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Polymer Recycling – Status and Perspectives

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INTRODUCTION

Newspaper headlines like "Used plastics turn into business" [1], "Planned recycling capacities are much bigger than the collected tonnage" [2] or the statement "At least for Germany the recovery of plastics has to be considered in principle as being solved" [3] may surprise in relation to the still continuing discussion about recycling and recovery of plastics. This the more, as government legislation actions in the mid-80's and following regulations first led to decisive problems for plastics processors, converters and consumers and then multiple efforts were started at many places to avoid and reduce and to recover polymer waste. In Germany, a collection and recovery system called DSD (Duales System Deutschland) was established and manufacturers of automobiles experimented with dismantling and materials recovery plants.

The most important objective of recycling is saving of resources. Necessary recycling cycles (circulations) going from the chemical feedstock over the raw material and the product to the final waste at the end of the product life can be of different quality (Fig. 1).

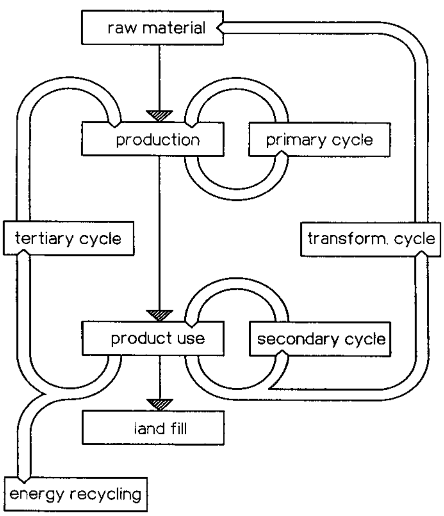

Fig. 1: Recycling cycles

Four recycling cycles have to be differentiated. In the primary cycle, waste from the production process is directly transformed into a reusable material. In general this is called "in-plant recycling". In the secondary cycle, potential waste is used in a new or another product. An example for this is a worn car tire which is now being used as a fender at the quay of a harbor. The multiway bottle is also included according to the above definition in the secondary cycle. The tertiary cycle, or material (mechanical) recycling, includes production and product usage as well as preparation of wastes and reuse as

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secondary material. The chemical feedstock recycling of wastes and their new usage as secondary materials is the fourth recycling cycle, also called conversion cycle.

With the length and duration of the recycling cycle, the energy consumption for preparation and transport increases which, in turn, has a direct influence on the economics and ecological value of the selected recycling method.

FRAMEWORK OF PLASTICS RECYCLING

Polymers are a group of organic macromolecular materials with a very broad and diversified spectrum of properties. The present existence of multiple (and hard to count) types of polymers and their very broad and diversified application spectrum definitely raises some problems concerning their collection and processing during recycling. To discuss this, it is good to keep in mind first that just about all polymers are derived from crude oil (Fig. 2).

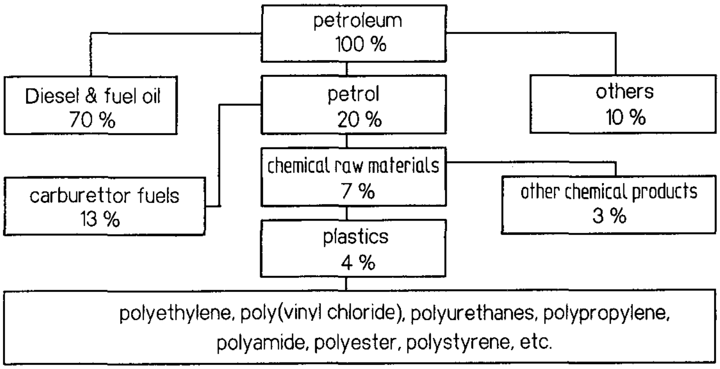

Fig. 2: From petroleum to plastics

This figure might be known but it is of significant importance in relation to very frequent, rather emotional discussions about plastics and their recyclability. Analyzing the content of that figure by applying a so-called ABC-analysis to reduce the consumption of oil and thus to save energy, the necessary savings have to start with car fuel and heating oil. The German Airlines (Lufthansa) consumed in 1989 1.3 % of all the fuel used for transportation in Germany. These 1.3 % were equivalent to 29 million ton/year of kerosine. In relation to this, there was an amount of 0.8 million ton/year of plastics waste from packaging materials [4,5].

AMOUNT OF PLASTICS WASTE PER ANNUM IN GERMANY

The annual plastics waste in Germany amounts up to about 3 million tons. There is a significant difference between the amount of production and that of waste due to the different period of usage of the specific products. Depending on the product, there can be a more or less significant delay of the material flowing back into the recycling cycle.

Today about 65 % of all plastics are used in "long-life" products (e.g., pipes, window-frames). If all plastics with a medium service life of about up to 8 years (automotive, electrical application) are included, the result is that 80 % of all polymers are used in medium and long-term applications. The rest remains of about 20 % are those having a service life lower than one year, which is characteristic of packaging materials [6].

In 1993, about 3 million tons of plastics wastes were generated. The proportion of packaging materials was the biggest with 1.4 million tons. The remaining 1.6 million tons of plastics wastes were coming from automotive applications (180 000 t), electric and electronic products (410 000 t), buildings (180 000 t), plastics synthesis and processing (660 000 t) and non-specified (210 000 t) [6]. Compared with the overall amount of domestic waste from households and industries of about 35.6 million tons [7], the ratio of plastics was about 8 % by weight and about 20 % by volume [6]. In 1996, the DSD system recovered 535 000 t of plastics waste, a part of that being recycled outside Germany. In 1997, all the collected material is supposed to be recycled within Germany.

WHAT HAPPENS WITH THE PLASTICS WASTE ?

Of the 3 million tons of plastics wastes, 1 million tons was deposited (landfill), about 600 000 t being used energetically [8]. More than 1.4 million tons were recycled mechanically [8]. The recycled plastics wastes in 1993 were about 60 % from production and conversion of wastes and about 40 % from the used products [6]. The recovered plastics are finding their market in diversified products. The most important are films, pipes, hoses, construction elements, and packaging products as well as household, industry and consumer products.

RECYCLING METHODS FOR USED PLASTICS

The recycling of plastics wastes can be classified according to the specific objective and technology (Fig. 3).

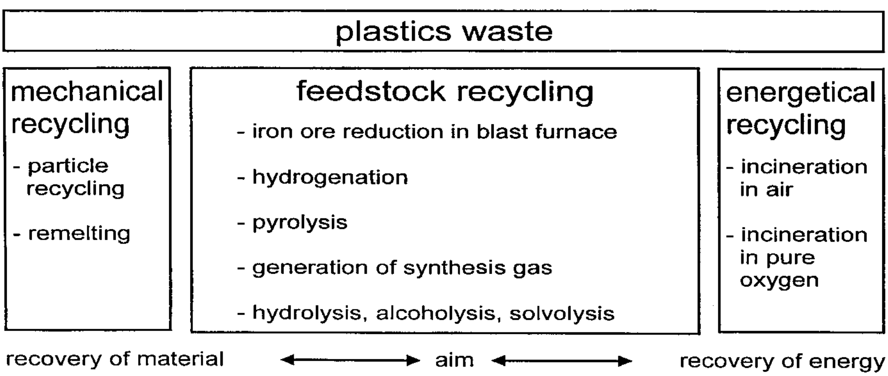

Fig. 3: Possibilities of plastics recycling

Depending on the degree of sorting, degree of contamination and the amount of material to be recovered, one has to differentiate between the following recycling processes [6].

MECHANICAL RECOVERY

Mechanical recycling is the domain for well-sorted waste from one (hopefully!) type of polymer as it is often in production and processing (conversion). Mechanical recycling of thermoplastic polymers means a remelting of the used polymer, production of new pellets and conversion into a new product. In general, there is a reduction in the quality of the material due to remelting, contamination and imperfect sorting of the plastics wastes before. That is the reason why this process is best suited for clean, well-sorted and large parts and lots of production wastes. With thermosets, mechanical recycling can be done via particle recycling. The crosslinked thermosets are ground and then added as a filler to new materials [6].

FEEDSTOCK RECOVERY

In feedstock recovery, the costs of sorting and cleaning the plastics wastes can be kept at a minimum. The material is degraded from a macromolecular structure to low-molecular-weight products which can be returned into a refinery or chemical process as a feedstock. The following chemical recycling technologies are used [6]:

- Hydrogenation: In the presence of hydrogen plastics are cracked at temperatures of about 300 - 500 ^{o}C and pressures of 100 - 400 atm. The final product are low-molecular-weight oils and gases which are then processed in refinery/chemical plants.
- Pyrolysis: In this thermal cracking process, polymers are transformed into gaseous, liquid or waxy carbon hydrocarbons at temperatures of about 500 to 900 ^{o}C in the absence of oxygen.
- Synthesis gas: at high temperatures (ca. 450 ^{o}C), plastics wastes together with oxygen are transformed into synthesis gas. The gas can be used for energy generation or for the production of methanol, ammonia and other products.
- Hydrolysis, alcoholysis, glycolysis: Polymers which were synthesized by polycondensation reactions are split back into their original substances.
- Iron ore reduction in blast furnaces: Plastics wastes can be used for the reduction of iron ore (iron oxides). They substitute heavy oil, which is used to save coke. At temperatures of about 2000 ^{o}C, the plastics waste is instantly gasified and acts as a reducing agent (up to 60 %). The rest of it supplies energy.
- Degradative extrusion: The plastics waste is heated in an extruder by conduction and especially by dissipation (shearing) to such high temperatures that the macromolecules are destroyed and low-molecular-weight fractions (gases, liquids) are obtained.

ENERGY RECOVERY

If the plastics wastes are crosslinked, high-filled or are contaminated with problematic substances, the energy recovery is perhaps the most meaningful solution. In the process, the material is burnt and its energy content used to generate steam and electricity [6].

In an optimum recovery of plastics wastes, the described technological processes are equally important in contributing to the recycling of polymers. They are already in use [9] and it is expected that in the near future, the attitude of certain groups of our society to the plastics will change if it is understood that the described three recycling options definitely give more possibilities to recover than it is feasible for other groups of materials (e.g. steel). It can be foreseen, though it still might look a little grotesque today, that polymers will be accepted as *those* materials which are really recyclable.

SELECTED ASPECTS OF MECHANICAL RECYCLING

So far the mechanical recycling has been mainly applied to thermoplastic materials since they allow a new transformation into a melt or a solution which enables an easy processing. Thermosets and elastomers cannot be treated that way due to their crosslinked molecular structure; this often leads to their reuse via energy recovery.

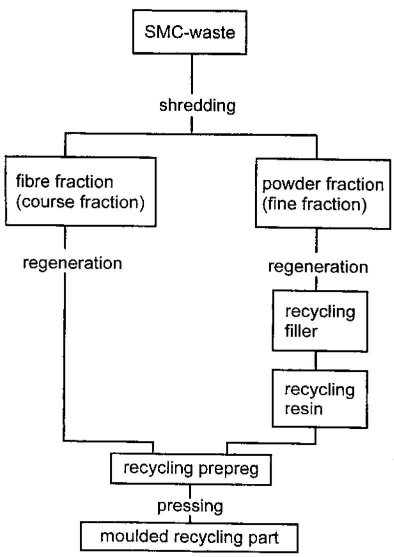

Fig.4: Particle recycling of sheet moulding compound waste

Nevertheless, it is worth mentioning that for glass-fiber-reinforced thermosets, a recovery company has been set up. The initiators of this company called ERCOM are German sheet moulding compound (SMC) and bulk moulding compound (BMC) manufacturers. The reinforced parts are collected and ground to a powder and short-fiber fractions and again used as fillers in SMC/BMC (Fig. 4) which even improve mechanical properties of the newly compounded material (Fig. 5) [10]. The prerequisite for this impressive example is a good sorting and a low degree of contamination of the recycled material.

Returning to thermoplastics, the recycling of one sorted-out type does not pose any severe technical problems. But it still has to be kept in mind that molecular degradation during the recovery affects the product quality. This can, for instance, be seen by studying the long-term behaviour of the material for pressure-loaded polyethylene pipes as given in Fig. 6 [11].

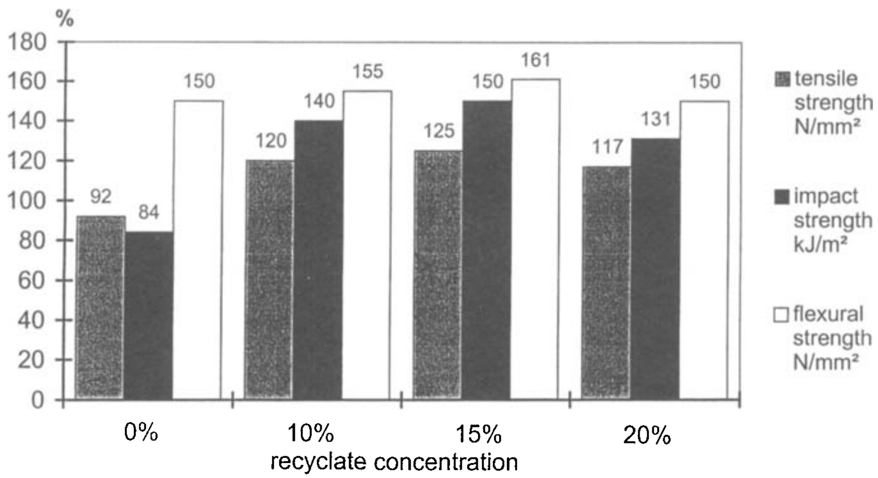

Fig. 5: Sheet moulding compound properties depending on recyclate concentration

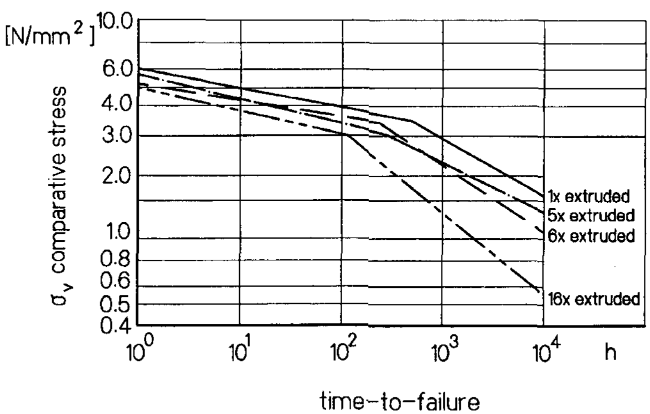

Fig. 6: Creep-rupture test of internal pressure on pipes of repeatedly extruded PE [10]

Therefore it is not possible, in most cases, to expect the same quality for the recycled as for the new material. This leads to applications of the material in products which require a lower mechanical performance.

Plastics waste containing mixed and foreign substances are still problematic since the identification, separation, sorting and cleaning of such materials is from the economical (and often also ecological) point of view not meaningful. Even if mixed polymer fractions contain no foreign substances like oil, paper, metal, their recovery is perhaps difficult. One of the reasons might be a different spectrum of processing temperatures (Fig. 7) [12] which again requires a good sorting; another reason might often be a rather poor compatibility of the individual polymers.

type of plastics		processing range	melt temperature [°C]
polystyrene	PS	wide	180 - 280
polyethylene soft	LDPE	wide	160 - 260
polyethylene hard	HDPE	wide	200 - 300
polypropylene	PP	medium	230 - 270
poly(vinyl chloride)	PVC	very narrow	180 - 210
polyamide	PA 6	narrow	230 - 280
polyamide	PA 66	very narrow	260 - 320
polycarbonate	PC	narrow	280 - 320

Fig. 7: Selected processing temperatures for injection moulding [12] (For high-quality brands of the same type, the melt is more viscous and therefore a higher processing temperature is needed)

Compared with other materials, the distance between macromolecules is rather large in polymers, which imparts them a low density and makes them permeable to many substances, a part of which being absorbed. This again creates certain problems in recovery and requires special equipment like vented extruders to recycle HDPE material from "gasoline-soaked" automotive fuel tanks.

The preparation technologies in mechanical recovery of plastics wastes consist in general of identification, sorting, grinding, washing, drying and finally extrusion and pelletizing (Fig. 8) [13].

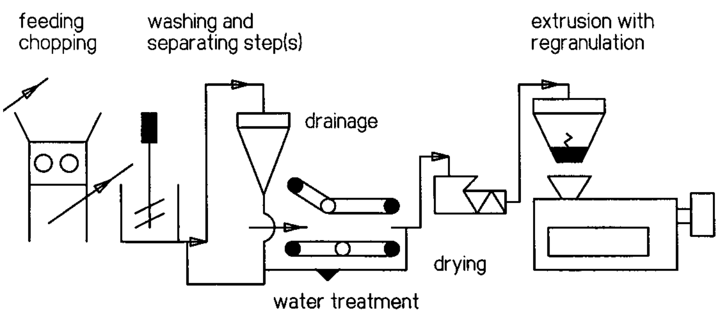

Fig. 8: Process diagram for a plastic preparation and compounding unit [13]

The extrusion step allows an upgrading of the recovered material by adding fibers, mineral fillers, stabilizers, pigments, flowing aids, compatibilizers, etc. (Fig. 9) [14].

The market for recycled thermoplastics has been growing since several years. In particular the demand for high-quality materials cannot be satisfied by the plastics recycling industry. Many questions on influences of polymer mixtures and contaminations on material properties and processability are still open. Therefore, a research group called MARECK (Material recycling of non-reinforced thermoplastics) has been established at the Aachen University of Technology (RWTH Aachen), funded by the German Research Foundation DFG (Deutsche Forschungsgemeinschaft) [15].

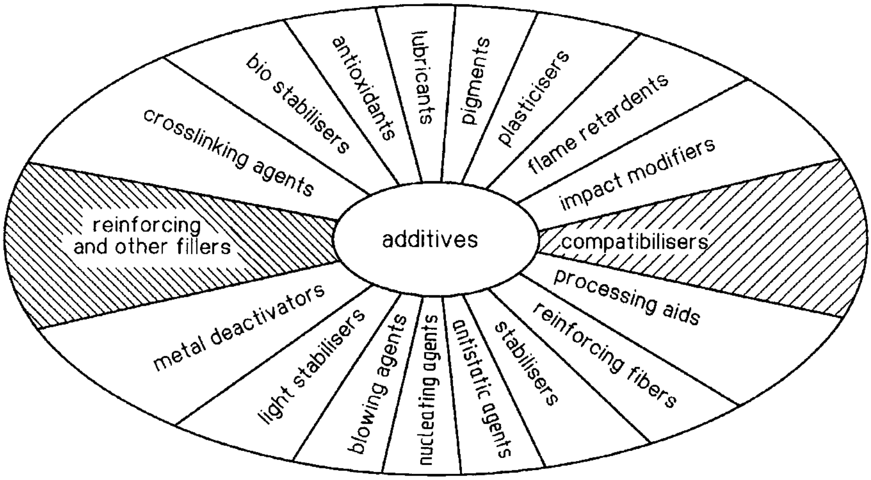

Fig. 9: Plastics additives [14]

To give an extensive contribution to the complex problem, the group covers the entire recycling process, beginning with pretreatment and separation of plastics, identification of plastics by infrared spectroscopy, chemistry and chemical analysis up to reprocessing and regranulation of plastics (Fig. 10) [15]. Therefore the group involves the four institutes of the RWTH Aachen [15].

The quality improvement already starts in the pretreatment of the plastics. Several methods to separate plastics have been developed and analyzed. Specifically in the fields of electrostatic and pneumatic table separation, extensive research has been done to separate the polymers and to remove contaminations such as paper and aluminium and others [15].

For the analysis of plastics, near infrared spectroscopy (NIR) is used. Various methods have been implemented to correlate and evaluate the spectroscopical data. These evaluation methods in combination with precise analytical instrumentation are the basis of an effective quality control system for polymers. NIR spectroscopy is used on line in the pretreatment as well as in the reprocessing by extrusion to detect the composition of the material. In addition, it is used off line to analyze the material in an input monitoring before reprocessing. Clearly, such a technique is not applied at three positions of the recycling process but the goal is to find out at which place it is the most effective and also the most economical [15].

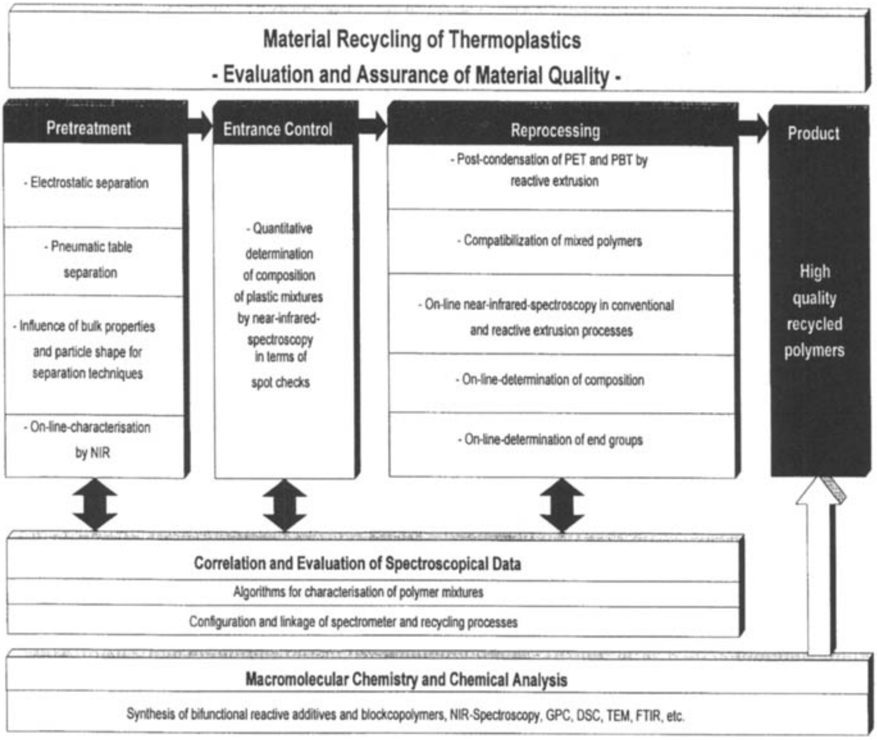

Fig. 10: Material recycling of thermoplastics [15]

The reprocessing of the plastics is the step following pretreatment on the route to a recycled high-quality material. Several approaches have been pursued in this area. For polycondensates, it is possible to increase their molecular weight by reactive extrusion. Extensive work on postcondensation of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) with melt degassing and bifunctional reactive additives has been done [15].

By conventional extrusion, model mixtures of different polymers and potential contaminants have been processed and later on, also real package waste fractions from the DSD which are mainly mixtures of polyolefins. Material tests have been done to find out the influences of the material composition on its quality and to estimate the effort which has to be taken in pretreating the plastics. Within the near future, on-line NIR will be used to determine the composition in the extrusion process [15].

Quite an impressive amount of material is being directly recycled within the plastics processing plant. Non-contaminated and well defined production waste is ground and directly fed back into the extruder or injection moulding machine. During processing, polymers are more or less degraded depending on the thermal and mechanical (shearing) loading, which negatively influences the properties. Therefore, there is always an uncertainty about how much a recycled (or just ground) material may be added to a new material without changing significantly the properties of the products. Most converters follow in this situation the advice of the raw material manufacturers, mixing new material with a maximum of 15 - 30 % reground.

Figure 11 also shows that not all mechanical properties of a product change with repeated (four times) processing. In these examples, only the impact properties are dramatically influenced. From this it also follows that one specific testing method is perhaps not sufficient to describe the performance of a recycled material.

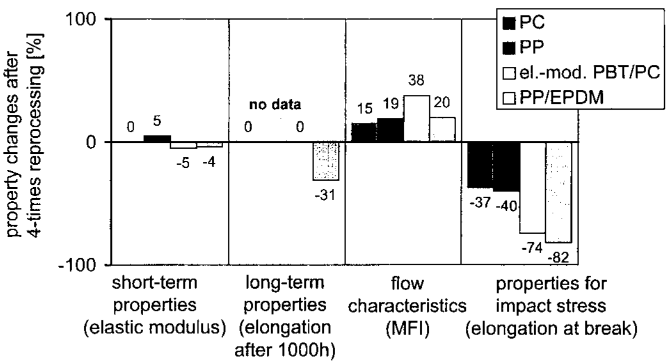

Fig. 11: Influence of repeated processing for injection moulding of various thermoplastics

In the past, we studied the mechanical performance of mechanically recycled plastics and could find the following rules of thumb [16].

- Very often during remelting/reprocessing, not all product properties are changed; often, the former application range of the material is not restricted.
- The use of recycled polymers has to be analyzed critically if impact and oscillating (dynamic) loading conditions occur in application.
- Maximum purity of the polymer type in the recycled material should be achieved, if possible.
- If there is significant molecular degradation during processing, the recycled material should be considered a "new" one, which requires an adaptation of the processing conditions.
- If contamination cannot be avoided, it has to be checked whether they can be considered as "faulty spots" in the product initiating early failure.
- Mixing recovered and new material might lead to satisfying material properties in a specific product application.

- To determine the profile of properties of a recovered material, the analysis of the molecular degradation or a single mechanical test is mostly not sufficient.
- High-speed tensile and impact tests are suitable for rapid understanding the influence of contamination and molecular degradation on the mechanical properties of the product.

These remarks concerning mechanical recycling should not hide the fact that only 15 - 20 % of the collected plastics waste of the future is handled this way. A much bigger proportion will be recycled by the feedstock (chemical) or energy way.

SELECTED ASPECTS OF FEEDSTOCK AND ENERGY RECYCLING

An interesting material for recycling is poly(methyl methacrylate) (PMMA). Although its quantities are small relative to standard plastics, the recycling problem has been a subject of considerable interest for many years. This is due to the relatively high market prices of PMMA.

As with most thermoplastics, post-consumer products made from PMMA can be ground and reprocessed by remelting (except for cast glass). But even with production scrap, which is usually clean and sorted, the recycled material shows a serious loss of quality. Even slight contamination and thermal degradation lead to a severe deterioration in optical quality. This form of material reprocessing is therefore referred to as downcycling [17].

In addition to this method, there is another option with PMMA in which the polymer molecules are broken down into their starting monomer. In this depolymerization, the polymerization reaction can be almost completely reversed. If appropriately purified, the monomers can be reused for polymerization to PMMA virgin material [18].

A number of processes for the depolymerization of PMMA has been known, such as dry distillation [19], the use of superheated steam as a heat transfer medium [20], melting in single-screw extruders and feeding into a pyrolysis reactor [21], and fluidized-bed pyrolysis [22]. However, the method most frequently used is depolymerization in molten metal and metal salt baths [23,24]. The various methods differ in their efficiency in terms of energy input [17].

With thermal and mechanical energy input, depolymerization of PMMA can be carried out on a corotating, closely intermeshing twin-screw extruder (Fig. 12). This type of machine allows continuous operation of the process. The PMMA waste is fed through a gravimetric metering station, melted in the extruder and further heated to depolymerization temperature. The corotating twin screws permit a particularly effective input of thermal and mechanical energy through the use of kneading blocks and left-hand thread elements.

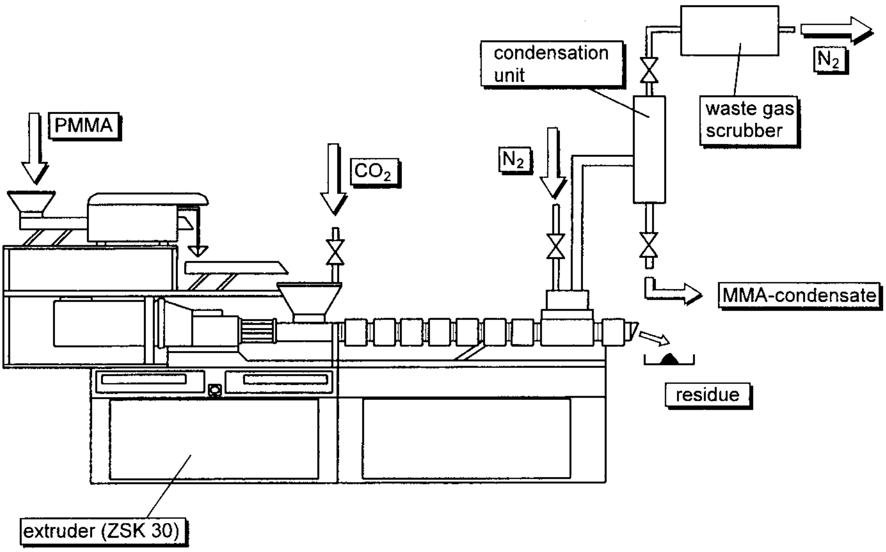

Fig. 12: Extrusion plant for depolymerization of PMMA waste [25]

The released monomer gases are removed via a vent that leads into a condensation unit. When the gas has condensed at atmospheric pressure below about 100 °C, it can be stored in the liquid state. The closely intermeshing twin screws have a self-cleaning action. Thus residues of non-depolymerized PMMA, contamination and extraneous polymers do not impair the continuous operation [25].

As can be seen from Fig. 13, up to 98 % of the MMA monomer could be recovered from the PMMA waste at processing temperatures between 380 and 400 °C [26]. The melt output rate in the tests was 5 kg/h and the specific energy input at maximum reaction temperature was 1.5 kWh/kg. The conversion curves for different PMMA fractions were relatively close, with the most effective conversion being with the cast PMMA (glass) sheets.

A crucial factor for feedstock recycling is the purity of the recovered monomer. This depends on the condition and origin of the waste fractions [26]. The purity values obtained in the tests were determined by capillary gas chromatography. In all cases they were between 89 and 97 % [17].

The degradative extrusion process is perhaps also an interesting option to prepare mixed plastics wastes in a way that a liquid stream is directly conveyed into a blast furnace to use the degraded polymer as a reducing agent for the iron ore and also as an energy source.

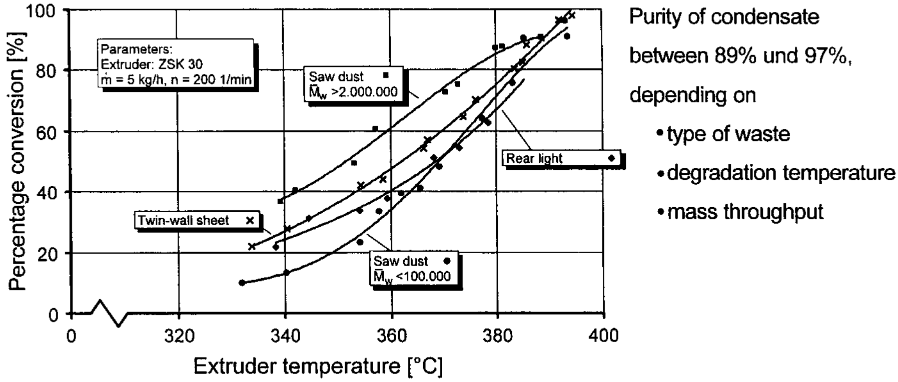

Fig. 13: Percentage conversion for various PMMA waste fractions [26]

Logically, mechanical and feedstock recovery require energy. Whatever the recycling process is, it has to be kept in mind that the costs of additional energy for recycling have to be lower than those for a new material. Ecological balances sometimes help to answer this rather complex question. Anyway, it can be stated that with highly contaminated (difficult to sort) waste materials, the energy recovery by burning them instead of oil or gas (which still could be a good source for synthesizing new polymers) is the most logical as well as ecological approach.

OUTLOOK

Within one decade of extreme activities, quite a bit has been achieved in polymer recycling but there are still challenges for science and transfer of findings into novel technologies in our industries. Nevertheless, the many and other options (more than other materials have) in polymer recycling are contributing to improvement of the acceptance of polymers in our societies.

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