DOI: 10.1002/cssc.201300898

Recycling of Polymers: A Review

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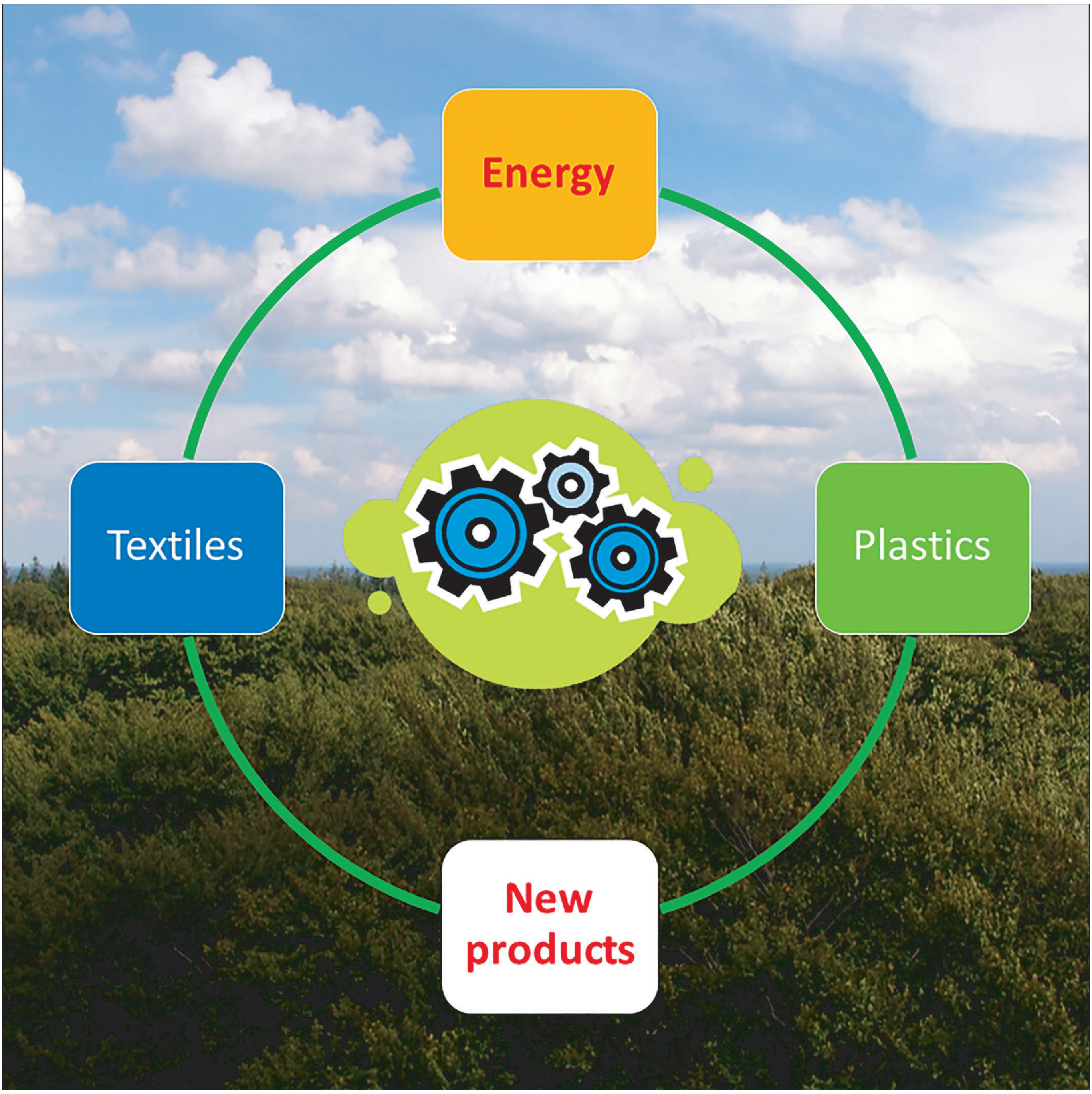

Plastics are inexpensive, easy to mold, and lightweight. These and many other advantages make them very promising candidates for commercial applications. In many areas, they have substantially suppressed traditional materials. However, the problem of recycling still is a major challenge. There are both technological and economic issues that restrain the progress in this field. Herein, a state-of-art overview of recycling is provided together with an outlook for the future by using popular polymers such as polyolefins, poly(vinyl chloride), polyurethane, and poly(ethylene terephthalate) as examples. Different types of recycling, primary, secondary, tertiary, quaternary, and biological recycling, are discussed together with related issues, such as compatibilization and cross-linking. There are various projects in the European Union on research and application of these recycling approaches; selected examples are provided in this article. Their progress is mirrored by granted patents, most of which have a very limited scope and narrowly cover certain technologies. Global introduction of waste utilization techniques to the polymer market is currently not fully developed, but has an enormous potential.

1. Introduction

Production of polymers has always been coupled with the challenge of their further utilization after use. A slower development within the field of recycling creates a serious problem: tens of millions of tons of used polymeric materials are being discarded every year. It leads to ecological and consequently social problems. Waste deposition in landfills becomes increasingly unattractive because of its low sustainability, increasing cost, and decreasing available space.[1] Dumping from ships at sea has already been prohibited in 1990.[2] Moreover, unsustainable methods lead to the exclusion of significant amounts of materials from the economic cycle. Thus, recycling can not only solve the first two problems, but can also be economically very beneficial as the market price of waste plastics as starting materials is at present particularly low.

At present, the added value created by recycling is also rather low; as a result, large amounts of used plastics and synthetic textiles can be only partially returned to the economic cycle. Moreover, recycling of polymers, in contrast to metals and ceramics, is largely impossible today without at least some downgrading of properties. On the other hand, it does not imply that nothing could improve the quality of products made from recycled polymers up to a desired level.

In the future, voluminous streams of used polymers can become an important source of raw material for production of plastics and textile applications, monomers for the synthesis of other polymers, and also fuel and energy.

Waste streams can be divided in end of waste (EOW), end of live (EOL), and post-consumer (PC) streams. EOW streams are generated during production and recycling within technological processes. Such pre-consumer waste can be valorized through the development of energy- and material-saving methods. EOL—and PC—waste streams consist of products that are at the end of their useful lifetime. Typical examples of such waste constituents are short-life packaging materials (bags, bottles, etc.), used goods (computers, cell phones, furniture, cars, etc.), demolition materials from buildings (insulation, flooring, pipes, etc.), and disposables. Valorization of these streams can be optimized through the application of methods that allows producers to recognize their products in waste mass (e.g., use of tracers), more efficient sorting and purification of different materials, and identifying sustainable solutions for streams of undesired components. The latter problem can be solved, for example, by extraction of such components from waste or encapsulation of undesirable components in products made from recycled materials. Therefore, efficient recycling should provide new opportunities for reintegration of discarded materials into the economic cycle, increase of the added value of products from recycled materials, creating a sustainable solution of the polymer waste problem, and decrease of the dependence on businesses utilizing oil to obtain raw materials and energy. The most common recycling methods are mechanical and chemical recycling and combustion. Their positions in a lifecycle of a product and its fabrication are demonstrated in Scheme 1, and their relevant properties are summarized in Table 1.

Sustainability should, of course, not be limited to separate optimization of recycling and recovery of materials and energy. Maximal reduction of usage of nonrenewable materials and energy in products and processes as well as durable optimization of consumption of energy sources and fuel remain important challenges for our society. These two principles of sustainable development are very general and relevant, in particular, for recycling and material isolation from waste recovery processes. Recycling technologies that consume no or small amounts of energy and do not create secondary environmental issues are regarded as sustainable recycling technologies.

The purpose of this Review is to provide a snapshot of the state of art, relevant social developments and market evolutions, and research and development activities in the field of recycling. Our study is aimed mostly, but not exclusively, at recycling of discarded polymers that are available in large amounts or can be particularly efficiently reused and reinte-

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grated into industrial processes. Therefore, recycling technologies are illustrated through examples of processing of the polyolefins (PO) polypropylene (PP) and polyethylene (PE), polyurethane (PU), hard and soft poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET).

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Bob Vander Beke received his Master in Chemistry (KU Leuven) in 1970 and his Master in Business Administration (MBA Vlerick School Gent) in 1984. He joined Centexbel, the Belgian Textile Institute, in 1976. From 1976 until 1981, he was research associate in the field of textile coatings. From 1981 until 1998, he was a senior consultant. In 1998, he accepted the position of M&S director at Centexbel, leading a group of 20 consultants. From 2009, a large part of the consultancy work has been reoriented towards the improvement of sustainability in textile companies: Recycling of polymers, REACH compliancy, and detoxification of formulations and masterbatches become more and more important.

2. Recycling Methods and Supporting Technologies

2.1. Primary mechanical recycling

Primary mechanical recycling is the direct reuse of uncontaminated discarded polymer into a new product without loss of properties. In most cases, primary mechanical recycling is conducted by the manufacturer itself for post-industrial waste.[3] Therefore, this process is often termed closed-loop recycling. In principle, post-consumer waste can be also subjected to primary recycling; however, in this case, a number of additional complications may arise, such as necessity of selective collection[3] and rough (manual) sorting.[4] Such issues may significantly increase the costs of recyclates.[3] Thus, in general, this method is unpopular among recyclers.

Before reintegration of a used material into a new product, it normally requires grinding, that is, shredding, crushing, or milling. These processes make the material more homogeneous and easier to blend with additives and other polymers for further processing. Broken-down material can also be integrated in a more controllable way into a common production process. Moreover, it becomes easier to purify. An additional cleaning step could be useful or even necessary to avoid problems that might otherwise occur with the final products.[5]

A recyclate can be given a new shape after melting. The best-known methods of this type of processing of mechanical recyclates are injection molding, extrusion, rotational molding, and heat pressing.[3,5,6] Therefore, only thermoplastic polymers, such as PP, PE, PET, and PVC, can normally be mechanically recycled.

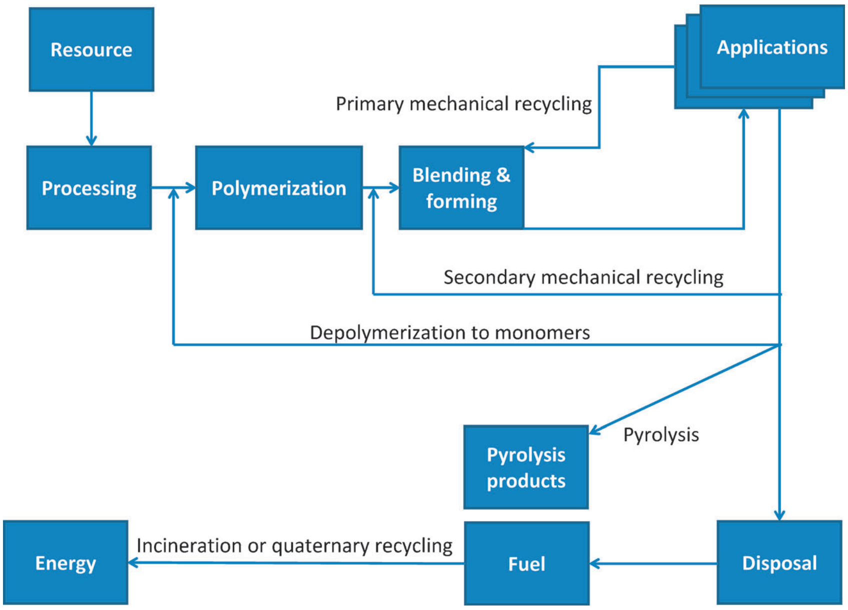
Closed-loop recycling can be efficiently realized as following:

- discarded materials are integrated quickly back into the production cycle
- impurities can be removed directly or easily, do not play any role in the end product or in the layer of recycled material in the end product
- the polymer is stable enough to again perform high-temperature processes
- recycled materials are processed in (almost) the same way as virgin materials.

An interesting case of closed-loop recycling has been recently demonstrated at the University of Leuven (KU Leuven).[7] Back covers of flat-screen TV sets that consisted of blends of polycarbonate with acrylonitrile butadiene styrene with phosphor-based flame retardants were converted into new back covers and testing bars by means of primary recycling. The authors further demonstrated the economic feasibility of the recycling process.

2.2. Secondary mechanical recycling

Exact content and purity grade of EOL- and PC-steams are frequently not known; therefore, they are processed through secondary mechanical recycling, which involves separation/purifi-



Scheme 1. Most common polymer recycling methods and their position in a lifecycle of an application.

cation in contrast to primary recycling. As well as in the case of primary recycling normally only thermoplastic polymers can be reprocessed.

The polymer is not changed during the secondary recycling, but its molecular weight falls owing to chain scissions, which occur in the presence of water and trace amounts of acids. This may result in the reduction of mechanical properties. This phenomenon can at least be partially counteracted by intensive drying, application of vacuum degassing, and use of various stabilizing additives.[8]

Another reason for the drop in mechanical properties after recycling is the contamination of the main polymer (matrix) with other polymers. Most of the polymers are not compatible with each other (i.e., their blends have mechanical properties that are inferior to those of the pure constituents).[9] Examples are PET impurities in PVC, in which solid PET lumps form in the PVC-phase. This leads to significantly downgraded properties[10] and consequently less-valuabale end products.

Efficient separation of different materials before integration into a new product is a solution. Fourier-transform and near-infrared spectroscopy are frequently used to determine the polymer type, whereas an optical color recognition camera is a popular tool to separate clear and colored materials from each other.[10] X-ray detection is used to identify and subsequently isolate PVC[11] to avoid the undesired formation of HCl during reprocessing at elevated temperatures.

A new detection method for electrical and electronic equipment waste and car scrap is laser sorting. It is also capable of separating different plastic types from each other,[10] whereas another upcoming technology is electrostatic detection.[12]

As well as in the case of primary recycling, waste is ground without prior purification, optionally cleaned after grinding, and integrated into the end product, mostly through melting.

Important factors of secondary recycling are:[3,5,10,12]

- availability of waste materials for recycling (logistics, volumes), costs of (selective) collection, storage, and transportation
- form or shape (blades, fibers…)
- composition (mono or complex, difference between melting points of components)
- purity grade (presence of certain admixtures can have negative effects on recycling or even make it impossible)
- price difference between virgin and recycled materials (secondary recycling of even small amounts of expensive technical polymers can be very attractive from a financial point of view)
- presence of desired and undesired additives (the odor and the color of recyclate frequently determines possibilities of integration of recyclate into end products; purification, deodorizing, and decolorizing are reasonable as long as the prize of the end product is significantly higher than that of the starting materials)
- availability and costs of techniques and processes (detection, separation, purification, compounding)
- ecological aspects (generation of dust, noise pollution by grinding, energy consumption, toxicity of applied solvents).

Table 1. Most common polymer recycling methods.

Input	Option	Process	Output
EOW/EOL/PC	preparation for recycling	collection and preparation	input for recycling, recovery of material and energy
EOW	material recovery	primary mechanical recycling	recyclate or (semi) ready product
EOL/PC	material recovery	secondary mechanical recycling	recyclate or (semi) ready product
EOW/EOL/PC	material recovery	tertiary or feedstock recycling	chemicals (mono- and oligomers, other substances/ reaction mixtures in form of gas, liquid, or solid)
EOW/EOL/PC	energy recovery	direct or controlled combustion (quaternary recycling)	heat, steam, or electricity

Automotive shredder residue from shredded car components is a typical material for secondary recycling. The resulting products can be further used in the form of composites for new car components.[13] Secondary recycling is also widely used for recycling of post-consumer PU foam, for which the foam is first crushed into flakes and then given a new form by remolding. However, the quality of the end product is often not satisfactory as a result of polymer degradation.[14] To tackle this issue, Papaspyrides et al.[15] used commercially available stabilizing additives (e.g., Recyclossorb 550) to conserve the chain length in closed-loop recycling of post-consumer streams of polypropylene (PP) and high-density polyethylene (HDPE). These additives contain antioxidants and various other stabilizing components. Particularly encouraging results were achieved in the reuse of HDPE bottle crates.[15b]

A special form of mechanical recycling is the so-called dissolution/reprecipitation method: a mixture of polymers is dissolved in a suitable organic solvent, which is followed by a selective precipitation of one or some of the components by addition of a nonsolvent.[16] Achilias and co-workers have demonstrated the effectiveness of this approach for blends of low-density polyethylene (LDPE), HDPE, PP, polystyrene (PS), PVC, and PET on a lab scale. They used xylene, toluene, dichloromethane, and benzyl alcohol as solvents and *n*-hexane and methanol as nonsolvents.[16a]

The VINYLOOP process envisages such a method for processing PVC containing additives. It can be applied in the reuse of electric cables, truck awnings, and other materials with PVC coatings.[17] Currently, Ferrari operates an industrial installation for the processing of PVC-coated textiles. A life-cycle assessment of PVC coatings has been performed in cooperation with Solvay, demonstrating the advantages of the VINYLOOP process.[18]

When secondary recycling becomes too expensive or complicated, waste is converted into fuel or incinerated directly.

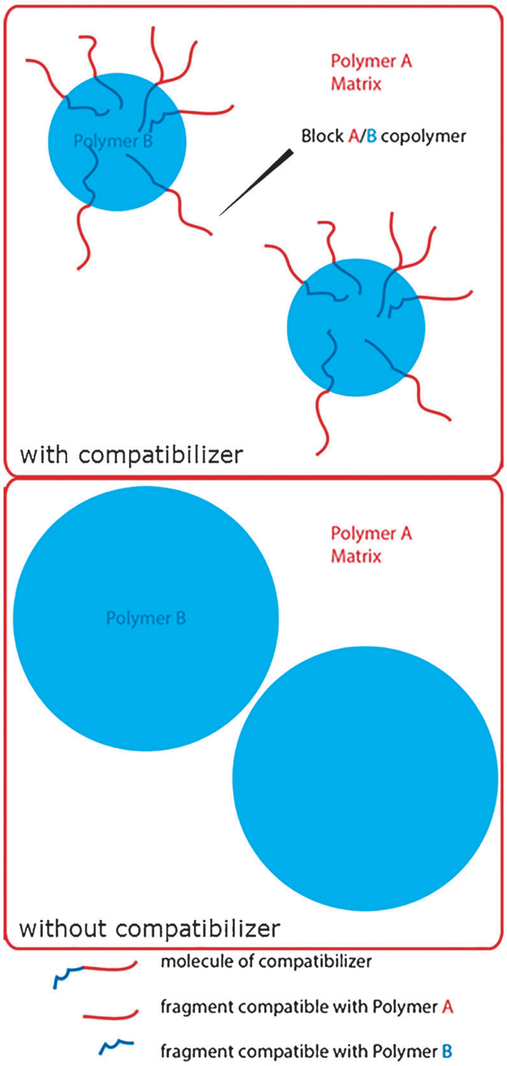


Figure 1. Compatibilization of polymer A and polymer B by a hybrid material.

2.2.3. Compatibilization

The above-mentioned technologies require the use of pure polymers or envisage preliminary separation or purification of waste. However, mechanical recycling can be improved by so-called compatibilization, which allows skipping separation.[19]

The compatibilization methodology has been mentioned in various publications since the occurrence in the 1950–60s: different polymers are mixed together, and a suitable third component, the so-called compatibilizer, is added.[20] Thus, mechanical properties of the final polymer–polymer composite can be improved significantly. The compatibilizer tends to be a copolymer containing a compatible molecular fragment for each blend component. Therefore, compatibilization is based on physicochemical interactions of waste polymers with this hybrid material. The presence of compatibilizers results in a finer dispersion of the contaminating polymer in the matrix. A graphic explanation of this process is presented in Figure 1.

For many polymer couples, suitable compatibilizers can be found in the patent literature. Most of the patents also mention the names of commercial compatibilizers. A good example is the compatibilizer ethylene–propylene diene rubber (EPDM) for PP and PE, typical materials for bottles.[21] It is available, for example, as Keltan 5170P from Lanxess. Another commercially obtainable compatibilizer is Kraton FG1901X from Kraton Performance Polymers Inc., which is maleated styrene–ethylene–butylene–styrene. This additive is suitable for thcompatibilization of PET with PP.[21b]

There are also solutions for rare combinations such as poly(1,1-difluoroethylene) (PVDF) and PVC: an ethylene terpolymer Elaloy HP 661 from Dupont.[22] Another field is compatibilization of non-thermoplastic materials (cork, paper) and rubber with plastics. One patent, for example, provides a solution for rubber combinations with polyolefins,[23] whereas another provides one for cork with various plastics.[24]

There are reports as well on the use of radiation-oxidized polymers as compatibilizers. For example, compatibilization of PE and polyamide 6 (PA-6) in the presence of modified polyethylene has been demonstrated by different research groups.[25]

2.3. Tertiary or feedstock recycling

Feedstock or tertiary recycling is a type of polymer recycling in which the polymer chains are converted to smaller molecules through chemical processes. Examples of such processes are hydrolysis, pyrolysis, hydrocracking, and gasification.[3,12,26] Typical conversion products are liquids and gasses, which can be used as feedstock for the production of fuels, new polymers, and other chemicals. Industrial implementation of this technology requires subsidies because of the low prices of feedstock materials compared with plant and processing costs incurred by depolymerizing the plastics.[27]

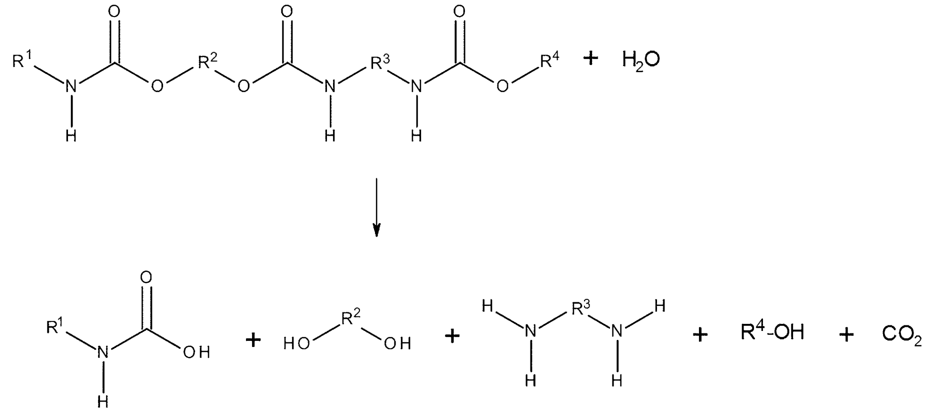


Figure 3. Hydrolysis of PU.

Polymers formed through polycondensation reactions (Figure 2), such as polylactic acid (PLA), PET, and PU, can be efficiently depolymerized through catalytic reactions; thus, the obtained monomers can be reused to synthesize the original polymers.[28]

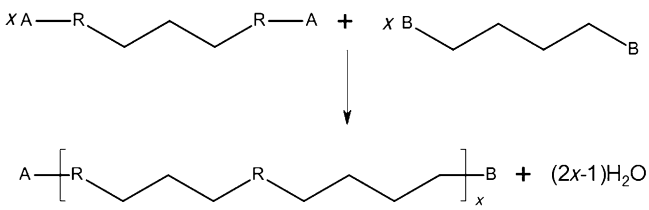


Figure 2. An example of polycondensation.

Achilias et al. achieved an efficient depolymerization of PET[29] and a polycarbonate[30] made from bisphenol A (PC/BPA) into their monomers and oligomers under microwave irradiation. One of the catalysts proven to be efficient for solvolysis of both plastics is aqueous NaOH.[29c,30]

An important feature of PU hydrolysis is that it can produce both polyols and amines (Figure 3). Polyols can also be used as fuel, whereas both can be reused as starting materials for the synthesis of new PU. However, hydrolysis of PU is uneconomical, mainly because of the high energy consumption: the temperature during the process has to be above 280 °C.

A more practical approach is glycolysis of PU, that is, reaction with diols at a temperature above 200 °C (Figure 4). The main goal of this process is the recovery of polyols used for PU synthesis.

Another frequently used polymer, which can be depolymerized using this method, is PC/BPA. Liu and co-workers[31] achieved over 95 % depolymerization of the polymer into its monomer bisphenol A in the presence of the ionic liquid 1-butyl-3-methylimidazolium acetate as catalyst.

Other polymers such as PE or PP can generally not be depolymerized to their monomers following the above-discussed method. They can, however, be degraded through a free radical mechanism at high temperatures, but this does not result in the formation of monomers as a major product in most cases but rather very diverse products owing to random breakdown of the C–C bonds. [8] As a result, heterogeneous mixtures of gasses, liquids, and tar are produced, which can be further utilized in petrochemical and chemical industries or used as combustible gas.[32] In the presence of catalysts, their degradation goes through a carbenium-ion intermediate, and it is possible to control the major product types through selection of the catalyst.[33] For example, pyrolysis of PE results in the selective formation of aromatic products in the presence of the zeolite H-ZSM5 and aliphatic compounds in the presence of the montmorillonite K10.[34]

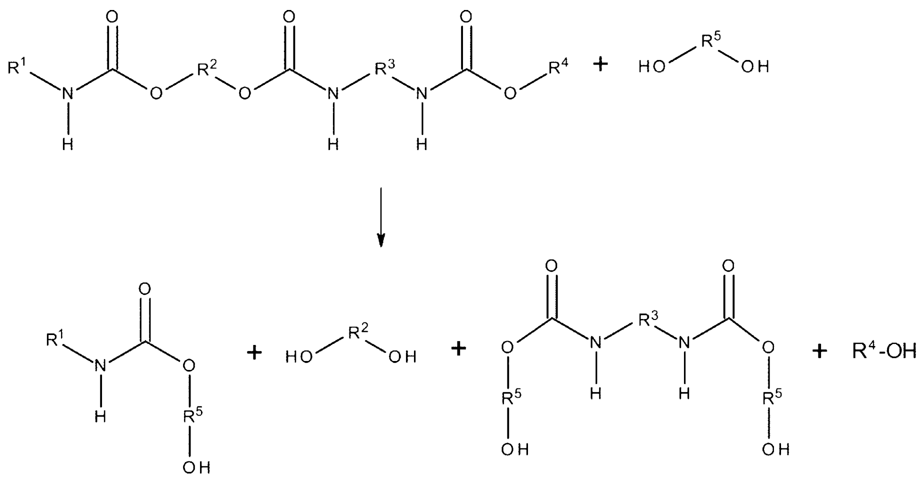


Figure 4. Glycolysis of PU.

The essential part of a polymer cracking process is pyrolysis in a fluidized bed reactor. It leads to formation of a fluid fraction (wax), which is chlorine and heavy metal free. This fraction is then transferred to thermocatalytic and catalytic crackers of a refinery for further reprocessing.

Preparation for cracking includes grinding, removal of metals, and other coarse components. Then, the plastic waste is fed into a fluidized bed pyrolysis reactor at a temperature of 500 °C for cracking. Dust is removed from the gas phase by a cyclone. Subsequently, HCl, which is generated by pyrolysis of chlorine-containing polymers such as PVC, is quenched over a CaO bed. The gas phase is cooled to isolate its condensable part. The condensate (wax) is further processed in a refinery. The non-condensable fraction (C_1–C_4) is pressurized, heated, and transported into the reactor as fluidization material. The excess is used for heat generation.[28]

Certain environmental impacts (e.g., emission of dioxins)[35] and intensive energy consumption[36] explain why feedstock recycling is mostly limited to small-scale pilot projects or big industrial-scale projects under very strict conditions.

Gasoline-, diesel-, and kerosene-range chemicals were produced by Panda and Singh from waste PP through pyrolysis in the presence of kaolin clay as the catalyst in a batch reactor.[37] The maximum oil yield was 87.5 %.

An interesting alternative example of pyrolytic recycling is plasma torching: diverse plastic waste is degraded by plasma in an oxygen-starved chamber into an harmless slag, which can be used in the construction industry, and valuable syngas. This method has already been applied on large scale in Japan.[38]

Another interesting method to enhance pyrolysis is to conduct it in the presence of a suitable solvent. This way, it is, for example, possible to increase selectivity towards desired products.[39] For example, Vicente et al.[40] have performed thermal cracking of HDPE at 400 °C in the presence of phenol, which promotes this reaction by supporting random scissions and chain reactions. The main products of this process are olefins, which are very valuable for the petrochemical business.

Zhuo and Levendis performed a survey of another promising form of the pyrolytic feedstock recycling: the synthesis of nanotubes from polymer waste.[41] According to this technology, a discarded plastic (e.g., PE, PP, PS, and many others) can be pyrolyzed in the presence of an appropriate catalyst, for example, nickel[42] or other transition metals, resulting in the formation of carbon nanotubes at suitable conditions. A one-pot synthesis is possible.[41] These nanotubes have a tremendous application potential in such fields as electronics,[43] composites,[44] and biotechnology[45] and form a very interesting possibility to upgrade plastic waste material.

2.4. Biological degradation

Certain polymers can be degraded in the presence of air and water[46] into smaller molecules by bacteria,[47] fungi,[48] and some other microorganisms that biosynthesize relevant enzymes.[49] This form of degradation is considered by some researchers[10,41,50] as a form of recycling (an improved form of the above-discussed tertiary recycling[10]) as it also clearly preserves the intrinsic value of waste materials and returns them into the biological cycle.[50b]

In most of the cases, naturally existing polymers and those purposely designed to resemble them are biodegradable.[51] However, there are exceptions from this principle. For example, polythioesthers are synthesized by bacteria through polymerization of mercaptoalkanoic acids in the presence of polyhydroxyalkanoate synthase and cannot be biodegraded.[52] On the other hand, the biodegradable aromatic polyester poly(butylene adipate-co-terephthalate) is a petroleum-derived product,[53] and it is also possible to design enzymes can biodegrade PET at a reasonable rate.[54]

Process parameters (pressure, presence of certain microorganisms, pH, etc.) determine whether polymers can be easily converted into compost or other substances.[55] In general, biosynthesized polymers (cellulose, chitin, etc.) can be efficiently biodegraded under a wide range of process parameters.[56] There is a labeling system for the classification of polymers that are biologically degradable and or compostable.

Mathew et al.[57] have demonstrated an efficient biodegradation of PLA and some of its composites in soil. Another example of degradation in soil has been reported by Tserki et al., who combined Bionolle 3020 (copolymer of succinic and adipic dimethylesters with 1,4 butanediol) with flax, wood, and hemp fibers and then demonstrated an increased biodegradation rate of the resulting composites.[58] This result can be attributed to hydrophilic lignocellulosic fibers transporting water into the composite and thus stimulating degradation of the composite.

2.5. Incineration or quaternary recycling

Incineration as a method to recover energy may be also classified as a form of recycling.[8,41,59]

Incineration (or quaternary recycling) still remains a very popular method for waste volume reduction and for energy recuperation.[60] In Europe, it is the most common method of utilizing discarded plastic.[10,12] This method is especially used for processing of mixed and heavily contaminated wastes, which cannot be easily and/or economically recycled by any other method.[3] Burning of energy-dense waste can create heat, electricity, or other forms of energy, which can be directly used in technological processes or for heating of buildings.

Quaternary recycling reduces the waste volume to roughly 1 % of the initial volume[3] and decomposes toxic and contagious waste. It is thus ideal for recycling of medical applications and packaging of hazardous goods.[61] Inorganic constituents are converted to inert slag through incineration and can be used for the construction of roads.[12]

Various setups and methods are used to perform incineration. Plastic waste is used as an energy-dense fuel for high-temperature processes: the calorific value of synthetic polymers is generally higher than that of coal.[62] It is suitable, for example, for cement furnaces, chemical waste incineration facilities, and metal melting ovens. Integration and clustering of incineration facilities directly in factories can make use of heat and electricity more efficiently.[3]

The design of incinerators and a strategy for their installation has been significantly influenced by the problems associated with the emission of soot, polycyclic aromatic hydrocarbons, and also dioxins in case of halogen-containing plastics.[63] Chung et al. have proposed an interesting approach to reduce the formation of 1,2-dichlorobenzene, CO, and potentially dioxins, which resemble chemical structure and toxicity of the former one, by exploiting the synergistic catalytic effect between Ti and Fe: through the addition of Fe_2O_3nanoparticles covered with a porous layer of TiO_2 into PE or PS followed by incineration in a packed bed reactor significantly less noxious gasses were detected after the processing in the presence of the mixed catalyst in comparison to Fe_3O_4 or TiO_2 alone or no embedded particles in the polymers.[64]

2.6. Cross-linking

Cross-linking is a technique that can be used to improve the mechanical properties of discarded polymer blends: special chemical agents are used to create chemical bonds between polymer chains during reprocessing, for example, in reactive extrusion.[65] These agents are mostly chemically active systems that interact with polymer chains, resulting in a decrease in or absence of degradation of properties.

Such hardening or “stitching” can solve the problem of incompatibility, but makes future recycling of cross-linked material very challenging because of full or partial loss of thermoplasticity, that is, the ability to undergo indefinite inelastic deformations at elevated temperatures. Cross-linking transforms the thermoplastic polymer into a thermoset, which cannot be easily reshaped.[66] However, such thermoset polymers can be mixed with analogous thermoplastic virgin materials after grinding and subsequently be integrated into end products. This integration can be also improved by chemical or thermal binding.

Fang et al.[67] tested cross-linking for the treatment of a blend of LDPE, PVC, PP, and PS, which resembles a typical tetra-component mixture of discarded polymers. They demonstrated that dicumyl peroxide is a suitable recycling agent for a combination of these plastics: mechanical properties of the blend were significantly improved after compounding.

Another example, which can be relevant for polymer recycling, is the Monosil process, developed by BICC Limited and Establishments Maillefer SA in 1974. Polyethylene is grafted with vinyltrimethoxysilane and subsequently cross-linked, which is induced by moisture.[68]

Another industrial application of cross-linking is hardening of PE using silanes, peroxides, and erythritol-bis-carbonate. Cross-linked PE, commonly designated as PEX, is used in electric cables and gas pipes because of its good thermal resistance.[69] BASF produces cross-linking agents for cotton and polyester compatibilization (Kaurit). These agents are aqueous adhesives made up of urea and formaldehyde or melamine and formaldehyde.[70]

An alternative approach is to use radiation instead of a chemical cross-linking agent. A successful compatibilization of EPDM with natural rubber (NR) through exposure to γ-rays (^{137}Cs) at various doses (up to 300 kGy) has been demonstrated by Zaharescu et al.[71] In this case, free radicals are generated by interaction between radiation and molecules, leading to the formation of chemical bond bridges between different polymer chains. This approach might also have potential in recycling.

3. Examples of European Projects

This list is based on publications on the online portal of the European Commission (http://europa.eu) and includes selected cases. In addition, the websites of the projects were consulted when available. Original reference numbers and designations of the projects are used throughout the text.

In the German project LIFE 00 ENV/D/000348, a pilot plant has been built for the production of wood–plastic composites. For the preparation of these products, up to 100 % recycled PP was used. Decorative finishing of these composites with thermoplastics using a belt press system was also investigated. The products can be used, for example, for flooring and resonance boxes.

LIFE 04 ENV/DK/000070 is a Danish project on complete conversion of scrap-tire powder to superior rubber products by using dense phase techniques. Bad-smelling oils are removed from milled car tires by extraction with supercritical CO_2. After this purification, the treated material is impregnated by means of the same technology using suitable monomers and polymer precursors. The reactor is subsequently depressurized, and CO_2 is recuperated. The thus recycled material is inter alia usable for preparing flooring of sport fields, rubber materials, and asphalt. A patent application has been submitted to protect this technology.

L-FIRE is a Dutch project focused on recycling of long fibers from ropes and optical cables in which Kevlar is used. Kevlar and other hard components such as optical glass fibers, aluminum, and steel make it difficult to shred these materials. In L-Fire, an alternative solution, the peeling of different components, is investigated.

FP7-ENV-2010: IRCOW is a Flemish project conducted by the Flemish institute for technological research (VITO). The goal is to develop new strategies for high-grade material recovery from construction and demolition waste.

FP7-ECOMETEX: 2012–2015 involves three institutions: European carpet and rug association (ECRA), Belgian textile research center (Centexbel), and the Fraunhofer society. The topic of this research is to develop an environmentally friendly methodology for recycling textile coverings used in the European construction and transport industry.

Polymer recycling is investigated at the polymer research center of the University of Surrey. Its topic is a life-cycle and process optimization approach in the selection and integrated chain management of polymer materials. Research is focused on complex materials: PVC-coated cables, laminated glass, toner containers, and plastics from electronic waste.

SUPERCLEAN, a project conducted at the Fraunhofer Institute, focuses on recycling of plastics that comes into contact with food. It deals mostly with colored and co-extruded PET bottles. In the context of this project, researchers are trying to develop an online system for detection of contaminations that grow from oxo-degradable additives.

Solid-state shear pulverization (S3P) is a new technology being developed at the polymer technology center of the Northwestern University in the USA. Some commercialization projects have already been undertaken in Europe. Using this method it would be possible to convert multi-colored unsorted waste, industrial scrap, and virgin resins to a uniform, light-colored, partially reactive powder of controlled particle size and particle-size distribution.

A British project (DEVULCO2) has been conducted within the field of high added-value sustainable products from used tires. The exact goal is to develop a novel, continuous, and effective devulcanization system based on the combination of supercritical CO_2, chemical devulcanization agents, and extrusion equipment.

PEGASUS is a Spanish project about integrated technologies, which is relevant for the European automotive sector, and aims at developing special materials for in situ coloring to replace conventional lacquers. Moreover, attention has been paid to the application of so-called "debond-on-command" additives.

ECO/10/277225 SUPERTEX is a European project within the field of integration of recycled PET into textiles. Next Technology (Italy), Centexbel, Devan Chemicals (Belgium), Leitat Technological Center (Spain), and other organizations have contributed to this study.

The presented examples of projects illustrate an implementation of the present innovative industry-orientated and multidisciplinary approach generally investigated on a semi-industrial scale. Moreover, the researchers elucidate the trend of further R&D in this field, which can serve as starting point for new projects.

4. Patents Overview

Patents and patent applications remain an important source of information about specific methods and technologies for polymer reuse or conversion into raw materials and energy. Expired and refused patents can be used without limitations. The current status of such documents can be easily checked online. A retrospective of aged documents can be very useful for the development of fresh technologies, and old methods can be applied in new fields, for example, in combination with modern methods.

Clearly, it is important to perform an elaborate patent search during a start of a new project to determine the freedom of operation. This analysis can be efficiently performed, for example, by a collective R&D center or by a special University service.

In our overview, we are focusing on the most frequently applied polymers: PO (PE and PP), PET, PU, and PVC. On the other hand, we have also taken into account less-known technologies.

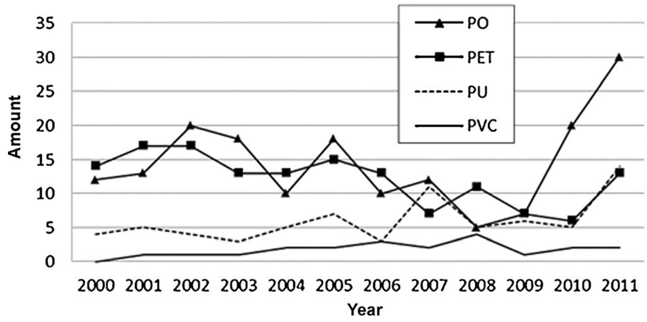


Figure 5. Evolution of the amount of granted recycling patents per material in 2000–2011.

Figure 5 demonstrates the evolution of the amount of patents covering recycling of four industrially relevant plastic materials in between 2000 and 2011. In three out of four cases (PO, PET, PU), a significant growth is recorded in the last three years. Recycling of PO is the topic of most patents. The biggest part of patents about PO and PU has been filed by petrochemical multinational companies such as BASF, Bayer, Basell, Mitsubishi, Shell, BP, China Petroleum, and Phoenix Technologies. The last one produces recycled PET for packing materials, including bottles, on a large scale and is an active filer of patents.

Almost all granted patents cover a specific recycling technique or method. A lower percentage of patents is focused on recycling of a specific waste stream such as bottles, fibers, coated materials, or plastics from car scrap. A highly limited number of patents covers the integration of recycled polymers into specific applications: decorative panels or artificial leather. Production of fixed raw materials (production of paraffin from PO) is also described in a small fraction of patents. Only two patents are dedicated to the application of particular additives that can be introduced before or during recycling: EP1801148 (UV-tracer for PP-bottles)[72] and WO9730112 (stabilizer for PO).[73]

This patent overview complements the project examples described above (Section 3) and also demonstrates in general a growing interest in polymer recycling, especially from big international companies. However, PVC recycling remains traditionally not developed. It should also be noted that patents mostly do not offer an integral scheme, that is, "waste→end product" (they are not linked with a certain waste stream and not oriented towards an end product from recycled materials).

5. Markets for Recycled Materials

Technical as well as nontechnical drivers and barriers influence collection, sorting, recycling, and reuse of polymers. Important factors among others are availability of materials, logistics and infrastructure, energy consumption, and legislation.[74]

In this part of the Review, we will discuss economic aspects of involved markets and some other relevant topics.

5.1. Polymer market: A general overview

The total worldwide production of polymer materials used as thermoplastics (ca. 65%), textile fibers (ca. 13%), PU foams (4%), thermosets, coatings, or glues reached 260 million tons in 2007. Approximately 24% is produced in Europe. The most typical applications of polymers are packaging (40%), construction materials (20%), and textiles (13%).

Low weight and specific properties such as thermal and electrical isolation and favorable gas-barrier properties are important advantages explaining the wide use of polymers and composites in vehicles, wind turbines, construction business, packaging, and electronics.

The most important polymers in Europe and their contribution to total production of polymers are PO (PE and PP; 48%), PVC (11%), PET (8%), PS (8%), and PU (7%). These materials (price <2 € per kg) also form the major fractions of polymer waste. To improve performance (e.g., UV resistance, impact strength) of polymers, additives or polymer blends are used. These factors can make recycling of EOL streams more difficult.

Market shares of less popular polymers such as polycarbonate, polyimide, or polyether ether ketone are naturally significantly smaller. Recycling of these polymers requires in most of the cases special equipment. Owing to their prices ($>$ 4–10 € per kg) they are normally recycled almost exclusively by the producers themselves or by specialized services. Very rarely can such materials be found in mixed streams unless they were initially mixed with or encapsulated in other polymers.

In general, virgin polymers demonstrate better properties than recyclates and the market price of the former creates a natural upper limit for the price of the reused material. This price difference is one of the key factors in market relevance of recycled polymers. The production price of virgin materials is determined by the oil price, which has increased significantly in the last few years. The latter issue has made recycling more economically viable.[10] Moreover, environmental costs of polymer manufacturing, such as CO_2 emission, should be taken into account and compared with corresponding effects of recycling.[75] However, a standard evaluation system has still to be developed and generally adopted.

Another nuance worth to be mentioned is that compatibilization of two or more polymers forming a waste stream can lead to the appearance of an advantageous combination of properties and/or new properties, which is/are present in the initial material.[76] For example, contamination of PLA with linear low-density polyethylene results in a significantly improved impact resistant when these two polymers are compatibilized.[77] It may even lead to a possible price premium for recycled materials.

Moreover, information about availability, quality, and sustainability of recycled polymers can also play a significant role. This positive trend may continue into the future with the help of R&D: technological progress may decrease recycling costs through advances in process efficiency and significant improvements in the quality of recycled materials.[10]

5.2. Packaging materials

Packaging, with its market share of 40%, is the biggest application of plastics. The most important polymers used in packaging are PO, especially PE in the form of foil, and PET, which is used predominately in drinking bottles and flacons, which have a very short lifetime of about two months.

In many countries, plastic packaging is collected separately from the rest of the waste. In most of the container parks, there are also special systems for hard plastics, foils, and Styrofoam.

Used industrial packaging (which is normally clean enough and with known content) and post-consumer packaging (which is frequently very contaminated with remains of packed materials) are easily available and, therefore, an important source of recyclates.

The application of recyclates for food packaging is rather limited because of high safety requirements: toxic chemicals can be adsorbed into the polymers and diffuse later into the food. However, recycled polymer parts that have not come into direct contact with food can still be used.[78] Moreover, with sufficient cleaning, it is possible to reuse polymers in food packaging without limitation as demonstrated with PET.[79]

5.3. Construction materials

Construction is the second biggest application of plastics with a market share of 20%. In contrast to packaging, construction materials (pipes, frameworks, insulation…) and interior elements linked with building (carpeting, shades, mattresses…) have an average lifetime of more than 10 years. Therefore, manufacturers' efforts within the field of ecodesign of such articles can have an impact on recycling only on a long-term basis.

Taking into account its big scale and the existing demand for building materials, construction can be considered as a potentially large and promising area for the application of recyclates. The most frequently used polymers in construction are PVC (doors, frameworks, cables, pipes), PU and expanded polystyrene foams (insulation materials), and PO (pipes, carpets, geotextiles).

Certain waste streams, for example, PVC, are sorted directly on the construction site.[80] Discarded PVC products are collected selectively in many countries. A project by European PVC producers Recovynil has been started to advance collection and recycling of used PVC. Stichnothe and Azapagic[81] revealed the environmental benefits (e.g., less CO_2 emission) of using recycled PVC in new window frames. This approach is still in its embryonic state, and suitable market stimulation is needed for its development and implementation. Another important polymer in this context is HDPE. Lu and Korman conducted a study that demonstrated the potential of recycled HDPE reinforced with industrial hemp fiber for the use in construction.[82] It is also interesting to mention that recycled PS has been proven by Wang and Meyer to be usable as a substituent for sand in cement mortar.[83]

5.4. Textiles

With 13% of the market share, textiles are also an important source of man-made polymers. The share of synthetic textile fibers continues to grow. Reasons for this are an increase of the world population and a general increase in wealth in the BRIC countries (Brazil, Russia, India, and China), where textile consumption per capita is higher, shifting from natural to man-made materials (e.g., wool carpets are being replaced by PP carpets), higher hygienic awareness, which requires more disposable nonwoven towels, and a growing number of technical textile applications (pipes, carpets, geotextiles, materials for cars).

A relatively high portion of the textiles creates fresh opportunities for recycled polymers to be reintegrated into end products. For example, the Hong Kong Green Label Scheme encourages fabrication of new textile products (http://www.greencouncil.org) from reused polymers.

Interesting research has been conducted in South Korea by Kim and co-workers: they mixed recycled PET (obtained from discarded PET bottles) supplied by the TK Chemical Corporation with virgin PET for the production of PET fibers.[84] One of the positive results of their approach is an improved thermal stability of the final material.

5.5. European market data

In 2009, almost 25 million tons of post-consumer waste were collected in Europe. Specific governmental initiatives (taxes, legislature, etc.) and rising environmental awareness in the societies results in an increased volume. More than 90% of collected materials are thermoplastics and approximately 55% of these polymers are POs (PE and PP). Seventy percent of all collected polymeric materials are components of used packaging.

A part of collected post-consumer polymeric waste (exact quantities vary from country to country and fluctuate between 1.2 and 22.2%) were mechanically recycled to raw materials in 2010. Another fraction was thermo-recycled (1.5–31.5%), and the rest was landfilled (2.7–45.8%).[85]

Conversion of collected waste into feedstock, materials, and energy is influenced by the following factors:

- selectivity of collecting
- purity grade
- difference between prices of recyclates and virgin materials
- economic demand in certain countries for streams of specific plastics.

Secondary mechanical recycling is one of the most popular methods of recycling. In Europe, there are approximately 3000 companies dealing with mechanical recycling, and approximately 100 companies that receive mechanically processed recycled plastics. This type of recycling results predominantly in intermediary products or half fabricates such as pellets and flakes. Only 13% is directly integrated into end products, which are mostly low-value floor coverings, grilles, and plant pots.[86] However, the amount of mechanically recycled materials has grown annually by more than 10% over the last couple of years. The reasons for this are effective collection of drink packaging and improvement of related technological processes.

According to the Institute for Prospective Technological Studies of the European Commission, there is an annual capacity in the EU of 5 million tons for mechanical recycling and only 50000 tons for chemical recycling. Existing consumption of 62 million tons per annum in Europe dwarfs both numbers and existing systems cannot fulfill even 10% of the demand for reused polymers.[87] Currently, only around 30% of all collected polymeric waste are effectively converted into feedstock and new materials.

For example, in Flanders recycling of polymers is executed only partially within the country: 27% of the collected material is recycled abroad. In 2007, 84000 tons of used packaging were exported for recycling, which made Belgium the fifth biggest exporter in Europe.[87]

Organization of a recycling system is defined by local legislature, rules, application of certain fiscal rules (e.g., so-called "green points"[10]), and habits. In Europe, the recyclates market is certainly not yet mature: a more intensive and efficient interaction is needed between recycling businesses and end-product producers. The following aspects clearly require attention:

- most of the recycling companies are small and medium enterprises with a limited capacity
- availability of desired recyclate and flow of recycled materials from recycling companies to industrial recipients are frequently seriously hampered; if a supplier is uncertain, then export of recyclates will be preferred or already established specific contacts with eventual recipients will be used
- for a company processing recyclates, quality of input material is of very high importance to manage its own production.

A dramatic increase in the demand for plastics (especially for food packaging, construction, agriculture, and nonwoven hygiene products) and a great availability of EOW and EOL streams in Europe should become important assets for our companies. Intensification and optimization of recycling can also decrease the dependence on oil-based raw materials.

Consolidation and integration of the complete value chain are essential to limit costs of waste collection, processing, and application of recycled materials and to create a high enough added value to an end product. All of these aspects are substantial for keeping new value chains economically feasible. Momentarily, a direct cooperation between manufacturers, retailers, and recyclers is still unusual in the EU. It results in an inefficient transfer of information about the exact content of the product. This phenomenon seriously hampers the development of the recycling industry.[88]

Conversion of used short-lifetime packaging in products with a long lifetime is a very interesting option for the sustainable development with regard to, among others, reduced consumption of natural resources and energy or lower CO_2 footprint. For example, a large fraction of PET bottles are converted into PET textile fibers, which are frequently integrated into fleece products.[89] This can be a clothing item with a lifetime of more than three years or a (car) carpet felt with a lifetime of more than seven years. Moreover, producers of drink bottles are becoming more and more interested in self-recycling their own products into new bottles. This specific PET recycling has increased the price of recycled PET, which is momentarily comparable with the price of virgin PET.

A large part of collected polymers with a high calorific value is currently recycled mostly for energy recuperation as mentioned above (through simple incineration, as fuel for cement furnaces and for metal recycling) or depolymerized by thermocracking into feedstock used inter alia in petrochemical industry.

Some plastics are halogenated and form highly toxic dioxins when incinerated. Because of this, such materials are less suitable for energy recuperation. European producers and processing plants of PVC have recently created some new recycling efforts aimed at both hard and soft PVC. The Vinylplus program is one example; a minimum of 800 000 tons of PVC are planned to be recycled by 2020.

In contrast to mono-component materials, separation, purification, and recycling of thermosets, mixed materials, composites, coated and laminated plastics, and textiles remain a big challenge. Various methods have been developed for small-scale recycling of such complex materials, but they are too selective, difficult, and not yet economically feasible. Incineration, export, and landfilling remain unfortunately still common. Through legal amendments, societies are trying to limit or stop these activities.

6. Outlook

The speed of waste generation is expected to increase in the future owing to a growing world population, increasing living standards, and consequently, increasing demand for polymers.[90] Polymers continue to replace traditional materials (wood, glass, metal, etc.) because of their lower weight, flexibility, and simple processing. The plastics industry has been hampered by the global recession in 2008, but a steady growth has been detected since 2009.[12] The rate of recycling of polymers is expected to exhibit a trend similar to their production.[10]

The existing recycling business is mainly determined by economic interests with less attention paid to environmental issues. However, new legislations are expected to improve the current situation and increase the incentives to recycle.[12] Moreover, it is more economically advantageous to apply intensive processes with reduced waste generation.[90a] A thorough life-cycle analysis will become a useful tool for strategic planning and estimation of technological processes and it can give a boost for the production of goods from recycled materials.[74]

The amount of incinerated waste is expected to decrease: incineration can be a solution to reduce landfill volumes, but does not reduce the demand for fossil fuels as most of the industrial polymers are made of oil products.[91] Furthermore, this method has negative environmental and health-related side effects because of the emission of toxic gasses.[92] The latter problem can be at least partially solved by the use of catalysts to oxidize noxious gasses in situ.[93] Therefore, design of new active and selective catalysts for these oxidation reactions can significantly contribute to the solution of the recycling problem in the future.

Current trends reveal that regulations to reduce dumping at sea have been relatively successful. However, the rising demand for plastics is expected to lead to a worsening of the existing situation with a significant increase in plastic debris volume anticipated to occur even in the deep sea.[2] Therefore, a creative solution is needed for the challenge of efficient collection and reuse of polymeric waste from the oceans.

Curbside collection schemes, a waste collection system for domestic waste, can be complemented by a new “on-the-go” and “office recycling.” Bring schemes are less efficient unless people are highly environmentally conscious or a direct deposit refund is provided. The public attitude is determined, among other factors, by responsible usage of terms such as “recyclable” and “recycled” by companies and governments: overstated claims can undermine confidence.[10]

On the other hand, it is essential to limit plastics consumption, for example, through usage of high-quality products with long lifetimes (shopping bags, head phones), and to develop more bio-based and biodegradable alternatives in the future. This way, waste accumulation would be partially prevented. In general, societies and industry have to pay attention to the cradle-to-cradle loop closure, which envisages that all products are fully recyclable or biodegradable.[94]

Further improvement of the online detection of polymer type and subsequent automatic separation are expected to advance recycling efficiency and eco-friendliness. Collection of single-polymer products, for example, in rigid containers can significantly simplify recycling: no separation or isolation step would be required.[10,95]

Another promising method is the incorporation of molecular fragments into polymer chains, which enables depolymerization by an external trigger. For example, integration of light-sensitive fragments into polymer chains can be used to induce and improve UV-initiated degradation.[96] On the opposite side, further development of stabilizing additives[15] containing antioxidants and light stabilizers and their wider implementation in recycling may help to preserve the chain length of reused polymers and, consequently, the initial level of performance. Therefore, future research in these opposite fields can be very useful for polymer recycling.

Development of recycling technologies should be coupled with research on the combination of both the most effective and environmentally benign developments.[12] It is especially important for the recycling of composites purposely designed to be stable even under extreme conditions.[97] For this type of materials it may be reasonable to identify pioneering ideas in the future to be able to efficiently isolate inorganic constituents after use. In one such example, Kamavaram et al. reported successful recycling of an aluminum metal matrix composite through electrolysis in 1-butyl-3-methylimidazolium chloride.[98]

Biomass starts to be considered as a raw material for new biodegradable plastics (PLA, starch-based materials). A big-scale introduction of such materials to the market, which is possible in the future, would require large volumes of bio-based feedstock. Currently, only 5% of the European chemical production uses raw biological material.[99] Amongst those, half of all textile applications is already bio-based.[90a] Subsequently, a serious adjustment of waste management will be essential to ensure efficient recycling of non-biodegradable bio-based polymers and the controlled degradation of biodegradable plastics.[90b,100]

Furthermore, gasification of biomass combined with conventional plastics into fuel gasses is a low-threshold technology: it increases recovered content of hydrogen gas and decreases the yield of toxic carbon monoxide.[101] Another interesting approach has been applied by Pang and co-workers on a lab scale: They successfully performed biodegradation of a PP/thermoplastic starch blend by burying it in soil.[102] In the future, this or a similar techniques of mixing bio- and synthetic polymers for recycling may be applied on a large scale for a wide spectrum of discarded polymers.[96] Likewise, more research on breeding of plastic-degrading microorganism strains is also a potential solution.[96,103] Later, it may be possible to introduce them for example into plastic land fill zones after careful testing of their impact on the environment. Thus, further development of fundamental knowledge of the processes occurring in gasification, biodegradation of non-biodegradable plastics in soil, and plastic degradation by microorganisms are needed to widen the available options for dealing with the polymer waste problem.

Mixed plastics still remain one of the biggest challenges of current waste management. Processing of such blends without prior separation normally leads to products with poor mechanical properties.[10] Prospective solutions can be compatibilization and the dissolution/reprecipitation method.[19a] Another option would be catalytic feedstock recycling.[33d,104] This method is, in principle, economically feasible,[12] and for example, development of more efficient and selective catalysts[3,105] including enzymes[96] can improve the applicability of this route in the future. Therefore, further research in polymer compatibilization and catalytic/enzymatic depolymerization can have a major impact.

Radiation can be also used to improve feedstock recycling of various waste types.[106] For example, Zhao et al. studied the pyrolysis of PP after exposure to γ-rays from ^{60}Co in air. They observed that pyrolysis can then be conducted at lower temperatures, allowing better control over the final products.[107] Similar techniques could be tested on plastic blends to establish applicability, to develop a better understanding of the underlying processes, and to develop more efficient techniques.

Ionic liquids (ILs) provide an alternative approach within the context of feedstock recycling. Seddon and co-workers performed efficient catalytic cracking of PE to light alkanes in chloroaluminate(III) ILs.[108] Kamimura and Yamamoto depolymerized polyamide plastics in several ILs, underlining the recyclability of the latter ones.[109] Use of ILs in general reduces the required temperature, pressure, and amount of catalyst required for a reaction.[110] The development of benign ILs for these applications and efficient separation technologies to recover the reaction products would certainly offer real tangible progress and potentially have a large impact.

7. Concluding Remarks

In this Review, we have discussed various established recycling technologies and examples of their big-scale implementations. However, the problem of plastic waste still remains to a large extent unsolved as many fundamental issues, for example, plastic blends, have not been solved both scientifically and economically. Moreover, logistical issues such as garbage collection schemes and interaction between recycling businesses and recyclate recipients are not always well managed.

The above-mentioned problems result at present in vast amounts of discarded polymer materials, especially in third-world countries. Moreover, water areas, such as lakes and oceans, also become significantly contaminated.

Therefore, more R&D activities are required to reverse this increasing waste problem. They should include large-scale tests and careful economic analyses. More attention has to be paid also to less-known techniques, such as radiation methods, compatibilization, cross-linking, and application of ionic liquids. The latter ones are expected to become significantly more economically attractive in case of their wider industrial application and efficient r-use in the future.[110a,111] In general, application of lab-based methods may lead to the development of new unexpected but at the same time practical solutions for the recycling industry.

List of Abbreviations

EOL	end of life
EOW	end of waste
EPDM	ethylene–propylene diene rubber
IL	ionic liquid
HDPE	high-density polyethylene
NR	natural rubber
PC	post-consumer
PC/BPA	polycarbonate made from bisphenol A
PE	polyethylene
PET	poly(ethylene terephthalate)
PLA	polylactic acid
PO	polyolefines
PP	polypropylene
PS	polystyrene
PU	polyurethanes
PVC	poly(vinyl chloride)

Keywords: plastics · polymers · recycling · textiles · waste management

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Received: August 23, 2013
Revised: December 9, 2013
Published online on May 8, 2014