Polyester Recycling

Based on: http://www.polyester-technology.com/index.html - Collection of Publications - "Recycling Concepts for Polyester"

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1. Kinds of polyester recycling

Polymer recycling always means that the polymeric material was already transformed, somehow, into semi-finished or end products and will be reused for production of similar or identical products. When recycling polyethylene terephthalate or PET, two ways generally have to be differentiated:

A: The chemical recycling into initial raw materials purified terephthalic acid (PTA) or dimethyl terephthalate (DMT) and mono ethylene glycol (MEG) where the polymer structure is destroyed completely, and

B: The mechanical recycling where the initial polymer properties are being maintained or reconstituted.

Chemical recycling will become cost-efficient only applying high capacity recycling lines of >> 50,000 tons/year. Such lines could only be seen, hitherto, within the production sites of very large polyester producers. Several attempts to establish such chemical recycling plants are made but without resounding success till 2008. Even the promising chemical recycling in Japan became not an industrial break through till now. The two reasons for this are at first the difficulty of consistent and continuous waste bottles sourcing in such a huge amount at one single site and at second the steadily increased prices of collected bottles. The prices of baled bottles increased between the years 2000 and 2008 from about 50 Euro/ton to over 500 Euro/ton in 2008.

Mechanical recycling or direct circulation in the polymeric state is operated in most diverse variants today. These kinds of processes are typical of a small and medium-sized industry. Cost-efficiency can already be achieved with plant capacities within a range of 5 000 – 20 000 tons/year. In this case, nearly all kinds of recycled-material feedback into the material circulation are possible today. These diverse recycling processes are being discussed hereafter in detail.

Besides chemical contaminants and degradation products generated during first processing and usage, mechanical impurities are representing the main part of quality depreciating impurities in the recycling stream. Due to the trend that recycled materials are increasingly introduced into manufacturing processes, which were originally designed for new materials only, efficient sorting, separation and cleaning processes become most important for high quality recycled polyester.

2. Impurities and material defects

The number of possible impurities and material defects which accumulate in the polymeric material is permanently increasing - when processing as well as when using polymers - taking into account a growing service life time, growing final applications and repeated recycling. As far as polyester is concerned, the defects mentioned can be sorted in the following groups:

Reactive polyester OH- or COOH- end groups are transformed into dead / not reactive end groups, e.g. formation of vinyl ester end groups through dehydration or decarboxylation of terephthalate acid, reaction of the OH- or COOH- end groups with mono-functional degradation products like mono-carbonic acids or alcohols. Results are decreased reactivity during re-polycondensation or re-SSP and broadening the molecular weight distribution.

The end group proportion shifts toward the direction of the COOH end groups built up through a thermal and oxidative degradation. Results are decrease in reactivity, increase in the acid autocatalytic decomposition during thermal treatment in presence of humidity.

Number of poly-functional macromolecules increases. Accumulation of gels and long-chain branching defects.

Number, concentration and variety of non polymer-identical organic and inorganic foreign substances are increasing. With every new thermal stress, the organic foreign substances will react by decomposition. This is causing the liberation of further degradation-supporting substances and coloring substances.

Due to service life of products made of polyester in the presence of air (oxygen) and humidity, as well as supported by ultraviolet light, hydro peroxide groups build up at the polymer surface. During an ulterior treatment process hydro peroxides are a source of oxygen-radicals which are source of oxidative degradation.
Destruction of hydro peroxides is to happen before the first thermal treatment or during plasticization and can be supported by suitable additives like antioxidants.

Taking in consideration the above mentioned chemical defects and impurities, there is ongoing a modification of the following polymer characteristics during each recycling cycle, which are detectable by chemical and physical laboratory analysis.

In particular:

→ Increase of COOH end groups
→ Increase of color number b
→ Increase of haze (transparent products)
→ Increase of oligomer content
→ Reduction in filterability
→ Increase of by-products content such as acetaldehyde, formaldehyde
→ Increase of extractable foreign contaminants

→ Decrease in color L
→ Decrease of intrinsic viscosity (IV) or the dynamic viscosity
→ Decrease of crystallization temperature and increase of crystallization speed
→ Decrease of the mechanical properties like tensile strength, elongation at break or elasticity modulus
→ Broadening of molecular weight distribution

3. Purification and decontamination – the most important processing steps during polyester recycling

The success of any recycling concept is hidden in the efficiency of purification and decontamination at the right place during processing and to the necessary or desired extent.

Generally, the following applies: the sooner foreign substances are removed, in the process, and the more thoroughly this is done, the more efficient the process is.

The high plasticization temperature of PET in the range of 280°C is the reason why almost all common organic impurities such as PVC, PLA, polyolefins, chemical wood-pulp and paper fibers, polyvinylacetate, melt adhesive, coloring agents, sugar and proteins residues are transformed into colored degradation products which, in their turn, might release reactive degradation products additionally.
Then, the number of defects in the polymer chain increases considerably. Naturally, the particle size distribution of impurities is very wide, the big particles of 1 000 - > 60 µm - which are visible by naked eye and easy to filtrate - representing the lesser evil since their total surface is relatively small and the degradation speed is therefore lower. The influence of the microscopic particles, which – because they are many - increase the frequency of defects in the polymer, is comparable bigger.

The motto "What the eye does not see the heart cannot grieve over" is considered to be very important in many recycling processes. Therefore besides efficient sorting the removal of visible impurity particles by melt filtration processes is playing a particular part in this case.

In general one can say that the processes to make PET bottle flakes from collected bottles are as versatile as the different waste streams are different in their composition and quality. In few of technology there isn't just one way to do it. There are meanwhile many engineering companies which are offering flake production plants and components and it is difficult to decide for one or other plant design. Nevertheless there are principles which are shearing most of these processes. Depending on composition and impurity level of input material the general following process steps are applied:

→ Bale opening, briquette opening
→ Sorting and selection for different colours, foreign polymers especially PVC, foreign matter, removal of film, paper, glass, sand, soil, stones and metals.
→ Pre-washing without cutting
→ Coarse cutting dry or combined to pre-washing
→ Removal of stones, glass and metal
→ Air sifting to remove film, paper and labels

→ Grinding, dry and / or wet
→ Removal of low density polymers (cups) by density differences
→ Hot wash
→ Caustic wash
→ Caustic surface etching, maintaining IV and decontamination
→ Rinsing
→ Clean water rinsing
→ Drying
→ Air sifting of flakes
→ Automatic flake sorting
→ Water circuit and water treatment technology
→ Flake quality control

See also [2]
"Current Technological Trends in Polyester Recycling", ISBN-10: 3-00-019765-6; PETplanet Publisher GmbH, Heidelberg, Germany
ISBN: 978-3-9807497-4-; 9th International Polyester Recycling Forum Washington / Sao Paulo

and [3]

"Polyester Bottle Resins Production, Processing, Properties and Recycling" by Dr. Ulrich K. Thiele; PETplanet Publisher GmbH, Heidelberg, Germany ISBN: 978-3-9807497-4-9; chapter H, 2007

4. Recycling to the initial raw materials

Glycolysis and partial glycolysis

In the field of glycolysis and partial glycolysis, the polyester which has to be recycled is transformed into an oligomer by adding ethylene glycol or other glycols during thermal treatment. The aim and advantage of this way of processing is the possibility of parting the mechanical deposits - this system being directly connected to the glycolysis - through a progressive filtration; the filtration fineness of the last filtration step has a decisive effect on the quality of the end product.

Taking partial recycling with partial glycolysis as an example, it is to be demonstrated how bottle waste can successfully be recycled in a continuously operating polyester line with which pellets for bottle applications are manufactured.

The task consists in feeding 10% bottle flakes and maintaining at the same time the quality of the bottle pellets which are manufactured on the line. This task is solved by degrading the bottle flakes - already during their first plasticization which can be carried out in a single- or multi-screw extruder - to an IV of approx. 0.30 dl/g by adding small quantities of ethylene glycol and by subjecting the low viscosity melt stream to an efficient filtration directly after plasticization.
Furthermore, temperature is brought to the lowest possible limit. In addition, with this way of processing, the possibility of a chemical decomposition of the hydro peroxides is used by adding a corresponding P-stabilizer directly when plasticizing.

The destruction of the hydro peroxide groups is, with other processes, already carried out during the last step of flake treatment for instance by adding H_3PO_3 , see also [4] DE-Patent DE19503055.
The partially glycolysed and finely filtered recycled material is continuously fed to the esterification reactor, the dosing quantities of the raw materials are being adjusted accordingly.

The treatment of polyester waste through complete glycolysis to convert the polyester to bis-beta hydroxy-terephthalate, which crystallizes or which could be vacuum distilled and can be used, instead of DMT or PTA, as a raw material for polyester manufacture, has only executed on experimental production.

Hydrolysis

Recycling processes, through hydrolysis of the PET to PTA and MEG, are operating under high pressures under supercritical conditions. In this case, PET-waste will be directly hydrolyzed. Purification of crude terephthalic acid will be carried out by re-crystallization in acetic acid / water mixtures similar to PTA purification. Industrial-scale lines based on this chemistry have not been known to date.

Methanolysis

Methanolysis is the processing which has been practiced and tested on a large scale for many years. In this case, polyester waste is transformed with methanol into DMT, under pressure and in presence of catalysts. After this an efficient filtration of the methanolysis product is applied. Finally the crude DMT is purified by vacuum distillation. Because polyester production based on DMT shrunk tremendously and with this DMT producers disappeared step by step during the last decade the methanolysis is only rarely carried out in industry today. See also [5] Stoyko Fakirov; „Handbook of Polyester“, ISBN 3-527-30113-5 – Wiley-VCH, Weinheim, 2002, pages 1223 ff

5. Processing examples for recycling polyester

Recycling processes with polyester are almost as varied as the manufacturing processes based on primary pellets or melt.
Depending on purity of the recycled materials polyester can be used today in most of the polyester manufacturing processes as blend with virgin polymer or increasingly as 100% recycled polymer.
Some exceptions like BOPET-film of low thickness, special applications like optical film or yarns through FDY-spinning at > 6000 m/min or microfilaments and micro-fibers are produced from virgin polyester only.

a) Simple re-pelletizing of bottle flakes

This process consists in transforming bottle waste into flakes, in drying and crystallizing the flakes, in plasticizing and filtering, as well as in pelletizing.

Product: amorphous re-granulate of an IV in the range of 0.55 - 0.7 dl/g, depending on how complete pre-drying has been done.
Special feature: acetaldehyde and oligomers are contained in the pellets; the viscosity is low, the pellets are amorphous and have to be crystallized and dried before further treatment.
Processing: Spinning to non-woven,
Staple fibers,
Filaments
Carpet yarn
A-PET film for thermoforming
Packaging stripes
BOPET packaging film
Bottle resin by SSP
Engineering plastics
Addition to PET virgin production

Choosing the re-pelletizing way means having an additional conversion process which is at the one side energy intensive, cost consuming and causes thermal destruction. At the other side the pelletizing step is providing the following advantages: Quality unitizing
Processing flexibility
Product selection and separation by quality
Intermediate quality control
Intensive melt filtration

b) Manufacture of PET-pellets for bottles (B-2B) and A-PET

This process is, in principle, similar to the one described above; however, the pellets produced are directly (continuously or discontinuously) crystallized and then subjected to a solid state polycondensation (SSP) in a tumbling drier or a tube reactor. During this processing step, the corresponding IV of 0.80 – 0,085 dl/g is rebuild again and, at the same time, the acetaldehyde content is reduced to < 1ppm.

The fact that some machine manufacturers and line builders in Europe and USA make efforts to offer independent recycling processes, e.g. the so called bottle-to-bottle (B-2-B) process, such as URRC or BÜHLER, aims at generally furnishing proof of the "existence" of the required extraction residues and of the removal of model contaminants according to FDA applying the so called challenge test, which is necessary for the application of the treated polyester in the food sector.
Besides this process approval it is nevertheless necessary that any user of such processes has to constantly check the FDA-limits for the raw materials manufactured by him for the process he is running.

c) Direct conversion of bottle flakes

In order to save costs, one is working on the direct use of the PET-flakes, from the treatment of used bottles, with a view to manufacturing an increasing number of polyester intermediates. For the adjustment of the necessary IV, besides an efficient drying of the flakes, it is possibly necessary to also reconstitute the IV through polycondensation in the melt phase or solid state polycondensation of the flakes. The latest PET flake conversion processes are applying twin screw extruders, multi screw extruders or multi rotation systems and coincidental vacuum degassing to remove moisture and avoid flake pre-drying. These processes allow the conversion of un-dried PET flakes without substantial IV-drop caused by hydrolysis.

Looking at the consumption of PET bottle flakes the main portion of about 70% is converted to fibers and filaments. When using directly secondary materials such as bottle flakes in spinning processes, there are a few processing principles to obtain.

High speed spinning processes for the manufacture of POY normally need a spinning IV of 0.62 - 0.64 dl/g. Starting from bottle flakes, the IV can be set via the degree of drying. The additional use of TiO_2-masterbatch is necessary for full dull or semi dull yarn. In order for the spinnerets to be protected, an efficient filtration of the melt is, in any case, necessary. For the time being the amount of POY made of 100% recycling polyester is rather low because this process requires high purity of spinning melt.

Staple fibers are spun in an IV-range which rather lies somewhat lower and which should be between 0.58 dl/g and 0.62 dl/g. In this case, too, the required IV can be adjusted via drying or vacuum adjustment in case of vacuum extrusion. For adjusting the IV, however, an addition of chain length modifier like glycol can also be used.

Spinning non-woven - in the fine titer field for textile applications as well as heavy spinning non-woven as basic materials e.g. for roof covers or in road building - can be manufactured by spinning bottle flakes. The spinning IV is again in the range of 0.64 dl/g.

A special field where recycled materials are used is the manufacture of high tenacity packaging stripes - and monofilament. In both cases, the initial raw material is a mainly recycled material of higher IV. High tenacity packaging stripes as well as monofilament are then manufactured in the melt spinning process