Polyester Recycling Industry

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1. Introduction

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 or polyester, two ways generally have to be differentiated:

A: The chemical recycling back to the initial raw materials purified terephthalic acid (PTA) or dimethyl terephthalate (DMT) and mono ethylene glycol (MEG) where the polymer structure is destroyed completely, or in process intermediates like bis-ß-hydroxyterephthalate

B: The mechanical recycling where the original 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, if at all, within the production sites of very large polyester producers. Several attempts of industrial magnitude to establish such chemical recycling plants are made in the past but without resounding success till 2008. Even the promising chemical recycling in Japan became not an industrial break through so far. 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 and price volatility of collected bottles. The prices of baled bottles increased for instance 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 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.

When talking about polyester recycling industry we are concentrating mainly on recycling of PET bottles which are meanwhile used for all kinds of liquid packaging like water, carbonated soft drinks, juices, beer, sauces, detergents, household chemicals and so on. Bottles are easily to distinguish because of shape and consistency and separate from waste plastic streams either by automatic or hand sorting processes. The established polyester recycling industry exists of three major sections which are

1. PET bottle collection and waste separation – waste logistics
2. Production of clean bottle flakes – flake production
3. Conversion of PET flakes to final products – flake processing

Intermediate product from section one is baled bottle waste with a PET content of > 90%. Most common trading form is the bale but also bricked or even loose, pre-cut bottles are common in the market. In the second section the collected bottles are converted to clean PET bottle flakes. This step can be more or less complex and complicated depending on required final flake quality. During third step PET bottle flakes are processed to any kind of products like film, bottles, fiber, filament, strapping or intermediates like pellets for further processing and engineering plastics.

Aside this external polyester bottle recycling numbers of internal recycling processes exist, where the wasted polymer material does not exit the production site to the free market and where the waste is reused at one and the same production circuit. In this way for instance fiber waste is directly reused to produce fiber, preform waste is directly reused to produce performs and film waste is directly reused to produce film.

2. Market

When we examine the development of the polyester recycling market development cross the World, we can find some interesting correlations, impacts and similarities.

As frontier of many industrial developments the USA started the first substantial PET-recycling during the late 70th. Low raw material cost – at that time used PET bottles where rubbish – and environmental activities of a highly developed society have been the major driving forces to develop within a relatively short time an US polyester recycling industry.

The saturation of this development came during the late 90th and the first years of the new century. The achieved collecting level of 20 – 25% became stagnant for several reasons. Mainly driven by the sharply rising prices of baled bottles and the general down trend of the US-textile-industry the interest in PET-recycling shrunk. Driving force behind was the exploding textile industry in China connected to a tremendous price increase of collected/baled PET-bottles.

As point of remembering: During the years 1995 – 2000 the price of one ton baled bottles was between 20 and 50 €. Today one must pay approximately ten times of this price!

Today mainly the brand owners in USA like Coca Cola keeping the PET recycling running on an dissatisfactory level by forcing the bottle producer to apply a fix amount of 10 – 30% of recycled polymer in each new bottle.

Quite different the development in Europe. After a slow start in Europe during 90th other mechanisms came in force which where the very strict plastic waste regulation of Germany like the green dot and the “Verpackungsverordnung” as well as similar EU regulations. Together with a “green – environmental” driven politics and similar movements in public relations Europe was overhauling the USA in collection rate and the total amount of collected PET bottles.

To understand the recycling market better it might be interesting how the source of the collected waste bottles, the PET bottle resin is developing. Table 1 is providing a summary. After this North Americas will lead the resin production till 2010. But looking at table 2 which is showing the estimated PET bottle recycling market development one can see, that the collection rate of the USA will be further stagnant (2006 15% and 2010 16%) Europe in the opposite will increase the collecting rate from 22,7% in 2006 to 28% in 2010.

Completely different the situation in Middle East, Asia, Africa and South America, let us say the low developed or fast developing countries like China or India. Here we see a rapid increase of the collection rates from about 4% in 2006 to 33% in 2010.

Chinese (unofficial) sources are claiming a collection rate of more than 90%! In China because of a large number of very poor migrant workers PET bottles are picked up everywhere they are dropped.

The tables 1 and 2 are providing a complete summary about PET resin production and bottle PET recycling cross the World.

The triumphal procession of the PET bottle started during the 90th of the last century and we have not jet reached the stage of saturation. Table 1 is showing the expected market development of the bottle resin between 2004 and 2010.

Table 1: Bottle PET resin production 2004 – 2010 [1]

PET Resin Capacity [kt/a]	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**
North America	3.685	3.745	3.923	4.595	4.595	4.595	5.000
South America	513	500	500	725	950	950	1.200
Europe	2.411	2.894	3.515	3.766	4.005	4.005	4.205
Africa, Middle East	308	338	499	604	843	843	843
Asia (ex China)	4.107	4.411	4.636	4.636	4.636	4.636	4.636
China	1.469	2.490	3.217	3.255	3.255	3.255	3.255
Total WORLD	**12.493**	**14.378**	**16.290**	**17.581**	**18.284**	**18.284**	**19.139**

The huge potential of PET bottle recycling is becoming obvious by comparing data of resin and flake production in Table 1 and 2. Provided the estimated production amount of 5 Mio t in 2010 is realistic the rate of recycling achieved world wide is a little more than 25% only

Table 2: World PET recycling capacity [1]

R-PET Capacity all in [kt/a]	**1999**	**2002**	**2003**	**2004**	**2006**	**2010**
North America	470	480	500	550	600	800
Europe	211	350	430	680	944	>1200
ME, Asia, South America, Others	218	370	470	680	1 700	3 000
World R-PET Bottle Flakes	899	1200	1400	1 900	3 100	**5 000 ↑ ??**
World PET-resin	7 100	9 900	11 800	12 500	16 300	19 200
Recycling potential	**6 201**	**8 700**	**10 400**	**10 600**	**13 200**	**14 200**

Off cause the data concerning the emergence of collected bottles within several areas of the World are to handle with care, but the trends are becoming obvious and comparable:

- → As higher the standard of living as more difficult the voluntary collection
- → As higher the standard of living as more governmental, political and public pressure are required
- → As higher the price of collected bottles as lower is the incentive to step in polyester recycling processing activities – bottle or flake selling is more easy
- → As higher the price of collected bottles as more trading volume will occur

→ As higher the price of collected bottles as more interesting are final products of high value like for instance A-PET film, strapping, food grade bottle resin or “GREEN” products like staple fiber made of 100 recycle.

→ As higher the flake prices as more attractive are vertical integration from collection to intermediate products like fiber, film, strapping and resin

→ As lower the standard of living (in developing countries) as higher the voluntary collection rate

3. The PET bottle recycling

3. 1. 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℃ is the reason why almost all common organic impurities such as PVC, PLA, polyolefin, chemical wood-pulp and paper fibers, polyvinyl acetate, 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 [2]:

→ Bale opening, briquette opening
→ Sorting and selection for different colors, 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

3.2. Impurities and material defects

The number of possible impurities and material defects which accumulate in the polymeric material is increasing permanently - 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 recycled PET bottles are 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 [3].

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

The recycling of PET-bottles is meanwhile a industrial standard process which is offered by a wide variety of engineering companies. Technology provider of PET recycling processes are collected in Table 3 [3].

Table 3: Collection of hard ware and technology provider from components to turn key recycling lines

Conmpany	Country	Internet site
Sorema - Plastic Recycling Systems	Italy	www.sorema.it
Amut SpA	Italy	www.amut.it
Herbold Meckesheim GmbH	Germany	www.herbold.com
Sikoplast GmbH	Germany	www.sikoplast.de
Krones AG		www.krones.de
Hunkler Systeme	Germany	www.hunkeler-systems.com
Retech Recycling Technology AB	Sweden	www.redoma.com
OCI GmbH - Navarini	Switzerland	www.navarini.com
Zhangjiagang Xinke Machinery Co., Ltd.	China	http://xinkeplas.fuzing.com
RRT Design & Construction	USA	www.rrtenviro.com
PPS Recovery Systems Ltd	UK	www.pps-ltd.com
Polymer Recovery Systems, Inc	USA	www.prsi.com
United Resource Recovery Corp.	USA	www.urrc.net

4. Processing examples for recycled 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, by drying and crystallizing the flakes, by plasticizing and filtering, as well as by pelletizing.
Product is an amorphous re-granulate of an IV in the range of 0.55 - 0.7 dl/g, depending on how complete pre-drying of PET flakes has been done.
Special feature are: acetaldehyde and oligomers are contained in the pellets at lower level; the viscosity is reduced somehow, the pellets are amorphous and have to be crystallized and dried before further processing.

Processing to:

- Non-woven,
- Staple fiber,
- 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 uniformization
Processing flexibility increased
Product selection and separation by quality
Intermediate quality control
Intensive melt filtration
Modification by additives

b) Manufacture of PET-pellets for bottles (B-2-B) 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 vertical 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 himself for his process.

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 to protect the spinnerets, an efficient filtration of the melt is, in any case is 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. Most of the time a blend of virgin and recycled pellets is used.

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 ethylene glycol or diethylene 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 within a range of 0.58 - 0,65 dl/g.

One field of increasing interest where recycled materials are used is the manufacture of high tenacity packaging stripes - and monofilaments. 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

5. Recycling back to the initial raw materials

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 separating the mechanical deposits directly and efficient through a progressive and stepwise 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 which is manufacturing pellets for bottle applications.

The task consists in feeding 10%- 25% bottle flakes and maintaining at the same time the quality of the bottle pellets which are manufactured on the line. This aim is solved by degrading the PET 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 possible 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].
The partially glycolysed and finely filtered recycled material is continuously fed to the esterification or prepolycondensation reactor, the dosing quantities of the raw materials are being adjusted accordingly.

The treatment of polyester waste through total glycolysis to convert the polyester to bis-beta hydroxy-terephthalate, which is vacuum distilled and can be used, instead of DMT or PTA, as a raw material for polyester manufacture, has been executed on an industrial scale in Japan as 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 applying for instance supercritical water steam. 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 recycling process which has been practiced and tested on a large scale for many years in the past. 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. The methanolysis is only rarely carried out in industry today because polyester production based on DMT shrunk tremendously and with this DMT producers disappeared step by step during the last decade. See also [5].

Literature:

The publication “Polyester Recycling Industry” is mainly based on:

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

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[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

[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] DE-Patent DE19503055.

[5] Stoyko Fakirov; „Handbook of Polyester“, ISBN 3-527-30113-5 – Wiley-VCH, Weinheim, 2002, pages 1223 ff