developed, by far the most important being glycolysis and regrinding. New trends in chemical recycling of PU waste have been focused on two aims: new recycling agents and new sources for process activation. Nowadays it is tried to recycle the PU waste without regarding the waste separation, selection, etc. A number of successful laboratory glycolysis processes have been carried out utilizing two different types of PU foams recovered from shredder residue:

- a. The best case scenario: handpicked PU foams from SR with >80% conversion into liquid initiator.
- b. The worst case scenario: mixed PU materials separated by an automated separation process from shredder residue with 50% conversion into a liquid initiator.

Both TDI- and PMDI-based flexible foams are prepared from the novel recycled polyols prepared by propoxylation of the glycolyzed products (initiators) obtained from the mixed PU materials [129].

New chemical agents are now researched for PU recycling. Microporous PU elastomers have been recycled by tris(1-methyl-2-chloroethyl) phosphate-induced degradation. The phosphorus-containing degradation products would be transformed into reactive intermediates by reaction with propylene oxide and are used for the preparation of rigid PU foams [130]. Split-phase glycolysis of isocyanate derived cold cure PUF is also performed with glycerin as a new glycolyzing agent. The process has been reported to be simple and economically attractive among material recycling processes. Glycerin has been used as a green destroying solvent and sodium hydroxide as the catalyst in the chemical recycling of PUF wastes [131]. Results showed the performance of the method in recovering monomer in high yield and purity. The spectroscopy techniques have been used in order to elucidation of chemical structures and data compared with an authentic sample data.

Chemical structures were fully adaptable with commercial polyols' structures and prepared foams had properties same as foams prepared with virgin one polyol. The merit of this method was the replacing of DEG with glycerin as a green and safe destroying agent. In addition, using fast and convenient method, namely microwave irradiation, has been introduced as a new energy source for the glycolysis process [132–136]. Reported results showed the performance of the method in successful polyol recovery and the using of recycled polyol in the new foam formulations. Data were comparable with foams prepared by virgin polyol data. Then the energy source would decrease the time required for a chemical recycling process to be performed, yielding high-quality products. In the meantime, the PU recycling studies are increasing, because of the lack of economic efforts for recycle marketing: until reasonable size markets for PU waste materials can be created the final destination for most PU wastes will be landfill, for years to come, until this is halted by legislation. It seems, due to increasing petrol-based chemical prices, that using novel technologies and methodologies in chemical recycling of monomers from polymeric wastes can be open a new window in environmental protection, as well as recovering valued monomers and oligomers.

## 7. Conclusion

Recycling of PU is motivated in order to minimize wastes and reduce environmental pollution. There are several methods for chemical and physical recycling of PU wastes, by far the most important being glycolysis and rebinding, respectively. The recovered of polyol in glycolysis process may replace up to 50% of virgin polyol material for PUF foams formulation. Also in the regrinding route there is a factor that limits the amount of scrapped PUF that can be recycled by this method, that is, the viscosity of the polyol–fine particle mixture. The major advantage of recycling processes for waste processing is that of economy and investment cost. Trends in PU recycling research are increasing, because of the lack of economic efforts for recycle marketing. Until reasonable markets for PU waste materials can be created the final destination for most PU wastes will be landfill. By means of recycling and as its main aim is to recover polyols from waste PU, it is possible to produce new materials and it is noticeable that this process can reduce environmental pollution and affect job creation for human resources.

## References

1. M. Szycher, *Szycher's Handbook of Polyurethanes*. CRC Press, Boca Raton, FL (1999).
2. G. Oertel, *Polyurethane Handbook*. Hanser Publishers, Munich (1993).
3. Z. Wirpsza, *Polyurethanes: Chemistry, Technology and Applications*. Ellis Horwood, London (1993).
4. <http://www.psrc.usm.edu/macrog/index.htm> (accessed 2010).
5. R. P. Lattimer, M. J. Polce and C. Wesdemiotis, *J. Anal. Appl. Pyrol.* **48**, 1 (1998).



6. J. Troitsch, *International Plastics Flammability Handbook*, 2nd edn, J. Troitsch (Ed.). Hanser, Munich (1990).
7. M. Ogawa, H. Fukazawa and Y. Ogawa, US Patent No. 5,035,833 (1991).
8. Gobi, *New Forecasts for Polypropylene, Polystyrene and Polyurethane*. Gobi International, London (2002), available at: [www.gobi.co.uk](http://www.gobi.co.uk).
9. V. Walter, <http://www.poliuretanos.com.br/Ingles/Chapter1/11Market.htm> (accessed 2010).
10. C. Kliwer and C. Kittel, US Patent No. 6,228,478 (2001).
11. R. Zevenhoven, *Treatment and Disposal of Polyurethane Wastes: Options for Recovery and Recycling*. Energy Engineering and Environmental Protection Publications, Espoo (2004).
12. J. Scheirs, *Polymer Recycling: Science, Technology and Applications*. Wiley, Chichester (1998).
13. E. Weigand, in: *Properties and Applications of Recycled Polyurethanes Recycling and Recovery of Plastics*, J. Branderup, M. Bittner, G. Menges and W. Micheali (Eds), Section 7-10. Hanser Publishers, Munich (1996).
14. Bayer, *Rebonded Foam on the Basis of an NCO Prepolymer*. Bayer, Leverkusen (1987).
15. T. Jeschke, A. Kriesmann, U. Bruns, W. Scholz, M. C. Luderwald and H. Peuker, US Patent No. 5,891,927 (1999).
16. C. Diessel, C. Kliwer, G. Burak, E. Blumel and C. Kittel, US Patent No. 5,185,380 (1993).
17. H. Stone, R. Villwock and B. Martel, in: *Proceedings of the Polyurethanes Conference*, Boston, MA, p. 3 (2000).
18. R. Villwock, in: *Proceedings of the Polyurethanes Expo*, Columbus, OH, p. 373 (2001).
19. M. P. Neuray, H. M. Sulzbach and J. Wirth, in: *Proceedings of the Polyurethanes Conference*, Boston, MA, p. 37 (2000).
20. Fact Sheet, *Recycling and recovering polyurethanes: Re-grinf-Powdering*, available at: [www.isopa.org](http://www.isopa.org) (accessed 2010).
21. J. Jensen, in: *Proceedings of the Polyurethane Foam Association Conference*, Arlington, VA, 6 pages (2000).
22. W. J. Farrissey, R. E. Morgan, M. R. I. Tabor and M. Zawisza, *Am. Chem. Soc. Symp. Ser.* **513**, 272 (1991).
23. N. D. Duggan, D. S. Loren, A. C. Kirk and B. G. Naik, in: UTECH 96, paper 17 (1996).
24. N. H. Nodelman and D. D. Steppan, US Patent No. 6,258,867 (2001).
25. F. E. Mark and A. Kamprath, in: *Society of Automotive Engineers Conference*, paper 2000-01-1514 (2000).
26. A. J. Hulme and T. C. Goodhead, *J. Mater. Process Technol.* **139**, 322 (2003).
27. <http://www.warwick.ac.uk/atc/materials/recyclecentre/seminar/paper7> (accessed 2010).
28. G. M. Gebreselassie, H. G. Wolf Jr., V. Sendijarevic, Q. Anjum, D. Klempner and K. C. Frisch, US Patent No. 6,576,176 (2003).
29. G. M. Gebreselassie, H. G. Wolf Jr., K. C. Frisch, D. Klempner and V. Sendijarevic, US Patent No. 6,299,811 (2001).
30. C. B. Chang, US Patent No. 5,478,865 (1995).
31. F. Mark and A. Calori, Technical Report 8028. APME, Brussels (1998).
32. L. A. A. Schöen, M. L. Beekes, J. van Tubergen and C. H. Korevaar, *Mechanical separation of mixed plastics from household waste and energy recovery in a pulverized coal-fired power station*. Technical report. APME, Brussels (2000).
33. F. E. Mark, *Polyurethane Energy Recovery and Feedstock Recycling Technology, A Summary Overview of Latest European Technologies*. DOW Europe, Horgen (2005).

34. A. Tohka and R. Zevenhoven, *Processing Wastes and Waste-Derived Fuels Containing Brominated Flame Retardants*. Energy Engineering and Environmental Protection Publications, Espoo (2002).
35. Y. Rogaume, F. Jabouille, M. Auzanneau and J. C. Goudeau, in: *Proceedings of the 5th International Conference on Technologies and Combustion for a Clean Environment*, Lisbon, p. 345 (1999).
36. R. Zevenhoven, E. P. Axelsen, P. Kilpinen and M. Hupa, in: *Proceedings of 39th IEA FBC Meeting*, Madrid, p. 104 (1999).
37. R. Zevenhoven, E. P. Axelsen, M. Elomaa, V. P. Liukkonen, P. Kilpinen and M. Hupa, in: *Proceedings of the 40th IEA FBC Meeting* (2000).
38. R. Zevenhoven, E. P. Axelsen, M. Elomaa, P. Kilpinen and M. Hupa, *Waste-to-Energy Technology Program*. Finnish National Technology Agency, Helsinki (2003).
39. R. P. Lattimer, M. J. Polce and C. Wesdemiotis, *J. Anal. Appl. Pyrol.* **48**, 1 (1998).
40. J. W. Wu, W. F. Sung and S. H. Chu, *Int. J. Heat Mass Trans.* **42**, 2211 (1999).
41. R. Font, A. Fullana, J. A. Caballero, J. Candela and A. García, *J. Anal. Appl. Pyrol.* **58**, 63 (2001).
42. D. Y. Takamoto and M. A. Petrich, *Ind. Eng. Chem. Res.* **33**, 3004 (1994).
43. E. J. Im, S. H. Kim and K. H. Lee, *J. Anal. Appl. Pyrol.* **82**, 184 (2008).
44. C. Branca, C. B. Di, A. Casu, V. Morone and C. Costa, *Thermochim. Acta* **399**, 127 (2003).
45. J. Scheirs and W. Kaminsky, *Feedstock Recycling and Pyrolysis of Waste Plastics*. Wiley, Chichester (2006).
46. D. A. Hicks, D. J. Soderberg, J. D. Winter and H. Cantero, *Cell. Polym.* **15**, 172 (1996).
47. *Modern Plastics Encyclopedia*. McGraw-Hill, New York, NY (1996).
48. G. Behrendt and B. W. Naber, *J. Univ. Chem. Tech. Metallurgy* **44**, 3 (2009).
49. *Alliance for the Polyurethanes Industry*, available at: <http://www.polyurethane.org/recycling> (accessed 2010).
50. K. Kodama, K. Murayama, T. Kumaki, F. Kasuya, Y. Nagase, M. Nakata and S. Nishida, US Patent No. 6,660,236 (2003).
51. L. R. Mahoney, S. A. Weiner and F. C. Ferris, *Environ. Sci. Technol.* **8**, 135 (1974).
52. <http://inventors.about.com/library/inventors/blpolyurethane.htm> (accessed 2010).
53. <http://www.apcoaviation.com> (accessed 2010).
54. <http://www.corrosion.com/madison/polyurethane2.html> (accessed 2010).
55. O. B. Johnson, US Patent No. 4,025,559 (1977).
56. G. A. Campbell and W. C. Meluch, *Environ. Sci. Technol.* **10**, 182 (1976).
57. L. S. Yang and D. A. Macarevich, US Patent No. 5,208,379 (1993).
58. Z. Dai, B. Hatano, J. Kadokawa and H. Tagaya, *Polym. Degrad. Stabil.* **76**, 179 (2002).
59. L. R. Mahoney, US Patent No. 4,196,148 (1980).
60. J. S. Robert and C. D. Clifford, US Patent No. 4,328,368 (1982).
61. S. Nishida, O. Kato, Y. Nagase, R. Fukuzato, M. Yamagata, K. Kodama, T. Matsuda, S. Suzuki and T. Naito, US Patent No. 6,630,517 (2003).
62. J. L. Gerlock, J. Braslaw, L. R. Mahoney and F. C. Ferris, *J. Polym. Sci. Polym. Chem.* **18**, 541 (1980).
63. S. Mishra, V. S. Zope and R. D. Kulkarni, *Polym. Plast. Technol. Eng.* **43**, 1001 (2004).
64. M. Modesti and F. Simioni, *Polym. Eng. Sci.* **36**, 2173 (1996).
65. K. C. Frisch, *Advances in Plastic Recycling*, Vol. 1. Technomic, Lancaster, PA (1999).
66. K. C. Frisch and D. Klempner, *Advances in Plastic Recycling*, Vol. 2. Technomic, Lancaster, PA (2001).
67. J.-J. Ge and S. Kokki, *J. Wood Sci.* **44**, 103 (1998).

68. K. Kanaya and S. Takahashi, *J. Appl. Polym. Sci.* **51**, 675 (1998).
69. T. Fukaya, H. Watando, S. Fujieda, S. Saya, C. M. Thai and M. Yamamoto, *Polym. Degrad. Stabil.* **91**, 2549 (2006).
70. H. Watando, S. Saya, T. Fukaya, S. Fujieda and M. Yamamoto, *Polym. Degrad. Stabil.* **91**, 3354 (2006).
71. J. Braslaw and P. Pai, US Patent No. 4,159,972 (1979).
72. J. L. Gerlock, J. Braslaw and J. Albright, US Patent No. 4,316,992 (1982).
73. T. Munzmay, H. Nefzger, W. Rasshofer and W. Meckel, US Patent No. 5,508,312 (1996).
74. H. R. Van der Wal, *J. Reinf. Plast. Composit.* **13**, 87 (1994).
75. K. Kanaya and S. Takahashi, *J. Appl. Polym. Sci.* **51**, 675 (1994).
76. K. Kodama, K. Murayama and T. Kumaki, US Patent No. 6,489,373 (2002).
77. M. M. Alavi Nikje, M. Haghshenas and A. Bagheri Garmarudi, *Polym. Plast. Technol. Eng.* **45**, 569 (2006).
78. C. Molero, A. de Lucas, F. Romero and J. F. Rodríguez, *J. Appl. Polym. Sci.* **109**, 617 (2008).
79. M. M. Alavi Nikje and F. A. Mohammadi, *Polimery* **54**, 541 (2009).
80. C. H. Wu, C. Y. Chang, C. M. Cheng and H. C. Huang, *Polym. Degrad. Stabil.* **80**, 103 (2003).
81. P. C. Kierkus and K. You, US Patent No. 5,763,692 (1998).
82. S. Held, D. A. Hicks and M. Har, in: *Proceedings of R'99 Recovery Recycling Re-Integration*, Geneva, p. 92 (1999).
83. K. K. You, D. T. Durocher, P. C. Kierkus and T. L. Fishback, *J. Cell. Plast.* **34**, 261 (1998).
84. Y. Yoshio, K. Makoto, T. Kazunobu and M. Shuichi, *Chem. Sus. Chem.* **1**, 133 (2007).
85. G. Parrinello, D. Thorpe, G. Verhelst, J. F. G. Hopper and W. M. B. A. De, US Patent No. 5,605,935 (1997).
86. T. Munzamy, W. Rasshofer, K. H. Dorner and U. Limna, US Patent No. 5,338,763 (1994).
87. V. Sendijarevic, US Patent No. 6,750,260 (2004).
88. V. Sendijarevic, AU0143354A5 (2001).
89. V. Sendijarevic, WO/2001/064778 (2004).
90. C. Molero, A. de Lucas and J. F. Rodríguez, *Polym. Degrad. Stabil.* **93**, 35 (2008).
91. M. M. Alavi Nikje, M. Haghshenas and A. Bagheri Garmarudi, *Polym. Bull.* **56**, 257 (2006).
92. M. M. Alavi Nikje, M. Haghshenas and A. Bagheri Garmarudi, *Polym. Plast. Technol. Eng.* **46**, 265 (2007).
93. M. M. Alavi Nikje and A. Bagheri Garmarudi, *Iran. Polym. J.* **19**, 287 (2010).
94. R. M. Machado and B. Farrell, US Patent No. 5,300,530 (1994).
95. J. Borda, A. Racz and M. Zsuga, *J. Adhesion Sci. Technol.* **16**, 1225 (2002).
96. B. Naber, V. Neiss, M. Gassan and W. Deutsch, US Patent No. 6,069,182 (2000).
97. B. Naber and M. Lezius, US Patent No. 5,556,889 (1996).
98. M. Modesti, F. Simioni, R. Munari and N. Baldoïn, *React. Funct. Polym.* **26**, 157 (1995).
99. M. M. Alavi Nikje, M. Haghshenas, A. Bagheri Garmarudi, N. Barzandeh and K. Taheri, *Int. J. Pure Appl. Chem.* **1**, 407 (2006).
100. J. Datta, *J. Elast. Plast.* **42**, 117 (2010).
101. C. H. Wu, C. Y. Chang and J. K. Li, *Polym. Degrad. Stabil.* **75**, 413 (2002).
102. H. Benes, J. Rosner, P. Holler, H. Synkova, J. Kotek and Z. Horak, *Polym. Adv. Technol.* **18**, 149 (2007).
103. C. Molero, A. de Lucas, F. Romero and J. F. Rodríguez, *J. Mat. Cycl. Waste Manag.* **11**, 130 (2009).
104. H. Stone, Recycling of flexible polyurethane foam, in: *Advances in Plastic Recycling, Vol. 1: Recycling of Polyurethanes*, K. C. Frisch, D. Klempner and G. Prentice (Eds), p. 244. Technomic, Lancaster, PA (1998).

105. B. U. Kettemann and M. Melciorre, US Patent No. 5,684,054 (1997).
106. R. A. Berard, US Patent No. 6,837,950 (2005).
107. O. Kinoshita, US Patent No. 3,632,530 (1972).
108. F. F. Frulla, A. Odinak and A. Sayigh, US Patent No. 3,738,946 (1973).
109. B. Tucker and H. Ulrich, US Patent No. 3,983,087 (1976).
110. O. Kondo, T. Hashimoto and H. Hasegawa, US Patent No. 4,014,809 (1977).
111. M. B. Sheratte, US Patent No. 4,110,266 (1978).
112. H. Ulrich, B. Tucker, A. Odinak and A. R. Gamache, *J. Elast. Plast.* **11**, 208 (1979).
113. F. Simioni and S. Bisello, *Cell. Polym.* **2**, 281 (1983).
114. F. Simioni, M. Modesti and S. A. Rienzi, *Cell. Polym.* **6**, 27 (1987).
115. F. Simioni, M. Modesti and C. A. Brambilla, *Cell. Polym.* **8**, 387 (1989).
116. M. Modesti, F. Simioni and S. A. Rienzi, *J. Elast. Plast.* **24**, 288 (1992).
117. F. Simioni and M. Modesti, *Cell. Polym.* **12**, 337 (1993).
118. J. Krescher, H. Schwager, W. RaBhofer and R. Pfefferkorn, in: *Chemical Recycling of an All-Polyurethane Instrument Panel — Industrial Realisation*, Utech, p. 22 (1996).
119. J. Borda, G. Pasztor and M. Zsuga, *Polym. Degrad. Stabil.* **68**, 419 (2000).
120. F. Simioni, M. Modesti and S. A. Reinzi, in: *Proceeding of International Conference of Cellular Polymers*, London (1991).
121. M. Gassan, B. Naber, V. Neiss, P. Moeckel and W. Weissflog, US Patent No. 5,357,006 (1994).
122. N. Asahi, K. Sakai, N. Kumagai, T. Nakanishi, K. Hata, S. Katoh and T. Moriyoshi, *Polym. Degrad. Stabil.* **86**, 147 (2004).
123. J. Gerlock, J. Braslaw and M. Zinbo, *Ind. Eng. Chem. Res.* **23**, 545 (1984).
124. J. Braslaw and J. Gerlock, *Ind. Eng. Chem. Res.* **23**, 552 (1984).
125. J. L. Gerlock, J. Braslaw and J. Albright, US Patent No. 4,316,992 (1982).
126. S. S. Kang, US Patent No. 7,125,199 (2006).
127. H. R. Mansouri and A. Pizzi, *Holz Roh-Werkstoff* **65**, 293 (2007).
128. V. V. Bestuzheva, N. V. Sirotinkin and N. V. Tokarev, *Russ. J. Appl. Chem.* **80**, 1120 (2007).
129. V. Sendijarevic, *J. Cell. Plast.* **43**, 31 (2007).
130. G. Grancharov, V. Mitova, S. Shenkov, A. Topliyska, I. Gitsov and K. Troev, *J. Appl. Polym. Sci.* **105**, 302 (2007).
131. M. M. Alavi Nikje and M. Nikrah, *Polym. Bull.* **58**, 411 (2007).
132. M. M. Alavi Nikje and M. Nikrah, *Polym. Plast. Technol. Eng.* **46**, 409 (2007).
133. M. M. Alavi Nikje and M. Nikrah, *J. Macromol. Sci. Pure Appl. Chem.* **44**, 613 (2007).
134. M. M. Alavi Nikje, M. Nikrah and M. Haghshenas, *Polym. Bull.* **59**, 91 (2007).
135. M. M. Alavi Nikje, M. Nikrah and F. H. Agha Mohammadi, *J. Cell. Plast.* **44**, 367 (2008).
136. M. M. Alavi Nikje and F. H. Agha Mohammadi, *Polym. Plast. Technol. Eng.* **49**, 818 (2010).