The Role of Chemistry in Plastics Recycling

A Comparison of Physical and Chemical Plastics Recycling

Today plastics recycling is usually only classified as being either mechanical or chemical. This view ignores the fact that the main difference between the two is whether physical or chemical reactions are taking place. However, precise differentiation is crucial for any assessment of the possibilities and limitations of plastic recovery processes and whether materials are actually being recycled or merely their raw materials recovered.

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Plastics recycling has been enjoying a considerable boom since 2016. This has been driven, on one hand, by players such as the Ellen Mac Arthur Foundation, which at the 2016 World Economic Forum in Davos, Switzerland, drew attention to the inadequate collection and recycling of plastic waste and formulated a vision for a closed loop recycling economy for polymers and, on the other hand, by numerous alarming images of plastic waste in rivers, the oceans and on what were once idyllic beaches. The topicality of the issue is intensifying the challenges that the recycling industry has faced for decades, such as the completeness of collection, problem-oriented sorting, and the availability of large quantities of consistently high-quality recycled plastic products under high cost pressure. At the same time, however, it is also bringing change to the market. Recyclers have begun to recognize the need for high-quality recycling and manufacturers are discovering the opportunities afforded by these secondary raw materials and the need for closed-loop-recycling management systems, while consumers are increasingly calling for sustainable products. It is just not clear yet who should bear the costs.

Plastics recycling serves primarily to maintain the value of polymer materials already in the value chain. This lowers the high costs incurred in processing crude oil into basic chemicals and new polymers and, in the case of mechanical recycling, eliminates the energy-intensive polymerization process, thus saving substantial quantities of CO_2 equivalents. This is reflected in the hierarchy of waste-recycling processes, which places mechanical recyc-

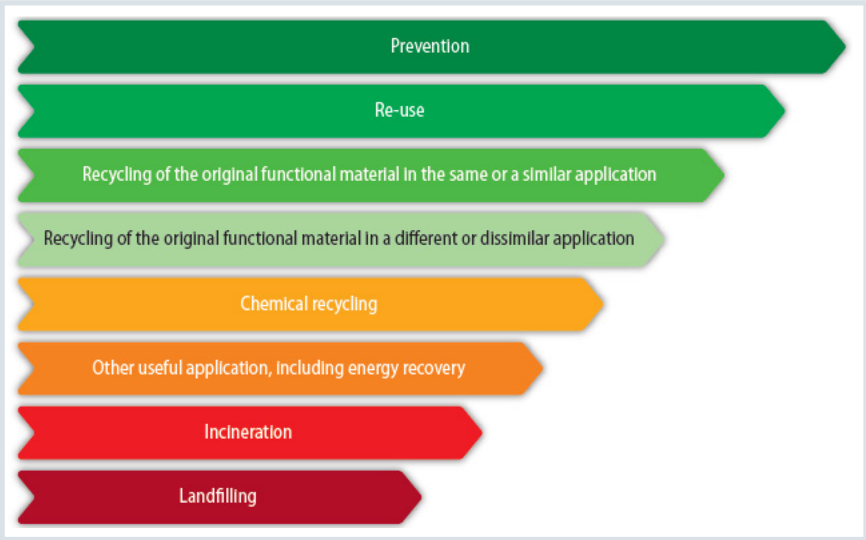

Fig. 1. Modified 8-step waste hierarchy according to Defra 2011 [13] Source: Fraunhofer IVV, graphic: © Hanser

ling above chemical recycling and immediately below direct re-use (**Fig. 1**).

The Physical and Chemical Processes Involved in Plastics Recycling

All plastics recycling involves waste pretreatment to a greater or lesser extent, even though this is often only associated with the mechanical type. The pre-treatment primarily consists of a cascade of physical steps, such as shredding and sorting with the aid of screens, magnets, eddy current units, separating tables, and optical sensors [1, 2].

Aside from these dry-mechanical processes, wet-mechanical washing and separation are common. These employ chemical additives, such as salts (separation via density), surfactants and alkalis, which work by initiating surface interactions, removing adhering dirt, coatings, labels and adhesives. However, they have no chemical effect on the matrix polymer and leave the polymeric structure intact.

Mechanical and solvent based recycling processes are physical in nature. With these, only the physical state (solid, liquid) changes, as the composition of the polymer remains unchanged. More strictly speaking, mechanical recycling is a thermal re-melting process in which thoroughly cleaned plastic input is melted in an extruder, the melt is treated with any necessary additives, filtered and then pelletized.

Solvent based recycling, as already mentioned, is physical in nature, too. By virtue of their polarity, the solvent molecules interact with the polymer macromolecules to form a polymer solution. Intensive purification of this solution at the molecular level is followed by precipitating the polymer, heating to remove the solvent and returning the entire polymer to the loop. The recycled product is a purified polymer that has not undergone any chemical changes during the process [3].

Both, mechanical recycling and solvent based purification belong to the class of "material recycling" based on physical interactions, which do not affect the composition of the polymer material.

In contrast, chemical recycling always alters the basic polymeric structure of the plastic and yields smaller feedstock molecules from which plastics can be produced again in the course of further chemical processes (**Fig. 2**). Depolymerization breaks down the polymers into their monomers, which are purified and returned to the polymerization process. Thermolysis, on the other hand, generates oils and gases that can serve as chemical feedstocks for petrochemicals or polymer manufacture or energy supply. Biodegradation (composting), too, consists of a series of (bio)chemical processes, even though it does not give rise to new recycled polymer product.

Mechanical Recycling

The quality of mechanically recycled product relies heavily on the sorting and separation technology employed in the upstream processing methods. The more inhomogeneous the waste stream, »

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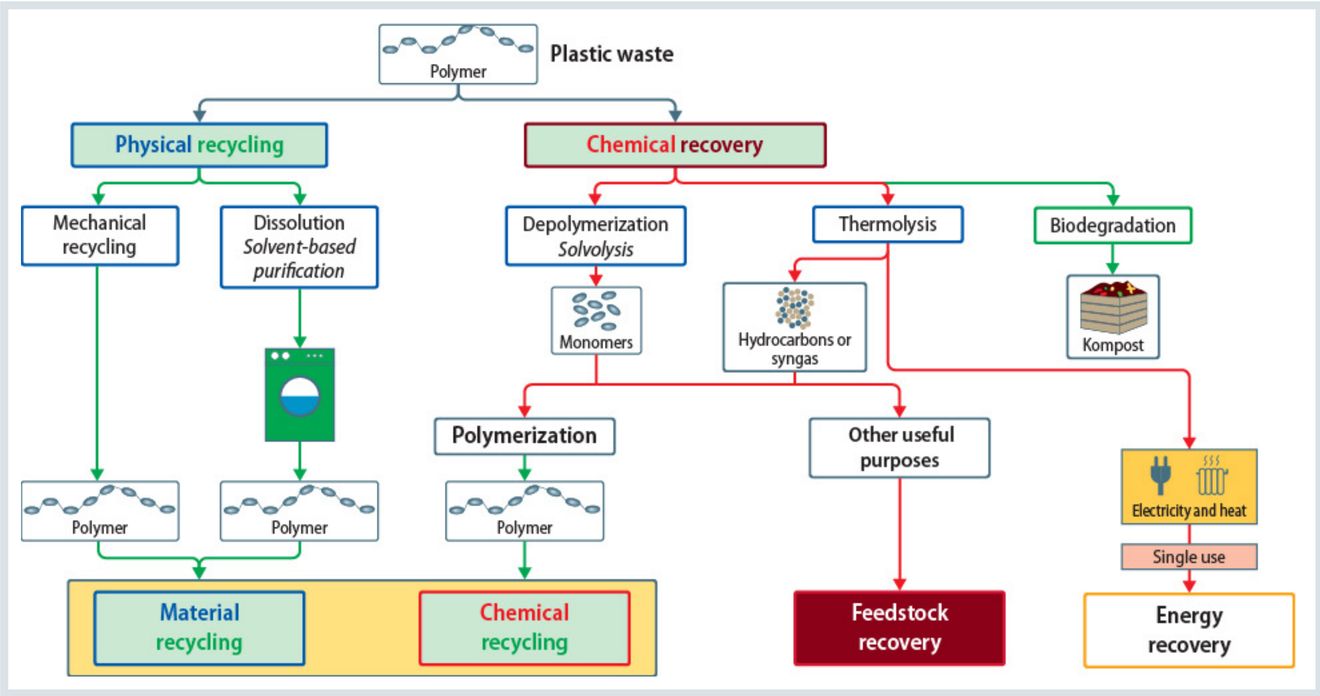

Fig. 2. Process steps involved in physical and chemical recycling: while physical recycling uses the material direct, chemical recycling only serves to recover feedstocks and requires an (energy-intensive) polymerization step before these can be reused in plastics Source: Creacycle, graphic: © Hanser

the worse is the quality. Also essential for highly sorted, homogeneous waste streams are upstream conditioning technologies that employ chemicals. For example, saperatec GmbH, Bielefeld, Germany, uses a special liquid based on chemical mixtures to separate flat plastic composites (beverage cartons, aluminum-plastic composites, PV modules, etc.) [4]. The subsequent washing step uses chemicals to remove residues adhering to the separated materials. The success of the process technology depends on the availability of highly sorted waste input.

Chemicals are also used to remove printing inks. For example, Cadel Deinking, a startup based in San Vicente del Raspeig, Alicante, Spain, has a process that deinks surface-printed plastics and delaminates and separates the various layers. This process is also used for deinking labels [1]. The quality of the resulting recycled product is enhanced by pigmenting and re-stabilization. Compatibilizers are used to produce a homogeneous mix of polymers [2]. If insufficient use is made of chemicals in the case of composite materials or contaminated waste, the recycled product is often of inferior quality. Examples are mixed polyolefins reclaimed from post-consumer packaging waste or polystyrene from recycling of odoriferous fish boxes [2].

In practice, it is the so-called bottle-to-bottle recycling that generates high-quality recycled products because the waste fraction is both readily sortable and highly sorted. It passes through a multi-stage, highly effective washing step involving chemicals, such as sodium hydroxide (NaOH), and surfactants. This step is so effective that PET (polyethylene terephthalate) beverage bottles or milk and juice bottles made from HDPE (high density polyethylene) can be recycled to high-grade products [5]. The recycled PET can even be re-used for direct food contact and can be employed in a closed loop [6].

Solvent Based Recycling (Dissolution)

Solvent based recycling as a method of plastics recycling has been applied and patented since the 1990s, but is not yet widely represented on the market. Until now, the accepted explanation has been, on one hand, the higher investment and process costs compared with those of mechanical recycling and, on the other, the fact that it is cheaper to incinerate or export plastic waste. However, current developments, and especially the demand both for technologies for recycling complex waste and for high-quality recycled product, suggest that this promising technology is about to make a breakthrough. From 2002 to 2018, composites of polyvinyl chloride (PVC) and plasticized PVC, sourced mostly from the construction sector, have been recycled by Solvay's Vinyloop process at the largest plant for this technology, which was located in Ferrara, Italy, and had a capacity of around 10,000 t/a. APK AG, Merseburg, Germany, runs a solvent-based operation for recycling polyethylene (PE) and polyamide (PA) in post-industrial composites packaging waste and can process complex composite structures such as multilayer film and beverage cartons, and has a comparable processing capacity of 10,000 t/a.

The CreaSolv Process developed by the Fraunhofer Institute for Process Engineering and Packaging IVV in Freising, Germany addresses a wider range of applications and polymers. It employs CreaSolv Formulations supplied by Creacycle GmbH, Grevenbroich, Germany, to selectively dissolve high-quality polymers out of mixed waste and composites found in different applications, such as polyolefins, polystyrene (PS) and PET in scrap packaging, styrene copolymers in scrap electrical appliances, expanded polystyrene (EPS) in insulating materials [7] or engineering polymers such as polyamides, and polybutylene terephthalate (PBT) present in post-industrial composite waste [8].

In late 2019, Unilever Indonesia started up a CreaSolv Pilot plant (1000 t/a) for the recycling of polyolefins sourced from landfilled post-consumer multilayer film packaging [9]. A smaller pilot plant is currently under construction in Neunburg vorm Wald in North-East Bavaria, Germany. The European cooperative PolystyreneLoop is currently erecting a demonstration plant with a capacity to recycle 3300 t/a EPS insulation materials, by separating the flame retardant additive hexabromocyclododecane (HBCDD), which is currently classified as a persistent organic pollutant (POP), in order to physically recycle polystyrene. The bromine is recovered from the separated HBCDD by chemical means [7]. According to Annex IV A of the Basel Convention, this is a D9 technology (physicochemical treatment) and facilitates downstream production of POP-free, recycled EPS. A lifecycle analysis conducted by the TÜV Rheinland independent inspection service shows that the CreaSolv Process outperforms the reference scenario of thermal recovery, with 47 % fewer greenhouse gas emissions and 51 % lower consumption of fossil raw materials [10].

Procter&Gamble's proprietary PureCycle process focuses on the recycling of polypropylene (PP). The process dissolves the PP present in composite waste such as waste carpet, as well as packaging waste, and reputedly yields colorless and odorless product grades. Building on the positive experience which it has gained on a pilot scale, Procter&Gamble is currently drawing up plans for an impressive 50,000 t/a plant in Ohio/USA.

Chemical Recycling

Solvolysis constitutes the first group of chemical recycling processes. This produces monomers by variously using alcohols, alkalis, acids, and amines to reverse the condensation reaction employed in the production of polymers such as PET, PA, polycarbonate (PC) and polyurethane (PU) [11]. With proper process control, these can be produced to a high level of purity and incorporated into the polycondensation stage of virgin material production. However, the 'reversing' reactions place high demands on the purity of the plastic waste to be processed, because secondary reactions with foreign polycondensates would affect the purity of the monomers produced.

These processes have been around for a long time and, in response to the demand for high-quality recycled plastics, are currently being discussed in particular for highly sorted PET or PA waste [2, 11]. Aquafil S.p.A., Arco, Italy, commissioned a plant for recycling PA6 from waste carpet in Phoenix, AZ/USA, in 2019. Among the many chemical recycling activities currently underway the Demeto consortium is a good example with the development of a scalable production setup for ethylene glycol and terephthalate based on microwave-assisted hydrolysis. Plant engineering and services related to the chemical recycling of PU are offered by Rampf Eco Solutions GmbH & Co. KG, Pirmasens, Germany [12].

Thermolysis (pyrolysis, thermocatalysis, hydrocatalysis and gasification), by contrast, entails temperatures in excess of 300 °C and is mainly used to convert polyolefin-rich waste into hydrocarbon mixtures. Pyrolysis and thermocatalysis work in inert gas, the latter with the help of catalysts that considerably narrow the complex spectrum of products yielded by pyrolysis. This principle is at work, for example, in the Quantafuel technology implemented for the first time in Skive, Denmark, which is expected to process around 18,000 t/a of plastic waste in 2020.

Hydrocatalysis additionally uses hydrogen gas to generate short-chain and saturated hydrocarbons even more selectively, while gasification oxidizes the plastic waste in oxygen or air at 10 to 90 bar and at 700 to 1600 °C to form synthesis gas (a mixture of mainly hydrogen and carbon monoxide) that can then be processed to methanol and subsequently to polyolefins. However, the latter technology is reputedly economical only at very large capacities in excess of 100,000 t/a.

Thermolysis of polystyrene constitutes a special case, because in this case it enables production of styrene monomer under certain conditions. This approach is being pursued by Ineos Styrolution Köln GmbH with partners under the German Resolve research project. In the USA (Chicago), Ineos Styrolution and Agilyx are planning plant capacities for processing up to 100 t/d polystyrene waste.

Conclusion

Physical and chemical steps dominate the recycling of plastics. However, the term "chemical recycling" technically only applies to those processes which yield chemical or monomeric feedstocks and polymerize them back into plastics. If this is not the case, the process is called feedstock recovery. Thus, these processes differ substantially from mechanical recycling and solvent based recycling (dissolution) of plastics, which do not alter the molecular structure of the polymer and allow the re-use in the original or similar application. That is why chemical recycling processes are not currently factored into calculations of recycling rates in accordance with the German packaging act.

According to a Conversio study (2018), some 6.2 million t of plastic waste are generated in Germany every year, from which around 1.8 million t of recycled plastics are produced. The planned capacity expansions for plastics recycling processes listed in this article add up to far less than the unutilized 4.4 million t, with the result that waste volumes will not generally act as a constraint on plant operation. However, it is important to note that a competitive situation could arise in the future, especially in the case of polyolefinic waste plastics, as they are currently being used in mechanical and solvent-based recycling technologies (APK, CreaSolv) and will also be employed in chemical recycling in the future. As chemical recycling plants are often designed for very large capacities, it is expected that these technologies will be mutually exclusive within a given collection area. Otherwise, they would stand in the way of increasing the recycling rate.

In the future, however, these technologies will not only coexist. They will also be combined, with advantage. Mechanical recycling might be employed for less challenging waste. The remaining volumes will be treated by solvent based recycling (dissolution) and/or chemical recycling. Excess energy recovered from chemical recycling, such as pyrolysis, would in turn be used direct for mechanical recycling. This is currently the object of the Circular Plastics Economy (CCPE) excellence cluster operated by the Fraunhofer-Gesellschaft e.V. ■