SENBIS
POLYMER INNOVATIONS

Evaluating recycled PET grades and making them Fit for Purpose

Inhoud

1. Why this white paper?

The PET market is highly dynamic these days. Consumer awareness about plastic waste is shifting, the PET collection, separation & refund schemes are gaining ground and the use of single-use disposables is increasingly restricted by EU regulations. These trends both result in an increasing supply and demand volume of recycled PET (rPET) on the market. The total recycled PET (rPET) volume demand in Europe is expected to increase from about 1.1 million ton/year in 2015 to about 1.5 million ton/year in 2022 [3]. The demand for virgin PET in Europe is expected to be stable at around 3.5 million ton/year [1]. Therefore, the importance of rPET in the total PET demand in Europe is steadily increasing.
However, recycling PET can be challenging. Recycling processes need to be effective in purifying PET waste streams from solid impurities, minimizing the occurrence of non-intentionally added substances (NIAS) like limonene or acetaldehyde, discoloration, and thermal degradation. Therefore, solutions and expertise is needed to control and monitor the challenging aspects during PET recycling in order to obtain the right price-performance ratio.
This paper will provide insights how recycling processes affects the rPET quality. For each challenge, solutions and expertise will be described to control and deal with these challenges in order to create new business opportunities.

2. The differences in mechanical and chemical recycling of PET

PET can be recycled by means of:

- Mechanical recycling (with or without solid state polymerization)
- Chemical recycling

2.1. Mechanical recycling

The most economical and common way to recycle PET is mechanical recycling. During mechanical recycling, the collected and sometimes colour sorted PET is shredded into PET flakes. The flakes are washed and dedusted to remove surface contamination, labels and caps effectively. Afterwards, the PET flakes are molten and melt-filtrated to remove pigment and contaminations in the molten state as much as possible. Afterwards, PET granulate can be obtained. After mechanical recycling, the rPET molecular weight or IV can be further increased by means of Solid-State Polymerization (SSP). SSP is a process executed at high temperatures but below the melting point of PET at zero oxygen level with nitrogen purging or at deep vacuum. During the SSP a polycondensation reaction occurs “repairing the polymer chains” while volatiles (and volatile contaminants) are removed. This results in a desired and controlled IV and in a purer rPET that can meet the European (EFSA) food contact demands.

2.2. Chemical recycling

Chemical recycling of recycled PET yields chemically identical rPET like virgin PET made from the original fossil sources. Chemical recycling of recycled PET is done by means of depolymerization of the recycled PET into one of its monomers. Afterwards, the obtained monomers are purified intensively by different purification process technologies. After purification, re-polycondensation of the monomer can take place to polymerize PET again. The obtained chemically recycled PET can chemically not be distinguished from virgin PET made from fossil sources. As a result, chemically recycled PET has identical properties and can be recycled again and again. However, chemically recycled PET is expected to be more expensive than mechanically recycled and virgin PET.

Chemical recycling is not widely applied on commercial scale yet, but it is gaining increasingly more importance due to a large number of start-ups, scale-ups and R&D consortia projects active in this field. Currently, the three mostly applied technologies to depolymerize PET, its obtained monomers, and some companies (NB. not a complete list!) active in this segment are summarized in table 1.

Depolymerization technology	Obtained monomer	Active companies
Hydrolysis	Terephthalic acid (PTA)	BP Infinia Gr3N - Demeto
Glycolysis	Bis(2-Hydroxyethyl) Terephthalate (BHET)	PerPETual Cure Technologies Ioniqa DuPont – Teijin Films
Methanolysis	Dimethyl Terephthalate (DMT)	Eastman Chemical Loop Industries

3. Mechanical recycling challenges

3.1 rPET still contains impurities and mostly shows less properties.

Presence of solid impurities.

When PET is recycled, labels, caps, papers, glue, inks, pigments, dyes, and other polymers needs to be separated from the PET polymer. However, depending on the PET recycling process and the source of recycled PET, solid contaminants will still remain behind to a more or lesser degree. Polymer impurities might affect the intrinsic viscosity, the transparency (haze) and the crystal nucleation rate. As a result, impurities can affect the final rPET properties. In addition, contamination can cause PET filament or foil breakage during respectively yarn and foil extrusion.

Thermal degradation.

During the melting of rPET in the extrusion step, the rPET polymer chains can be broken into shorter chains. This results into a decrease in the intrinsic viscosity and molecular weight distribution. Consequently, this yields in a decrease in mechanical properties. In addition, thermal degradation can cause the occurrence of non-intentionally added substances, such as acetaldehyde.

Senbis solutions

3.2 How Senbis can help you improving and controlling the rPET quality.

Senbis can offer several solutions to improve and control the rPET quality. These solutions are:

- Our unique quantification of solid particle impurities in PET: Partisol (particles in solution)
- Standard filtration test
- Solid State Polymerization (SSP)

3.2.1 Unique quantification of particle contaminations: Partisol (particles in solution)

Partisol is based on detection of dirt particles and other contaminants in a solvent. This is a laboratory technique where the rPET flakes, foil or yarn samples are dissolved in the very strong solvent hexafluoroisopropanol (HFIP) with a very low refractive index. The low refractive index results in large contrast between non-dissolved particles (for example PE, PP, PVC, glue, paper) and background, ensuring particle detection with a high sensitivity: The lower detection limit of the particles is about 3 micrometer. An image with some calibration particles is shown in figure 1.

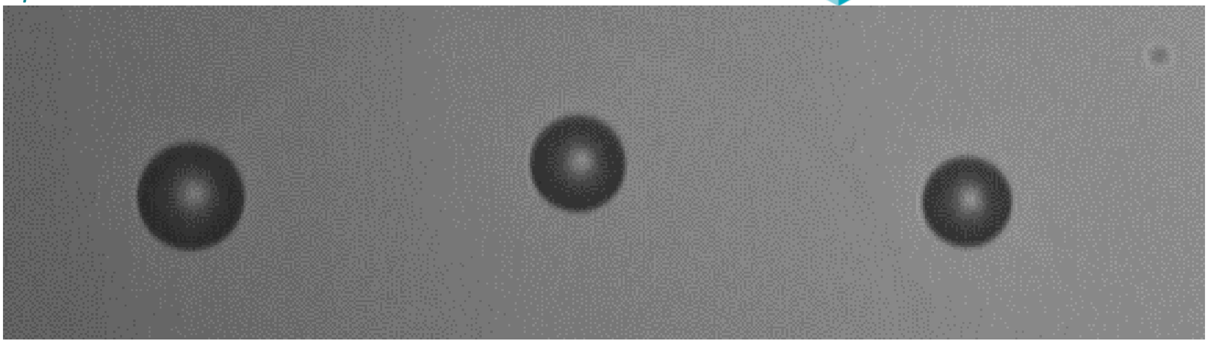


Figure 1: Image of Partisol calibration particles

The Partisol analyses results in a histogram with a particle size distribution of the contaminations, see figure 2. Typically, about 11,000 particles in 10,000 measuring images are detected in rPET samples. In virgin PET, typically about 1,000 particles in 10,000 measuring images are detected. That is significantly lower than in rPET!

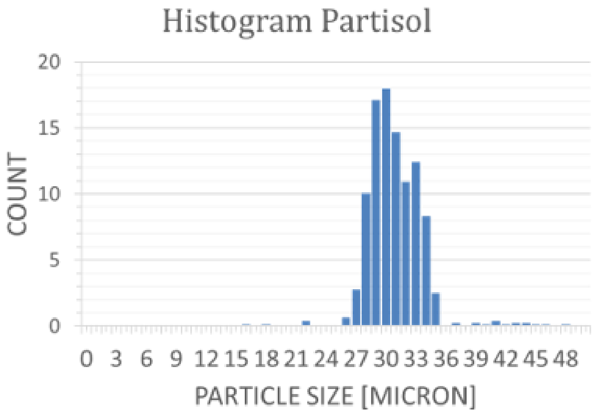


Figure 2. Particle size distribution of a Partisol measurement

3.2.2 Standard melt filtration test

As mechanically recycled PET contains significantly more solid particle impurities than virgin PET, effective melt filtration in PET processing technologies is vital. Performing melt filtration on recycled plastic can have multiple purposes and advantages:

- Basic melt filtration achieves a purer granulate that can be used for critical rPET converting techniques such as yarn spinning and foil extrusion. Depending on the applied mesh size of the filter, melt filtration gives an indication about the purity of the final rPET granulate on an industrial scale.
- By melt filtration you can collect a high concentration of particles on the filter. By means of SEM-EDS electron microscopy examination of the filter residues, the origin & nature of the impurities can be detected. In addition, Senbis can execute the standard filtration test to monitor the degree in pressure

increase during melt filtration in time depending on the rPET process conditions, see figure 3. As a result, the rPET quality can be determined and the rPET process conditions can be optimized.

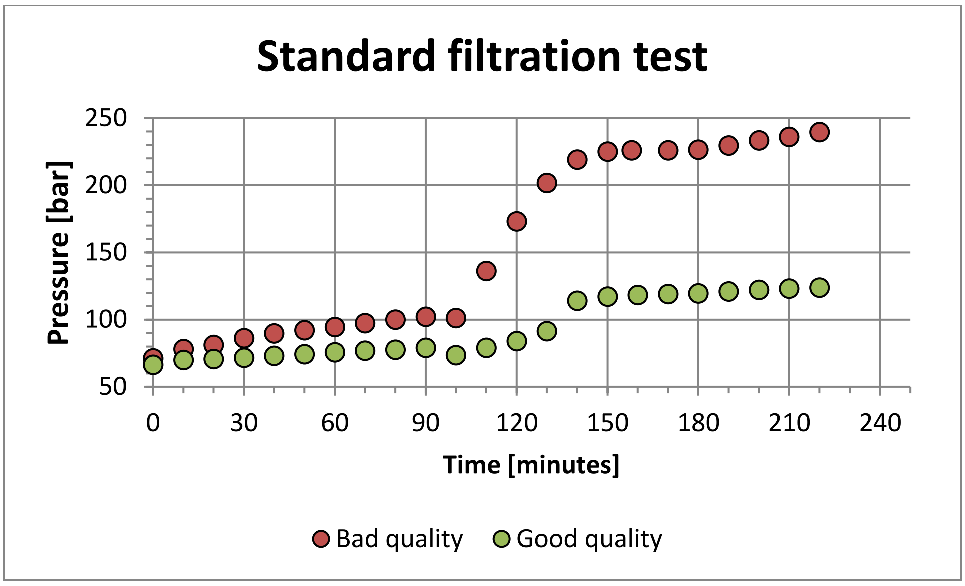


Figure 3: Visualization of increased extruder pressure by pollution for different PET grades

3.2.3 Solid -State Polymerization

Solid -State Polymerization (SSP) of rPET is carried out by heating the rPET at temperatures below its melting point but above its glass transition temperature. Usually, a temperature in the range between 210-230ºC is applied for about 8 hours. Post-condensation occurs and the condensation by-products can be removed by applying vacuum or inert gas. Polymers obtained usually have high(er) molecular weight, low(er) carboxyl end-groups and acetaldehyde content. The intrinsic viscosity (IV) can be increased up to even 1,50. After SSP, the acetaldehyde content can be below 1 ppm compared to 2 – 5 ppm after mechanical recycling of rPET. Therefore, SSP improves not only the rheological and mechanical properties but also the rPET's purity. As a result, by means of SSP high-quality and food-compliant rPET can be obtained for application in beverage bottle or industrial yarns. Senbis can assess the quality improvements of rPET after SSP on lab-scale (3 kg capacity per batch) and pilot plant scale (60 and 120 kg capacity per batch).

Figure 4. Pilot plant scale SSP reactor

4. Chemical recycling challenges

4.1 How to assess high-purity monomers for PET polymerization purposes.

High purity PET monomers after chemical recycling

During chemical recycling of PET, depolymerization of PET waste is a necessary step to obtain one of its monomers, preferably with high yields above 95%. Usually, this appears not to be the most critical step. The most critical step is the purification of the monomer. For purified terephthalic acid (PTA), obtained via PET hydrolysis, a purity of over 99.99% needs to be obtained. The alkali metal content is not allowed to exceed 10 ppm; Chlorine content needs to be avoided completely due to possible corrosion attack of the process equipment. In addition, the PTA color needs to be white and meet strict requirements (b < 2.5). Only by applying high-purity monomers, good and efficient (re-)polymerization of PET polymer can be achieved.

A number of start-ups or companies active in the chemical recycling of PET waste do not polymerize PET polymer in a polycondensation reactor themselves. They license their depolymerization & purification technology or sell the monomers to PET polymer manufacturers. However, it is vital to test the polymerization behaviour of the monomer to show the polymerization effectiveness of the chemically recycled PET.

Senbis solutions

4.2 How Senbis can help you to create chemically recycled PET.

Senbis has a polycondensation autoclave available for trials up to 1kg. Currently we are investigating the options for a bigger pilot plant facility with a capacity of 5 kg per batch. The current autoclave facility has a one-reactor glass vessel. This kind of batch-type operation allows researchers to study the polymerization process parameters (e.g. foaming, discoloration and the influence of catalysts/additives on the polymerization). When finished the polymer is extruded from the vessel and cooled in a water bath. The chemically recycled PET strand is then pelletized into chips. In this way the intrinsic viscosity, thermal behavior and PET color can be assessed. Polyesters can be produced starting from DMT (dimethyl terephthalate) and purified terephthalic acid (PTA). NB. In addition to PET, the autoclave is also suitable to polymerize and assess the technical feasibility of other polyesters such as PEF, PEN, PTT, PBT or PBS.

Figure 5. Polymerization autoclave

5. Yarn spinning of rPET

The proof of the pudding is in the eating. Off all the different polymer processing technologies, yarn spinning is considered one of the most sensitive and critical.

Senbis can perform spinnability trials on rPET granulates as received or we can perform a melt filtration as mentioned above. Flakes are usually first regranulated before processing. Spinning trials can be performed with 100% rPET or with blends (for example with higher quality virgin material). Both the yarn spinning stability as the mechanical performance of the yarn give a good indication of the rPET quality.

The evaluation of the mechanical properties versus the draw ratio is shown in figure 7. The drawing ratio is the ratio of the speed of the front roller to the back roller: The speed of the back roller is higher than of the front roller, causing an additional yarn orientation & tenacity.

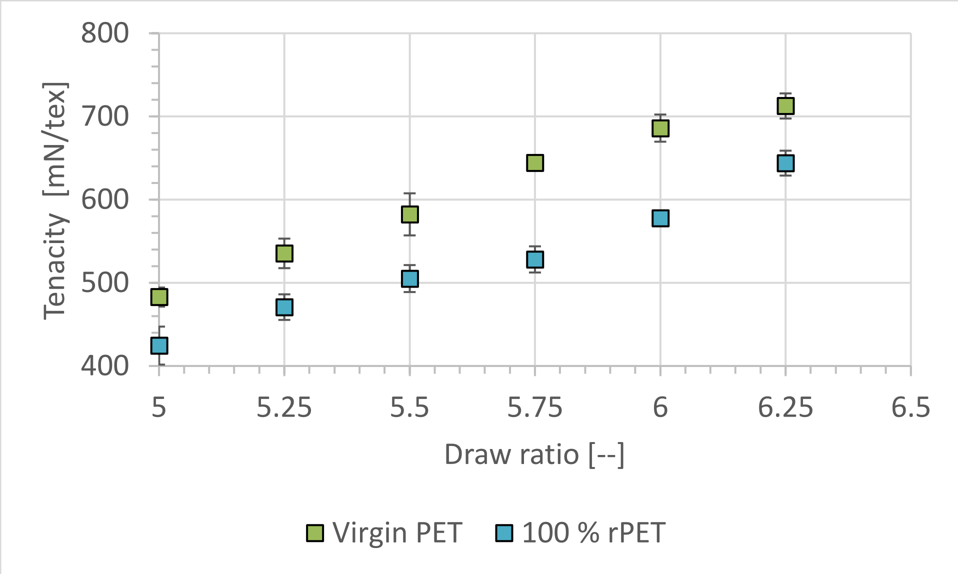
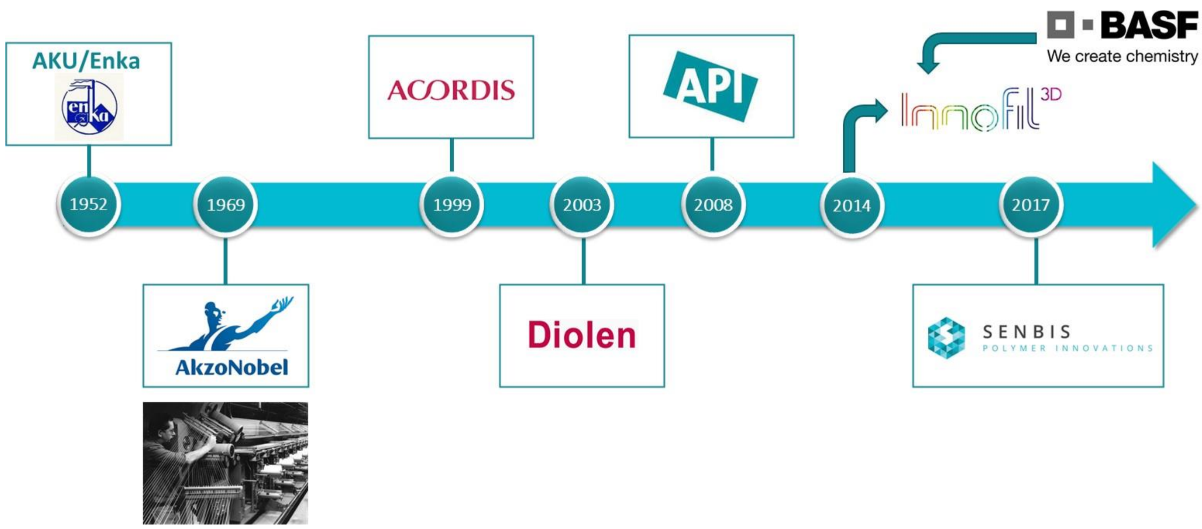


Figure 6: The evolution of the yarn tenacity vs the draw ratio

6. Senbis Polymer Innovations history at a glance

Senbis is a Dutch company that divides its activities between R&D services and the production of sustainable polymeric products. Senbis Polymer Innovations B.V. provides third party research to the plastic industry and Senbis Sustainable Products B.V. produces and sells our own developed sustainable products. Our own products are made out of biodegradable plastics made for applications that have a high likelihood of ending up in nature, where they cause lasting harm to our environment.

Senbis is the continuation of the former R&D department of Akzo Nobel. The combination of decades of experience in fiber and yarn development, the flexibility of a start-up and an extensive modernized lab and pilot plant facility gives us unique innovation potential.



7. Interested to know more about Senbis Polymer Innovations? Please contact us!

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