VOLUME 1

RECYCLING OF POLYURETHANES

ADVANCES IN PLASTICS RECYCLING

Edited by

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Introduction

THE safe disposal and reuse of industrial and urban wastes is a serious challenge in terms of the environment and public health. There is increasing pressure brought about by governments around the world to utilize safe disposal of industrial and postconsumer plastics wastes as well as to seek alternate routes to disposal by landfilling. The costs for landfilling have increased as has resistance of communities to this type of disposal.

Options of technologies for waste disposal of plastics other than landfilling are: recycling, reuse and incineration (waste-energy).

Recycling of industrial thermoplastic waste is practiced throughout the plastics industry, although it has certain limitations with regard to the number of recycles and the type of plastic. The recycling of thermosets presents a different problem since they cannot be reprocessed in general by conventional melting processes such as extrusion or injection molding. However, today even thermosets such as polyurethanes have been successfully recycled by both chemical and physical processes.

A so-called "critical mass" is necessary to make recycling commercially viable, i.e., the amount of recyclate should be large enough to carry out a continuous process. Another important consideration is the location of the recycling plant, which should be near a waste-producing facility in order to minimize transportation costs.

Recycling of waste materials can be classified according to the following categories.

Primary Recycling refers to the recycling of waste materials back to the original application. The presence of contamination in the recycled product, mixed plastic wastes, and partial degradation of the material as the result of repeated thermal processing are some of the problems encountered.

Secondary Recycling refers to the use of recycled material in less demanding applications that do not require the physical properties of the original materials.

Tertiary Recycling involves the degradation of the waste material to the basic chemical monomers or low molecular weight oligomer employing thermal and chemical processes. It also includes decomposition of the waste to fuels (both gaseous and liquid).

Quaternary Recycling refers to energy conversion by means of incineration. This is usually carried out when dealing with commingled plastic wastes or when no other recycling process is feasible. The combustion must be carried out in plants with suitable scrubbers to meet environmental regulations.

The first volume of this series is focused on the recycling of polyurethanes. Although there are thermoplastic polyurethanes (TPUs), the majority of polyurethane applications involve thermoset polyurethanes such as foams, elastomers, RIM and SRIM, and coatings.

The recycling of polyurethanes can be classified as follows:

(1) Physical recycling: The processes used in physical (mechanical) recycling can be categorized as:
   - flake and particle bonding (especially flexible PU foams—carpet underlay)
   - use of PU granules as fillers
   - compression molding
   - thermoplastic processing (where applicable)
   - thermoforming (e.g., flexible, semi-rigid, rigid foams and elastomers and composites)

(2) Chemical recycling: A number of different processes have been studied that are used for the recovery of urethane polymer components. In general, they can be classified as follows:
   - pyrolysis
   - hydrolysis
   - glycolysis
   - recovery with alkanolamines
   - petrochemical feedstock processing

   A combination of these processes can also be used such as pyrolytic hydrolysis or hydroglycolysis. In general, chemolysis or chemical recycling involves treatment, at elevated temperatures, of manufacturing and post-consumer scrap with a glycol or alcohol, water, amine or alkanolamine as well as mixtures thereof, to generate materials which may be used again in the manufacture of a second generation urethane product. Catalysts are usually used in these processes. The resulting products usually consist of complex mixtures of products which may require separation or a separate second process. Pyrolysis may also be considered a chemolysis operation, since it generates either useful products or may lead to the production of useful fuel feedstocks.

There are of course other forms of chemolysis such as oxidation, photolysis and hydrogenation, and work is also being carried out on these approaches.

(3) Energy conversion: Energy recovery is an important element of the waste management of polyurethanes, as is the case for all polymeric materials. Today's modern incinerators for the conversion of polymeric materials into energy meet all health, emission and environmental standards. The choice of utilizing PU scrap for energy recovery is a viable option when the PU products are contaminated and commingled with other products in such a way that an economic separation would not be feasible.

This book is a compilation of the present ongoing studies on recycling of urethane and, in general, isocyanate-based polymers. The focus is on thermosetting urethane polymers and includes most of the above options.

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Present State of Polyurethane Recycling in Europe

E. WEIGAND[1]
W. RAßHOFER[1]

INTRODUCTION

POLYURETHANES (PUR) are a class of polymers that is produced by the polyaddition of polyisocyanates and polyols.

$$n\,\text{OCN-R}_1\text{-NCO} + n\,\text{HO-R}_2\text{-OH} \rightarrow [\,\text{CONH-R}_1\text{-NH-CO-O-R}_2\text{-O}\,]_n$$

Polyisocyanate Polyol Polyurethane

They were discovered by Otto Bayer et al. in the 1930s. Since then, they have found a multitude of applications, e.g., as flexible foams for upholstery purposes in furniture and mattresses; as rigid foams for thermal insulation of refrigerators and buildings; but also as microcellular elastomers or structural foams for interior and exterior automotive parts, for shoe soles and for sports articles [1]. Polyurethanes are therefore a whole family of specialty polymers that covers a wide range of physical properties. In addition to their versatility, they are noted in most applications for their durability. The contribution to a long product lifetime and the corresponding resource conservation are important environmental considerations that favor the selection of polyurethanes. PUR consumption in Western Europe in 1995 was 1.3–1.5 million tons (excluding adhesives, surface coatings and fibers). This represents about 5% of all plastics in Western Europe. A breakdown of PUR consumption by branch,

[1]Bayer AG, Leverkusen, Germany.

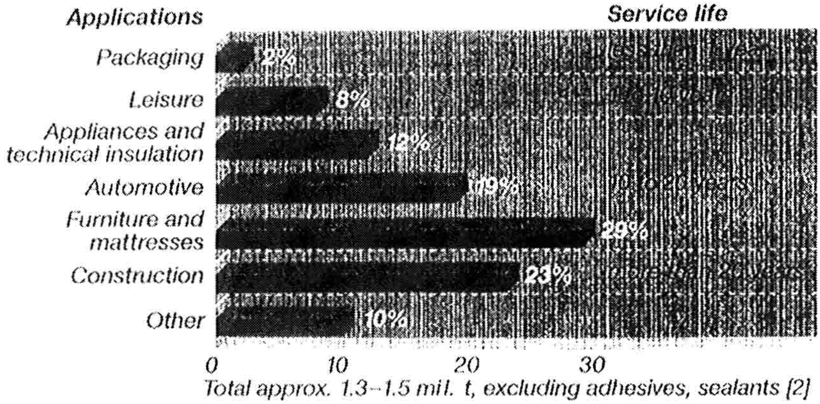

Figure 1.1 Polyurethane applications and product lifetimes in Western Europe in 1995.

together with an indication of the respective service life [2], is provided in Figure 1.1.

The long lifetimes of polyurethane-containing products, sometimes exceeding 30 or even 50 years, mean that the return of these products as postconsumer waste materials is a slow process, still not fully under way today. Indeed, in the construction industry, which uses rigid foam panels and boards, postconsumer waste may be anywhere between 5% and 15%. This is a rough estimate; statistics are not available. It is therefore not surprising that the major part of recycled polyurethanes today is made from the much more readily available production waste.

Thermoplastic polyurethanes (TPU), which are processed on injection molding machines or extruders, account for a comparatively small part of the total polyurethane consumption. Most polyurethanes are made by reaction pouring or reaction injection molding (RIM) methods [1]. In these cases the high molecular weight polymer is made by mixing two or more liquid components at the PUR processor's premises. This is in contrast to thermoplastics, where the raw material manufacturer makes the polymer.

Polyurethanes are mainly chemically crosslinked polymers. Although the degree of chemical crosslinking varies from high for rigid foams to low for PUR elastomers, they are usually nonmeltable, i.e., thermosets. For this reason, again in contrast to thermoplastics, they often cannot be reprocessed by one general process such as remelting. Rather, a whole range of different recovery methods is employed. The best method may vary from case to case, and depends on the properties of the polyurethane, the intended application for the recycled material, the availability of the necessary equipment and, above all, on logistical, economic and ecological factors.

TERMINOLOGY AND METHODS FOR RECYCLING AND RECOVERY

In Western Europe the plastics industry is promoting the following terminology:

(1) "Recovery" comprises:
- mechanical recycling
- feedstock recycling (and chemical recycling)
- energy recovery (or energy recycling), sometimes referred to as combustion

(2) "Disposal" comprises:
- incineration (without energy recovery)
- landfill

Whereas some politicians want to see these recovery and disposal options in hierarchical order, it is industry's view (based on first-hand experience) that mechanical and feedstock recycling and energy recovery ought to be given equal importance within a balanced approach to plastics waste management. *All* recovery options should be exploited to the maximum possible degree, paying due respect to local conditions as well as to the limitations arising from logistics and market capacities. "Simple" incineration and landfill are following as the lesser and least preferred options. Regulations have already been passed or drafted that will exclude organic materials from being landfilled in the future.

The tailor-made polyurethanes can be recycled and recovered by a multitude of processes covering all three recovery categories from above (Figure 1.2). Before going into the details for the industry branches that make use of polyurethanes in one form or another, a brief description of the individual processes shall be given. For more details see References [2,3].

MECHANICAL RECYCLING

Rebonding

Rebonding is the oldest way of recycling polyurethanes. Ever since the large-scale production of flexible foam began, scrap has been cut into flakes and used to produce rebonded foam primarily for carpet underlay. The flakes are coated with a polyurethane binder (approx. 10–15 wt%) and compressed to a predetermined degree, e.g., in large rectangular or cylindrical molds (Figure 1.3). Curing of the PUR binder is achieved by hot steam in most cases.

Adhesive Pressing

Using particle board technology, rigid foam particles (among others), rang-

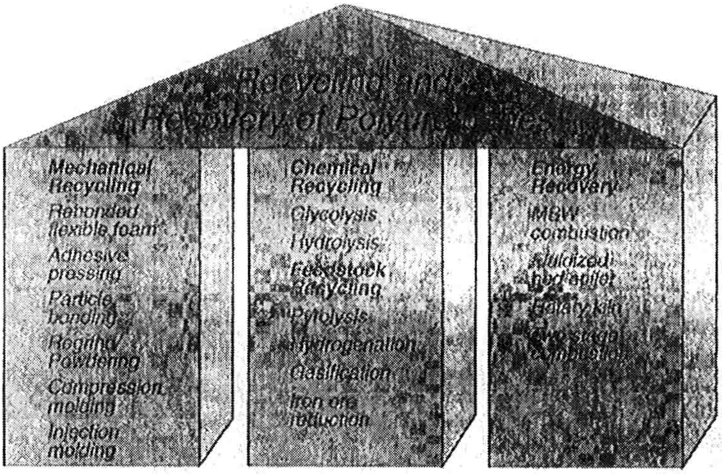

Figure 1.2 Recycling and recovery of polyurethanes.

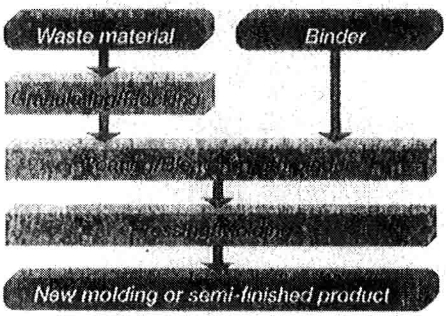

Figure 1.3 Process steps for rebonding, adhesive pressing, and particle bonding.

ing in size from small granules to a coarse powder, can be processed into press boards in a heated press (Figure 1.3). Normally, polymeric MDI is applied as the binder (approx. 10 wt%).

Particle Bonding

Polyisocyanates, together with polyols if necessary, are suitable for binding particles of many kinds of materials (whether sorted or unsorted) often under the influence of pressure. Particle bonding is thus a general recycling method that is not restricted to polyurethane particles but may also be used for recycling other wastes (Figure 1.3). Depending on the intended application of the new product, the polyurethane "binder" may constitute the matrix of the finished article (from 10 to 70 wt%). One particular application that is already well established is the binding of rubber particles with PUR for sports surfacing.

Regrind/Powdering

In regrind or powder incorporation PUR powder is added to a liquid reactant (generally the polyol) and used as a filler to manufacture new PUR products (Figure 1.4). While this opens up the possibility of recycling into the original application, the quantity of polyurethane filler added will generally be limited to 30% or less in the new product.

Compression Molding

Polyurethanes with a low degree of crosslinking can be formed into new parts by compression molding (Figure 1.5). For this process the milled polyurethane is first preheated and then subjected to a pressure of 350 bar or more

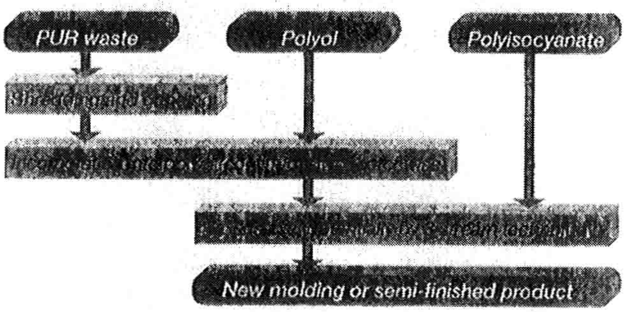

Figure 1.4 Process steps for regrind/powdering.

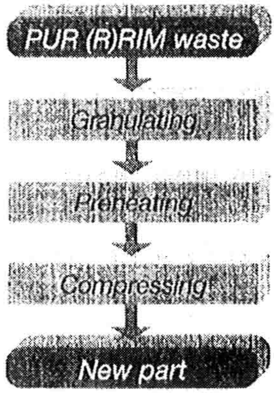

Figure 1.5 Process steps for compression molding.

in a mold at temperatures of around 180°C. Under these conditions, with high shear forces, the granules flow together and combine to form a new part without the use of any binder. This gives a recycle content of 100%. The process was applied commercially on a small scale in Germany as well as in the United States to reinforced RIM polyurethanes from exterior automotive applications. In the meantime it has been discontinued because of economic reasons.

Injection Molding

Traditional thermoplastics technologies like, e.g., injection molding (Figure 1.6) may be used not only for actual thermoplastic polyurethanes (TPUs) but also for other (moderately crosslinked) polyurethanes. Reportedly, solid PUR

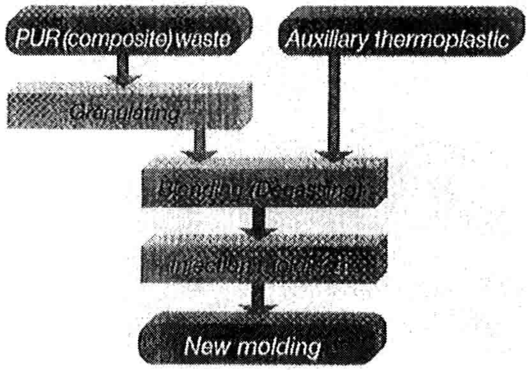

Figure 1.6 Process steps for injection molding.

shoe soles have been made from PUR shoe sole scrap by injection molding in Eastern European countries where virgin raw materials are in short supply. It is advantageous to add a certain amount of an "auxiliary thermoplastic." This technique is thus also suitable for processing composites of thermoplastics and polyurethanes without prior separation (e.g., automotive instrument panels). To the authors' understanding, these processes are currently not (or no longer) used on a commercial scale.

FEEDSTOCK RECYCLING/CHEMICAL RECYCLING

Feedstock recycling covers a range of chemical and/or thermal processes by which plastics can be broken down to basic hydrocarbon units or constituent monomers which can then be used again as raw materials in chemical or petrochemical processes. Large-scale feedstock recycling processes have been developed to recover oil and gas products from hundred thousand tons per year or more mixed plastics waste streams, of which polyurethane materials could be one, usually minor, constituent. These processes include pyrolysis, hydrogenation, synthesis gas generation and the reduction of iron ore in blast furnaces. For further details see References [2,3] and the references given therein.

When pure streams of particular polymers are available, "chemical recycling," "chemolysis" or "depolymerization" processes can be applied. These processes are suitable for recycling of the much smaller streams of polyurethanes or other polyaddition materials as well as to condensation polymers such as polyesters or polyamides. Steam in hydrolysis, glycols in glycolysis or amines in aminolysis can be used as reagents to break the urethane bonds. It is thus possible to obtain liquid degradation products from polyurethanes that are suitable, together with new material if necessary, for the manufacture of new polyurethanes.

Hydrolysis

Hydrolysis was examined back in the 1970s as a recovery method for flexible PUR foam [4] (Figure 1.7). The open-cell polyurethane material is converted by pressurized hot steam back into diamine and polyether polyol. Separation, cleaning and conversion of the diamine into the diisocyanate are process steps that require the well-trained personnel and the equipment found in the chemical industry. PUR feedstocks are obtained that, in principle, may be used again to make flexible polyurethane foam. However, the process was unable to establish itself beyond the pilot plant scale. Poor economics was not the only reason. Rather, there is no market for the mixed polyols and mixtures of diamines of varying composition that would result from recycling the large number of different types of flexible foams without previous sorting. Sorting