

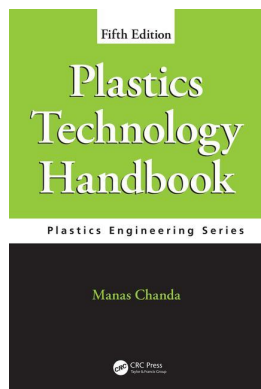
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Recycling and Disposal of Waste Plastics

6.1 Introduction

The quantity of plastics consumed annually all over the world has been increasing phenomenally, with around 4% of annual petroleum consumption globally being used to produce plastics (with an additional 4% employed to power manufacturing processes for plastics production). The main reasons for this rapid growth of plastics are their exceptional and wide-ranging attributes like user-friendly features, unique flexibility, processing and fabrication possibilities, immense durability, and cost-effectiveness. Plastics thus find extensive use in both domestic and industrial fields, covering such diverse areas as packaging, automotive, aerospace, transport, medical delivery, biomedical instruments, health care, artificial implants, laboratory wares, sports goods, water desalination, household appliances, communication, and electronics as also in countless new emerging applications that range from improving food safety and distribution efficiency to helping create lighter, more efficient vehicles [1].

According to the United Nations Environmental Program and the Worldwatch Institute (an independent research institute, founded in 1974 by Lester Brown and devoted to global environmental concerns with a network of international partners in more than a dozen countries), solid plastics production grew from 5 million tons in the 1950s to 110 million tons in 2009 and then to 300 million tons in 2013, as plastics continued to replace other materials, notably metals and glasses. Where do these plastics go when we are done with them? In the United States alone, 33.6 million tons of plastics are discarded each year, but only 6.5% of it is recycled and 7.7% is combusted to generate heat and electricity from garbage. The rest ends up in landfills where it may take centuries to decompose and potentially leach pollutants into the soil and water. The plastics content of municipal solid waste (MSW) has grown rapidly over the years. This is evident from the fact that, according to the United Nations Environmental Program, while plastics comprised less than 1% of MSW in 1960, by the first decade of the 2000s, it had reached double figures and now worldwide a range between 22% and 43% of plastics is disposed of in landfills [1].

The oceans of the Earth are also not spared. According to the results of the global study released at the World Economic Forum (2016) in Davos, 8 million tons of plastics end up in the oceans each year, and it is also estimated there are 100 million tons of plastics debris floating around in the oceans, threatening health and safety of marine life. The Pacific Ocean is home to the world's biggest "landfill"—the *Great Pacific Garbage Patch*, which has been formed between California and Hawaii by air and ocean currents, generating a huge, slow-moving spiral of plastics debris that accumulated through decades from all corners of the globe. The plastics do not biodegrade, but they photodegrade, breaking up into tiny bits, called *nurdles* or "*Mermaid tears*," which are reported to outnumber plankton, six-to-one, and, mistaken as food, they pose a serious threat to marine life. According to a study cited by the Worldwatch Institute, there are 5.25 trillion plastics particles weighing a total of 268,940 tons, currently adrift in oceans around the world. The economic impact of this situation, with losses in fisheries and tourism as well as cost of

cleaning beaches, amounts to \$13 billion per year [1]. A new report further warns that the amount of waste plastics in oceans will outweigh fish in just 30 years unless drastic action is taken.

The direct economic impact of dumping plastics after a single use is also too great to be ignored. For example, it may be noted that while about 56 million tons of poly(ethylene terephthalate) (PET) were produced worldwide in 2013 alone, an overwhelming 95% of plastics packaging worth \$120 million a year is lost to the economy by discarding after a single use. Relatively little plastics recycling is done in practice because there are various types of plastics with different chemical compositions, and recycled plastics can be contaminated by the mixing of types. Waste plastics are also contaminated by non-plastics, such as paper, cloth, wood, glass, and metal. Separating plastics from non-plastics and different types of plastics from each other and cleaning to remove labels, decorative markings, paints, and so on before the recycling process is labor-intensive and there is no easy solution.

To simplify the identification of common polymers used in some applications such as disposable containers, the Society of Plastics Industry developed an identification code, which shows a “chasing arrows” triangle enclosing a number to indicate the polymer type, for example, 1 for PET, 2 for HDPE, 3 for PVC, 4 for LDPE, and 5 for PP. In reality, however, only two—PET used for synthetic fibers and water bottles and HDPE used for jugs, bottle caps, water pipes, and so on—are routinely recycled. In more and more cities, LDPE plastic bags are now being recycled too. In addition, the increasing use of near-infrared spectroscopy by the recycling industry for fast and easy identification of the chemical composition of plastics is improving the speed and efficiency of plastics recycling.

Although the plastics industry practiced recycling for many years, attention was mainly focused on the recycling of industrial scraps and homogeneous post-consumer plastics, which are easy to collect and reprocess. However, more recently, the plastics industry accepted the challenge of recycling heterogeneous plastics waste based on new technologies of separation and reprocessing. Scientific research, scarcely visible only a few years ago, is now a very active, fast-growing discipline, contributing to the development of newer processes. An excellent review of various recycling and recovery routes of plastics solid waste can be found in Ref. [2]. According to the type of product obtained from the recycling process and the percentage of the economic value recovered, the following broad classification of recycling technologies for solid waste plastics (SWP) has been made:

1. *Primary recycling*. Also known as *re-extrusion*, the process refers to the reprocessing of SWP (such as scrap, industrial, or single-polymer plastic edges and parts formed as by-products of processing or fabrication) into same or similar types of product from which it has been generated. While this definition commonly applies to the processing line itself, injection molding of defective or out-of-specification products by grinding and re-introduction into the recycling loop or the final stages of the manufacturing is also considered as an example of primary recycling.

Primary recycling is used when the plastic waste is uniform and uncontaminated and can be processed as such. Only thermoplastic waste can be directly reprocessed. It can be used alone or more often added to virgin resin at various ratios. Widely performed by plastics processors; primary recycling is often considered an avoidance of waste rather than recycling. The main problems encountered in primary recycling are degradation of the material resulting in a loss of properties as appearance, mechanical strength, chemical resistance, and processability. Contamination of plastic scrap and handling of low-bulk density scrap such as film or foam are additional problems in primary recycling.

Primary recycling can also involve the re-extrusion of post-consumer plastics. Generally, households are the main source of such waste. However, primary recycling of household waste calls for selective and segregated collection of mixed SWP from a large number of sources, which may be challenging and uneconomical.

2. *Secondary recycling*. Also known as *mechanical recycling* (since no chemical alteration of polymer is involved), the process refers to the mechanical and nonchemical processing of SWP (generally

reduced in size, such as pellets, flakes, or powders, depending on the source, shape, and usability) into products with less demanding properties. The concept was promoted and commercialized all over the world back in the 1970s. For single-polymer SWP, for example, PE, PP, PS, PVC, PU, and PET, mechanical recycling opens an economic and viable route for SWP recovery, especially in the case of foams and rigid plastics [3]. A number of plastics products found in our daily lives come from mechanical recycling of single-polymer SWP, such as grocery bags, pipes, gutters, window and door profiles, shutters and blinds, and so on.

In a typical example of secondary recycling of polyurethane (PU) foam, PU recyclate made by shredding PU waste, mixing with binder and compressing, is added to polyester molding compounds as filler, which gives added toughness to the material, yielding a variety of products such as carpet underlay and athletic mats. Another common example of secondary recycling is flexible PVC waste, which is recycled into powder and used as filler in the production of floor coverings of various kinds. As much as 75% of PET waste in the United Kingdom and the United States is used for secondary recycling to manufacture fibers for carpets, apparel, and bottles.

One of the main issues that face mechanical recyclers is the degradation and heterogeneity of SWP. Degradation, such as polymer chain length reduction and chain branching, can be caused by photo-oxidation and/or mechanical stresses as well as harsh natural weathering conditions.

For post-consumer *mixed* plastic wastes (MPW), which are unsuitable for direct use, the industry often resorts to secondary recycling methods. There are various technical approaches to secondary recycling of MPW. These include reprocessing based on melt homogenization in specialized equipment; using ground MPW as filler; and separation of MPW into single homogeneous fractions for further processing, such as partial substitution of virgin resins and blending with other thermoplastics using suitable compatibilizers.

Generally, the first step in secondary recycling involves (a) size reduction of SWP to a more suitable form (pellets, powders, or flakes), which is usually achieved by cutting, milling, grinding, or shredding [3,4]. It is followed by (b) *contaminant separation* (i.e., separating paper, dust, and other forms of impurities from plastics, usually in a cyclone), (c) *floating* (i.e., separating different types of plastic flakes in a floating tank according to their density), (d) *washing and drying*, and (e) *extrusion* (i.e., extruding to strands followed by pelletization).

3. *Tertiary recycling*. In this process, also known as *chemical recycling* (since it occurs by an alteration in the chemical structure of the polymer), polymers are chemically unzipped (depolymerized) or thermally cracked in order to recover monomers or petrochemicals indistinguishable from virgin materials [5]. Tertiary recycling procedures offer viable alternatives for utilizing commingled (heterogeneous) plastics with limited use of treatment.

Processes similar to those employed in the petrochemical industry, for example, noncatalytic thermal cracking (pyrolysis), gasification (in the sub-stoichiometric presence of air, usually leading to CO and CO₂ production), liquid–gas hydrogenation, steam degradation, or catalytic cracking, are used in tertiary recycling of SWP, producing various fuel fractions. A number of polymers, by their nature, are advantageous for this treatment. For example, condensation polymers PET and certain polyamides nylon-6 (PA-6) and nylon-6,6 can be efficiently depolymerized to produce monomer units, while PE, in particular, has been targeted as a potential feedstock for fuel (gasoline) production as degradation produces a mixture containing numerous components for use as a fuel. Conditions suitable for pyrolysis and gasification have been researched extensively [6]. There is also a growing interest in developing value-added products such as synthetic lubricants via PE thermal degradation as this would increase the economic incentive to recycle polymers [7]. Different thermolysis schemes, main technologies, and their main products are described by Al-Salem et al. [2].

Some plastics, because of their nature, are more suitable for recycling via pure chemical routes as opposed to thermochemical treatment routes described above. These chemical routes can be

summarized by the following technologies (see later): hydrolysis (PA-6, PU), glycolysis (PET), ammonolysis (PET), methanolysis (PET), and acid cleavage (PA-6).

4. *Quaternary Recycling*. Also known as *energy recovery recycling*, it refers to the recovery of energy from SWP by burning to produce energy in the form of heat, steam, and electricity. It is considered to be only sensible way of waste treatment when material recovery processes fail because of economical constraints.

The importance of plastics recycling and safe disposal in the environmental context in today's world, apart from its economic impact, cannot be overemphasized. Plastics recyclers provide many benefits environmentally as well as to the economy. Using recycled material in place of virgin material leads to environmental benefits in terms of the reduced demand for raw resources as well as decreased energy required for processing. Not only does recycling help keep waste plastics out of landfills, the materials obtained by recycling processes are more energy efficient in terms of producing than new material, while avoiding consumption of new resources. For example, the US Environmental Protection Agency (EPA) estimates that plastics recycling results in significant energy savings amounting to 50–75 MBtus per ton of recycled material versus production of new plastics using virgin materials [1].

Substantial progress has been made over the last 25 years in the recovery rate of waste plastics as well as in the efficiency of the recycling industry, accompanied by sophisticated sorting and recycling systems developed to automate and upgrade the process. In addition, researches have continued to explore innovative ways to derive more value from waste plastics ranging from plastics conversion to energy to plastics conversion to oil. There are now a number of treatment and disposal methods for waste plastics (although when most people think about waste disposal, it is typically the landfill that comes to mind). Treatment techniques that act to reduce the volume and toxicity of solid waste, transforming it into more convenient form for disposal besides deriving fuel from it, have been developed. The major treatment and disposal methods are thermal treatment, dumps/landfills, and biological waste treatment.

Thermal waste treatment refers to processes that use heat to treat waste materials. The most commonly used thermal waste treatment technologies, as described above, are *incineration*, *gasification*, and *pyrolysis*. The former involves combustion of waste material in the presence of oxygen, while the last two refer to methods that decompose waste material by heating to very high temperatures in the presence of very low amount of oxygen (for gasification) or no oxygen (for pyrolysis).

Open burning is another thermal waste treatment that is commonly practiced. The incinerators used in such process often have no pollution control devices and smoke is released into the open air directly along with harmful gases that include hexachlorobenzene, dioxins, carbon monoxide, volatile organic compounds (VOCs), polycyclic aromatic compounds, and ash. Open burning is therefore regarded as very harmful, environmentally. Still, this method is practiced by many local authorities to reduce the volume of wastes very quickly, without incurring much collection and transportation costs.

Sanitary landfills and controlled dumps, which are the most common waste disposal fields, are designed to eliminate or reduce the risk of environmental and/or public health hazards owing to the discarded waste. These landfills are thus built usually in areas where land features provide natural buffers between the landfill and the surroundings.

Composting, the most frequently used biological waste treatment method, refers to the controlled aerobic decomposition of organic waste materials by the action of small invertebrates and microorganisms. Some of the most commonly used composting techniques are static pile composting (organic materials placed on a pile and left to decompose over a long time with no human intervention), vermin composting (process of composting using various worms), windrow composting (mixture of composting materials placed in long narrow piles called windrows that are agitated or turned on a regular basis to enhance natural or passive aeration), and in-vessel composting (methods that confine the composting materials within a building, container, or vessel).

As there has been a big surge in plastics consumption over the last few decades, it has brought with it an urgency to recycle greater amounts of waste plastics and thus divert them from landfills. However, our

collective ability to effectively recycle increasing amounts of waste plastics has lagged and a high percentage of the waste still goes to landfills, for many reasons [1], including lack of awareness of municipal recycling programs, inconsistent state laws, and local confusion over what is or is not recyclable, as well as other issues. According to the Worldwatch Institute, only 9% of post-consumer plastics, amounting to 2.8 million tons, was recycled in the United States during 2012. The balance, totaling 32 million tons, was sent to landfills or otherwise discarded. The picture is relatively better in Europe, where recycling absorbed 26% of post-consumer plastics generation, or 6.6 million tons, while 36% of post-consumer plastics was burned to generate energy and the balance 38% ended up in landfills.

The aforesaid scenario of plastics recycling, notwithstanding, the recycling industry has continued to expand and significant progress has continued to be made in the recovery rate for waste plastics. For a systematic approach to plastics recycling, however, the entire product life cycle is to be considered. The challenge before the plastics industry is thus to fully leverage the amazing attributes of plastics, while creating a system that prioritizes design for recycling and more effective recovery [1].

6.2 Outline of Recycling Methods

Post-consumer plastic wastes can be divided into two different groups depending on their source: (1) mixed plastics from the household waste and (2) plastics from the industrial sectors. The first category involves the medium-/short-life articles that are used in food, pharmaceutical, and detergent packaging, shopping, and others. The majority of these articles are composed of thin protective films: a variety of bottles for soft drinks, food, and cosmetics, sheeting for blisters, strapping and thermoformed trays.

There are basically five different polymers that contribute to the total amount of domestic plastic waste, namely, PE, PP, PS, PVC, and PET. The composition of this MPW can change depending on the regional habits and seasons of a year, and also on the mode of waste collection. A typical composition may be PE 39%, PVC 22%, PET 19%, PS 8%, and PP 12% (by wt).

The collection of plastics wastes always yields a polluted product, and this fact poses the need for the first operation of the recycling process, namely the cleaning of foreign bodies. The machinery required at this stage may be either manual or automatic type, the former being simpler from the standpoint of installation. The operations following the first step of clearing are determined by the type of recycling process to which the material is to be subjected. There are basically two main recycling processes: recycle of heterogeneous MPW and recycle of selected polymers separated from MPW.

A direct solution to disposal of domestic MPW can be the reuse of the heterogeneous mixture by processing through extrusion or injection molding technologies using traditional machineries. However, when MPW is processed, one of the main problems is to find the best compromise between homogenization and degradation. The optimal processing condition must ensure a good dispersion of the materials with high melting point (such as PET) in a continuous phase of molten polymers (such as PVC), avoiding gas bubbles, low-molecular-weight compounds, and cross-linked residues that are formed by thermal degradation. Some possible applications of such molded mixed plastics are injected tiles for paving, and extruded profiles for making structural articles such as benches, garden tables, bicycle racks, fences, and playing facilities. However, because of the incompatibility of the various components in mixed plastics, the mechanical properties of the molded or extruded products are rather poor.

The market of park benches, playgrounds, fences, and so on, cannot absorb, in the long run, the massive amounts of MPW that are produced every year. Hence the possible route to recycling of MPW to obtain secondary materials with acceptable mechanical properties could be to blend them with virgin polymers, or, at least, with recycled homopolymers. For example, experimental results [8] of processing and properties of blends of virgin LDPE and MPW have shown that all mechanical properties, with the exception of elongation at break, are very similar to those of the virgin material if the MPW content does not exceed 50%.

The possibility of using MPW as filler for both LDPE and HDPE has been considered [9] as such an approach may offer two important advantages: (1) improvement of the use of huge amounts of MPW that

are generated by municipalities and industries; and (2) savings in nonrenewable raw materials and energy, both associated with the manufacturing of the virgin materials that can be replaced by plastics waste. Even if the percentage of plastics waste used as a filler cannot be higher, its common use may absorb sizable amounts of waste.

A widespread solution, in terms of application and market volume, can be the recycling of single materials or homogeneous fractions obtained from a differentiated collection system and/or a separation process of the mixture. Molded products from single or homogeneous fractions usually show a general performance far greater than that of products from mixed plastics. To obtain single or homogeneous fractions, it is useful to separate the mixed domestic plastics into four fractions, namely, polyolefins, PS, PVC, and PET.

An important preliminary to separation of mixed domestic plastics is the cleaning and selection operation. A simple method to perform this operation consists of a selection platform where a number of trained sorters separate the different types of plastics by visual assessment. Because manual selection is liable to human error, selection platforms may be equipped with detectors such as electronic devices to check the quality of the selected material.

The drawbacks of the manual platforms—which range from high labor cost to the complexity of labor management—may be avoided by resorting to automatic platforms. The machines required for such automation are related to the quality of the collected material. Essential machines are rotary screen, light-parts separation equipment, heavy-parts separation equipment, and aluminum rejection equipment. All such machines are preliminary to the stage of separation into homogeneous plastic fractions.

Bottles constitute the largest high-volume component of post-consumer plastics and need special attention in reclaim operation. Since 1988, developments in bottle reclaim systems have made recycling post-consumer plastics more efficient and less costly. Municipalities, private organizations, universities, and entrepreneurs have worked closely to develop new collection, cleaning, and sorting technologies that are diverting larger portions of plastics from landfills to recycled resins and value-added end products.

To collect the high volume-to-weight ratio post-consumer plastics economically, truck-mounted compactors have been developed that seem to have the most promising future for mobile collection. They are self-contained and offer, on average, a reduction ratio of 10:1. Simple to operate, compactors accept all types of plastics, including film, and perform equally well with milk jugs and PET bottles as with mixed plastics.

Using compactors for on-board truck densification can thus be a cost-effective part of multimaterial collection programs. Another noteworthy development is that of flatteners and balers, which have also proven cost-effective under certain conditions. An integrated baler developed by Frontier Recycling Systems (USA) is fully automatic and capable of handling the plastic throughput of larger and costlier systems without the corresponding expenditures of space and labor. By producing smaller, high-density bales, it allows for lower transportation costs of recyclables shipped to market.

In keeping with the progress in densification options, efficient sortation systems have also been developed. The Poly-Sort integrated sorting line developed by Automation Industrial Control (AIC), Baltimore, is capable of sorting mixed stream of plastic bottles at a baseline rate of three bottles per second, or 700 kg/h. With expected advances in scanning and detection, the sorting rate of the system could double to 1400 kg/h.

Designed to sort compacted bottles, the Poly-Sort system employs conveyors for singulation, and two devices for color and chemical composition identification. A vibratory conveyor singulates bottles; a read conveyor transports bottles to an ultrasonic sensor that detects their position; a near-infrared system detects the resin type; a camera detects the color of the container; a computer integrates data and makes an identification; air jets divert bottles to the appropriate segregation conveyor or hopper.

The above type of separation is a macroseparation. It may be noted that the methods of separation into homogeneous fractions fall into three groups: molecular separation, microseparation, and macroseparation. Molecular separation is based on the dissolution of the various plastics in selective solvents, while microseparation is a method by which a suspension medium is used to separate plastics with density higher or lower than the suspension medium. Macroseparation, which is the separation of

plastics when waste materials are still in initial form, appears to be the most conveniently applicable system, considering the increasing possibilities of automation it offers. The key to this separation process is the development of an efficient detector system that can distinguish between type and quality of different plastics in waste materials.

Different types of detectors have been developed and many are under development. These are based on distinctive physicochemical properties of plastics and employ different techniques such as x-ray, near-infrared spectrophotometry, fluorescence, and optical measurement of transparency and color. Automatic systems consisting of a platform for selection according to plastics topology, a number of identification and detection steps, and adequate checks on the efficiency of separation following detection have been developed. The Poly-Sort system described above is one such example.

Recycle installations take up the separated plastic flakes for further processing. Various elements that normally compose the item to be recycled are caps made of PE, PE with PVC gaskets, aluminum, labels of tacky paper with different types of glue, and residues and dirt that have been added during the waste-collection phase. Various operations that are carried out in a specific sequence because of the problems posed by the type of material are: grinding to ensure homogeneity of the product, air flotation for separation of flakes with different specific weight and removal of parts of labels freed by grounding (such as separation of PVC labels from PET bottle flakes), and finally washing to remove residues. The washing system consisting of a range of equipment that includes centrifugal cleaners, washing tank, settling tank, and scraping machines is part of a know-how of various manufacturers.

The majority of municipal solid waste consists of plastics waste, which is often contaminated with significant amounts of paper. This is not only the case with plastics fraction of municipal solid waste (PFMW), but also with such industrial waste as used packaging materials, laminates, and trimmings. The reprocessing of plastics waste contaminated with more than 5% paper is difficult using conventional plastics processing machinery, and becomes almost impossible at paper levels exceeding 15%. The sorting operation at a municipal plant normally aims at removing the paper component from the light plastics fraction to a level well below 1%. However, this operation has not been quite successful because the material handling side has been difficult and the costs have far exceeded the price of virgin polyolefins.

A simpler solution to the problem of contamination may be to allow for a paper component in the plastics fraction and to use a processing method that can disintegrate the cellulose fibers into small fragments such that they act as particulate fillers in the plastics. Such a method has been developed at Chalmers University of Technology, Gothenburg, Sweden. Known as the CUT-method, the process makes it possible to reprocess both the PFMW and a number of different industrial plastic waste materials contaminated with paper [10,11]. The CUT-method, consisting of a prehydrolytic treatment of the paper component, is an industrially applicable method of reprocessing paper-contaminated plastics waste of various origins.

The main advantage of the CUT-method is that the plastics fraction and the paper component do not need to be separated as the hydrolysis does not degrade the plastics component but reduces the chain length of the cellulose component to a level at which the cellulose fiber becomes extremely brittle and the shear forces generated in normal plastics processing machinery (compounding extruders and molding machines) can easily disintegrate the paper parts into small fibrous fragments. It is the disintegration of the embrittled paper component into an almost pulverized substance that is the key to the success of the method, since this results in greatly enhanced melt flow properties, better homogeneity, and thus in improvement in the mechanical properties of the material [12].

The method of hydrolysis used in the CUT-method offers an efficient and economical way of processing plastic waste, both post-consumer municipal waste and industrial waste, contaminated with a cellulose component. The presence of cellulose gives a desired stiffness to the final product, as studies have shown [11,12]. Such plastics product can be used in several applications, such as artificial wood.

Because of the advantage in design and functionality, plastics are now an indispensable part of any kind of car; the amount of polymers employed to build a car has risen to about 20% from a mere 5% in 1973, with a corresponding increase in the quantity of nonmetallic waste during scrapping. The main problem of plastic wastes from all industrial sectors, and in particular the car industry, is the large variety of

materials employed to build a single component or system, for example, a dashboard. This takes place because of the sophisticated and complex mission that the system must perform. The large number of plastics used and the disproportionately high costs in the dismounting of the different plastic pieces of a car represent an intractable waste-recovery problem and thus have a negative impact on the recycling process. As a result of this, often only the metallic fraction is recovered, while the plastic materials are eliminated by deposition in refuse dumps.

An alternative approach to the recovery of automotive plastics is therefore to use them as large, easily removable components that offer potential for reclamation as well-characterized individual polymers. Some particularly complex components such as vehicle front- and rear-end systems, exhibit special suitability for manufacture in plastics instead of metals because of their ease of production and assembly. It is generally recognized that improvements in automotive scrapyard economics may be best achieved by the prior removal from vehicles of such large polymeric components and their recycling as well-characterized plastic fractions. For example, plastic fuel tanks of HDPE are now in common use and represent the most common recyclable plastic component. Trials with material recovered from used plastic fuel tanks have shown promising results for the manufacture of new tanks [13].

A concept that is being developed to solve the recycling problems of plastics from industrial sectors, and in particular the car industry, is based on the use of materials of the same family for all components of the plastic systems to be recycled at the life end. This allows an easy and direct recycling of the scraps and the recovery of the whole system. Greater recycling efficiency can be obtained when the following two basic requirements are satisfied: (1) materials compatibility through materials homogeneity, and (2) easier disassembly through planned design. This concept has been first applied to the automotive sector, where the environmental problems have become of primary importance; however, it could be also applied to other products, i.e., appliances and building materials. There are two tasks in developing this concept: to develop new advanced materials in individual categories of polymers and to promote new technologies.

Consider, for example, the automotive industry. Although many polymers are used in cars today, the industry tends to favor more and more polypropylene use due to a large range of properties available. New developments in polyolefin-based materials have thus created a family of polypropylene products with a wide range of physical properties, including the ability to be easily recycled. When utilized by automotive and product designers as a part of a design for disassembly strategy, these compatible materials will yield large subassemblies that can be reclaimed with a minimum of handling [14,15]. In each project, the design incorporates readily identifiable hard point connections between the polypropylene components and the metal automobile subframe. This allows personnel in recycling centers to remove these parts quickly and in large pieces that can be completely reground and recycled. This concept has been applied to car dashboards and interior vehicle components like floor covering, trim, and door panels, as well as bumpers.

Lead-acid batteries from automotive applications normally have a shorter service life than the car itself. The logistics system for used car batteries is geared to lead recycling. However, the first battery reprocessing step yields not only lead but also polypropylene in a form of the casing fragments. Accordingly, the polymer is available without additional cost. As the casing makes up a substantial part (7%) of the total battery, the quantities of polypropylene obtained are sufficient to warrant the operation of a plastics recycling plant.

Polyolefins and poly (ethylene terephthalate) (PET) are the most frequently recycled polymers obtained from both the domestic and industrial plastics wastes, and as such they have received most attention in the recycling research and technology. PET is one of the largest recycled polymers by volume [16], because it is suitable for practically all recycling methods [17]. Over 50% of the PET film produced in the world is used as a photographic film base. The manufacturers of these materials have long been interested in PET film recovery. An important motivation for this has been the fact that photographic films are usually coated with one or more layers containing some amount of rather expensive silver derivatives.

Silver recovery makes PET-base recovery more economical. In a typical way of operation, PET film recycling is thus coupled with the simultaneous recovery of silver, for example, by washing with NaOH and follow-up treatment. PET-recycling by direct reuse, if the washed PET-film scrap is clean enough to be recovered by direct reextrusion, is by far the most economical process. However, this process is most

suited for the recovery of in-production wastes. For customer-recollected PET-film, which may have a higher degree of contamination, other technologies are to be applied.

There exists a hierarchy in PET-film and plastics recycling technologies depending, first of all, on the degree of purity of PET scrap to be handled, and secondly, the economics of the process. For the cleanest PET grade, the most economical process, i.e., direct reuse in extrusion, is self-explanatory. For less-clean PET waste, it is possible to reuse them after a modification step (partial degradation, e.g., by glycolysis) at a reasonably low price. More-contaminated PET waste must be degraded into the starting monomers, which can be separated and repolymerized afterwards, of course at a higher cost.

Polyethylene films from greenhouses, although highly degraded by UV radiation, are recycled by various means leading to manufacture of films and molded products with low mechanical properties. Problems in the recycling of greenhouse films arise from the presence of products of photooxidation, which significantly affect the properties of a recycled material. An interesting possibility of the use of photooxidized PE in blends with nylon-6 to improve blend compatibility has been demonstrated [18,19].

Chemical means such as glycolysis, methanolysis, and hydrolysis are good at unzipping only the condensation polymers—such as polyester, nylon, and polyurethanes—to facilitate chemical recycling. Addition polymers, such as vinyls, acrylics, fluoroplastics, and polyolefins, can hardly be reprocessed except that, if they are sorted, they may be converted into powder by grinding operation and mixed with respective virgin resins for remolding into finished goods or, in some cases, blended with other resins using suitable compatibilizers to make useful end-products of commercial value.

Tertiary recycling of addition polymers require pyrolysis, which is a more aggressive approach. For mixed or unsorted plastics in particular, it is a practicable way of recycling. Pyrolysis is the thermal degradation of macromolecules in the presence of air. The process simultaneously generates oils and gases that are suited for chemical utilization.

The advantage of pyrolysis over combustion (quaternary recycling) is a reduction in the volume of product gases by a factor of 5–20, which leads to considerable savings in the gas conditioning equipment. Furthermore, the pollutants are concentrated in a coke-like residue matrix. It is possible to obtain hydrocarbon compounds as gas or oil.

The pyrolysis is complicated by the fact that plastics show poor thermal conductivity, while the degradation of macromolecules requires considerable amounts of energy. The pyrolysis of mixed plastic wastes and used tires has been studied in melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, cooking chambers, and fluidized bed reactors [20,21].

Rotary-kiln processes are particularly numerous. They require relatively long residence times (20 min or more) of the solid wastes in the reactor. Moreover, due to the large temperature gradient inside the rotary kiln, the product spectrum is very diverse. For this reason, the gases and oils generated by the pyrolysis are normally used for the direct generation of energy and the process may well be considered as a quaternary recycling process.

For chemical recycling of mixed plastics, the fluidized bed pyrolysis has turned out to be particularly advantageous. The fluidized bed is characterized by an excellent heat and mass transfer as well as constant temperature throughout the reactor. This results in small dwell times (a few seconds to a 1.5 min maximum) [21] and largely uniform product spectra. The fluidized bed is generated by a flow of air or an inert gas (nitrogen) from below through a layer of fine-grained material, e.g., sand or carbon black. The flow rate is sufficient to create turbulent motion of particles within the bed. Using a fluidized bed pyrolysis, 25–45% of product gas with a high heating value and 30–50% of an oil rich in aromatics could be recovered [21]. The oil is comparable to that of a mixture of light benzene and bituminous coal tar. Up to 60% ethylene and propylene are produced by using mixed polyolefins as feedstock. Moreover, depending on the temperature and the kind of fluidizing gas (nitrogen, pyrolysis gas, and steam) different variants of the fluidized bed pyrolysis process can be carried out, yielding only monomers, BTX-aromatics, high boiling oil, or gas.

A promising concept that has received much attention is recycling plastics to refinery cokes, where pyrolysis units and a well-developed infrastructure are already in place. The main hindrance to the execution of this concept is the presence of contaminants (including chlorine and nitrogen) in the plastics

stream, as well as the need to turn plastics into a liquid form that the refinery can handle. Projects are in place to address these issues. Initial small-scale pyrolysis, dissolving plastics into other refinery feedstocks, or turning solid wastes into a slurry, are some of the options that have received attention. Efforts have also been made in some refineries to convert mixed plastics into a petrochemical feedstock by catalytic hydrogenation. In the refinery, the aim of tertiary recycling is not to displace regular refinery capacity, but to use plastic waste as a very minor stream. However, even if all refineries with cokers took only 2% of their capacity as plastic waste, it would be extremely significant.

Mention should be made of a plastics liquefaction process that has been developed jointly by the Japanese Government Industrial Laboratory, Hokkaido, Mobil Oil Corporation, and Fuji Recycle Industry. The process can treat polyolefinic plastics (polyethylene, polypropylene, and polystyrene) or their mixtures by a combination of thermal and catalytic cracking to produce gasoline, kerosene, and gas oil fractions of about 85%. Recovered liquid and gas are separated by cooling and the gas is used as in-house fuel. The technology is unique in using proprietary Mobil ZSM-5 catalyst and has been described as an ultimate recycling technology [22].

A brief overview of several important aspects of plastics recycling and development in the field has been given above. Some of the topics that have been highlighted in this review will now be elaborated further in the following sections. In addition, waste recycling problems and possibilities relating to a number of common plastics will be discussed.

6.3 Recycling of Poly (Ethylene Terephthalate)

The largest use of poly (ethylene terephthalate) (PET) is in the fiber sector, with PET film and PET bottles representing only about 10% each of the total PET volume produced annually. A large percentage of the total PET output comprising films, plastics, and fibers is recycled by various methods and for several applications, which makes PET one of the largest in volume of recycled polymers in the world. Contributing to this is the suitability of PET for practically all recycling methods, which include direct reuse, reuse after modification, recovery of monomers and other low-molecular-weight intermediates, and incineration. Any particular method is selected on the basis of the quality of waste and scrap, the economy of the process, and the convenience of the operation.

Contamination of post-consumer PET (POSTC-PET) is the major cause of deterioration of its physical and chemical properties during reprocessing. POSTC-PET is contaminated with many substances: (1) acid producing contaminants, such as poly(vinyl acetate) and PVC; (2) water; (3) coloring contaminants; (4) acetaldehyde; (5) other contaminants such as detergents, fuel, pesticides, etc., stored in PET bottles.

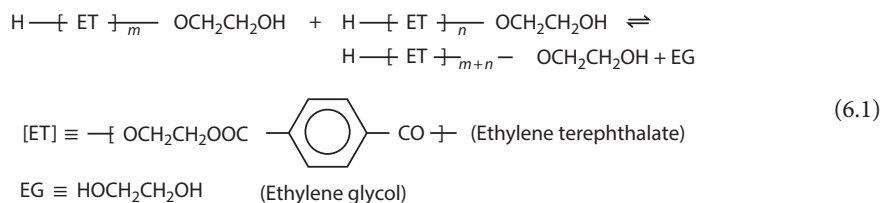
The most harmful acid to the POSTC-PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, and hydrochloric acid produced by the degradation of PVC. The acids act as catalysts for the chain scission reactions during POSTC-PET melt processing. Thus, the presence of PVC, as little as 100 ppm, would increase POSTC-PET chain scission [23]. Water reduces molecular weight (MW) during POSTC-PET recycling through hydrolysis reactions at the processing temperature (280°C). Moisture contaminants should be below 0.02% to avoid such MW reduction [24].

Acetaldehyde is present in PET and POSTC-PET, as it is a by-product of PET degradation reactions. The migration of acetaldehyde into food products from PET containers was a major concern in the early stages of developing the recycling process. Acetaldehyde being highly volatile, it can be minimized by processing under vacuum or by drying. Stabilizers such as 4-aminobenzoic acid, diphenylamine, and 4,5-dihydroxybenzoic acid are added to PET in order to minimize the generation of acetaldehyde [25].

6.3.1 Direct Reuse

This method, also called recycling by re-extrusion or melt recovery, is used for relatively pure PET waste such as cleaned consumer bottles or in-house waste. The method is based on the same principles as the

original equilibrium polycondensation reaction:



As polymer buildup and polymer degradation are taking place in the melt simultaneously, the reaction conditions have to be controlled very carefully in order to obtain the desired molecular weight and molecular weight distribution for the end use. In theory, this seems rather simple; in practice, however, a large amount of determining parameters (temperature, environmental atmosphere, holding time in a melt state, amount of impurities, type of used catalysts, stabilizers, etc.) have to be kept under control.

Customer-recollected waste from fiber and textiles consists mainly of continuous filaments or staple fibers, which may be contaminated with dyestuffs, finishes and knitting oils, and other fibers such as cotton, wool, rayon, nylons, and acrylics; they are the most difficult-to-recover products.

A different picture can be presented for the PET bottles. In the environmentally active states in the U.S., 80–95% of the PET bottles sold are recollected and recycled. In Europe and in Japan where recycling were started earlier than in the U.S., various reclamation and reprocessing methods have been worked out and applied in practice. Because these processes are usually proprietary, the details of their operation are not known.

The larger use of PET film is as a photographic film base, which accounts for over 50% of the PET film produced in the world. The manufacturers of these materials, mainly Agfa-Gaevert, Eastman Kodak, DuPont de Nemours, Fuji, 3M, and Konishiroku, have long been interested in the recovery of PET film because of its content of rather expensive silver derivatives. Recycling of PET-film waste in production, which may amount to 25–30% of the total output, is almost complete by these manufacturers.

In a typical way of operation, PET film recycling is coupled with the simultaneous recovery of silver, as represented schematically in Figure 6.1. In the first step of the process, photographic emulsion layers containing silver are washed with, for example, NaOH, and after separation, silver is recovered on one side and cleaned PET waste on the other side [26]. Careful analysis is necessary to ensure that the washed PET-

film scrap is clean enough to be recovered by direct extrusion.

The most obvious way of adding the recycled PET flakes is after the usually continuous polymerization and before the PET melt enters the extruder screw [27]. Such a procedure, however, has two main drawbacks: first, the highly viscous melt is difficult to filter (to eliminate possible gels or microgels); and second, other impurities (e.g., volatiles, oligomers, and colored parts) cannot be eliminated any more. In order to remove these disadvantages, several alternative modes have been worked out. A method to add recycled PET to the polymerization batch reactor during the esterification step was described by DuPont as early as 1960 [28]. Such a method shows the following advantages over the method described above: filtration can take place in the low-viscosity phase, and volatiles can be eliminated during the prepolymerization phase.

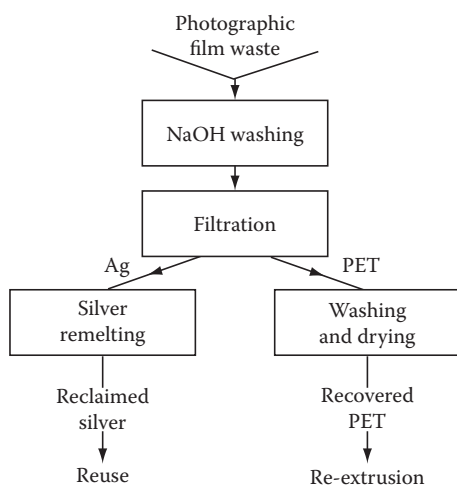


FIGURE 6.1 Combined recovery of silver and PET. (After De Winter, W., *Die Makromol. Chem., Macromol. Symp.*, 57, 253, 1992. With permission.)

PET recycling by direct reuse, as described above, is by far the most economical process. However, it is useful in practice only for well-characterized PET wastes that have exactly known chemical composition (catalysts, stabilizers, and impurities). Therefore, the method is ideally suited for the recovery of in-production wastes, but it may not be suitable for post-consumer PET film.

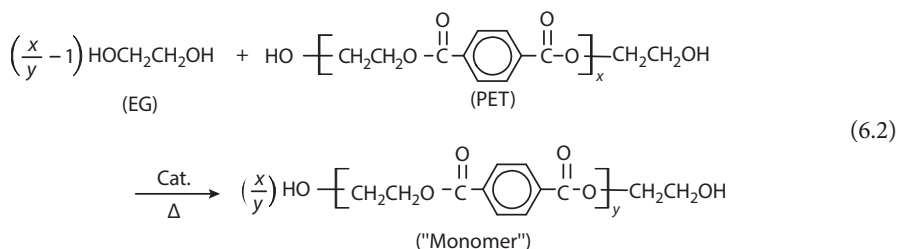
6.3.2 Reuse after Modification

For post-consumer PET waste having a higher degree of contamination, technological processes based on degradation by either glycolysis, methanolysis, or hydrolysis can be used. These yield products that can be isolated. The principles of chemical processes involved in these methods are schematically represented in Figure 6.2.

Hydrolysis and methanolysis of PET regenerates the starting monomers. Thus, terephthalic acid (TPA) along with ethylene glycol (EG) are obtained by hydrolysis, while methanolysis yields EG and dimethyl terephthalate (DMT) among other products. Stopping short of complete depolymerization, glycolysis degrades long polymer chains (with typical repeat sequences of 150 units) into short-chain oligomers (repeat sequences of 2–10 units) having hydroethyl end groups.

6.3.2.1 Glycolysis

The addition of EG–PET reverses the polymerization reaction. This can be stoichiometrically represented by



where x = average number of repeat units in polymer and y = average number of repeat units in "monomer." When $y = 1$, monomer = dihydroxyethyl terephthalate (DHET).

Glycolysis thus represents a compromise between regeneration of starting ingredients by methanolysis or hydrolysis and direct melt recovery. It is less costly than the former and more versatile than the latter.

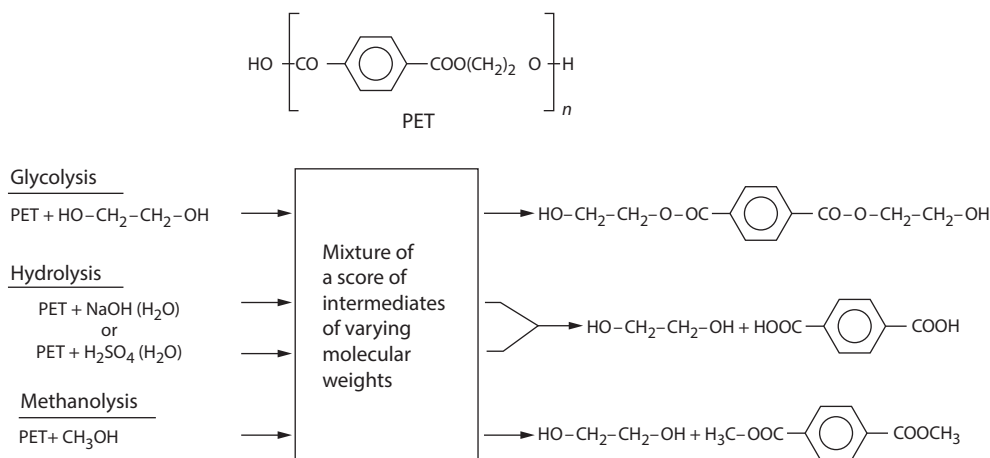


FIGURE 6.2 PET degradation by glycolysis, hydrolysis, and methanolysis. (After De Winter, W. 1992. *Die Makromol. Chem., Macromol. Symp.*, 57, 253.)

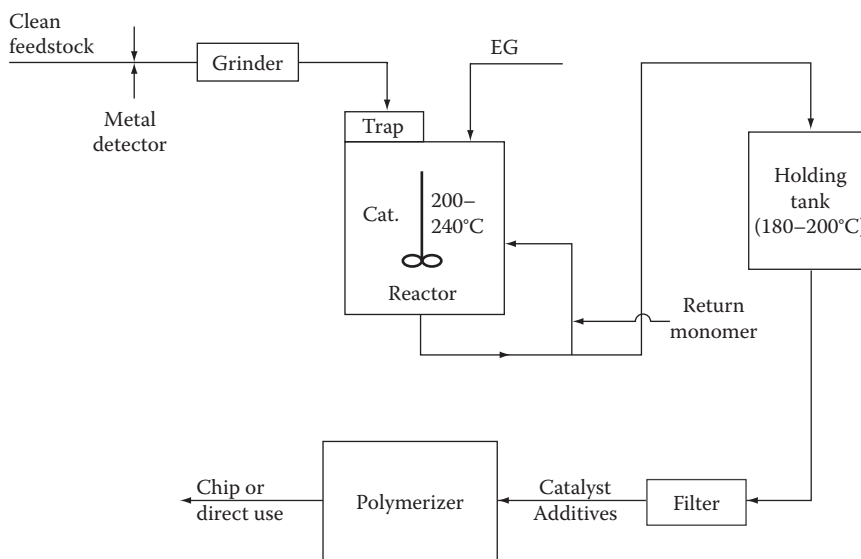


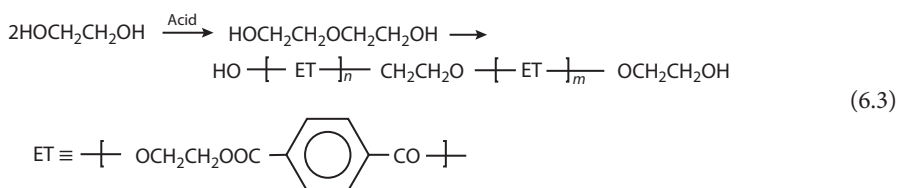
FIGURE 6.3 Flow diagram of a typical system for glycolytic recycling of PET waste. (After Richard, R., *ACS Polym. Prepr.*, 32(2), 144, 1991. With permission.)

The resultant, easily filtered, low viscosity “monomer” can be repolymerized to a useful higher molecular weight product. A typical flow sheet of the process is shown in Figure 6.3.

PET scrap suitable for glycolytic recycle includes production waste, fibers, film, flake, and bottles. In a practical system, major contaminants are separated from feedstocks, e.g., bottle waste is cleaned and separated from a polyethylene base, paper labels, metallic caps, and liners. For many end uses, colored PET must also be segregated. (Highly modified copolymers, glass-reinforced resin, fiber, or fabric blends are not suitable for glycolysis. These can only be recovered by methanolysis/hydrolysis.) Since reaction time depends on surface area, PET feedstocks must be reduced to relatively small particles by grinding, cutting, etc.

The DuPont company [29] published many details covering the glycolytic recycling of PET. Goodyear has also developed a PET recycling process based on glycolysis that is called REPETE [30]. In a batch process, a molten “monomer” heel is left in the reactor to allow the feedstock/glycol mixture to reach optimum reaction temperatures. In a continuous process (Figure 6.3) some of the molten “monomer” is recycled to a stirred reactor to accomplish the same function. High glycol/terephthalate (G/T) ratios lead to more complete glycolysis but lower the maximum temperature, increasing the reaction time. A ratio of 1.7–2.0 G/T is a practical compromise [31]. An ester exchange catalyst as zinc or lithium acetate is usually added to increase the rate of glycolysis. Reaction temperatures of 220–240°C and times of 60–90 min are typical. The reactor is operated under a positive pressure to prevent forming an explosive mixture of air and glycol vapors.

The major side reaction is the production of ethers:



Since this reaction is acid catalyzed, it can be minimized by adding a buffer such as sodium acetate or by adding water [32]. Lithium acetate catalyst also produces less ethers than zinc acetate. Some other side

reactions are the formation of aldehyde, cyclic trimer of ET, and dioxane. Oxidation of glycol ends produce aldehydes that lead to colored compounds. Traces of dioxane can form from the cyclization of glycol.

If other glycols, such as diethylene glycol, are substituted for ethylene glycol, the corresponding oligomers are formed. These can subsequently be polymerized with aliphatic diacids as adipic or 4,4'-diphenylmethane diisocyanate to give rigid elastomers [33]. Additive to control luster, color, and so on can be added in the usual manner before and after polymerization.

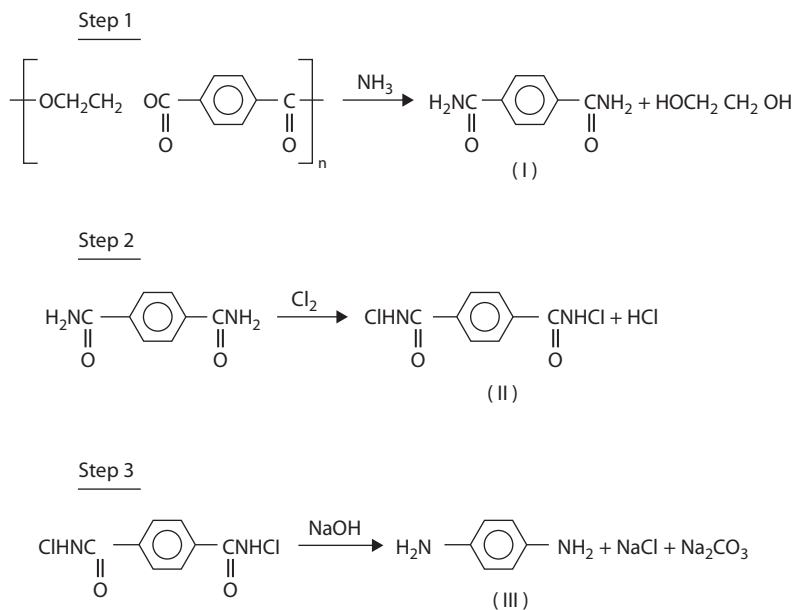
Primary uses for PET from glycolytic recycle are geotextiles, fibers for filling products, nonwovens, and molding resins where color, strength, and control of dyeability is not important. Recovered polymer can be added to virgin polymer for films, fibers, and molding resins.

6.3.2.2 Methanolysis

PET waste obtained in the form of film, bottles, and fibers can be very conveniently converted into its raw materials dimethyl terephthalate (DMT) and ethylene glycol (EG) by methanolysis. The process involves heating the PET waste with methanol at 240–250°C and 20–25 kg/cm² pressure in the presence of catalysts such as metal oxalates and tartrates. Once the reaction is completed, DMT is recrystallized from the EG-methanol molten liquor, and distilled to obtain polymerization-grade DMT. Also EG and methanol are purified by distillation. Eastman Kodak has been using such a process for recycling of x-ray films for many decades and it has improved the process [34], e.g., by using superheated methanol vapor to allow the use of ever more impure PET waste. Important factors that have to be dealt with in this process are avoiding coloration due to aldehyde formation and minimizing the formation of either glycols.

6.3.2.3 Ammonolysis

PET wastes can be converted via ammonolysis to paraphenylenediamine, which is a basic raw material for the high-modulus-fiber Kevlar or for high-value hair dyes. The chemical basis for this process is a modified Hoffman rearrangement. The synthesis may be done via the following three stages [35]:



In the first step, granulated PET is suspended in ethylene glycol and treated with gaseous ammonia at 100–140°C. In this reaction, the ethylene glycol also acts as a catalyst. The product terephthalimide (I) is insoluble in the medium and thus may be isolated. In the second step, terephthalimide (I) is suspended in water and chlorinated vigorously with chlorine gas. The resulting terephthalic bis-chloramide (II) is treated with NaOH solution to obtain paraphenylenediamine (III). An important aspect of this process is that paraphenylenediamine so obtained is completely free from its ortho and meta isomers and its production cost is much less than the market price. ICI has reported an alternative single-step process for conversion of PET to paraphenylenediamine by ammonolysis in the presence of hydrogen gas.

6.3.2.4 Hydrolysis

PET can be completely hydrolyzed by water at higher temperatures and pressure in the presence of catalysts (acidic as well as alkaline) to regenerate the monomers, terephthalic acid, and ethylene glycol. While both acid- and base-catalyzed systems are completely realistic, their usefulness under practical production conditions remain controversial. As far as acid hydrolysis is concerned, the large acid consumption and the rigorous requirements of corrosion resistance of the equipment make profitability questionable. Moreover, the simultaneous recovery of TPA and EG, requiring the use of ecologically undesirable halogenated solvents, is difficult and not economical. For the alkaline hydrolysis process, also, the profitability is strongly determined by the necessity of expensive filtration and precipitation steps. In spite of the fact that the majority of newer industrial PET-synthesis plants are based on the TPA process rather than on the DMT process [36], the hydrolytic method of PET recycling has not gained favor.

6.3.2.5 Depolymerization in Supercritical Fluids

The supercritical fluid over its critical point has high density, such as in liquid state, and high kinetic energy as in a gas molecule. Therefore the reaction rate is expected to be higher than the reaction under liquid state conditions. PET is depolymerized quickly by solvolysis in supercritical water [37] or supercritical methanol [38]. The main products of PET depolymerization in supercritical methanol are dimethyl terephthalate (DMT) and ethylene glycol (EG), as shown in Figure 6.4. The depolymerization is carried out typically at temperatures between 543 and 603 K under pressures of 0.1–15 MPa for a reaction time of 3–60 min. For example, at 573 K, sample/methanol ratio 1/5 (by wt) and reaction pressure 14.7 MPa, DMT yield is reported [39] to be 98 per cent in 30 min.

It has been suggested that random scission of polymer chain takes place predominantly in the heterogeneous phase during the initial stage of PET depolymerization in supercritical methanol producing oligomers, whereas specific (chain end) scission to monomers proceeds predominantly in the homogeneous phase during the final stage.

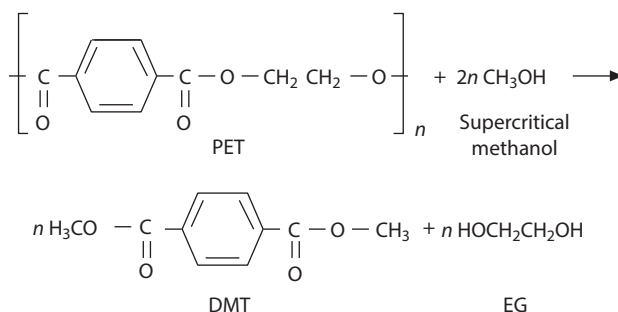


FIGURE 6.4 Main reaction of PET depolymerization in supercritical methanol.

6.3.2.6 Enzymatic Depolymerization

In 1977, Tokiwa and Suzuki reported that some lipases, which are extracellular enzymes that usually cleave esters in oils and fats, are also able to attack ester bonds in some aliphatic polyesters and can depolymerize such materials [40]. Aliphatic polyesters, however, exhibit only limited useful properties for many applications. Aromatic polyesters, such as PET and PBT, which are widely applied because of their excellent properties, are not attacked by hydrolytic enzymes. This led to the development of aliphatic-aromatic polyesters as biodegradable plastics that present a compromise between biodegradability and material properties [41]. Later, however, Müller et al. [42] isolated a hydrolase (TfH) from *Thermofibida fusca* which was able to depolymerize the aromatic polyester PET at a high rate in contrast to other hydrolases such as lipases. They demonstrated for the first time that commercial PET can be effectively hydrolyzed by an enzyme at a rate that does not exclude a biological recycling of PET. The effective depolymerization of PET with the enzyme TfH will result in water soluble oligomers and/or monomers that can be reused for synthesis. In contrast, a microbial treatment of PET may not be appropriate for recycling purposes, since monomeric and oligomeric depolymerization products would be consumed by the microorganisms involved or inhibit their action and growth [42].

It is likely that the degradability of PET with hydrolases such as TfH strongly depends on the polymer crystallinity and the temperature at which the enzymatic degradation takes place [42]. The effective enzymatic PET hydrolysis will thus be expected to occur only below a certain critical degree of crystallinity. However, for bottle manufacture polyesters with low crystallinity are preferred for high transparency, thus increasing the susceptibility of PET to enzymatic attack.

One reason for the high activity of TfH hydrolase towards PET may be the high temperature (55°C) optimum, which is a result of its origin from a thermophilic microorganism. However, differences in the degradation behavior between TfH and the other lipases may also be due to differences in the structure of the enzymes, possibly enabling TfH to attack less mobile polyester segments and degrade PET at a surprisingly high rate.

6.3.3 Incineration

For PET wastes containing a large amount of impurities and other combustible solids it is more profitable to resort to quaternary recycling, that is, energy recovery by burning. Research along this line has been performed, particularly in Europe and Japan, since the early 1960s. Strong emphasis has been laid on the optimization of incinerators with regard to higher temperature of their operation and reduction of the level of air pollution.

Having a calorific value of ca. 30.2 MJ/kg, which is about equivalent to that of coal, PET is readily suited for the incineration process. However, like other plastics its combustion requires 3–5 times more oxygen than for conventional incineration, produces more soot, and develops excessive heat that thus calls for special incineration equipment to cope with these problems.

Several processes have been developed [43–45] to overcome the technological drawbacks of plastics incineration cited above. These include continuous rotary-kiln processes; a process for glass-reinforced PET; a combined system for wood fiber and PET to provide steam to power equipment; and a fluidized system for pyrolysis, in combination with silver recovery from photographic film. Incineration of photographic film raises the additional problem of the formation of toxic halogenated compounds due to the presence of silver halides.

Incineration of PET is usually carried out at temperatures around 700°C, since at lower temperatures waxy side products are formed, leading to clogging, while at higher temperatures the amount of the desirable fraction of mononuclear aromatics in the condensate decreases. A representative sample pyrolyzed under optimum conditions yields, in addition to carbon and water, aromatics like benzene and toluene, and a variety of carbon–hydrogen and carbon–oxygen gases. Studies have been made [46] relating to the formation of dioxines and residual ashes containing heavy metals and other stabilizers.

While most problems arising during incineration of PET can be resolved, it is evident that quite a few hurdles remain to be overcome before an economically feasible and ecologically acceptable industrial technical process becomes available.

In conclusion, it may be said that there exists a clear hierarchy in PET-film recycling technologies. Two most important criteria of classification are the degree of purity of PET scrap to be handled and the economics of the process. While for the cleanest PET grade the most economical process is direct reuse in extrusion, for less-clean PET samples it is still possible to reuse them after the modification step (partial degradation, e.g., by glycolysis) at a reasonably low price. More-contaminated PET waste must be degraded into the starting monomers, which can be separated and repolymerized afterwards, of course, at a higher cost. For this operation, mostly the methanolysis process has been exploited industrially. Finally, the most heavily contaminated PET wastes have to be incinerated or brought to a landfill.

6.4 Recycling of Polyurethanes

Polyurethanes are by far the most versatile group of polymers, because the products range from soft thermoplastic elastomers to hard thermoset rigid forms (see Chapter 4). Although polyurethane rubbers are specialty products, polyurethane foams are well known and widely used materials. While the use of plastics in automobile has increased steadily over the years, a major part of these plastics is polyurethane (PU), which is used for car upholstery; front, rear, and side coverings; as also for spoiler. In fact, about half of the weight of plastics in modern cars is accounted for by PU foams. Accordingly, in addition to production scrap, large quantities of used PU articles are now generated from automotive sources. Though most PU plastics are cross-linked polymers, they cannot be regarded as ordinary thermosetting plastics, owing to their chemical structure and physical domain structure. Thus in contrast to typical thermosetting plastics, various methods are available today for recycling PU scrap and used products.

There are basically two methods for recycling polyurethane scrap and used parts, namely, material recycling (primary, secondary, and tertiary recycling) and energy recycling (quaternary recycling). The former methods are preferred since in this way material resources are replenished. After multiple uses the material can finally be used for energy recovery by high-temperature combustion or gasification.

Among several processes described for PU material recycling, thermopressing and kneader recycling [47] have attracted much attention. By the thermopressing process, granulated PU wastes can be converted into new molded parts, while in the kneader recycling process a thermomechanical operation causes partial chemical breakdown of PU polymer chains that can be subsequently cross-linked by reacting with polyisocyanates. Hydrolysis and glycolysis are important tertiary recycling processes for PU wastes.

6.4.1 Thermopressing Process

Thermopressing, or molding by heat and compression, is a direct method of material recycling that is designed such that elastomeric, cross-linked polyurethanes can be recycled in much the same way as thermoplastic materials [48]. The principle of thermopressing is based on the realization that polyurethane and polyurea granules are capable of flowing into each other and building up new bonding forces under the influence of high temperature (185–195°C), high pressure (300–800 bar), and strong shearing forces. The granules generally used for this purpose have a diameter of 0.5–3 mm. They completely fill the cavities of a mold meaning that moldings with new geometries can also be manufactured.

Unlike injection molding of thermoplastics for which a cold mold is used, in the thermopressing process, the mold is kept constantly hot at a temperature of $190 \pm 5^\circ\text{C}$ and no release agent is used for demolding. This relatively simple technique will permit 100% recycling of polyurethane RIM and RRIM moldings, particularly when the formulations of RIM systems to be used in future have been optimized for recycling. The steps in the thermopressing process are shown in Figure 6.5.

The molded parts obtained by thermopressing of granulated PU waste exhibit only slight reduction in hardness and impact strength but significant reduction in elongation at break. The last named

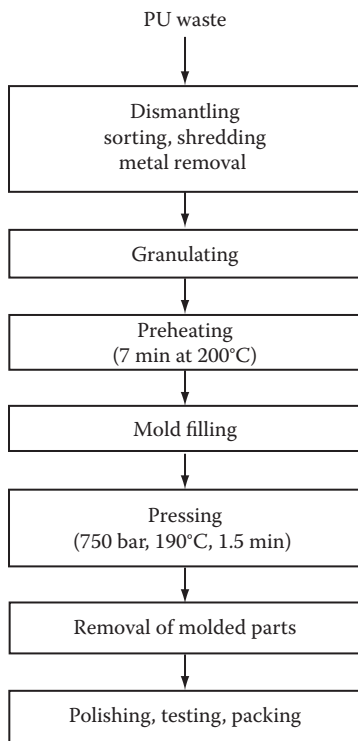


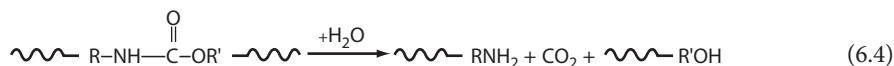
FIGURE 6.5 Reprocessing of polyurethane waste by thermopressing. (After Müller, P. and Reiss, R., *Die Makromol. Chem., Macromol. Symp.*, 57, 175, 1992.)

polyisocyanate (e.g., Desmodur TT or 44 of Bayer) and molded into desired shapes by compression molding at 150°C and 200 bar pressure. The scheme of the recycling process is shown in Figure 6.6.

Partial breakdown of PU network in the kneader results in highly branched molecules with many functional groups necessitating addition of polyisocyanate in relatively high concentration for subsequent cross-linking to produce molded articles. The process thus yields products of high hardness (with Shore up to 80) and high tensile strength (30 MPa), but small elongation at break (6–8%).

6.4.3 Hydrolysis

Hydrolysis of PU waste results in the formation of polyethers and polyamines that can be used as starting materials for producing foam. In this process, powdered PU waste is reacted with superheated steam at 160–190°C and the polymer gets converted in about 15 min to a liquid heavier than water. The liquid is a mixture of toluene diamine and propylene oxide (polyether diol), the former accounting for 65–85% of the theoretical yield:



The recovered polyether can be used in formulations for making PU foam, preferably in admixture with virgin polyether [49].

A continuous hydrolysis reactor utilizing a twin-screw extruder has been designed [49] that can be heated to a temperature of 300°C and has a provision for injection of water into the extruder at a point

property, for example, drops to about 10% of the original value if painted PU wastes are used. Moreover, because of the use of granulated feed, the resulting molded parts lack surface smoothness and thus should be used preferably in those areas where they are not visible. In a passenger car, there are many such parts that are not subjected to tensile stress but require dimensional and heat stability—properties fulfilled by PU recycled products. Examples of application are wheelboxes, reserve wheel covers and similar other covers, mudguard linings, glove boxes, and casings.

6.4.2 Kneader Process

The basic of the kneader recycling process is a thermomechanical degradation of polymer chains to smaller-size segments. The hard elastic PU is thereby converted into a soft, plastic (unmolten) state, which is achieved with a kneader temperature of 150°C and additional frictional heating. This leads to temperatures above 200°C and causes thermal decomposition into a product that is soft at 150–200°C but becomes brittle at room temperature, enabling it to be crushed to powder in a cold kneader or roller press. The resulting powder can be easily mixed with a powder form

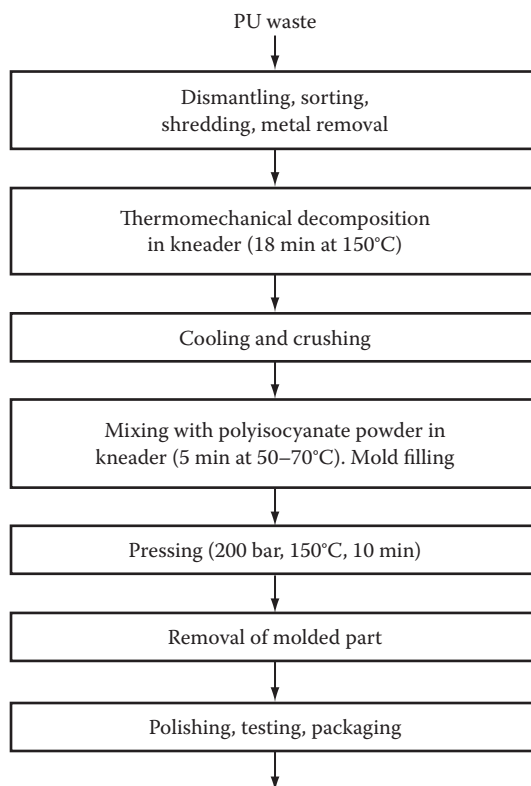


FIGURE 6.6 Recycling of polyurethane waste via partial decomposition in kneader. (After Müller, P. and Reiss, R., *Die Makromol. Chem., Macromol. Symp.*, 57, 175, 1992.)

where the scrap is almost in the pulp state. Polyurethane scrap in powder form is fed into the extruder and residence time is adjusted to 5–30 min. Separation of the two components, polyether and diamine, in the product may be effected by fractional distillation, by extraction with a suitable solvent, or by chemical means. The PU foams made from these recycled products can be used in several applications, one example being protection boards for construction sites. Hydrolytic recycling has not, however, found much application, since virgin raw materials are cheaper than the regenerated products.

6.4.3.1 Glycolysis

Extensive studies have been made on glycolytic degradation of PU wastes. In a glycolytic process, powdered PU waste is suspended in a short-chain glycol and heated to a temperature of 185–210°C in nitrogen atmosphere. The glycolysis reaction takes place by way of transesterification of carbonate groups in PU (Figure 6.7). The reaction product is predominantly a mixture of glycols and does not need any further separation of the components, unlike in the hydrolytic process. The cost of producing such recycled polyol is reported to be low enough to make the process economically viable [49].

The mixed polyols resulting from glycolytic degradation of PU waste is suitable mainly for the production of hard foam, such as insulating foam for houses.

6.4.3.2 Ammonolysis

Chemical recycling of polyurethanes by ammonolytic cleavage of urethane and urea bonds under supercritical conditions has been described [50]. It is well known that a number of low-boiling materials give enhanced solubility and reactivity under supercritical conditions. Ammonia has a critical point at 132.45°C and 112.8 bar (11.28 MPa) with a density of 0.235 g/cm³. Being able to act as hydrogen-bond

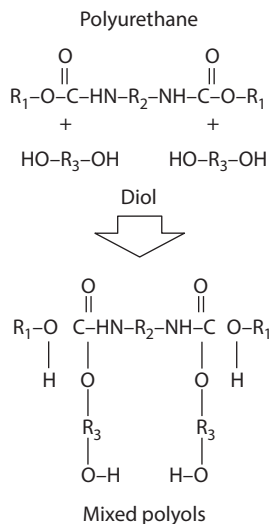


FIGURE 6.7 Alcoholysis of polyurethane (PU) waste. By the action of small-chain alcohols (e.g., diol), PU is decomposed yielding homogeneous, liquid, and mixed polyols.

donor and acceptor, it provides good solubility for polyurethanes and dissolves their hard segment domains thus enabling a homogeneous reaction. Ammonia is also a reagent having greater nucleophilicity than, for example, water or glycol is; since it is added in a huge molar excess compared to the urethane or urea groups of the materials to be cleaved, the equilibrium is shifted towards the ammonolysis products. The stoichiometry of ammonolysis reaction of a polyetherurethane is shown in Figure 6.8.

The typical reaction parameters of an ammonolysis process are temperature of 139°C, pressure of 140 bar, and reaction time of 120 min. The ammonolysis reaction transforms derivatives of carbonic acid into urea. Ether bonds as well as hydroxy groups are inert towards ammonia under the reaction conditions applied. Hydroxy compounds like polyols and diol chain extenders that do not contain ester groups are recovered as such. The C=O fragments of urethane and urea functional groups are converted to unsubstituted urea.

After ammonolysis, ammonia is evaporated and can be reused after liquefaction, while degradation products of polyurethane hard segments (e.g., amines and chain extenders) and urea are removed by extraction. The pure polyol is left in the reactor. It can be removed mechanically or by extraction with liquid ammonia in which it is soluble. The recovered amines can be converted to the corresponding isocyanates and can be reused, along with polyols, in the same applications as before. A flow scheme of the recycling process is shown in Figure 6.9.

Among the various material recycling methods for PU scrap and wastes described above, the thermopressing and kneading processes are especially significant, because these simple processes render

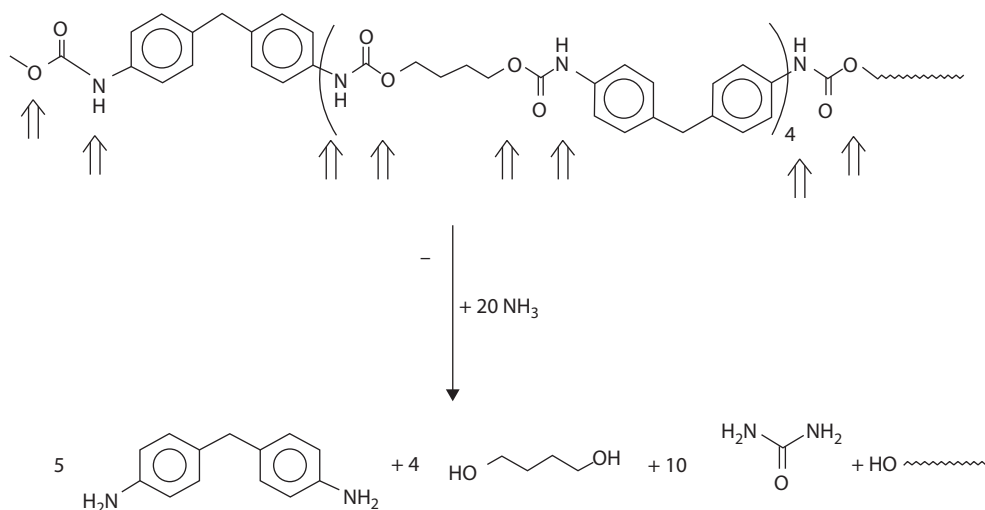


FIGURE 6.8 Stoichiometry of ammonolysis reaction of a polyetherurethane. (After Lentz, H. and Mormann, W. 1992. *Die Makromol. Chem., Macromol. Symp.*, 57, 305.)

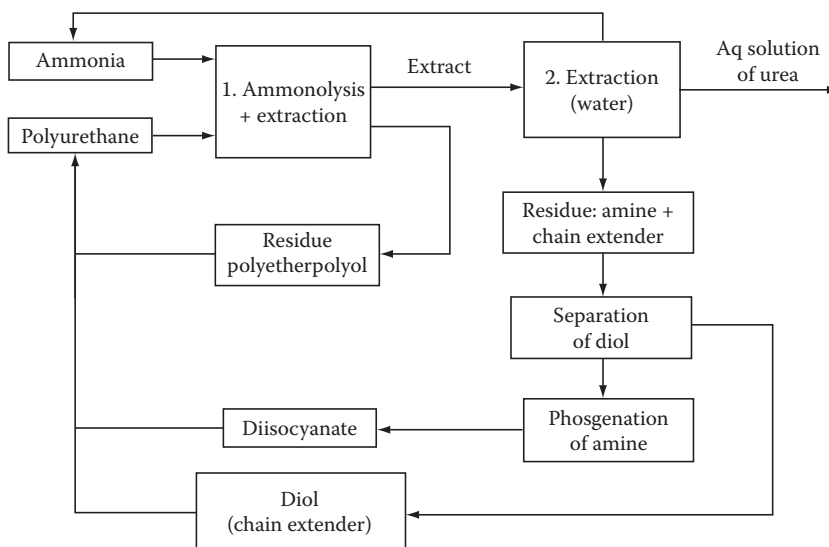


FIGURE 6.9 Flow scheme of a chemical recycling process based on ammonolytic cleavage and separation of polyol by supercritical ammonia. (After Lentz, H. and Mormann, W., *Die Makromol. Chem., Macromol. Symp.*, 57, 305, 1992.)

the recycling of cross-linked PU products equivalent to that of thermoplastic products. Lack of surface smoothness and some reduction in mechanical properties are to be tolerated, especially when painted PU wastes are recycled. However, good values of E-modulus, structural rigidity, and hot and cold impact resistance permit use of the molded components of recycled PU in many applications, e.g., in unsighted parts of automobiles, instruments, and machineries.

6.5 Recycling of Poly (Vinyl Chloride)

Aside from the polyolefins, poly (vinyl chloride) (PVC) [51] and some other chlorine-containing polymers belong to the most widely applied thermo-plastic materials. There are many applications of rigid and plasticized PVC. In the building sector, for example, very large amounts are used for pipes, profiles for windows, floor coverings, roofing sheets and so on. By the end of the lifetime of these articles, large amounts of scrap have been produced. It is of economic and environmental interest to recycle this PVC waste as much as possible. Disposal of PVC waste by incineration has its special problems. Due to the high chlorine content of PVC, its incineration yields large amounts of HCl gas in addition to the possibility of formation of toxic dioxines and furans. On the other hand, it is a great advantage that many sources produce large amounts of PVC scrap of the same origin and with similar composition, which simplifies the reuse possibilities from a logistic point of view.

Dealing with post-consumer mixed PVC waste involves special considerations. Reprocessing PVC-containing plastics waste without separation will normally entail dealing with mixtures in which large proportions of polyolefins (mainly polyethylene) are present. In view of the poor compatibility of polyolefins with PVC, this is not a particularly attractive practical proposition, with respect to processing and the resulting product. Selective reclamation, i.e., separation from waste mixtures with other plastics, and subsequent reprocessing are complicated by the wide variety of PVC formulations, and the increased susceptibility to heat degradation in reprocessing. The main factors in the latter are the heat history already acquired; the possible presence of polymer already partly degraded in the course of past heat treatments and/or service; and the remaining stability of PVC articles before their recycling, which often

necessitates an additional stabilization by addition of heat stabilizers. Moreover, about 1/3 of the used PVC is plasticized by various types of plasticizers. Therefore, for the recycling of such PVC types the concentration of plasticizers should be known. Due to these considerations, it is important to have rather detailed information about a PVC scrap before use.

6.5.1 Characterization of Used PVC

Since several chemical reactions occur during processing and use of PVC, which can change the properties of the polymer, it is necessary to characterize PVC scrap before deciding about the reusability.

Under the influence of heat and light (and also oxygen), PVC chains can be degraded or even cross-linked, which results in changes in the molecular weight and distribution and thus in the mechanical properties of PVC. For determining the molecular weight distribution, gel permeation chromatography is the most applied method, but in many cases the measurement of solution viscosity after separation of all insoluble components, including cross-linked PVC, will suffice.

Because practically no PVC is processed and used without the addition of stabilizers, one should know the residual stability of a used PVC product. For this the best way may be the determination of the hydrogen chloride elimination at 180°C under air or nitrogen [52]. The conversion-time curves so obtained provide indication of the residual stability from the induction period and also enable calculation of the rate of HCl split-off after consumption of the stabilizers. In some cases, however, it may be sufficient to use a simple Congo Red test (e.g., according to DIN 53 418) instead of the apparatus for measuring the HCl elimination.

The dehydrochlorination of PVC results in the formation of polyene sequence that can be responsible for discoloration and also act as starting sites for further degradation and cross-linking reactions. For some applications it may thus be useful to have some knowledge about the unsaturated structures that have been formed in PVC during the use. For this purpose, the investigation of the UV-VIS spectra that give at least semiquantitative information about the dehydrochlorination and the application of ozonolysis [53], which results in cleavage of the unsaturated sequences in PVC, may be useful.

In the case of reuse of plasticized PVC, it is important to determine the residual plasticizer content. This can be obtained by extraction with ether or similar nonsolvents for PVC and determination of the chemical nature of the plasticizers by thin-layer or gas chromatographic methods. The determination of the glass transition temperature by differential thermal analysis also gives information on the efficiency of the residual plasticizers.

6.5.2 In-Line PVC Scrap

Normal recirculation, in the same process, of the clean PVC scrap generated (e.g., edge trim in calendaring) is widely practiced, in particular with PVC for noncritical applications. General PVC scrap, both from internal and external sources, is also converted by some processors into such products as cheap garden hose or core composition for cables.

Two possibilities have been investigated for the recycling of die-cutting scrap produced in the processing of PVC sheet: production of secondary sheet and production of extruded profiles or pipes. First the scrap is ground up in a grinding mill. The stabilizer used in the original process is added again in a premixer, and pigments are often added to achieve a uniform, desired color. This premix is fed into the compounding unit.

If the regrind includes rigid, semirigid, and plasticized PVC, the rigid and semirigid fractions can be charged into the compounding unit through a first-inlet opening and plasticated in an initial kneading zone. The plasticized PVC scrap is then fed into this fluxed stock, which ensures the gentlest and most homogeneous processing (Figure 6.10). Any additional plasticizer required is injected directly into the kneading zone of the compounding unit by a pump. This is done because the plasticizer cannot diffuse in

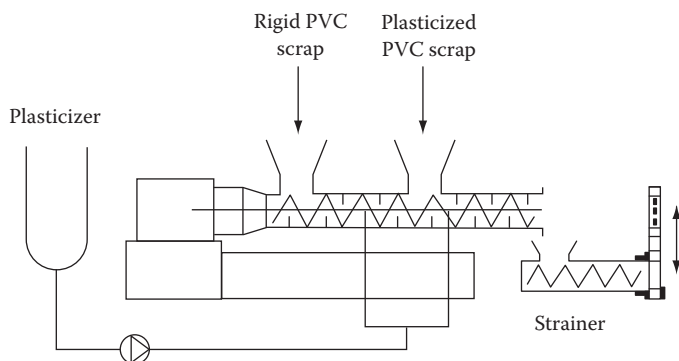


FIGURE 6.10 Recycling of PVC film scrap.

the PVC regrind within a reasonable time, which it can in the case of virgin PVC. It is advisable to use a strainer in order to remove any contamination from the stock. Afterwards, the calendering process is carried out as usual.

For the production of profiles and pipes, the homogeneous stock is pelletized following compounding. The pellets are fed to an extrusion line.

In the cable sector, compounders are often confronted with the problem of recycling copperless insulation and sheathing scrap. An approach that may be taken in this case is to use this scrap for producing filling core mixtures. The purpose of the filling cores is to fill out the cavities between a cable's conductors (Figure 6.11). Since their composition is not subject to any special electrical or mechanical specifications, it is normally made as inexpensive as possible, usually receiving a high level of chalk filler. The PVC in this case acts mainly as binder for the filler. For compounding such cable filler cores, the reground PVC scrap, with a particle size of 5–10 mm, is fed into the first inlet of a compounding unit designed specifically for this application (Figure 6.12). The reground scrap is plasticated homogeneously in the first kneader zone, enabling it to absorb the high filler loading fed into the second inlet opening without any difficulty. For increased flexibility of the filler cores, plasticizer may be injected into the kneading chamber by a pump (see Figure 6.12). The homogenized stock is pelletized following compounding.

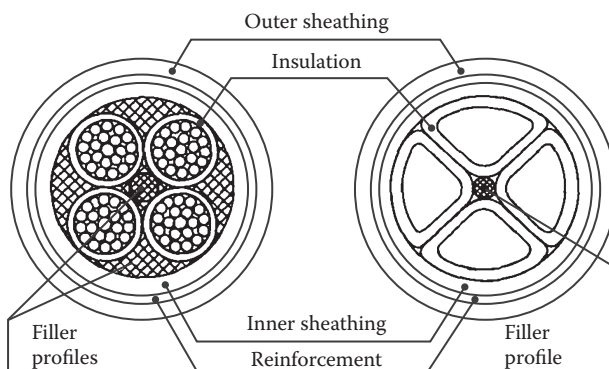


FIGURE 6.11 Schematic of cable design. (After La Mantia, F. P. ed. 1996. *Recycling of PVC and Mixed Plastic Waste*, p. 265. ChemTec Publishing, Toronto-Scarborough, Canada.)

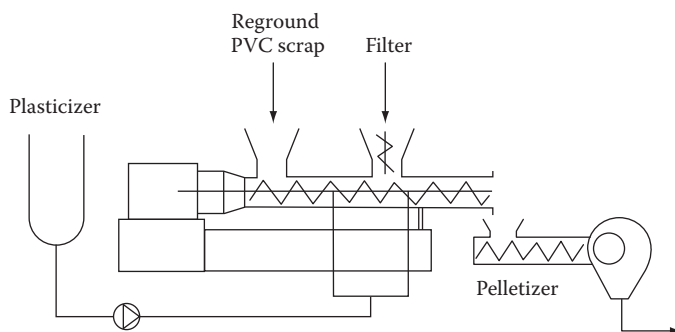


FIGURE 6.12 Compounding of cable filler cores.

6.5.3 PVC Floor Coverings

PVC floor coverings are a combination of a number of constituents that together comprise the recipe for a floor covering. Typical floor covering recipes are for the most part made up as follows: PVC 28–50%, plasticizer 10–20%, stabilizers 0.5–1%, slip agents less than 1%, filler 25–60%, and pigments 1–5%. Further, many floor coverings are provided with additional textile- or glass-fiber—containing carrier layers. Given an average service life of 10–17 years, old PVC coverings represent a large reserve of raw materials.

To exploit these large reserves of raw materials on an industrial scale, one needs a network for systematic collection of old coverings, a system of transport logistics, and the ability to build technically feasible recycling plants. In order to undertake this work in Europe, about 20 producers of PVC raw material and floor coverings from Germany and other European countries joined together in April 1990 to form the Society for the Recycling of PVC Floorings.

The main operations carried out in a recycling plant for old PVC floor coverings are sorting, cleaning, shredding, purifying, powdering, mixing, and packaging [54]. The purification unit essentially comprises a hammer mill and a downstream vibrating screen. The function of the hammer mill is to knock off any residues of screed or adhesive still adhering to the floor covering, and the vibrating screen then separates off these residues. The shredding material that has been purified in this way is first passed to a cutting mill, which enables it to be precomminuted to granules that are first homogenized in a mixing silo and purified by means of zigzag sifters before being processed to PVC floor covering powder in the powder mill. The powder can be upgraded by the addition of plasticizer, PVC, or filler to give powder recipes suitable for calendering to make new floor coverings; this depends on the quality of the batch in question. Other possible uses of the powder are for products, such as mats for cars, mud flaps, and soft profiles.

6.5.4 PVC Roofing Sheets

A major use of PVC in the building industry is for roofing sheets. These sheets are produced on calenders and contain in most cases two plasticized PVC foils that are reinforced by glass fiber or polyester fabrics. The used sheets show different properties, depending on whether they are applied under direct influence of light and weather conditions.

After a lifetime of 10–20 years, the roofing sheets have to be replaced by new ones, which is normally done by the same firm(s). Therefore, the recycling of used roofing sheets is rather easy from the logistic point of view and has been common practice for many years. New PVC roofing sheets may contain up to 10% of the recycled material [54].

6.5.5 Post-Consumer PVC

Some post-consumer PVC sources are water, food, pharmaceutical, and cosmetic bottles, and film. Another significant source of post-consumer PVC is used electric cable, coming principally from plant demolition and, to a lesser degree, from manufacturing scrap and offcuts.

Most end-use markets for recycled plastic bottles require that they be separated by resin type and color. This ensures high end-use value for new products incorporating substantial amounts of the recycled resin. PVC bottles, like PET bottles, are very recyclable. Manual sorting of nonpigmented PVC and clear PET bottles is difficult because they look alike. When the two types are received commingled, the reprocessor can experience quality deficiencies due to rheological incompatibilities between these two resins. Therefore, all attempts to separate and remove these two resins must be made prior to recycling.

Manual sorting techniques are inadequate to meet the market's needed quality standards, so new techniques have been engineered that will detect and separate bottles made from either of these two resins. A simple device senses the presence of chlorine atoms as a means to detect PVC bottles. Once detected, PVC bottles are pneumatically jettisoned from the commingled bottle feed-stream by a microprocessor-based air-blast system.

The step after sorting is baling or granulation. Granulation is the preferred method of intermediate processing since the material so processed commands the highest market value. For upgradation of the resin from the recycled PVC bottles, several steps are explored depending on the results of characterization tests as discussed earlier. These include incorporation of virgin resin (10–90%), restabilization against UV and heat, and incorporation of processing aids, impact modifiers, lubricants, plasticizers, and antioxidants.

The recovery of electric cable is long established because of its valuable copper content. After this conductor material has been extracted, the residue consists of sheathing and insulation that may contain rubber and polyethylene as well as PVC. These other materials can be largely removed from grinding, by flotation, vibration, and filtration, but rubber is especially difficult to remove entirely, so that applications for material recycled from cables containing it are limited to areas such as car mats and carpet underlay.

6.5.6 Vinyloop and Taxyloop Processes

Vinyloop is a technology that enables recycling difficult-to-treat PVC waste from different sources. It produces recycled PVC (R-PVC) compound that can be considered as virgin material in terms of quality and property consistency. In addition to preserving nonrenewable resources, the Vinyloop process avoids landfilling or incineration of post-consumer PVC waste and consequent addition to carbon footprint. For each kilogram of PVC compound recovered through the Vinyloop process, the production of 1 kg of virgin PVC compound and the incineration of the corresponding amount of PVC waste are avoided.

From a selection of raw, heterogeneous waste, the Vinyloop procedure allows homogeneous regenerated PVC compounds to be produced. There are several varieties of regenerated PVC compounds, depending on the recycled material or origin of the waste. Commonly used recycled materials include waste from cables, frames, roller shutters, and agricultural film, while the following could also be recycled: wallpaper, floor covering, roofing membranes, blister packaging, and so on. The average PVC content in the waste must be at least 70%.

The Vinyloop procedure has proved to be the only recycling method available for regenerating the PVC contained in composite structures as it has been impossible so far to recover it using traditional methods. It allows the PVC compound to be separated from other materials such as natural textiles, polyester fibers, polyolefins, rubbers, metals, and many others. The recycling is based on the principle of selectively dissolving the PVC using a solvent that is constantly recycled in a closed circuit.

Taxyloop is the polyester PVC composite material recycling technology based on the Vinyloop process. It provides a recycling solution for PVC composite textiles, which, until the advent of this process, were not fully recyclable owing to difficulty in separating the PVC from polyester fibers. The Taxyloop process

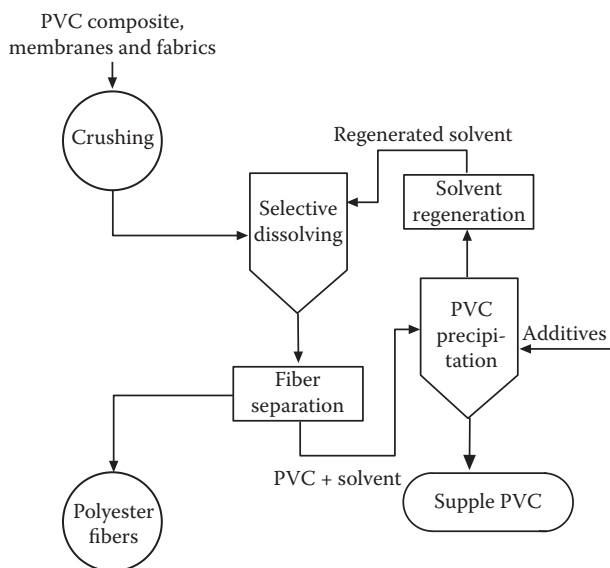


FIGURE 6.13 Texyloop process for recycling PVC.

ensures 100% recyclability of PVC textiles into clean and reusable materials, thereby reducing raw material consumption and minimizing landfill or pollution through incineration.

The recycling project was commenced in 1997 by Ferrari in partnership with the Solvay Group and eight years of research and development led to the construction of a recycling plant at Ferrara, Italy, in 2005. The Texyloop process consists of five main steps in a “Closed Circuit” based around Solvay’s Vinyloop process (Figure 6.13): (a) crushing, (b) selective dissolving, (c) fiber separation, (d) PVC precipitation, and (e) solvent regeneration.

6.6 Recycling of Cured Epoxies

Thermosetting plastics are difficult to dispose because of their network structure. Chemical recycling is a promising route for converting these plastic wastes by returning them back to their original constituents. However, thermosetting resins are usually reinforced by reinforcement such as glass fiber to modify their brittleness and increase their strength, forming composite materials with complex structure. The presence of reinforcement in the cured composite thus makes the recycling of the matrix resin more difficult.

An approach to chemical recycling of amine cured epoxies using nitric acid solution has been proposed [55,56]. In order to investigate the practical applicability of the proposed research, glass fiber-reinforced bisphenol F type epoxy resin (cured with 4,4'-diaminodiphenylmethane) was decomposed in nitric acid solution and the decomposed organic products as well as the fiber were recovered. In a typical experiment, the glass-reinforced epoxy composite was cut into small pieces and kept immersed in 4 M nitric acid at 80°C till the matrix resin dissolved completely, yielding a yellow solution and leaving behind the inorganic (glass) residue which was separated and recovered. When the yellow solution was cooled in ice no crystal was formed. However, if nitric acid solution of higher concentration, such as 6 M, was used for immersion, crystals separated out because of breakage of the main chain of epoxy resin and subsequent nitration under the attack of nitric acid [57].

The yellow solution was subjected to neutralization with sodium carbonate, extraction, refinement, and drying to obtain neutralized extract (NE) which was then repolymerized to prepare the recycled resin. Since NE could contribute hydroxyl groups to bond with phthalic anhydride (curing agent), it was employed to

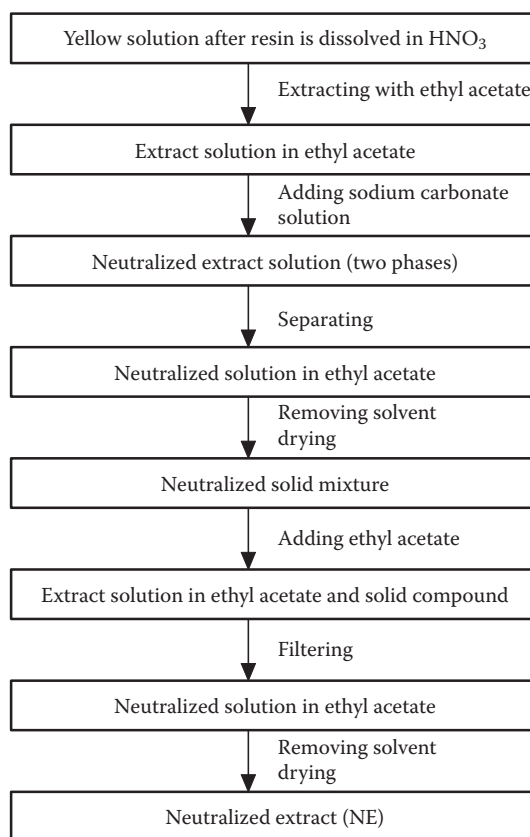


FIGURE 6.14 Process of extraction of epoxy resin dissolved in nitric acid and neutralization of the extract. (After Dang, W., Kubouchi, M., Sembokuya, H., and Tsuda, K., *Polymer*, 46, 1905, 2005. With permission.)

substitute a part of epoxy resin. The proportions of NE addition ranged from 5 to 30 wt% (the ratio of weight of NE to the total weight of NE and epoxy resin). The process of neutralization and refinement of the acid extract is presented in Figure 6.14.

6.7 Recycling of Mixed Plastics Waste

Commingled plastics currently represent an estimated two-thirds of today's recycled plastics streams. That fraction can be expected to shrink somewhat with the development of more successful identification and segregation technologies in the future. However, commingled plastics streams will continue to make up a significant volume for several reasons: proliferation of grades and types of commodity; profusion of polymer blends and alloys; contamination of recycle plastic parts with metals, coatings, and laminates; and practical cost considerations. Mixed plastics wastes can be divided into two groups depending on their source: mixed plastics from household or municipal solid wastes and plastics from industrial sectors.

The first category (post-consumer mixed plastics) involves the articles that are used in food, pharmaceutical and detergent packaging, shopping, and others. The majority of these are composed of films, sheeting, strapping, thermoformed trays, as well as a variety of bottles for soft drinks, food, and cosmetics. There are mainly five different polymers—PE, PP, PS, PVC, and PET—that contribute to the total amount of plastics waste. The composition of mixed plastics can change depending on the regional habits and the seasons of the year. Also the mode of waste collection can influence its final composition.

The category of postindustrial wastes concerns articles like the products of the car, furniture, and appliances industries. The problems of these sectors are a wide variety of engineering materials and a high number of components employed to build a final system.

6.7.1 Direct Reuse

A direct solution to the problem of plastics disposal can be the reuse of a heterogeneous mixture of plastics directly obtained from an urban collection. Today there are extruders specifically designed for reprocessing post-consumer and postindustrial waste materials. The waste material can have many forms and can range in bulk density from approximately 1 to 35 lb/cu ft. The form, bulk density, moisture content, contamination level, and process-temperature restrictions all affect the design of the extruder to be used. For example, due to the presence of PVC resin, the melting temperature must be kept below 210°C and the barrel residence time must not exceed 6 min. Furthermore, in the mixture, the relatively high content of semicrystalline polymers like PET, whose melting point is above the processing temperature, influences the extruder design or the final properties of the manufactured product. Large injection gates and mold channels must be used in order to avoid undesirable occlusions in the channels.

Standard single-screw extruders are no longer adequate to recycle or reclaim this wide range of materials in a cost-effective manner. There are now special extruders designed to process the lighter-bulk-density materials. Low-bulk-density materials are the various forms of film, fibers, and foams commonly used in the packaging industry. Due to their low-bulk density, such materials typically require an auxiliary device to facilitate proper feeding into the extruder throat. There are several varieties of such feeding mechanisms available [58]. Two of them are a rotating screw-type crammer and a piston-type ram. The crammer and ram systems both act on the same principle; that is, an auxiliary feeding device is used to convey and to compact the low-bulk-density materials into the feed section of the extruder screw.

The screw-crammer system uses a conical hopper with a screw that is driven by a separate gear reducer and variable-speed drive motor. The output and effectiveness of the crammer are determined by the screw configuration and the available speed. The ram-type system, on the other hand, uses a pneumatic ram to stuff material into the screw. The ram is a piston-driven unit with the stroke timing adjustable by setting a series of timers located in the control panel. The feed section used by the ram system has an opening that is 12–14 times larger than that of a standard screw extruder. This allows low-bulk-density material to flow freely into the feed throat where the ram can compress it into the screw. Depending on the extruder size, the ram can compact materials with a force of 2000–9000 psi.

Feed materials usually need to be supplied to either the crammer or the ram system in a chopped form. The size and bulk density of the chopped particles affect the performance of the crammer and ram, and thus ultimately the output of the extruder. Both these systems can also be used to process higher-bulk-density products.

A third method of processing low-bulk-density materials is through the use of a dual-diameter extruder [58]. This system has two distinct sections: a large diameter feed and a small diameter processing section. The large-diameter section acts as a cramming device—compacting, compressing, and conveying the feed material—while the smaller-diameter section is used to melt, devolatilize, and pump the extrudate into a die. In the feed section, the screw can have deep flights, allowing low-bulk-density materials to flow freely, while in the processing section the screw resembles that of a typical extruder. The screw is available in one of several configuration: single-stage, two-stage, or barrier design. Depending on process needs, these designs optimize output and raise product quality.

The feed section of a dual-diameter extruder can be equipped with feed-assist components that in some cases work in conjunction with specially designed screws to allow processing of a wide variety of feedstocks that are fed to the machines in roll form. Among these possible feedstocks are loose bags, handle cutouts from bag making operations, and continuous web products such as blown and cast film scrap. This ability eliminates the cost of shredding, grinding, and densification of many materials. A dual-diameter

extruder is also capable of processing materials with a high-bulk density. The crammer, ram, and dual-diameter systems do not differ widely in equipment costs, or production rates.

It is well established that a strong incompatibility is typical of polymers usually found in commingled waste (PE, PP, PET, PVC, and PS). This incompatibility gives rise to materials that have inferior mechanical properties, particularly with regard to tensile, flexural, and impact strengths. This means a strong limitation of applications, in particular in the case of thin walls and manufactured products that have to work under flexural and tensile stresses. However, by adding to the mixture specific components like other polymers from homogeneous recycling, fillers (talc), fibers, or promoters (compatibilizers) that increase the compatibility, it is possible to improve the tenacity or stiffness, product aesthetics, and processability.

Addition of glass fibers, for example, is found [59] to yield products with very high stiffness (e.g., elastic modulus $E \approx 2800$ MPa with 30% glass fiber), higher than that with talc ($E \approx 1250$ MPa with 20% talc) and far better than that of the original mixture ($E \approx 950$ MPa). Addition of LDPE and styrene-butadiene-styrene copolymer, on the other hand, improves the tenacity (showing, typically, a 30–90% increase in elongation at break). Extruded profiles have thus been made that can be employed to build benches, garden tables, bicycle racks, fences, and playing facilities for park. Coextrusion technology can be used very effectively to improve surface properties like puncture, impact and weather resistance, as well as appearance. One interesting application for mixed plastics, because of their large market volume, is the production of injected tiles for paving [59].

A new and exciting technology has been developed in the fabrication of composite materials made with commingled plastics. It followed the discovery in 1986 by the scientists and technologists at GE Plastics that useful products could be fabricated using Radlite technology (Figure 6.15) if the powdered feed consisted of two or more resins. While compatibilization of dissimilar resins is typically brought about by chemical means, this is not the case with Radlite technology products where compatibilization appears to take place by physical means, i.e., the binding of dissimilar resin domains through the fibers. A conceptual model of physical compatibilization is shown in Figure 6.16.

The rolls or sheets made by Radlite technology using commingled plastics and chopped glass fibers (0.25–1.0 in.) can be converted to finished parts by conventional forming technologies such as compression molding (typically 200–290°C, 3–5 MPa, 2–4 min). These are fully consolidated, essentially void-free products with specific gravities that would be calculated on the basis of resin type and glass fiber content. The physical properties of the consolidated structures from commingled plastics are in general similar to standard grades of SMC composites.

Foamed network structures (lofted structures) are also prepared in a compression press using Radlite technology. In this case, after applying full temperature and pressure for the requisite 2–4 min, the platen gap is opened 1.5 times the original setting (for primarily open-cell structure) or 1.1–1.2 times the original

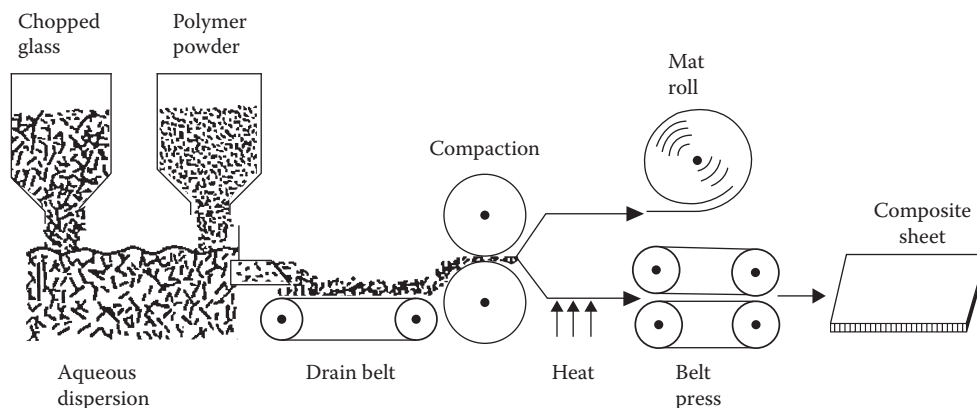


FIGURE 6.15 Schematic of Radlite technology.

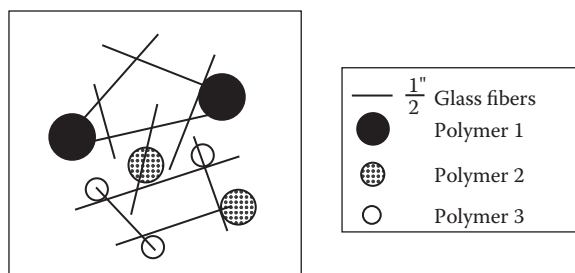


FIGURE 6.16 Conceptual model of physical compatibilization.

setting (for primarily closed-cell structure). Foamed structures have the aesthetic and physical appearance of particle board, a common material of construction. Application possibilities of products made by the Radlite technology include highway signs and sound barriers, substructures for bathtubs and shower stalls, pallets and tote boxes, and flooring products and building fascias.

A novel application of mixed plastics is to toughen road surfaces. In 1986, the Ragusa Laboratories of ECP Enichem Polimeri in Italy investigated the use of mixed plastics waste to reinforce bitumen. Sorted municipal waste with a polyethylene content of approximately 60% was mixed with bitumen in varying proportions up to 20%. The properties of the resultant bituminous concrete were improved in two important ways: better wear resistance and raised softening point. Use of bitumen modified with mixed plastics waste of high polyethylene content as an experimental road surface under heavy traffic has established its notable superiority over unmodified bitumen for road surfacing.

6.7.2 Homogeneous Fractions

A widespread solution, in terms of application and market volume, could be the recycling of single materials or homogeneous fractions obtained from a separation process of the mixture. In fact, the samples obtained from single homogeneous fractions show a general performance far greater than that of samples produced from mixed plastics. Separation of post-consumer mixed plastics (municipal waste) into four fractions—polyolefins (PO), PS, PVC, and PET—is commonly adequate.

The improvement of tenacity is, in particular, evident when considering impact resistance of PO as compared to mixed plastics. Samples subjected to impact tests show an increase in elongation at the breaking point from 7% to above 100% [60]. The samples of recycled PVC fraction are comparable with those of a common virgin, with only marginal reduction in mechanical properties.

With regard to PET fraction, the potential applications are strongly dependent on its purity (as discussed earlier). Applications like films, fibers, or straps are not recommended when a high concentration of impurities are present. In this case, the PET fraction can be employed for structural applications as an engineering polymer with the addition of other components like glass fibers, impact modifiers, and/or nucleating systems. However, reuse of the PET fraction implies that the amount of residual PVC must be kept below 50 ppm to avoid undesirable polymer degradation that results in poor surface appearance and loss of mechanical properties of the manufactured products.

Mixed waste consisting of PET and PE can be converted into useful products using compatibilizers such as LDPE and LLDPE with acid and anhydride groups grafted on the backbone. A range of products can be made with such compatibilized blend, e.g., office partitions, roofing, slates for benches and chairs, and generally any extruded or molded sections needing mechanical load-bearing capacity similar to aforesaid applications.

With advances in cleaning, sorting, and other recycling technologies, more products with recycled plastics content are being manufactured. Some recent developments include using recycled PP and HDPE to produce a wide range of products. For example, multimaterial PP bottle scrap (typically, 90% PP, 5%

ethylene-vinyl alcohol barrier resin, and 5% olefin adhesive) can be added in varying amount (3–12%) to recycled HDPE and processed on a single-screw extruder to form pellets for compression molding to a range of products. The multimaterial resin can also be sandwiched between two layers of virgin HDPE using a three-layer extrusion blow-molding process. Bottles made in this way from 75% virgin resin and 25% post-consumer blend are found to be suitable for normal commercial trade [61].

6.7.3 Liquefaction of Mixed Plastics

There have been many research activities on plastics liquefaction because oil is easy to store, transport, and use. Most promising among them is the liquefaction technology jointly developed by the Japanese Government Industrial Development Laboratory (Hokkaido), Mobil Oil Corporation, and Fuji Recycle [60]. The process features a combination of thermal and catalytic cracking using a proprietary Mobil ZSM-5 catalyst. It can treat polyolefinic plastics, PE, PP, PS, or their mixtures, producing relatively low pour and highly aromatic liquid at a yield of about 85%. The produced oil contains many aromatics including benzene, toluene, and xylene.

Waste plastics are crushed, washed, and separated from other plastics that cannot be liquefied (e.g., PVC) by utilizing the difference of specific gravities against water. Plastics that can be liquefied mostly float in water while plastics that contain a lot of chlorine, carbon, and oxygen have high specific gravities and sink in water. However, some PVC floats and is recovered with PE or PP. Therefore, after separating, the feedstock for liquefaction may still contain 3–7% PVC. Fuji Recycle has developed liquefaction technology to treat such PVC contaminated mixtures [62].

For liquefaction, polyolefinic plastics are warmed to about 250°C, melted and transferred to the melting vessel by a heated extruder. In the melting vessel, plastics are further heated to about 300°C by heat transfer oil and transferred to the thermal cracking vessel. In the thermal cracking vessel, melted plastics are heated to about 400°C by the cracking furnace. The thermally cracked gas phase hydrocarbon passes through the catalytic reactor containing ZSM-5, where it is cracked and converted to higher-value hydrocarbon. The recovered liquid and gas are separated by cooling and the gas is used as in-house fuel.

Because of the pore structure of ZSM-5, the produced hydrocarbons are composed of low molecular species (4 carbons to about 20) which are in the gasoline, kerosene, and gas oil boiling range. In comparison, the carbon numbers of hydrocarbons produced only by thermal cracking range from 4 to 44. Polystyrene in the feedstock enhances the yield of ethylbenzene, toluene, and benzene, while producing gas that is predominantly propane/propylene.

6.8 Post-Consumer Polyethylene Films

Driven by consumer and legislative pressures, post-consumer film recycling has gained momentum and is now one of the fastest-growing segments of the recycling industry. Post-consumer films consist of LDPE, LLDPE, and HDPE, which are accounted for mostly by grocery sacks, stretch and shrink wrap, agricultural film, packaging, and blow-molding drums, and have thicknesses ranging from 0.2 to 5.0 mils. Film recycling was first developed in Europe for agricultural film, which is relatively easy to process due to its high-bulk density and minimal contamination. Today, interest in recycling systems for film of varying thickness and resin types has changed the design of a recycling line to one that uses both high and low-bulk-density material.

The primary challenge to recycling film is contamination. According to an industry estimate, up to 25% of all grocery bags are contaminated and require very thorough washing in the recycling process. A typical route for recycling plastic bags is shown in Figure 6.17.

Bales weighing 600–800 lb, collected by commercial haulers, film-generating business, or the solid-wastes-handling industry, are first fed into a breaker-shredder. The shredded material then passes over a vibratory conveyor or through metal-detection systems to remove ferrous and nonferrous contaminants.

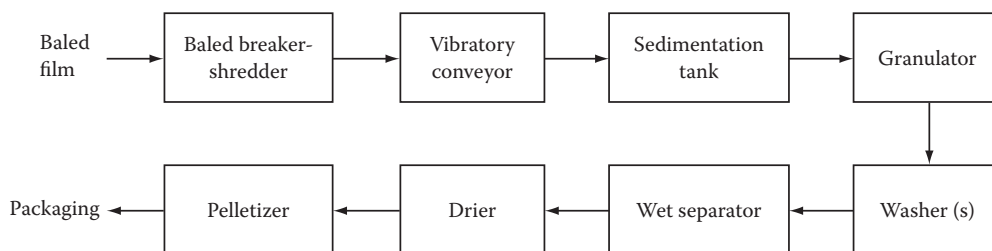


FIGURE 6.17 Typical route for recycling plastic bags.

Film is next sent to a sedimentation tank for removal of rocks or dirt before going into the granulator (usually wet) for size reduction. Granulated into flake, the material then passes to a hot wash for removal of glue, residues, and remaining labels. Depending on the feedstock and the extent of contamination, the film may go through more than one wash cycle.

After the wash, the material moves to the separation stage. Two most common methods for separating plastics by resin type are float-sink and hydrocyclone. The float-sink method is less costly but requires a relatively large tank size in order to realize volume effectiveness. A hydrocyclone is more costly, but uses less water, has no moving parts, and generally takes up less space than the older float-sink method.

The flaked material from the wet separator, described above, goes through a drying and dewatering stage to an extruder, where in the melt phase the plastics can be mixed with dyes and other product enhancements, and then filtered and forced through a die for fabrication of free-flowing pellets. Depending on the mixture of LLDPE, LDPE, and HDPE, the pellet can be tailored for specific markets. Low-quality pellets are often sold as a commodity in the general marketplace. High-quality blends of polyethylene are suitable for many nonfood film applications.

One major market for recycling film is packaging. Many consumer-products companies have already turned to detergent bottles and other packaging made with significant percentages of recycled HDPE. Another fast-growing outlet is coextruded blown film used in trash bags, in which post-consumer resin is sandwiched between virgin layers of high-molecular-weight HDPE. The coextrusion technology allows high percentages of reprocessed material to be incorporated into virgin resin.

In many countries, legislation is a key driving force behind greater recycling efforts. Several states in the U.S. have passed recycling content standards mandating that virgin plastics used in some applications, such as grocery and trash bags, contain a certain percentage of recycled material. In California, for example, trash bags are required to have 30% recycled post-consumer content. Germany requires that 64% of all packaging materials be recycled. Under the German system, all types of plastics packaging are collected together and subsequently segregated into several categories: rigid containers; films; cups, trays, and blister packaging; and foamed material. The materials are then offered back to industry for recycling purposes at no charge.

6.9 Recycling of Ground Rubber Tires

Discarded tires represent a significant component of the overall plastics recycling challenge. They are an easily segregated, large volume part of the waste stream and present their own, somewhat unique, waste recycling problems. Some of the methods of utilizing scrap tires that have been investigated [63–65] are: burning, pyrolysis, use in cleaning up oil spills, road surfaces, roofing materials, and playground surfaces. While some of these approaches have been put into practice, the scrap tire disposal problem is clearly a case where supply far exceeds available use, pointing to the need for new methods of utilization and/or technological advances to extend the existing ones.

One area that has the potential to utilize large volumes of discarded tires is the need for a filler in polymer composites. Although the use of ground rubber tire (GRT) as a filler in polymer blends is a

potentially attractive approach, it is fraught with a number of difficulties. Generally, when the large GRT particles are added to either thermoplastic or thermoset matrices, there is a large drop in mechanical properties, even at relatively low filler loadings [66]. Since the approach here is to use the GRT as a low-cost additive, and as there are a number of other materials competing in this regard, overcoming this large drop in properties has to be accomplished with little added cost (both in terms of additives and additional processing). This has proven to be quite a challenging task.

In order to be used as a filler in polymer composites, tires are first ground into a fine powder on the order of 100–400 μm , which is accomplished typically through either cryogenic or ambient grinding. The large rubber particle size used in GRT composites is reported to be one of the two major factors (the other being adhesion) contributing to the poor mechanical properties generally observed for GRT-polymer composites. In general, a low particle size is desired for optimum composite properties. In GRT-polymer composites, however, the particle size is quite large. Since there is very little breakdown of the particles under normal melt blending conditions due to the highly cross-linked nature of GRT, the particle size is to be controlled only by the grinding process, which in turn, is influenced by process choice and economics.

In order for GRT to be used as an economical filler, the particle size has to be kept as large as possible to minimize grinding costs. Typically, the lower limit on particle size necessary to produce economical composites lies in the 40–80 mesh (≈ 400 – $100 \mu\text{m}$) range, while for rubber toughening applications it is generally reported [67] that the optimum particle size for toughening brittle polymers is in the 0.1–5 μm range. Thus the size gap is large. Though it adds to the cost, there may be some advantage in going to smaller particle sizes if significant gains in mechanical properties are realized. The detrimental effects of adding GRT to cured rubbers decreases as the particle size is decreased [68]. For GRT recycled back into tires, for example, the detrimental effects are almost eliminated [68] with the use of ultrafine (20 μm) rubber.

As mentioned above, simple addition of GRT to most polymers results, in general, in significant decreases in mechanical properties due to large particle size and poor adhesion. Since lowering particle size to effect any substantial improvement in material properties adds significantly to grinding costs, strategies for overcoming the deleterious effects of adding GRT to polymers have focused on methods of improving adhesion. The poor adhesion is, at least in part, due to a high degree of cross-linking in the GRT particles. The highly cross-linked nature of the particles inhibits molecular diffusion across the interface so that there is little or no interpenetration of the phases, resulting in a sharp interface. There have been a number of reports of processes that claim to improve properties of GRT-polymer composites through enhancing adhesion. The use of an aqueous slurry process using a water-soluble initiator system to graft styrene to GRT has been reported [69]. The styrene-grafted GRT particles are found to give composites with properties superior to straight mechanical blends.

Precoating of GRT particles with ethylene/acrylic acid (EAA) copolymer is found to improve the mechanical property, which is attributed to an interaction (H bonding) between the EAA copolymer and functional groups on the GRT surface, resulting in increased adhesion [70]. Thus a blend of 40 wt% EAA coated GRT particles (4 wt% EAA) with LLDPE was shown to have impact and tensile strengths 90% of those for pure LLDPE, representing increases of 60% and 20%, respectively, over blends with uncoated particles. The use of maleic anhydride grafted PE (PE-g-MA) resulted in increases in the impact strength of LLDPE-GRT composites of as much as 43%, without the need for a precoating step [70].

Electronic spectra for chemical analysis (ESCA) of GRT surface reveal an oxygen surface content of 5–15%, which may indicate the presence of $-\text{OH}$ or $-\text{COOH}$ functionalities. Since the epoxy group readily reacts with a wide range of functional groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{SH}$, $-\text{NH}_2$, the use of ethylene-co-glycidyl methacrylate (EGM) as a coupling agent [70] has been investigated. A significant increase in impact behavior has been observed. It is seen that judicious selection of a compatibilizing agent can lead to composites with quite reasonable mechanical properties at significant levels of GRT (as high as 50–60 wt%). Because added compatibilizer levels are low (4–7 wt%) and no specialized processing steps are necessary, these higher-value composites can be produced at little additional cost over simple GRT-polymer blends.

It has been observed recently [71] that special treatment of GRT by bitumen confers outstanding mechanical properties on thermoplastic elastomers (TPEs) produced using the treated GRT. Typically the reclamation of GRT by bitumen is carried out by preheating the GRT/bitumen blend (1/1 by weight) at 170°C for 4 h in an oven, followed by rolling on mill rolls at about 60°C for 40 min. Thus, high performance TPEs, based on recycled high-density polyethylene, ethylene-propylene-diene monomer (EPDM) rubber, and GRT treated with bitumen has been prepared. It has been concluded that bitumen acts as an effective devulcanizing agent in the GRT treatment stage. In the subsequent steps of TPE production, bitumen acts simultaneously as a curing agent for the rubber components (EPDM/GRT) and as compatibilizer for the blend components.

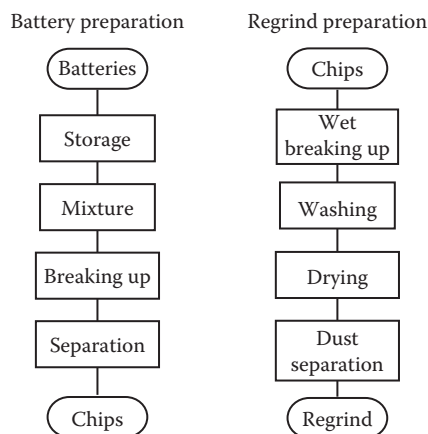


FIGURE 6.18 Process steps in preparation of polypropylene regrind.

6.10 Recycling of Car Batteries

Polypropylene (PP) is obtained in segregated form as casing fragments from reprocessing of used lead-acid batteries from automotive applications. Because the casing makes up about 7% of the total battery and the used batteries are recycled primarily for lead recovery, PP is obtained without additional cost and in substantial quantities to warrant the operation of a plastics recycling plant.

In the first step of a typical recycling operation, the batteries are processed through a crushing and separation system operating on the TONOLLI principle (Figure 6.18), which has been successfully employed in various battery recycling plants in Europe and North America. The heavy fraction (lead, lattice metal) and ebonite are then separated from the light fraction (PP and impurities). The PP at this stage has a purity of 97%, which is still insufficient for its further processing. It is therefore sent to an upgrading stage, where it is further reduced in size in a wet-type rotary grinder and subsequently separated from water by sedimentation. After passing through two series-connected driers and a cyclone separator, the PP is available as so-called regrind with a purity of 99.5%. As the regrind consists of various types of PP differing in their formulation, molecular composition, and stabilizer content, it has a broad spectrum of characteristics. Suitable mixing can be done to obtain an intermediate product with a narrowed range of statistically uniform product characteristics.

In the next step, the regrind is routed to a compounding plant where—with controlled addition of additives, polymers, and fillers—the feed mix can be adjusted to suit the specific customer requirements. This feed mix is then metered into a special twin-screw kneader where it melts under the dual action of an external heater and internal shear forces, producing a homogeneous compound. Volatile matter is vented and unmolten impurities are filtered out. The melt is subsequently palletized in a melt granulator and the resulting granulate is quenched in a water bath, centrifuged, and finally passed through a hammer mill to break up lumps. The end product is a granular secondary raw material and suitable for injection molding.

6.11 Plastic Recycling Equipment and Machinery

While the plastics recycling activity, driven by consumer and legislative pressures, is all but certain to increase, the key variables in the rate of growth are the plastics industry's ability to develop an economical material-collection infrastructure and to improve the methods for handling and processing of contaminated

scrap. Techniques for selection and recycling of post-consumer plastics are, however, closely related to the characteristics of plastics containers consumption, which vary greatly according to the geographical areas and the relevant law regulations governing activities in this sector.

Consumption features play a major role in the choice of the materials to be recycled. In the United States and Canada, the materials chiefly recycled are PET bottles and PE containers; in France, on the contrary, recycling of PVC got priority on account of the large quantity of such material used in the packaging of drinks. In Australia, recycling includes primarily PET and PE, whereas in Japan it is mainly PET. In Italy, the plastics recycled are mostly PET, PVC, and PE. In short, the material to be recycled and the enforced legislation determine the choice of collection system. In many countries such as United States, Canada, Australia, France, Austria, and Switzerland, some fractions of post-consumer plastics are collected in the most homogeneous way possible. In other countries, plastics are collected more heterogeneously, that is, different types of plastics out of different types of manufactured articles, such as foil, containers, bottles, are collected together.

The outcome of the collection system constitutes the raw material for the recycling process. The degree of purity of this raw material evidently depends on how selective the collection is.

6.11.1 Plastocompactor

For voluminous scraps such as light film, textiles, fleece, and foam, it is advantageous to increase the density, which may be in the range of 20–40 kg/m³, to about 400 kg/m³ for transport reasons and for further processing. With thermoplastics and thermoplastic mixtures, a *plastocompactor* can be used for this purpose. It is, however, more useful for homogeneous fractions of thermoplastics. The process agglomerates the material without plastifying it. By heating the material locally for a short period to a temperature above the softening point, the soft components begin to adhere. The material is then compacted into a condition very similar to the virgin material.

In a typical agglomeration plant, the loose material is usually fed to a granulator, which is also fitted with a nip roll device for feeding continuous material such as fleece or film from the roll. A blower transports the flakes from the granulator to a holding silo. The discharge screw in the silo transports the flakes to the feed hopper from where they are carried by a blower to the plastocompactor. A dosing and pressing screw feeds the actual agglomerator part of the machine. This comprises essentially two discs—one rotating and the other stationary—between which the flakes are compacted by using heat from friction and pressure. The agglomerate leaves the discs through the outer gap in the form of warm soft sausages and is cooled immediately by an air stream. It is then fed, in a semisoft state, to a hot melt granulator where it is reduced to a free-flowing granulate.

6.11.2 Debaling and Initial Size Reduction

The first operation of the recycling process is the cleaning of foreign bodies. It requires a number of operating steps, the first being normally a debaling operation as the collected material, for transport reasons, is reduced into bales. Debaling is still often carried out manually. The reason often given for using a manual method is that the workman can also check the baled scrap for large pieces of foreign matter at the same time. However, there exist very efficient debalers for making the task automatic, and the best brands are equipped with specific devices designed in accordance to the composition of the bales to be loosened. Such factors as the forms of plastics items; the proportion of PE, PET, or PVC in the bales; the collection features; the container typology; and the share of foil plastics determine the type of debaler construction technique.

Two simple debaling services are a grab truck and a screw shredder. A grab truck can normally be used for bales of film. Sitting in his machine, the workman can break open the bales using three hydraulically operated grabs fitted to an extension arm. Checks for large pieces of foreign material can also be conducted. Using the same grabs, the loosened material can then be placed onto the feed conveyor fitted with a metal detector.

For bales containing individual items of scrap such as bottles and other hollow items, the use of a screw shredder offers many advantages. This machine is fitted with a very large feed hopper and can be fed directly with a large bucket loader or similar device. The feed material is reduced by a tearing process in the shredder between independently driven screw shafts fitted with shredding teeth. Screw shredders are manufactured with up to six adjacent shafts and are thus suitable for the feed of very large bales or a large number of bales at one time.

After debaling, the material passes through initial size reduction units to separation and selection operations. Most size reduction tasks can be performed by the following machines: shredder, cutter or guillotine, screw shredder, and granulator.

6.11.2.1 Shredder

Shredders have been in use for a long time in many sectors for the recovery of scrap. To a large extent they draw in the material automatically, and are suited for film, sheets, solid pieces, hollow items, cables, etc. The stresses caused by the tough and partly high-strength material are enormous. Extremely sturdy units designed for this technology are thus required for the treatment of plastics. It is important that the cutting shafts run at a suitable speed so that cutting and tearing processes occur.

Models of shredders are offered with from one to six cutting shafts. Machines with a capacity of many tones per hour are available. They are able to reduce complete bales of film fed by forklift without any difficulty. Also, hollow items such as rubbish bins and barrels can be reduced when a ram is fitted to the feed. Another field of application is the shredding of cables to allow the separation of plastics and metal. Generally, a trough fed by a forklift or conveyor is located above the shredder shafts. After the material is reduced to a practical size in the shredder, it is transported to subsequent process stages by means of a conveyor or other mechanical device.

6.11.2.2 Cutter or Guillotine

Some plastics scraps are not suited for initial reduction in a shredder described above. These include fibers, long pieces of material, rolled strips, and lumps of rubber. A guillotine is better for these applications.

The material is fed manually in a trough or on an open conveyor to the guillotine. The latter operates as opposed to the shredder, on a stroke principle. A cutter, usually hydraulically operated, is lowered from above to cut the material in slices of the desired thickness. The complete cutting process including the material feed is best operated under a programmed control.

6.11.2.3 Screw Shredder

The screw shredder mentioned earlier as a machine for debaling is also used for the initial size reduction of plastic items, and in particular when these are very voluminous and not too tough. It is suited for very large items or bundles of material and has the advantage of being fitted with a very large feed hopper that can be filled by bucket loader or similar device.

The machine is fitted with two shafts, rotating independently. It can be constructed, however, with up to six adjacent screw shafts, each shaft having its own drive via gears and electric motor. The shafts are equipped with shredder teeth for reducing the feed material in a crushing and tearing process. Not being a cutter, the machine is best suited for materials that can be broken or torn. When overloaded, a special control stops the respective shaft and switches it into reverse gear for a set time before returning to normal operation.

6.11.2.4 Granulators

Granulators can be seen as the most versatile size-reduction machine for the complete sector of plastics size reduction, and are used for the dry reduction of plastics. The machines used for this application are therefore designed to meet the special demands of job conditions, which are sturdy mechanical design, quick knife replacement, easy cleaning, and high capacity.

Since the reduction process is subject to the generation of a considerable amount of heat, it is necessary to water-cool parts of the machine or remove the heat with it. It is advantageous to fit the granulator with an open or semiopen rotor and a strong suction device to ensure that the grinding chamber is cooled intensively so that water-cooling is not required and the air is used at the same time for discharging the size-reduced material. All granulators should be equipped with a screen that can be easily removed. The screen opening determines the top size limitation of the size-reduced product. Material is fed to a feed hopper manually, or on a feed conveyor, screw, or similar device.

As an example, all granulators supplied by Herbold GmbH Maschinenfabrik (Meckesheim, Germany) have the following characteristics: (1) welded steel construction; (2) externally mounted bearings; (3) hinged two-piece housing with split point around the shaft; (4) easily replaceable screen; (5) double cross-cutting action; and (6) preadjustable knives. These characteristics offer a number of advantages, as explained below.

Due to the welded construction, the machine is resistant to extreme stresses caused by any foreign matter that may enter the granulator despite all precautionary measures taken, and fractures are avoided although the housing may be deformed. As the bearings are mounted outside the granulator housing, it is not possible for the feed material to enter the bearings or for grease to contaminate the material. The hinged housing allows easy and quick cleaning necessary when feed is changed and simplifies servicing and knife replacement. This is a significant advantage particularly in scrap recycling, where increased wear and more frequent knife replacement are to be reckoned with. For double cross-cutting action, all knives on the rotor are mounted at an inclined angle in a straight line to the rotor axis while all bed knives are set at the same angle but in an opposed inclined direction, also in a straight line. Complete sets of resharpened rotor- and bed-knives can be readjusted to the exact gap required between them to achieve the desired reducing action. This advantage, in conjunction with the good accessibility due to hinged housing, allows knife replacement to be carried out very quickly.

6.11.2.5 Fine Grinding

Fine grinding also offers solutions for the recycling of plastic scrap. Different types of machines are used, two common types being universal blast mills and disc pulverizers. In a universal blast mill, plastic scarp is reduced between the beater wings of a blast disc and a screen or the grooved grinding track of a grinding chamber. The hole size of the screen determines the fineness of the plastic powder. This usually has an upper size limitation of 500–800 μm .

In an impact disc pulverizer, which has much lower power consumption than the blast mill, the material is size reduced to an upper limit of about 800 μm between a fixed and a rotating disc. If a lower top size limitation is required, a screener may be used to return the coarse material continuously to the grind process. The finely ground powder is separated in a cyclone.

6.11.3 Cleaning and Selection

Cleaning, separation, and selection operations that usually follow the initial size reduction are determined by the type of recycling process to which the material is to be subjected. Basically there are two main recycling processes: recycle of heterogeneous plastics and recycle of selected polymers. The former process leads to the manufacture of extruded or injected products by direct reuse or in mixture with other components. The latter process consists of separation of the mix of collected plastics into homogeneous fractions, subjected to further processing that brings their characteristics and purity as near as possible to those of the original polymers.

The simplest method to perform the cleaning and selection operation consists of a selection platform where a number of trained sorters separate the different types of plastics on the basis of visual assessment. Though this is a hard and unpleasant job, the advantage of manual selection is that sorters operate to a degree of intelligence that the automatic equipment cannot reach. On the other hand, manual selection is, understandably, always liable to human error. To counter this problem, selection platforms are often equipped with

detectors to check the quality of the selected material. These may be electronic appliances capable of recognizing, for example, PET in flux of PVC, and vice versa, and detectors able to identify traces of metal overlooked during manual sorting, such as aluminum from caps and rings. The material manually selected and then electronically checked is therefore of best quality and can be sold at the maximum market price.

The most serious drawback of manual platforms lies in the high cost of labor and the need to manage a large number of workers when considerable quantities of material are to be sorted. Such drawbacks may be avoided by resorting to automatic platforms.

Automation is introduced at the stage of debaling. In order to obtain a product suitable for the recycling process, operations to remove undesired impurities must be carried out. The machines required are manifold and the necessity to employ them is related to the quality of the collected material. A few essential machines are: (1) rotary screen, by which parts of the desired dimension are sorted out, separating them from smaller and larger ones; (2) light-parts separation equipment, in which lighter parts such as films are separated by air blowing from the plastic material to be recycled; (3) heavy-parts separation equipment, in which heavy particles are separated and the operation is carried out by means of air that shifts the material selectively; and (4) aluminum rejection equipment, which normally consists of an electromagnetic drum placed in a suitable location on the train of operations. All such machines are preliminary to the stage of selection into homogeneous plastics fractions.

6.11.3.1 Dry Separation

The cleaning of plastics is often combined with the separation of other types of plastics and is performed by either dry or wet process depending on the quality of the collected material. A significant advantage of dry cleaning with air, as compared to wet cleaning, is that it has a lower power consumption. Loose adhering dirt—and this is the only type of sorting that can be removed in a dry process—is loosened and pulverized by the impact and rubbing caused during size reduction. The dirt, then as dust, can be separated by using an appropriate equipment. Examples of this are screen units and air stream separator.

The screen unit is the most economical means of removing the dirt. By selecting a screen with suitably sized openings, it is possible to minimize the amount of plastic discharged with the dust. Electrostatic charge can however cause too many dust particles to adhere to the plastic. The air separator (Figure 6.19) is then the more suitable device to use. Lighter-weight dust is carried out of the unit by the opposed directional air stream.

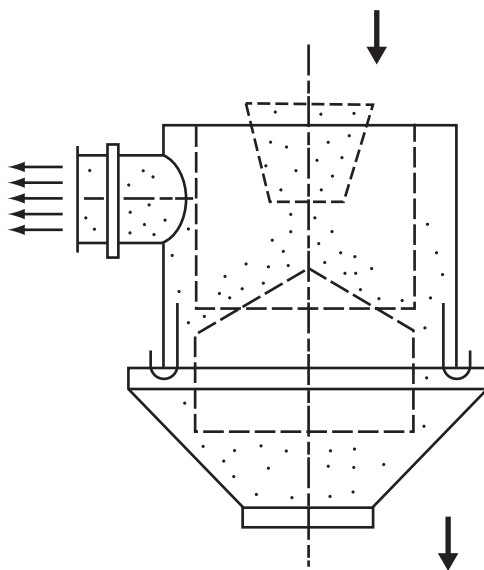


FIGURE 6.19 Schematic of air-stream separator.

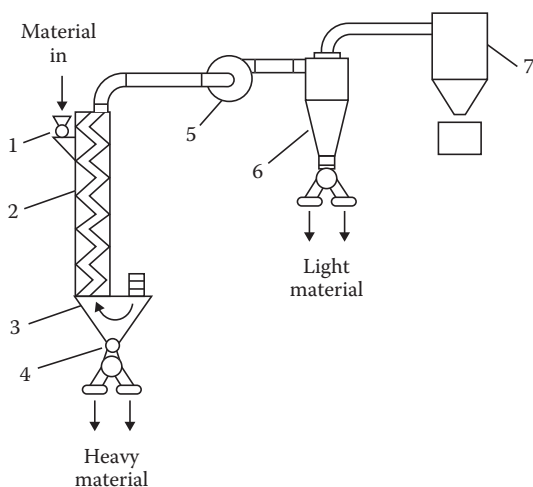


FIGURE 6.20 Schematic of air-stream (cascade) separator. 1, Gate valve; 2, cascading (zigzag) channel; 3, container with air suction; 4, gate valve; 5, blower; 6, cyclone; 7, filter with particle container.

below (Figure 6.20). The material to be separated is fed to the top end of the channel into the air stream. The separation point is set by adjusting the air-flow rate. Material turbulence occurs in each section of the air stream channel, with lighter material being carried upward by air stream to discharge and heavy material moving downward from step to step. Fine particles are loosened from the larger ones and also from each other each time impact with side wall occurs. Cascade separators produce more efficient separation than single-stage units due to dispersion taking place at each kink in the channel. Typical applications for the cascade separator are the separation of fibers and insulation film or foam and soft film.

The principle of operation of a fluidized air bed separator is shown in Figure 6.21. The material to be separated is carried uphill by the orbital vibration in the separation channel designed with a rectangular cross section. An adjustable air stream is passed through the sieve surface in the channel where it lifts the material. The particles that are lifted higher in the air stream (that is, jump higher due to elasticity) flow

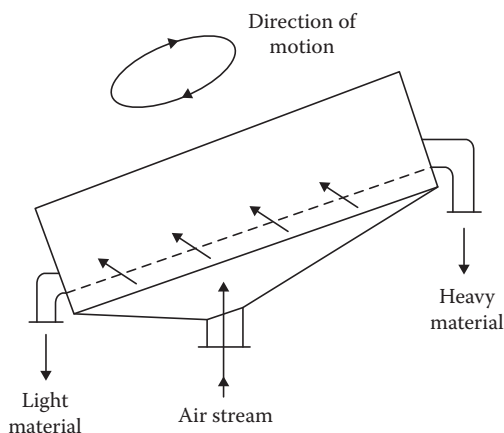


FIGURE 6.21 Schematic of vibrating air separator.

Mixed plastics, including various types of composite materials, that are to be dry-separated are first size-reduced (e.g., in a granulator) before the different constituents are separated. The separation is done in a process based on differences in material densities or shape and size of particles.

Screening may follow size reduction, depending on the material and the particle size distribution. In the screen unit, all of the mixed material is divided into two or three size fractions, e.g., 0–2, 2–4, and 4–6 mm. This is necessary since small heavy particles and large light pieces behave in the same manner, as do heavy flakes and light conical pieces. The separation based on density difference is easier or only then possible when all particles are of similar size.

Dry separation using air can be repeated several times, and the process is then classified as a cascade separator. A cascade separator, also known as a zigzag separator, uses an air stream passing through a rectangular zigzag channel from

downhill and are discharged from below. This type of fluidized air bed separation process can also be enhanced by using a multistage plant. A typical application for this unit is the separation of rubber from rigid thermoplastics or aluminum from plastics.

6.11.3.2 Wet Separation

Wet separation of plastics is a *microseparation method* in which a suspension medium is used to separate plastics with density higher or lower than the suspension medium. For example, water can be used as medium to separate PE from PVC or PET. In this case, special tanks are used in which various types of plastic flaks are mixed with water and then given a sufficient time to position themselves in the most suitable way according to their density. Materials are subsequently extracted separately from the top or bottom. This method is, however, not suitable for separating PVC from PET, because they have similar density.

Researchers at Rutgers University [72] studied a method of PVC microseparation from PET, by which PVC is subjected to a process of selective bulking that causes it to float. Such a method may be applied for separating small quantities of PVC from large quantities of PET, as normally is the case in the U.S., but is not suitable when PVC is a major component of the containers mix. Another wet method applicable to PVC and PET containers, previously reduced to flakes, is flotation with surface active agents.

6.11.3.3 Other Methods

Need for using microseparation techniques arises in critical situations where minute concentrations of identified contaminants adversely affect the post-consumer resin's usefulness in high-value end-uses. In many cases, microseparation, or the ability to sort resins by type, can be accomplished by air elutriation techniques (e.g., dry separation techniques, described above), wet separation techniques (such as sink/float tank technologies and hydrocyclones), magnets, electrostatic and electrodynamic methodologies, and optical scanners. Air aspiration and elutriation systems work well for separating light-density foams and films from denser reground plastics, while density-based methods are better for separating polyethylene from PET and denser resins.

Challenges to separate materials having similar densities, for example, PVC from PET regrind, or polypropylene from polyethylene, remain. Examples of microsorting techniques commercialized so far include electrostatic separation devices designed to sort by way of resin's conductivity, supercritical fluids which alter the separation fluid's density, froth flotation using the alteration of a liquid's surface tension to separate various solids, and chemical dissolution based on the difference in solubility of various plastics in selective solvents. Another development is a novel method to separate diverse resins by taking advantage of their differences in stick temperature.

BASF's Kali and Salz AG company, which has extensive experience in electrostatic separation of salts, employs its own electrostatic separation process (ESTA) to the separation of plastics. Using density separation, paper and plastic residues from labels and crowns are separated first. Then, following pretreatment with surface active substances designed to enhance the electrostatic properties, the homogeneously milled particles are charged electrically as they rub against each other. The extent of electrostatic charge depends on the plastic. The particles then fall through a high-tension field and are diverted at different angles depending on the charge, resulting in separation.

6.11.4 Resin Detectors: Type and Configuration

Detectors fall into four categories—x-ray, single-wavelength infrared (IR), full-spectrum IR, and color. The earliest automated systems used x-rays, which are still the most effective means of determining the presence of PVC. The chlorine atom in PVC emits a unique signal in the presence of x-rays by either x-ray transmission (XRT) or x-ray fluorescence (XRF). The XRT signal passes through the container, ignoring labels and other surface contaminants, and is capable of detecting a second container that may be stuck to the first. XRF, on the other hand, bounces off the surface of the container and is useful for finding any PVC, including labels and caps.

Systems for separating multiple types of plastics utilize a single wavelength of the near-infrared (NIR) spectrum. These systems work on the basis of a simple determination of opacity and separate the stream of mixed containers into clear (PET and PVC), translucent (HDPE and PP), and opaque (all pigmented and colored materials) streams.

The most sophisticated detectors, however, employ full spectrum NIR. Since all plastics absorb IR to different degrees and each resin has a unique “fingerprint,” these detectors can accurately separate each of the resins. In later developments, filters for individual wavelengths are used for rapid identification and there is promise for even faster, lower-cost systems.

The color detectors are, in fact, very small cameras capable of identifying a number of colors. When combined with a resin-specific detector, they allow a variety of sorts based on both resin type and color.

Containers must be separated and presented to a detector in order to collect data on each unit. That information is then integrated via computer, and the container is tracked down the conveyor until it reaches the appropriate ejection point, where it is removed by a timed blast of air. The two primary techniques for presenting containers to a detector are full-conveyor or single-file systems. Containers delivered in a full-conveyor system can achieve higher throughput rates and are normally used to remove a single material from the mixture. A singulated stream, on the other hand, has lower throughputs, but allows sorting into a number of streams on a single pass.

Detectors are usually arranged in one of three configurations. The first is single detector/single container (Figure 6.22a): this is the simplest setup for singulated containers. As each container passes the detector, several readings are taken instantaneously and a decision is made by the computer. While

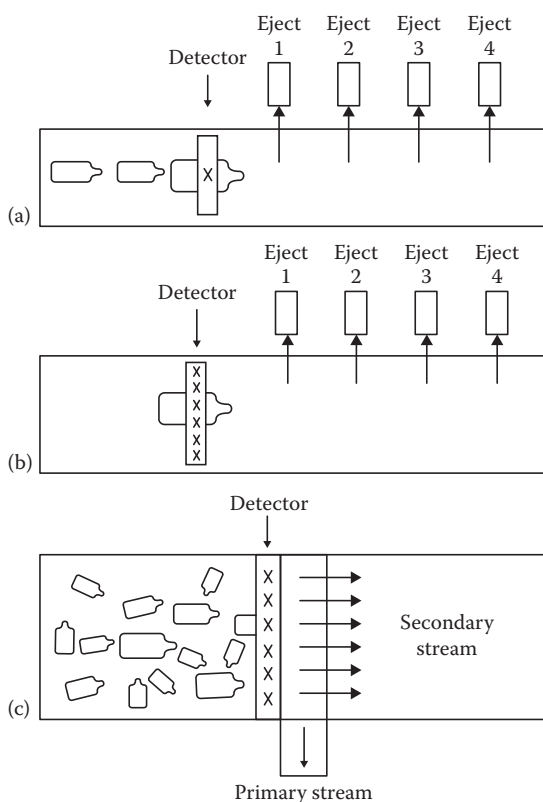


FIGURE 6.22 Typical separation and sorting setups using three main detector systems: (a) single detector/single sample; (b) multiple detector/single sample; and (c) multiple detector/multiple sample. (After Tomaszek, T. 1993. Automated Separation and Sort, *Modern Plastics*, 34–36 (November).)

usually accurate, this process is subject to error if the container has a large label blocking the signal and thus restricting data input to the computer. The second configuration is multiple detector/single container (Figure 6.22b): as each container passes the detector assembly, it is read by a number of detectors resulting in a more accurate reading. The third is multiple detector/multiple container (Figure 6.22c): This is the standard configuration for a mass-flow system and has detectors spaced to cover the width of the conveyor. When the target material is spotted, its position on the belt is noted and accordingly an ejector removes it before falling off at the end of the belt.

Further development in autosort technology is represented by particulate-sorting units capable of sorting by color. Applied in combination with the aforesaid resin detectors this facilitates autosorting according to both resin-type and color.

6.11.5 Automatic Sortation

Most end-use markets of recycled plastics require that they be separated by resin type and color. For post-consumer bottles, all lids, caps, and closures should also be removed because they are often of different colors, and made of different resins than the bottle. The goal of any sorting process is to obtain the highest purity, consistency, and quantity of a particular consumer resin type. This ensures the highest end-use value for new products incorporating substantial amounts of the recycled resin.

In the widely used manual method of sorting, employees known as material handlers are stationed at predetermined locations alongside the sort conveyor to remove the desired bottles for recycling. All caps and closures still affixed to the bottles are manually removed by the handlers prior to or during sorting. These manual methods of sorting, however, face many challenges, some of which are economic and others environmental and aesthetic. Among the key hurdles are high cost of the labor-intensive process, exposure of employees to the residual household and industrial chemicals contained in some of the collected bottles, difficulty in sorting look-alike resins, and subjective material quality standards resulting from manual sorting. Automating the container sorting process to overcome these hurdles has thus been a major goal of the recycling industry.

An automatic separation process that includes various systems employing detectors currently available in the market is ideally suited to *macroseparation* or *macrosorting* (separation of plastic fractions before size reduction) when waste materials are still in the initial form (such as post-consumer bottles). Macrosorting is one of the fastest-growing segments of the plastics recycling industry. Although automated sorting, by resin type and color, can be accomplished after size reduction, most commercial automated-sorting machines are designed to sort plastics containers in whole form before size reduction. Some of the automated bottle-sorting systems are designed to sort certain bottles such as look-alikes, while others are designed to separate all plastics bottles by resin type and color. The most commonly encountered look-alike bottles are those fabricated from nonpigmented PVC and clear PET.

6.11.5.1 PVC/PET and Commingled Plastics Sortation

Both PVC and PET bottles are very recyclable. However, when the two types are received commingled, the reprocessor can experience quality deficiencies due to rheological incompatibilities between these two resins. This has been of special concern to the PET bottle reclaimer because, as the PET is heated to its processing temperature, trace amounts of PVC can cause severe deterioration in the quality of the reprocessed PET resin. Therefore the two resins must be separated prior to recycling.

Manual sorting of look-alike PVC and PET cannot meet the market's needed quality. Therefore new techniques have been engineered that will detect and separate bottles made from either of these two resins. The first detector was developed by Tecoplast in Casumaro, Ferrara-Italy, to separate PVC from PET. The application of this system resulted in the introduction of an automatic plant, processing drink plastic bottles using the AZZURRA machine. The Tecoplast detector consists of an x-ray source and a receiver that measures the bottle absorption while passing between the source and receiver. PVC has a higher

absorption compared to the other plastic due to the presence of a chlorine atom. The value of PVC absorption, electronically processed through algorithms, makes it possible to detect its presence and consequently to eject bottle.

Another detector is employed to line up bottles using a suction robot. The aligning process enables bottles to be arranged in a suitable way for measuring transparency and color. Using this technology, Tecoplast developed the first optical detector capable of establishing the quality of PET, thus allowing the separation between clear PET and colored PET, besides the aforesaid separation from PVC. In a later development, Govoni's technology employed detectors performing these separations without alignment.

Other detectors have been developed in the U.S. A leading manufacturer of plastics sortation equipment, ASOMA Instrument Inc. (Austin, TX), developed a simple operator-friendly device for sensing the presence of chlorine atoms contained within the PVC resin. This sensor identifies PVC by x-ray fluorescence as bottles fall through a chute or move on a belt conveyor, at the end of which either the PVC or PET bottles are extracted—in most cases, by a burst of compressed air-jet actuated by the device, although mechanical devices have also been employed. The x-ray fluorescence sensitivity is so reliable that a 10 ms analysis is all that is needed to make proper selection. Single-unit systems have been developed that both detect and separate commingled bottles at production rates of 800–1200 lb/h, which corresponds to between two and three bottles per second. As is the case with most macroseparation devices, singulation (that is, alignment of bottles in a single file) is critical for this system to function at high production rates while maintaining rigorous quality standards. With x-ray detection, sorted PET streams having less than 50 ppm of PVC have been consistently produced, while, in contrast, manual separation generally results in PET with 2000 ppm PVC [73].

Another example is a system made by National Recovery Technologies (NRT) Inc. (Nashville, TN) [74]. This apparatus incorporates a proprietary electromagnetic screening process that also detects the presence of chlorine as found in PVC bottles. Once detected, PVC bottles are pneumatically jettisoned from the commingled bottle feed stream by a microprocessor-based air-blast system. The NRT technology permits bottles to be delivered to the unit in a mass sort concept in either crushed or whole form. This system does not require any special positioning or orientation of the bottles in order to achieve high efficiency rates.

An optical detector developed by Magnetic Separation Systems (MSS) Inc. (Nashville, TN) incorporates an optical sensing device with a transmission output range of 200–1500 nm to detect both the resin composition and the shape of the inspected container. Additionally, a video camera is employed to identify colored containers via computerized spectrographic matching. This information is also processed through a high-speed microprocessor that has the ability to perform algorithmic analyses and alarm the programmable logic controller (PLC) to actuate an ejection apparatus to sort the desired bottle. Finally, an x-ray fluorescence sensor is used to sort PVC bottles from the PET bottle fraction. The MSS detector system is thus designed to obtain separation of commingled plastics into homogeneous material fractions, including PVC, clear PET, colored PET, multicolored HDPE, and translucent HDPE.

A modular sorting system of MSS, BottleSort, incorporates a sensory apparatus designed to detect and mechanically separate commingled plastic bottles in a process that includes several functions: debaling, screening, sensing, separation, and electronic control. Sensing is performed both optically and with x-ray fluorescence. Each BottleSort modular unit can process 1250 lb/h. Systems have been commercially installed incorporating four units having a combined capacity to sort 5000 lb of commingled bottles each hour.

A near-infrared spectrophotometry detector, developed by Automation Industrial Control (AIC) of Baltimore, MD, allows identification of resin type, such as PET, HDPE, PVC, PP, LDPE, and PS. The equipment is connected with another detector for color determination and the resulting data are processed by computer with highly sophisticated software. The equipment thus enables separation of a container mix into various components with a high degree of selectivity in regard to typology and color. This type of detector, however, requires material singularization and lining up.

The PolySort automatic plastic bottle sorting system introduced by AIC is designed to receive commingled plastic bottles in either baled or crushed form. At the heart of this sorting system is a sophisticated video camera and color monitor incorporating a strobe to detect and distinguish colors in the inspected plastic bottle. This optical scanning device interfaces with a computer to match the color of the bottle against a master. The detector is reputed to detect and match up to 16 million shades of colors. In addition, the system can be programmed to disregard labels on the bottles. Following color detection, a near-infrared detection system scans the single-bottle stream at a rate of approximately 3000 times a minute, to determine in less than 19 ms the primary resin found in each one. This is achieved by matching the interferogram produced by the bottle to a known master for each base resin as stored in the system.

Computations are coordinated through the use of a rotary pulse generator and sensing light curtain to impel the qualified bottle to a discharge chute located on the sort conveyor. Although the standard PolySort system is designed to detect and sort about 1500 lb of compacted bottles each hour, higher production rates can be obtained by feeding multiple lines from one debaler.

A point of consideration is the efficiency of separation that could nullify the high efficiency of a detection equipment. Detection must be unfailingly followed by rejection of the detected bottle, and in reality this does not always occur. Delivery systems in use today are effective but not 100% accurate. Most errors that occur with an autosort process are due to mechanical delivery errors rather than error related to detection. Therefore, a check on the operations of selection of the detected product is of primary importance. Detectors with 99% or greater efficiency, if installed in series and in number of at least two units, can bring the level of impurities within the limits required. For example, with a mix in the proportion of 90% PET and 10% PVC, two detectors with 99.5% efficiency placed in series enable one to obtain a level of impurities of 2.5 ppm, whereas with efficiency of 99% the value of residue is 10 ppm.

6.12 Upcycling of Waste Plastics

Recycling generates some worth (usually less than the original material) from waste materials but ultimately they end up in landfill. From this realization, the German industrialist Reiner Pilz coined a new phrase in 1994 with his statement: "Recycling? I call it *downcycling*. What we need is *upcycling*, where old products are given more value, not less." Generally, plastic only downcycles, losing significant strength once it is melted, whereas upcycling is the new concept of converting the waste plastic into something more valuable. Ideally, upcycling may thus be called a green solution to the problem of plastic waste.

It is well known that chemical recycling partially converts some plastics into their monomers, or into hydrocarbon fractions, which can then be used either as feedstock for polymerization, or in other chemical processes. Since in the traditional chemical industry process, new materials may account for 60% to 90% of production costs, inexpensive feedstocks yielded from chemical recycling provide a pathway to reduce the cost of manufacturing value-added products. Only if the quality/value of the final products is upgraded could the processes involved therein be termed *upcycling*. Thus, the established technology of converting petrochemical waste plastics to petrochemical plastics, such as polystyrene (which could be produced by polymerization of cheaper styrene derived from post-consumer polystyrene waste), is to be termed *recycling*, whereas their conversion to higher value commodities such as biodegradable plastics would be termed *upcycling*. A typical example is the conversion of waste poly(ethylene terephthalate) to the biodegradable polymer polyhydroxyalkanoate (PHA).

PHA is the general term for a range of diverse polymers that consist of polyesters of (R)-3-hydroxyalkanoic acids. These biodegradable polyesters are distinguished from each other by the chain length of their monomers, two common well-known polymers being polyhydroxybutyrate (PHB) and poly(hydroxyvalerate) (PHV) derived from 4-carbon and 5-carbon monomers, respectively. In one method of upcycling of PET to PHA [75], PET is pyrolyzed at 450°C, resulting in the production of solid, liquid, and gaseous fractions. The liquid and gaseous fractions are burnt for energy recovery, whereas the solid fraction, terephthalic acid (TA), is used as the feedstock for bacterial production of PHA, using selective new strains that are capable of accumulating medium chain length PHA (mcl PHA) from TA as

the sole source of carbon and energy. The biopolymers, incl PHA, thus obtained by bacterial production have monomers of 6–14 carbons long and are elastomeric with molecular weight ranging from 74 to 123 kDa. These biopolymers are of interest owing to a broad range of applications and the fact that they are completely biodegradable.

Carbon being the major constituent of plastics, waste plastics can provide a carbon source for carbon-based value-added products, such as light hydrocarbons [76,77], carbon black/activated carbon [78], carbon fibers [79], fullerenes [80], carbon nanotubes [81], and graphene [82]. Converting waste plastics into such value-added products is a good example of upcycling.

According to the US Environmental Protection Agency, Americans use more than 100 billion plastic bags annually, but only about 13% are recycled. Moreover, conventional recycling methods are not effective because different types of plastics, for example, polyethylene and polystyrene, are not miscible and hence the quality of the recyclate is typically poor. In this context, a new process developed at Argonne National Laboratory [83] converts a wide range of waste plastics into a fine black carbon powder. In this environmentally benign solvent-free autogenic process, various waste plastics (LDPE, HDPE, PET, PS, or their mixtures) are inserted into a specially designed closed reactor and heated to 700°C. The thermal dissociation of these individual or mixed waste plastics in the reactor under autogenic pressure (1000 psi) produces dry powder of carbon microspheres (CMSs), which are pure, conducting, paramagnetic, and about 2–5 μm wide (1/20th the width of a human hair). Moreover, if a cobalt-based catalyst is added during the heating, the powder forms carbon nanotubes (CNTs). Both carbon spheres and CNTs have many industrial applications. They are used to manufacture lithium-ion batteries, which power cell phones, laptops, and other products. The batteries are also used in electric cars, while the properties of CMSs make them useful in water purification, in the tire industry as also in the manufacture of various carbon-based products like paints, printer inks, and toners.

One-pot conversion of plastics into CNTs has been explored by many workers [84]. The process typically starts with solid plastics, which are mixed with catalysts. Heat is applied by either electric furnaces or combustion of fuels to pyrolyze the plastics. The decomposed products, either in liquid or gaseous phases, serve as sources of carbon for the growth of CNTs on the catalysts. Polymers such as PE, PP, PS, PVA, PVC, PTFE, PET, and PF have been studied by this method. Various catalysts have been examined, including transition metals in either elemental form (Ni, Fe, etc.) or chemical compound form (nickel oxides, ferrocene, ferrous chloride, cobalt acetate, etc.).

The one-pot process features simultaneous plastics decomposition and the CNT synthesis. It has been suggested that the one-pot synthesis can be greatly facilitated by utilizing a combination of metal catalysts and solid acids, since the latter can provide intermediate proton acidic sites to assist breaking down the molecular chains of the plastics and favor the formation of CNTs. Thus, whereas conventional methods for large-scale production of CNTs (either CVD or combustion synthesis) require intensive combustion of premium feedstocks, such as methane, ethylene, carbon monoxide, and hydrogen, the aforesaid upcycling of waste plastics through the use of inexpensive feedstocks can contribute to the cost reduction of CNT production, thereby promoting larger CNT use in consumer/industrial products.

Studies on upcycling waste plastics into high-value-added carbon nanomaterials have further led to the finding [85] that graphene flakes (GFs) can also be synthesized in high yield by catalytic carbonization of waste polypropylene using organically modified montmorillonite (OMMT) as degradation catalyst and template at 700°C. This simple approach opens up a new way to transform waste plastics into high-value-added GFs, which have potential applications in many fields including catalysis, composites, energy, and environment.

6.13 Plastics Waste Disposal in Landfills

Because plastics do not decompose biologically, the amount of plastic waste in our surroundings is steadily increasing. For example, more than 90% of the articles found on the sea beaches contain plastics. Disposal of plastic waste has thus emerged as an important environmental challenge. The current

methods of plastics waste disposal are dumping in landfill, recycling/reusing, and incinerating to generate energy (gasification, pyrolysis, and thermal depolymerization).

Landfills are the most common way to dispose of municipal solid waste (MSW), a significant part of which is now accounted for by plastics. In the United States, plastics made up only 1% of MSW in 1960, but it increased to 12% (30 million tons) in 2008, 43% of this being in containers and packaging, 22% in nondurable goods, and 35% in durable goods. This means that nearly 13 million tons of plastics ended up in landfills in a year only in the form of containers and packaging. A landfill is looked upon as just a big hole that we fill with all types of solid waste hoping that it will slowly disappear. Common plastics do not biodegrade, however; so once in a landfill, it will sit there for decades, maybe for centuries, and possibly forever.

It is generally agreed that recycling is a preferred method of dealing with plastics. However, only 7% of plastics that are disposed of are recovered, compared to 55% of paper board. Of PET soft drink bottles, only 37% is recycled and only 28% of HDPE milk containers and large water bottles are recovered. All in all, bottles alone account for about half of the plastic materials that appear in dumps and could have been recovered [86].

As a way to dispose of solid waste, landfills have several advantages, especially in countries like the United States with large open spaces. Compared to materials recovery and incineration processes that require extensive investments in infrastructure and manpower, landfills have fewer fixed, or ongoing, costs and, in addition, landfill gas can be upgraded to natural gas, promoting landfill gas utilization as a potential revenue stream. In some countries, landfill gas recovery is extensive. In the United States, for example, more than 850 landfills have active landfill gas recovery systems.

On the other hand, landfills also have the potential to cause a number of issues having social and environmental impact, such as infrastructure disruption, damage to access roads by heavy vehicles, pollution of water courses, contamination of groundwater or aquifers, and harboring vectors such as rats and flies that can cause infectious diseases. Moreover, methane that is naturally generated by decaying organic wastes is a potent greenhouse gas, besides being flammable and potentially explosive.

There would not be a better solution than if the plastics that go to landfills could simply disappear, leaving behind products that could fuel homes, schools, offices, and industrial areas. This raises the question: can plastics biodegrade in a landfill?

There are a number of plastic products already in the market that have passed the test for biodegradability. These products range from water bottles to garbage bags to amenities and are made from traditional plastics in conventional processing plants [86]. To make plastics biodegradable, an additive (EcoPure) can be added to the material during the normal manufacturing process. It does not affect the mechanical strength, clarity or recyclability of the original plastic. EcoPure additives are tested using the ASTM D5511 test method and proven to biodegrade plastic at a highly accelerated rate. The additives are designed to start the biodegradation process only after reacting with microbes found in landfills.

BASF's bioplastic ecovio is a high-quality, fully compostable polymer product. It consists of the biodegradable BASF polymer ecoflex and polylactic acid (PLA), which is derived from corn, and also consists partially of renewable raw materials. In contrast to simple starch-based bioplastics, ecovio is more resistant to mechanical stress and moisture. It can be molded as easily as conventional non-biodegradable plastics and products are just as high-performing and strong in use. An ecovio product can take the same load as its polyethylene counterpart. It has mainly been used as mulch film, shopping bags, and certified compostable bags for collection of organic waste that make disposal more hygienic and convenient. Injection molding grade ecovio has been used for compostable coffee capsules and an aroma-tight outer packaging.

Since MSW normally does not contain enough moisture to react with biomass, modern landfills use leachate circulation and bioreactors to incorporate liquid management and pumping systems to achieve close to 40% moisture, which is enough for anaerobic bacteria to thrive [86]. A side effect of the biodegradation process that cannot be ignored, however, is the production of "landfill gases"—CO₂ and CH₄,

recognized as greenhouse gases. Hence, all modern landfills are required to install and operate landfill gas collection and control systems.

Compost sites also generate methane. However, only very few (<10%) compost sites would have adequate controls in place to collect the generated volatile organic compounds (VOCs) and methane because these controls are so expensive to implement. In view of this, landfilling is often considered to be a better option.

6.14 Energy Recovery from Waste Plastics

It is estimated that 200 billion pounds of plastics are produced in the world every year to fabricate myriads of products for diverse uses. Because of technical limitations or inconvenience of recycling, only a fraction of that material reappears in new plastic products. Discarding a plastic may thus only doom it to the fate of a thousand years in a landfill. However, waste plastics have high energy potential as they are high value “captured energy” with significantly more captured energy than wood, paper, or even coal and this energy can be converted to electricity, synthetic gas, fuels, and recycled feedstocks for new plastics as also other products of chemistry [87].

A range of energy recovery technologies are being used to complement recycling in helping to divert more amount of valuable post-consumer plastics from landfills. A novel process [88] has been developed to make fuel nuggets called *Plastofuel* by forcing waste plastics through a heated extrusion die, thereby melting a thin jacket that locks unmelted pieces within. A hot knife cuts the extruded material into easily stored and readily shipped nuggets, which can be burnt with coal in a coal-fired boiler or eventually combusted directly in a boiler system. High-temperature combustion (2000°F) ensures clean burning with minimal emissions. A key feature of *Plastofuel* is that the production process is tolerant of dirt and debris, and since only the outer portions are melted during processing, it requires only about one-tenth the energy to form as compared to production of plastic pellets.

A novel high-temperature plastic fueled burner, called “Eco-Clean Burner,” was invented in Seoul (South Korea) in 1999 by GR Technologies. This technology has been used by Eco-Clean Burners Inc. (Pittsburgh) to make industrial burners that are about the size of household ovens and can create energy to fire up industrial boilers using pellets made from old soda bottles and other plastics that are not suited to typical recycling processes (e.g., bottles that contained detergents or even water bottles that are colored) and would otherwise end up in landfills. The Eco-Clean Burner system is a clean energy source that can be retrofitted to most of existing commercial hot water heating systems with minimal disruption.

Polymer Energy LLC, a division of Northern Technologies International Corp., has developed a system to convert waste plastics by catalytic pyrolysis into liquid hydrocarbons, coke and gas, which can then be used as boiler fuel for power generation. The technology uses significantly lower temperature than gasification, so it is more energy efficient to produce. In the presence of proprietary catalytic additives, the reactor melts and vaporizes waste plastics in one step at temperatures between 840°F and 1020°F. It is reported that, on average, 78% of every pound of plastics fed into the Polymer Energy system is converted to liquid hydrocarbons, coke, and gas. The resultant coke can be further processed to produce additional fuel oil.

Polymer Energy has several advantages [89]:

- (i) The system is modular in design, each module typically producing 775 liters of crude oil for every ton of waste plastics processed. A single module can process between 250 and 400 tons of waste plastics per month, the throughput capacity being directly dependent on the quality of the input waste plastics. The system is designed to be a self-cleaning process. Thus, any contaminant in the input waste plastics stream is automatically removed from the system as an ash by-product, which can be safely disposed of in a landfill.
- (ii) The Polymer Energy system is robust in design and can process a wide range of waste plastics such as used agricultural/mulch film, silage wrap and other solid agricultural plastics, metallized plastics, plastic laminates, printed plastics, wet plastic by-products, and even heavy recycled

plastics. The non-plastic contaminants are converted into ash, which is automatically removed from the system during the normal cleaning cycle.

- (iii) The waste plastics do not need to be pre-sorted, cleaned, or dried before processing and the system can tolerate high amounts (up to 30% of the mix) of the following contaminants in the input waste plastics stream—mineral impurities such as sand and dirt, hard impurities such as glass and small metal parts, fibrous impurities such as cellulose and clothing, as well as water and oil residue. The process thus saves on the cost of pre-sorting, cleaning, and drying, thereby reducing the total cost of operation.

The output crude oil of the Polymer Engineering system is of high grade and can be further processed in a refinery or used to power low-rpm machineries such as electric generation turbines.

6.15 Disposal of E-Waste Plastics

“Electronic waste,” or “e-waste” for short, is a generic term embracing various forms of electric and electronic equipment that have ceased to be of any value to their users. This term is often used synonymously with the term “WEEE,” which is an abbreviation for waste electrical and electronic equipment. The scrap plastics generated by recycling electronics and referred to as “e-waste plastics” constitute one of the most challenging types of material to manage in the recycling industry.

As the use of electronic devices has proliferated in recent decades, the quantity of electronic devices such as PCs, mobile telephones, and entertainment electronics that are disposed of is growing rapidly throughout the world. For example, in the United States alone, it is estimated that 400 million units of consumer electronics are scrapped each year. With rapid advances in technology, electronic products are now becoming obsolete more quickly; this coupled with explosive growth in sales of consumer electronics means that more products are being disposed, even if they still work [90].

E-waste contains a range of materials of which plastics constitute a significant fraction. According to the European Topic Center on Research and Management [91], iron and steel are the most common materials found in electrical and electronic equipment and account for almost half of the total weight of WEEE, while non-ferrous metals, including precious metals, represent approximately 13% of the total weight of WEEE (with copper accounting for 7%). Plastics, however, are the second largest component by weight representing approximately 21% of WEEE. About 26% of these plastics are of flame-retardant type and the rest are non-flame-retardant.

The chemical composition of e-waste varies depending on the age and type of the discarded item. For example, a discarded personal computer (PC) with a CRT monitor typically weighs 25 kg and consists of metal (43.7 wt%), plastics (23.3%), electronic components (17.3%), and glass (15%) [92]. Heavy WEEE items, such as washing machines and refrigerators, which are mostly composed of steel, may contain fewer potential environmental contaminants than e-waste items, such as laptop computers, which may contain high concentrations of flame retardants and heavy metals.

E-waste recycling involves disassembly and destruction of the equipment, with mechanical separation being the first step. Recycling can recover 95% of the useful materials from a computer and 45% of materials from cathode ray tube monitors [93]. In rich countries, such as Japan, high-tech recycling operation functions well with little environmental impact [94]. Modern techniques can recover high-Pb glass from discarded CRT with minimal environmental impact [95]. Valuable metals may be recovered from e-waste by pyro-, hydro-, and bio-metallurgical processes [96].

E-waste plastics are considered to be an environmental hazard since harmful chemicals are leached from them when discarded in landfills or elsewhere. These chemicals are used in the e-plastics manufacturing process—most notably the brominated flame retardants, namely, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE). Brominated chemicals have been linked with endocrine and neurological damage in both animals and humans, causing infertility and thyroid disorders in adults and impaired physical/mental development in children. Worse still, brominated

flame-retardants bioaccumulate. This means that the compounds that have leached into the environment do not degrade or dissipate over time, and the pollution builds.

Typically, plastic shares in WEEE product categories are estimated [97] as follows: mixed consumer electronic devices (without television), 28%; cathode ray tube (CRT television sets and monitors), 30%; liquid crystal display (LCD) monitors, 35%; personal computers/servers, 8%; laptops, 28%; printers, 30%; and large copying machines, 7%. The following plastic types (in order of decreasing share) have been identified to be dominant in the different WEEE product categories—consumer electronics, including television sets (HIPS, ABS); information technology devices (ABS, HIPS, ABS/PC, PPO/PS); large electrical appliances (PP, PUR, ABS, PS, HIPS); small electrical appliances (PP, HIPS, ABS); and cooling appliances (ABS, HIPS, PUR, PP, PVC). It is reported in a Swiss study [98] that, in 2007, the most prominent plastic types in Swiss WEEE were ABS and HIPS (6870 tons and 6570 tons, respectively), followed by PP (4530 tons), ABS/PC-blend (2240 tons), and PUR (1500 tons).

The results of the aforesaid Swiss study [98] also show that approximately 80% (w/w) of all WEEE are dominated by the plastic types ABS, ABS/PC, HIPS, PP, and PUR. Particularly in large and small household appliances, cooling appliances, as well as in other consumer electronics, printers, CRT monitors, and television sets, these plastic types appear to possess a relevant theoretical recycling potential. On the other hand, they are suspected to contain brominated organics like deca-BDE, octa-BDE, and/or cadmium in concentrations exceeding RoHS (Restriction of Hazardous Substances) limits directive.

Though some post-consumer e-plastics can be melted down and used to manufacture new items, most kinds of plastics are not recycled in this way, and, instead, “down-cycled,” that is, used to make lesser-value products. E-waste plastics are so challenging to recycle because the brominated flame retardants prevent these plastics from being down-cycled. The e-waste plastics that contain these banned chemical additives cannot be reused and must be disposed.

A collection center, if available, facilitates collection of e-waste from households and organizations for sending to authorized e-waste recyclers. A certified recycler must make sure that, when possible, e-waste plastics are processed and reintegrated back into the manufacturing process, while all unusable e-waste plastics, like those with banned brominated flame retardants, are disposed under carefully controlled conditions in a properly equipped facility.

While proportions may vary from place to place or country to country, most e-waste today still goes to landfills and incinerators. For example, EPA estimates that, in 2011, while the United States generated nearly 3.4 million tons of e-waste, only 25% of that was collected for recycling; the other 75% went to landfills and incinerators, despite the fact that hazardous chemicals in them can leach out of landfills into groundwater and streams, or that burning the plastics in electronics can emit poisonous dioxins and furans. Another concern is that a large part of e-wastes that is collected in developed countries for recycling and disposal is simply shipped overseas to developing countries where they are dismantled and disposed under horrific conditions, poisoning the people, land, air, and water.

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