Polyethylene terephthalate (PET) in the packaging industry

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Abstract

Polyethylene terephthalate (PET) is the third most widely diffused polymer exploited in the packaging industry, monopolizing the bottles market for beverages, and covering almost the 16% of the European plastic consumption in the packaging industry. Even if PET primarily derived from fossil sources and remains not-biodegradable in the environment, novel advancements in the field pointed out the possibility of producing PET in a more sustainable way (e.g., from biomasses) or the possibility of biodegrade this polyester through the enzymatic action of specific genetically-modified/isolated bacteria/enzymes. By considering also the high recyclability of PET, and the possibility of potentially indefinitely re-use this material, one can assume that the future of PET is still to be written. Therefore, all aspects involving the industrial production (with traditional and sustainable chemical routes), intrinsic physicochemical/thermal/mechanical properties, undesired degradation phenomena, chemical/mechanical recycling processes, and processability of PET are here critically discussed. A particular emphasis has been dedicated to the role of PET in the packaging industry. The main achievements in the PET processing for food packaging are presented, analyzing advantages and disadvantages of each technology. This document aims at providing a useful instrument that collects past, present, and future of the PET: a well-consolidated material that has been able to renew itself over time.

Keywords: Bottle recycling; Engineering plastics; Packaging; Polyesters; Thermoplastics.

1. Introduction

Polyethylene terephthalate (commonly abbreviated as PET, PETE, or by the resin identification (recycling) code #1) is one of the most diffused thermoplastic polymers available on the market [1–3]. PET relies on the polyester family, which is a wide category of polymers characterized by having esters functionalities within the macromolecular main chains [4,5]. Apart from PET, the polyesters family gathers also other oil-derived as well as naturally-occurring polyesters (e.g., the PHAs subgroup produced through bacterial-mediated fermentative processes) [6].

According to PlasticsEurope (i.e., the European plastics producers' association) [7], the global plastics production in 2018 reached ca. 360 million tonnes, and the European contribution results being ca. 62 million tonnes (i.e., 17%). In the same year, the European plastics demand surpassed 50 million tonnes, mainly absorbed by the packaging industry, which is the main relevant industrial segment (ca. 40%), followed by the construction and building industry (ca. 20%), and the automotive (ca. 10%). Among polymeric materials, PET occupied 7.7% of the European market (ca. 4 million tonnes), making this polymer the sixth per importance (after PP, LDPE, HDPE, PVC, and PUR) [7]. In a recent report, PET has been pointed out as the third most commonly used plastic in the packaging industry (covering ca. 16% of the European consumption) with a continuous growing demand [8]. The industrial exploitation of PET by end-segment evidenced that this polymer is mainly used for the production of bottles/containers for beverages, such as water (ca. 26%), carbonated soft drinks (CSD, ca. 26%), or other drinks/juices (ca. 18%), in the shape of sheets/films (ca. 14%), in the food industry (ca. 9%), as well as in non-food uses (e.g., cosmetics, ca. 6%) [9]. Further important end-segments for PET (not-discussed in this document) are the production of fibres for textiles (e.g., polar fleece, or advanced fabrics) [10–12], biomedicine (e.g., hernia-repair meshes, or scaffolds) [13–16], composites [17–

20], separation science (e.g., membrane technology) [21–23], automotive [24], FDM 3D printing (by using a glycol-modified PET, PETG) [25].

Currently, the release of fossil-based non-biodegradable plastics in the marine ecosystems with formation of floating islands (e.g., the Great Pacific garbage patch) due to the synergic action of both the sadly known anthropogenic pollution and ocean currents [26,27], together with the release of plastics fragments and debris (i.e., microplastics) affecting both surface water and the living animals (and, consequently, the human diet) [28–30] is becoming the main environmental concern that deserves worldwide attention and rapid solution. In order to try to mitigate this issue, several directives (and laws) were approved by international organizations (and countries) aiming at reducing/replacing fossil-derived plastics by means of more sustainable bio-based and biodegradable materials [31]. Hence, it clearly emerged how the end-life fate of fossil-derived polymers became an important criterion for selecting materials, especially in the packaging industry. Therefore, before continuing with the entire discussion, it is fundamental to reply to the following question: is PET enough sustainable to deserve attention? The answer is yes, with some reservations [32].

First of all, PET is a thermoplastic polymer, which means that can be easily re-processed at high temperature. Furthermore, PET can be easily recycled as almost the entire bottles' production industry for drinks (i.e., water and CSD) uses extensively this specific polymer (as previously discussed). In particular, the PET recycling industry is very efficient and the PET processing allows obtaining different scenarios, all of them potentially interesting, namely: i) chemical recycling to the initial monomers [33], ii) chemical recycling with conversion-to-polyol by transesterification mechanism and addition to PUR [34], iii) mechanical recycling by exploiting its thermoplastics nature for the production of new bottles (see Ref. [35] and references therein), iv) the production of fibres and carpets or non-food containers [36], v) incineration for energetic gain [37]. The use of recycled PET (named Re-PET or R-PET) as an alternative to "virgin" PET or glass-made bottles significantly rose up in the last decades due to its indefinitely recyclability. Many companies offer bottles containing from 50 to 100% of R-PET, thus covering ca. 1.4 million tonnes of the packaging market in the 2018 [38]. However, even if this solution guarantees a significant improvement in the direction of the environmental sustainability, bio-based bioplastics (e.g., PLA or PHAs) are the best (and ideally preferred) technological alternatives to fossil-based polymers with the only limitation being not always economic sustainable. In this context, it should be reminded the definition of "bioplastic" provided by the IUPAC (International Union of Pure and Applied Chemistry) federation, which is "bio-based polymer derived from the biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow" [39]. Therefore, aiming at providing a more sustainable version of PET, experts developed a bio-PET, which is obtained by merging ethylene glycol (EG) obtained through more sustainable processes (mostly from sugarcane, thus bio-based, vide infra) and terephthalic acid (largely still from fossil-source) [40]. According to the European Bioplastic report, this bio-PET (containing 30% of biomass, due to EG) covers ca. 40% of the bioplastics production in 2011 (doubling the PLA), and attests itself being a real valid protagonist in the bioplastic framework [41]. However, it should be reminded that even if fully and in principle 100% recyclable (R-PET) and with a growing bio-based content (bio-PET), PET still remains non-biodegradable, and if non-properly treated still potentially dangerous for the environment. To overcome this intrinsic issue of fossil-derived polymers, a recent study by Yoshida et al. [42] reported the discovery of a bacterium (Ideonella sakaiensis) able in hydrolyzing PET, thus opening towards promising bioremediation scenarios.

Once defined that PET deserves attention since enough sustainable, it should be remembered also the reasons why PET is the sixth polymer per importance (or fifth if LDPE and HDPE where considered as a single polymer) and the "king of the bottled drinks end-segment" (i.e., 87% of bottled water sold in Europe in 2016 is preserved in PET containers) [43], namely:

- PET is colourless and can be transparent (if amorphous) or translucent (if semi-crystalline). This is a very important characteristic as it allows consumers seeing the content within the bottles.

- PET is lightweight. The weight of a 1L PET bottle designed for containing water is ca. 25 g. For comparison, a 750 mL wine bottle made by glass is ca. 360 g weight, and a 500 mL aluminium can typically use for CSD is ca. 18 g weight.
- PET is thermoplastics, robust, semi-rigid to rigid, mechanically resistant to impact, and stretchable during processing.
- PET shows gas-barrier properties against moisture and CO_2 (this is important for CSD).
- PET is extremely inert compared to the other plastics, and free from plasticizers (on the contrary, in the case of PVC the use of plasticizers is essential).
- In order to improve specific properties, PET can be blended with other polymers (e.g., with PC, PP, PP copolymers, and PBT) or surface modified (through physical and chemical treatments).
- PET can be copolymerized (e.g., PET-G).

Therefore, for all these reasons, PET remains (and will remain) one of the main polymeric materials to be exploited in the packaging industry. This study aims at summarizing in a single document the main achievements obtained by using PET in the packaging industry, in particularly focusing on the bottle processing methods.

2. History and commercialization of PET

The history of synthetic polyester dates back to the discoveries by the American chemist Wallace H. Carothers (1896–1937) on linear thermoplastics polymers performed at the laboratories of the DuPont Company [44]. In particular, the first activities related to polyesters fibres were performed by a strict collaborator of Carothers: the American chemist Julian W. Hill (1904–1996). In 1929s, both Carothers and Hill synthesized polyesters by reacting dicarboxylic acids (octadecanoic acid) with diols (propylene glycol) obtaining macromolecules with molecular weight up to 25,000 Da by removing the water molecules generated as by-products during the condensation reactions (vide infra) [4]. However, the birth of PET is due to the work by the English chemist John R. Whinfield (1901–1966) and his assistant James T. Dickson in the 1941 at the Calico Printers' Association of Manchester (a British textile company). Both scientists synthesized (and patented) PET by performing condensation processes involving the two monomers (i.e., terephthalic acid and EG). Additionally, in the same year, this discovery has been applied for the production of the first PET fibre called Terylene (patent right granted by the Imperial Chemical Industry, ICI), and later as film named Melinex. In the 1950s, PET was also produced by DuPont Company for the American market (purchasing the U.S. right in 1945 for further development) by adapting the technology already exploited for the production of polyamides, developing a PET fibre for the textile industry named Dacron. Also the USSR manufactured PET in 1949 in the laboratories of the USSR Academy of Sciences under the trademark Lavsan. Subsequently, DuPont developed also a biaxially-oriented PET film named Mylar in 1952 [45,46]. Actually, the owner of these brands is DuPont Teijin Films (founded in 2000), but different trade names were provided depending on the company producer. The exploitation of PET in the field of beverages is due to the work by the American engineer Nathaniel C. Wyeth (1911–1990) at the DuPont Company [47]. In particular, Wyeth invented/patented 25 products/processes and reached (for the first time) the degree of Senior Engineering Fellow at the DuPont Company (which the highest technical position available). The highest contribution by Wyeth to the field is the idea of storing CSD (i.e., pressurized liquids) into biaxially-oriented PET blow moulded bottles (patented in 1973), which opened toward the enormous development of PET in the bottled drinks end-segment [47,48]. Lastly, the recent progress made in the PET recycling processes has favoured the use of R-PET also in the beverage industry. In the early 1990s, R-PET has been approved for food contact in the U.S., and the Coca-Cola Company (leader industry in the field of CSD) began the production of plastic beverages bottles introducing R-PET in its formulation [49,50].

3. Synthesis of PET

The traditional production of PET relies on the use of EG and terephthalic acid (or better its dimethyl ester, named DMT) derived from crude oil (traditional oil refinery) [51,52]. The two monomers were obtained through the following mechanisms:

1) EG is produced from ethylene by means of the catalytic oxidation of ethylene with oxygen in presence of silver supported onto alumina as catalyst, thus forming ethylene oxide (EO). Subsequently, the simplest procedure consists in performing the hydrolysis reaction of EO in presence of water at acid pH, thus forming EG. An alternative process developed by Shell (named OMEGA process) consists in the carbon dioxide-mediated hydrolysis of EO yielding firstly ethylene carbonate and subsequently EG with stripping of the volatile carbon dioxide [53,54]. In countries rich in coal deposits (e.g., China), it can be interesting the exploitation of CO (derived from coal's syngas) to generate oxalates and subsequently EG. As reported by Dong and co-workers [55], CO-mediated routes can generate two different processes: either the N_2O_3-mediated carbonylation of alcohols (e.g., methanol) to dialkyl oxalates by means of Pd complexes (and subsequently hydrogenation to EG in presence of a Cu catalyst) [56], or the methanol carbonylation in presence of oxygen by using a Pd/V/Ti catalytic system [57].
2) Terephthalic acid is widely produced through the AMOCO (American Oil Company) process which consists in the oxidation of paraxylene (isolated from the catalytic reforming of petroleum as BTX aromatics fraction) with oxygen in acetic acid medium in presence of a corrosive Co–Mn–Br catalytic system, whereas DMT is produced either through esterification of terephthalic acid with methanol or directly from para-xylene following a multi-step process (Witten process) involving a preliminary oxidation of a mixture of paraxylene and methyl para-toluate in presence of a Co–Mn catalyst, and subsequent esterification with methanol [58].

Alternatively, different chemical routes are exploitable for the sustainable production of EG and terephthalic acid (or DMT) starting from biomass. As well-documented by Pang and co-workers [59], EG can be obtained from four main routes, namely: the conversion of ethanol (via dehydration to preliminary form "bio"-ethylene), glycerol and sorbitol (via catalytic hydrogenolysis with Ru-based catalytic systems), or other lignocellulosic biomasses (in presence of Ru/Ni/W catalysts). On the contrary, terephthalic acid can be ideally obtained through seven "green" pathways, namely: the synthesis of para-xylene from bio-based ethylene (complex multi-step reactions involving trimerization, catalytic disproportionation, Dield-Alder reaction, and dehydrogenation), 5-hydroxymethylfurfural (HMF, through hydrodeoxygenation and Dields-Alder reactions with ethylene or acrolein by means of zeolite catalysts), or isobutanol (through multi-step dehydration, oligomerization, and dehydrocyclization reactions), followed by oxidation to terephthalic acid, the catalytic pyrolysis/reforming of biomass (and further BTX reforming by using properly modified zeolite catalysts) followed by oxidation to terephthalic acid, as well as the direct synthesis of terephthalic acid from isoprene and acrylic acid (through Diels-Alder mechanism followed by dehydroaromatization and oxidation reactions), limonene (via dehydrogenation to para-cymene and subsequently oxidation to terephthalic acid), or furfural (through a very complex multi-step mechanism involving six reactions, in presence of a homogeneous/corrosive catalyst). The main advantages and disadvantages of these sustainable processes are summarized in Table 1 (see Ref. [59] and references therein).

As depicted in Table 1, most of the processes present several criticalities (e.g., harsh conditions, limited feedstock availability, and high costs of raw substrates), thus making these technical solutions still exploitable only at the laboratory scale. Up-to-now, the industrial feasibility has been reached only in the case of EG with two processes, namely: the production of EG from ethanol thanks to the abundant availability of bio-ethanol plants in Brazil/Asia (e.g., the production of PlantBottle™ by the Coca-Cola Company) [59,60] as well as the production of EG from sorbitol in China (by Changchun Dacheng Industrial Group Company Ltd., China) [59], very attractive due to the economic advantages provided by the primary product formed (i.e., 1,2 propylene glycol). Concerning terephthalic acid, only one process reached the level of demonstration scale production: this is the case of the biomass pyrolysis/reforming technology to obtain para-xylene (and subsequently terephthalic acid) developed by Virent Inc. (Wisconsin, U.S.A.) to produce bio-PET [61].

Table 1. Comparison of sustainable processes for obtaining the two monomers useful for the PET synthesis, namely EG and terephthalic acid (data from Ref. [59] and references therein).

Monomer	Feedstock	Yield	Selectivity	Criticalities	Feasibility
EG	Ethanol	High	High	High costs	Commercial
	Glycerol	Medium-low	-	Limited feedstock	-
	Sorbitol	Medium-low	-	Limited feedstock	Commercial
	Biomass	High	High	Diluted conditions	Laboratory
Terephthalic acid	Ethanol	Medium	Low	Harsh conditions	Laboratory
	HMP	High	-	High costs	Laboratory
	Isobutanol	Low	-	High costs	Pilot plant
	Biomass	Low	Low	-	Demonstration
	Isoprene/Acrylic acid	High	-	Limited feedstock	Laboratory
	Limonene	-	-	Limited feedstock	-
	Furfural	Low	-	Harsh conditions	Laboratory

Independently from the origin of the monomers, the mechanism involved in the production of PET is a prepolymerization followed by a step growth polycondensation, and depending on the monomer adopted can be rationalized as an esterification (involving terephthalic acid) or a transesterification (involving DMT) [10]. The reaction mechanism is summarized in Fig. 1. In details, the pre-polymerization step involving the diacid terephthalic acid and the diol EG (esterification, path a) consists in a heterogeneous reaction as terephthalic acid is insoluble in EG at moderate pressure (ca. 3–6 bar) and high temperature (ca. 250 °C). High temperature favoured the solubilisation of terephthalic acid within EG. The process is conducted without adding any catalysts as the diacid functionalities self-catalyze the esterification reaction with the diol. On the contrary, the process involving DMT and EG consists in a transesterification performed at lower temperature (ca. 150–200 °C) in presence of a catalyst (below 0.5 wt%) in an excess of EG. Usually the catalyst selected typically contains antimony. Even this route deserves the removal of the sub-product (methanol) through distillation, in order to push the equilibrium reaction toward the desired product: the prepolymer bis-(2-hydroxyethyl)-terephthalate. During the second step, the polycondensation of the prepolymer is performed by heating at high temperature (ca. 300 °C) under vacuum to remove the EG released during condensation in presence of the antimony oxide (Sb_2O_3) as catalyst. In order to maximize the degree of polymerization in step growth polycondensation reactions for linear polymers, it is important to maintain the equimolar ratio between the two monomers. In fact, the stoichiometric excess of one monomer respect to the other significantly reduces the material’s degree of polymerization (i.e., the presence of a limiting reagent can be used to control the final molecular weight) [3].

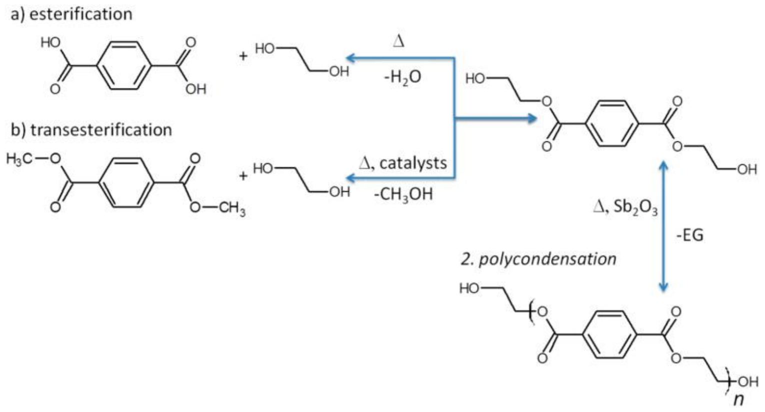

Fig. 1. Schematic representation of the PET polymerization mechanism.

However, these processes present several criticalities and side reactions. In particular, the more commonly-occurring side reaction is the dimerization (via etherification) of EG into DEG (diethylene glycol) during the preheating, and subsequently incorporated as co-monomer during the polymerization [4]. The formation of DEG is catalyzed by the carboxylic functionalities of terephthalic acid. The presence of DEG units within the PET chain, strongly influences the physicochemical and mechanical properties of the final polymer as well as its processability, thus it is mandatory to control it. During synthesis/processing of PET at temperatures above the melting point (ca. 260 °C), it is possible to form chain scission involving terminal ends with consequent release of undesired acetaldehyde (for details, please refers to the dedicated paragraph, vide infra) [62].

However, PET thus produced still present too low properties for being exploited in the packaging industry. Thus, in order to increase the PET physiochemical/mechanical properties, amorphous pellets should be processes following a solid-state polymerization (SSP) step, which is carried out by heating the pre-polymer chips at temperature nearby the melting point (e.g., 220–230 °C) in presence of an inert gas [63,64]. This way, PET characterized by having high molecular weight, melting point, crystallinity, and viscosity were obtained [4,10]. For more details on the synthesis of PET, please refers to Ref. [51,65–67]. For the production of R-PET from the chemical recycling of PET waste, please refers to the dedicated paragraph (vide infra).

4. Physicochemical, thermal and mechanical properties of PET

Table 2 reports a comparison between the main relevant physicochemical, thermal and mechanical properties of PET as a function of the crystalline degree (i.e., amorphous vs. semi-crystalline), according to the CES database [68]. The data summarized in Table 2 clearly evidenced several important characteristics of this polymer, which make it absolutely useful for our daily applications, namely:

1) Density: PET density values are higher than water one, thus this indicates that this polymer sinks in water (independently from the crystalline degree).
2) Optical properties: the crystalline degree affects the optical properties of PET. In details, amorphous PET is transparent, whereas semi-crystalline PET is opaque (white). Such loss in transparency in crystalline polymeric materials is given by the formation of crystalline spherulites which scatter the light [69]. Moreover, the transparency of amorphous PET is very appealing for its application in the beverages industry. In microcrystalline materials, crystallites dimensions are small enough to avoid alteration of the optical transparency in the final object, thus this way it is possible to design transparent bottles/containers, which favour the consumer seeing the desired content [70].
3) Gas-barrier properties: PET is widely used in the packaging industry due to its proper low permeability against several gases (e.g., oxygen, nitrogen, and hydrogen). The barrier property of PET against oxygen is estimated being ca. 1.5 cm^3 mm/m^2 day atm, whereas HDPE, LDPE and PP ones are 60, 200 and 70 cm^3 mm/m^2 day atm, respectively [71]. Such barrier properties might be influenced by several parameters, one above all crystallization (e.g., the higher the crystallization,

the lower the permeability) [10,72,73], thus preserving foods and beverages sensitive to oxidation (e.g., organoleptic, nutritional, and colour alterations) [72]. Additionally, PET presents good barrier properties against several organic aroma compounds and due to its CO_2 barrier properties compared to other plastics, PET can be used for packaging CSD [74].

4) Thermal properties: The aromatic rings and the polar groups forming the PET main chain favoured an improved thermal stability and a general stiffness of the polymer. As reported in Table 2, the melting point (or T_m, which corresponds to the crystalline solid-to-liquid transition) of a semi-crystalline PET is in the 255–265 °C temperature range (which is quite high for being a polymer). Furthermore, the glass transition temperature (or T_g, which corresponds to the glassy-to-rubbery state transition, i.e., from brittle to viscous materials) of amorphous PET is ca. 67 °C, for semi-crystalline PET is ca. 80 °C, whereas in the case of crystalline and oriented PET chains it raised up to ca. 125 °C [10,75]. This trends confirmed that the higher the order degree within the polymer structure, the higher the T_g. This is also reflected by the temperature of maximum service (or T_{max}, which corresponds to the highest temperature at which the polymeric material can be used for an extended period of time without significant problems). In fact, higher crystalline content induced an intrinsic higher thermal stability and consequently a higher T_{max} (i. e., ca. 115–120 °C for semi-crystalline PET and ca. 55–65 °C for amorphous PET). Fundamental for the processability of PET is the mould temperature (or T_{mould}, which corresponds to temperature of the mould surface for processing the polymer) that in the case of amorphous PET is nearby RT (namely, 20–30 °C), whereas in the case of semi-crystalline PET is ca. 125–145 °C.
5) Chemical stability: PET is chemically inert toward several solvents and reactants; however, it is sensible toward strong acids and bases, weak bases and hydrocarbons. PET is soluble in *orto*-chlorophenol, trifluoroacetic acid, and hexafluoroisopropanol [10] Additionally PET is sensitive to hydrolysis at temperature above T_g [76].
6) Mechanical properties: PET mechanical performances are strongly influenced by several parameters, such as the polymer crystalline degree, processing (i.e., orientation) and shaping (e.g., bottles, films, fibres). In general, PET shows high mechanical strength compared to traditional polymers (i.e., higher stiffness), with a Young's modulus of ca. 3.0 GPa (i.e., for comparison HDPE is ca. 1.1 GPa, and PP ca. 1.4 GPa). Moreover, the lower the crystalline degree, the higher the elongation at break (see data in Table 2). Additionally, Fig. 2 reports a typical stress vs. strain curves for a PET film [77]. As highlighted by this curve profile, it is possible to enhance the mechanical properties of PET by forcing the polyester's chain orientation applying a stretching direction at temperatures comprises between T_g and the crystallization temperature (i.e., in the polymer's rubbery state). According to Ansari and co-workers [77], orientation (deformation) enhances the polymer toughness over five times than standard PET. It is possible to rationalize this peculiar behaviour by following the curve profile and distinguishing two regions, namely: strain softening region (Region I) and strain hardening region (Region II), respectively. In the strain softening region (which corresponds to the first segment of the curve), the stress increases until reaching a yield point, than remains almost constant for large deformations. Once the strain hardening point has been reached (and this is a function of the orientation conditions selected), the strain hardening region (second segment) finally starts. In this region, the stress increases rapidly, thus confirming a strain induced alignment of the polymer's macromolecular chains, leading to chain orientation (hardening). As well-documented by the literature [77,78], this hardening is strongly influenced by the strain rate (high strain rate enhances PET hardening) and temperature (high temperature decreases PET hardening). The explanation of this strain-induced phenomenon is attributable to the specific chemical structure of PET, and in particular to the presence of aromatic rings and polar functionalities (esters) along the main chain. In detail, once macromolecules chains are subjected to such strain-induced orientation, these functionalities are able in interact between each other (through π-π coupling between the aromatic

groups, and H-bonding between esters), and favouring a crystalline organization, with progressive orientation of the aromatic rings parallel to the direction of the deformation [79].

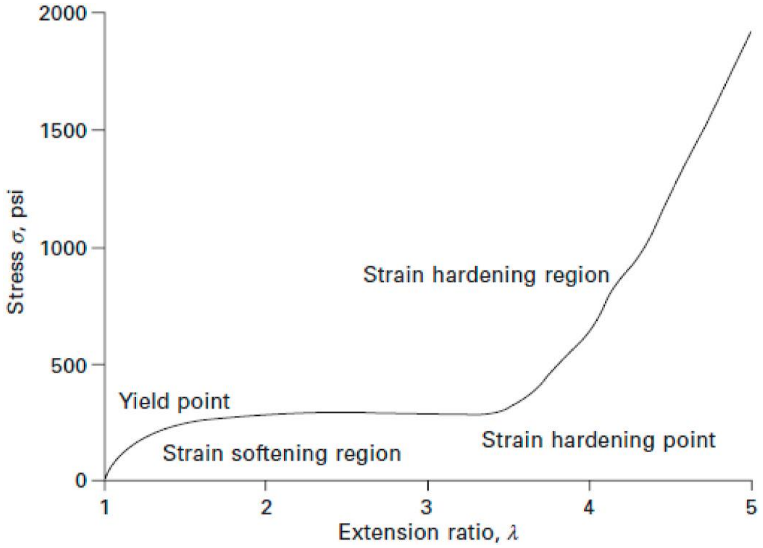

Fig. 2. Typical stress vs. strain curve for a PET film at temperature above the T_g. Reprinted with permission from Ref. [77].

Table 2. Physicochemical and mechanical properties of PET according to the CES Database [68].

PET	Physicochemical					Thermal			Mechanical		
	Density (g/cm^3)	Transparency	Permeability, 25°C		T_g (°C)	T_m (°C)	T_{max} (°C)	T_{mould} (°C)	E (GPa)	σ_{max} (MPa)	ε_b (%)
			O_2	CO_2							
Amorphous	1.29-1.39	Transparent	1.2-2.8	15.7	60-84	-	55-65	20-30	2.8-3.0	55-60	280-320
Semi-crystalline	1.37-1.40	Opaque	1.2-2.8	14.0	68-80	255-265	115-120	125-145	2.8-3.1	70-75	65-75

Abbreviations: T_g: glass transition temperature; T_m: melting point; T_{max}: maximum service temperature; T_{mould}: mould temperature; E: Young's modulus; σ_{max}: ultimate tensile strength; ε_b: elongation at break.

Note: Permeability is expressed as (cm^3 mm)/(m^2 day atm).

5. Degradation and recycling of PET

Degradation processes in polymers occur by means of several (environmental) factors over a period of time, such as: moisture (hydrolytic degradation), temperature (thermal degradation), chemicals (chemical degradation), mechanical stresses (mechanical degradation), radiation sources (radiative degradation), enzymes/living organisms (biochemical degradation), or a combination of them [80], resulting in a significant deterioration of chemical structure of the organic polymers, with relative loss in terms of (thermo)mechanical stability and morphologic alteration at the macro/microscopic level (e.g., colouring, crazing, surface roughness, (micro)cracks and debris formation, change in the molecular weight, crystalline degree, cross-linking) [80,81].

PET, as being a polyester, is sensitive to hydrolysis reactions from moisture at temperature higher than T_g. The hydrolytic degradation acts on the ester bonds of the amorphous section within the main chain inducing ester bonds scission, and reformation of acid and alcoholic functionalities, with consequent reduction of the molecular weight (as in Fig. 3, reaction a). This reaction obviously is influenced by the polymer permeability toward water molecules. In this context, the presence of crystalline phases contrasts this mechanism since being impermeable to water molecules. However, it should be reminded that this mechanism is catalytically enhanced in the presence of acid or alkaline environment [82].

Thermal degradation of PET in absence of oxygen (anoxic conditions at temperature higher than T_g, generally at temperatures in the 250–350 °C range) involved again a random scission of the ester groups within the main chain, with consequent chain scission and formation of carbonyl and vinyl ester (double bonds at the end groups through β-scission involving the methylene group at the β position respect to the carbonyl groups, as in Fig. 3, reaction b). This mechanism proceeds with a transesterification of the vinyl ester groups with formation of vinyl alcohol and subsequent conversion into volatile acetaldehyde through tautomerization [83]. As already discussed in the previous paragraphs, the possible release of acetaldehyde is a critical issue in the bottled water industry as it can alter the taste/flavour of water when it diffuses in the contained products [84]. Interestingly, the thermal degradation of PET allows obtaining also other degradation products, such as ethylene, benzene, substituted aromatics, other aldehydes, cyclic oligomers, CO and CO_2, and so on [85].

Conversely, the thermal degradation of PET in presence of oxygen (i. e., thermo-oxidative degradation) started with the extraction of an -H by oxygen molecules and formation of hydroperoxides along the main chain as pendant groups (as in Fig. 3, reaction c) [80,81]. This mechanism, named Bolland's cycle, proceeds with the thermal scission of the hydroperoxides with formation of macroradicals within the main chain, and subsequent formation of other O-containing species through further radical reactions [86]. However, it should be remembered that this Bolland's cycle has been theorized to explain the thermal- and photo-oxidative degradation of long chain olefins at the liquid phase [87]. Even if the literature suggests using this mechanism to polymers, in several recent studies [88–91] it has been demonstrated that this mechanism is too simplistic, and other unknown/more complex reactions might take place (e.g., the direct formation of other oxidised species rather than hydroperoxides in the case of HDPE/LDPE and PP).

In the case of PET photo-degradation (where UV light is the radiation source), the literature suggests the occurring of Norrish-I, Norrish-II, and photo-Fries reactions [92,93], with radical-induced breaking and subsequent formation of carbonyl end-groups, volatiles (such as CO and CO_2) and cross-linking points (Fig. 3, reaction d) [81]. The formation of vinyl esters end groups due to degradation phenomena can also act as cross-linking sites, with formation of polyenes and other conjugated coloured species which causes a yellowish colouring of the degraded material (Fig. 3) [94].

Apart from acetaldehyde, another important (and often underestimated) product released from degraded PET is residual antimony (Sb) from the catalyst used during PET polymerization (see Fig. 1) [95]. Several studies confirmed that PET bottles can contain a residual Sb concentration of ca. 200–300 mg/kg [95–97].

However, the Sb migration from PET bottles to bottled water/drinks depends on the storage conditions, and in order to respect the EU standards limits (5 ppb) [98], temperature should be maintained below ca. 70 °C over a period shorter than ca. 72 days [97].

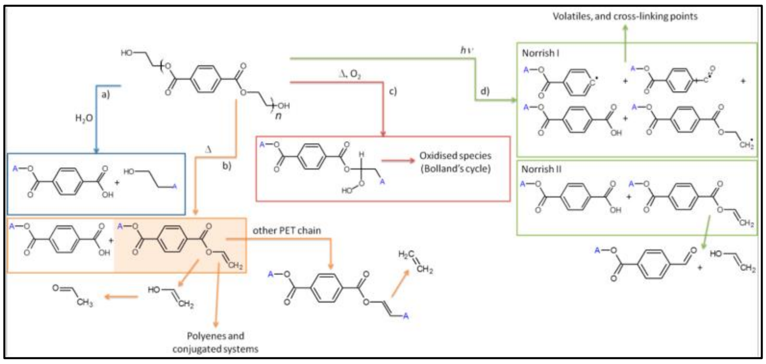

Fig. 3. Schematic representation of the PET degradation mechanisms, namely: hydrolysis (a), thermal (b), thermo-oxidative (c), and photo-degradation (d). Note: the symbol “A” refers to the macromolecular chain prolongation.

Concerning the biodegradation, and in analogy to most of the fossil-derived plastics, PET is not readily biodegradable and it takes years for complete degradation, with risk of accumulation in the hydrosphere [99]. However, quite recently, several (very promising) studies have confirmed the possibility for some specific micro-organisms to biodegrade PET and other recalcitrant fossil-derived plastics (e.g., the bacterium *Ideonella sakaiensis*) [42]. The biodegradation of plastics requires the following multistep approach: i) initial microbial attachment at the polymeric surface with formation of microbial biofilm (plastisphere formation, this step is strongly influenced by the polymer’s surface area as the polymer-bacteria interaction is surface mediated), ii) secretion of endo-/exo-enzymes (biodeterioration agents) and exo-polysaccharides (adhesive agents), iii) enzymatic depolymerisation with conversion to oligomers and monomers (biofragmentation), iv) mineralization of monomers into microbial biomass, CO_2, H_2O and CH_4 (depending on the polymer composition) [99,100]. According to the literature, the living organisms that are able in biodegrade PET are fungi (e.g., *Pestalotiopsis microspora*), actinobacteria (e.g., *Thermobifida fusca*), alphaproteobacteria (e.g, *Rhodococcus ruber*), betaproteobacteria (e.g., *Ideonella sakaiensis*), and bacteroidetes (e.g., *Muricauda*) (see Ref. [101] and references therein). Interestingly, biotechnological studies involving these living organisms pointed out the possibility of genetic engineering/isolating specific enzymes to be exploited for the enzymatic hydrolysis of PET plastics (e.g., PETase and MHETase enzymes) [102–104]. The biodegradative enzymatic mechanism of PETase against PET macromolecules is proposed in Fig. 4 [103].

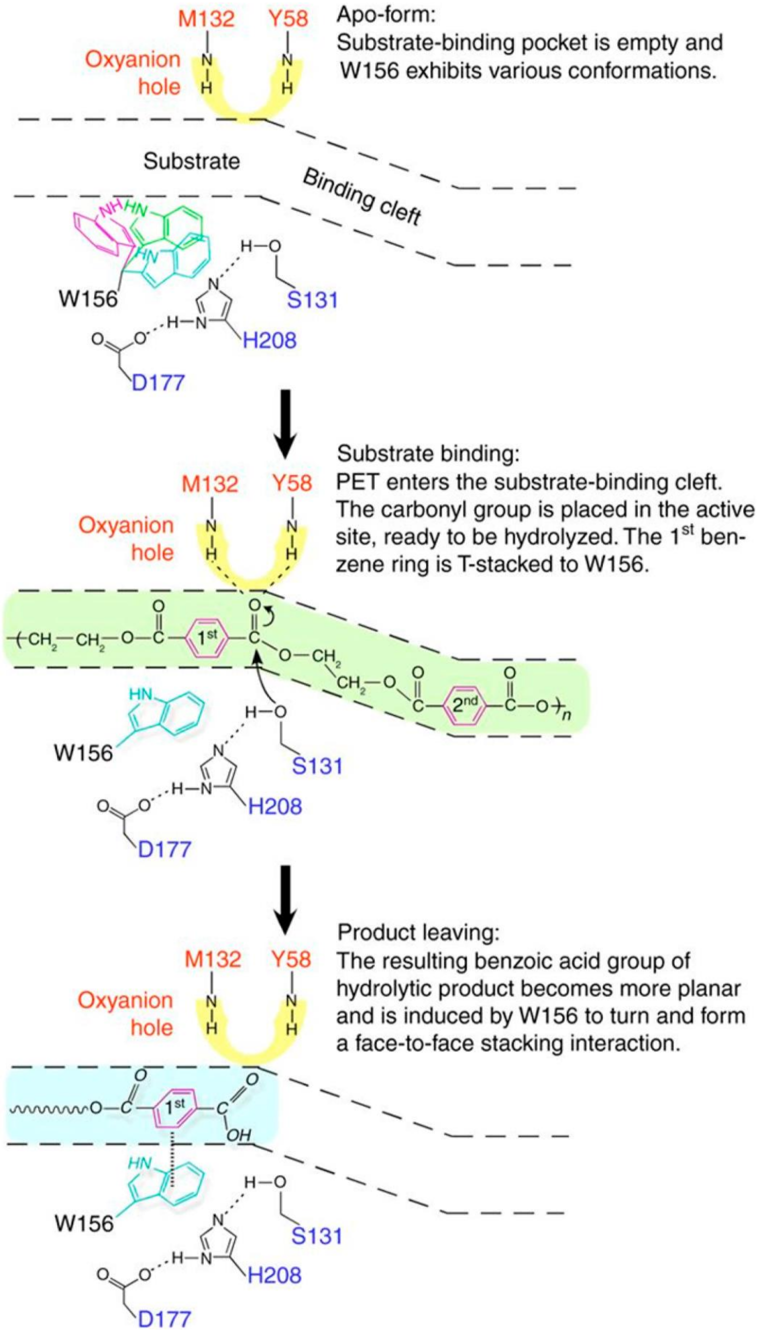

Fig. 4. Proposed mechanism of PETase: interaction between the enzyme active site and PET macromolecular chain. Reprinted with permission from Ref. [103].

Furthermore, as previously discussed PET can be efficiently recycled through different methods, namely: chemical routes to obtain the initial monomers [33] or by converting PET-to-polyol by transesterification mechanism and addition to PUR [34], as well as following mechanical routes by exploiting its thermoplastics nature for the production of new bottles (see Ref. [35] and references therein) or for the production of fibres/carpets/non-food containers [36].

Concerning the chemical routes, the first approach consists in the depolymerisation of post-consumed PET through hydrolysis/methanolysis/glycolysis to obtain the starting monomers (namely, EG, terephthalic acid, DMT, or BHT) [49]. As reported in the literature [4], hydrolysis might be carried out under different conditions, namely: i) under high pressure water/steam, ii) under strong bases (NaOH aqueous solution) at high temperatures (180–250 °C) and pressure (1–2 MPa), iii) under strong acids (HNO_3, H_2SO_4) at high temperatures (85–150 °C). On the contrary, methanolysis involved the use of methanol in presence of a catalyst at high pressure and temperature for long times (3–5 h), whereas glycolysis involved the use of EG at high temperatures (180–250 °C) [105]. The mechanism is always to open the ester bonds within the macromolecular chains. Once obtained the monomers/oligomers, these units were re-polymerised by polycondensation reactions, following the reaction path in Fig. 1. The main advantage of this chemical route is the possibility of purifying (through distillation/crystallization steps, or surface/vacuum treatments) monomers/oligomers by removing possible post-consumer contaminants (decontamination process), and consequently directly re-using these monomers for the production R-PET again for food applications (e.g., new bottles/containers) [49]. Additionally, for a correct processing, it should be remind the importance of obtaining macromolecules with the same high molecular weight.

An alternative chemical route for the recycling of PET is to convert the aromatic polyester chains into polyols, exploitable in the production of rigid PUR foams [105–107]. The production of such aromatic polyesters polyols (APPs) from PET waste consists in transesterification reactions with DEG (or other glycols, such as: propylene glycol, or polyethylene glycol) in presence of specific catalysts (e.g., metal acetates, or sodium sulphate) [108,109]. Sometimes, specific additives (e. g., adipic acid, glycerol, or poly(propylene glycol)/hexanediol system) were added to confer a specific rheology (i.e., viscosity) [107]. Such PET-derived oligomers were used to produce PUR [110] or polyurethane dispersions [111] by polymerization with diisocyanate species, as well as for the production of unsaturated polyester resins [112,113], epoxy and alkyd resins [114,115]. In particular, these PET-based polyurethane systems found valuable applications as coatings and/or adhesives [116, 117], whereas PET-derived resins were mainly exploited as matrices for the development of fibre-reinforced composites (FRCs) for automotive or other technological sectors [118].

The mechanical recycling of PET involved the melt reprocessing of PET waste (typically by extrusion or injection moulding) with addition of virgin PET (ca. 20 wt%) [35]. However, this thermo-mechanical recycling generates several undesired (ir)reversible reactions which modified the final PET architecture, through hydrolysis, esterification, transesterification mechanisms involving primarily the ester functionalities and chain's end groups, thermo-oxidation/degradation to monomers/oligomers, hydroxylation involving aromatic rings, and polyaddition reactions (see Ref. [35] and references therein). These undesired macromolecular changes might affect the mechanical and rheological properties of the mechanical recycled PET, with formation of high content of volatiles organic compounds (VOCs, mostly acetaldehydes). Studies evidenced that during extrusion the main undesired mechanism are thermo-oxidative pathways (occurring at the well-oxygenated zones, namely feeder and die sectors, Fig. 5 zones 1 and 3) and chain coupling/branching (occurring at the poorly oxygenated zones, namely in the middle sectors, Fig. 5 zone 2) [35,119,120].

However, the feed purity requirement for application in the food packaging makes difficult the re-use of mechanically-recycled PET, whereas these limitations are not compulsory in other uses. For all these reasons, usually the mechanical recycling of PET is typically exploited in production of fibres and carpets (which constitute ca. 60% of PET global market) or, eventually, non-food containers [36]. Following this process, the conversion of PET bottles-to-fibres consists in a washing step for the removal of contaminants/dirt affecting the wasted material and grinding into flakes, drying, sorting by colour and density, and finally by conversion into fibres for the production of nonwoven textiles [121,122] or fillers in composites [123,124]. In general, PET fibres are obtained though melt extrusion systems [36,122]. There are two different types of PET fibres: staple fibres and partially-oriented yarns (produced by properly varying the operating parameters) [125]. As reported by Dulmalik et al. [126], partially-oriented fibres are obtained through melt extrusion of the polyester filament from a capillary die and then pulling it by filament winding at high speed, followed by air cooling. A detailed discussion on the fibres production is out of the scope of this document (for details, please refer to Ref. [127]); however, some important evidences deserve discussion. In particular, compared to the chemical recycling routes, the mechanical recycling of PET guarantees several advantages in terms of processability (simple technology and low-cost of the process). The main drawbacks still remain the degradation-related phenomena previously discussed (i.e., colouring, oxidation and cross-linking reactions).

In the case of particularly contaminated polymers very difficult to be fully recycled (e.g., PET laminates), it is still possible to obtain an energetic gain by simply proceeding with the thermovalorization of PET objects through incineration (heat value of PET 22.95 MJ/kg) [37].

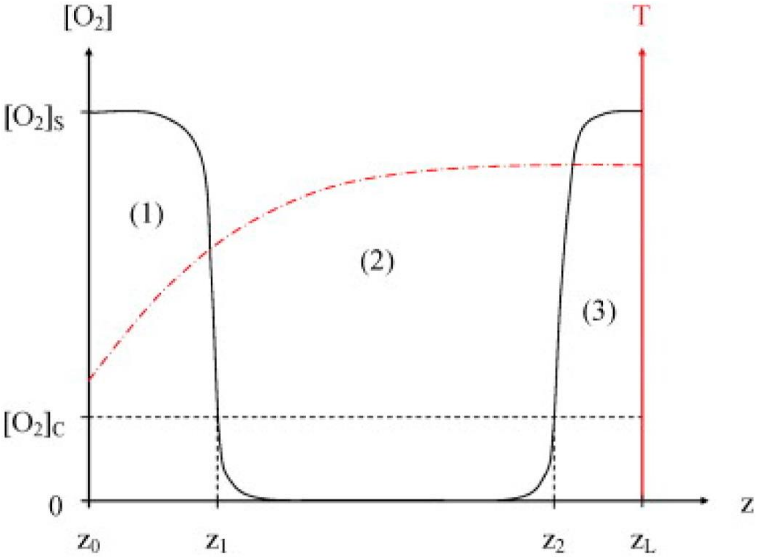

Fig. 5. Schematic representation of an extruder: oxygen concentration $[O_2]$ and temperature T gradient within the length of the extruder. Position (1) corresponds to the feeder, (2) to middle sections, and (3) to die sector. Note: $[O_2]_C$ refers to the oxygen critical concentration, whereas $[O_2]_S$ to the equilibrium oxygen concentration. Reprinted with permission from Ref. [35].

6. PET "process-ability" in the packaging industry

The processability of PET for the packaging industry passed through the main forming techniques, namely: extrusion, thermoforming, compression moulding, injection/extrusion (blow) moulding, and more interestingly (single-stage/double-stage) stretch blow moulding [3]. A complete discussion concerning the theory of each type of forming techniques is out of the scope of this document due to the huge amount of literature and key-concepts necessary. Thus, for a detailed discussion, the author suggests to consult specific (and more generalist) books and reviews specifically dedicated to each technique. For those Italian speaking interested onto these topics, the following books might be extremely useful [128–130]. Furthermore, the international English speaking literature is very broad, and in this sense it can be useful to consider the *Encyclopedia of Polymers Science and Technology* [131] as well as other dedicated books (e.g. Ref. [1]).

6.1. PET extrusion and films' (biaxial) orientation

Polymer extrusion consists in melting one (or more) polymer(s) pellets/flakes (eventually, together with other additives/compounds), mechanically forcing the melt passing through a die with a particular opening (which confers a specific shape), and subsequently cooling down the extrudate to maintain the final shape [132–137]. However, it should be remember that this process (i.e., extrusion) is fundamental for the correct comprehension of the other processing techniques. Fig. 6 reports the scheme of a typical extrusion set-up [132]. In general, once materials were introduced in the hopper, polymers enter the feeding zone and then solid is transported by the rotary motion of either single-or twin- (co- or counter-rotating, depending on the direction) screw system. Afterwards, polymers are melted (and mixed) by the combined action of barrel heaters (in the melting zone) and by additional shear heating (in the metering zone, this last phenomena is provided by the conical shape of the screw that progressively push the melted polymer against the barrel). Lastly, the melt is forced into the die to confer a specific shape. Sometimes the shaping can be also induced by connecting to the die other equipments, such as: water tank and calendaring (for rods and pipes), chill-roll (for sheet films), bubble (for blown films), spinneret (for fibres), and so on [138]. Even if this process seems simple, in reality it is quite complex due to several factors that might influence negatively the final material homogeneity and, consequently, its final characteristics/properties.

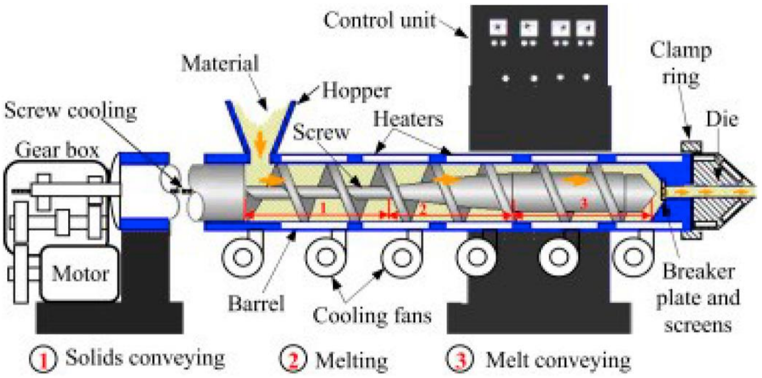

Fig. 6. Scheme reporting a single-screw extruder set-up. Reprinted with permission from Ref. [132].

As reported by Shrivastava [133], the extrusion process can be simplified in three main actions: solid conveying, homogeneous melting, and melt pumping. The choice of the correct screw system (e.g., length/diameter L/D ratio, number and type of screw, geometry) as well as the technical parameters (e.g., rotating screw speed and temperature profile) is fundamental for regulating the feeding/mixing zones, and consequently for determining the homogeneity of the material. Furthermore, the dies design and configuration plays an important role in the final material shaping. During the process, it is possible to manually regulate the thickness of the extrudate (i.e., the distance between the two sides of the die). In general, this action should be balanced with the polymer flow (feeding, melt viscosity, temperatures), thus the operator experience plays a major role in optimizing the operating conditions. Depending on the desired final shape of the material, T-shaped dies are used for flat products (e.g., sheet films), whereas ring-shaped dies are used for cylindrical products (e.g., pipes). Eventually, when specific dimensions were reached, it is possible to cut the extrudate without stopping the continuous flow. Quite interestingly, die swelling is a common phenomenon occurring during polymers (i.e., viscoelastic fluid) extrusion that should be taken into account [139, 140]. In fact, during extrusion, the melt (and consequently the macromolecules forming the polymeric melt) is (are) subjected to mechanical stresses (traction, compression, shear). On the contrary, at the end of the extrusion process, when coming out from the die, macromolecules are subjected to elastic relaxation by recoiling, with consequent contraction of the extrudate along the flow direction and growth in the normal direction (due to the action of several effects, such as: normal stress, elastic energy, entropy enlargement, orientation, and memory effects). The literature suggests that the swelling phenomenon can be reduced by: i) decreasing the extrusion rate, ii) increasing the melt temperature, iii) increasing the length of the die, iv) reducing the die entry angle, v) increasing the draw down ratio, and vi) adding lubricants (i.e., low molecular weight polymer fractions) to the formulation [141].

Concerning PET, typically extrusion is used to produce sheet films intended for a subsequent thermoforming process to produce bags and other containers [142]. Prior to proceed with the extrusion, PET granules must be pre-treated as this polymer is hygroscopic and the presence of residual moisture at high temperature can lead to hydrolysis reactions (as pointed out in the previous dedicated paragraph) [80,81]. Hence, to prevent this undesired phenomenon, PET granules must be pre-dried at 120–180 °C inside an oven for 6–24 h and the moisture content reduced to 0.005 wt% (dew point ca.-60 °C) [143,144]. Furthermore, as PET is sensible to thermal-oxidation, drying temperature should not exceed 180–190 °C [144]. Extrusion temperature depends on the polymer intrinsic thermal properties (see Table 2). In the case of amorphous polymers it should be higher than the T_g, whereas in the case of semi-crystalline polymers it should be higher than the melting point T_m [3]. Zhang and co-workers [143] reported for a medium molecular weight PET the following extrusion parameters: single screw rotation speed 20–50 rpm, feed zone temperature 290 °C, compression zone temperature 260 °C, metering zone temperature 260 °C, die temperature 260 °C, and take up speed 10–20 m min^{-1}. The choice of a high temperature (but still below 300 °C to prevent degradation) in the feeding zone is to achieve a constant feeding during extrusion, whereas the choice of 260 °C as extrusion temperature is correlated to the melting point (256 °C experimentally measured, thus slight below the one selected for processing). Too high temperatures may induce degradation phenomena, with enlargement of the polymer's molecular weight distribution, and reduction of the average molecular weight (quite often polymers require the addition of specific additives, namely: thermal stabilizers, antioxidants, and flame retardants) [145]. Depending on the viscosity of the melt, it is possible to regulate the macromolecular chain orientation and subsequently the crystallization (during cooling), thus influencing the mechanical properties and the dimensional stability of the final object [143,146]. For these reasons, the comprehension of the flow behaviour of the selected polymer is mandatory for the correctness of the entire processing. Apart from the temperature profile, also the screw rotation speed and the take-up speed are fundamental as influence both crystallinity and chain orientation. In general, higher speed induced higher elongation flow and, consequently, higher crystallinity/orientation. However, crystallinity is not always a desired property. In fact, high crystallinity is not desirable during further processing of PET bottles as affects the polymer transparency (see Table 2) and the workability (crystalline regions act as cross-linking points) [119,143]. Therefore, the cooling speed is a real critical point as influences number, shape, and dimension of crystallites, the presence of different crystalline phases, and the filming capacity [3]. As a general rule, high crystallinity betters the barrier properties and mechanical properties, but worsens the material's workability and the transparency.

Furthermore, PET films can be stretched along one or more specific directions to confer a specific anisotropic response in terms of morphology and mechanical properties [3]. Such stretching can be along a single direction or, more frequently, biaxial (along the direction of the machine and in the orthogonal direction). Biaxially-oriented PET (BoPET) films are largely used for their superior tensile strength and barrier property [147,148]. To manufacture such biaxially-oriented films, three different processes can be applied: the one-step (simultaneous) tenter technique, the two-step (sequential) tenter technique, and the double bubble technique [3].

In general, both tenter-based techniques required that the polymer extrudate (under the shape of sheet film) is processed on a quenched chill roll and rapidly cool down to maintain an amorphous state. At this point, the two approaches differ from the stretching one. In the case of the one-step tenter process (less commonly used), the sheet films are maintained suspended by tenter clips while simultaneous stretching applied in both directions [149]. Conversely, for the two-step tenter process, the sheet film is drawing along the machine direction using heated rollers (above the polymer's T_g) rotating at speed progressively faster than the previous one (machine direction oriented, or MDO). Then, for the transverse direction, the sheet film enters inside a temperature-controlled tunnel in which the films edges are gripped by tension clips running on divergent path (transverse direction orienter, or TDO). Subsequently, clips continue to carry the oriented film (still applying uniform tension along both directions) through an annealing oven, and thick edges cut off [150–152]. A scheme reporting the two-step (sequential) tenter process is reported in Fig. 7 [152].

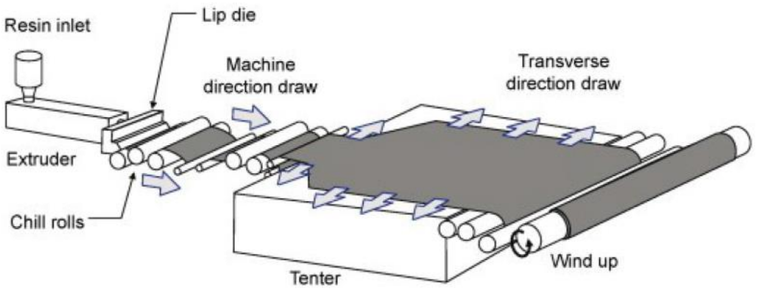

Fig. 7. Two-step (sequential) tenter technique for biaxial oriented film production. Reprinted with permission from Ref. [152].

Double bubble process, instead, consists in extruding the melt through a circular die to generate a tubular extrudate, rapidly cooled down in a water bath to maintain the amorphous state [3]. Afterwards, the tubular film is heated (above the T_g) through heat air or IR radiation, and inflated with compressed air to generated a second bubble. In this step, the film is biaxially-oriented through the simultaneous transversal stretching due to the inflation and the longitudinal one due to the different rotating speed of the rolls [153,154]. A scheme reporting the double bubble process is reported in Fig. 8 [154].

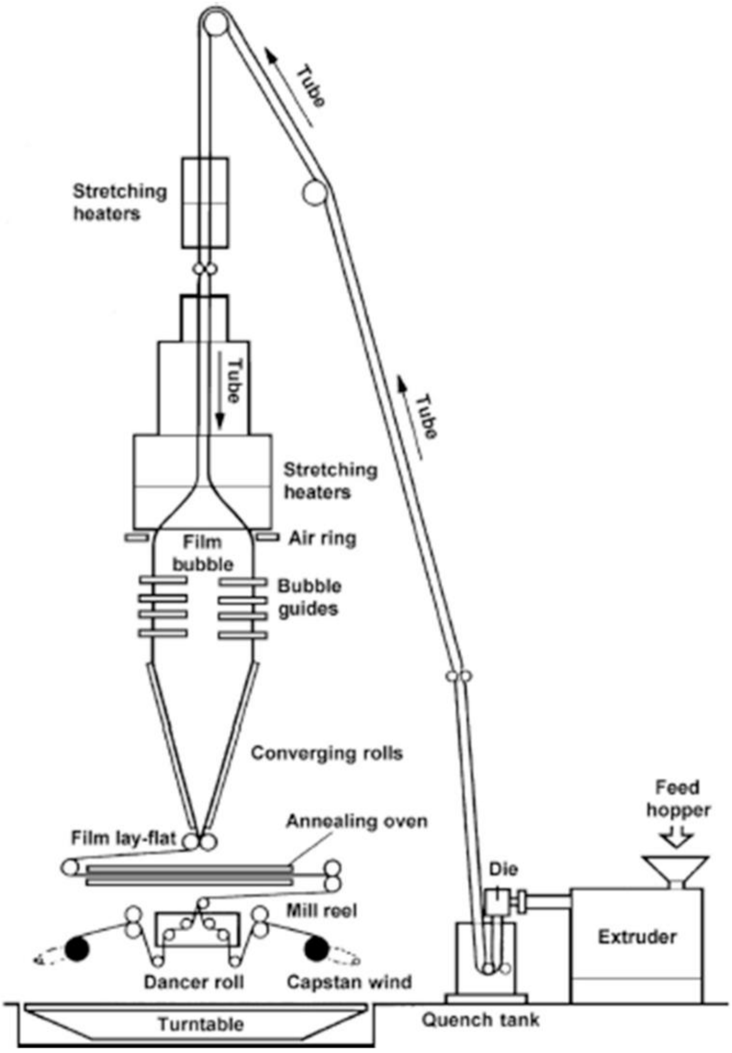

Fig. 8. Double bubble technique for biaxial oriented film production. Reprinted with permission from Ref. [154].

Parameters influencing the effectiveness of the orientation are the stretching temperature, the stretching speed, the stretching ratio, and the cooling rate. As a general rule, the stretching temperature should be slight higher than the polymer T_g and stretching speed very fast, in order to avoid the macromolecular chain rearrangements. Moreover, the film orientation increases with both stretching ratio and cooling rate [3].

As reported by Breil [153], BoPET films are the second most diffused polymeric oriented films available on the market (production: 2 million tons per year). Due to the improved mechanical properties (strength) and chemical/temperature stability, BoPET films are widely exploited in packaging industry (ca. 40% of the BoPET market, e.g., food packaging, coffee bags, shrinkable films), in industrial uses (ca. 28%, e.g., cable wrapping, adhesive tapes, stiffeners, thermo-transfer films for bar code), and in the magnetic fields (ca. 13%, e.g., magnetic tapes, flexible circuits and capacitors). In particular, BoPET films are often subjected to lamination or other coating processes (metallization) to improve the barrier properties in food wrapping (e.g., by metalizing it is possible to reduce the oxygen permeability value of two order of magnitude). For example, in the case of coffee wrapping, the BoPET film is laminated with aluminium foil (as barrier layer) and PE film (as sealing layer).

6.2. PET thermoforming

Thermoforming consists in converting a sheet material into a shell preform by clamping the heated sheet over a mould cavity and (by different approaches) irreversibly deforming the sheet in order to follow the mould cavity shape. Subsequently, the mould cavity is opened and the deformed material cooled down [154]. According to the literature (see Ref. [154] and references therein), three main forming forces can be used, namely, by supplying vacuum, by applying positive air pressure, or by direct power press between male/female moulds (where male stands for punch solid mould, and female for a cavity forming the mould). In the vacuum forming, when the heated sheet material enters the mould, the vacuum (ca. 85–90% of theoretical maximum) forced the sheet to contact with the mould internal surface, by generating a force nearby ca. 90 kPa. Conversely, in the case of pressure forming, pressurized air (ca. 550–700 kPa) is applied on the non-mould side of the sheet, thus pushing it against the mould wall. Lastly, in the case of matched mould forming, the sheet material is constrained between the two side of the mould (male and female) pushed together by applying a moderate force (ca. 1–4 MPa). The male mould side is also exploitable to confer a pre-shaping of the object. Fig. 9 summarized all these three processes (i. e., vacuum, pressure, and matched mould forming).

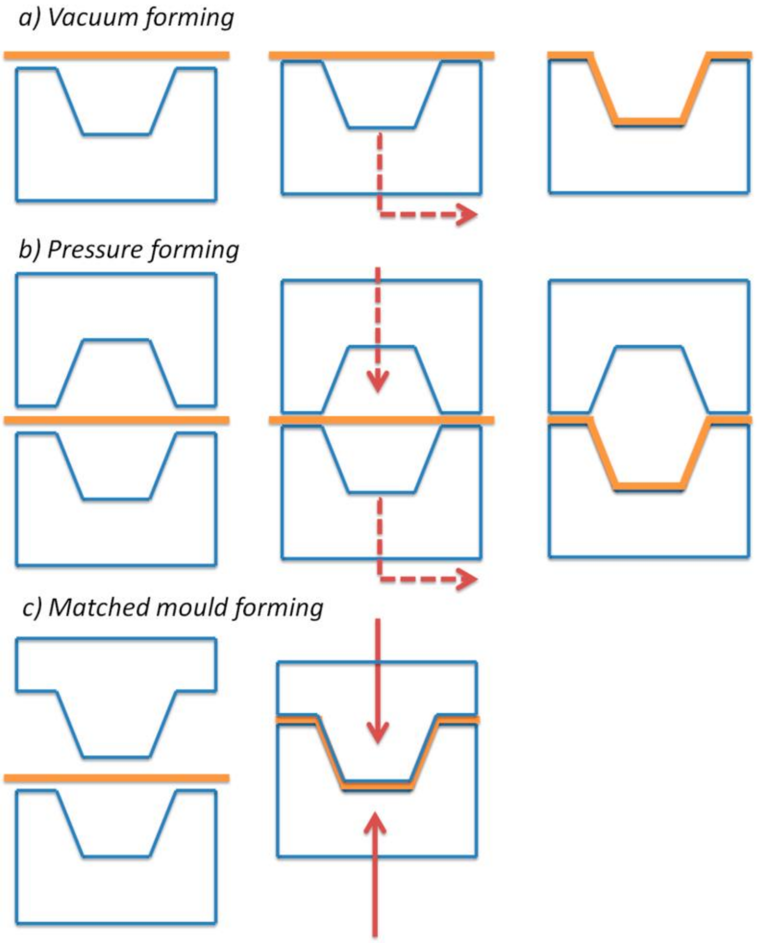

Fig. 9. Schematic representation of the different thermoforming methods, namely: a) vacuum forming, b) pressure forming, and c) matched mould forming. In the figure, the polymer sheet is in orange, whereas the moulds are in blue. Forces applied are: route a) vacuum applied from the bottom; route b) applied air pressure from the top and vacuum/vent from the bottom; route c) applied forces on both sides.

Usually thermoforming is positioned after an extrusion system (necessary to produce sheet films) or after a preheating system. Sometimes, particularly in the case of complex shapes, sheet films required a pre-stretching step by means of a shaping punch. Depending on the crystallinity degree of the material, semi-crystalline polymers can be processed by setting the forming temperature below (solid phase thermoforming) or above (melt phase thermoforming) the polymer melting point (however, in general the temperature range goes from the T_g to the T_m) [3]. Interestingly, melt phase guarantees several advantages, one above all a reduced distortion degree if compared to the solid phase approach. Concerning the heating mode, sheets can be heated either on one side or on both sides, by using different systems based on IR radiation (most diffused), conduction, or convection phenomena. This forming technique is quite simple, and typically adopted for manufacturing simple-shaped objects (e.g, plastic cups and plates, or fresh pasta and yogurt containers).

As reported by Morris [151], the temperature selected for the thermoforming process and its uniformity has a significant role on the effectiveness of the processing. In the case of solid phase forming, the polymeric material should be soft enough to deform, but not too much as it may cause problems during the process (e.g., blow out from the mould). In the case of amorphous PET this range of temperature should comprises between 125 °C and 165 °C (see Table 2). Interestingly, thermoformed PET can be used for “boil-in-the-bag” products due to its high thermal stability [155]. Such steamable bags are usually laminates of different materials, containing PET in the outer layer, and other polymers in the inner layer [156]. Typical multilayer films produced through thermoforming are made by (Bo)PET/PE, (Bo)PET/PP, (Bo) PET/PE/EVOH/PE, (Bo)PET/PP/EVOH/PP, (Bo)PET/Aluminium/PE, (Bo)PET/Aluminium/PP, and many other combinations. These PET-based laminates are very appealing solution for food packaging as the PET layer provides enough gloss and transparency (ideal to support printed material) and it is also suitable for productions performed on sterile environments (e.g., see the portfolio products in Ref. [157]).

6.3. PET compression moulding

Compression moulding consists in directly shaping polymer powders/pellets or preforms within a mould. By applying heat and pressure, the material softens and is deformed following the moulds shape (as in the case of thermoforming). Subsequently, by cooling down the mould, the polymer hardens (fixing the desired shape) and, finally, the formed object is pushed out from the moulds by through ejector pins [154]. These equipments are characterized by having integrated thermal apparatus to regulate the heating (through electricity, or vapour steam) and cooling (cold water) systems. Compression moulding can be fully automatic, semiautomatic or hand mould. The core of these systems is the cavity design, which can be flash type, fully (direct) positive (i.e., single cavity, the gap between male/female parts is close), landed positive (i.e., multi-cavity), semi-positive horizontal flash (most commonly adopted), and semi-positive vertical flash (i.e., adopted in the case when a visual flash line scar is present, i.e., flash is the excess of material that should be removed). In the latter two cases (namely, both semi-positive systems), it is present a land to carry the material in excess [154,158]. The main advantages of compression moulding is the low pressure applied necessary for shaping the objects (ca. 7 MPa) and the possibility of producing large items. Conversely, the main disadvantages of this technique are the long time for completing a cycle (if compare to the other forming techniques) and a significant limitation in terms of possible geometries to confer to the final objects.

In general, this technique is widely used for moulding thermoset-based composites [159,160]. Concerning PET, a new technology has been developed for the production of PET bottle preforms through compression moulding named preform advanced moulding (PAM) [161]. One of the main advantages of this technique is the integration of extrusion step with low energy consumption. Fig. 10 shows a typical PET preform. For clearness, it should be remember that the parison, instead, is a preform without a screw thread (*vide infra*).

Fig. 10. PET preform and cup.

6.4. PET injection moulding, and (stretch) blow moulding processes

Injection moulding consists in mechanically injecting (though high pressure) a fixed volume of molten material inside a mould cavity of the desired shape [3,162]. Fig. 11 reports a scheme showing the main features of this process [162]. The first step (plastification step) involves the heating of the polymeric material until reaching the state of viscous melt (at high torque and low rotational speed) and the recoiling of the screw-type plunger, thus allowing the accumulation of the polymer melt. Then, as the screw-type plunger advances through the nozzle, the molten material is forced (via high force and medium speed) into a closed mould (injection step). Subsequently, the mould is cooled down below the freezing point in order to solidify the polymer within the mould (packing/cooling step). Lastly, the mould is opened and the solid object ejected though the use of pins (ejection step). By means of this technique, it is possible to use moulds with single cavity or more complex cavities connected with flow channels. During injection moulding, several parameters might influence the properties of the object, such as the melting temperature and mould temperature. The crystallinity of the moulded object is controlled by the cooling rate and time [163], whereas the value and timing of pressure applied during injection affect the final shape of the object [3].

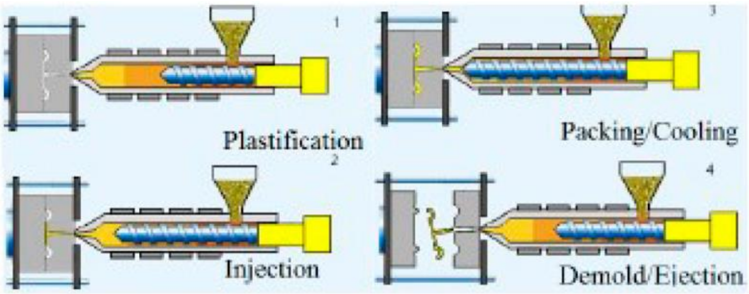

Fig. 11. Conventional injection moulding process. Reprinted with permission from Ref. [162].

In general, injection moulding is one of the most economical processes for obtaining polymeric objects [164]. However, even if widely diffuse and economic, injection moulding requires sensibilities by the operators since the behaviour of polymeric materials under heat and pressure can be significantly different. Therefore, when using new polymeric mix or when filling new moulds, it is recommended performing several preliminary trials involving the selected polymeric mixture and mould, to optimize the injection speed, pressure and temperature (thus, avoiding undesired voids or degradation and burning phenomena). Additionally, due to the high speed of the melts at the mould surfaces, there is the risk of inducing particular orientations. Such orientation can be “freeze” by the fast cooling at the mould surfaces rather than in the middle area of the object (where the macromolecules have time to further re-organize themselves). This phenomenon can induce a certain degree of heterogeneity as well as mechanical properties depletion. Lastly, such thermal gradients within the object might induce distortions and warping phenomena. To avoid these thermal-induced concerns, it is possible to extend the cooling time or by increasing the mould temperature, but conversely both choices might negatively affect the cycle timing (and costs) of the entire process [3]. As always in processing, every modification of the process condition is a trade-off between quality of the products and final costs of the product/process.

Blow moulding is a large family of processes related by the fact that all processes required air inflation to generate hollow objects (e.g., bottles) [3,154]. A complete analysis of all the different processes is out of the scope of this document; however, a quick resume is here reported. In details:

1) Extrusion blow moulding consists in connecting an extruder to a parison head (which acts as a die) for the production of the parison (i. e., without the screw thread) necessary for the moulding process. This way, the extrudate (parison) is generated within the blow mould. Subsequently, mould is closed

and a pressurized air is injected within the parison, thus increasing the dimensions of the parison covering entirely the inner surface of the mould and shaping the object. This process can be single-stage (continuous or representation of the extrusion blow moulding process is reported in Fig. 12A [154].

2) Injection blow moulding consists in using an injection moulding machine to produce the preforms. This way, the injection unit generates the preform, the blowing unit moulds the preform to the desire shape by pressurized air, and finally the final object is ejected. The main advantage of this technique is that the neck presents already the desired screw thread. A schematic representation of the injection blow moulding process is reported in Fig. 12B [165].
3) Stretch blow moulding is an interesting variation of the conventional blow moulding processes as the preform/parison is subjected to an axial stretching induced by the movement toward bottom of a stretch rod inside the preform/parison and a circumferential stretching induced by the pressurized air (as in the other conventional blow moulding). This way, a biaxilly oriented hollow object has been obtained. This technique can be obtained by means of extrusion moulding apparatus (extrusion stretch blow moulding, starting from a parison) or injection moulding apparatus (injection stretch blow moulding, starting from a preform). The latter one can be single-stage (where injection moulding and stretch blow moulding are integrated) or two-stage (where the two steps are separated). In general, two-stage injection stretch blow moulding machines are organized in rotary operation set-up. A schematic representation of both single-stage and two-stage injection blow moulding processes is reported in Fig. 12C and D, respectively [152,154].

According to the literature (see Ref. [3] and references therein), the choice of the best blow moulding technology is strictly correlated to the material properties, geometry of the designed object, and the manufacturing precision required.

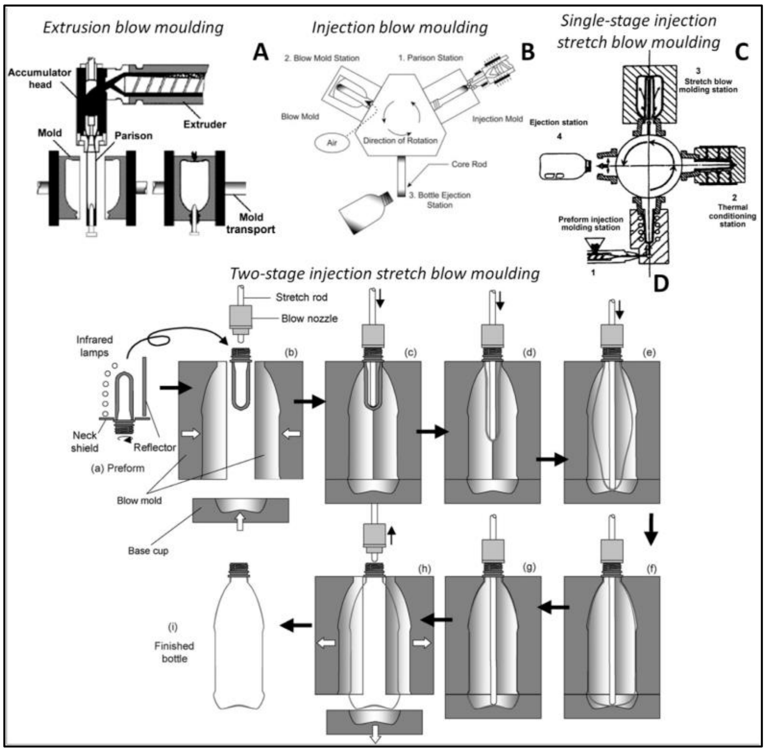

Fig. 12. Schematic representation of the blow moulding processes, namely: (A) extrusion blow moulding, (B) injection blow moulding, (C) single-stage injection stretch blow moulding, and (D) two-stage injection stretch blow moulding. Panels A) and C) reprinted with permission from Ref. [154], Panel B) reprinted with permission from Ref. [165], and Panel D) reprinted with permission from Ref. [152].

In the case of PET, depending on the process selected for the manufacturing of hollow objects for packaging (e.g., bottles) different parameters might influence the goodness of the PET processability. One is the choice of the correct moulding temperature. In fact, depending on the temperature selected it is possible to induce a specific crystallinity. However, since crystallinity influences the optical properties (crystalline domains induce a white opaque colouring, see Table 2), the thermal crystallization rate during the injection stage correlated with the preform production (for injection moulding and injection blow moulding processes) should be minimized [119]. As pointed out in the literature [166], the possibility of inducing a thermal crystallization of the neck can be consider as an advantage in terms of resistance to thermal distortion (this effect is properly induced through heating only the neck at 125 °C, and then cooling down). In general, blow moulding is performed at 120–145 °C (as in Table 2), whereas temperature higher than 145 °C might leave a deposit on the bottle walls and reduction of the transparency. However, in order to check the effectiveness of the processing to produce bottles, technicians should examine the variation of the wall thickness as a function of the temperature, the planar extension (assumed as the product of the extension ratios in the first and second directions) and consequently the stress concentration. An increment of the planar extension results in a more orientation of the polymeric chains and consequently a strain-induced crystallization with surpassing of the hardening point.

Due to the adsorption properties, in general IR lamps used to heat PET preforms are set over 80% of their capability (due to the high melting point of PET). Additionally, it should be remember that sometimes it is required to pasteurize the products for food market (in general heating at 120–140 °C for few seconds, and cooling down). As highlighted in Ref. [166], once liquid is cooled down to RT, it shows a volumetric reduction of ca. 3%, thus causing a vacuum that can distort the PET bottle. Therefore, to reduce the risks related to bottle distorting and humidity absorption, final bottles should have a certain degree of crystallinity (e.g., 30%) to improve their thermal stability. Furthermore, considering the optical properties, even the dimensions of the crystallites influence the light refraction (optical properties). In particular, strain-induced crystallites are small enough to do not alter the optical transparency of the final object. Therefore, for all these reasons, stretch blow moulding is largely preferred (when economically convenient) to the different blow moulding processes for the production of PET bottles.

7. Conclusions and future perspectives

In this study, the main features concerning the use of PET in the packaging industry has been deeply analysed, and solutions investigated. In particular, the analysis of the European market pointed out the key role of PET in the packaging sector as it covers almost the 16% of the European plastic consumption. Even if PET is a fossil-derived material, several important insights were discovered in the latest period, making PET “more sustainable” than in the past. In fact, novel advancements in the field unveiled the possibility of:

1) Producing PET through polymerization mechanisms involving monomers (EG and terephthalic acid/DMT) isolated from biomasses (i.e., sustainable resources): this form of PET is named bio-PET.
2) Fully-recycling PET through advanced chemical methods, which enable its direct re-utilization again and again in the packaging industry: this form of PET is named R-PET.
3) Biodegrade PET via enzymatic reactions involving bacteria/enzymes properly isolated (e.g., the bacterium *Ideonella sakaiensis* or the enzyme PETase).

All these achievements seem justifying the remarkable use of this polyester. However, the use of PET in the bottled water/drinks sector presents some drawbacks that should be faced too. In particular, the high sensitivity of PET esters bonds against water molecules as well as all its possible degradation products (one above all the release of acetaldehyde) still remain critical issues that deserve attention by experts, especially considering the high use of this polymer in the packaging industry for food contact.

In this document, all aspects involving the industrial production (with traditional and sustainable chemical routes), intrinsic physicochemical/thermal/mechanical properties, undesired degradation phenomena, chemical/mechanical recycling processes, and processability of PET are critically discussed. In particular, one of the main achievements reached by PET is its high processability by means of different well-consolidated techniques, namely: extrusion, thermoforming, compression moulding, injection/extrusion (blow) moulding, and more interestingly (single-stage/double-stage) stretch blow moulding. This last technique is strictly correlated with the peculiar chemical functionalities forming the PET macromolecular chains: when mechanically deformed, PET shows a certain hardening capability due to the strain- induced chain orientation by means of aromatic rings and polar esters bonds. This orientation can be very interesting for the production of biaxially-oriented films or containers for food packaging as it enhances the polymer's barrier properties. However, all processing techniques present advantages and drawbacks, thus making the correct choice of the exact technique always a trade-off between the final products characteristics (product design) and the process cost (economic analysis).

In conclusion, it is not possible to predict the fate of PET, as it strongly depends on the future scenario involving the entire packaging industry. The direction provided by worldwide countries and supranational institutions is to proceed following the green chemistry dictates and (as soon as the technology is able to) reaching the maximum compromise between feasibility and environmental sustainability. This way, it seems that the future of PET should be the same of the other polymers (e.g., HDPE, LDPE, PP, and PS). However, this document clearly pointed out the increased sustainability of PET respect to the other "plastics". These new advancements still encourage the exploitation of PET in the packaging industry, making PET a well-consolidated material able to renew itself over time.

CRediT authorship contribution statement

Roberto Nisticò: Conceptualization, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

APPs: aromatic polyesters polyols; bio-PET: bio-based polyethylene terephthalate; BoPET: biaxially-oriented polyethylene terephthalate; BTX: benzene, toluene, and xylene isomers; CSD: carbonated soft drinks; DEG: diethylene glycol; DMT: dimethyl terephthalate; HDPE: high-density polyethylene; HMF: 5-hydroxymethylfurfural; E: Young's modulus; ε_b: elongation at break; EG: ethylene glycol; EO: ethylene oxide; FDM: fused deposition modelling; FRCs: fibre-reinforced composites; IR: infrared; LDPE: low-density polyethylene; MDO: machine direction orienter; MHET: mono-(2-hydroxyethyl) terephthalate; PAM: preform advanced moulding; PBT: polybutylene terephthalate; PC: polycarbonate; PHAs: polyhydroxy alkanoates; PET: polyethylene terephthalate; PETG: polyethylene terephthalate glycol-modified; PLA: polylactic acid; PP: polypropylene; PUR: polyurethane; PVC: polyvinyl chloride; R-PET: recycled polyethylene terephthalate; σ_{max}: ultimate tensile strength; SSP: solid-state polymerization; TDO: transverse direction orienter; T_g: glass transition temperature; T_m: melting point; T_{max}: maximum service temperature; T_{mould}: mould temperature; VOCs: volatile organic compounds.

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