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# A Review on the Formulation and Rupture Properties of Polyethylene Terephthalate in a Mechanical Recycling Context

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# A review on the formulation and rupture properties of polyethylene terephthalate in a mechanical recycling context

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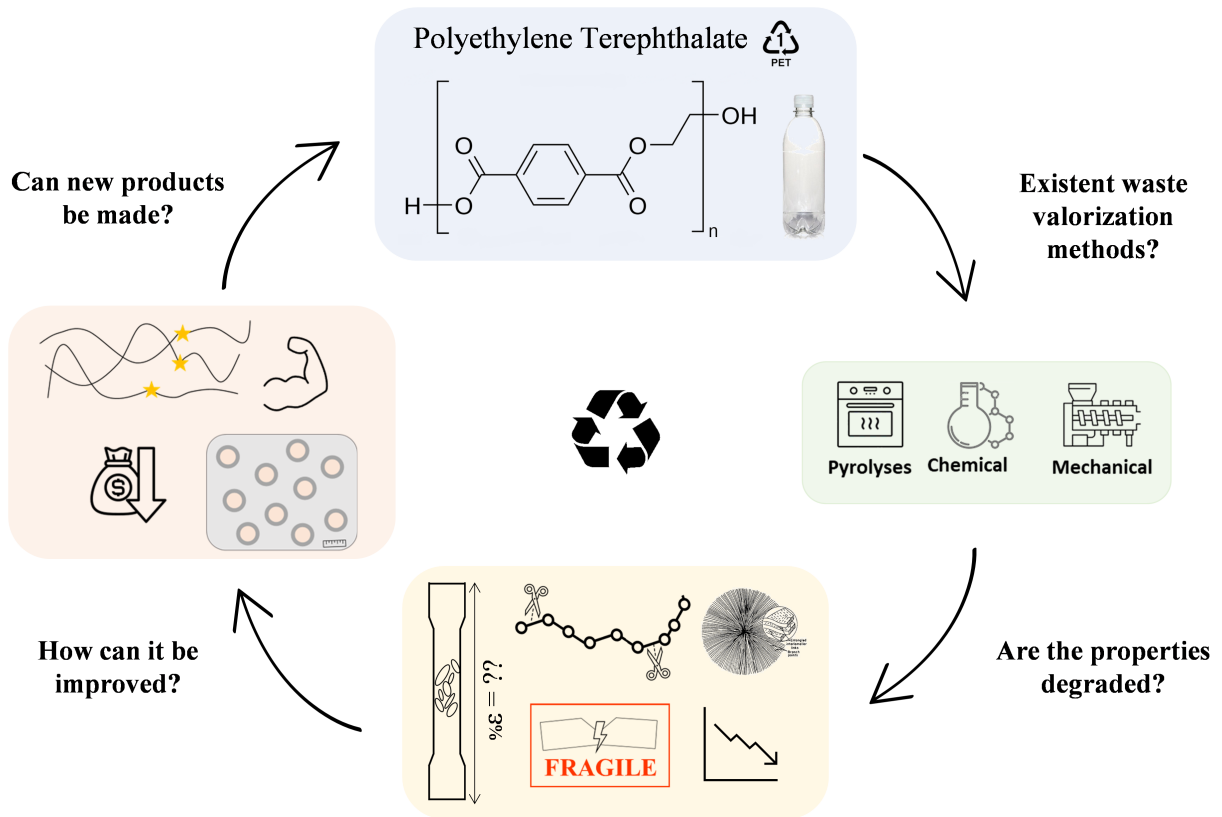
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## Abstract

The environmental stress caused by climate change has provided an impetus to the search for greener solutions. A striking example of this is plastic pollution. One of the main difficulties in finding alternatives is maintaining an ecological balance along with economic viability. Other than reducing the consumption of plastics, recycling is today one useful approach. In this context, polyethylene terephthalate (PET) is in the spotlight. This saturated polyester with unique properties is one of the most used plastics, and its use is increasing year by year. Plus, it is the most recycled polymer in the world. Among different recycling methods used, the well-established equipment for mechanical recycling is today the most efficient process and has the lower carbon footprint. However, despite the effort spent on recycling PET and the extensive number of published papers on this matter, many challenges still restrain its industrial development. One of the reasons for this is a lack of understanding of the structural modifications caused by processing and the effect on the properties of the

final product. This review presents an overview of PET's intrinsic properties, before and after mechanical recycling. By focusing on the mechanical process, the different degradation mechanisms and their effects are described. Widely used reinforcement techniques are explained along with their possible drawbacks. A better view of what is yet to be understood might guide new solutions for PET's processing and reuse.



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## Glossary

- $M_c$  Critical molar mass. 4, 9, 48
- $M_n$  Molar mass in number. 4, 9, 13, 46–48, 58
- $M_w$  Molar mass in weight. 4, 9, 26, 32, 33, 46, 48, 49, 57, 58, 60
- $P_{O_2}$  Partial oxygen pressure. 4, 33
- $T_c$  Crystallization temperature. 4, 20, 45, 61
- $T_{cC}$  Cold crystallization temperature. 4
- $T_g$  Glass transition temperature. 4, 9, 18, 20, 26
- $T_m$  Melting temperature. 4, 9, 18, 20
- $T_{BD}$  Ductile-brittle transition temperature. 4, 50
- $[\eta]$  Intrinsic viscosity symbol. 4, 37
- %RH Percentage of residual humidity. 4, 17, 28, 38
- $\chi_c$  Degree of crystallinity. 4, 20, 32
- 1.3-PBO** 1,3-phenylene-bis-oxazoline. 4, 54
- ATR** Attenuated total reflection. 4, 26
- BDT** Brittle-ductile transition. 4, 50
- BHET** Bis(2-hydroxyethyl) terephthalate. 4, 10, 11
- CBC** N,N'-carbonylbiscaprolactam. 4, 54
- Cp** Heat capacity. 4, 18
- D/L** Diameter over length of an extruder screw. 4, 44–46
- DEG** Dimethylene glycol. 4, 13
- DMA** Dynamic rheological measurements. 4, 55
- DMT** Dimethyl terephthalate. 4, 10, 11
- DP** Degree of polymerization. 4, 11, 12

**DSC** Differential scanning calorimetry. 4, 17–20, 28, 44, 45, 60, 61

**EBA** Ethylene butyl acrylate. 4, 58, 59, 61

**EG** Ethylene glycol. 4, 10, 11, 41

**EPR** Ethylene-co-propylene rubber. 4, 57, 58

**EU** European Union. 4, 8, 35, 36, 60

**FTIR** Fourier-transform infrared spectroscopy. 4, 25, 26

**GC-MS** Gas chromatography–mass spectrometry.. 4, 29

**GMA** Glycidyl methacrylate. 4, 55, 57–61

**IPA** Isophthalic acid. 4, 13

**IPCC** Intergovernmental Panel on Climate Change. 4, 7

**IR** Infrared spectroscopy. 4, 13, 17, 32

**IV** Intrinsic viscosity. 4, 11, 17, 25–27, 43, 52, 54, 58, 59, 61, 62

**M<sub>e</sub>** Entanglement molar mass. 4, 50

**MA** Methyl acrylate. 4, 57, 60

**MAF** Mobile amorphous phase. 4, 44

**MBS** Methacrylate-butadiene-styrene copolymer. 4, 60

**MFI** Melt flow index. 4, 43

**Mt** Million metric tons. 4

**NMR** Nuclear magnetic resonance. 4, 13, 29

**NR** Natural rubber. 4, 59, 60

**PE** Polyethylene. 4, 15, 37

**PEF** Poly(Ethylene Furanoate). 4

**PET** Polyethylene terephthalate. 4, 7–13, 15–17, 19–29, 31–35, 37–49, 52, 54–64

**PLA** Polylactic acid. 4, 51

**PP** Polypropylene. 4, 15

**ppm** Parts per million. 4, 17, 22, 24, 37

**PVC** Polyvinyl chloride. 4, 37, 40, 42, 45, 60

**RAF** Rigid amorphous phase. 4, 44

**rPET** Recycled polyethylene terephthalate. 4, 39, 41, 42, 46, 53, 57, 58, 60–64

**rpm** Rotations per minute. 4, 32, 34, 43, 44, 47, 57, 59

**SAXS** Small angle X-ray scattering. 4, 17, 50

**SEBS** Styrene-ethylene butylene-styrene. 4, 57, 60

**SEC** Size exclusion chromatography. 4, 25, 29, 32

**SEM** Scanning electron microscope. 4, 55

**SSP** Solid state polymerization. 4, 10, 12, 13, 28, 38, 53, 54, 60–64

**TGA** Thermogravimetric analysis. 4, 29

**TPA** Terephthalic acid. 4, 10

**TPP** Triphenyl phosphite. 4, 54, 55

**UV** Ultra-violet (for a wavelength going from 100 to 400 nm). 4, 32, 38, 47, 48

**vPET** Virgin polyethylene terephthalate. 4, 9, 10, 44, 46, 49, 54, 60, 62, 63

**WAXS** Wide angle X-ray scattering. 4, 17

**wt%** Percentage by weight. 4, 12, 13, 26, 27, 37, 53, 55, 57–60

# Introduction

On April 2022, for the first time in history, the climate change that society is facing today was incontestably related to human activities. This was one of the six big findings provided by the sixth report from the Intergovernmental Panel on Climate Change (IPCC).<sup>1</sup> This scientific group, brought together by the United Nations, is responsible for assembling data and monitoring the global conjuncture related to several aspects of climate change. More than 34,000 studies were examined to conclude that the environmental impact is much more widespread and severe than expected. Using the tools of data processing, the IPCC explored different scenarios. Aspects such as greenhouse gas emissions in different socio-economic pathways were used as inputs. These projections allowed a better understanding of the risks of the current way of living, producing, and consuming. In addition, they allowed evaluating the impact of different actions that governments will face at some point. They have shown that some risks related to increased temperatures, loss of biodiversity, and drought, for instance, can escalate much quickly and cause irreversible damage to the ecosystem and to society as a whole.

A striking example of such a deterioration of the environment is pollution by petroleum-based plastics. Plastic products have become a crucial part of our daily lives due to their unique combination of properties, such as resistance, lightness of weight, and relatively low price, when compared to other materials.<sup>2</sup> It is estimated that since the 1950s, 83,000 million metric tons (Mt) of virgin plastic has been produced.<sup>3,4</sup> By 2050, the demand is estimated to quadruple.<sup>4</sup> This trend has become even more acute with the the COVID-19 pandemic, where the amount of polymer-based personal protective equipment, such as masks and latex gloves, skyrocketed.<sup>5</sup>

Plastics are usually meant for a very short life-cycle and mainly for a single use. This poses a challenge for waste management.<sup>3</sup> It is estimated that 79% of the global production has now accumulated in natural environments, such as landfills and oceans.<sup>6</sup> On European beaches alone, 80% of the marine litter is composed of plastics, of which 50% are single-use items.<sup>7</sup> Their very slow decomposition may be a danger to marine life and contaminate the water. Exposure to sunlight and humidity, for instance, can break polymeric chains into small parts. These will form the so-called micro-plastics, which will also be a part of the marine litter in considerable amounts.<sup>7,8</sup>

To modify this reality, countries' climate policies have to be implemented and join the effort to reduce the consequences of human activities. Looking for alternatives to today's linear-based economy, heading to a more circular economy, is certainly one of the pathways to solve some of these problems.<sup>3,6</sup> Focusing specifically on the plastic pollution, the Environment Protection Agency developed strategies to approach a zero-plastic-pollution policy, with seven main actions to be implemented. They consist on minimizing the commercialization of single-use plastics and replacing the petroleum based options by bio-based ones. They also lean on the rising capacity of collection, sorting and recycling of polymeric post-consumer products.<sup>6</sup>

European legislation is already improving in this direction by promoting the use of a minimum amount of recycled resins. For example, Polyethylene terephthalate (PET) bottles starting from 2025 shall contain 25% recycled resin. This amount will rise to at least 30% after 2030. Commercializing single-use plastics for the production of cutlery, straws and



food containers, for example, has also become prohibited in the European Union (EU) since 2022.<sup>7</sup>

In the context of this ecological transition, PET is of a major importance. It is considered as one of the most important polymers for the last two decades because of its extensive use in many of the products of our daily life.<sup>2,6</sup> Its unique characteristics, such as its excellent mechanical properties, thermal stability, action a gas barrier, and transparency, make it the perfect material for uses ranging from packaging to engineering applications.<sup>2,9</sup> Added to its properties, PET is one of the most collected materials on curbside bins.<sup>6</sup>

For these reasons, PET is one the most recycled plastics in the world, representing 40% of the total recycled amount. However, only 9% of the total world production of plastic has really been recycled.<sup>6,9</sup> The primary challenge to increasing this quota is the laborious effort involved in collecting and separating it from other polymers, additives, and contaminants.<sup>6</sup> The second and main problem is modifying PET and other materials into economically reusable forms without losing ecological balance. The difficulty of today's methods of recycling is related to this: either the processes are too expensive to provide an attractive price or the obtained materials are strongly modified and can't be used as new.

Despite these challenges, the massive production of PET since the 1950s has made this material extensively available. This strategic advantage means that all the efforts on the development of new solutions for its recycling and reuse will directly have a more significant impact on society and will gather more interest from industrial actors. Since the 1970s, when the effort to recycle PET began, a lot has been done. But there is still a lack of understanding of the structural modifications caused by reprocessing. Reducing its cost could also be an important step for the democratization of PET recycling and its effect on its further processability and on its final properties.

The present review paper aims to give an overview of the status quo of the recycling of PET and the current state-of-the-art related to the understanding of this very complex material in the literature. The degradation of its properties after mechanical recycling is the focus of this paper. Throughout this study, the terms *reprocessing* and *recycling* will be employed to characterize the various processing cycles applicable to this material. Due to the often unclear origin and lack of control over recycled material, which may involve a blend of different grades, tracking degradation throughout the product's life cycle can be challenging. Consequently, we will specifically highlight instances where this information is well documented, while otherwise, our focus will remain on the degradation resulting from the processing itself. The most used strategies for the reinforcement of the matrix, before or after recycling, will also be discussed. Establishing a relation between structural modification and the mechanical properties of the recyclates may allow the development of techniques for tuning and improving specific drawbacks resulting from the processing.

# 1 Polyethylene Terephthalate

## 1.1 Overview

Polyethylene terephthalate is a semi-crystalline polyester with a large presence in the polymer market. Its linear chemical structure, shown in Figure 1, is composed of a short alkyl chain

and an aromatic ring, which provides the material with rigidity and great cohesion to the molecule.<sup>9,10</sup> These characteristics give this material excellent tensile behavior, significant chemical and thermal stability, the possibility of transparency, and a great permeability barrier for gases. Table 1 summarizes some of the average thermal and intrinsic properties of this material. Most of these can be modified by methods of synthesis and processing, which will notably affect the crystallinity and molar mass.<sup>9</sup>

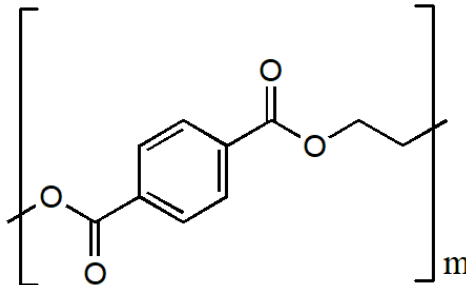


Figure 1: Polyethylene terephthalate repeating unit.

Table 1: Standard intrinsic properties of virgin polyethylene terephthalate (vPET).

Properties	Average values	References
$T_g$ ( $^{\circ}\text{C}$ )	$\approx 76\text{--}83$	9, 11, 10, 12, 13
$T_m$ ( $^{\circ}\text{C}$ )	243–265	9, 10, 12, 11, 13
$\mu$ ( $\text{kg}/\text{m}^3$ )	Amorphous $\approx 1330$ / Crystalline $\approx 1410$	9, 6
$\varepsilon$ (dL/g)	Fibers $\approx 0.55\text{--}0.68$ / Bottles $\approx 0.80$	9, 6
$M_n$ (kg/mol)	Fibers $\approx 15\text{--}20$ / Bottles $\approx 24\text{--}36$	9, 12
$M_w$ (kg/mol)	$\approx 45$ (30–80)	12
$M_c$ (kg/mol)	17 (10–18)	14, 15, 16, 17

The chief demand for PET is found in food applications for the manufacture of transparent bottles and packaging. This accounts for up to 40% of total production.<sup>18</sup> It also arises from other fields, such as the textile industry, as electrical insulators and electronic components, and in the automotive and medical fields, among others.<sup>2,9</sup>

Due to its economic importance, PET accounts for around 8.4% of the total market for plastics, corresponding to a total demand of around 4.14 Mt in 2020.<sup>19</sup> A recent study by the strategic consulting and market research firm BlueWeave Consulting<sup>20</sup> revealed that the global polyethylene terephthalate resin market was 80.9 million tons in 2021. It is projected to reach 114.7 million tons by 2028, with an annual growth rate of 5.2%. The increasing interest in this material can be easily explained by the growing concern for the development of a greener economy. Moreover, the legislative pressure on the plastics market and waste treatment makes it mandatory to find new solutions. Indeed, PET is a non-degradable but recyclable material, that can be easily reprocessed by many techniques.

The significant presence of PET in our daily lives makes this material one of the most recycled polymers in the world.<sup>2,21</sup> As already mentioned, according to a report published

by The Waste and Resources Action Program<sup>22,23</sup> in 2018, PET made up almost 40% of what is recycled in the United Kingdom.<sup>18</sup> But a lot of progress still has to be made in order to extend not only the fields of application of the reprocessed polymer but also to make it economically viable, as nowadays vPET is still much cheaper and has a stabler cost than recycled PET..<sup>9</sup>

Before talking about the recycling process, it is first important to understand the reactions that lead to this widely used material. The next section will, then, be focused on the methods of its synthesis and the experimental conditions for the production of PET.

### 1.1.1 Ways to synthesize PET

Although natural polyesters have been used for a very long time, the first synthesis of PET only took place in 1942, by the Whinfield and Dickson company, in the United Kingdom.<sup>6,12</sup> During the Second World War, PET took an important place in the manufacture of synthetic fibers. But it was only at the end of the 1970s, with the development of the stretch-blow method of molding, that the production of bottles became possible, henceforth the demand skyrocketed.

The manufacture of PET is done by an initial esterification or transesterification, followed by a polycondensation in the melt state. For a further increase in the molar mass, a solid state polycondensation can also take place.<sup>10,12,24</sup> Each one of these stages will be described below.

### 1.1.2 Esterification reaction

Esterification is a reaction between an alcohol and an acid. This takes place in the formation of PET by reacting a terephthalic acid (TPA) with an excess of ethylene glycol (EG) to obtain BHET (see Figure 2). This reaction takes place at temperatures between 240°C and 260°C, as well as with a pressure between 300 and 500 kPa for 3 to 4 hours.<sup>9</sup> The high concentration of terminal carboxyl groups, given by the reactants, makes this mechanism possible without the addition of further catalysts.<sup>25</sup> During this synthesis, the excess of EG, as well as the water formed, are progressively eliminated.

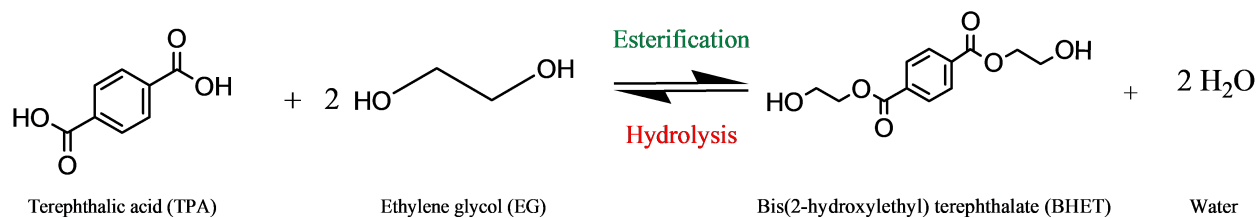


Figure 2: Esterification reaction between terephthalic acid (TPA) and ethylene glycol (EG).

The esterification reaction, depicted in Figure 2 is an equilibrated reaction with hydrolysis. The understanding of this reversible mechanism is very important for the recycling and the degradation processes of this polymer.<sup>12</sup> The prepolymer resulting from a TPA-based process is preferable for a SSP reaction as it produces higher carboxyl end groups when compared to a DMT-based one<sup>26</sup> (see Part 1.1.5 Solid state polymerization below).

### 1.1.3 Transesterification

Transesterification is the second possible way to obtain BHET: it involves a reaction between ethylene glycol (EG) and dimethyl terephthalate (DMT). In this case, a pressure of 100 kPa and temperatures between 160°C and 180°C are necessary, with a residence time of around 3 to 4 h<sup>27</sup>, and the addition of a catalyst. The most used catalysts are metal salts, such as antimony oxide.<sup>9,10,12,28</sup> Their presence added to the high temperatures are needed for the displacement of the reaction equilibrium towards the ester products. This exothermic reaction accounts for 70% of the global production of PET, due to the ease of purifying the products in comparison to esterification.<sup>12</sup> The reaction scheme is shown in Figure 3.

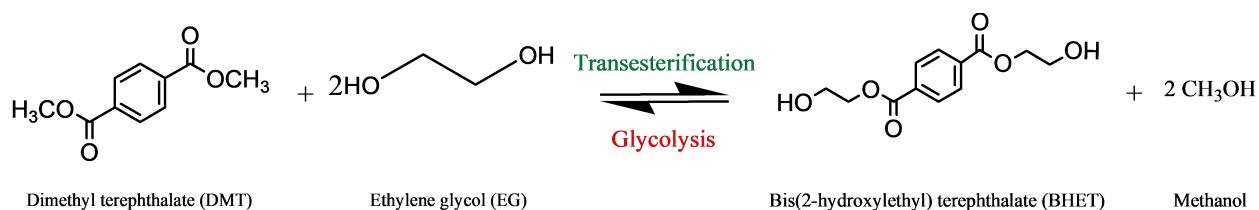


Figure 3: Transesterification reaction between dimethyl terephthalate and ethylene glycol.

### 1.1.4 Polycondensation

The next usual step for either of these reactions is a polycondensation under vacuum. Since this is a transesterification reaction, the same metal catalysts, such as Sb<sub>2</sub>O<sub>3</sub> or Ti(OBu)<sub>4</sub>, are commonly used. The main difference between polycondensation and transesterification is its reaction product, which is not a methanol as described above, but an ethylene glycol (see Figure 4).<sup>10,12,24</sup>

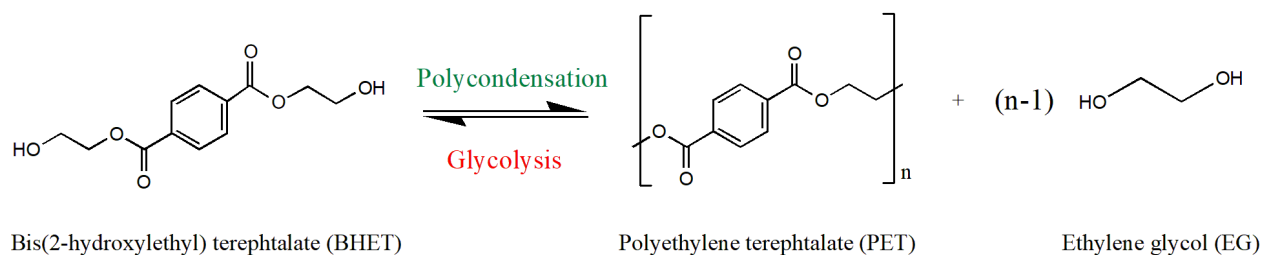


Figure 4: Polycondensation to produce polyethylene terephthalate.

The synthesis of PET on the melt state can be divided into two steps. The first one consists of a transesterification reaction of two BHET molecules, at temperatures between 250°C and 280°C and pressures around 2–3 kPa. This step allows the formation of a PET with a degree of polymerization (DP) of around 30.<sup>9,28</sup> A further step with the formed PET oligomer increases the DP up to 100 due to reactions at around 280°C–290°C under vacuum.

PET polymers are produced by either a semi-batch or continuous process. Either way, after melt polymerization, the obtained molar masses are between 16 and 19 kg/mol and with intrinsic viscosities (IV) between 0.6 and 0.7 dL/g.<sup>9</sup> As a result, polycondensation allows PET which can be applied in films and fibers. For other more specific uses, where a

higher molar mass is required, a final synthesis step can be employed, which will be described below.

### 1.1.5 Solid state polymerization

Solid state polymerization (SSP) consists of an additional polycondensation step to obtain higher molar masses, between 27 and 38 kg/mol.<sup>12,29,30</sup> The use of high temperatures allows sufficient collisions between the functional groups, which can thus further react so as to increase the molar mass.<sup>26</sup> Often used for the manufacture of bottles or technical applications, a standard post-condensed PET can have intrinsic viscosity values between 0.7–0.8 dL/g, with a DP of around 150.<sup>12</sup>

This transesterification in the solid state can be theoretically done at temperatures between the glass transition and the melting point of the polymer, in the presence of an inert gas or at low pressures.<sup>12,29</sup> But, according to Bamford et al.<sup>30</sup>, no reaction is perceptible before 150°C. As the temperature window is rather low, in order to maximize the reaction rate, the experimental conditions must be controlled at all times. The higher the temperature, the faster the formation of long polyester chains but getting too close to the melting temperature can cause the sticking of the polymer particles and/or thermal degradation.<sup>12</sup>

Other factors, such as the crystallization rate of the pellets, the molecules' mobility within the crystal lattice, the particles' size, and the presence of impurities, will have a large effect on the reaction rate of the SSP.<sup>30</sup> The initial concentrations of the carboxyl or hydroxyl will also greatly affect the reaction in the solid state.<sup>26</sup> A maximum SSP rate was determined to occur when the concentration of the OH groups is twice as large as the COOH units.<sup>31,32</sup> Duh et al. also showed that the SSP rate is inversely proportional to the concentration of carboxyl end groups.<sup>26</sup> One of the reasons for this is the loss of efficiency of the Sb catalysts used on the transesterification reaction in the presence of this functional group.<sup>26</sup> According to their work, the optimal proportion of COOH ends is between 0.25–0.40, but can vary with other aspects such as the size of the pellet and the required increase in the intrinsic viscosity.<sup>26</sup>

In a continuous solid-state polycondensation processing, at temperatures around 210°C, the residence time is between 10 to 20 h. Because of this long time and large consumption of energy, reaction accelerators are commonly used. Sterically hindered hydroxyphenylalkylphosphonates, such as calcium bis-ethyl-3,5-di-*t*-butyl-4-hydroxyphosphonate (commercial name *Irganox 1425*<sup>®</sup>, named *Irgamod 1425* in reference<sup>12</sup>), well known as antioxidant, is also described for its accelerator properties (see Figure 5). Used at concentrations between 0.1–0.5 wt%<sup>12</sup>, it can also contribute for the yellowing reduction of PET resins and act as a heat stabilizer.<sup>12,33</sup> The use of toxic solvents for the extraction of side-products may also complicate the SSP procedure.<sup>12</sup> But, by working in a solid state, issues related to the homogenization of high viscosity mixtures, for example, are eliminated. In addition, PET degradation mechanisms are limited and considered negligible due to its being in the solid state at relatively low temperatures.<sup>26</sup>

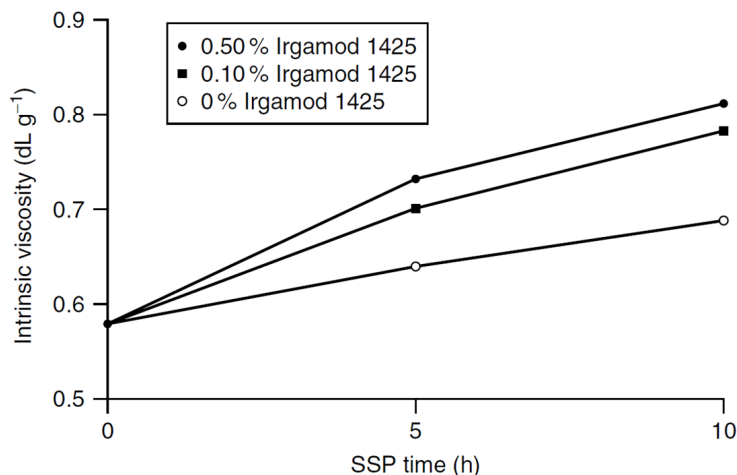


Figure 5: Intrinsic viscosity evolution as a function of SSP time in the presence of a commercial accelerator *Irganox 1425*® (named *Irgamod 1425* in the cited paper) based in a hindered phenolic aromatic phosphate. Data obtained from Ciba Specialty Chemicals. Reprinted with permission from reference.<sup>12</sup> Copyright 2004 John Wiley and Sons.

### 1.1.6 Side products in PET melt polymerization

In order to obtain a PET with a controlled molar mass, it is mandatory to limit the undesirable side products that can occur. The presence of oligomers is often described in the literature, at levels up to 3% by weight after polymerization.<sup>27</sup> These short chain molecules, that can be either linear or cyclic, will usually induce processing issues. To avoid that inconvenience, a purification step by solvents can be added. However, oligomers tend to be reformed during thermal treatments so constant care must be taken. For instance, as little as 1 to 2 wt% of diethylene glycol (DEG) can considerably reduce the thermal and light stability and increase the polymer's crystallinity.<sup>27</sup> Comonomers as such can deliberately be added in order to completely suppress the crystallization of PET in injection and stretch blow molding applications. As little as 5 mol % of DEG or isophthalic acid (IPA) is enough to attain the production of a clear bottle.<sup>12</sup>

Peebles et al.<sup>34</sup> found a direct correlation between the molar mass in number ( $M_n$ ) and the formation of cyclic oligomers at typical synthesis temperatures around 290°C. A “back-biting” mechanism (cyclodepolymerization) has been proposed for that kind of by-product and they have shown that their production is favored for decreasing  $M_n$ . Therefore, for recycled PET, where a chain scission process occurs, the presence of cyclic oligomers can be higher.<sup>12,34</sup> The thermal conditions will also play a key role in the side reactions. For temperatures between 150°C and 270°C, linear oligomers are increasingly formed, probably due to hydrolytic degradation reactions. The cyclization is only favored at higher temperatures and for a PET containing small amounts of water.<sup>12</sup>

There are several quantitative methods used to control the concentration of the by-products. Some examples are NMR spectroscopy, IR spectroscopy, and gas chromatography.<sup>27</sup> The degradation reactions suffered by PET will be discussed in detail in Part 2. But, first, PET's morphology and crystalline structure will be explained in detail below.

## 1.2 Morphology and microstructure

### 1.2.1 PET's crystalline structure

Unlike thermosets, thermoplastic materials can be melted and reprocessed many times. During these transformations, the polymers can partially crystallize, by always keeping an amorphous phase. This mechanism can either happen by cooling from a melted state, at a temperature between the glass transition point and the melting point, or by heating from the glassy state. Another possibility for inducing crystallization is mechanical stretching and solvent evaporation.<sup>9,10</sup>

In the solid state, the crystal structure is the most thermodynamically stable structure. However, not all polymers can crystallize. For an alignment of the molecular chains to take place, they must have a minimum length with a certain flexibility. Plus, when pendant groups are present, they must have a certain stereoregularity. This is the reason why atactic polymers usually cannot crystallize.

When all the proper conditions are fulfilled, the atoms in a macromolecule are organized in the three spatial directions to form a crystal network. These organized regions are called *crystallites*. Their average thickness is around 10 nm, which is smaller than the usual molecular length of a polymer. This means that the chains are folded in order to align within one another. These structures are called *lamellae*.<sup>35</sup>

If no mechanical stress is applied to the crystallizing material, these lamellae radiate outward from a nucleus to form a complex spherical structure called a *spherulite* (see Figure 6). These objects spread at the expense of amorphous regions and their growth is limited by the contact with other growing spherulites. This is the primary crystallization. This step is then followed by a possible secondary crystallization, involving the improvement and growth of other crystals, which are completely immersed and mixed with amorphous regions, which accommodate the unfolded and unorganized chains.<sup>12,35,36</sup>

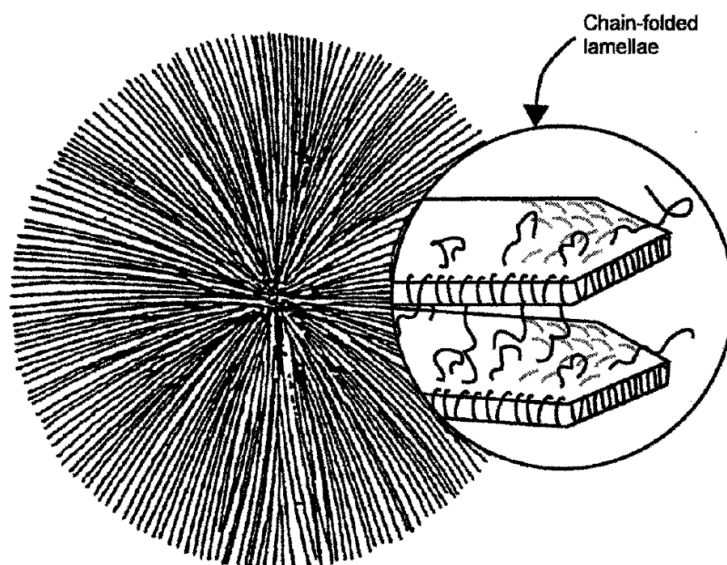


Figure 6: Schematic representation of the structure of a polymer spherulite. Reprinted with permission from reference.<sup>12</sup> Copyright 2004 John Wiley and Sons.

The presence of these spheroidal shapes is often associated with opaque materials due to the light scattering which they may cause. However, transparency can be obtained even for crystallized materials, when the crystalline entities are relatively small (smaller than the visible spectrum region).

Several authors have studied the crystallization kinetics and their influence on the macroscopic properties.<sup>10,37</sup> The spherulite structures prove to be less sensitive to solvents, mechanically and thermally more resistant than the unorganized portions, giving overall better properties for certain final applications.<sup>38,39</sup> Polymers with higher crystallinity have a high Young's modulus, are more resistant to solvents, and have a better toughness, usually followed by less impact strength. The link between the crystalline structures and the amorphous regions can also have an effect on the impact resistance of the bulk. The presence of these *tie molecules*, that join these two phases together, can be compared to entanglements in amorphous thermoplastics. Therefore, they can induce a reinforcement of the spherulite structures, resulting in a higher mechanical resistance of the polymer.<sup>40</sup>

It is usually agreed in the literature that the size of the spherulite is inversely proportional to the impact strength.<sup>40</sup> The failure sites are usually concentrated at the boundary of these spherical-shaped structures. So, increasing its size and complexity tends to influence the cracking mechanisms observed.<sup>40</sup> For example, Ohlberg et al.<sup>41</sup> found a linear relation between the size of the spherulites and the loss of impact strength of linear polyethylene (PE).

Friedrich et al., studying polypropylene (PP), showed that crack propagation was eased with bigger structures (around 500  $\mu\text{m}$  of diameter).<sup>40</sup> Increasing exclusively the molar mass of the PP (and keeping the same spherulite size) helped to create a stronger intercrystalline link, which benefits the impact resistance. The increase of the molar mass with a constant level of crystallinity has also proven to be an efficient way to improve impact strength on a nylon 610 and 66, according to Starkweather et al.<sup>40,42</sup> The impact behavior and failure phenomenon will be discussed in more detail in Part 4.

Lu et al.<sup>37</sup> also observed the effect on tensile properties of a crystallized PET. They established that the increase in the yield stress and loss of elongation at break were related to a reinforcement effect of the crystalline regions on the amorphous portion. The same conclusion was reached by Zhou et al.<sup>43</sup> (cf. Figure 7). In other words, the higher the crystallization, the lower the ductile behavior of PET.<sup>37</sup> In addition to the mechanical properties, the glass transition temperature was also affected by the crystallization, and went from 67°C for amorphous PET up to 81°C for crystalline PET.<sup>44</sup>



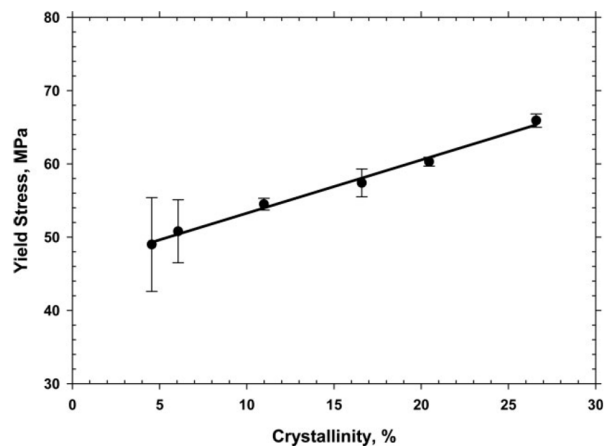


Figure 7: Yield stress of PET as a function of its crystallinity. Samples were crystallized in a circulation air oven at 115 °C. Tensile test performed at 12.7 mm/min. Reprinted with permission from reference.<sup>43</sup> Copyright 2009 John Wiley and Sons.

PET crystallizes in the triclinic crystal structure, as represented in the schematic in Figure 8. The cell parameters are given in Table 2.<sup>10,38</sup> These parameters give PET a crystalline density around 1.455 g/cm<sup>3</sup>, with an amorphous density of 1.335 g/cm<sup>3</sup>.<sup>12</sup> In isothermal conditions, its crystallization is usually described as a two-step process. The primary crystallization consists in this three-dimension spherical growth on heterogeneous nuclei followed by a linear growth of the spherical structures already formed.<sup>37</sup> The maximum growth rate observed for PET was 73 nm/s with an isothermal at 178 °C, according to Phillips et al.<sup>45</sup>

Table 2: Triclinic PET unit cell parameters.<sup>38</sup>

Edge lengths (nm)	Interaxial angles (°)
a = 0.456	$\alpha = 98.5$
b = 0.594	$\beta = 118$
c = 1.07	$\gamma = 112$

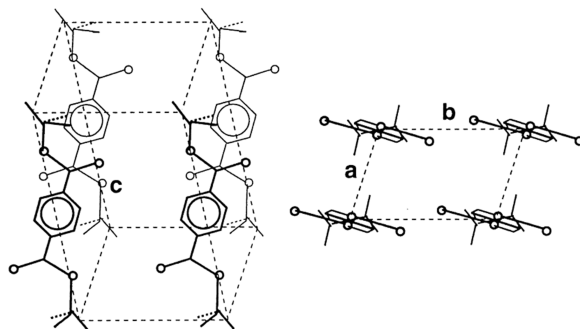


Figure 8: Schematic diagram of the triclinic PET unit cell. Reprinted with permission from reference.<sup>38</sup> Copyright 2000 Elsevier.

Several factors will affect the crystallization of PET. Its anisothermal behavior was studied by, among others, Jabarin.<sup>46</sup> As for other polymers, it has been found that the crystallization speed is inversely proportional to the length of the chains: the longer the chains, the slower their diffusion and organization, so the crystallization is slowed. The molar mass will therefore have an effect on the minimum cooling rate needed for a noncrystalline PET. According to them<sup>47</sup>, a cooling rate of 400°C/min is required for a PET with intrinsic viscosities of around 0.7 dL/g, whereas 130°C/min is enough for higher values of IV.

The polycondensation catalyst system used during synthesis will have an even stronger effect than the molar mass.<sup>47</sup> An antimony catalyst will slow the crystallization rate when compared to the same molar mass PET synthesized with a Ti-Mn system. The moisture content will also have an effect on the nucleation rate, but won't affect the growth of the spherulites. The half-time of crystallization is reduced by more than one-half (to something on the order of a few seconds) for humid samples (residual humidity %RH > 2000 ppm) at 120°C.<sup>48</sup>

The crystal arrangement of a polymer can be studied by several techniques. *Wide or small angle X-ray scattering (WAXS or SAXS)* can be used respectively for determining interatomic spacing within the unit cell, orientation and crystallinity, or the spherulite radius and the thickness of the lamellae.<sup>49</sup> Optical microscopy equipped with polarizers can also be a fast and easy way to identify the growth of spherulites. This technique, which only allows the observation of objects bigger than 1  $\mu m$ , takes advantage of the birefringence in the crystalline lamellae, which allows revealing the spherulites as maltese crosses. If no waveplate is used, the amorphous moieties will show completely dark while the the semi-crystalline parts that are not in the direction of the polarizer appear white. Using a hot stage, by following the radius of the formed objects, the growth rate of the crystalline lamellae can be determined.

Differential Scanning Calorimetry (DSC) is also a powerful tool to quantify the crystallization and its effect on thermal transitions. By tuning the analysis parameters, it allows measuring the melting and crystallization temperatures. Furthermore, it reveals the effect of nucleating agents on the thermal stability for example. Infrared Spectroscopy (IR) can also be used to quantify the biaxial orientation in PET films: for examples, see.<sup>49</sup>

As discussed in this section, the degree of crystallinity can be affected by, among other things, molecular length and structure, the molar mass, and the functional groups composing the polymer. It can also have an effect on other properties, such as the mechanical behavior. In the next section, the relation between crystallinity and the glass transition will be discussed. The definition and effect of physical aging will be addressed.

### 1.2.2 PET's physical aging

One of the most important transitions for a polymer is that to the glassy state. Unlike liquids, because of its thermodynamically out-of-equilibrium state, this reversible phenomenon concerns only the amorphous moiety of a polymer. And, also unlike a liquid, the glassy state does not have enough Brownian motion to allow molecular rearrangements. Only small portions of the molecule are concerned in this transition, with an overall free volume that remains constant.<sup>50</sup>

The glass transition can be obtained either by cooling a polymer from the melted state or by heating a solid material. In both ways, the glass transition temperature ( $T_g$ ) is used to define the crossover point between the metastable equilibrium state and the out-of-equilibrium one (cf Figure 9).<sup>50,51</sup> The  $T_g$  also marks the evolution of a material from a “solid” state to a liquid “rubbery” one.<sup>50</sup> A discontinuity of the coefficient of thermal expansion can be observed during this transition, leading to a change in the heat capacity ( $C_p$ ) that is generally detected by DSC analysis.<sup>50,52</sup>

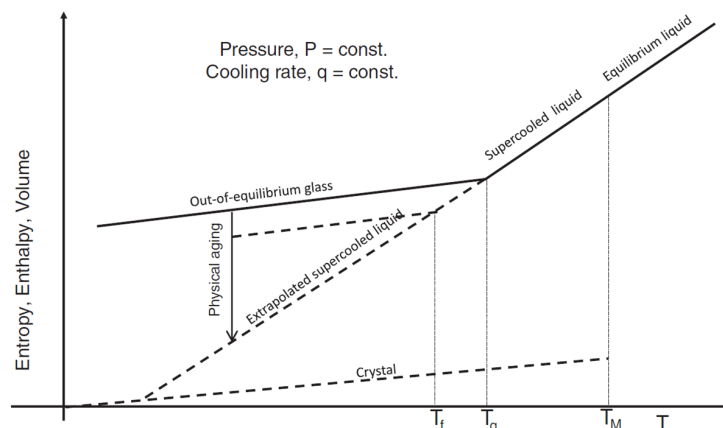


Figure 9: Schematic representation of the glass transition temperature.  $T_m$ : melting temperature,  $T_g$ : glass temperature,  $T_f$ : temperature at equilibrium. Reprinted with permission from reference.<sup>51</sup> Copyright 2016 Elsevier.

The molecular structure and the presence of pendant groups might modify this transition temperature. Crystallinity can as well, as it can restrict the molecular movements of semi-crystalline polymers.<sup>53</sup> The difference in the segmental mobility of the bulk amorphous phase and that of the portions in immediate contact with the crystal structures will induce a distribution of glass transition temperatures.<sup>53</sup> The midset  $T_g$ , for instance, will probably be shifted to higher temperatures.

The glass transition represents an excess of free volume, enthalpy and entropy.<sup>54</sup> So, over time, a structural relaxation can happen. And when the time scale of observation is sufficiently long with respect to the molecular motion, such surplus of energy can be released in order to spontaneously evolve towards an equilibrium state, as predicted by thermodynamics.<sup>54,55</sup> This tendency to approach the supercooled liquid equilibrium will continue till a new equilibrium is established. This phenomenon is called “physical aging”.

Since it has a reversible nature, this transition can be erased by heating above  $T_g$ , which is termed rejuvenation.<sup>54</sup> However, it can become persistent even for temperatures above  $T_g$  with semi-crystalline polymers, where the molecular mobility is not completely homogeneous, as explained before. Some of the molecules still in the glassy state can continue to undergo this enthalpic relaxation.<sup>56,57</sup>

When the chains relax towards a lower level of energy, they have a loss of the internal entropy, releasing a small amount of energy. This relaxation is manifested by an endothermic peak at temperatures around  $T_g$  and can be measured by DSC as shown in Figure 10. The measured enthalpy of this peak is proportional to the recovery of free volume caused by

the relaxation of chains.<sup>55</sup> Therefore, the sensitivity of a sample to physical aging can be easily evaluated by the increase in the relaxation enthalpy measured with DSC. In Figure 11, Zhou et al.<sup>55</sup> witnessed the effect of crystallinity on the physical aging of PET. As one can conclude, this relaxation over time is more significant for more amorphous samples after aging for different times at 65 °C.

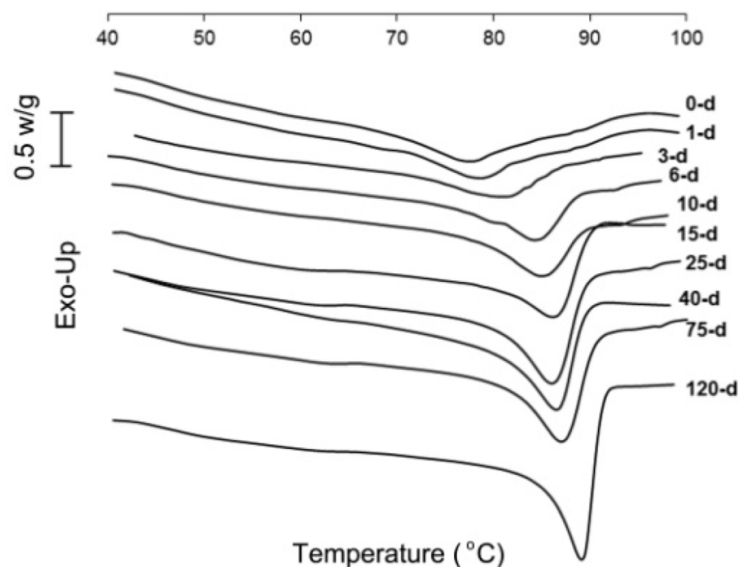


Figure 10: DSC thermogram of a 28% crystalline PET after several aging duration at 45 °C. Heating rate used for measurement: 10 °C/min. Figure from Farhoodi et al.<sup>57</sup>

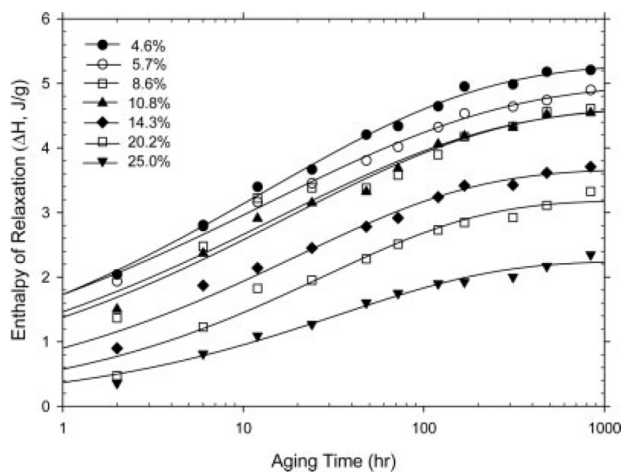


Figure 11: Evolution of the enthalpy relaxation over time of different PET samples aged at 65 °C. Samples with different levels of crystallinity were achieved at 115 °C. The evaluation of physical aging was made by modulated DSC measurements with a heating rate of 1 °C/min, a temperature amplitude of 1.5 °C, and a period of 120 s. Reprinted with permission from reference.<sup>55</sup> Copyright 2007 John Wiley and Sons.

Such as the  $T_g$ , the relaxation endothermic peak can also present a distribution of temperatures with different intensities. That behavior is attributed to the location of the amorphous regions, which can either be between spherulites or in the interlamellar region. For intraspherulitic regions, the endothermic relaxation peak will be at lower temperatures with higher intensities.<sup>43,58</sup>

Physical aging is a phenomenon of major importance, since mechanical, viscoelastic, optical and electrical properties can be strongly modified over the storage time.<sup>51,59</sup> The thermal response will also be affected.<sup>57,60</sup> Farhoodi et al.<sup>57</sup> studied the effect of physical aging on PET's  $T_g$  by DSC. They showed that the  $T_g$  of a bottle-grade PET ( $\chi_c = 28.2\%$ ) could be modified from 73.26 °C to 86.33 °C after 120 days of aging at 45 °C. The crystallinity was also strongly affected, achieving 34% after this same aging period.<sup>57</sup> However, storage at room temperature did not affect the  $T_g$  and the crystallinity to the same extent, inducing only a small increase ( $\chi_c = 30.6\%$ ) over the same period of aging.

The modification in the crystallization kinetics is related to the changes in the molecular mobility and morphology.<sup>58</sup> Plus, the energy released by the enthalpic relaxation of chains can contribute to the process of primary nuclei formation and the rearrangement of chains that will form the crystallites.<sup>57,60</sup> According to Lu et al.<sup>60</sup>, aged samples following an isothermal crystallization at different temperatures experienced an increase in the rate of crystallization while being heated between  $T_g$  and  $T_m$  (without melting). This modification of the crystallization was also highlighted with a slight  $T_c$  decrease of 3 °C–4 °C while heating, more pronounced for aging temperatures close to  $T_g$ .<sup>60</sup>

In what concerns the mechanical response, the overall consequence of physical aging is the embrittlement of the materials, attributed to a densification of the polymeric chains.<sup>43,56,61</sup> This relaxation over time can also have a great effect on environmental stress cracking, which happens when a low stress is applied over a long period of time.<sup>43</sup>

In the case of a semi-crystalline PET, Tant and Wilkes<sup>62</sup> established an increase in both the Young's modulus and the yield stress after several aging durations at 23 °C (from 10 to 70000 minutes). This phenomenon was less significant the more crystallized the samples were before the tensile test.<sup>62</sup> These observations are in accordance with the lower molecular mobility of aged samples, which will have a slower response to the applied stress and will, therefore, have a more fragile behavior.<sup>62</sup>

Other studies focused on the effect of aging on the strain–stress behavior. Zhou et al.<sup>43</sup> investigated the effect of aging on unoriented PET samples with levels of crystallinity going from 4.6% to 26.6%. The crystallinity difference itself already has an impact on the mechanical response of the samples. The yield stress increase from 49 to 65.9 MPa was further enhanced by the aging duration at 45 °C, 52 °C and 60 °C<sup>43</sup> (see the previous section). The overall elongation at break was reduced by this phenomenon, witnessing to the stiffness of the aged samples. For example, the results showed a loss of 82% of the elongation at break of samples aged 14 days at 52 °C with a level of crystallinity of 26.6%.<sup>43</sup> They also established a relation between the enthalpy relaxation and the brittle–ductile transition for PET samples with differing crystallinities. This parameter tends to decrease linearly with the level of crystallinity. The time of aging required for brittle failure followed the same tendency. Plus, as expected, increasing the aging temperature (below  $T_g$ ) also accelerated their embrittlement.

The evolution of properties over storage time can have a negative effect on the final product and has to be taken into account. Other external factors can also have a great influence on the mechanical and other properties of a polymer. The next section is dedicated to summing up some of the processing methods that PET usually undergoes for specific applications.

### 1.3 PET's processing methods

As stated before, PET is a very common polymer, used for several applications, going from products used in daily life to those with more technical uses. On top of the method of synthesis and the microstructure, which will determine most of the material properties, the processing methods will also have a great impact on the final product. Each application will require specific procedures.

Extrusion is the simplest transformation method for several thermoplastics. It consists in forcing a molten material through a die with a specific dimension and shape, using a single- or twin-screw system. The screw profile will have an important effect on the uniformity of the temperature and the degradation of the polymer. There are several types of extrusions to produce sheets, films, foam, or extrusion molding.<sup>9</sup> This last procedure allows the fabrication of larger objects with glass-filled toughened resins.<sup>12</sup>

Another processing option is injection molding. This discontinuous process allows the production of parts with variable dimensions and complexities. It consists in injecting a molten material into a cavity, then cooling it under a certain applied pressure to give it a specific shape.<sup>63</sup> Under gravity, the stored pellets on the hopper are fed into a reciprocating screw. This screw will plasticize the material and move backwards at the same time, in order to accumulate a chosen volume of the molten polymer ahead of it. This deposit is called *shot*. Once the correct amount is obtained, the screw will move forward to inject the material inside the mold by applying an injection pressure.<sup>63</sup> Once the material is solidified, the mold opens and the object is ejected using ejector pins. This manufacturing imposes a high shear on the molten material, causing the orientation of polymeric chains along the direction of the flow.<sup>63</sup> In addition, the contact of a hot material with a cold mold can often cause an anisotropy in the properties of the final product because of the remaining orientation of the macromolecular chains in the amorphous phase and also an orientation of the crystalline entities. The mechanical properties, such as tensile strength, tend to be higher in the direction of the orientation.<sup>63</sup>

Generally, PET processed by this transformation method has low mechanical properties, inducing a brittle material. This can be explained by its well known slow crystallization rate, which will also induce too long molding cycles, not applicable in an industrial context.<sup>9,12</sup> The injection cycles, as with many other processing methods, can also induce several degradation mechanisms, caused for instance by water and high temperatures. Many possibilities allow convenient processing of PET as such. For instance, the use of a cold mold, with temperatures between 15 °C to 40 °C. In this temperature range, the produced material is mostly amorphous but a further thermal treatment allows improving its crystallinity. Nucleating agents and/or crystal growth accelerators can be added as well for this purpose. These molecules will also positively affect the material by homogenizing the crystal structure and inducing the formation of smaller and more stable crystals. Some of the nucleating

agents include talc, long diols (co-diols such as 1,5-pentadiol, 1,8-octanediol in a concentration range of 0 to 10 mol%)<sup>64</sup>, titanium dioxide and certain sodium salts such as sodium stearate. Formulating PET with glass fibers or mineral reinforcements is also a common technique to reduce brittleness.<sup>12,64,65</sup>

For bottle production, however, the method used is blow molding, developed in 1970, with a DuPont patent. The success of PET resulting from this processing method is due to its possible crystallization, with a relatively slow kinetics and its strain-hardening characteristics, which guarantees a homogeneous distribution of the thickness throughout the preform.<sup>66</sup>

The bottle manufacturing starts with an injection of PET into a cold mold to obtain a tubular preform. This obtained parison can be directly transferred to an air-blowing unit to be stretched with air into a mold, or by a two-stage injection (see Figure 12). This blowing operation is also responsible for a biaxial orientation that can affect both the mechanical and optical properties plus the permeability of the final object.<sup>63</sup> This good barrier ability combined with a mechanical resistance are desirable in the food and beverage industry.<sup>9,10,12</sup> The obtained crystal organization also allows transparency even with a crystallinity up to 25% , due to the organization of chains into small objects.<sup>9,10,12</sup>

Usually a drying unit is directly attached to the injection molding machine to guarantee a moisture content of around 50 ppm. According to Gupta et al., without proper drying, a drop of 0.2 dL/g is expected only after the preform injection.<sup>66</sup> Plus, the difficulty is in finding the perfect temperature window to avoid the preform haze.

The drawback of all processing methods is the degradation of the material. Tuning the manufacturing parameters, such as the temperature, screw speed, and humidity, allows better controlling and predicting the properties of the product. However, a modification in the structure of the material can often occur, so it is very important to be aware of the different mechanisms that can take place. PET's most important degradation reactions will be discussed in the next section.

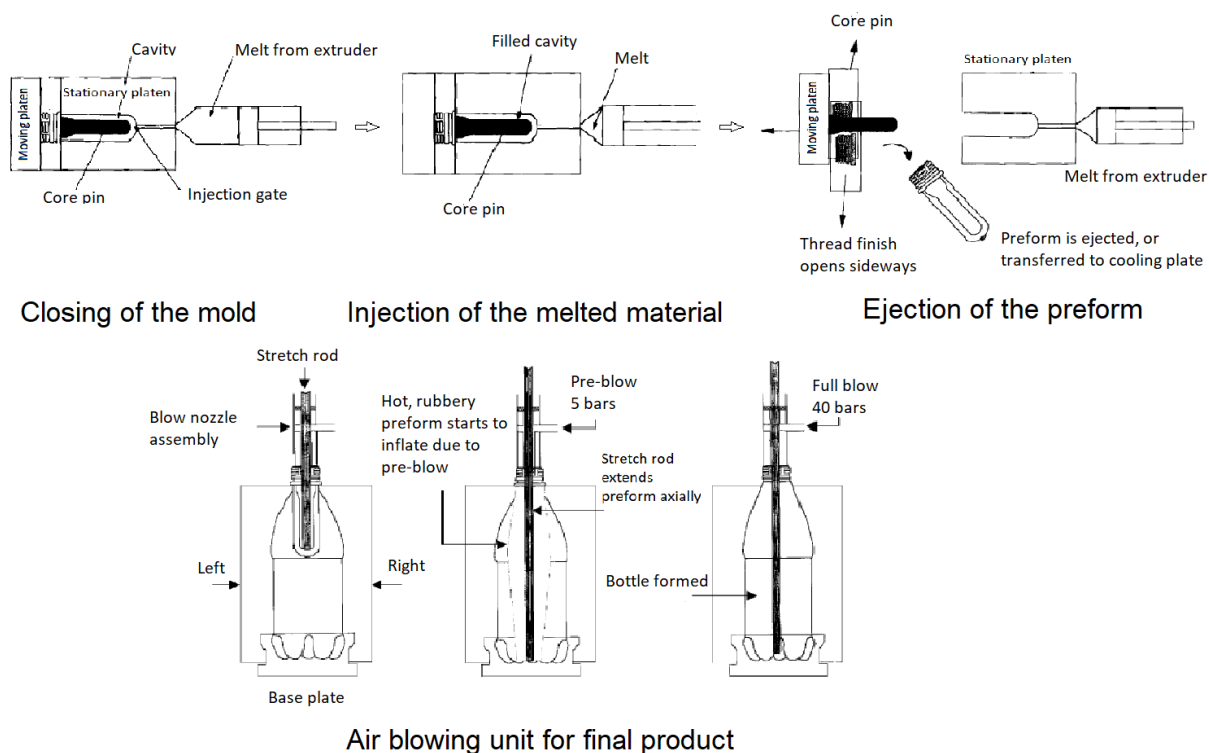


Figure 12: Schematic representation of the injection blow molding unit for bottle production. Adapted from the *Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends, and Composites*. Reprinted with permission from reference.<sup>66</sup> Copyright 2002 John Wiley and Sons.

## 2 Degradation mechanisms of PET

In order to be used in several applications, materials can be manufactured and modified in many ways before a final object is obtained. After their life cycle, they go to waste and ideally should be treated and re-used as many times as possible. During production and use, materials are exposed to the environment or to specific workloads that can induce different degradation mechanisms. These involve modifications of the material's original properties, usually by means of macromolecular cleavages and/or branching. This degradation can start with the formation of an active center through an initiation process or by reaction with other species, such as water. Such initiators can be radicals formed either thermally, photochemically, by mechanical shear, or through an oxidative process.<sup>67</sup> Reaction with other molecules, such as water, can also engender degradation mechanisms, resulting in structural modifications.<sup>12</sup> Some of them can be losses in molar mass, revealed sometimes by a drop in the intrinsic viscosity, and a yellowing of the material.

To better control and predict those changes, it is essential to study the main degradation mechanisms that can occur. This review paper specifically addresses the degradation occurring during the processing of PET, reducing the scope by not considering the product's entire life cycle. Below, three reactions, well known in polyester chemistry, will be discussed,



with examples of some of the modifications that they can generate.

## 2.1 Hydrolytic degradation

Polyesters are known to be very hygroscopic materials, which will generally absorb the moisture and water in its surrounding environment.<sup>12,65</sup> The presence of an ester functional group, that can be easily attacked by water, will lead to chain scission and the production of carboxyl and hydroxyl end groups. This reaction with water (see Figure 13), namely hydrolysis, corresponds to the reversible reaction of condensation. To a certain extension of the degradation, only the amorphous structure will be concerned by this reaction. It becomes more significant at temperatures equal to or above 160 °C, easily reached during processing.<sup>68</sup>

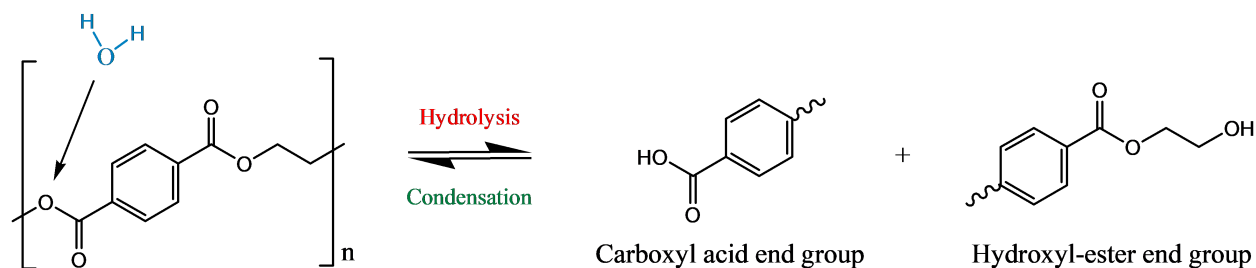


Figure 13: PET hydrolysis reaction.

What is also called hydrolytic degradation is often described as an auto-catalyst process, being activated by the presence of its reaction products like carboxyl acids.<sup>10,69</sup> However, Launay et al.<sup>68</sup> showed that the auto-catalyst behavior has a very limited effect on the loss of molar mass, but the presence of water at high temperatures will indeed cause several modifications in the structure of PET.

For example, it is well established that hydrolysis reaction damages the material, with a rapid decrease in molar mass.<sup>70,71</sup> An increase of the crystallization due to chemocrystallization is also an often observed modification. This can be explained by the presence of smaller chains, which can compromise the overall entanglement in the amorphous phase, facilitating the entrance of those mobile portions into the crystalline structure.<sup>68</sup> These changes have been much studied and might restrict the range of uses of the material. The geometry and size of the pellets will also affect the aptitude for moisture absorbance and thermal and oxidative degradation, according to Thumsorn et al.<sup>72</sup> and Cardi et al.<sup>73</sup> They've shown that powders, for example, would have a stronger absorption rate due to their larger surface area, although drying could be facilitated too.<sup>65,72</sup> The same conclusion is applied to scraps, when compared to pellets.<sup>73</sup> The roughness of the ground particles might also increase the interaction with the surrounding water molecules according to these researchers, strongly affecting the hydrolysis rate.<sup>72</sup> Buxbaum et al.<sup>74</sup> explain that hydrolysis is a two-step process, via adsorption and diffusion to the interior of the polymer. According to their research, the adsorption of water on a PET cube of length 0.4762 cm is 250 ppm after half an hour.

The evolution of the moisture content over time of a dried PET is presented in Figure 14. However, it is noteworthy that the crystallinity of these pellets and scraps might possibly differ and also contribute to these observed water recovery kinetics over time.

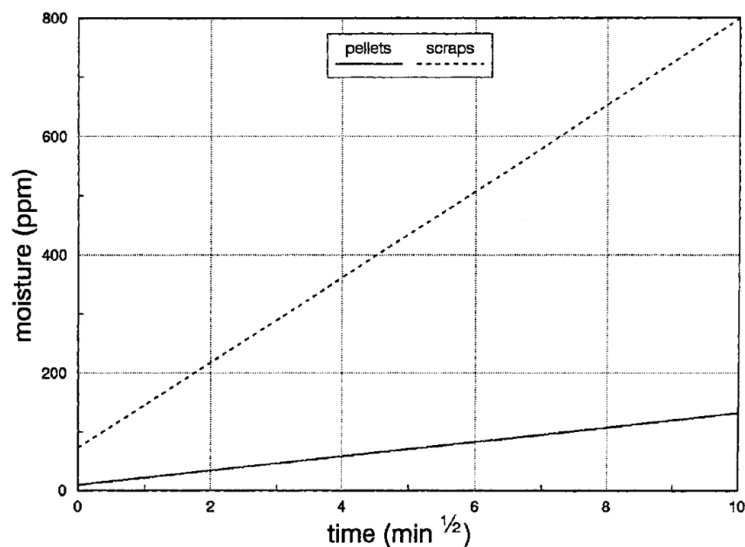


Figure 14: Moisture content of a dried PET (4 h at 180 °C, unknown atmosphere) as a function of time of exposure in air at 28 °C and residual humidity of 50%. Reprinted with permission from reference.<sup>73</sup> Copyright 1993 John Wiley and Sons.

The most common ways to quantify the modifications caused by hydrolysis are, first, molar mass measurements by size exclusion chromatography (SEC) and by IV measurements.<sup>68,71</sup> Another standard method is carboxyl end-group titration, usually by using Pohl's method, an acid-base titration.<sup>75</sup> FTIR can also be applied to identify some of the products' functional groups such as O-H and carboxylate absorbance. Density and crystallinity measurements are also usually employed, as these parameters will strongly influence the degradation mechanisms. However, their modification has to be studied with caution, as they can be caused by other reasons such as processing parameters (temperature, screw speed, etc.) and the presence of additives.<sup>70,71,76</sup> Below, several examples of these techniques described in the literature are summarized.

Launay et al.<sup>68</sup> studied the PET hydrolysis reaction kinetics in a bath of 100°C distilled water after drying for 24 h in a 50°C vacuum oven. The degradation of the material was identified after 25 days of exposure, accompanied by a rapid increase in crystallinity. The polydispersity index was also decreased. Some of these observations are presented in Figure 15.

Zimmerman et al.<sup>69</sup> found an increase of the COOH groups with the decrease of intrinsic viscosity after hydrolysis. They stated that PET samples with more than 100 to 150  $\mu$  eq. COOH/g PET could not be used anymore for technical applications. Partini et al.<sup>76</sup> also proved the effectiveness of infra-red spectroscopy, with a transmission technique, for the quantification of hydrolysis mechanisms. By immersing different samples in a basic aqueous solution, they were able to track the presence of carboxylate groups formed by the base catalyzed reaction of the ester groups. The corresponding peak centered at around 1570  $\text{cm}^{-1}$  was then used to quantify the degradation products and its linear increase with time was related to the progress of the hydrolysis reaction. They confirmed that this chemical reaction is the limiting factor, instead of the diffusion of molecules as suggested by

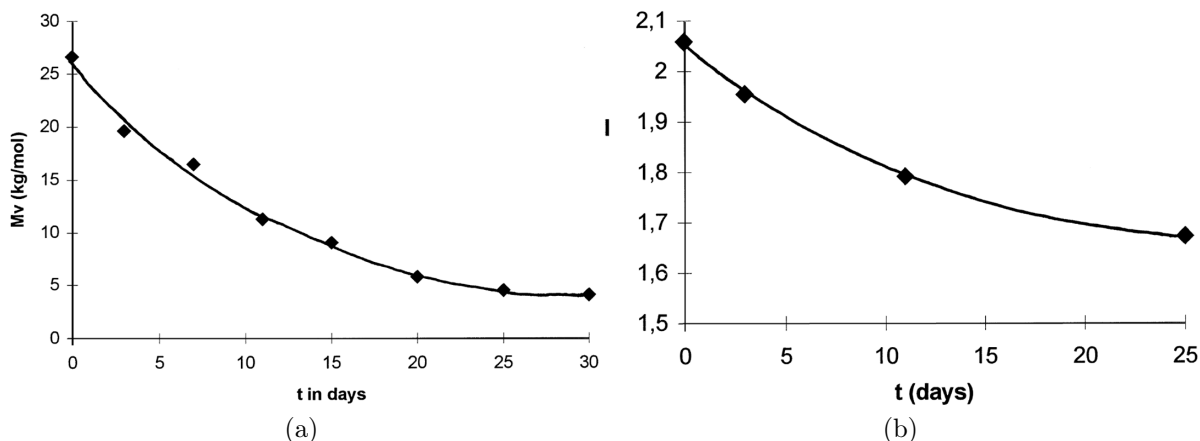


Figure 15: (a) Loss of PET molar mass measured by viscosimetry and (b) variation of PET polydispersity index of a sample exposed in boiling water for several days. Reprinted with permission from reference.<sup>77</sup> Copyright 1999 Elsevier.

some authors. In this study, they also suggested that the molar mass, calculated with a Mark–Houwink equation via IV measurements, had a strong impact on the sensitiveness to hydrolysis. Polymers with lower  $M_w$  and lower polydispersity index were less prone to degradation.<sup>76</sup>

In other studies, FTIR also proved to be a useful and fast technique with a good correspondence with the number of chain scissions per unit mass. For example, Du et al.<sup>78</sup> studied the carbonyl regions by a peak resolving technique to avoid saturation and the overlapping of esters and hydrolysis products. The hydrothermal aging was induced by an immersion of injected PET parts in deionised water at temperatures between 70°C to 95°C for different time intervals. Tests were conducted on samples conditioned at room temperature with 50% humidity. Due to the use of an ATR accessory, they found a two-step degradation corresponding to, first, the water absorption and then the hydrolysis mechanism itself. Samples aged at temperatures higher than the glass transition (here, 85°C), had their first stage much faster with an overall higher degradation than for temperatures below  $T_g$ . By combining FTIR and molar mass measurements, Du et al.<sup>78</sup> found the auto-acceleration nature of this reaction due to the increase of hydrophilicity, as established before by Launay et al.<sup>68</sup>

Even though hydrolysis can have a severe effect on the material properties, there are several ways to avoid or slow down this degradation caused by humidity. A drying of the material is regarded as an essential step not only for processing but especially for recycling, as some properties such as the impact strength can be drastically modified, as is emphasized in Figure 16.<sup>12</sup> The usual targeted amount of water allowed on PET to avoid catastrophic loss of properties is around 0.02 wt%.<sup>9</sup>

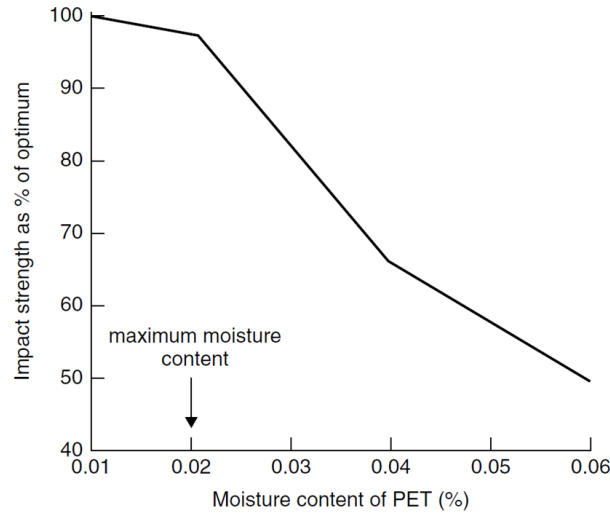


Figure 16: Notched impact strength as a function of the moisture content of PET according to Scheirs and Long. Reprinted with permission from reference.<sup>12</sup> Copyright 2005 John Wiley and Sons.

Regardless of the nature of this step, the reported drying conditions of PET vary a lot in the literature. It is often reported that temperatures of around 140°C to 170°C for 3 to 7 h are enough to obtain the minimum amount required, but several other conditions have been suggested.<sup>6,9</sup> As an example, Nait-Ali<sup>10</sup> reported that 15 h at 120°C in a vacuum oven was enough to reach 0.02 wt%, using the method of Karl Fischer for this measurement. According to the obtained results, extending the drying time to 15 h had no positive effect on reducing the measured residual water amount of PET (see Figure 17).

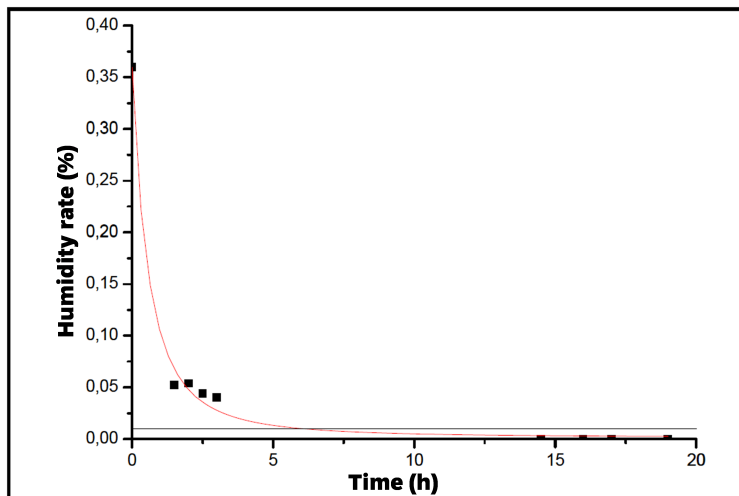


Figure 17: Humidity rate as a function of the drying duration in a vacuum oven at 120 °C. Measurement according to Karl Fischer titration for PET pellets (size around 8 mm) with an IV of 0.76 dL/g.<sup>10</sup>

Improving crystallinity is also a common way to reduce the moisture content, as it is mainly the amorphous regions that absorb water.<sup>73</sup> This can be done, for instance, by the SSP process or by the addition of fillers. Negoro et al.<sup>65</sup> incorporated fillers such as talc and glass beads as nucleating agents in recycled PET during compounding to lower the hydrolysis content. They concluded that samples with fillers had a higher crystallinity and lower moisture absorption at 25°C and relative humidity of 50% (see Figure 18). Hydrolysis stabilizers and acid-and-water scavengers can be used for the same purpose. Polycarbodiimides, for instance, decrease the initial acid value of polyesters to maintain acceptable values for processing.<sup>12</sup> Desiccant additives like treated calcium oxide can also be used to trap water molecules during extrusion for instance.<sup>12</sup>

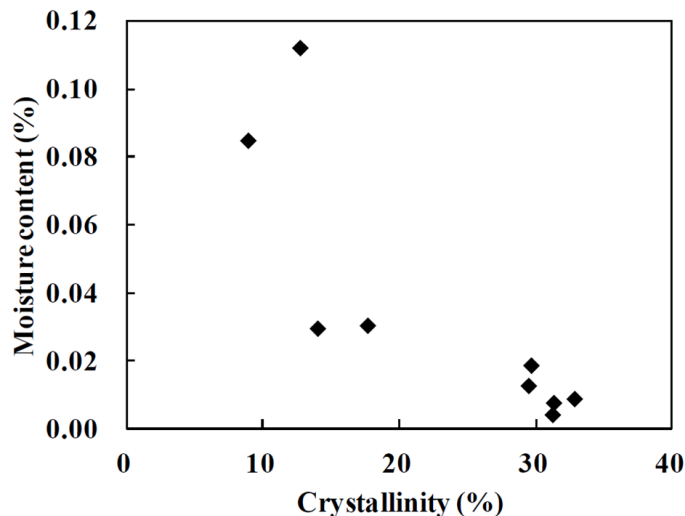


Figure 18: Relation between crystallinity and moisture content of recycled PET compounds according to Negoro et al.<sup>65</sup> Moisture content analyzed by Karl Fischer titration at 25 °C and relative humidity of 60%. Crystallinity measured by DSC from 30 °C to 300 °C with a heating rate of 10 °C/min under nitrogen. Reprinted with permission from reference.<sup>65</sup> Copyright 2016 Elsevier.

## 2.2 Thermal degradation

Another possible degradation is one that is initiated thermally. For PET, between 100°C and 120 °C with %RH = 100%, the relative rate of hydrolysis is some 10000 times faster than the thermal process in the same temperature range.<sup>74</sup> Yet this mechanism can also strongly affect PET and cause undesirable side reactions that can negatively affect the growth of the molecular chains during polycondensation.<sup>12</sup> It can also affect the duration of the SSP, as reaction temperatures have to be limited to favor molar mass increase instead of a chain scission.<sup>12,69,75</sup>

Thermal degradation is exclusively studied in inert atmosphere at temperatures above the melting point, in order to separate its mechanism from the oxidation reaction. It is an irreversible reaction that predominates in long-term processing conditions. Temperature

amplifies the intermolecular vibrations and conformational changes, causing homolytic dissociation of chains and inducing end-group radicals that can allow a depolymerization to occur.<sup>67</sup> With polyesters, the energy offered by elevated temperatures causes a rearrangement of the ester moiety, inducing a cleavage of the ester bond and the formation of acids and vinyl-ester end groups (see Figure 19). According to Paci et al.<sup>79</sup>, this degradation becomes measurable only at temperatures higher than 270°C.<sup>9,12</sup> The transition state can be activated by metal catalysts, such as zinc and antimony, usually added during the polycondensation reaction and sometimes still present if not consumed.<sup>69</sup>

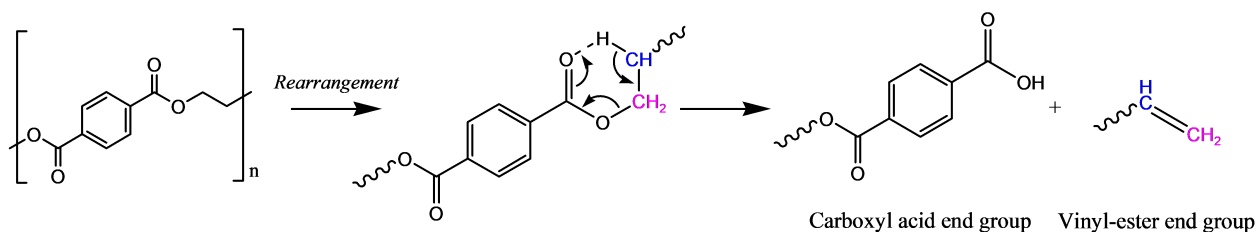


Figure 19: Thermal degradation mechanism established by Zimmermann et al.<sup>69</sup>

The random chain scission nature of the thermal degradation is also responsible for a decrease in the molar mass. Therefore, the analytical techniques used to quantify this mechanism are similar to what can be done for hydrolysis, namely SEC and viscosimetry. Thermogravimetric (TGA) analysis can complete the understanding, by observing the various decomposition products at different temperatures. Coupling this technique with NMR, gas-chromatography mass-spectroscopy GC-MS or SEC measurements, allows an even better understanding of the product's structure.<sup>10-12</sup>

As long as sufficient amounts of hydroxyl groups are present in the PET chain, the reaction products can undergo secondary processes. The carboxyl acid can be esterified for the production of an ester ( $\text{HO}(\text{O}=\text{C})-\text{C}_6\text{H}_4-\text{R} + \text{PET}-\text{OH} \longrightarrow \text{R}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{PET} + \text{H}_2\text{O}$ ) and the vinyl ester group can be transesterified into another ester.<sup>12,80</sup> However, the hydroxyl content is low, an anhydride and acetaldehyde are generated which can also further react into esters and carboxyl ends.<sup>12</sup>

That is why some of the typical volatile thermal degradation products formed are mostly aldehydes, such as acetaldehyde and formaldehyde (see Figure 20).<sup>10,80,81</sup> In applications to packaging and bottles, these molecules can be very disturbing, as they can cause a modification of the smell and taste if they migrate to the food or drink. Because aldehydes are small molecules present in low concentrations, they are usually trapped inside the crystal structure, being therefore very hard to quantify.<sup>10,82</sup>

Other by-products can be formed at even higher temperatures, around 400–500 °C, such as carbon monoxide, aromatic and aliphatic hydrocarbons.<sup>80</sup> The use of stabilizers such as carboxylic acid, anhydride and isocyanate can help to reduce the thermal degradation by trapping free radicals and by blocking hydroxyl chain ends.<sup>82</sup>

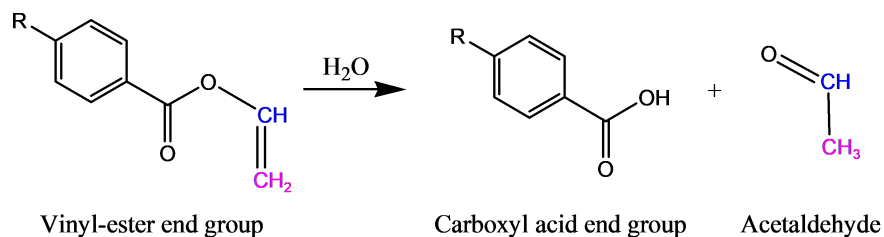


Figure 20: Proposed mechanisms for the formation of acetaldehyde from PET degradation.<sup>81</sup>

## 2.3 Thermal-oxidative degradation

When the reaction at elevated temperatures (above the crystallization temperature) involves the presence of oxygen, what is called thermal-oxidative degradation is the main mechanism taking place. Generally, the first stage of a typical oxidation mechanism is the formation of radicals (RH represents a polymer chain)<sup>67,83–85</sup>:

1. Heat initiation on the polymer chain:  $\text{RH} \longrightarrow \text{R}^\cdot + \text{H}^\cdot$
2. Heat initiation of hydroperoxide units:  $2 \text{ROOH} \longrightarrow \text{ROO}^\cdot + \text{RO}^\cdot + \text{H}_2\text{O}$
3. Oxygen initiation:  $\text{RH} \xrightarrow{\text{O}_2} \text{R}^\cdot + \text{HOO}^\cdot$
4. Basic radicals can also react with oxygen:  $\text{R}^\cdot + \text{O}_2 \longrightarrow \text{ROO}^\cdot$

The basic radicals formed go through a propagation stage for the formation and accumulation of hydroperoxide groups (-OOH). As these molecules are highly unstable, they tend to decompose to form radicals, resulting in an autocatalytic phase<sup>84,85</sup>:

5. Formation of peroxides:  $\text{ROO}^\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}^\cdot$
6. Homolytic decomposition of formed peroxides:  $\text{ROOH} \longrightarrow \text{RO}^\cdot + \text{HO}^\cdot$
7. Peroxide radicals can react with chains forming new radicals and chain branching:  
 $\text{RO}^\cdot + \text{RH} \longrightarrow \text{R}^\cdot + \text{ROH}$  or  $\text{HO}^\cdot + \text{RH} \longrightarrow \text{R}^\cdot + \text{H}_2\text{O}$

Once a certain concentration of peroxide is reached, these molecules can rapidly participate in bimolecular decomposition and start the termination step.<sup>67</sup> In this type of degradation,  $\beta$  scissions are favored, yielding fragments with aldehydes, ketones, alcohols, and vinyl end groups.

8.  $\text{ROO}^\cdot + \text{ROO}^\cdot \longrightarrow \text{ROOR} + \text{O}_2$
9.  $\text{ROO}^\cdot + \text{R}^\cdot \longrightarrow \text{ROOR}$
10.  $\text{R}^\cdot + \text{R}^\cdot \longrightarrow \text{R-R}$

In the case of PET, even though the reaction mechanisms are not completely understood, they are known to follow the same chemistry starting with the formation of a hydrogen peroxide (functional group ROOH) at the methylene group in the diester linkage (see Figure 21). This portion of the molecule is favorable because the methylene function is considerably more reactive than the aromatic CH.<sup>17</sup> Unlike the other two degradation mechanisms mentioned above, in this case, the reaction products work as initiators of the reaction (see the propagation phase with reactions 5, 6 and 7 above): the initial slow reaction kinetics increases with its production, causing an irreversible degradation of the material.<sup>10,12</sup>

The literature has not reached unanimity about the reaction mechanism for this degradation. It is usually asserted that the initiation of the reaction comes from a unimolecular decomposition of the hydrogen peroxides followed by a propagation by R<sup>•</sup> and ROO<sup>•</sup> radicals. At temperatures above 250 °C, ROOH groups are no longer stable, and tend to go through a fast rearrangement for the formation of new radicals (see Figure 21 and reaction 9 above). This mechanism will cause a fast chain scission of the material. The absence of crosslinking on neutral conditions probably originates from an insignificant production of the radical R<sup>•</sup> on the alkyl portion. Another possibility is the bimolecular termination of the alkyl radicals, associated with the combination of two alkyl radicals of a polymer chain, in a crosslinking process (also see Figure 21 and reaction 10 above).<sup>10,86</sup>

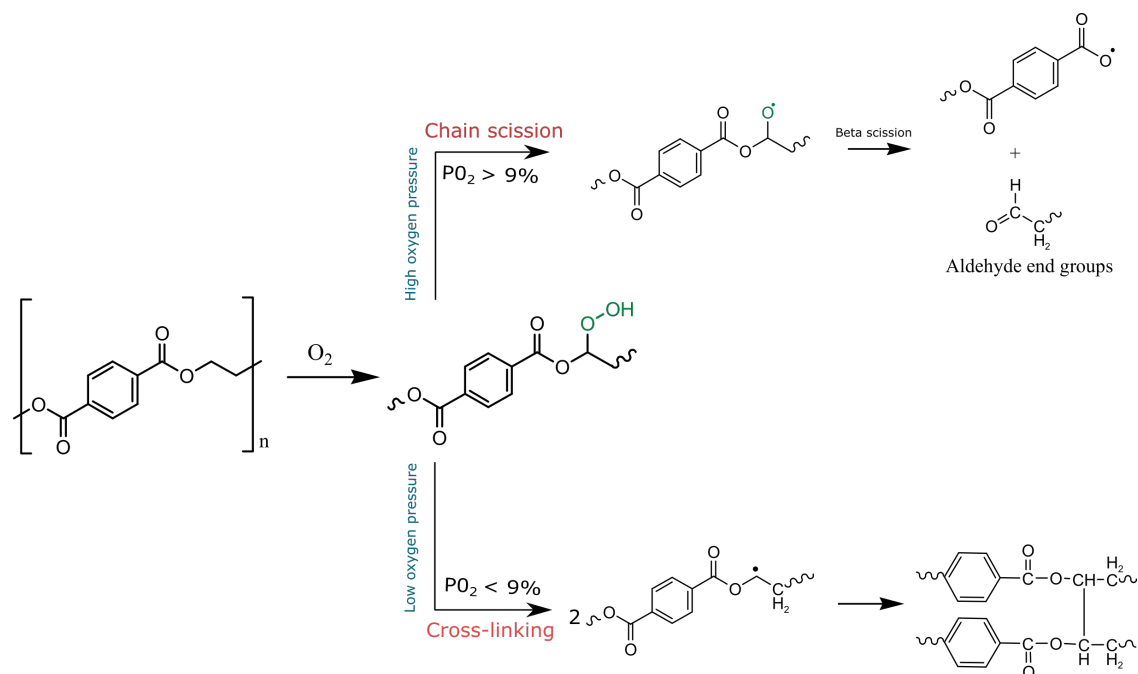


Figure 21: Simplified thermal-oxidative degradation of PET with two different mechanisms according to the partial oxygen pressure.

Because of the unpredictable nature of the secondary reaction (either forming branched chains or causing chain scissions), the oxidative degradation has sometimes been described as the main source of problems during the manufacture of PET.<sup>17,87</sup> Plus, the reaction products can also undergo a decarboxylation, hydrogen transfer, and transesterification, at different temperatures. These reactions are responsible for the formation of volatile groups, as listed



in Table 3.<sup>80</sup>

Assadi et al.<sup>17</sup> studied the competition between chain scission and crosslinking during processing by extrusion. By varying the oxygen concentration in a single screw, they could establish its effect on the molar mass of dry PET (starting  $M_w = 55$  kg/mol and  $\chi_c = 33\%$ ) during processing. The single screw was set at 40 rpm, with a temperature ranging from 240 °C to 280 °C and a residence time of around 1.30 min. The techniques used for characterization were multiple detection SEC (refractometer, UV absorption and viscosity), rheological tests, and IR spectroscopy. Due to these characterizations, they found that PET materials could undergo both chain scission and cross-linking during extrusion, the latter procedure predominating as the number of processing cycles increased, until arriving at a gelation point.

Table 3: Concentration of thermal-oxidative secondary reaction products as a function of the temperature. A bottle grade PET granulate was used for testing. Samples were placed in a tubular furnace kept in isothermal conditions with an air flow of  $0.025$   $m^3/h$  for 20 min at each temperature. Oxygen partial pressure is not indicated but should be around 21%. Volatile products were analyzed by gas chromatography and colorimetric methods. Reprinted with permission from reference.<sup>80</sup> Copyright 1998 John Wiley and Sons.

Substance	Temperature (°C)					
	200	300	400	500	600	700
	Concentration (mg/m <sup>3</sup> )					
Acetaldehyde	< 0.2	1.3	302.5	235.8	84.5	73.0
Formaldehyde	0.3	0.8	31.0	44.0	13.4	12.8
Benzaldehyde	< 0.8	< 0.8	1.1	3.2	4.6	10.7
Benzene	< 0.1	0.1	2.0	12.0	47.5	95.0
Toluene	< 0.2	< 0.2	0.7	1.2	6.8	17.4
Ethylbenzene	< 0.2	< 0.2	0.3	1.0	2.3	10.4
Styrene	< 0.5	< 0.5	0.8	2.4	6.5	26.0
C <sub>1</sub> -C <sub>4</sub> aliphatic hydrocarbons	< 0.1	< 0.1	2.0	15.0	43.0	51.0
Dioxane	< 0.8	< 0.8	5.0	10.8	4.2	2.0
Methyl acetate	< 0.8	< 0.8	1.5	3.0	14.8	20.5
Methyl alcohol	< 0.5	< 0.5	1.8	4.5	1.8	1.0
Carbon monoxide	< 5	62	1240	2480	3400	3540

In an initial approach, experiments were made in a nitrogen atmosphere, as extrusion is usually considered an anaerobic process with hardly measurable reductions in intrinsic viscosity over time.<sup>79</sup> By perfectly controlling the conditions of the atmosphere, Assadi et al.<sup>17</sup> showed that with high concentrations of nitrogen, a viscosity increase was predominant, mainly related to a polycondensation process, as shown in Figure 22. Without oxygen, the insignificant production of radicals could not cause any chain cleavage, so polycondensation and an increase in molar mass were observed. However, as the reaction time increased, a random chain scission happened, causing a decrease of viscosity, associated with a thermal degradation. The first moderate decrease of viscosity at the beginning of the study was attributed to structural irregularities.<sup>17</sup> This study confirms that an effect on the Newtonian viscosity could be visible even in anaerobic conditions, as crosslinking becomes predominant during long-term processing.<sup>17</sup>

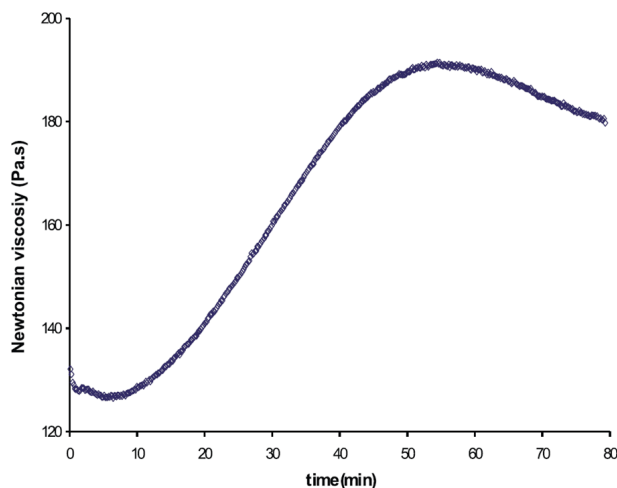


Figure 22: Evolution of melt Newtonian viscosity in dry nitrogen atmosphere at 280 °C of three times reprocessed post-consumer PET. Reprinted with permission from reference.<sup>17</sup> Copyright 2004 Elsevier.

In another approach, to simulate the contact of PET with air at both extremities of the extrusion, a rheological characterisation was performed (parallel plate geometry, frequency sweep from 1 to 500 rad/s at 280 °C with 3% strain) with different concentrations of oxygen. The results are presented in Figure 23(a). To better show these effects, changes of  $M_w$  are plotted as a function of the exposure time during processing (cf. Figure 23(b)). The notably different behavior depending on the oxygen partial pressure  $P_{O_2}$  are summarized below:

- At low oxygen pressure ( $P_{O_2} < 9\%$ ): a sufficient concentration of radicals induces predominately an oxidative crosslinking. The overall viscosity increases during the time of exposure, with a gelation point at around  $P_{O_2} \approx 6\%$ .
- At intermediate partial pressures, around 9% ( $9 \cdot 10^3$  Pa): the crosslinking effects equilibrate those of the chain scissions, giving an almost constant viscosity over time;
- At high oxygen pressure ( $P_{O_2} \gg 9\%$ ): a fast chain scission process takes place, decreasing the overall molar mass and viscosity.

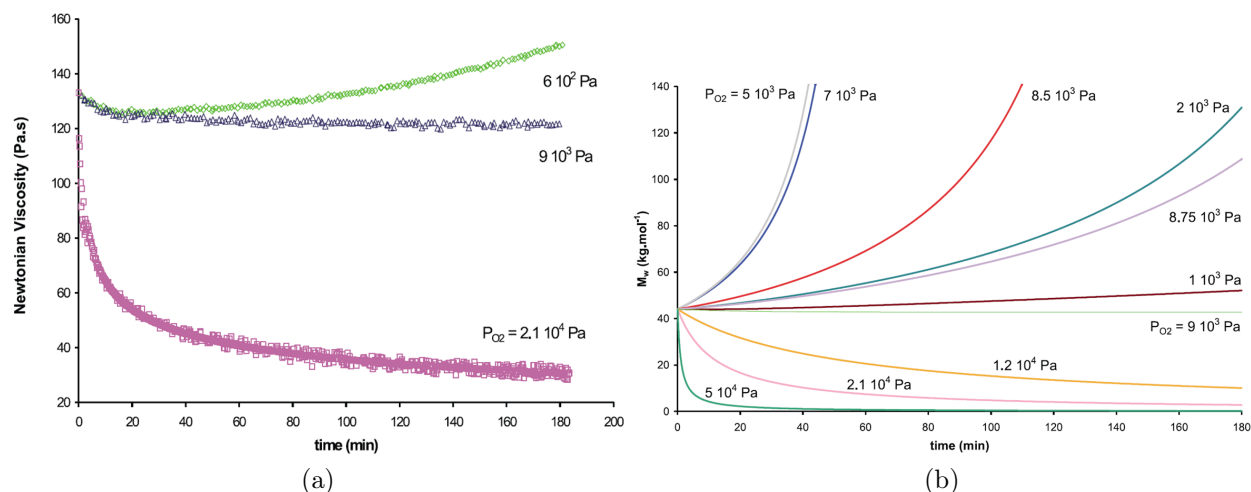


Figure 23: Modifications of (a) Newtonian viscosity and (b) weight average molar mass over time at various oxygen partial pressures. Reprinted with permission from reference.<sup>17</sup> Copyright 2004 Elsevier.

As demonstrated by Assadi et al.<sup>17</sup>, the thermal-oxidative degradation can have strong effects on the material's viscosity and molar mass, giving sometimes unpredictable behavior related to the different partial oxygen pressures of the environment. When compared to other degradations that can take place for PET, it has been demonstrated by Paci et al.<sup>79</sup> that oxidation is by far one of the most important. They studied a knife-milled post-consumer PET in a Brabender mixing bowl under different conditions. In this way, they showed that, with appropriate processing conditions, an increase of the molar mass is possible even when omitting the drying step recommended before PET processing. This is possible due to a polycondensation reaction that outweighs the chain scission reaction (see Figure 24). They also established that increasing the mixing speed from 30 to 130 rpm could also generate a polycondensation reaction by influencing the reaction kinetics.<sup>79</sup>

The use of antioxidants at high temperatures is often a way to improve the stability of PET over time during processing. Phenols, phosphites, phosphates, and phosphonates are the most effective ones.<sup>88</sup> Carboxyl acid scavengers or chain extenders can also be used to reduce both hydrolytic and thermal oxidative degradation, according to Bikiaris et al., who stated that these have a promoting effect on both these degradation mechanisms.<sup>88</sup>

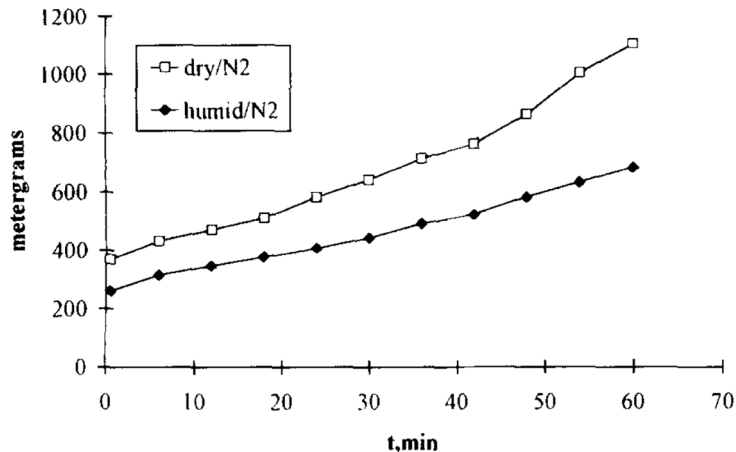


Figure 24: Measured torque in PET in a mixing bowl over time in dry or humid (residual humidity between 50%–60%) nitrogen atmosphere. Reprinted with permission from reference.<sup>79</sup> Copyright 1998 Elsevier.

The structural changes caused by the described mechanisms can cause embrittlement and completely modify the structure of the polymer. These modifications are even more severe for the final properties when the material is in a post-consumed state or has already suffered from reprocessing degradation. In the next section, an overview of polyethylene terephthalate recycling methods will be treated, with a focus on the mechanical process.

### 3 PET recycling and valorization methods

It is estimated that between 1950 and 2015, the total accumulated amount of plastic was about 6.3 billion tons.<sup>89,90</sup> And according to the Conversio Market & Strategy GmbH, the total collected plastic in post-consumer waste in 2020 in Europe was only about 29.5 Mt. Plus, only a small portion of this waste was really transferred to recycling units, inside and outside of the EU.<sup>89,90</sup> This obviously insufficient amount of collection and recycling creates a tremendous need for the improvement of techniques that could reduce the environmental impact of polymer materials, and a lot of work is in progress.<sup>4</sup>

Figure 25 summarizes the main pathways for waste management. Its evolution in Europe is also represented in Figure 26 and it shows already a very promising feature. The amount of plastics sent to landfills fell by almost 50% in the last years. For instance, since 1995, the PET collection rate has been increasing year after year, according to Petcore data in 2011. In the UK, for example, between 2015 and 2016, PET made up almost 40% of all collected waste from the curbside.<sup>2,6,18</sup>

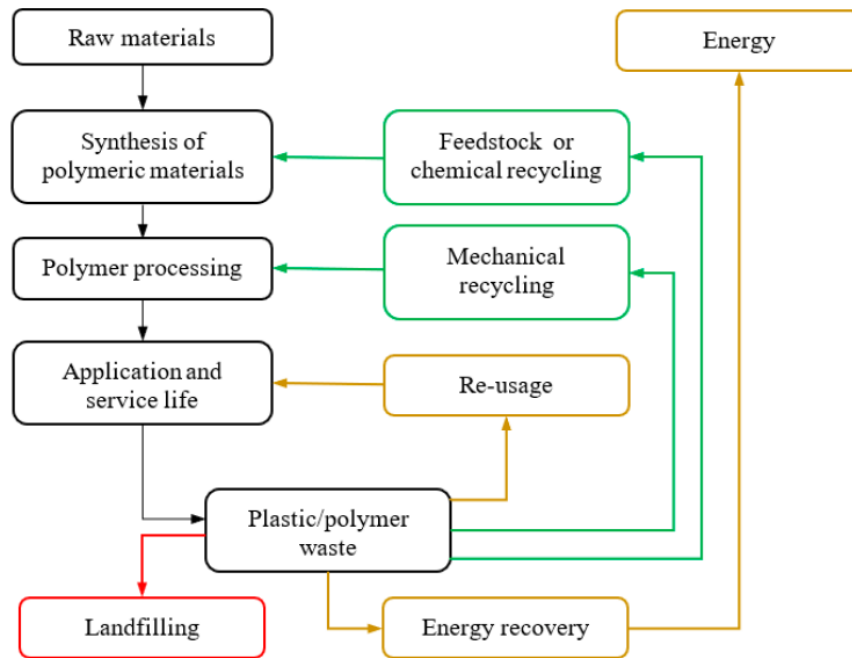


Figure 25: Schematic representation of different waste management choices from Vilaplana and Karlsson<sup>91</sup> and Moens et al.<sup>92</sup> Red arrows represent the less desirable pathways; yellow the processes that have to be minimized, and green the most preferable ones.

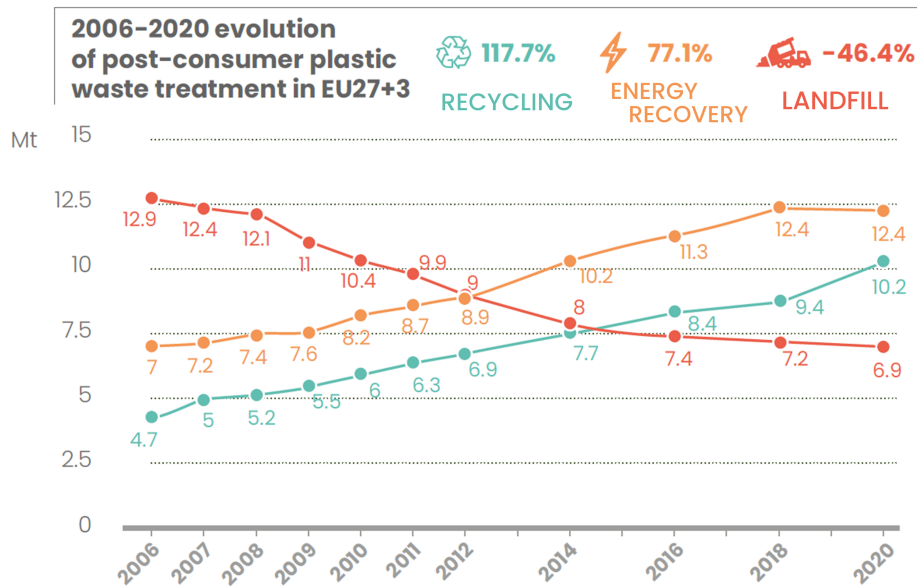


Figure 26: Evolution of post-consumer plastic waste treatment in the EU, Norway, Switzerland, and the United Kingdom from 2006 to 2019.<sup>93</sup>

This polyester can be easily reprocessed multiple times and is usually used alone and in great amounts for different applications, such as fibers, packaging and carbonated soft

bottles, which facilitates its recycling.<sup>6,12</sup> The first recycling attempt of post-consumed PET in the world was in 1977 and since then, a lot of effort has been made to improve different recycling techniques.<sup>9,94</sup>

Three of these recycling strategies used for PET will be detailed below.<sup>6</sup>

### 3.1 Methods and requirements

According to the Environmental Protection Agency, plastic recycling means either the direct re-use of the materials or a physical or chemical treatment. Waste collection is the first and common step for all those treatments and can usually be divided into two schemes: curbside collection and drop-off locations.<sup>2</sup> The first one makes up almost 60% of the recyclables and it relies on the citizens' sorting the waste, collected then by reclaimers. The second method consists in the disposal of household wastes in specific locations, which makes up almost 15% of the total collection rate. However, it has the inconvenience of having a higher contamination level, up to 30%, which will have a huge impact on the reprocessing scheme.<sup>95</sup> A third most recent method is the use of refundable deposits for PET bottles<sup>96</sup>, being today the most reliable method to avoid contamination, but still in development in most countries.<sup>97</sup> By ensuring a mono-collection system with only food-grade PET products, high quality recycled materials can be obtained with a closed-loop approach.<sup>98</sup> In recent years, PET has been replacing other materials such as PE, which could further contribute to recycling possibilities by unifying the waste composition for recycling.<sup>99</sup>

In order to achieve a successful recycling, materials that have been collected have to meet certain minimum technical requirements. These are summarized in Table 4. And, even by adding a sorting of PET materials, to avoid pollution from other plastics, many contaminants might strongly modify the recyclate. For instance, the presence of polyvinyl chloride (PVC) can be hazardous as it contributes to an acid production after chain cleavage. Those acids can act as catalysts for chain scission reactions in the melt state. Authors such as Paci et al.<sup>79</sup> reported that amounts around 100 ppm of PVC would already be enough to accelerate hydrolysis, for example.

Table 4: Minimum requirements for recycling of post-consumer PET according to Awaja et al.<sup>9</sup>

Property	Value
$[\eta]$	$> 0.7$ dL/g
Melting temperature	$> 240$ °C
Water content	$< 0.02$ wt%
Flake size	$0.4 \text{ mm} < d < 8 \text{ mm}$
Dye content	$< 10$ ppm
Yellowing index	$< 20$
Metal content	$< 3$ ppm
PVC content	$< 50$ ppm
Polyolefin content	$< 10$ ppm

Some of the methods used for avoiding contamination are the identification and separation by near-infrared spectroscopy, color and density differences. Artificial intelligence may also be a useful tool for identification of non-PET products.<sup>96</sup>

Another requirement that can be relatively easily met is the avoidance of water pollution. In processes where melted polyester is in contact with humidity and/or water, hydrolysis can occur (see Part 2). In manufacturing sites, drying conditions are usually around 140 °C to 170 °C between 3 to 7 h in order to reduce the residual humidity (%RH) to less than 0.02%.<sup>9,12</sup> But, as stated before, those conditions vary a lot in the literature and usually the evolution of water absorption over time is not well understood or quantified. A drying step in a vacuum oven might also be beneficial by reducing the acetaldehyde content formed as a side product during degradation, being easily extracted due to its volatile nature. It is important to avoid possible migrations, specially in food-contact applications.<sup>6,9</sup> Following the same logic, the presence of heavy metals, such as lead, nickel, cadmium, and antimony, originating from labels and adhesives in poorly sorted PET materials, can cause serious health problems.

The European legislation for use in food-contact applications stipulates that all recycling methods have to be individually approved by the European Food Safety authority. The maximum amount of a non-food PET in recycling processes for food-grade uses is 5%.<sup>100</sup> Franz and Welle<sup>101</sup> reported, however, that this amount could be increased to 20% without safety concerns.

Coloring contaminants are also often found in post-consumer products, especially in packaging and bottles. Those pigments, added to UV stabilizers and oils, used against photooxidation for example, might contribute to molar mass reduction with decreasing intrinsic viscosities associated to chain cleavages. As a result, some companies have started to shift to uncolored transparent plastics and to change their brand image to a more ecological one, according to Petcore Europe.<sup>6,9</sup>

Because of all these specificities that traditional recycling methods have, new methods are being developed. For instance, the *PET Super-Clean Recycling Process* is focused on the total removal of contaminants on PET surface. Coupled with that, the SSP technology might be used for further cleaning and to improve the crystallinity.<sup>6</sup>

Recycling appears not only as a strong tool for waste management but also as a key to decrease the demand for fossil fuels and the emission of greenhouse gases.<sup>102</sup> As an example, bottles made entirely of recycled PET would engender a relative reduction of 27% CO<sub>2</sub> emission (from 446 to 327 g of CO<sub>2</sub>).<sup>102</sup> A smaller but still significant reduction can be obtained even for mixed plastics recyclates.

However, even if this review paper focuses on recycling for PET waste management, it is important to note other solutions that are also being developed and contribute to circularity. One example is the direct re-use of PET products, which could be an eco-friendly solution that contributes to a better space management with weak energy consumption.<sup>28,103</sup> The limitations of this option, however, are similar to those of recycling, namely a collection system that must be developed and coupled with strong washing to avoid contamination. Even by reducing the presence of hazardous substances, the direct re-use of products would hardly allow the use of food-contact applications for safety concerns.<sup>96,103</sup> One recent technology that could help in the traceability of products is the presence of a watermark on labels to better control its life-cycle. Information such as product specifications, number of layers, origin of used materials and number of reprocessing cycles, etc., could allow an easier

re-use.<sup>96</sup>

Another way to reduce energy consumption is on-site manufacturing to avoid the transportation of empty containers between different production sites. Other examples, such as investing in light-weighting of products through an eco-design approach, technological advances for energy consumption reduction in processing units, and the development of bio-sourced resins, show the numerous existing approaches.<sup>99</sup> Notably, there the cooperation between multiple techniques and technologies would also be a valuable option to cover the maximum amount of waste treatment, and this shows a general commitment towards increasing sustainability.

### Other aspects of recycling advances

In order to replace the use of virgin polymers at industrial scale, recyclates must have at least a comparable performance, be available in large amounts, with a competitive price.<sup>99</sup> A recent study conducted by Hundertmark et al.<sup>104</sup> predicted the economic benefit of a fourfold increase in today's recycling rate. With a fixed oil-barrel price of \$75, in 2030 plastic reuse and recycling could lead to a profit of \$60 billion for the petrochemical and plastic sectors. However, to reach that amount of recycling, the plastics waste recovery rate would have to reach 50% of the total produced amount, which would require \$15 to \$20 billion dollars of investment per year. Following this scenario, by the year 2050, one-half of the demand for resins could be covered by recycled ones. The oil-barrel price and the world's economical and political context will, obviously, have an influence on those predictions. Advances in recycling technologies can also close the price gap between a virgin and a recycled PET.<sup>99</sup>

Indeed, in order to achieve such a significant recycling rate and recovery, investment in this sector must be done. Effective collection systems have to be put in place along with an alignment with the industrial sectors business model, adapted to this changing conjuncture.<sup>104</sup> Factors such as easier data access about availability and quality of rPET can also encourage their use by industrial actors.<sup>102</sup> Additionally, available information on how to prioritize each of the different approaches according to waste origin, geographic region, and economical means, can help to better guide policies. Thus, technological advances should work side-by-side with the evolution of legislation on the matter.<sup>99,102</sup>

Focusing on the technical aspect, the next sections will develop in more detail three of the recycling methods that can be applied for PET and other polymers.

## 3.2 Energy recovery

One traditional method used for waste management is energy recovery. It consists in using the calorific content of waste for electrical or thermal energy through complete or partial oxidation.<sup>89,105</sup> This, also called incineration, leads to a total destruction of the material and the production of water and carbon dioxide, as do classic petroleum based fuels. It also produces gaseous fuels, oils, chars, and ash as by-products.<sup>105</sup>

Plastic materials are usually considered a convenient energy source because of their relatively high energy content. For example, standard polyolefins have a calorific content of around 46.6 MJ/kg against 45.2 MJ/kg for gas oil and 42.3 for petroleum. PET however, has a much weaker energy production, between 13 to 24 MJ/kg for packaging products.<sup>89,105,106</sup>



The complete combustion of this polymer is achieved at temperatures between 800 °C to 1000 °C. At around 500 °C, high yields of liquid products can be obtained, even though the majority consists of gaseous species<sup>89</sup>, being less adapted for oil extraction for example.

Incineration is capable of reducing the quantity of the original waste by 90%–99%, needing therefore a much smaller disposal area when compared to other recovery methods.<sup>105</sup> This can be a huge advantage for countries such as Japan, where only a limited area for landfill is available<sup>89</sup> and excavation is difficult because of the geological nature of the ground.<sup>102</sup> Plus, it can be a useful technique for highly mixed plastics in applications such as electronic wastes<sup>102</sup>, as no sorting is demanded. According to Stallkamp, Christoph, et al.<sup>107</sup>, energy recovery of plastics is an interesting process from an economical point of view. Studying automotive plastic waste, they have shown that the processing costs are lower than for chemical recycling via pyrolysis (around 0.05 to 0.02 euros/kg waste input for energy recovery against 0.05–0.08 euros/kg waste input for pyrolysis).

From an environmental point of view, however, the energy recovery process is much more damaging. It is responsible for emitting greenhouse gases and the formation of toxic combustion residuals such as fly ash.<sup>89</sup> Plus, it produces volatile organic compounds, particle-bound heavy metals, and carcinogenic substances, such as poly aromatic hydrocarbons and dioxins.<sup>105</sup> The presence of mixed plastics such as PVC can also induce the formation of halogenated compounds, increasing the risk of pollution.<sup>102</sup> Capture and removal of these pollutants is a major problem and is dealt with either by the addition of substances such as ammonia, acid neutralization or activated carbon, or through a filtration process.<sup>105,108</sup> Anyhow, the overall climate change impact has been estimated to be twice as high than for advanced recycling for automotive plastic waste (1.17–1.25 against 0.57–0.64 kg CO<sub>2</sub>e/kg waste input respectively).<sup>107</sup> When it is feasible, prioritizing chemical or mechanical recycling can be a better solution for a circular economy and an ecological balance of plastic waste in general, PET included.<sup>105,107</sup>

### 3.3 Advanced recycling

Advanced (or chemical) recycling consists in a depolymerisation process followed by a purification and a repolymerisation to obtain the final product.<sup>109</sup> It allows breaking long polymer chains to come back to the initial monomers or oligomers. The vulnerability to solvolytic chain cleavage with different degrading products makes several polymer families (polyesters, polyamides, and polyurethanes) very suitable for this technique.<sup>109</sup> The increasing interest in this recycling method is reflected in the number of published papers on the subject, being, since 2015, more than 70% of the literature about PET recycling.<sup>99</sup>

Chemical recycling has been used for PET by taking advantage of the reversible reaction equilibrium of polycondensation or by intentionally choosing specific conditions to engender the already discussed degradation. Some of the reactions that can take place during chemical recycling are hydrolysis, glycolysis, methanolysis and ammonolysis (see Figure 27), consisting in reactions of the ester group with different molecules.<sup>94</sup>

The main advantage of this type of recycling is the fact that the final properties of the obtained products are not dependent on the origin of the waste and will not suffer from losses in the properties, as a repolymerisation step takes place. This means that almost no waste sorting is necessary and several condensation polymers can be reused. The fact that it

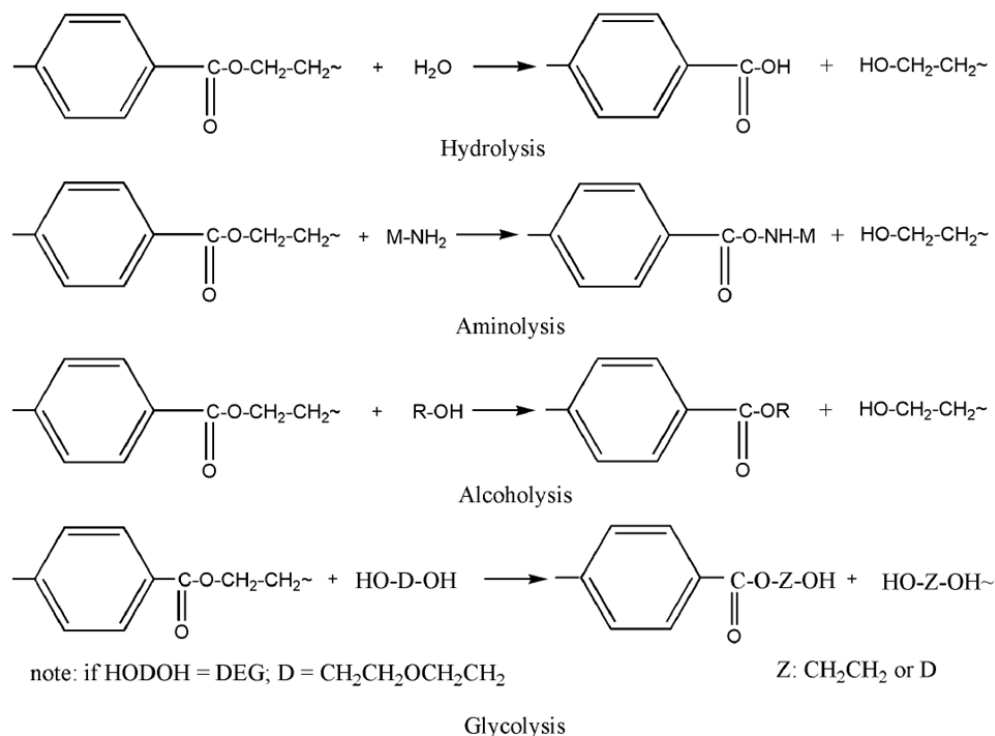


Figure 27: Possible routes for chemical recycling of PET. Figure from Jankauskait et al.<sup>94</sup>

is suited for food-contact applications also increases its interest.<sup>110</sup> Plus, polymers that have already been exhausted by the mechanical recycling process, for instance, can be recycled by a pyrolysis pathway, which can also easily treat mixed polymer sources.<sup>28,103</sup>

Furthermore, by coming back to monomers, it allows a wider scope of uses. After depolymerisation and purification, the collected monomers can react with EG under specific conditions to reproduce PET. Other applications for glycolysis PET products are, for example, use as starting materials for the rigid polyurethane foam industry. Another possibility is use as a matrix for fiber-reinforcement composites. Recycled PET is used for the fabrication of polymer concrete and mortars. Plus, rPET might also be applied as radiation curable oligomers, a greener option for reducing the solvent emissions for the inks and coatings industry.<sup>94</sup>

Even with these diverse applications, chemical recycling makes up only a small portion of the total recycled PET. One of the reasons for this is the energy-intensive nature of the depolymerisation reactions such as methanolysis, as they need high temperatures in vacuum reactors to take place.<sup>102,103</sup> For example, in order to have a hundred percent conversion in glycolysis, the ideal conditions are 190 °C for 1.5h with a catalysis system. Another disadvantage in the aminolysis reaction, for instance, is the use of hazardous chemical substances such as amines. Their presence will demand a purification step to remove catalyst residues, additives and dyes, increasing the ecological footprint of the process.<sup>28</sup> Additionally, in some cases, a further resizing to flakes and decontamination phase before a glycolysis reaction is necessary. This common step with mechanical recycling reduces the overall interest in the advanced method for mixed recycle sources.<sup>28</sup>

Because of those reasons, the overall cost related to that method is relatively high, producing therefore recycled monomers that are much more expensive than the virgin ones.<sup>18,94,102</sup> It has been calculated that for chemical recycling to be economical, it has to have a minimum throughput of 15 kilo tons per year.<sup>110</sup>

### 3.4 Mechanical recycling

The third and most used method for PET is mechanical recycling.<sup>99,102,104</sup> Also called physical recycling, this relatively cheap method uses standard extrusion lines to produce regranulated materials from plastic waste. Its simplicity and low investment costs for the recycling facilities contributes not only to its profitability but also to lower its carbon footprint when compared to above-cited techniques.<sup>102,111</sup> Life-cycle analyses have shown that mechanical recycling has a greater positive impact from an environmental point of view when compared to energy recovery, advanced recycling, and landfill.<sup>102</sup>

This already implemented and in expansion industry<sup>99,104</sup> has as the first step (after waste collecting) a washing procedure. Using caustic soda or detergents, it seeks to reduce the amount of contaminants, such as dirt, labels and glues. Other plastics are also separated using their differences in densities and color, by a combination of automated and manual processes.<sup>2,6,18</sup> Due to its very similar density, PVC cannot be removed as such, so a two-stage process is done industrially. By taking advantage of its different solubility in a concentrated solution of a derivative of *n*-octyl butane with an inhibitor<sup>112</sup>, PVC can be selectively separated from PET.<sup>112</sup>

After decontamination, PET is retreated either by cutting to resize it to flakes or through extrusion to produce granules. Before that step, it is very important to correctly follow the drying procedure to reduce the residual humidity to 0.02%, as established by most manufacturers (see Part 2). Other subsequent processes, such as coloring or sizing, are often applied before manufacturing the end product. The mechanical recycled materials are usually used for the production of packaging films, sheets, containers, fibers and floor covering.<sup>6,113</sup>

Even though this type of reprocessing is already in large scale use and is well established, there is an important challenge to the use of rPET. Indeed, in an extrusion process, the material suffers from important shearing at high temperatures, which will engender several degradation as discussed above. The final properties of the recyclate will then be modified. It is often said that it induces an embrittlement of the structure, related mostly to a chain scission and/or branching. Therefore, to meet commercial demands, rPET is usually mixed either with virgin polymer or with additives such as chain extenders and toughening agents, which will be discussed in the last part.

However, there is no consensus on the effect of recycling on the final mechanical properties. To some extent, this might be related to the fact that PET is found in several commercial grades, which will react differently during the process. Plus, it is possible to control these mechanisms only by tuning the extrusion parameters such as temperature, screw speed, and the extrusion profile.<sup>18</sup> Anyhow, an overview of what is most commonly described in the literature related to the modifications caused by reprocessing is presented below.

## Physical and structural modifications to the PET

The effect of multiple extrusions on the rheological and mechanical properties have been described by La Mantia et al.<sup>87</sup>, using granules once transformed with a knife mill. As can be seen in Figure 28, they have found an important viscosity drop (from 400 for virgin to 200 Pa.s) after only two extrusions with a single screw (equipped with a Brabender unit, rotational speed of 100 rpm and thermal profile 210 °C–230 °C–260 °C–270 °C).<sup>87</sup> The viscosity stabilizes once the molar mass reaches a critical value, which was not given in the paper.<sup>87</sup> The extrusion parameters also have important repercussions on the viscosity drop, being higher for faster rotational speeds. Water exacerbates this mechanism of hydrolytic chain scission, even though it would also take place in a dry environment, caused by the thermomechanical degradation.

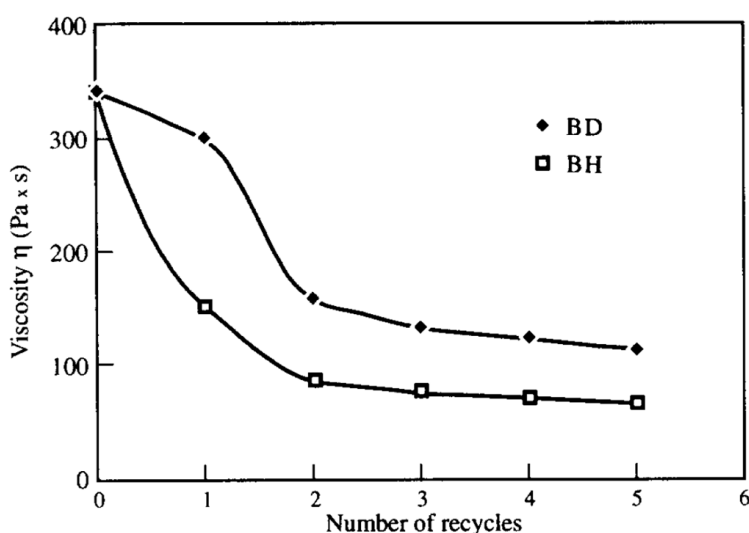


Figure 28: PET viscosity evolution as a function of the number of extrusions in two different environmental conditions. B: bottle grade (IV between 0.73 and 0.82 dL/g), D: dry (3 h at 100 °C) and H: humid (no drying). Reprinted with permission from reference.<sup>87</sup> Copyright 1994 Elsevier.

An end-group titration can also be a valuable tool to quantify the downgrading of PET, and has been used by several authors.<sup>114</sup> In more industrial applications, a Melt Flow Index (MFI) measurement can be a fast and safe test as it does not require a complex sample preparation nor dissolution in hazardous solvents. It allows revealing the viscosity loss of a polymer, coming as a complement to more complete methods such as cone-plate rheometry. The increase in the yellowing index, caused by the presence of chromophoric by-products, is sometimes described as a way to quantify the degradation as well (cf. Table 5).<sup>114</sup>

Table 5: Mechanical properties of virgin and reprocessed PET. Reprocessing consisted of a single-screw extrusion ( $D/L = 30$ ,  $D = 32$  mm, five heating zones: 220–260–285–290–295 °C, 102 rpm) followed by water quenching and chopping. After injection molding of pellets (feeding temperature of 270 °C, nozzle temperature 280 °C and 20 s cooling) for mechanical characterization. Reprinted with permission from reference.<sup>114</sup> Copyright 2001 John Wiley and Sons.

Processing Cycle	Crystallinity Degree (%)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Yellowing Index (a.u.)
0	24	25.0 ( $\pm 0.7$ )	112 ( $\pm 23$ )	63.0 ( $\pm 2.9$ )	9
1	27	26.0 ( $\pm 0.6$ )	167 ( $\pm 42$ )	60.0 ( $\pm 1.6$ )	14
2	35	27.0 ( $\pm 1.9$ )	140 ( $\pm 45$ )	60.0 ( $\pm 1.7$ )	17
3	38	52.0 ( $\pm 3.1$ )	6.0 ( $\pm 0,7$ )	52.0 ( $\pm 2.9$ )	27
4	38	54.0 ( $\pm 2.1$ )	6.0 ( $\pm 0,2$ )	54.0 ( $\pm 2.0$ )	48
5	38	55.0 ( $\pm 2.3$ )	6.0 ( $\pm 0,3$ )	55.0 ( $\pm 2.2$ )	52

A modification of the crystallization is a widely described consequence of the mechanical recycling of PET. Usually the ease of crystallization is explained by three main factors: 1) the decrease of the molar mass, 2) the molecular orientation favored by the injection molding during processing and 3) the residual moisture content.<sup>80,114–116</sup> Those modifications can be noticed also in the mechanical behavior. The presence of a spherulitic crystallization, for example, may reduce the elongation and the impact strength of PET materials. Frounchi et al.<sup>117</sup>, confirmed this rise in crystallinity for PET that had endured several extrusion cycles, accompanied with an increase of the crystallization temperature when cooling from the melted state. In that specific case, the main explanation was related to a nucleation favored by a decrease in the length of the polymer chain.

Badia et al.<sup>118</sup> also tried to explain the modifications observed in the degree of crystallinity caused by the shortened PET chain using another concept, that of a rigid and a mobile amorphous phase (MAF and RAF respectively). Because of the lower molar mass of the mobile amorphous fraction, a reorganization is favored, modifying the overall periodicity of the material. The crystal modifications were observed, among others, by DSC analyses. An increase of a bimodal melting behavior, intensified with the number of reprocessing cycles, was associated with the formation of domains with smaller lamellar thickness (see Figure 29). Along with that, the crystallization temperature from the melt state by cooling was increased, indicating that successive recycled samples crystallize earlier and faster.<sup>116,118</sup>

A deconvolution process Figure 30(a) demonstrated that a first population diminishes with the recycling cycles in favor of a second and third populations with lower lamellae thickness (cf. Figure 30(b)). All those observations confirmed the heterogeneity of the chain lengths, worsened by humidity.<sup>118,119</sup> The same conclusion was observed by Spinacé et al.<sup>114</sup> in another study, who demonstrated a crystallization temperature increase of almost 40 °C for 5-times extruded samples compared to vPET (cf. Table 5) and a bimodal melting peak.

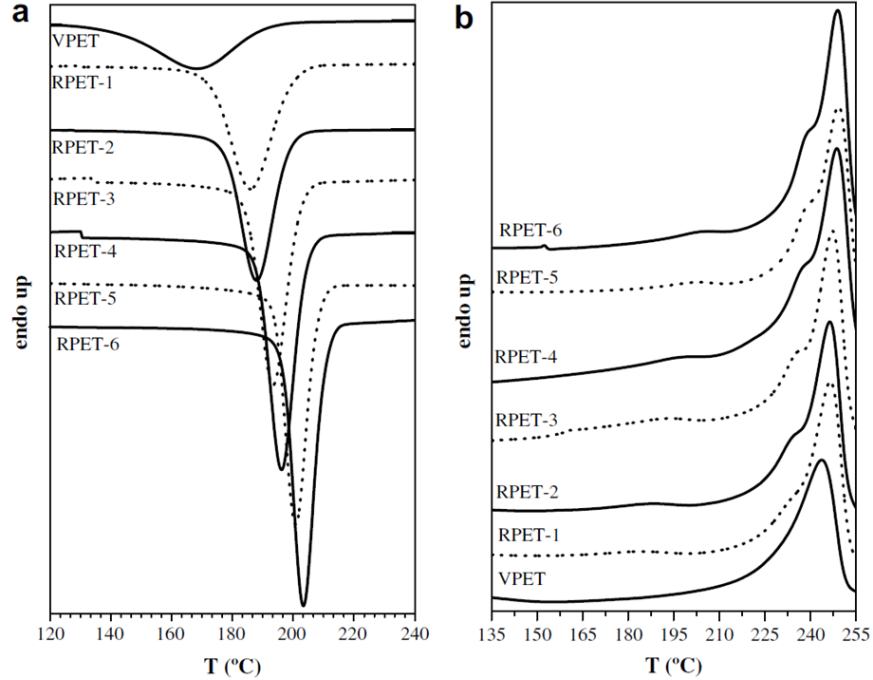


Figure 29: DSC thermograms for virgin and recycled PET. On the left, a crystallization scan and on the right, the melting scan. Reprinted with permission from reference.<sup>118</sup> Copyright 2009 Elsevier.

The presence of impurities of heterogeneous deposits might induce or accelerate some modifications.<sup>110</sup> For instance, post-consumer PET with high contents of contaminants, such as PVC, traces of labels and adhesives containing esters or ethylene/vinyl acetate copolymers, paper and aluminum scraps, etc.<sup>120</sup> will suffer a greater modification of their  $T_c$ , due to their action as nucleating agents.<sup>115</sup> PET's color and clarity may also be modified by their presence.<sup>110</sup> Those materials will also suffer even more after injection molding for instance, because the presence of impurities as such could increase the hydrolytic degradation as explained before.

The decrease in molar mass and the alterations in the crystallization will have direct impacts on the mechanical properties. The first consequence is the embrittlement of the material, with a rise in the modulus, described by most authors and related to both these micro-structural modifications.<sup>87,114,118,119,121,122</sup> This more fragile behavior can be easily seen in a drop of properties such the impact resistance and the elongation at break in a tensile test (cf. Figure 31). For example, La Mantia et al.<sup>87</sup> and Spinacé et al.<sup>114</sup> (cf. Figure 31 and Table 5 respectively) found important losses in the properties in both these parameters after two or three extrusion cycles. After a significant drop at the beginning, where the main chain scission happens, the material properties tend to arrive at a plateau (the chains are already too short to be further wounded).

Wu et al.<sup>119</sup> reached similar conclusions, finding a modest increase in the modulus after three reprocessing cycles by co-rotating extrusion (screw diameter of 25 mm,  $D/L = 40$ , profile temperature 190 °C–230 °C–260 °C–265(x4) °C–260 °C). Samples were dried in a vacuum oven at 140 °C for 8 h.<sup>119</sup> The main impact observed was also on the elongation

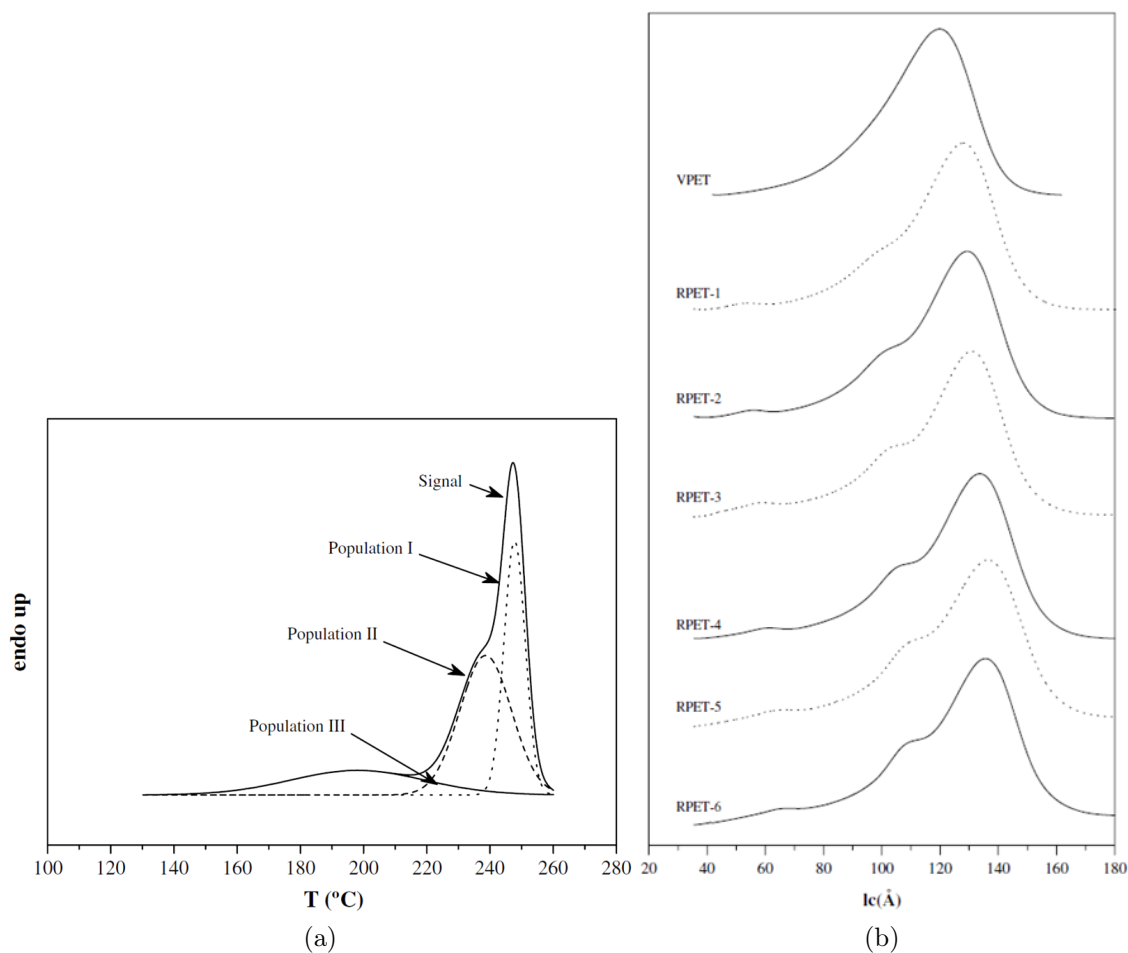


Figure 30: (a) Deconvolution of the melting thermogram into crystalline populations. (b) Lamellar thickness distribution for vPET and rPET. Reprinted with permission from reference.<sup>118</sup> Copyright 2009 Elsevier.

at break and on the impact strength, as can be seen in Figure 32, related to a higher crystallinity and processability. By comparing the conventional twin-screw extruder method with an eccentric rotor extruder (self-made extruder with a rotor diameter of 34 mm,  $D/L = 20:1$ )<sup>119</sup>, Wu et al. brought to light the influence of the processing method on the degree of degradation of recycled PET. The average processing temperature will also have an impact on PET obtained molar mass according to Fox et al.<sup>122</sup> They also confirmed the correlation of  $M_n$  and the impact strength on Izod configuration. It is worth noting that in this study, only the  $M_n$  was calculated by viscosity measurements. But the relation between the molar mass by number and the mechanical response must be done with care, as  $M_w$  is more appropriate in this case. The polydispersity index could be given to establish a relation between them.

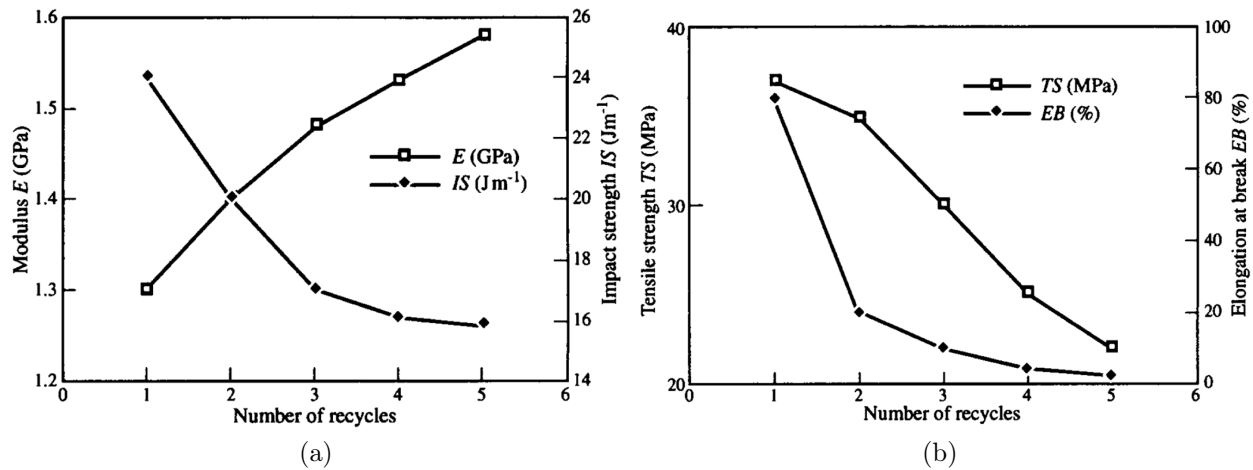


Figure 31: Impact of the successive extrusion recycling cycles on mechanical properties of PET. Extrusion conditions: temperatures between 120 ° and 140 °C and screw rotation of 40 rpm. (a) Young's Modulus ( $E$ ) and impact strength ( $IS$ ) (b) Tensile strength ( $TS$ ) and elongation at break ( $EB$ ). Reprinted with permission from reference.<sup>17</sup> Copyright 2004 Elsevier.

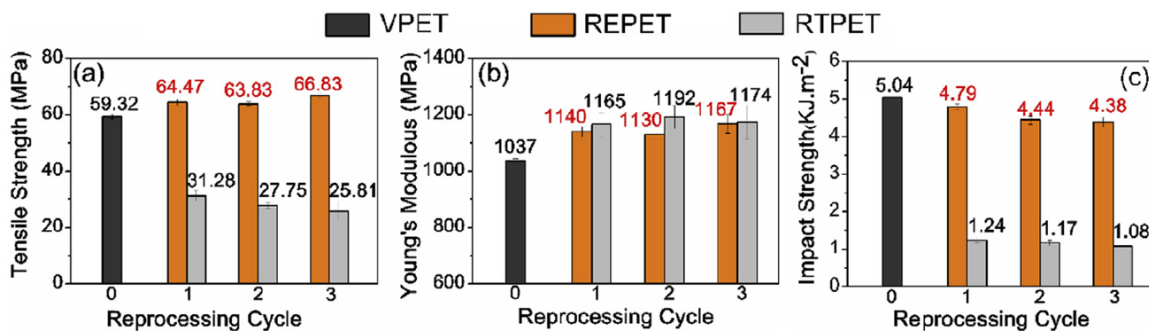


Figure 32: Effect of reprocessing by two different extrusion techniques. REPET for PET recycled by an eccentric rotor extruder and RTPET one recycled by convention twin-screw extruder. (a) Tensile strength (c) Young's modulus (c) Impact strength. Reprinted with permission from reference.<sup>119</sup> Copyright 2019 Elsevier.

Yet another study by Wang et al. confirmed the impact of a molar mass decrease on mechanical properties of UV-irradiated (irradiator with six) PET films under tensile stress.<sup>121</sup> Samples were irradiated using six fluorescent sunlamps with a spectral distribution between 280–400 nm and a single maximum of radiation at 314 nm for accelerated photodegradation, as PET's sensitivity to light starts at this wavelength.<sup>121,123</sup> They showed, however, that this photodegradation was mostly concentrated in a thin layer of 15  $\mu m$  and the the reason for a premature break was related to the ease of crack propagation under stress. Due to that study, three different  $M_n$  regimes could be established for the elongation at break (see Figure 33):



- Regime I where  $M_n$  is lower than 11 kg/mol: PET has a fragile behavior and a stress at break ( $\sigma_y$ ) around 125 MPa;
- Regime II for  $M_n$  between 11 and 17 kg/mol:  $150 < \sigma_y < 300$  MPa;
- Regime III for  $M_n$  higher than 17 kg/mol: the properties tend to stabilize ( $\sigma_y > 300$  MPa) without any further increase with the molar mass.<sup>121</sup>

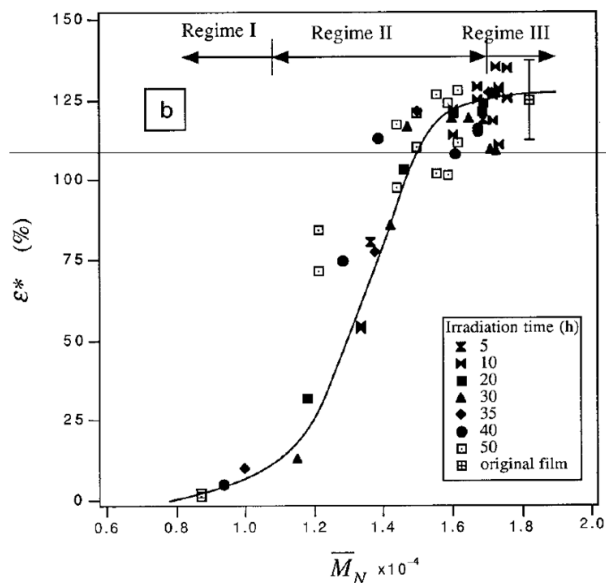


Figure 33: Strain at break as a function of the molar mass in number of different UV-irradiated PET film. Reprinted with permission from reference.<sup>121</sup> Copyright 1998 John Wiley and Sons.

Contrary to these observations, other authors have reported more modest modifications of the impact strength. Frouchini et al.<sup>80</sup>, for instance, showed that, even for a considerable molar mass loss (from  $M_w = 50.4$  kg/mol for virgin to 22.3 kg/mol for three extrusion-cycles on PET), only a slight modification of the material toughness was to be found, almost within the measurement error. In this particular study, they attributed this to the fact that the critical molar mass ( $M_c$ ) was not yet reached. This conclusion is in accordance with the  $M_c$  value of 17 kg/mol usually given in the literature for PET, even though there are only few studies that have confirmed this value.<sup>124</sup>

Another issue that might explain PET modifications, other than micro-structural changes, is the difficulty in obtaining a surface uniformity after injection. That challenge was reported by Mancini et al.<sup>125</sup> who mentioned shrinkage of tensile test samples during injection molding and a temperature gradient in flexural specimens, causing crystallinity differences. A more uniform mold could be obtained for samples of dog bone, allowing mechanical characterization by tensile tests. As with other researchers, they stated an increase in the modulus with a strong loss of the elongation at break, but in this case, after only the first injection cycle. However, they also brought to attention the standard deviation of these mechanical properties, which sometimes restrains any conclusion on the recycling effect, even though

they became smaller the more recycled the sample was. These observation might be related to the fact that the material reprocessed many times in that research originated from a uniform polymer, producing recycled samples with better qualities.

As one can see, the scientific community agrees on the fact that reprocessing causes chain scission of PET.<sup>126</sup> That was confirmed by several authors that used mostly molar mass measurements and carboxyl end group titration as a degradation marker.<sup>126</sup> Using rheology to measure the viscosity after processing was a valuable technique too. The increase of crystallinity was confirmed, although explanations for this feature varied a little bit between researchers.

Meanwhile, there is no agreement on the modifications of the mechanical properties. Some have observed a strong effect on the elongation at break and on the modulus, indicating a structural embrittlement.<sup>87,114</sup> Others concluded that only modest mechanical behavior differences were observed or that the standard deviation was too high to reach a conclusion.<sup>117,125</sup> The arrival at a plateau of those properties is not always observed after the same number of cycles either.

It is therefore mandatory to analyze the conclusions and the results in the literature with a very critical eye. For example, in none of those papers are the drying conditions and the extrusion processes the same. As an illustration, Frounchi et al.<sup>117</sup> would dry their pellets for 120 °C for 24 h whereas Spinacé et al.<sup>114</sup> reduced their granules humidity at 160 °C for 6 h. The water content after the drying procedure is almost never indicated in these papers. Plus, even something so little as the different forms (between powder and granules for example) can modify the surface residual humidity and ease of drying, because the crystallinity is not the same in those two states, but above all because the specific surface is very different.

With that in mind, a recent study conducted by Celik et al.<sup>127</sup> compared different commercial post-consumer PET recyclates in constant conditions. Taking advantage of a probability study, they stated that the impact strength, elongation at strain and melting temperature are not affected enough to allow an easy distinguishing between virgin and recycled materials, mostly because the vPET is already available in a wide range of properties. Only crystallinity and the glass transition temperature were considered distinct enough to allow a differentiation between these materials.

Anyhow, PET is inevitably modified after recycling and processing. It might be desirable anyway to overcome these losses or to improve the mechanical properties of virgin and/or recycled resins in order to meet the standards needed for specific applications. An example is the blow molding process, which will require higher molar masses than a PET used for the production of textile fibers, for instance.<sup>125</sup> The next part will discuss some of the strategies used with this purpose.

## 4 PET reinforcement strategies

PET undergoes several modifications after mechanical recycling, specially a drop in the  $M_w$  and therefore a loss of viscosity. Shortening and degradation of the chains may also cause modifications in the crystallization that affect the mechanical characteristics of the final product. Drying, formulating with stabilizers, and performing a decontamination step have already been discussed in Part 2. Other techniques to overcome these losses in properties,

extensively described in the literature, will be summarized below.

## 4.1 Impact Resistance: Theory and strategies

The impact resistance of a material is its ability to resist a sudden load without failure.<sup>40</sup> Two of the most important mechanisms of failure are shear banding and crazing (or cracking). The first one gives the material a ductile behavior whereas the second one engenders a mechanical failure in a brittle manner.<sup>128,129</sup> The brittle–ductile transition (BDT) is the switch from one failure mechanism to the other. At this specific point, the coexistence of both shearing and crazing can happen. Experiments carried out in a SAXS showed that their interaction can modify the material’s response according to Stoclet.<sup>130</sup> On a tensile test, another object, called deformation bands (or croids), can grow alongside with the existing shear bands. Their presence acts as retaining walls for the propagation of craze and no failure is obtained before a critical craze size is reached.<sup>130,131</sup>

The BDT is characterized by the *ductile–brittle transition temperature* ( $T_{BD}$ ). An application of a *critical stress* is also responsible for this transition. The time–temperature superposition principle allows establishing a link between these two modifications. At high test speeds or low temperatures, the brittle behavior is favored. Inversely, ductile failure is predominant at slow test speeds or higher temperatures.<sup>40</sup>

Other than the temperature and the test parameters (or specimen geometry), the material’s chemical nature and organization will influence its mechanical response. Indeed, a macroscopic failure starts at a molecular level.<sup>132,133</sup> Under stress, the chemical bonds that can no longer resist the applied load will break, leading to a crazing. According to Kausch<sup>133</sup>, the sample strength is proportional to its molar mass and chain orientation. A critical chain length allowing physical crosslinking (typically a few tens of kg/mol) is mandatory for macroscopic strength. Below this value, the chains tend to slip between each other and the overall strength is governed by the intermolecular attraction.<sup>133</sup> The mechanical behavior will, therefore, depend mostly on the microstructure, which can be tuned to some extent, for specific purposes, via processing for example.

This critical molecular length is related to the molar mass ( $M_e$ ) between entanglements, the value between two crosslinking points. When  $M_e$  is weak, the tridimensional network is very dense with a high crosslinking rate. A polymer as such will present on a tensile test a ductile mechanical behavior, driven by the presence of shear bands formed with an angle of 45° to the stress axis.<sup>134</sup> This mechanism is usually preferable as it produces a ductile response with a better energy dissipation.<sup>40,135</sup> It is worth noting that a polymer can have a high impact strength even with a brittle failure, but in most cases, ductility implies higher impact resistance.<sup>40</sup>

In contrast, when  $M_e$  is much higher, the crazing mechanism drives the fracture.<sup>136,137</sup> It has a characteristic formation of voids (cavitation) with fibrils (of the order of a nanometer), perpendicular to the axis of load. If the crazing phenomenon is localized in a small volume in the sample, a fragile fracture is observed. In that case, a linear relation between the impact load and the sample deflection is observed in experiments.<sup>40,132</sup> But if they occur in a relatively higher volume of the polymer, a ductile fracture happens, with a characteristic non-linear relation between the sample’s stress and deflection.<sup>40</sup> Studies have shown that a modification in the  $M_e$  won’t affect the craze geometry itself but mostly reduces its density

after stretching until a shear banding mechanism becomes favored.<sup>130</sup>

Polymeric materials can sometimes be resistant to craze initiation or propagation or both.<sup>40</sup> Preexisting defects in the material, such as surface irregularities, or the presence of voids and notches, may also weaken its resistance to stress.<sup>40,132</sup> For instance, semicrystalline polyesters are known to be notch sensitive, which means that mostly the craze propagation will be responsible for their brittle behavior<sup>138</sup> as crack initiation needs a significant energy to happen.<sup>139</sup>

As a consequence, a material that intrinsically has a fragile behavior can have this modified only by their molecular orientation. According to Xu et al.<sup>140</sup>, a brittle–ductile transition can be obtained by biaxial orientation of chains, in a pre-treatment before the tensile test with PLA (see Figure 34).

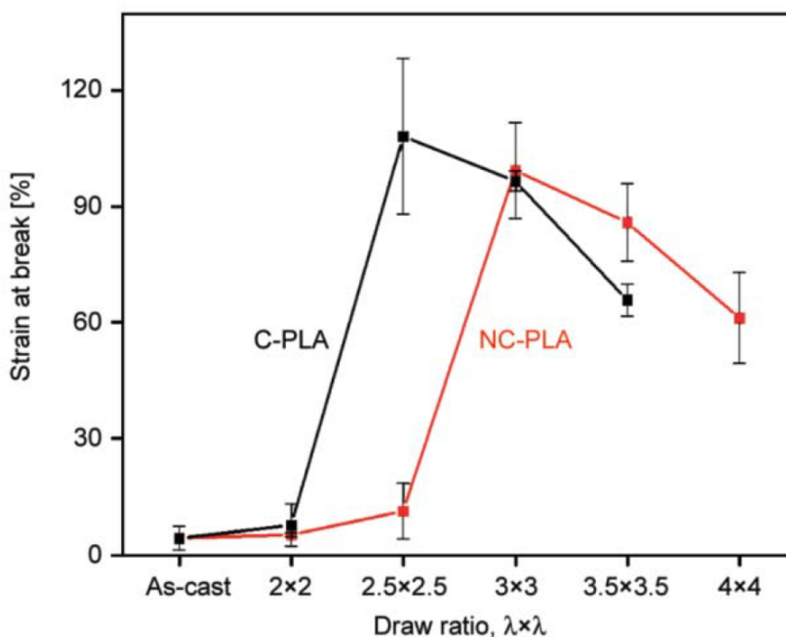


Figure 34: PLA strain at break as a function of the biaxial stretching. C-PLA = crystallizable PLA grade (2% D component) and NC-PLA = non-crystallizable PLA grade (8 to 10% of D component).<sup>140</sup>

The reason for this modification in the PLA is usually attributed to a crystallization induced by chain orientation.<sup>141</sup> However, Ouchiar<sup>142</sup> showed that even with an equal crystallinity after the sample preparation step, a ductile behavior was observed.<sup>142</sup> This was explained by the predominance of the shear banding over the crazing due to the orientation of the chains. They reached a critical value where the brittle–ductile transition took place. In other words, the critical strain needed for a crazing mechanism proved to be higher than for shear banding.<sup>130,142</sup>

In order to avoid premature failure of semi-crystalline polymers, the three most used strategies are a crystallinity modification, the use of dispersed rubber particles, and the increase of the molar mass.<sup>40,143</sup> The impact of the orientation of this organized phase and its morphology has been discussed in more detail in Part 1. In this section, the focus will

be placed on the addition of rubber toughening particles, its mechanisms and actions in polymers in general and in PET.

## 4.2 Chain extenders

Chain extenders are molecules with at least two functional groups, capable of reacting with the terminal groups of the polyester chain.<sup>9,144</sup> These also called coupling agents, and are capable of reversing the molecular mass loss caused by degradation. Combined with a mechanical recycling process, it can contribute to prevent degradation by stabilizing the molecule's terminal groups, preventing chain scissions, and increasing thermal stability.<sup>144-146</sup> Although, in principle, all bifunctional chemicals could be used as chain extenders, the presence of side reactions, resulting in undesirable by-products and branched and/or crosslinked structures, limit the possibilities of their use. Plus, the initial molar mass or the end-group concentration can guide the used functional groups. For instance, hydroxyl-reactive chain extenders are more effective for increasing the IV on low molecular weight PET obtained by melt-polymerization, where the hydroxyl terminals are present in greater concentration.<sup>144</sup> A recent study by Jang et al.<sup>145</sup> provides information about the strength and weakness of some chain extenders based on their functional group.

The processing allowing the reaction between a polymer and a chain extender is termed reactive extrusion or reactive chain coupling.<sup>9,12</sup> It has been gaining more interest as it can enhance the properties not only for virgin but also for reprocessed and recycled polycondensates.<sup>147</sup> Chain extenders are usually added in a single- or twin-screw extruder, making it a relatively easy and cost-effective procedure, especially when compared to solid state polymerization.<sup>147</sup> They allow the acquisition of a wide range of viscosities, starting from the same polymer. Also, the reactions occur faster than polycondensation, happening in only minutes instead of hours.<sup>9,12</sup>

However, in some cases, the use of a high vacuum and/or catalysts is mandatory for the completion of the reaction. Another drawback related to this kind of reactive species is the inefficiency of restoring the molar mass of very severe degradation undergone by post-consumer materials for instance.<sup>147</sup> In this particular case, where the extent of the deterioration of the material is too great, the added amounts become too large to preserve the economic viability of this method. In addition, undesired modifications can occur, such as alterations in color and haze, problems with processability, and instability during storage. Plus, some of these molecules can be hazardous because of their high reactivity and formation of by-products.<sup>144,147,148</sup> For the reactive extrusion reaction to work properly, great attention must be given to the stability of the operating system, in order to avoid disturbances to the reactions.<sup>149</sup> Parameters such as screw design<sup>149</sup>, residence time, die pressure, and temperature, must be controlled at all times.<sup>9,150</sup>

The most common chain extenders for PET are bifunctional dianhydrides<sup>151</sup>, diepoxides<sup>152</sup>, diisocyanates or bis(oxazoline)s.<sup>12,147,148,153,154</sup> Other authors have used molecules such as triphenyl phosphite<sup>155</sup> or diimidodiepoxides for chain extension. Multi-functional agents can also be used, although they have a very narrow processing window and can lead to catastrophic gelation caused by branching.<sup>147</sup> The structures of some of these chain extenders are summarized in Table 6, with comments on the structural modifications described in the literature.

For example, Villalobos et al.<sup>147</sup> added a commercial multi-functional styrene-acrylic oligomer called *Joncryl-ADR-4368* (from Jonshon Polymer, see Table 6) to a rPET. This polymer proved to be very effective for chain extension at concentrations around 1.5 wt%, without the addition of any catalyst or air-free conditions. They showed that, even if the reactions can induce crosslinking, Joncryl has a large gel-free processing window, even for very low intrinsic viscosities (see Figure 35). Furthermore, the overall price of this method proved to be lower than SSP.<sup>147,156</sup>

Table 6: Chain extenders - Bibliography examples.<sup>9,11,146,148,151,155,156</sup>

Product Commercial name	Function	Chemical structure	Amount (%wt)	Reaction with...	Structure	Comments	Reference
Joncryl ADR-4400 (BASF)	Epoxy		0,5 (vPET) 1% (rPET)	COOH	Linear or ramified	Samples with additives resist to several extrusion cycles without such a significant Mw loss. Joncryl is the most used chain extender on the PET industry.	Candal et al. [11]
Polyad PR 002 (Mix Joncryl 4368 et 4370)	Epoxy		0,5 (vPET) 1% (rPET)	COOH	Ramified		Duarte et al. [156]
Triphenyl phosphite (TPP)	Phosphates Phosphites		1% (vPET) 3% (rPET)	OH et COOH	Linear or ramified	Competition between chain extension and degradation, specially during storage	Cavalcanti et al. [155]
1,3-phenylene-bis-oxazoline (1,3 PBO)	Oxazolines		0,3-0,7% (vPET fiber grade)	COOH	Linear	Additives disturb PET crystallization mechanisms, thinner lamellae formed. Increase on storage and loss moduli plus complex viscosity	Berg et al. [148]
N,N-carbonyl bis caprolactam (CBC)	Bis-lactam		0,3% (vPET fiber grade)	OH			
Pyromellitic anhydride (PMDA) Nipon	Anhydride		0,05-2% (vPET fiber grade)	COOH	Linear or ramified	PMDA increase PET's intrinsic viscosity and reduce the carboxyl end group concentration to values close (or better) than for vPET. Used for bottle production.	Awaja et Daver [9] Incarnato et al. [151]
Bisphenol-A dicyanate (BADCy) Dow / Shell	Bisphenol-A		0,6 (vPET low IV)	COOH	Linear	Melting and crystallization temperatures were shifted to lower values with the addition of BADCy on PET. Interferes with the crystallization, giving unperfect crystals.	Zhang et al. [146]

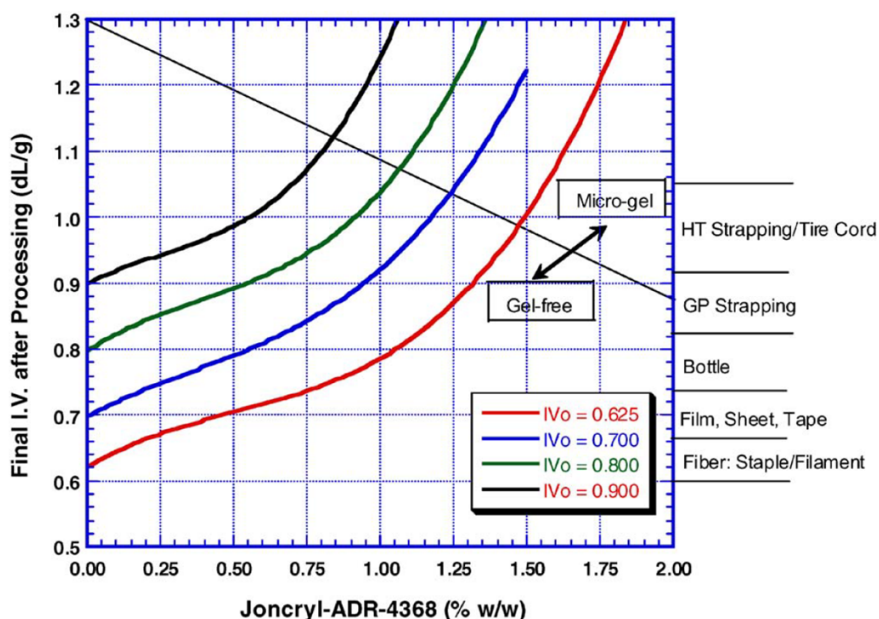


Figure 35: Final intrinsic viscosity as a function of the amount of Joncryl as a chain extender for different PET grades. IV 0.8 and 0.9 come from of a virgin resin, 0.7 from a post-consumer recycled bottle flake, and 0.625 from a SSP precursor. Reprinted with permission from reference.<sup>147</sup> Copyright 2006 Elsevier.

About this same additive, Duarte et al.<sup>156</sup> showed that, even if Joncryl seems to be less efficient for post-consumer PET than for the virgin resin, it will not interfere in the reprocessing of these materials. Plus, they also observed lower molecular mass losses after recycling when compared to a vPET without Joncryl. They demonstrated that, by exceeding the addition of the initial PET, the resulting materials from reprocessing might be “protected” of chain scission.

Chain extension will have an impact not only on the microstructure but also on the rheological behavior. Because of the longer chains formed, a higher Newtonian viscosity with a shear thinning behavior appearing at lower shear rate is observed, as reported by Berg et al.<sup>148</sup>. Reducing this effect is important for some applications such the spinning of fibers, imposing the use of only small amounts of these long molecules.

In this specific study, Berg et al.<sup>148</sup> used 1,3-phenylene-bis-oxazoline (1.3-PBO) and *N,N'*-carbonylbis-caprolactam (CBC), which can react respectively with PET’s carboxyl and hydroxyl end groups. The chain extension process proceeds in a linear way for both molecules, which is important for the production of fibers for instance. They showed that the presence of those additives also disturbed the formation of highly crystalline structures in the polymer, resulting in the formation of smaller objects. According to them, the lamellae are promoted by the hydrogen bonds between the end groups of different PET chains.<sup>148</sup>

Another molecule that can react with both end groups of PET (COOH and OH) is triphenyl phosphite (TPP), due to the available electrons in its chemical structure. Its use with recycled and virgin PET was investigated by Cavalcanti et al.<sup>155</sup> By optimizing the processing conditions (specially the temperature) for the addition of TPP to PET materials, a reduction of the degradation was possible, while promoting the chain extension. However,

TPP showed a very low stability during storage caused by the presence of degradation by-products, bringing to light a possible problem with this technique.

This chain extender was added to formulated PET (with glass fiber and elastomers) to improve the impact strength at various temperatures. The best improvement was accomplished by the addition of a core-shell polyester (containing a poly(butyl acrylate) and a poly(methyl methacrylate)).<sup>157</sup> Those additives can also be classified as impact modifiers, which will be discussed in more detail below.

### 4.3 Toughening agents for PET

The addition of rubber particles on notch sensitive polymers like PET is a common way to limit a brittle fracture and widen its possible uses.<sup>40,138,158</sup> These so called impact modifiers are generally elastomeric compounds often used as toughening agents to improve both the impact strength and the elongation at break.<sup>12,159</sup> The dispersion of a rubber phase within a matrix induces a brittle–ductile transition at lower temperatures. This avoids the localization of stress by inducing an overall deformation mechanism. There are many parameters that might influence the success of those additives. For instance, the particle size and the inter particle distance need to be within a specific range, which will be discussed below. Furthermore, the type of compatibilizer will have a repercussion.<sup>12</sup>

Impact modifiers can be reactive or non-reactive. Usually reactive impact modifiers are preferable as they allow a good dispersion in the matrix by a strong grafting.<sup>12</sup> This is possible due to functionalized end-groups that will not only actively connect the two distinct phases together, but also reduce the free energy in the interface of the additive, enhancing dispersion. They also help to avoid coalescence during processing.

According to Scheirs and Long<sup>12</sup>, for effective rubber toughening, it is advisable to maintain an interparticle distance between 50 to 300 nm with a particle diameter of around 3  $\mu\text{m}$ . Loyens et al.<sup>160</sup> showed that the interparticle distance strongly affects the brittle–ductile transition temperature in a PET blend with a copolymer of ethylene-propylene, graft with glycidyl methacrylate (8 wt%).

Usually, a morphological analysis like SEM is used to control the good dispersion and the particle size of the additives. As those compounds can also affect the thermal transitions, differential scanning calorimetry is used for comparison. This technique can also be coupled with X-ray diffraction for the characterization of the crystal structure. Dynamic rheological measurements (DMA) can also provide information about the interaction between the particles. According to the theory of Rohn<sup>161</sup>, if the elastic modulus is greater than the viscous one, it is possible to conclude that the particles are finely distributed in the matrix. This dispersion will also strongly depend on the processing conditions and will affect the mechanical properties, which are also important aspects to be considered for the use of impact modifiers.<sup>15,16,158,160,162,163</sup>

The most used reactive toughener is Lotader<sup>®</sup>, a terpolymer whose structure is presented in Figure 36. The ethylene-acrylic ester segments provide elastomeric properties while the glycidyl methacrylate (GMA) enable grafting with the PET matrix. Furthermore, this molecule will react with the carboxyl end groups already present in the PET structure or formed during hydrolytic and thermal degradation, stabilizing the material. By adding around 20 wt% Lotader<sup>®</sup> to a PET polymer, a fine morphology (cf. Figure 37) is obtained



with well dispersed particles, smaller than 1  $\mu\text{m}$  in diameter. This gives the polymer a “supertoughening” behavior, with an notched impact resistance above 700 J/m on an Izod test (with 1 J/m  $\approx$  8 J/m<sup>2</sup> for the ISO180:2000 norm).<sup>12</sup>

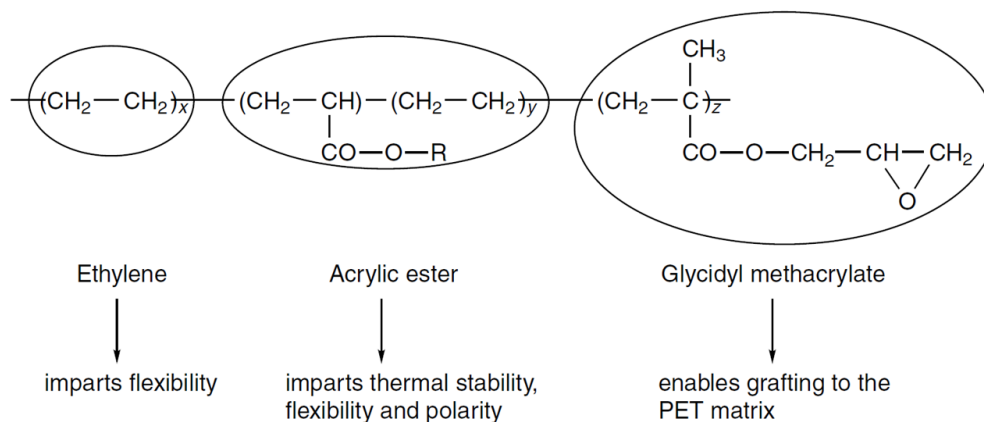


Figure 36: Lotader<sup>®</sup> simplified structure given by Scheir and Long. Each polymer has a specific impact on the final compound. Reprinted with permission from reference.<sup>12</sup> Copyright 2004 John Wiley and Sons.

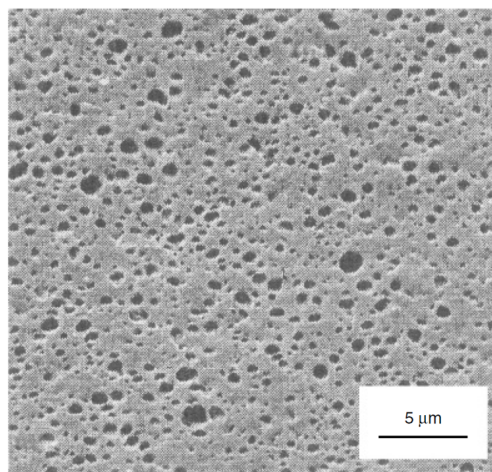


Figure 37: Image from electron microscopy of a selective etched by solvent PET sample with 20% weight of Lotader<sup>®</sup> AX8900. Reprinted with permission from reference.<sup>12</sup> Copyright 2004 John Wiley and Sons.

Another example is the use of a maleic-anhydride-functionalized styrene-ethylene butylene-styrene (SEBS), commercially called Kraton<sup>®</sup>. As little as 1 wt% of this toughener can increase the fracture strain by more than a factor of ten times, and lead to a far superior impact strength.<sup>164</sup> Zahier et al.<sup>162</sup> studied the influence of 20% by volume of SEBS-g-MA in a PET annealed at 150°C under vacuum for 5 h. Due to the reaction of PET's hydroxyl end groups with the maleic anhydride groups, the tensile resistance and impact strength were increased threefold, reaching 30 KJ/m<sup>2</sup>. These improved properties were also perceptible for recycled resins but were better for annealed rPET, especially because increasing the crystallinity reduced the hydrolysis.

Other authors have studied the effect of the polymer on the impact behavior of rubber toughened PET. Loyens et al.<sup>160</sup> studied a PET mix in a two-step batch mixer (first at 180°C, 50 rpm for 5 min and then at 280°C, 50 rpm for 10 min) with an ethylene-co-propylene rubber (EPR with a ratio of 78/22 : *E/P*) and a Lotader<sup>®</sup> grade as compatibilizer, the AX8440 (8 wt% GMA content). They found a correlation between the molar mass and the particle size, interfering with the interparticle distance. They concluded that the higher the molar mass the better the impact strength. However, this conclusion was not related to the matrix itself but to the effect of lower  $M_w$  on the blend morphology. The particle diameters would decrease with higher molar masses, giving a better dispersion and therefore a better impact strength. Below a critical value of 0.1  $\mu\text{m}$ , a clear transition from brittle to ductile can be seen for medium and high molar mass (cf Figure 38). The crystalline morphology of the matrix would also lead to a decrease in the brittle-ductile transition temperature.<sup>160</sup>

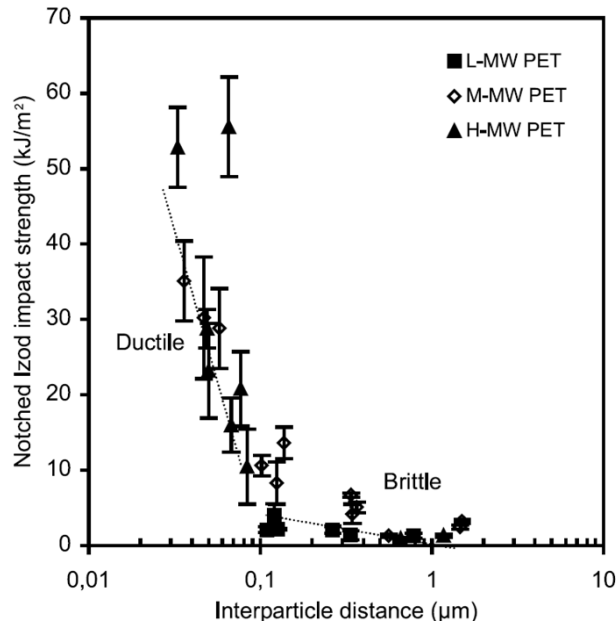


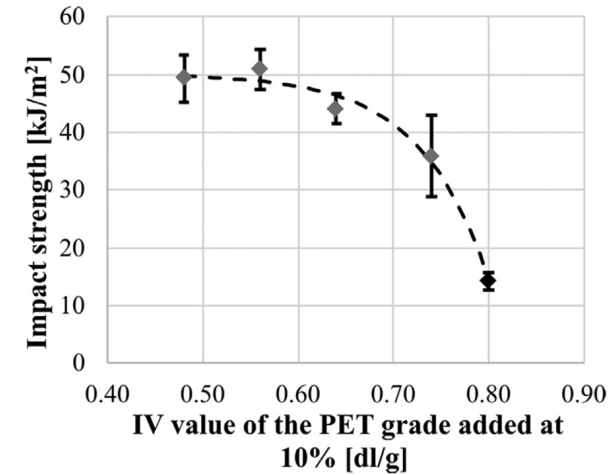
Figure 38: Notched impact strength as a function of the interparticle distance for the investigated PET-EPR-E-GMA (8% w:w of GMA but rubber content varies from 10 wt% to 30 wt%) blends with varying PET molar mass. A constant dispersed phase concentration was used but with a changing ratio of the two dispersed components. L = low ( $M_n = 18.5$  kg/mol), M = medium ( $M_n = 29.5$  kg/mol) and H = high ( $M_n = 38.4$  kg/mol) molar mass. Reprinted with permission from reference.<sup>160</sup> Copyright 2003 Elsevier.

Bocz et al.<sup>15</sup> showed that in some cases, the presence of lower molar masses from highly degraded PET can be beneficial for toughening properties. In Figure 39 (b), one can see the progression of the impact strength with 10 wt% of ethylene-butyl acrylate-glycidyl metacrylate (EBA-GMA, Elvaloy PTW<sup>®</sup>) of different PET grades (see IV and  $M_w$  losses in 39(a)). Indeed, the presence of a high concentration of hydroxyl end groups for the recycled material allows better compatibilization with the EBA-GMA functional groups. However, below a critical molar mass, usually stated to be 17 kg/mol in the literature<sup>124</sup>, the insufficient entanglement density prevents this mechanism from happening. The unreacted epoxy groups still present in the middle can therefore induce a crosslinking mechanism, which is catastrophic for processing.

The competition between crosslinking and compatibilization is key for a good linkage. But, if the crosslinking reaction takes place after the compatibilization has occurred, it can improve the fragmentation of the particles, further increasing the toughening. To sum up, in this particular mixture, both the crosslinking and the fragmentation are favored by the presence of shorter chains (see Figure 40). Due to these mechanisms, a formulated rPET with 20 wt% of EBA-GMA can catch up with the virgin standards in terms of impact strength.<sup>15</sup>

Sample code	Number of extrusion cycles	IV [g/dl]	M <sub>w</sub> [g/mol]	PDI
oPET		0.80 ± 0.02	27 400	2.71
rPET		0.56 ± 0.03	16 900	2.43
PET-1x	1	0.74 ± 0.02	25 200	2.80
PET-2x	2	0.64 ± 0.02	21 500	2.56
PET-3x	3	0.48 ± 0.02	14 850	2.38

(a)



(b)

Figure 39: Results of Bocz et al. (a) IV, average molar mass, and polydispersity index (PDI) of PET grades obtained after different numbers of extrusion cycles (temperatures between 245 °C and 270 °C, screw speed of 20 rpm). (b) Double-notched Izod impact strength of different PET grades with 15 wt% EBA–GMA content after injection (temperatures varying from 260 °C to 275 °C with a mould temperature at 60 °C).<sup>15</sup>

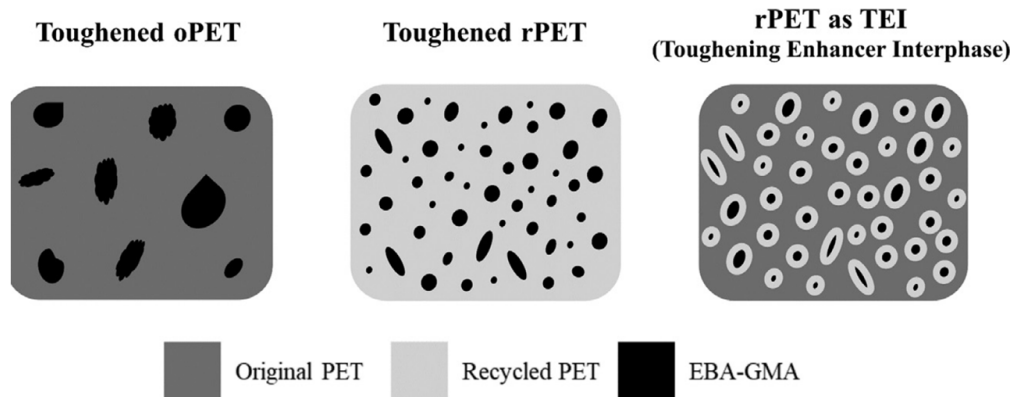


Figure 40: Schematic phase morphology of PET/EBA–GMA systems.<sup>15</sup>

The use of non-functionalized rubber is also a possible solution and can, in some cases, have a good dispersion with resilient final properties. Phinyocheep et al.<sup>163</sup> investigated the effect of a PET-Natural Rubber (NR) without the addition of compatibilization functions. They showed that a good dispersion could be obtained due to the presence of abnormal

groups of the NR chain that could react with the hydroxyl groups of PET via hydrogen bond. This interaction proved to be enough for toughening properties but is sometimes unpredictable, as it depends on the chemical nature of the NR.

Even though those reactive additives are very effective for toughening, one of the worst inconveniences is the presence of hazardous functions such as glycidyl methacrylate (GMA) in Lotader<sup>®</sup> for example. Furthermore, the compatibilization reaction that takes place can strongly modify the rheology of the PET and therefore its processability. They can also modify the material's thermal behavior, observed for several blends such as PET/SEBS-g-MA. The need of formulation with high concentrations of additive, around 20 wt% in some cases, can also cause a coalescence of droplets, even with compatibilization functions. Finally, the blend morphology cannot always be perfectly controlled, with a very specific interparticle distance and particle size, making it harder to toughen PET materials.<sup>138,160,162,163</sup>

Non-reactive impact modifiers have the advantage of not having dangerous monomers and being dispersed only by a physical process such as compounding. Plus, they offer a well-controlled blend morphology due to the emulsion copolymerisation process used for their fabrication. Core-shell elastomers are a good example of non-reactive molecules and have also proven their efficiency for PET and PVC. An example is a methyl methacrylate-butadienestyrene copolymer (MBS), whose commercial name is Paraloid EXL<sup>®</sup>. This additive can be very useful, especially for application where cold impact resistance is needed, without altering the thermal and other mechanical properties of the final material.<sup>12</sup> However, only a few studies of non-reactive additives are present in the literature, especially on what concerns virgin and recycled PET, separately and together. In what follows, the influence of virgin PET on recyclates will be discussed.

#### 4.4 rPET and vPET composites

Blending a recycled polymer with a virgin resin of the same nature is a commonly used technique to upgrade post-consumer materials.<sup>165</sup> Plus, the increasing amount of legislation in the EU, for instance, which imposes the use of a certain amount of rPET in bottles or packaging, makes it even more important to understand the mechanisms involved in that kind of composite. Even though not a lot of research has been focused specifically on PET blends, some studies for other polymers indicate that it is possible to achieve mechanical and rheological properties close to those of the virgin material, especially when following a SSP.<sup>165,166</sup> The characterization of those mixtures is usually similar to what can be done for the study of additives such as impact modifiers.

Elamri et al.<sup>165</sup> studied the effect of two different PET post-consumer sources for a composite with a fiber grade vPET. When compared with the virgin resin, some thermal transitions were modified, for instance a shift of the maximum melting peak to lower values. The crystallization of the composites was modified by the presence of the lower molecular weight of the recyclates in the mixture and the presence of contaminants which could work as nucleating agents. The rPET improved the overall crystallization, having a transition on DSC with a narrower and sharper curve. In other words, in that study, it was concluded that the higher the rPET content, the faster the crystallization kinetics. The effect of the lower  $M_w$  can also be observed by dynamic rheology measurements, where the increasing amount of rPET reduces the apparent viscosity.

Fann et al.<sup>166,167</sup> reported an improvement of almost ten times of the elongation at break when a recycled PET is added to the virgin matrix. The impact strength was also slightly improved. That was explained by the differences in the crystallinity induced during the synthesis, giving the recycled PET a more ductile characteristic (bottle grade with a crystallinity around 14% and rPET around 30%). The crystallization temperature was also modified but in that paper, contrary to what was reported by Elamri et al.<sup>165</sup>, the recycled samples presented a lower  $T_c$ . And following this logic, the more the recycled content, the lower is the crystallization temperature. This conclusion is exactly the opposite from that of other papers cited above, probably because of the nature of the PET used for reprocessing.

The modest number of papers studying the effect of blending virgin and recycled PET on the mechanical and thermal properties, varying their concentration, does not allow a conclusion on the matter. Furthermore, some of these existing studies give contradictory results, for instance on what concerns the crystallinity evolution. This might be a result of a larger difficulty concerning the recycling of PET, which is the huge number of parameters that might influence the properties of the PET itself. Plus, when it comes to recycling, the differences in the processing methods employed and the origin of the post-consumer PET will have a great influence on the final results. It is therefore very hard to establish a consistent progression of the properties that might help to better follow the evolution of the legislation on the matter. Plus, what is usually described in the literature is a mixture of these blends with impact modifiers or chain extenders, which makes it difficult to fully understand the separate modifications of the properties of the rPET. One good example, cited above, is Bocz et al.<sup>15</sup>, where the presence of short PET chains was beneficial for the compatibilization with EBA-GMA reactive modifier (see the last subsection).

The next subsection will discuss another possibility for modifying some of the degraded PET properties, extensively applied in the industrial scale.

## 4.5 Solid State polymerization

Solid state polycondensation is a process used for PET after a first polymerization in the melt state for a further increase of its molar mass.<sup>12</sup> This is done through esterification and transesterification by heating the polymer between its melting point and the glass transition temperature. By controlling the duration of this and the amount of catalyst, a panel of molar masses can be obtained.<sup>12,168</sup>

Cruz et al.<sup>168</sup> studied the use of SSP for post-consumer PET and confirmed the efficiency of this technique for increasing the molar mass and IV. They also demonstrated the success of this process by measuring the carboxyl end group concentration that decreased with the reaction time. By DSC, they found a modification of the melting peak after SSP. This endothermic transition became narrower when compared to a virgin resin, indicating that a homogeneity of crystals was obtained. A viscosity increase after SSP was determined by parallel plate rheometry measurements, a direct result of the molar mass increase. The dislocation of the crossover point of the storage and loss moduli was also an indicator of the success of the procedure. A narrowing of the molar mass distribution was observed. However, the viscosity loss over time is more significant for materials already suffering from a first recycling process, even for a similar molar mass obtained after a further polycondensation.<sup>168</sup>

In a recent study, Pinter et al. provided important results about the use of SSP for

a closed-loop bottle-to-bottle process.<sup>98</sup> The effect of eleven recycling cycles of a mixture of rPET/vPET : 75/25 was evaluated in terms of chemical, optical and intrinsic viscosity quality. Their simulation of an industrial recycling process involved a pre-drying step at 140 °C for the first extrusion, a SSP process (at 190 °C for 7 h), a second extrusion for adding additives (0.05% of an acetaldehyde blocking agent and an anti-yellowing colorant), and a final hot wash (1% NaOH and 0.2% detergent) before a new cycle. A filtration step using glass fibers was introduced when hazardous contaminants did not respect the legislative threshold. Due to the SSP, the  $\Delta IV$  between a virgin resin and a rPET that followed 11 reprocessing cycles was around 0.011 dL/g, maintaining an IV higher than the minimum required for bottle production of 0.8 dL/g. By adjusting the SSP conditions, the targeted IV could be reached even when higher IV modification happened, which was observed after nine cycles. Thereby, these researchers showed that using this recycling scheme could enable bottle production without compromising its final quality. However, in this study, no data about the mechanical behavior was provided.

Even though this process is very useful for compensating for the degradation mechanisms that PET can go through during processing and life-cycle, it is a very energy- and time-consuming technique. The reaction times will be even longer for more degraded polymers, which have higher COOH content from chain scission reactions.<sup>12</sup> As the concentration of carboxyl acid end-groups will either favor the esterification or the transesterification reaction, the SSP process in this case can last for more than 10 h at temperatures around 230 °C.<sup>12</sup> The use of very low IV (between 0.18 and 0.19 dL/g) can also slow down the reaction rate by 3 to 5 times, mainly by the modification of the crystallization behavior of PET.<sup>169</sup>

Another issue is the production of chromophore groups due to the high temperatures employed, leading to thermal degradation. These by-products increase the yellowness of the material. A further compounding can be done for the addition of colorants to compensate for these modifications<sup>98</sup>, amplifying the complexity of this recycling scheme. The loss of transparency in bottle production, where PET finds its main application, can also be an issue. Finally, SSP often counts on the use of catalysts which are usually expensive and hazardous. Hence SSP is a high-cost process from many points of view.<sup>9,12,168</sup>

## Conclusion

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic commonly used in everyday products. Important for packaging and disposable bottles, it is today one of the most popular plastics. It is well known as a very resistant material, with excellent impermeability to water and gas, attractive optical properties, and good processability.<sup>2,9,12</sup>

After the steps of its synthesis, mainly through a trans-esterification reaction, a further solid state polycondensation is used to increase the molar mass and a large range of intrinsic viscosities (IVs).<sup>9,24,28</sup> Each one of these synthesized grades will be used for specific applications. A PET with a lower IV can be used for the production of fibers, whereas higher viscosities can be used, for example, for industrial tire cords.<sup>9</sup> The crystallinity will also play an important role in PET's mechanical resistance, and can be tuned by different paths. On top of its physical characteristics, the processing method may be an asset for achieving specific requirements for final applications.<sup>9,12,119</sup>

Added to these possibilities, PET have gained an increasing interest due to its recyclable nature. Several operations that aim to recover this material and to convert it into new items can be considered as recycling.<sup>11,125</sup> By taking advantage of the reversible nature of the reactions producing PET, initial monomers can be restored for another life cycle.<sup>94</sup> This is called advanced recycling and has been gaining more interest due to its diverse scope of applications and the stability properties of the recyclates, without a specific sorting step.<sup>28,99,103,110</sup>

Mechanical recycling, another option for PET, is already established as a sizeable business and requires fewer investments, allowing a faster development of recycling facilities.<sup>99,104</sup> By using standard processing lines, washed collected materials can be resized to flakes for new manufacturing cycles.<sup>6,125</sup> Its overall positive ecological balance makes it a practicable option for waste management.<sup>99</sup> Challenges related to the modification of the structure of the polymer after recycling and the difficulty in sorting and avoiding contaminants from diverse sources can complicate this process.

Even if PET's degradation mechanisms are well known to the scientific community, the extent of structural modifications are sometimes hard to estimate. The fact that several mechanisms act simultaneously and can, occasionally, counteract each other, make it challenging to draw conclusions and to evaluate the significance of every parameter.<sup>17,76</sup> The effect of chain scission on the mechanical response of recycled polyethylene terephthalate (rPET) is a good example of contradictions found in the scientific literature. Some authors claim that the loss of molar mass greatly reduces its impact strength and elongation at break.<sup>17,87,114,118,119</sup> Others have not observed such modifications.<sup>117,124</sup> Other studies report very insignificant modifications, as if they were expressive, without taking into account analysis errors.<sup>17</sup>

Anyhow, after mechanical recycling, rPET has different properties than vPET. A modification of the crystallization is almost always observed, either because of the processing or because of the presence of shorter chains.<sup>72,80,82,118</sup> Losses in the molar mass, increasing concentrations of carboxyl and hydroxyl end groups, and yellowing, are some of the modifications that have been confirmed by studies in different contexts.<sup>75,114,170</sup> These physical and chemical modifications can be balanced or avoided with the use of additives.

Impact modifiers and chain extenders are widely used and have proven their efficacy in many studies. By applying some of these molecules to a virgin and a recycled blend, some studies have even found that the presence of very degraded polymers can be beneficial, opening other pathways for the recyclates.<sup>12,15,160</sup> But these reactants have important drawbacks.<sup>12</sup> They might reduce the possibilities of several reprocessing cycles, because of their unstable nature and the cross-linking that they can induce.<sup>15,82,155</sup> By-products can also be formed during reactions between the PET and the additives, which can modify the rheology and thermal stability.<sup>147,148</sup> It has been found to be difficult to develop non-hazardous functionalized molecules capable of enhancing properties with a fixed morphology.

Another possibility is a combination of several technologies. For instance, advanced and mechanical recycling can be complementary techniques to overcome the limits associated with each one of them.<sup>99</sup> Discarded PET from various sources can be converted into valuable products by chemical recycling. However, when less investment or more discrete amounts of waste are available, mechanical recycling, associated or not with solid state polymerization (SSP) and compounding with additives, can be the most eco-friendly way to increase the



circular life cycle of PET.<sup>99,102</sup>

After a careful analysis of the literature, partially expositied in the present paper, one can note that few studies have arrived at the same conclusions. From our perspective, there are several reasons for this. One of them is the vast number of processing methods that are ordinarily referred to as *mechanical recycling*. An example will be given for illustration. For some, rPET issues from pelletizing with a knife mill followed by an extrusion process and finally an injection blow-molding for the production of a new bottle.<sup>87</sup> Others will consider something directly after extrusion to be a recycled material, because new granules were obtained from a post-consumer product.<sup>125</sup> By comparison of these two methods, it is obvious that the first type of mechanical recycling will have a much more severe effect on the structure of the polymer. So, among the literature data, to make a meaningful comparison of the mechanical properties of rPET products, it is essential to take into account the respective processing methods.

More than technical advances, the evolution of the economic, legislative, and social aspects can also influence the viability of recycling.<sup>102</sup> The first obstacle is the insufficient number of collecting units for the huge amount of disposable waste produced every day.<sup>4,89,90</sup> Then, other factors, such as the lack of control of waste sources and the unclear picture of how to recapture and reuse discarded waste by the numerous available techniques shows the remaining need for more research on the matter. For instance, very few papers have compared advanced recycling and mechanical recycling<sup>99</sup> with respect to their viability in different circumstances and environments, for example. Industrial actors play a key role for this transition as well.<sup>99,102,104</sup>

In conclusion, PET is a very promising material from many points of view. It has gained attention and importance for the research community, which has been trying to understand and administer its multiple applications. A development of recycling has to be done not only to deal with the enormous amount of PET waste, but also as a circular-economy approach. While the occurrence of PET chain scission during use or processing and the effectiveness of drying or SSP in maintaining sufficient molar mass are well established, few studies have focused on quantifying the effect of varying the molecular parameters on the loss of mechanical properties, and this point would deserve to be clarified. Establishing these connections will permit a better targeting of the modifications that new technologies can bring to this polymer as well as the need the pressing need for greener solutions to address the effects of these modifications without compromising the recyclability.

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