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Acetaldehyde generation in preforms with the use of recycled PET

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This thesis is heartily dedicated, with a gratitude that knows no bounds, to my grandmother Luísa, for love, support, and countless prayers for my success since the day I was born.

RESUMO

O processo de produção e reciclagem de garrafas em polietileno tereftalato (PET) em vários continua a crescer exponencialmente, fruto de um processo de aperfeiçoamento constante. No entanto, aquando do seu processamento e transição para o estado fundido, ocorre degradação do material, particularmente quando se utiliza PET reciclado (rPET). O resultado das reações de degradação traduz-se numa queda acentuada no peso molecular, levando a uma falha na viscosidade intrínseca, resistência do fundido e processabilidade do mesmo. Por consequência, a degradação do material nestas condições resulta em pobres qualidades do material em serviço e uma baixa qualidade das garrafas obtidas. Um dos produtos de degradação mais comuns é o acetaldeído (AA). Devido ao seu baixo ponto de ebulição, 21 ° C, o AA é capaz de se difundir do PET para o conteúdo da garrafa. Este processo de difusão de AA é preocupante porque altera o sabor e odor do conteúdo embalado e pode ser facilmente detetados pelos consumidores.

O objetivo deste estudo é examinar a geração de AA, a falha na viscosidade intrínseca e a degradação de cor do rPET quando exposto a diferentes condições de secagem e moldação por injeção. Um modelo estatístico inicial foi desenvolvido para analisar a interação, magnitude e influência de cada condição de processamento de um sistema de moldagem por injeção e de secagem de dois tipos de rPET na produção de pré-formas. Foi encontrada uma condição ótima capaz de reduzir a concentração de AA na pré-forma, sem comprometer uma falha significativa da viscosidade intrínseca, com impacto mínimo na degradação da cor.

A modificação das condições existentes de secagem e moldagem por injeção foi aplicada sob o resultado ótimo obtido pelo modelo, onde estudos adicionais sobre o teor de humidade e viscosidade intrínseca foram posteriormente realizados. O AA foi reduzido em 61% após a secagem e a queda na viscosidade intrínseca foi significativamente reduzida pela preservação da temperatura de secagem estabelecida. Não houve impacto significativo na cor observada.

Atingiu-se um compromisso entre os resultados do programa estatístico e as tendências observadas na moldagem por injeção. A base foi lançada e foram feitas novas melhorias na produção industrial de pré-formas com 100% de teor de PET reciclado.

KEYWORDS

PET; reciclagem; acetaldeído; viscosidade intrínseca; secagem; moldação por injeção

ABSTRACT

The production and recycling process for polyethylene terephthalate (PET) bottles for packaging soft drinks and mineral waters is still growing worldwide and improving constantly. Although, during the melting and processing of PET, especially recycled PET (rPET), degradation of the material occurs. The result of the degradation reactions is a severe drop in the molecular weight, which leads to the failing of intrinsic viscosity, melt strength and melt processability and finally, to poor usage properties and a low quality of the bottles obtained. One of the most common degradation products is acetaldehyde (AA). Due to its low boiling point, 21°C, AA is able to diffuse out of PET into the beverage content of the PET bottle. The diffusion of AA into packaged contents is of concern due to its limited threshold for the taste and odour that can be detected by consumers.

The purpose of this study is to examine the AA generation, the failing of the intrinsic viscosity and the colour degradation from reprocessed rPET when exposed to different drying and injection conditions. An initial model was developed to analyse the interaction, magnitude and influence of each processing condition in a twin-tower desiccant dryer and a mono-cavity PET preform injection moulding system. It was found an optimal condition capable of reducing AA concentration in the preform, without compromising a significant failing of the intrinsic viscosity, with minimal impact in colour degradation.

The modification of an existing drying and injection moulding program was applied under the optimal result given by the model and additional studies regarding moisture content and intrinsic viscosity were conducted. AA was reduced by 61% after drying, while the drop in the intrinsic viscosity was significantly reduced by heat preservation of the settled drying temperature. There was no significant impact in colour observed.

An agreement between the modelling results and observed trends from mono-cavity injection moulding was achieved. The groundwork was placed and made further improvements in the industrial production of preforms containing 100% content of recycled PET.

KEYWORDS

PET; recycling; acetaldehyde; intrinsic viscosity; drying; injection moulding

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1. INTRODUCTION

Plastics are extremely durable and versatile, with outstanding physicochemical properties. However, one of its greatest strengths has become its greatest weakness – it is not degradable [1]. This is called the plastics paradox and the continued war against it, together with a heightened awareness of plastic pollution, has driven much of the attention on the use of recycled plastics, especially an unprecedented level of interest in recycled polyethylene terephthalate (rPET) [2]. In comparison to other polymers, polyethylene terephthalate (PET) has become the most favourable packaging material worldwide for drinking water, mineral water and carbonated beverages due to its unbreakability, high clarity as well as good barrier properties towards moisture and oxygen [3]. Additionally, it has a very inert character, which results in a low absorption of compounds during the first life of the packaging material [4]. In general, it can be seen that the desired properties for packaging applications are attained from the intrinsic properties of PET polymer [5].

For the reasons given, several recycling technologies have been developed to establish a bottle-to-bottle recycling of post-consumer PET bottles [6]. The recyclability of this material is unmatched and it is in the interest of any packaging industry to push for more recycling as it relieves the environmental pressure and ecological demands to improve waste management [7], [8]. However, for a long time, recycling of post-consumer packaging plastics into direct food contact packaging applications was not possible because of the lack of knowledge about contamination of the packaging polymers during first use or recollection [9]. In addition, the decontamination efficiencies of recycling processes were in most cases unknown, making the evaluation of the food law compliance status of the post-consumer recyclates impossible for a long time. For this reason, over the years, the recycling of post-consumer PET as a technology became a cross-disciplinary practice with many fields of science involved [6], [10], [11]. These include polymer chemistry and physics, process engineering and manufacturing engineering.

In a bottle-to-bottle recycling stream, the recollect PET bottles end up into new PET beverage bottles [12]. Several problems arise in this cross-disciplinary practice and the main concern is that substances from the beverages as well as hazardous compounds from potentially misused containers might be absorbed into the polymer [13]. If these absorbed post-consumer contaminants are not removed from the packaging polymer during recycling, they might migrate into foodstuff from the bottle [14]. In addition, other substances which are not approved for food packaging materials might enter the bottle stream if non-food packaging materials of the same polymer type were also re-collected and recycled together with PET [15].

One of the most important substances migrating from PET bottles is acetaldehyde (AA), a very volatile substance with a boiling point of 21ºC [16]. It is generated not only during the manufacture of the polymer but every time PET undergoes thermal and thermal oxidative degradation when heated above the melting temperature (approximately 265ºC) [17]. Acetaldehyde is particularly critical because it is inevitable on the stream and possesses a distinct odor and taste, which affects the organoleptic properties of non-carbonated mineral waters, being detectable in low concentrations by consumers [18]. It can be found in virgin PET and recycled PET, but it's usually at a higher concentration in rPET because the bottles have also been subjected to degradation agents such as ultraviolet light. Moreover, the bottles need to be shredded to produce the input flakes for further recycling, which results in some additional 'heat history' [19]. Therefore, the amount of acetaldehyde that is present within PET varies greatly during the polymer's lifecycle, particularly in a bottle-to-bottle lifecycle [20].

Although, it is possible to keep acetaldehyde in PET bottles at low levels during the manufacture by controlling the critical stages of production process. A PET bottle is produced in a two-stage process – injection and blow moulding. First, given the hygroscopic identity of PET, the resin absorbs environmental moisture during storage, which means that a careful drying operation needs to be done formerly to prevent the loss of properties, such as molecular weight, and further processing problems [21]. Then, the so-called preforms are manufactured by injection moulding at high temperatures of about 265ºC. Subsequently, the preforms are heated and blown into a mould with the shape of the bottle for the subsequent filling stage [22]. Material changes resulting from drying and further melt processing can affect significantly the generation of the species responsible for deteriorating the aesthetic and organoleptic properties of the preforms for the production of the bottles.

Hence, the general aim of this work has been to utilize a dehumidifying dryer and single-cavity injection moulding machine to explore the various parameters affecting the reaction mechanisms for AA generation, the degradation of PET polymer itself into a drop in the intrinsic viscosity, and the yellowing of the preforms.

These investigations can be extended to provide a theoretical background for establishing simulation and prediction models for any other injection moulding system.

1.1 Plastipak

Plastipak Packaging, Inc., a family own-business, is a world leader in the design and manufacture of high-quality, rigid plastic containers for the food, beverage, and consumer products industries.

Founded in 1967, Plastipak operates more than 47 production sites in the United States, South America, Africa, Asia and Europe, with a total of over 6,600 employees. Its customers include some of the worlds most respected and recognized consumer brands. Plastipak is also a leading innovator in the packaging industry, holding more than 1,500 patents globally for its state-of-the-art package designs and manufacturing processes. It also possesses the largest recycling capacity in the world with over 135 million kilos of recycled material produced annually.

Plastipak licenses various packaging technologies around the world. In North America, the Company is the exclusive supplier of plastic containers to Procter & Gamble for heavy-duty, liquid laundry detergents and the largest supplier of plastic containers to Kraft Foods for their salad dressings, barbecue sauces and grated cheeses.

For more than 50 years, Plastipak has worked as a strategic partner with the customers in the early stages of their new marketing initiatives. It provides integrated transportation and logistics services, and satisfies the customers' needs for recycling, reliability and dependability in plastic packaging. In addition, Plastipak has 5 global packaging centers, seen in figure 1, that provide packaging solutions through engaged hearts and minds.

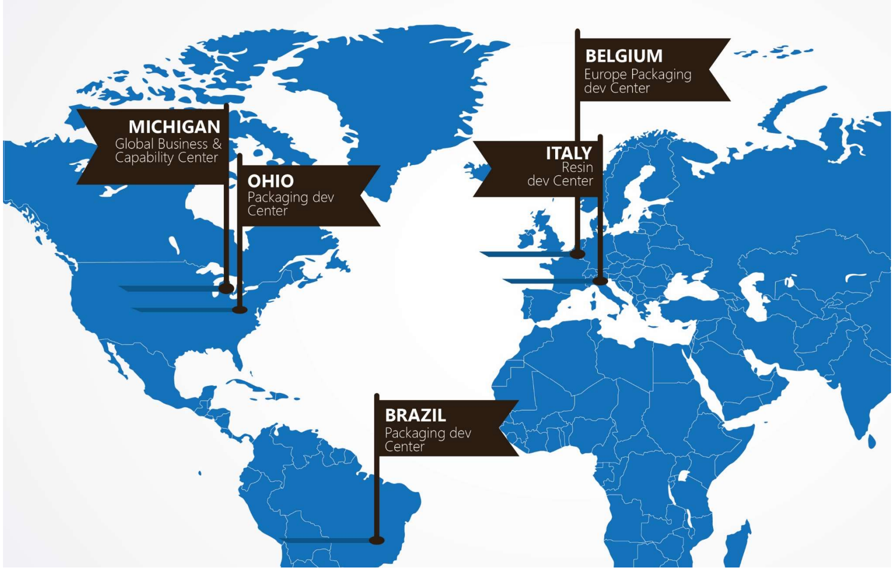


Figure 1 - Global packaging centers of Plastipak

Sustainability is a priority in Plastipak's processes to deliver top-quality, highly-functional packaging. With recycling, used plastic bottles are turned into resin to make new bottles, through the four recycling centers seen in figure 2. This bottle to bottle recycling approach creates a sustainable life cycle for plastic packaging, which is accomplished through the recycling company – Clean Tech.

Figure 2 - Plastipak global recycling footprint

Plastipak's global recycling centers utilize the most advanced recycling technologies globally in converting collected and recycled plastic containers into high-quality post-consumer recycled PET resin. Post-consumer recycled resin is converted back into containers for food, laundry detergent, household cleaners and other common products.

1.1.1 Objective

The goal is to improve sustainability of PET package for water filling companies by increasing rPET content on the preforms from two different recycling centers. The materials produced in these not only come from two different recycling technologies but the input post-consumer feedstock comes from two different countries, leading to significant output differences.

Thoroughly documented process recommendations backed up with data based on pilot and lab scale experiments, the aim of this thesis is to improve the knowledge about rPET colour degradation (yellowing/browning), thermal degradation leading to an intrinsic viscosity (IV) drop and the generation of organic volatile compounds such as acetaldehyde.

Therefore, a statistical software is used to find trends, predict patterns, and visualize the data interactions in order to identify the important factors and give background to further experiments or to modify the on-going processing conditions internally used.

2. LITERATURE REVIEW

2.1 Knowing PET

Polyethylene terephthalate, abbreviated as PET, is a polymer that, from a chemical point of view, is a polyester [23].

It is one of the fiber and film forming saturated polymer with commercial importance and it has become the most favourable packaging material world-wide for beverages [24]. The reason for this development is the excellent material properties such as high mechanical strength, low weight, low permeability to gases, relatively low manufacturing cost and non-toxicity [25].

In general, it can be seen that the desired properties for packaging applications are attained from the intrinsic properties of this polymer. PET provides good optical transparency and a negligible barrier against the permeation of carbon dioxide and water vapour [26], [27], making it perfectly suitable for packing liquids such as carbonated beverages, natural mineral and spring water. Therefore, too much additives are not required in the production of PET compared with the other plastics having the same application area.

Like all polymers, PET can be described chemically as large molecule consisting of chains of repeating units [28]. The PET used for bottles typically has about 100-140 of the repeating unit shown in figure 3, and as it can be seen, it contains at least one ester linking group per repeating unit, making it a member of the thermoplastic polyester family [29].

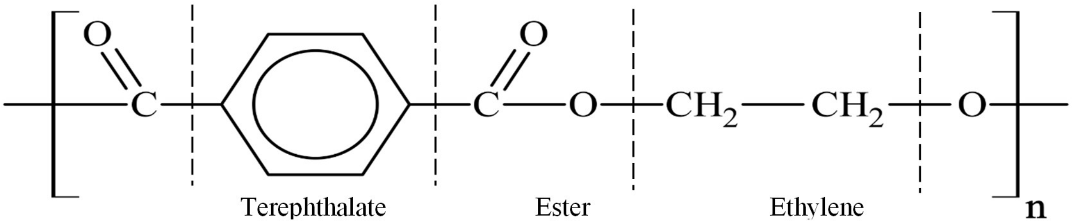


Figure 3 - Repeating unit of PET

The figure above represents the monomer in which, through a polymerization reaction, will establish chemical links with other’s same monomers in order to form the PET polymer chain.

The ring structure makes PET tough while the ethylene component gives it flexibility [30].

The properties of the PET polymer are strongly dependent on the average molecular weight or the average number of repeating units of the polymer chains [28], [29]. This is usually determined by measurement of the intrinsic viscosity (IV) in dilute solutions [31]. The relationship between molecular weight and IV is fairly linear. High-IV PET has a higher molecular weight than low-IV PET. The longer chains give better properties in the final product but also affect the processing in predictable ways [32].

In a processing environment and given the thermoplastic nature of PET, the application of heat causes its softening and deformation. The overall processing behaviour is established by an understanding of the molecular weight and molecular weight distribution [33].

The glass transition temperature of PET increases with molecular weight. This means that the temperature range at which the polymer can flow (processing temperature) also increases with molecular weight. On the other hand, the degradation temperature steadily decreases with increasing molecular weight [23]. Hence, it is necessary to find the molecular weight or the intrinsic viscosity that renders ideal material properties for the finished polymer product, while providing flow properties that make it easy to shape the material during the manufacturing process [14].

Molecular weight and IV have a huge influence on rheological and mechanical properties, and these are fundamental properties that determine end-use applications. Table 1 shows different examples of IV values on different PET final uses.

Table 1 - Range of IV values for different PET uses

Uses	**Intrinsic Viscosity (IV) (dL/g)**
Fibers and Textiles	0.5 – 0.65
Film and Tape	0.60 – 0.75
Bottles	0.73 – 1.00
Tire cord	0.85 – 1.00

Identification of the intended use is important because PET manufacturing techniques can vary depending on the IV that is desired. It is the ideal IV that renders ideal PET material properties for the finished product, while providing the adequate flow properties that make it easy to shape the material during the manufacturing process.

2.1.1 Physicochemical properties of PET

In summary, PET occurs in three different states [14]:

- Amorphous, non-oriented, and clear, such as preforms and melted plastic resin;
- Thermally (by means of temperature) crystallized, such as resin pellets;

- Strain-induced crystals, such as bottle sidewalls.

PET is transformed several times as it goes from pellet to preform to bottle, as well as its chain conformation shown in figure 4 [34].

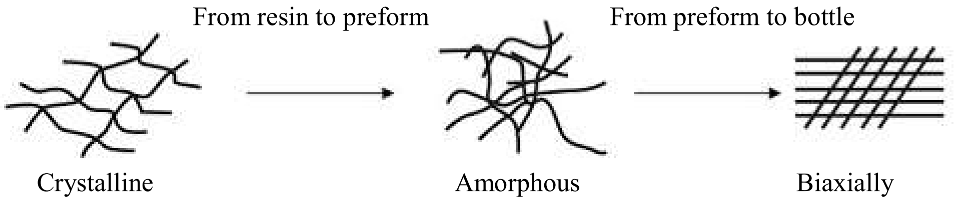


Figure 4 - Chain conformations from the resin to the bottle. Adapted from [35]

As resin pellets, PET is thermally crystallized to a level of 50-70%. Thermally induced crystals are arranged in spherulites, which reflect light. Therefore, PET appears white [35].

During injection process, these crystals are melted, resulting in an amorphous melt, which is injected into the preform mould cavities. The preform is rapidly cooled down to avoid recrystallization. Preforms therefore do not have a crystal structure, appearing in an amorphous state. Hereby, the molecular chains show no orientation and no crystallinity, which means that there is nothing to reflect light and the PET is clear [36].

In the reheat stretch blow machine to produce a bottle, PET can be bi-axially oriented by means of stretching both radially (width) and axially (length) at the same time. The material of the heated preform is forced into one direction by the stretch rod and compressed air is blown to orient in the axial and hoop direction, forming small, strain-induced crystals shown in figure 5.

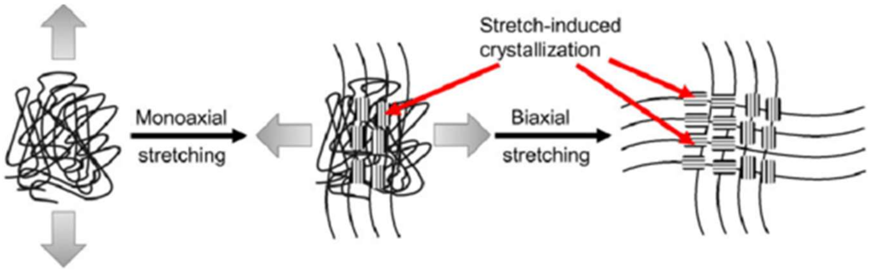


Figure 5 - Schematic representation of strain-induced crystallization in the production of a PET bottle. Adapted from [36]

These crystals do not reflect light and the bottle appears clear. It also has higher strength and barrier properties. Crystallization levels of up to 25% can be achieved in the bottle sidewall given the correct preform design and process conditions [36], [37].

Mechanical properties, storage stability, gas barrier, dye ability and transparency are the properties controlled by the nature of the degree of ordering in finished articles made from this material. Strength, durability, cohesion, gas barrier properties and heat setting are associated with crystalline regions. The non-crystalline regions are mainly responsible for extensibility, recovery, toughness and diffusion [38].

The properties of PET are determined basically by their chemical composition and molecular structures [33]. The main characteristics are summarized as follows:

- General characteristics – cooled to give clear amorphous state, crystallizable, high melting temperature, melt processable, moderate softening point, worldwide food approval, excellent clarity, colorless, excellent strength, good creep resistance especially when crystallized, good barrier properties, and excellent chemical resistance.
- Characteristics of stretched products (oriented) – excellent strength and stiffness (high modulus), good creep resistance, excellent clarity, colorless, good water vapor barrier, adequate CO_2 barrier, low taint, outstanding impact resistance, excellent chemical resistance, worldwide food approval, and favorable environmental impact [28], [29].

2.2 Manufacture of PET resin

As mentioned before in section 2.1., it is crucial the identification of the intended use for the resin because the manufacturing techniques can vary depending on the IV that is desired.

The manufacture of PET for bottle grade resin involves, generally, three steps. The first stage comprises the manufacture of ethylene glycol (EG), terephthalic acid (TPA) and/or dimethyl terephthalate (DMT), all from crude oil using catalysts, pressure and heat [39].

The second stage involves the formation of monomer bis-(2-hydroxyethyl) (BHET) via either the esterification of terephthalic acid with ethylene glycol or the transesterification of dimethyl terephthalate with ethylene glycol under heat and high pressure [39], [40].

The third, and final, stage of PET manufacture involves the synthesis of the polymer by melt-polymerization of the monomers followed by solid-state polymerization. The latter process is important in the production of beverage bottles since it involves the vacuum and high temperature treatment of PET granules at low moisture and oxygen levels, allowing the increase of the molecular weight of the polymer and the removal of migratory volatile reaction by-products [40].

2.2.1 Synthesis of the starting reactants

Ethylene glycol, classified as a diol or di-alcohol, is manufactured by oxidation of ethylene from the gas fraction of crude oil to ethylene oxide (oxirane), which is subsequently hydrolysed with water. The oxidation of ethene to oxirane takes place in the presence of a silver catalyst [41].

This work will focus in the synthesis of PET with terephthalic acid as a precursor. This compound is classified as di-acid, where p-xylene from the naphtha fraction of crude oil is oxidized to produce it.

EG and TPA, have two functional groups, which mean they can continue to link up to form long chains [41]. Therefore, the formation of the so-called pre-polymer or monomer BHET can be achieved by this chemical route, shown in figure 6 [26], [40]:

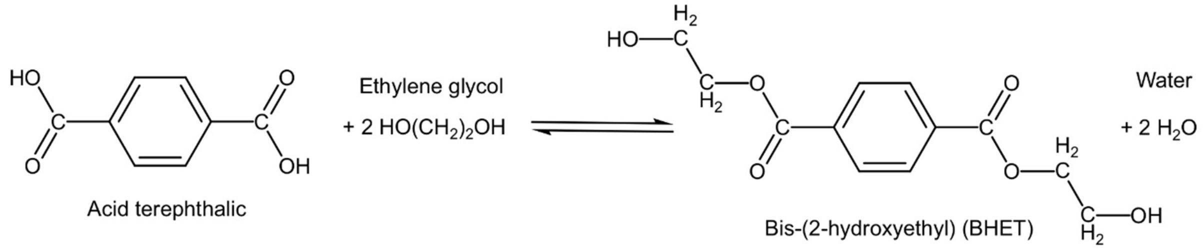


Figure 6 - Formation of bis-(2-hydroxyethyl)terephthalate (BHET) from acid terephthalic and ethylene glycol

It is characterized as a self-catalysed esterification reaction between TPA and EG in a nitrogen atmosphere at a temperate surrounding 240°C and 260°C. The pressure levels fall between 300kPa and 500kPa, giving water as a by-product [40].

The process forms intermediate precursors that contain the monomer BHET and short-chain oligomers [42], which must be polymerized to form PET.

2.2.2 Melt-phase polymerization

PET is obtained through a catalysed, high temperature transesterification reaction in the melt phase, shown in figure 7, releasing EG as a by-product. This reaction is an equilibrium reaction and for that reason EG must be removed to obtain a high yield of PET [40].

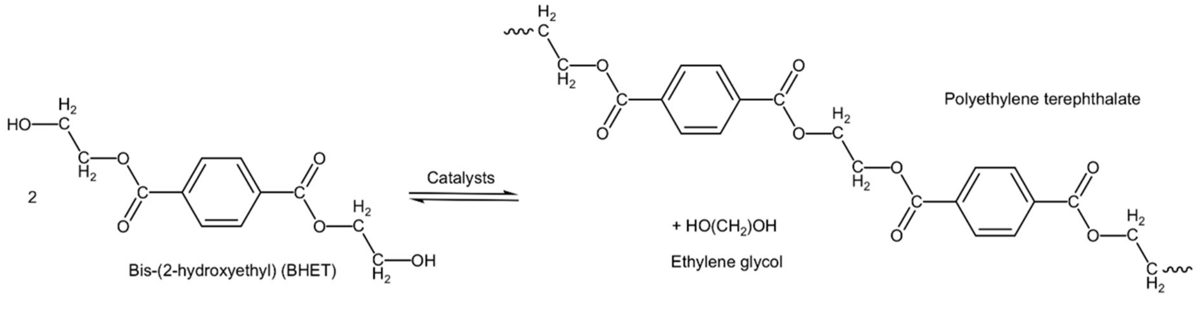


Figure 7 - Reaction scheme for the formation of PET from BHET

The short-chain oligomers and BHET are treated in a temperature between 270°C and 285°C in the presence of catalysts and high vacuum to form the polymer. Common catalysts used are acetates, substances of antimony, titanium or germanium [43]. The purpose of applying high vacuum during this polycondensation reaction is to drive the reaction forward by removing ethylene glycol side product [43].

After removing the alcohol (EG), the precursors enter a second stage reactor establishing condensation linkages at high temperatures to create a viscous, polymeric melt [26]. The use of the polymerization catalyst becomes essential at this point to allow the reaction to proceed to acceptable molecular weights [42]. It is also usual to add small quantities of melt stabilizers to reduce thermal degradation and colour formation.

The melted PET, after polycondensation, is introduced into the extruder and is granulated in a hot water bath, resulting in pellets with an amorphous structure. The overall reaction time, including pre-polymerization and polycondensation processes, is long and varies from 5 to 10h [44].

Although, traditional melt-phase polymerization techniques have a limit to the molecular weight, or IV, that can be achieved [45]. The constraint is due to the difficulty in removing the reaction by-products, particularly EG, BHET, and oligomers from the viscous PET melt [46]. Removal of these un-wanted by-products is needed to continually drive the equilibrium reaction forward and thus continually increase the degree of polymerization of the PET.

2.2.3 Solid-state polymerization

When higher IV PET is needed to manufacture resins for PET bottles, the IV needs to be increased beyond what melt-phase polymerization techniques can yield [47]. Therefore, a second polymerization technique is traditionally required for it and it is known as solid-state polymerization (SSP) [26], [27], [42].

During the SSP process, the solid amorphous pellets are heated well above PET's glass transition temperature but below its melting temperature, on a temperature range typically between 200 and 240°C, for 10-30h [48]. As the temperature is increased, mobility of the polymer chains also increases. This increases the likelihood/ability of the polymer chains' end-groups to find and react with one another, producing a chain extension of PET [26].

As the end-groups react with one another, more by-products are formed. Removal of these is achieved by a continuous positive stream of inert gas (typically nitrogen) or by applying vacuum pressure. As with melt-phase polymerization, by-product purging is a necessity to progress the SSP equilibrium reactions forward and ultimately reach the desired IV [49].

Therefore, the amorphous pellets, with the use of good agitation, anneal and develop a higher level of crystallinity (approximately 48%) [19]. Agitation prevents the amorphous and the non-annealed crystalline pellets to stick and sinter together during the whole process.

The fundamental difference between melt-phase and solid-state polymerization is the phase of the reactants during the respective polymerization. Table 2 shows the main differences and the achievements on the properties of PET by each method [39], [50].

Table 2 - Main differences of melt-phase polymerization and SSP on the properties of the PET resin

	Melt-phase polymerization	**Solid-state polymerization**
State of PET	Liquid melt	Solid/ Crystalline
Environment	Vacuum	Inert gas or vacuum
Typical temperature (ºC)	270 - 285	200 – 240
Range of molecular weight	16000 - 19000	27000 - 38000
Range of IV (dL/g)	0.58 – 0.68	0.69 – 1.20

At SSP conditions, PET is in a solid, rubbery state and not the viscous liquid seen during melt-phase polymerization [51]. This makes it much easier for a purging gas (or vacuum) to remove the volatile degradation products and reaction by-products that form during polymerization. The greater ease of by-product removal allows the polymerization process to progress beyond the limitation observed during melt-phase polymerization [52]. Additionally, the lower temperatures characteristic of SSP cause fewer side reaction to occur. The combination of less side reactions and easier by-product removal create a more efficient route for the end-groups of PET to react with one another and ultimately for the molecular weight to increase more rapidly [53].

The length of a molecular chain determines the molecular weight of the material and determines the properties and usage. IV becomes the practical measure of the molecular weight of the PET macromolecules. It indicates potential applications based on required properties and processing conditions, shown in table 3.

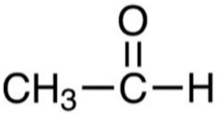
Table 3 - Intrinsic viscosity (IV) and applications

	IV (dL/g)				
	0.40 – 0.60	0.70 – 0.78	0.74 – 0.80	0.76 – 0.85	0.85 – 1.05
Grade	Fibers	Bottles	Bottles	Bottles	Extrusion
Polymer type		Homopolymer	Light copolymer	Copolymer	
Application		MW, EOS, other	MW, CSD, heat-seat	Hot-fill	
‘Solid-stating’	⟶	⟶	⟶	⟶	⟶

MW: mineral water; EOS: edible oils and sauces; CSD: carbonated soft drinks

2.2.4 Acetaldehyde formation during the manufacture of PET resin

Acetaldehyde can be naturally found in citrus fruits and vegetables, and can be produced as result of lactic acid fermentation in cheese and yoghurt, or alcohol fermentation in beer and wine [16]. It is known for having an acid, fruit-off taste and a distinct odour, having a low sensory detection threshold level. This small organic compound, shown if figure 8, is also very volatile, with a boiling point of 21°C [20].



$CH_3-C(=O)-H$

Figure 8 - Chemical structure of acetaldehyde

Acetaldehyde is a by-product of PET production and its presence within PET packages has been known to result in adverse effects. With a boiling point that is lower than room temperature, AA is able to diffuse out of PET and into either the atmosphere or into the packaged contents [54].

The diffusion of AA into packaged contents is a concern because many food products have a limited threshold for the taste of acetaldehyde. This is especially true when bottling water because the taste of pure water is so sensitive that even a small amount of AA is detectable by consumers [55]. This taste impairment through acetaldehyde does not play any role in the case of sweet beverages, juices and beer, as the concentration of AA in the actual beverage is already distinctly higher than the diffusion from a PET bottle [54], [55].

The prominent reason that creates acetaldehyde is the degradation occurring phenomena in the macromolecular chains of the PET polymer during its synthesis, where several PET degradation routes can be identified [56]. These AA producing chemical reactions result from two of the three core degradation mechanisms of PET: thermal degradation and thermal-oxidative degradation. The factors that drive these reactions are: temperature, hydroxyl end-groups, diethylene glycol (DEG) molecules, vinyl ester end-groups, oxygen, DEG linkages, and free radicals [57].

Researchers have shown that the most noticeable factor that leads toward the formation of AA is the concentration of vinyl ester, carboxyl and hydroxyl end-groups in PET [56], [57].

Prolonged heat treatment during the polymerization of PET results in a random chain scission reaction and the subsequent formation of carboxyl and vinyl ester end-groups. Then, a transesterification reaction occurs between the carboxyl and vinyl ester end-group, generating vinyl alcohol, which is rapidly transformed into a molecule of acetaldehyde. This reaction, shown in figure 9, is a characteristic of thermal degradation [58].

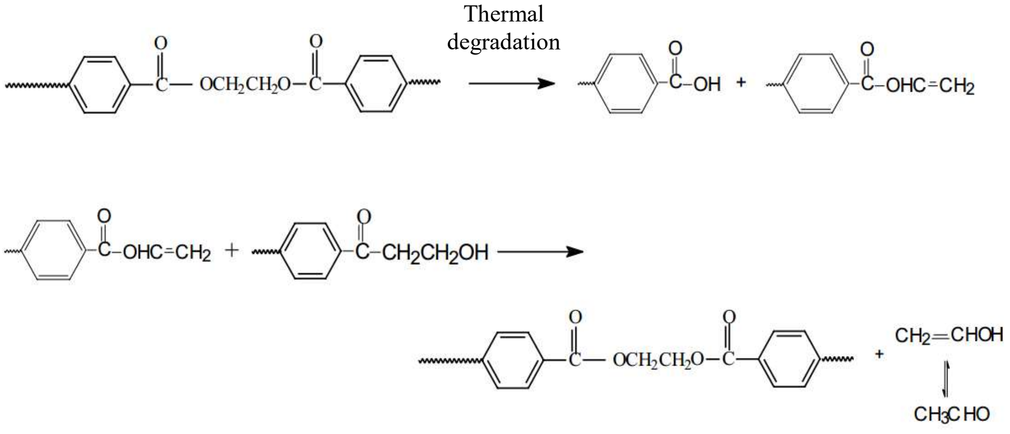


Figure 9 - Formation of acetaldehyde from carboxyl and vinyl ester end-groups. Adapted from [58]

Another route occurs when the PET chain terminated by a hydroxyl end-group reacts with the vinyl ester end-group. This reaction creates a larger PET chain, connected by an ethylene linkage, and a molecule of acetaldehyde, as illustrated in figure 10. Elevated temperature and the precursors mentioned are the prominent factors for this reaction [59].

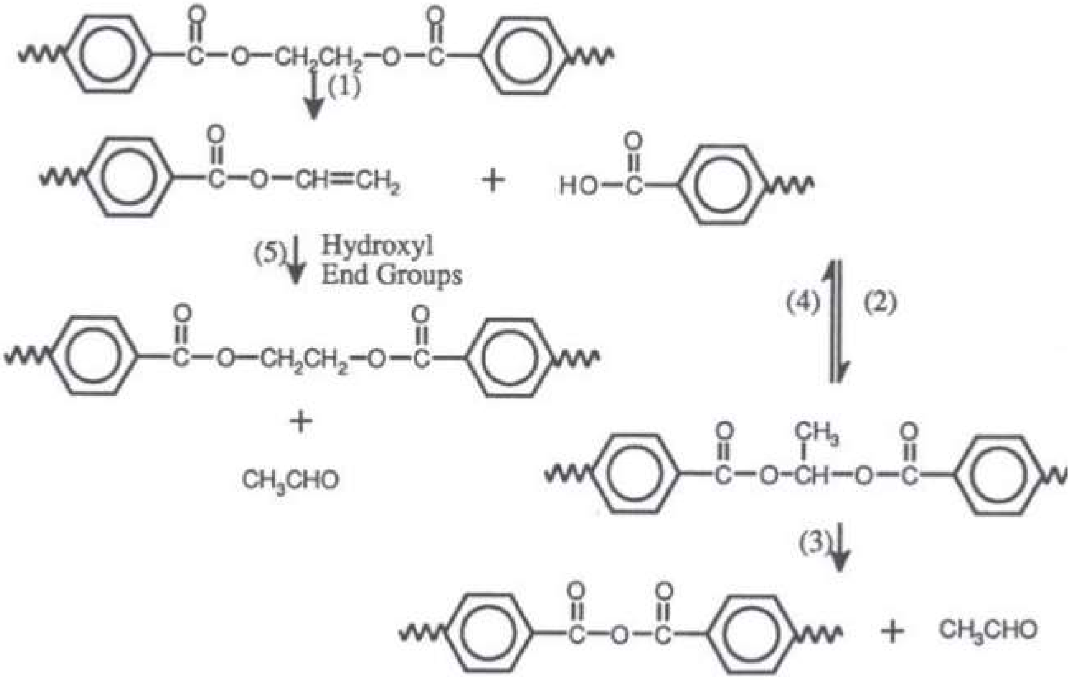


Figure 10 - Formation of acetaldehyde from hydroxyl and vinyl ester end-groups. Adapted from [59]

PET can also generate acetaldehyde due to the presence of DEG linkages within its chains [60]. Melt-phase polymerization is usually carried out between 270 to 285°C and, at these elevated temperatures, it is common for a small amount of ethylene glycol (EG) to react with itself to form diethylene glycol (DEG), making possible to DEG replace EG during the whole synthesis process [39]. When this occurs, a DEG linkage connects the terephthalate groups of PET rather than and EG linkage. The disadvantage of this linkage is that it is very susceptible to be attacked by oxygen, as shown in figure 11 [61].

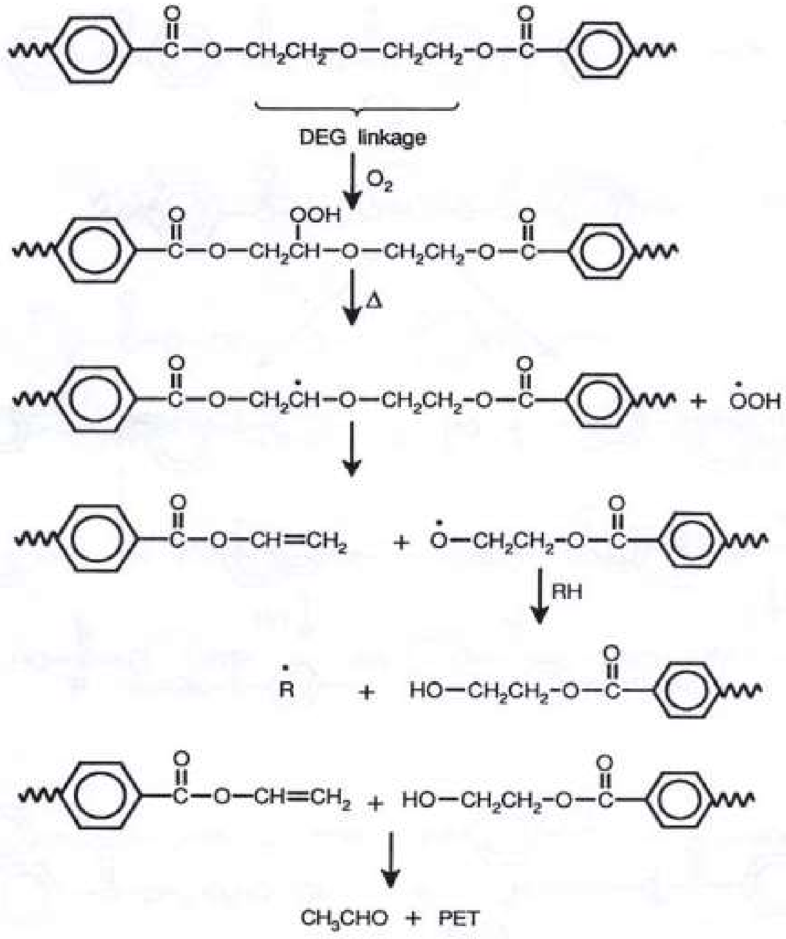


Figure 11 - Formation of acetaldehyde from diethylene glycol (DEG) linkage. Adapted from [61]

When oxygen attacks the DEG linkage it forms a hydro-peroxide group that with elevated temperatures decomposes to form free radicals [56]. In time, these free radicals lead to the formation of PET chains terminated by vinyl ester end-groups and hydroxyl end-groups that, as mentioned above, will produce a larger PET chain and a molecule of acetaldehyde.

The amount of acetaldehyde that is present with PET varies greatly during the polymer's lifecycle. Melt-phase polymerization yields an amorphous PET resin with a high amount of AA, typically above 20 ppm [54].

To reduce the amount of degradation by-products and prepare the resin for the second polymerization step, the amorphous pellets are subsequently dried and crystallized, reducing the amount of AA to less than 10 ppm [51].

The second polymerization step, SSP, is conducted to further polymerize the PET chains, increase its IV and perform a good removal of by-products and AA from the polymer's matrix. SSP can reduce the AA levels to less than 1 ppm [48], [54].

2.3 Introduction to the recycling of PET bottles

PET can be 100% recycled. As a thermoplastic, it can be melted down again almost as often as desired. PET bottle recycling is one of the greatest examples of successful polymer recycling. One factor contributing to this, in addition to increasing consumption of plastics in general, is the fact that is possible to use recycled PET in the production of new bottles, without any risk to the health of consumers [62]. An example of a very successful bottle-to-bottle lifecycle, from Plastipak' philosophy and technologies, can be attained from figure 12.

Figure 12 - Plastipak's bottle-to-bottle sustainable chart

This post-consumer PET recycling industry, in general, started as a result of environmental pressure to improve waste management. Ecological demands and pressure from the public community, together with the increasing amount of PET bottles all over the world, allowed a steadily increasing in recollection of post-consumer PET bottles and recycling.

However, post-consumer contaminants still have to be decontaminated to concentration levels of virgin PET materials. Contamination of post-consumer PET (PCR-PET) is the major cause of deterioration of its physical and chemical properties during re-processing. Minimizing the amount of these contaminants leads to better recycled PET quality [37], [62].

Therefore, the continuous development of sophisticated decontamination processes allow a bottle-to-bottle recycling lifecycle, which produces "super-clean" recycled material that can be integrated into the new PET bottles [63]. Super-clean processes ensure an effective decontamination process and a quality assurance concept that meets the European Food Safety Authority (EFSA) demands. PET bottles with recycled material are just as safe as virgin PET bottles, even with a recycled share up to 100% [9].

Although, techniques for selection and recycling of post-consumer plastics are closely related to the characteristics of plastic containers consumption, which are extremely diversified according to the geographical areas and the relevant law regulations governing activities in this sector. In each area, socio-economic and legislative features as a whole determine the first stage of the recycling process, which is re-collection [64]. This, in turn, influences the layout of the recycling plant which aims at the re-use of plastic materials re-claimed in the most economical way. A typical PET bottle production, consumption and disposal chain can be attained from figure 13 [65].

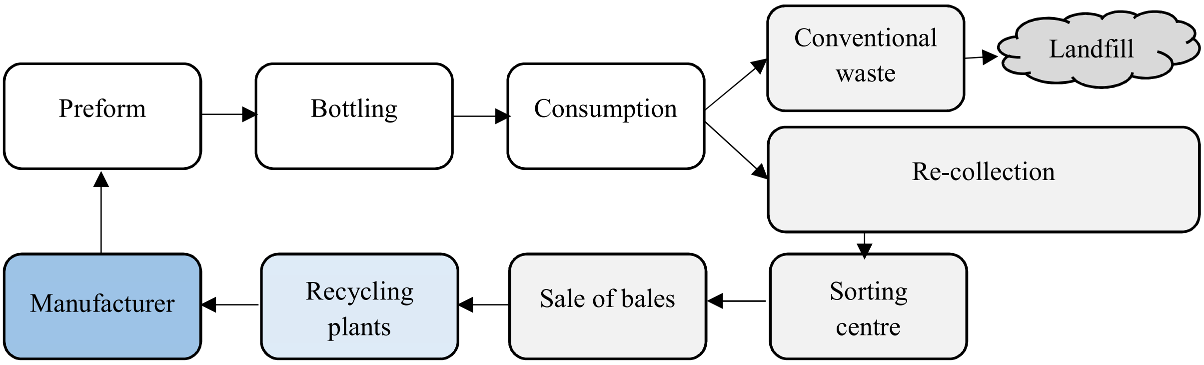


Figure 13 - PET bottle production - consumption - disposal chain

In short, the material to be recycled and the enforced legislation are determinants for the choice of the re-collection system. In many countries recollection systems for post-consumer PET bottles as well as for other packaging materials (paper and board, metal cans, glass, plastic packaging) have been established. In the US, Australia, France, Austria and Switzerland, different fractions of post-consumer bottles are collected in the most homogeneous way possible [66]. In other countries, on the contrary, bottles are collected more heterogeneously, in which different types of plastics out of different types of manufactured articles are collected together with PET bottles [67].

At any rate, re-collection must necessarily be a “differentiated” one, although the degree of differentiation may vary extremely [68]. The outcome of the re-collection system, therefore, constitutes the raw material for the recycling process. Consequently, the more selective the re-collection, the higher the degree of purity of the bottles from foreign bodies [69].

2.3.1 Sorting and separation technologies

The fact is that re-collection always yields a polluted product, and this fact poses the need for the first operation of the recycling process, namely the cleaning of foreign bodies by sorting and separation techniques [70].

The recyclables are conveyed to a facility for processing into a form suitable for sale as raw materials. Plastic and glass can first be separated from each other by mechanical or manually means, and then once more according to their type. Sorting is carried out in specially designed sorting plants which employ semi- or fully automatic processes, depending on the type, size, and technical standards of the plant [70]. The introduction and use of automated plastic sorting systems have lowered processing cost and improved the purity of the separated plastics over the past few years, thereby increasing the quantity utilization of recycled plastics [71].

The technologies for separating post-consumer plastics into their appropriate components fall into two categories: macroseparation and microseparation [72]. Macroseparation involves removing discarded materials from waste and separating them into different components by handling manually or automatically the individual items. Macroseparation allows separation of a wide range of materials from each other.

The following techniques and methods fall under these categories [72]:

- Gravity/Centrifugation;
- Methods based on the shape of the individual fragments (manual, 3D measuring devices);
- Optical (x-ray, IR, NIR, fluorescence, etc.);
- Metal detectors;
- Sonic techniques (ultrasonic technique).

Microseparation involves separating polymers by type after they have been shredded and chopped down to small pieces of approximately 1/8 to 1/4 inch in diameter [73]. This category comprises techniques based on:

- Geometry (air classification, micronization);
- Density (hydrocyclones, swim/sink);
- Melting point (heated rolls);
- Electrostatic; Mechanical (peeling);
- Solving behavior (temperature gradient).

Gravity and centrifugal techniques make use of different density (specific gravity) of the materials. Such a system is employed by Duales System, where the mixed plastics, after being cleaned, are suspended in water and enter the centrifuge as a suspension [74].

Particles with a higher density of water precipitate down to the centrifuge bowl while the lighter particles float on the surface and are extracted [74]. Sorting out specific types of plastic is feasible but the process has to be repeated with several centrifuges. Other methods employ rotating disks and inclined belts. The principles of plastic flotation show that it is more flexible than other techniques and could prove useful in separating mixture of plastics, but more research needs to be carried out for its successful implementation in the industry. Separation according to shape can be conducted manually [72]. As far as the optical methods are concerned, these are based on IR, UV and visible spectroscopy, laser induced plasma spectroscopy, x-ray spectroscopy, fluorescence and near infrared (NIR) detectors. Infrared spectroscopy uses the way different materials respond to infrared light for identification [75].

Generally, the recyclables enter the MRF and are sorted through a scheme similar to figure 14.

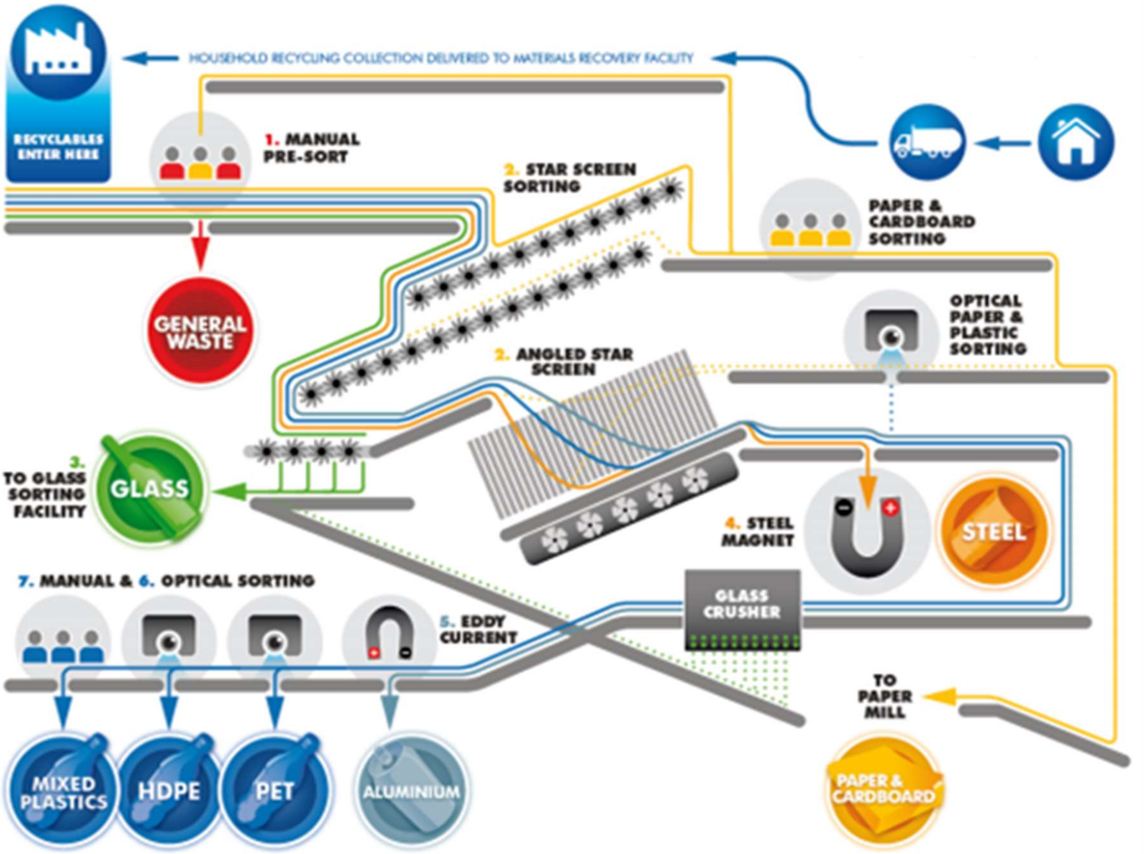


Figure 14 - Scheme of the sorting process of waste in a Material Recovery Facility (MRF)

First the MRF staff manually remove contamination (e.g. plastic bags) [76]. Fans and a series of shafts fitted with rotating start shaped discs propel paper and cardboard forward, while bottles, cans, and containers fall backwards. The glass is then sent for further sorting by colour. Next, a series of rotating magnets pick up steel cans. The eddy current repels, with an electromagnetic field, the aluminium cans off the conveyor belt [77].

Finally, through optical sorting techniques such as infrared sensors, the coupled air jets sort plastic types 1 and 2 (PET and HDPE, respectively). MRF staff manually sort the other plastic types (3 to 7). At the end of this process, the so-called bales of PET bottles, seen in figure 15, can be obtained [78].

Figure 15 - Bales of plastic PET bottles obtained from MRFs

The sorting and separation techniques are aiming at reducing the quantity of non-targeted plastic polymers and non-plastics that can be found together with PET bottles, in the bales [75]. These bales can lately suffer another step of sorting and separating techniques, producing flakes of PET of a high purity, seen in figure 16.

Figure 16 - Shredded flakes from PET bottles

Most European sorting plants consist of a mix of the above mentioned technologies to ensure an economical and efficient sorting of the input material with satisfying output quality. The exact composition of the specific plant should be adjusted according to input material as well as required output quality [9], [73], [75].

2.3.2 PET super-clean recycling technologies

So-called super-clean processes for PET bottle-to-bottle recycling are using further deep-cleansing steps to clean-up conventionally recycled PET flakes to contamination levels similar to virgin PET pellets [79].

As a general principle, potential post-consumer contaminants have to be mobilized in the PET matrix, so that they are able to diffuse to the surface of the PET pellet or flake, generally by heating up to temperatures of about 200°C. When the contaminants have reached the surface of the PET pellet or flake, they have to be removed from the recyclables stream with vacuum treatment or inert gas stripping [79]. The use of chemicals (caustic soda) removes parts of the PET surface. On the other hand, chemicals like ethylene glycol swell the PET polymer matrix so that the diffusion of the contaminants to the surface will be fasten up. In the last two decades several recycling technologies have been developed for the decontamination of post-consumer PET bottles [73].

2.3.2.1 PET super-clean recycling process based on pellets

The PET recycling processes based on pellets are using as main decontamination process the last step of the PET virgin processes, the solid-state polycondensation (SSP). As input material, conventionally recycled PET flakes, hot-washed, are used. A scheme of PET super-clean recycling processes based on pellets is shown in figure 17. The washed flakes are introduced into an extrusion machine to be processed and melted, with no drying step between.

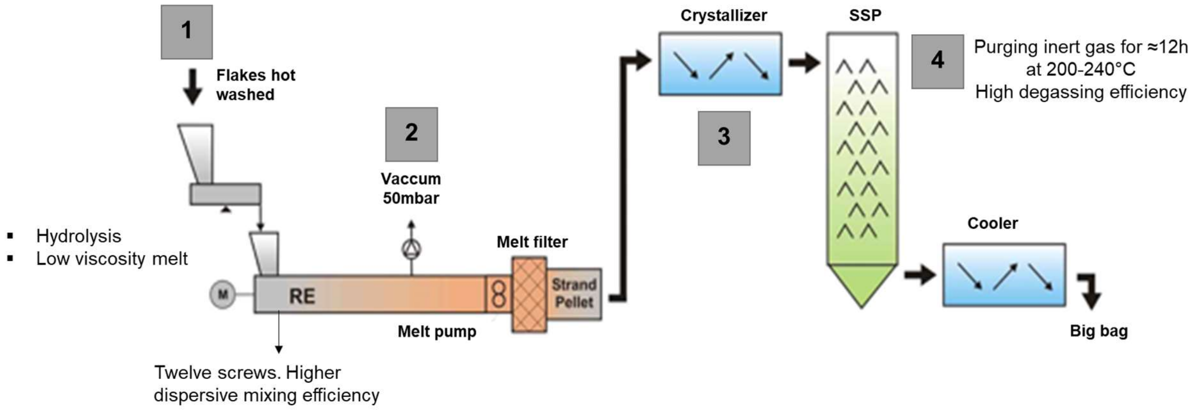


Figure 17 - Scheme of PET super-clean recycling process based on pellets

This re-extrusion process is characteristic of a high level of hydrolysis and a low viscosity melt is present. The melt is continuously filtered to remove solid particles (e.g. remaining paper, labels, aluminium, etc.) and a high vacuum (50 mbar) is applied in order to remove the moisture and other volatiles that may be generated in the melt-phase.

The configuration of the twelve screws arranged in a ring that turn in the same direction allow a high dispersive, degassing and mixing efficiency through the whole melt extrusion process.

The melt is pelletized and the pellets are then fed to a highly mechanically agitated horizontal reactor, in which they initiate primary crystallization under a combination of heat, positive flow of dry gas or a combination of gas and surface heaters. The residence time (around 10-15 min) and the agitation is controlled to ensure that the pellets do not sinter together and are completely crystallized.

The crystallized and preheated pellets are continuously fed to a counter-current reactor running under high temperature, in the range of 180°C and 200°C, and inert gas flow (typically hot nitrogen), for a predefined residence time between 12 to 20h. This defined operating parameters are dependent on the desired increase of the viscosity of the PET material.

Super-clean PET recycling based on pellets has some advantages. Due to the re-extrusion step, all PET pellets have the same size and the potential post-consumer contaminants are homogeneously distributed in the polymer. Also the PET matrix was homogenized. Therefore, the polymer properties can be controlled easily.

The distances, however, which the potential contaminants must move in order to reach the surface of the PET pellets are relatively long. In other words, the residence time of the PET pellets in the SSP reaction is dominated by the diffusion coefficients of the potential contaminants in the PET polymer at the decontamination temperature. The higher the temperature, the shorter is the minimum residence time in the solid state process.

On the other hand, moisture from the core of the PET pellets is also eliminated during the long residence times under vacuum and high temperature. As a result, the viscosity of the PET polymer typically increases to virgin levels during the SSP reaction.

Recycling processes based on SSP reactions are therefore used in such cases, where an increase of the viscosity of the PCR-PET is necessary.

2.3.2.2 PET super-clean recycling process based on flakes

The PET recycling process based on flakes is conventionally configured to decontaminate first the recycled PET flakes and subsequently re-extrude them to pellets. It is interesting to note that the residence time for decontamination of PET flakes is typically in the range of only 1 to

2h, which is significantly lower compared to the residence times of PET pellets in the SSP process. A scheme of super-clean recycling processes based on the decontamination of PET flakes is shown in figure 18.

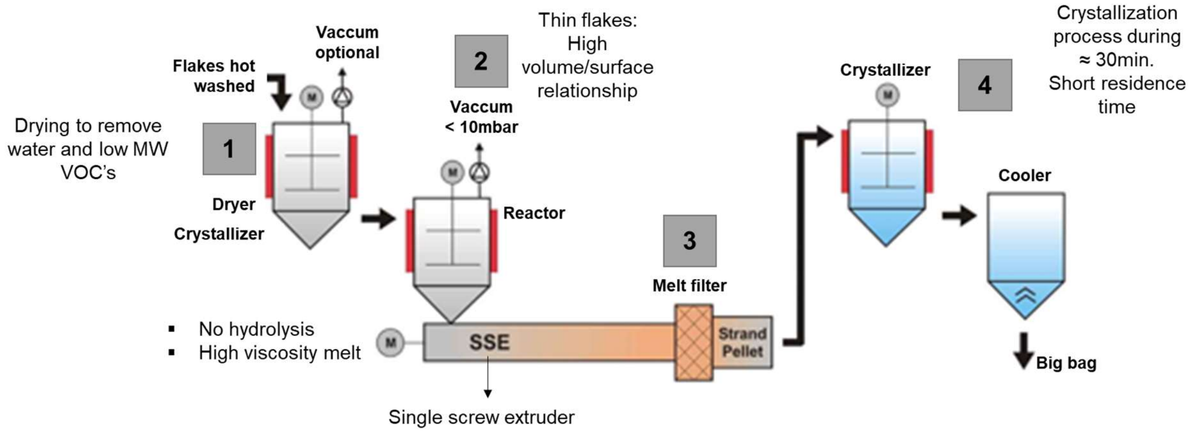


Figure 18 - Scheme of PET super-clean recycling process based on flakes

The amorphous washed flakes are introduced into a vacuum crystallization dryer where vacuum and temperature are applied for a predefined residence time, to achieve high levels of crystallinity. Then, the flakes are fed to a continuous reactor operating under high temperature and vacuum for a short period of time.

Moisture and low molecular weight volatiles are efficiently removed in this two batch mode.

The flakes coming from the reactor are melt in a single screw extrusion process and residual solid particles (e.g. paper, aluminium, etc.) are filtered out before pellets are produced. Subsequently, the melt is pelletized and the pellets reach a crystallizer, during 15 to 20 minutes, to develop crystallinity, an increase in viscosity and chain length.

As mentioned above, the residence time in the decontamination process is dominated by the diffusion coefficients of the migrants. The main reason for the significantly shorter residence times is that potential contaminants from the first use of the PET bottles are located near the surface of the PET flakes, which reduces the distances for the contaminants to move to the surface of the PET flakes significantly. In general, the smaller the flake size, the shorter the residence times in the decontamination processes.

Therefore, the time to decontaminate the PET flakes to levels found in virgin PET in a super-clean flake process can be influenced by the flake size.

2.4 Manufacture of PET preforms

Polymers attract moisture from the surrounding environment. Some materials only collect surface moisture while others actually absorb water vapour inside the pellets, like PET [80]. This polymer is highly hygroscopic and will attract moisture into its molecules, leading to chain breakage, and, therefore, a drop in the intrinsic viscosity [81]. The resin requires a drying step before it can be injected in order to produce a preform. The maximum amount of water that can be in the resin should be less than 30ppm to avoid IV drop levels between 0.03 – 0.04 dL/g . Higher moisture levels will lead to much higher IV drops, rendering the material unsuitable for the application and the end product will have either structural or appearance defects [21], [81].

Since acetaldehyde is a very volatile compound, the drying process of the PET resin can ultimately reduce its concentrations until less than 1 ppm, becoming a very important step not only for the moisture content factor but also for the low molecular weight compounds remaining from previous treatments that can additionally be removed [80].

2.4.1 The importance of drying

Anything that may degrade or lower the IV of PET during processing must be monitored and controlled. The most important issue is proper drying of the resin prior to melt processing, minimizing the hydrolytic degradation of PET and yield an AA concentration of less than 1 ppm [47]. Hydrolytic degradation is temperature dependent: it begins to occur in PET at temperatures as low as 150°C and the rate increases with temperature [17].

Higher temperatures lead to oxidation of the polymer, which shows up as yellowing of the pellets and/or a yellow tint to the preform [21]. In addition, if the residual moisture is too low, this leads to a tough melt when processing the resin, increasing the shearing within the material and causing a higher drive power of the injection machine. That leads thereby to a material damage and a reduction of the intrinsic viscosity by shear stress. Improper drying and the resultant high moisture in the melt phase lowers down the friction but increases hydrolysis and consequent drop in IV. This changes the inflation behaviour of the preform in that the preform will inflate under lower pressure because the natural stretch ratio is greater. In turn, this will lead to less orientation and weaker bottles [81].

Drying the material means removing its moisture while it remains undamaged. The correct and most important drying parameters are a combination of time and temperate at a certain airflow.

Heat is the driving force in drying. The pellets will not release its moisture without being heated. Heat causes the molecules to move about more vigorously, weakening the forces that bind the water molecules to the polymer chains. Above certain temperatures, the force that binds the water molecules to the polymer chains are reduced allowing free movement of the molecules to aid the drying process [21].

Dew point is the second fundamental drying parameter. It is the temperature at which moisture in the air begins to condense. The low vapour pressure (dew point) of the dry air surrounding the pellets causes the freed moisture molecules to migrate to the surface of the pellet [81].

Drying time is the third fundamental drying parameter. PET pellets do not dry instantaneously, there must be sufficient time for the water molecules to defuse to the surface of the resin [82].

Finally, the forth fundamental drying parameter is airflow, which carries heat or dry heated air to the material in the drying hopper. With hygroscopic materials, the low dew point heated air must be forced over the material to make the molecules of moisture disengage from the pellets and move to their surface where the airflow carries the moisture away [80].

There are dozens of drying processes technologies. Although, Dual Bed dryers used to be the most commonly purchased type of resin dryer. A schematic representation of how these dryers operate is shown in figure 19 [81]. This technology consists of two beds (or towers) of desiccant stainless steel beds, process and regenerative blowers, process and regeneration heaters and valves to re-direct the airflow. While one bed of desiccant supplies dry process air to flow through the drying hopper, the other bed – with saturated desiccant – is regenerated, by forcing hot air through it. When the regeneration is complete, that bed becomes the one supplying the dry process air and the first bed goes into the regeneration mode [21], [81].

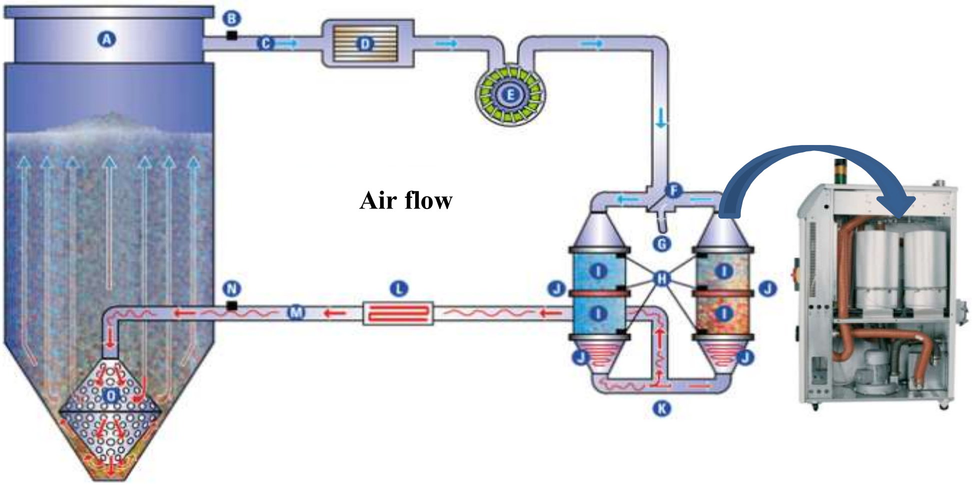


Figure 19 - Dual Bed drying technology scheme

Typically, PET is dried in the design dehumidifying dryer shown above, operating at a temperature of 160°C for a period of at least 4 hours [23].

2.4.2 Injection moulding of preforms

As a cycling process, a preform injection moulding system can be divided into four essential process steps: feeding and plasticizing, filling, packing-holding and cooling [23].

The first task of the injection machine is to transform the continuously feed dried pellets into a homogeneous melt [32]. There are three extrusion systems used in the production of PET preforms, although the scope of this section will focus on the standard reciprocating-screw technology, whereby the screw recovers and then pushes the material forward. These screws are manufactured with three distinct areas shown in figure 20. The configuration is purposeful, so that the root diameter increases along its length, ensuring that, as the resin melts, the decrease in occupied volume is accounted for so that the polymer continues progressively melting [80].

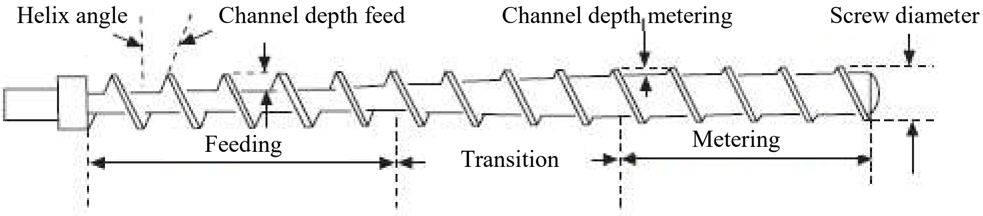


Figure 20 - Gradual transition screw. Adapted from [32]

The reciprocating-screw injection moulding machine is now the most widely used due to its reliable overall performance, such as improved melting rates, closer tolerances on shot size, and better control of temperatures [83]. It comprises an injection unit, a clamping unit, and a hydraulic unit, as schematically shown in figure 21 [22].

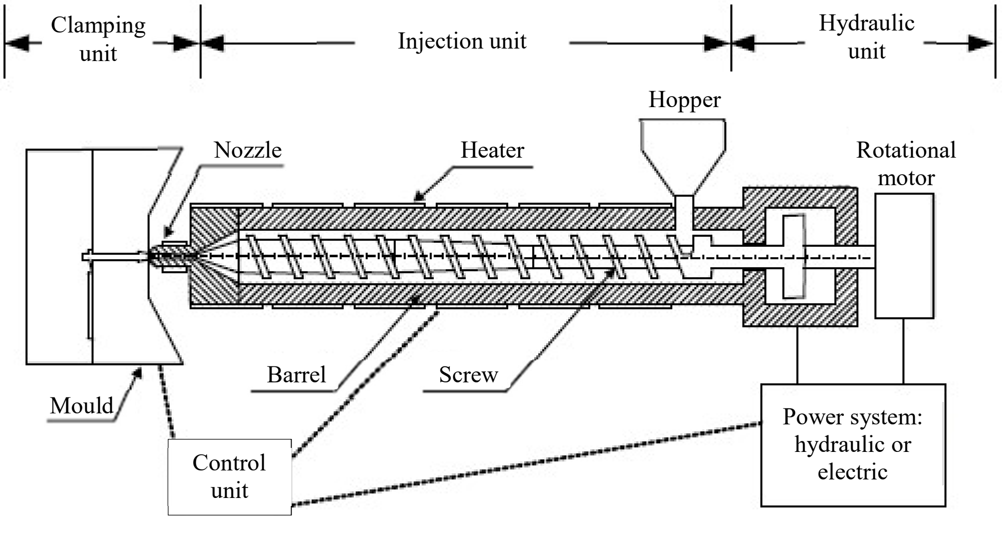


Figure 21 - Simplified schematic of a reciprocating-screw injection molding machine. Adapted from [83]

The whole system combines injection and plasticizing into a single unit, in which the screw is used to both plasticize the material and inject the melt into the mould. The clamping unit holds, opens, and closes the mould automatically and ejects the moulded preform at the end of the cycle [84]. The power unit generates and distributes either hydraulic or electrical power for every motion of the machine. The control unit controls the machine sequencing and the key processing variables that ensure the quality of the preforms [22].

As the pellets are feed to the screw from the hopper, they present themselves as a mix of crystalline and amorphous phases, and must be gently melted due to the temperature-sensitive nature of PET. This mix will travel along the heated barrel of the extruder [85]. Although, polymers melt at different rates. The more crystalline the polymer, the shorter the temperature range from start to completion of melting and, therefore, the quicker the volume loss [21].

Considering that, different temperatures and screw profiles are designed and applied to separate zones down the length of the outside of the extruder, ensuring that sufficient heat energy is applied to the resin. The melt temperature must be as uniform as possible and at the lowest achievable level in the flow channel [86].

Therefore, barrel temperature should be adjusted with a negative profile from 275-290°C between the feeding section and compression zone down to 260-275°C towards the screw tip [87]. This provides control of the melting behaviour by the barrel temperature setting [3].

A considerable enthalpy increase must be provided by the plasticizing process, through screw torque and heater bands in order to transforming the solid into the melt stage. All crystals must be melted because un-melted crystals would act as nuclei (starting points) of crystallization in the preforms [34]. This should be avoided as the goal is to have the preform completely amorphous and clear.

The melting of the resin is accomplished mainly by transferring the mechanical energy of the rotating screw into shear energy. By rubbing the spherulites against each other and against barrel and screw, the extruder brings on the necessary shear heat for melting [88].

Heat transfer from barrel through heater bands is only about 30%. Most of the heat (about 70%) comes from pellet inlet temperature (the temperature at which the pellets leave the dryer) and friction between the material, screw and barrel walls [22].

2.4.2.1 Filling

Filling is the second stage after a homogeneous melt is obtained, and begins with the mould fully closed, forming an empty cavity, schematized in figure 22 [83].

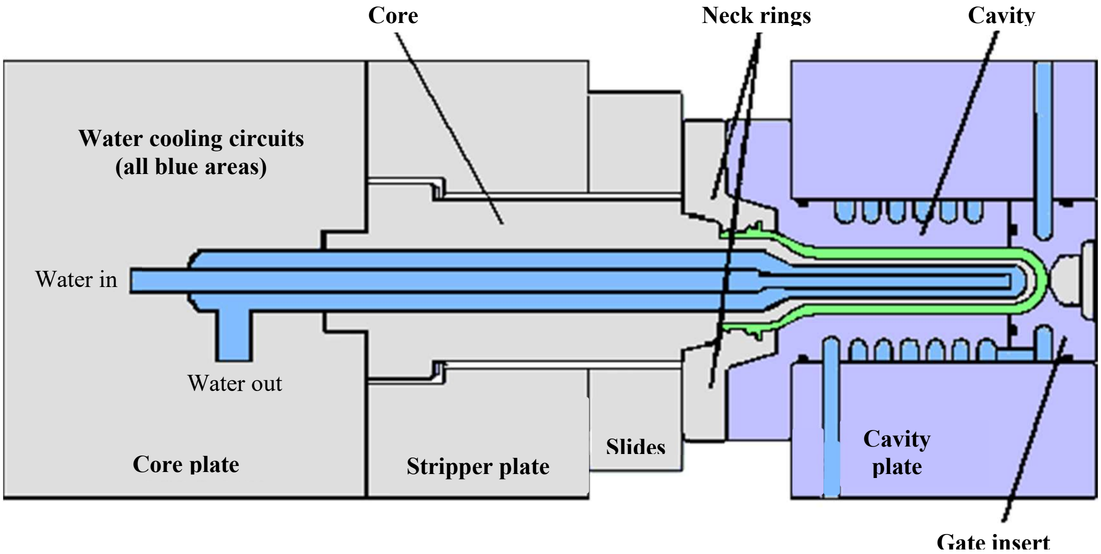


Figure 22 - Typical components of a preform injection mold. Adapted from [83]

During the filling stage, high pressure in the hydraulic cylinder forces the screw forward and pushes the material into the mould cavity until it is completely or nearly completely filled [83]. As the hot material hits the cold mould walls, seen in figure 23, the melt in direct contact with the wall freezes off and forms a boundary layer. The material in this layer will not change during injection [22].

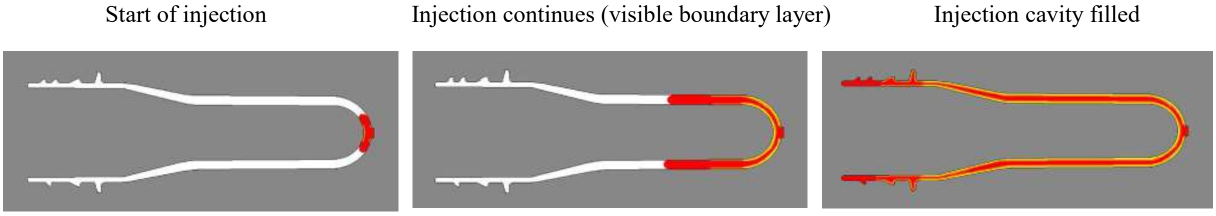


Figure 23 - Melt filling diagram of a preform. Adapted from [22]

As more material enters the cavity, the boundary layer expands along the length of the preform. The melted PET flows through the barrel, hot runner channel, nozzles and the mould cavity in a laminar flow. This flow is characterized by the highest shear rates occurring between the melted polymer and the surrounding channel walls. Shear deformation causes internal friction between adjacent entangled polymer chains, which results in shear heating. As the term implies, shear heating (also referred to as frictional heating) is defined as a local temperature rise due to friction [22], [34].

2.4.2.2 Packing-holding and cooling

Once the cavity is full, the added resistance causes the hydraulic pressure to increase, and it is here that the machine needs to be switched from injection to hold or packing pressure [22]. The material is “packed” into the mould cavity under pressure to compensate the shrinkage associated with cooling and solidification. The packing-holding stage continues until the material at the mould gate is frozen and the material inside the mould is no longer influenced by that at the injection nozzle [81].

The material is then cooled inside the mould until it is rigid enough to be ejected. Concurrently with the material solidification in the cooling stage, another injection cycle is being prepared whereas plasticisation is taking place inside the barrel, resulting in the melting and conveying of melted PET to the screw tip by the backwards screw rotation [89]. The screw rotation ceases after a sufficient amount of melt is generated in front of the screw. When the part in the mould becomes rigid enough, the mould opens and the preform is ejected [84].

2.4.3 Acetaldehyde generation in the injection moulding process

As discussed previously in section 2.2.4, acetaldehyde is a degradation product formed when PET is heated to its melting temperatures [20]. Even after reducing the AA content in the pellets to less than 3 ppm by SSP, more AA will be formed during the melt processing stage when the preform is injection moulded. Figure 24 shows a graphical depiction of how AA content changes until the injection moulding process [90].

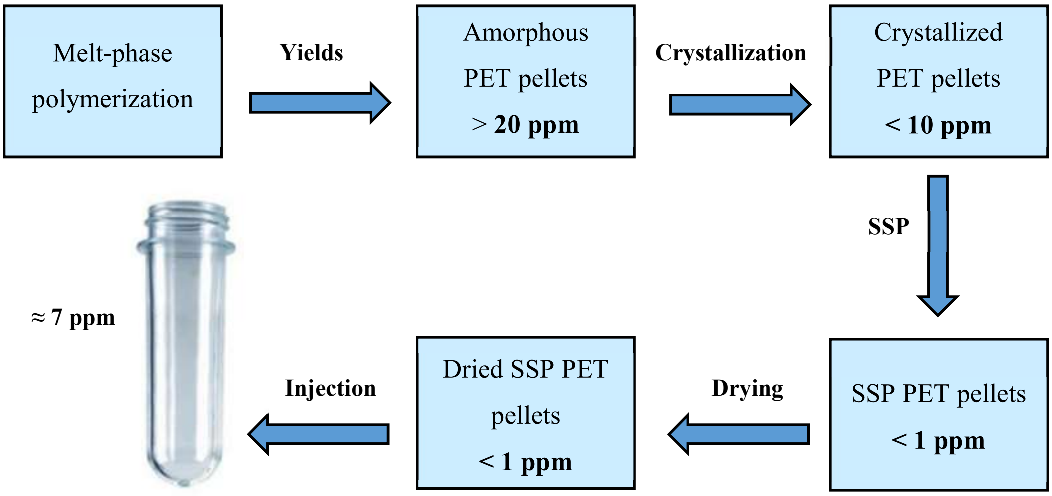


Figure 24 - Acetaldehyde concentration during lifecycle of PET

The amount of AA in PET is of great concern for manufacturers of food and beverage packaging. As it is easily perceptible at very low levels through its characteristic odour and taste, the organoleptic features of the end product may be changed. The most extreme scenario exists for bottled water companies. The taste of pure water is very subtle and is unable to mask the taste of even a few parts per million of AA [90].

Of all the AA producing degradation mechanisms discussed in section 2.2.4, thermal degradation has the greatest impact on the generation of AA. Thermal degradation leads to random chain scission reactions, resulting in the formation of vinyl ester end-groups [91]. The vinyl ester end-group concentration has been shown to have the most direct influence of the amount of AA that will be generated during lifecycle of PET [88].

AA is the low molecular weight by-product generated through the thermal degradation due the processing significantly elevated temperatures. Thus, control of the injection process parameters is critical to control and minimize the AA generation in the production of preforms. Therefore, besides the high melting temperature, other relevant factors related to thermal degradation and random chain scission have to be considered [26], [89].

The concentration of AA in the preform increases in proportion to the drying, barrel and mould cavity temperatures. The viscous polymer melt is also heated by friction within the barrel, the screw and the distribution channels, as it can be attained from figure 25 [30], [88].

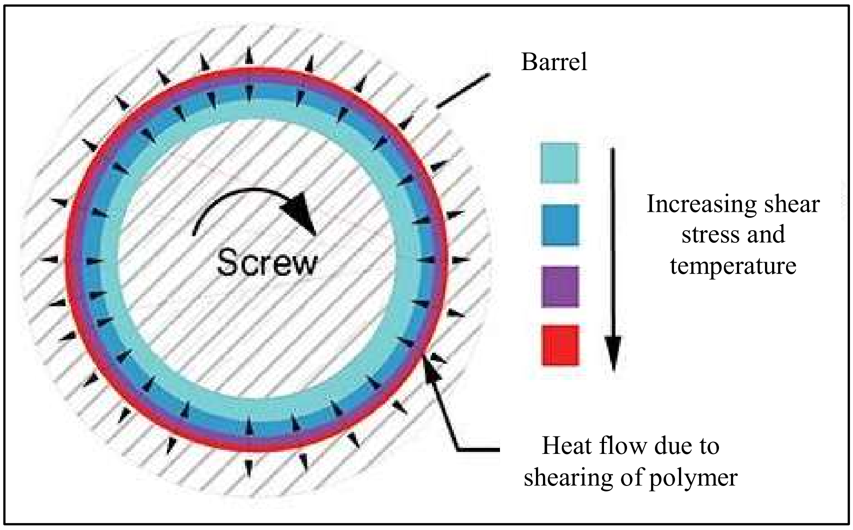


Figure 25 - Temperature variation and shear stress submitted to the polymer melt due during extrusion process. Adapted from [88]

This friction is much depending on the viscosity of the molten resin as the type and speed of the thread. Besides the heat generated by friction, shear stress can mechanically break the polymer molecules, thereby forming more vinyl ester end-groups [57], [87]. The lower the IV of the resin, lower will be the melt viscosity and allows the injection moulding machine to operate at lower temperatures, with less shear stress induced to the molten PET [83].

A parameter of almost equal importance to the temperature of the molten polymer to minimize the formation of AA in the preform is the residence time thereof. The AA generated is almost directly proportional to the residence time of the melt in the process. Thus, it is a good rule to minimize the cycle time to decrease the generation of AA [47].

Shukla, et all [92] performed an exhaustive study examining the effects that various injection moulding parameters can have on the degradation of PET and the generation of AA. Their work revealed that increasing the processing temperature by 10°C will cause the AA concentration within PET to double. In addition, it was shown that exist strong relationships between an injection moulder's shear rate and the generation of AA, as well as between the polymer's processing time and the amount of AA that is generated.

Intuitively, to minimize the effects of thermal degradation and the amount of generated AA, a balance must be made between the processing temperature, the residence time, and the shear heating that occurs during extrusion or injection moulding.

2.4.4 Intrinsic viscosity drop during the injection moulding process

As discussed previously, PET can be produced through an esterification reaction, using TPA and EG, as described in the following equation (1).

(1) Direct esterification TPA + 2EG = BHET + 2H2O

Water is a given by-product of polycondensation. Therefore, if a significant quantity of water molecules co-exist with PET macromolecules, as it can be attained from figure 26, water molecules will break PET chains into smaller ones, in a reverse reaction of the polymerization process called hydrolysis [58].

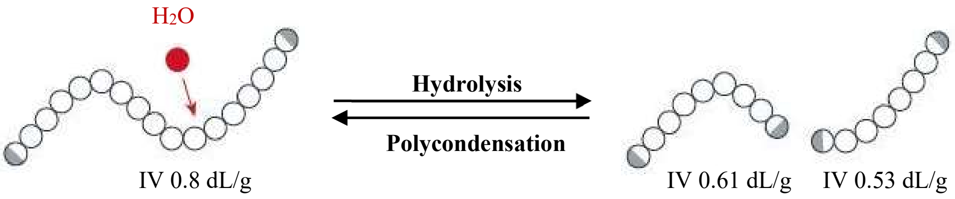


Figure 26 - Chain breakage of PET chains due to hydrolysis

Hydrolytic degradation of PET chains produces hydroxyl and carboxylic end-group. One molecule of water attacks the chain and causes a scission of the chain, creating a carboxylic end-group [56]. With these generated end-groups comes the reduction in the polymer's molecular weight and IV.

Intrinsic viscosity is a measure of molecular weight, using a solution of the resin rather than a melt as in the melt index test. A decrease of IV from pellet to preform means a reduction in molecular size due to the moulding process.

There are several undesirable consequences of more than a slight loss of IV: increased moulded part weight and faster crystallization, both resulting from lower melt viscosity; and decreased toughness in non-oriented parts of the finished bottle, related to lower molecular weight and the possibly higher preform crystallinity [21], [90].

The principal cause of IV drop is, of course, hydrolytic degradation of the polymers' chains due to moisture. In the melt state, the attack of water molecules on ester linkages is rapid and quantitative.

A secondary source of IV drop is shear heating [89], [92]. Separation of the effect of high shear stress and/or rate of the effect of dissipation of this energy as sensible heat in the resin is not easy and may not be necessary. Excessive screw speed, which generates high shear rates in flight clearances, has been observed to lower IV. A significant fact here is that PET's melt viscosity decreases but little as shear rate increases, so that high shear stress levels, high rates of viscous dissipation, and resultant high local temperatures are likely to occur together at high screw speeds. These conditions tend to promote rupture of PET macromolecular chains [83].

On the other hand, while hydrolytic degradation is reported to be the most aggressive form of PET, researchers have shown thermal-oxidative degradation to be as disruptive as thermal degradation in terms of IV [56], [93]. Thermal-oxidative degradation, as a rout to AA, occurs when oxygen reacts with PET at elevated temperatures. The exposure to elevated temperatures leaves the EG linkage of a PET chain susceptible to be attacked by oxygen, which will decompose and form free radicals. The formation of two free radicals causes the PET chain to split in two. Some end-groups will re-form a PET chain and a molecule of AA, but others will remain separated and the molecular weight is reduced [4], [94].

Just like AA, to minimize IV drop, a balance must be made to reduce the hydrolytic, thermal, thermal-mechanical and thermal-oxidative degradation that occurs during injection moulding. Incoming moisture level should be the lowest to minimize hydrolysis but just as enough to avoid a tough viscous melt and a consequent increase in shear stress. PET should also be melted and/or processed under an inert environment to displace any oxygen interactions.

2.4.5 Lack of clarity and discoloration of PET

PET is transparent when amorphous and it will crystallize only between 85°C and 250°C [21]. The change is very slow near the ends of this range, more rapid between 150°C and 200°C, but still slow enough to permit fast cooling from the melt to a clear preform. This rate of crystallization during injection moulding will determine the preform clarity [83].

The milder receives pellets that have been crystallized in the resin manufacturing process. In the extruder they must be heated and plasticized to melt out all crystallinity. If the inject melt is not clear, preforms will not be either. This amorphous melt in the sprue and runner system must be kept above 260°C to prevent recrystallizing [95]. Then, on filling the cavity, temperature must quickly be brought below 75°C, again to prevent crystallizing. The resin must navigate the crystallization temperature range fast enough to stay essentially amorphous. This is accomplished by mould design and moulding operation [86].

If the entire preform is hazy and not fully transparent, there are three possible: residual crystallinity in the injected melt, inadequate mould cooling and inadequate resin drying. Drying is implicated here because, as stated above, residual moisture causes a drop in IV and a lower IV resin crystallizes faster than high IV resin. The problem goes beyond clarity because bottle mechanical properties can be affected by crystallinity. Haze dramatically increases at very low crystallinity levels (over ≈ 3%) [81].

It is also known that the many additional degradation reactions that take place during the polymerization stage and injection moulding of PET resin participate in subsequent reactions, which may involve polymer chains, monomers, low molecular weight by-products, or all of the above. Both thermal degradation and thermal-oxidative degradation share many common traits. First, both mechanisms require excessive temperature to degrade the PET chains [56]. Second, for the most part, both degradation systems result in similar effects upon PET: reduction of IV or molecular weight, formation of carboxyl end-groups, generation of the low molecular weight compounds and, ultimately, discoloration [96].

Discoloration is a serious problem in the production of PET preforms and bottles since they must appear water-clear and as close as possible to colourless. A big requirement is the absence of any yellowing or other discoloration and interrelated decreasing properties. The colour degradation can start in the synthesis of BHET, the pre-polymer of PET. There are some catalysts used in the melt polycondensation step that have a tendency to produce a yellowish polymer, such as titanium-based catalysts [53]. Other polycondensation catalysts based on mixed oxides of titanium/silicon have a less pronounced yellowing effect but can still be visible.

Yellowing of the polymeric end product is a characteristic of noticeable levels of thermal and oxidative degradation [96]. Yellow-amber coloured products of those degradation side reactions are not only provided in the synthesis of PET but also in the treatment of the pellets and subsequent melt process. This organic degradation contaminants will remain in the molten polymer and, given time and temperature, they will continue to react and grow, to increase in complexity and conjugation, and to intensify in colour [97].

Discoloration mainly results from the vinyl groups and can increase if a significant content of DEG molecules is present. Also, when letter solid-state polymerization process continues for a substantial extra number of hours in order to lift the IV levels to bottle grade, some oxidative degradation and yellowing arise [98]. Under the same logic, if the pellets before being injected stay in the dryer under extreme periods of time at significantly high temperatures, side degradation reactions will produce a yellow/oxidized resin. On the other hand, when molten PET is being processed by a high injection speed, the shear rate controlled by this parameter will cause over-shearing, over-heating and yellow/brown colour is taking place [99].

All these problems are preventable by tighter production controls, such as minimization of temperature and time fluctuations, and timely and careful maintenance operations.

2.5 Limiting AA generation, IV drop and colour degradation

Typical of injection moulding, PET preform moulding involves many variables, most of them interacting mutually and with resin parameters. PET's somewhat different nature requires that its process responses be clearly factored into control of a quality preform production.

In solving moulding problems, a reasonable first approach is to associate IV drop with drying, acetaldehyde generation with heat history and colour degradation with both drying, heat history and oxygen interactions. However, a problem may have multiple or subtle or multilevel causes. Further, solving one may create another. Hence, there are two important principles of PET injection moulding: (1) it is the interaction of resin properties and machine conditions that determines results, and (2) any adjustment can have an effect beyond the intended one.

The preform manufactures seeks to minimize the AA content of preforms by using minimum injection temperatures (without sacrificing clarity), short cycle times, and low shear rates during injection moulding.

3. EXPERIMENTAL WORK

3.1 Materials

Acetaldehyde generation, IV drop and colour degradation of two materials were evaluated. rPET1 comes from a PET recycling process that use as main decontamination process the last step of the PET virgin process, the solid state polycondensation (SSP), as a decontamination step. In one of the first steps of the super-clean process, the washed PET flakes were re-extruded to pellets. The pellets were subsequently further deep-cleansed using the SSP technology.

On the other hand, rPET2 comes from a PET bottle recycling process where the re-extrusion and decontamination step exchanges. The conventionally recycled PET flakes were firstly decontaminated and subsequently re-extruded to pellets, with no SSP process.

The recycled PET resins were both purchased from recycling plants of Plastipak.

The initial values of AA, IV and colour of both materials are summarized in table 4.

Table 4 - Initial AA, IV and color values for the two recycled PET resins used

Property	Material	
	rPET1	rPET2
Acetaldehyde (ppm)	0,15	3,13
IV	0,792	0,794
(b) colour value	- 3,93	- 0,76

Both materials meet the Food and Safety requirements to be integrated into new PET bottles or other packaging containers for food and beverages.

3.2 Design of Experiments (DOE)

Design of experiments has been a very useful tool to design and analyse complicated industrial design problems. It helps to understand process characteristics and to investigate how inputs affect responses based on statistical backgrounds, as schematized in figure 27 [100].

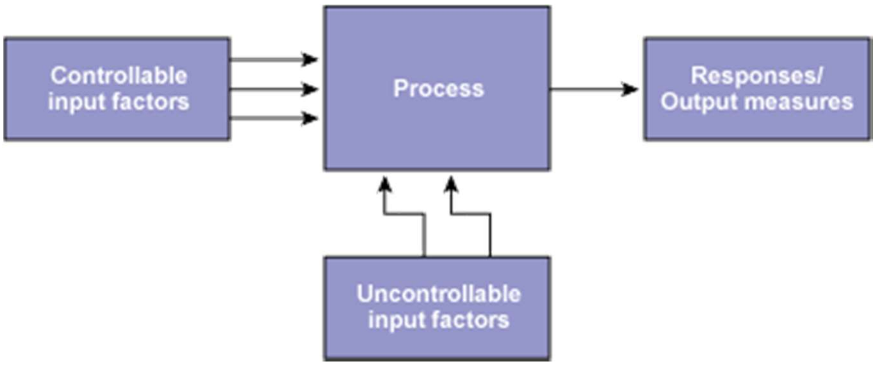


Figure 27 - DOE approach. Adapted from [100]

In addition, it has been used to systematically determine the optimal process parameters with fewer testing trials.

In general, there exist interactions among injection moulding factors. Thus related experiments must be designed to consider interaction effects appropriately. The present work concerns a DOE approach based on a response surface design for the proper consideration of interactions.

The response surface design, as an advanced set of design of experiments, is a technique that predicts responses for different factor designs, plots the relationships between the factors and the responses and finds the settings that optimize one or more responses [101].

The software used was Minitab and the approach was then applied to determine the optimal conditions for the injection moulding process of a preform containing recycled PET.

3.2.1 Drying DOE

There are four essential parameters, described in section 2.4.1, that affect the quality of the dried resin. Accordingly to the drying available equipment, drying temperature and time were considered for the screening DOE, in mutual interactions as well as with separate factors.

The number of levels was set to 2 (low and high) and are summarized together in table 5.

Table 5 - DOE setup for the drying exercise

Sample reference	**DOE Setup**	
	Drying temperature (°C)	**Drying time (h)**
A	120 (Low)	1 (Low)
B	120 (Low)	5 (High)
Middle point	150	3
C	180 (High)	1 (Low)
D	180 (High)	5 (High)

All evaluations were performed using the two materials individually.

PET is known to undergo hydrolytic degradation with a minimum moisture content and at temperatures exceeding 110°C. To avoid this, all resins were dried to moisture levels below 50 ppm, under the conditions described above. A PIOVAN DP 605 dryer, with a twin-tower desiccant beds as described in section 2.4.1, was used for this purpose.

Around 3kg of material was drained into a bucket in order to collect an adequate sampling size of approximately 100g from the bottom crucial point of the drying hopper.

The final moisture content of the samples was measured with an AQUATRAC-3E, seen in figure 28.

- Cover of reaction vessel
- Sample container
- Reaction vessel

Figure 28 - Main components of the AQUATRAC-3E®

The sample container contains 52g of the sample reference to be measured. The moisture analysis is performed by the schematized principle in figure 29.

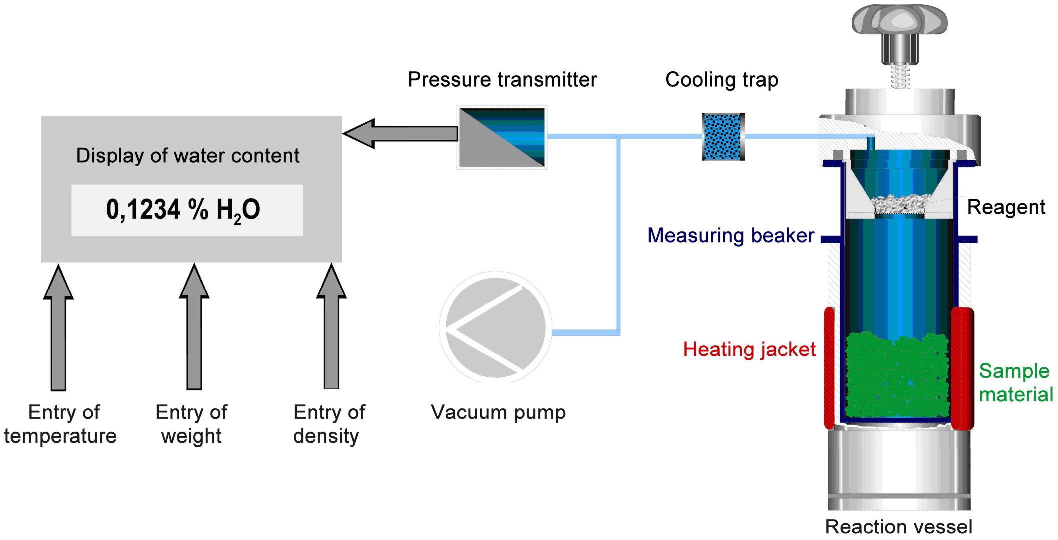


Figure 29 - Measuring principle of the AQUATRAC-3E®

The water contained in the sample evaporates due to the effect of temperature (160°C) and vacuum. The water vapor raises, penetrates the reagent granules in the reagent insert on top of the sample container, thus forming calcium hydroxide $Ca(OH)_2$ and hydrogen (gas), as it can be attained from the following equation.

$$CaH_2 + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ H_2$$

This reaction takes place in the closed reaction vessel and the cold volume of it is known.

The chemical reaction by-product, $Ca(OH)_2$ can be seen as a pale grey powder on the surface of the reagent. The pressure, generated by hydrogen as the other product of the chemical reaction, is measured by a built in pressure transducer. When the partial pressure of the water vapour in the system is finally zero, hence also hygroscopic substances will release their moisture completely.

For each sample drying set and with the moisture value checked, samples were collected, stored in aluminium bags and placed immediately in a freezer. This was to prevent any acetaldehyde from diffusing from the rPET pellets and into the atmosphere.

3.2.2 Injection DOE

Each injection parameter affects the preform quality in mutual interactions with the drying parameters as well as with separate factors. Considering the literature review, barrel temperature of the injection unit and residence time may have the most detrimental effect on the preform quality and the responses to analyse.

Therefore, for the screening of the injection DOE, four factors were selected with four levels – soft and hard in terms of drying, low and high in terms of injection. Nine runs were performed as listed in table 6.

Table 6 - DOE setup for the injection molding exercise

Sample reference	DOE Setup			
	Drying temperature (°C)	Drying time (h)	Barrel temperature (°C)	Residence time (s)
A	120 (Soft)	5 (Soft)	265 (Low)	21,4 (Low)
B	120 (Soft)	5 (Soft)	265 (Low)	31,4 (High)
C	120 (Soft)	5 (Soft)	285 (High)	21,4 (Low)
D	120 (Soft)	5 (Soft)	285 (High)	31,4 (High)
Middle point	150	4	275	26,4
E	180 (Hard)	3 (Hard)	265 (Low)	21,4 (Low)
F	180 (Hard)	3 (Hard)	265 (Low)	31,4 (High)
G	180 (Hard)	3 (Hard)	285 (High)	21,4 (Low)
H	180 (Hard)	3 (Hard)	285 (High)	31,4 (High)

The dried rPET pellets were introduced into the injection moulding machine with an automatic vacuum loading system connected with the drying unit.

All preforms were produced with a 50-ton, single-cavity, reciprocating-screw Arburg injection machine. For all runs, the injection speed and pressure was set at a constant value of 19 mm/s and 2500 bar, respectively. The mould temperature was controlled by circulating cooling water (± 9°C) flowing through the drilled channels in the mould cavity and core plates.

The mould cooling time and speed of PET in dosing/decompression was set accordingly to the DOE setup for each reference, as it can be seen in table 7.

Table 7 - Speed and cooling time variations

Injection parameter	References								
	A	B	C	D	Middle point	E	F	G	H
Speed on dosing/decompression	105	53	105	53	75	105	53	105	53
Cooling time	11	21	11	21	16	11	21	11	21

Extruder barrel temperatures were set to the same temperature described in table 6, to give a consistent temperature profile, for ease of analysis and interpretation of experimental data. The hot runner temperature was controlled to be 285°C, with a nozzle temperature of 320°C.

Under the exact same conditions as references A, B, C and D, four new references were produced with an high level of moisture surrounding 100 ppm, in order to analyse the influence of a significant elevated moisture content within the acetaldehyde levels, IVdrop and colour degradation of PET preforms containing 100% rPET.

For each injection set, the first preforms were discarded, allowing the machine to reach a steady-state until sample collecting began. Once the machine reached steady-state, just like the drying exercise, preforms were collected, stored in aluminium bags and placed in a freezer to avoid the diffusion of AA.

3.3 Headspace Gas Chromatography with FID detector

For this work, the quantification of acetaldehyde in each sample was performed by a headspace analysis technique. In this method, processed samples (either dried resin and injection moulded preforms) were immediately collected and placed in a freezer to prevent the AA from volatilizing out of the PET matrix. The analysis of acetaldehyde by headspace gas chromatography is therefore done on PET ground into small diameter particles. In order to obtain these small diameter particles, grinding the resin and the preforms is necessary.

Grinding the resin samples in the ZM 200 ultra-centrifugal mill, seen in figure 30, was achieved by the rebound and shear effect between the rotor and the stationary ring screen. A small amount of rPET pellets were submersed in liquid nitrogen in order to avoid the overheating of the samples during grinding that could impact the results. Then, they are fed to the rotor via the hopper equipped with a splash guard. Under the effect of centrifugal acceleration, it is projected outwards and pre-crushed in contact with the wedge-shaped teeth of the rotating rotor. This two-stage comminution process results in a fast and particularly gentle treatment of the material. The pellets to be shredded remain in the shredding chamber for a very short period of time, where its properties are therefore not affected by the grinding process.

Figure 30 - ZM 200 ultra-centrifugal mill for grinding resin samples

By using the ultra-centrifugal mill, 0.5-mm diameter particles of PET resin are obtained.

Grinding the preform samples in the FRITSCH Cutting Mill PULVERISETTE 15 was achieved by immersing the preforms in liquid nitrogen to, once more, avoid overheating. In this case, no liquid nitrogen must be transferred into the cutting mill seen in figure 31.

Figure 31 - FRITSCH Cutting Mill PULVERISETTE 15 for grinding preform samples

Particles of 2-mm are obtained with the rebound and shear effect of the rotating blades.

To prepare the grinded samples for analysis, ± 0,2000 mg is weighed in a 22-mL glass vial, properly closed with an aluminium cap on it.

Finally, the samples are ready to be analysed by Gas Chromatography (GC), where the process is schematized in figure 32. This analytical technique uses a carrier gas as the mobile phase and a solid column as the stationary phase. So, during GC, an inert gas moves the gaseous sample through a long column, which is stored within an oven. At this point, the analytes, such as acetaldehyde, are vaporized (if not already in the gas phase) by the high temperature maintained in the injection port. The analytes are kept in the gaseous state by maintaining all elements of the instrument at a temperature above the boiling point of the analytes. The gas phase analytes are then immediately swept onto the chromatographic column by the mobile phase. The mobile phase is comprised of an inert carrier gas, nitrogen.

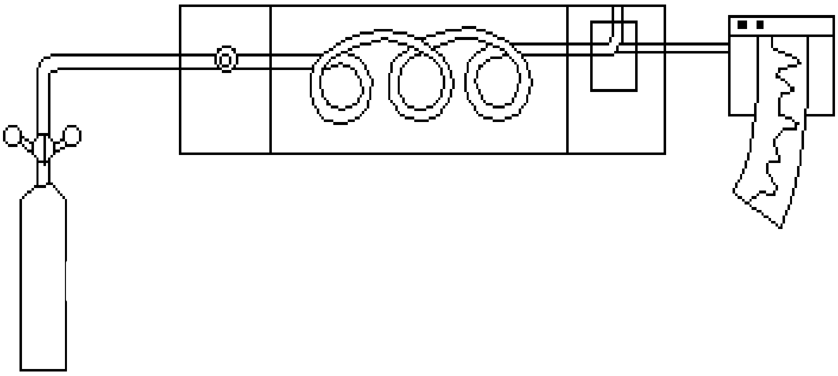


Figure 32 - Schematic of GC analysis

As the sample moves through the column, it separates into its individual chemical species based on the affinity that each individual chemical species has toward interacting with the column (stationary phase). Components of the mixture with a high degree of affinity for the stationary phase are strongly retained while components with low affinity for the stationary phase migrate rapidly through the column. As a consequence of the differences in mobility due to affinities for the stationary phase, sample components separate into discrete bands that can be qualitatively and quantitatively analysed.

As individual components of the mixture elute the chromatographic column, they are swept by the carrier gas to a detector. The detector generates a measurable electrical signal, referred to as peaks, that is proportional to the amount of analyte present. Detector response is plotted as a function of the time required for the analyte to elute from the column after injection. The resulting plot is called a chromatogram. Detector response is generally a Gaussian shaped curve representative of the concentration distribution of the analyte band as it elutes from the column.

The position of the peaks on the time axis may serve to identify the components and the area under the peaks provide a quantitative measure of the amount of each component.

3.3.1 Acetaldehyde analysis

The ground samples into small particles using the two grinding methods and a precise mass of ground sample are analysed with a GC Perking-Elmer AutoSystem XL Gas Chromatograph, seen in figure 33.

Figure 33 - GC Perkin Elmer AutoSystem XL for acetaldehyde analysis

This headspace analysis technique determines the amount of AA that remains trapped within PET in the resin, as well as the amount following processing into preforms.

The headspace sampler conditions where the ones summarized in table 8.

Table 8 – Perkin Elmer AutoSystem XL GC conditions

Column	SS + packing of Tenax 60/80
Detector	FID
Heating	20 minutes at 150°C
Column temperature	95°C
Detector temperature	250°C
Injector temperature	160°C
Retention time	1,82 min
Carrier gas N_2	32 psi

Measured in three replicates

During analysis, each sample is heated for 20 minutes at 150°C and at 32 psi, with nitrogen as the carrier gas. This temperature does not melt the PET, it simply volatizes the residual amount of AA that is trapped within the PET into the headspace of the glass vial. Once the twenty minutes has lapsed, the equipment injects a needle and extracts a sample of the gaseous headspace. This sample is sent through the GC column to be quantified.

The GC was calibrated with known amounts of AA treated in a manner similar to that of the ground resin and preform materials. Concentrations of AA where calculated by means of internal equations. It uses the experimental sample’s weight, the experimental sample’s resulting peak area, and the instrument’s response factor from the calibration standards to tabulate the AA content within the PET sample.

3.4 Rheological methods – determination of sample’s intrinsic viscosity (IV)

PET exhibits a molecular weight distribution, which means that is composed of molecules of different length. Therefore, a weighted average is taken. PET sample’s average molecular weight was characterized by measurements of its intrinsic viscosity in a solution, following the international standard ISO 1628-5. Pellets from resin samples were dissolved in meta-cresol, at a specified temperature. Small parts from the preforms were dissolved in dichloroacetid acid, also at a specified temperature. Conversion from melt viscosity to intrinsic viscosity was made by evaluating the melt viscosities of standardized samples that possess precisely known IVs.

This study based on IV changes during drying or the IV drop that the material suffers evaluates the intensity of the drying conditions and the degradation of PET as a result of processing through the injection moulding machine.

3.5 Colour analysis

Changes in colour, due to the processing into injected moulded preforms, as well as the changes in dried resin samples were analysed by means of a CM-3700d Spectrophotometer, seen in figure 34.

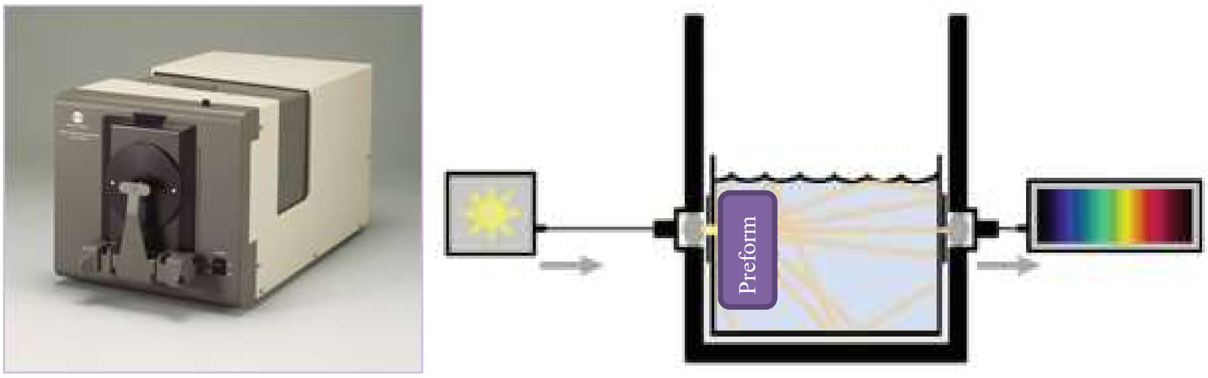


Figure 34 - CM-3700d Spectrophotometer for preform color analysis

When discussing the measurement of colour, in fact it is the variation in optical properties such as intensity, reflectance and transmittance over a spectral range. Both preform and resin colour analysis lays on the class of transmittance spectra. The amount of light transmitted by the sample is compared – wavelength by wavelength – with the amount of light transmitted by a standard medium, usually the air.

This method determines the amount of a parallel bean of light has made it through the sample without being absorbed or scattered.

The spectrophotometer captures, evaluates the colour and yields L, a, and b values for each preform sample. Table 9 gives an explanation of the L, a, and b values that are obtained from the instrument.

Table 9 - Explanation of L, a, and b values in color analysis

Variable	Meaning
L	Measures lightness and varies from 100, for perfect white, to 0, for black; approximately as the eye would evaluate it
a	Measures redness when plus, grey when zero, and greenness when minus
b	Measures yellowness when plus, grey when zero, and blueness when minus

These values were then converted to ΔL^2, Δa^2 and Δb^2 values; according to equations 2, 3 and 4, respectively. Then, the square root of the resulting value of equation 5 was used to calculate a yellowness index (ΔE).

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{2}$$

where:

$$\Delta L^2 = (L_{target} - L_{sample\ to\ analyze})^2 \tag{3}$$

$$\Delta a^2 = (a_{target} - a_{sample\ to\ analyze})^2 \tag{4}$$

$$\Delta b^2 = (b_{target} - b_{sample\ to\ analyze})^2 \tag{5}$$

If this value stays below 3, there is no significant impact in the colour of the preform.

4. RESULTS AND DISCUSSION

4.1 Acetaldehyde concentration

4.1.1 Residual AA in resin samples after drying

Under the drying conditions established in the drying DOE of section 3.2.2., a desorption phenomena of AA occurs. Acetaldehyde has a boiling point of 21°C, which means that it will volatize from the matrix of PET accordingly with the intensity of the drying process. However, it does not volatizes completely and a portion of AA remains residually trapped in the samples.

This residual AA was quantified by means of a procedure known as headspace analysis, described in section 3.3.1. Table 10 provides the comprehensive results for the drying DOE.

Table 10 - Residual acetaldehyde levels in rPET resin samples after drying exercise

Residual AA (ppm)		Sample reference				
	Start	A 120°C | 1h	B 120°C | 5h	Middle 150°C | 3h	C 180°C | 1h	D 180°C | 5h
rPET1	0,15 ± 0,02	0,15 ± 0,00	0,15 ± 0,00	0,14 ± 0,02	0,14 ± 0,01	0,13 ± 0,01
rPET2	3,13 ± 0,09	2,83 ± 0,02	2,50 ± 0,09	1,39 ± 0,04	1,91 ± 0,04	1,23 ± 0,09

In rPET2, it is possible to reduce 60,7% of the initial AA content, as it can be attained from reference D. In the case of rPET1, it becomes very difficult to reduce the AA level within the resin because the starting one is already considerably low. The former SSP process of this particular rPET resin reduces the initial value to a minimum. Therefore, there is no significant changes in AA volatilization, even at the highest temperature and higher drying time.

As expected, the minimum level of residual AA is achieved under the hardest drying conditions, for both materials.

By plotting this results in Minitab, regression equations can be obtained for the desorption phenomena of AA. Equations 1 and 2 express the acetaldehyde level in terms of drying temperature - T(°C) - and drying time - Time(h).

$$\textbf{rPET1} \quad \text{AA (ppm)} = 0{,}1645 - 1{,}25\times10^{-4}\ \mathbf{T(°C)} + 5{,}00\times10^{-3}\ \mathbf{Time(h)} - 0{,}42\times10^{-5}\ \mathbf{T(°C)*Time(h)} \tag{1}$$

$$\textbf{rPET2} \quad \text{AA (ppm)} = 4{,}43 - 0{,}0139\ \mathbf{T(°C)} + 0{,}092\ \mathbf{Time(h)} - 0{,}00146\ \mathbf{T(°C)*Time(h)} \tag{2}$$

These equations are the fitting mathematical formulas to a response surface design.

Figures 35 and 36 show the temperature and time dependent equations and effect on AA volatilization from the PET matrix, by means of factorial plots.

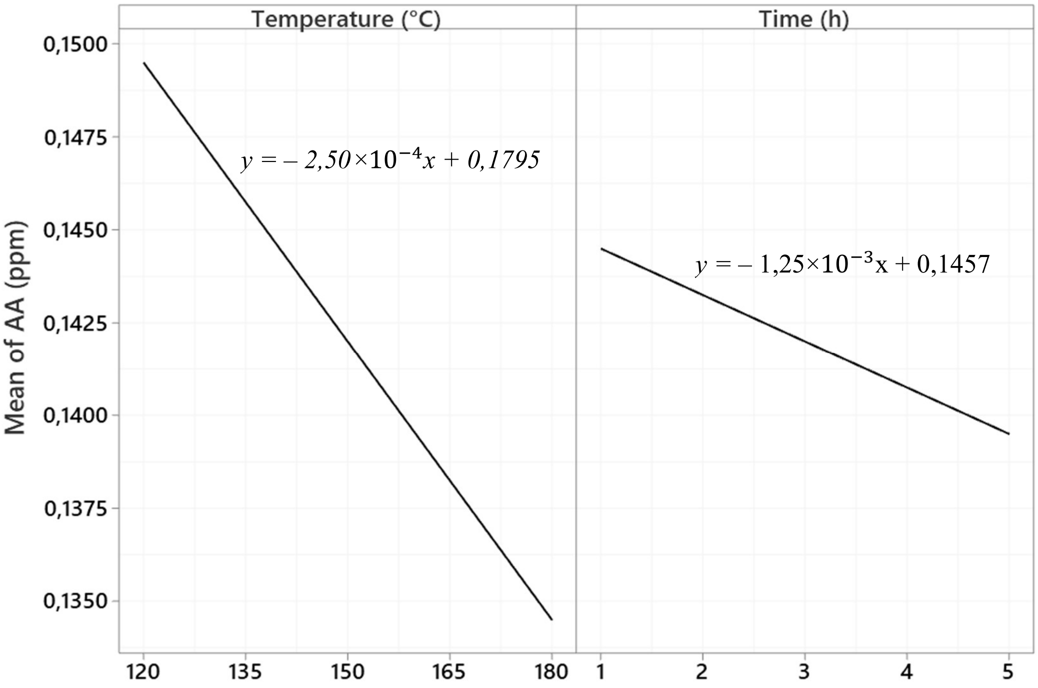


Figure 35 - Effect of temperature and time on acetaldehyde desorption with rPET1

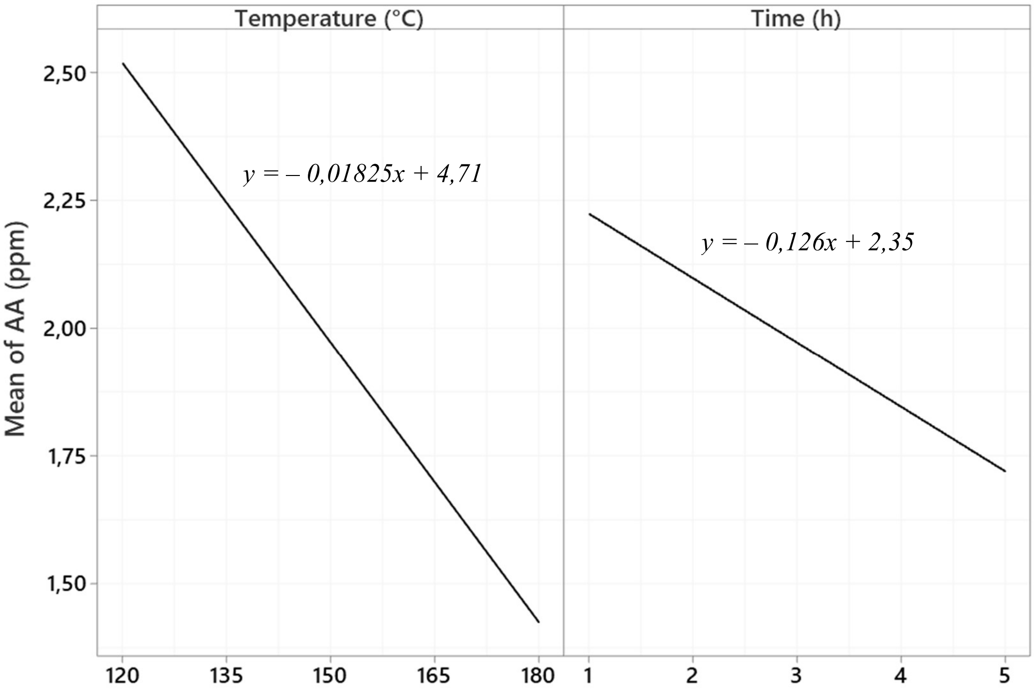


Figure 36 - Effect of temperature and time on acetaldehyde desorption with rPET2

The fitted means of the data collected show that temperature is the most significant factor on reducing AA content during drying in both materials. It is visible by comparing the slopes of each equation in each material.

4.1.2 AA generation in preforms

Figure 37 and 38 express the acetaldehyde levels before injection process, achieved with drying and the generated value after injection.

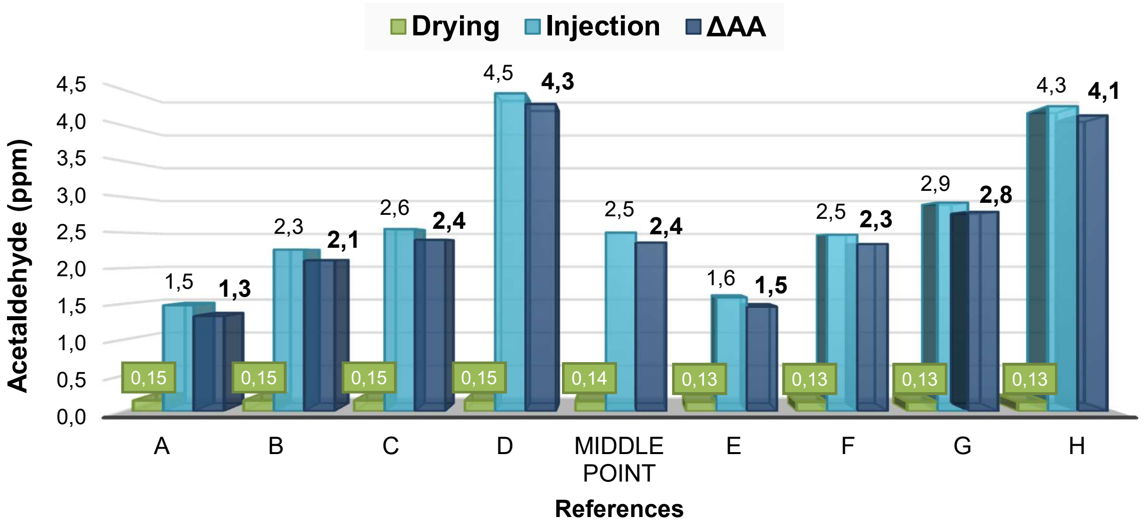


Figure 37 - Acetaldehyde levels in rPET1 before and after injection, with generated content

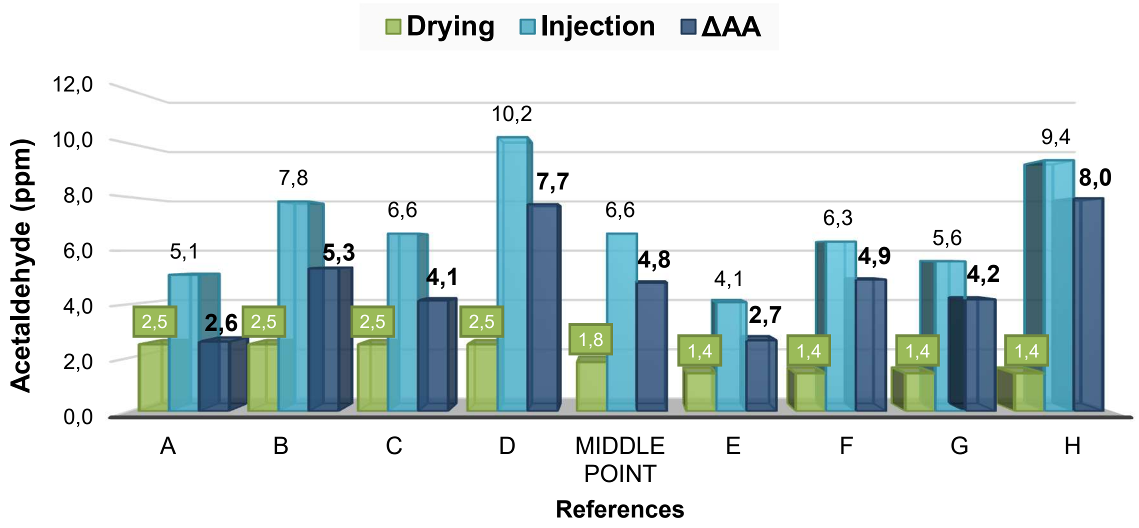


Figure 38 - Acetaldehyde levels in rPET2 before and after injection, with generated content

The first important observation that can be made from this plot is that for every rise in temperature, the AA generation rate nearly doubles. Secondly, the effect of barrel temperature on AA generation is far greater than the effect of residence time.

By plotting this results in Minitab, two regression equations can be obtained for the AA regeneration phenomena.

rPET1

$$\Delta AA\ (ppm) = 21{,}4 - 0{,}0130\alpha - 0{,}96\beta - 0{,}11\gamma - 1{,}084\delta - 0{,}0083\alpha\beta + 2{,}33\times10^{-4}\alpha\gamma - 4{,}00\times10^{-4}\alpha\delta + 8{,}63\times10^{-3}\beta\gamma - 7{,}50\times10^{-4}\beta\delta + 0{,}00462\gamma\delta \quad (6)$$

rPET2

$$\Delta AA\ (ppm) = 7{,}80 - 0{,}002\alpha + 1{,}63\beta + 0{,}0026\gamma - 1{,}999\delta + 0{,}0128\alpha\beta - 2{,}25\times10^{-4}\alpha\gamma + 8{,}72\times10^{-4}\alpha\delta - 0{,}01462\beta\gamma + 0{,}0334\beta\delta + 0{,}00743\gamma\delta \quad (7)$$

where α: drying temperature (°C); β: drying time (h); γ: barrel temperature (ºC); δ: residence time (s)

These equations are the fitting mathematical formulas to a response surface design of the generation of AA in preforms with 100% of two types of rPET content. These equations can be used to predict the generated AA in the preforms containing 100% of rPET 1 or 2, by specifying any drying and injection condition above, as long as the repeatability of the process is respected. Preform weight, machine and dryer should be kept, as well as the remaining drying and injection conditions, e.g. air flow, nozzle temperature, equal temperature profile for all the zones in the extruder barrel, etc.

In order to evaluate more clearly this generation phenomena of AA, contour plots depicted from figure 39 and 40 were created.

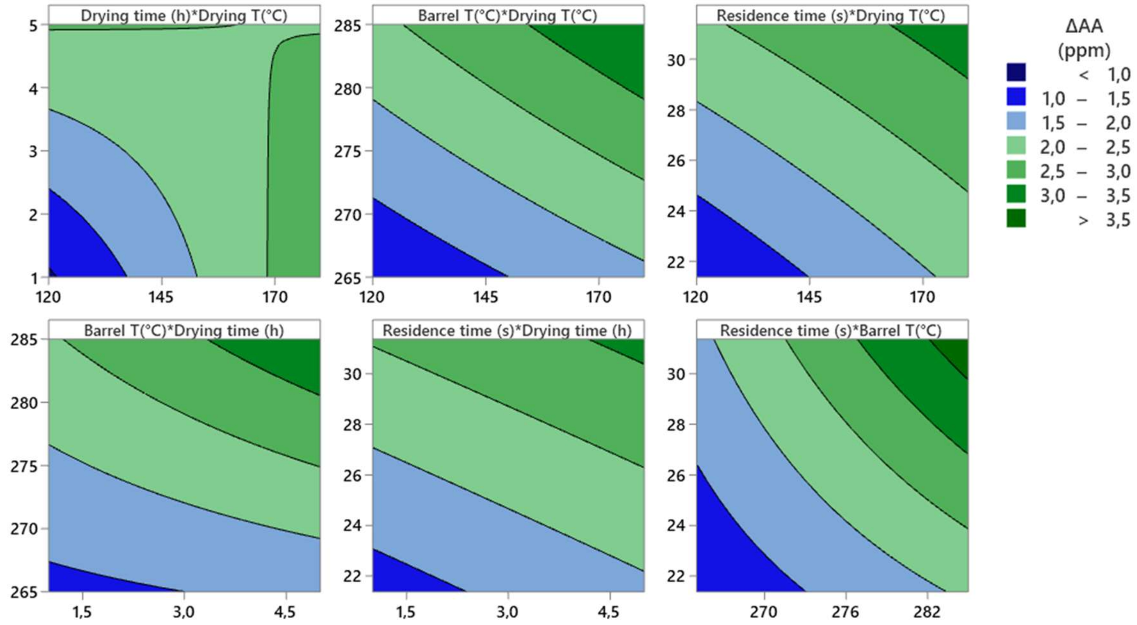


Figure 39 – rPET1 contour plots of acetaldehyde generated values in function of the drying and injection conditions

The lower acetaldehyde levels can be found in the references where the resin was dried under very mild conditions. This indicates that if a considerable level of moisture content it's present within the PET's matrix, the lower will be the generated AA in the preforms.

By increasing time and temperature during the processing, an increase in AA will follow.

It can be observed by the shape of the curves that the drying conditions are not as prominent as the injection ones. Drying is very important to volatize acetaldehyde but minimizing time and temperature of PET material inside the extruder barrel is the crucial to achieve the lowest AA generation rates.

The same can be observed for rPET2. The curves of drying temperature in function of both barrel temperature and residence time are almost horizontal, indicating that the temperature at which rPET2 is dried barely influences the generated AA value during injection.

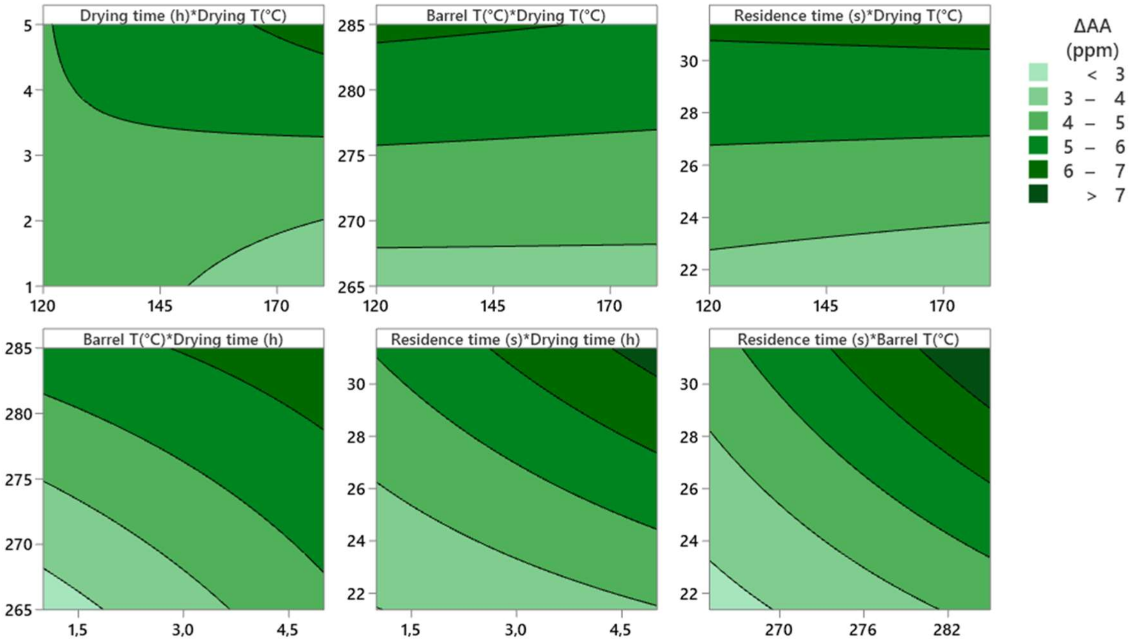


Figure 40 – rPET2 contour plots of acetaldehyde generated values in function of the drying and injection conditions

Drying process and moisture content are essential to reduce acetaldehyde levels in PET. A deeper study was conducted to analyse the influence of moisture levels in AA generation rates.

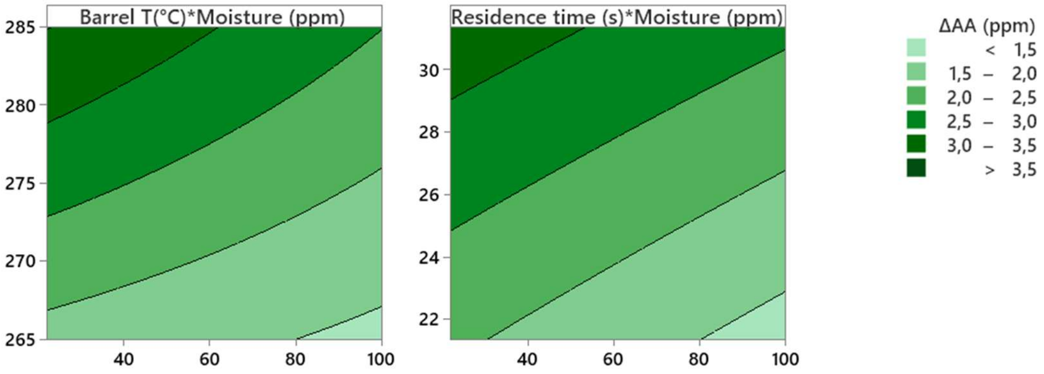


Figure 41 - Influence of moisture content in AA generation of preforms containing 100% of rPET1

Moisture indeed helps reducing the acetaldehyde content that it is generated during injection moulding. Above 60 ppm of moisture it is possible to increase both barrel temperature and residence time in 5°C and 2 seconds that the generated AA will remain in the same range of values – 1,5 to 2,0 ppm. From a point of view of processing savings and cycle optimization, it is a very valuable reduction that can be performed.

From figure 42 the shapes of the curves are much smoother, indicating a much prominent effect in reduction of the generated AA with elevated levels of moisture.

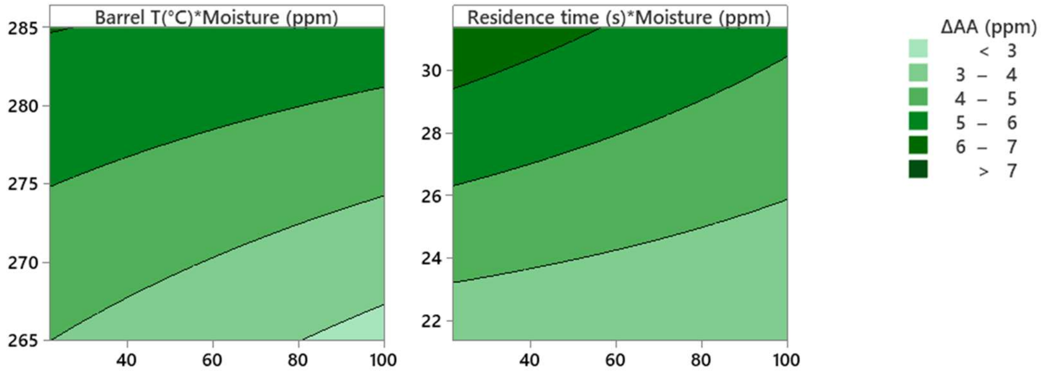


Figure 42 - Influence of moisture content in AA generation of preforms containing 100% of rPET2

In fact, almost 10°C and 4 seconds can be raised up that AA levels will not significantly change, as long as the resin contains a high level of moisture.

As it could be attained from figure 25 in section 2.4.3., the viscous polymer melt is also heated by friction within the barrel, the screw and the distribution channels. When a high level of moisture is present, the water molecules will act as a plasticizer [83], decreasing the resistance that the melt offers to flow and, therefore, reducing shear stress. Consequently, the generated AA values decrease with increasing moisture content, achieved by drying the rPET pellets very softly.

4.2 Intrinsic viscosity drop

Hydrolysis and thermal degradation are the most noticeable mechanisms that destroy the macromolecular chains of PET when its melt processed. As explained, it is the IV that renders the material for a specific application and anything that may deteriorate this property should be monitored and minimized. The failing in the intrinsic viscosity – IV drop – always occurs in a certain level. Moisture should be avoid, as well as the time that the material spends in its melt state. Temperature also provides a big role.

With the software utilized it is possible to analyse the results from a Pareto chart point of view. In this case, the Pareto determines the magnitude and the importance of the parameters used for the screening – moisture, barrel temperature and residence time, shown in figure 43 and 44.

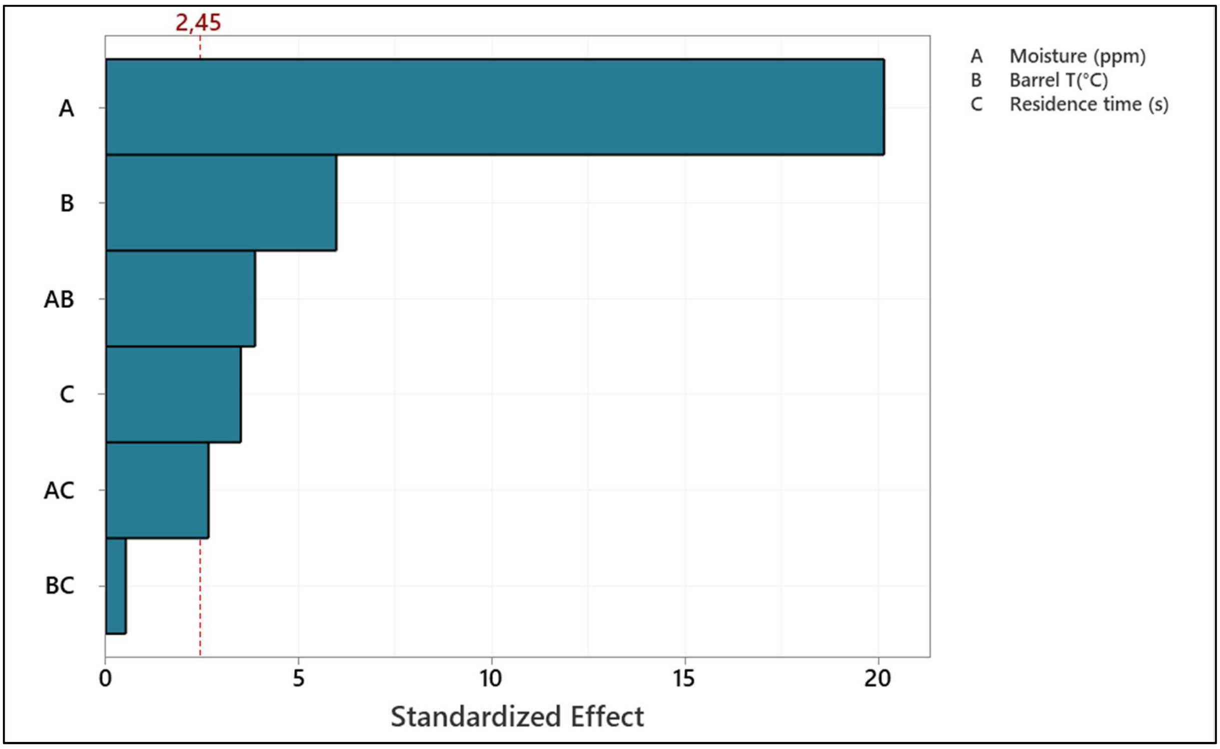


Figure 43 - Pareto chart of rPET1

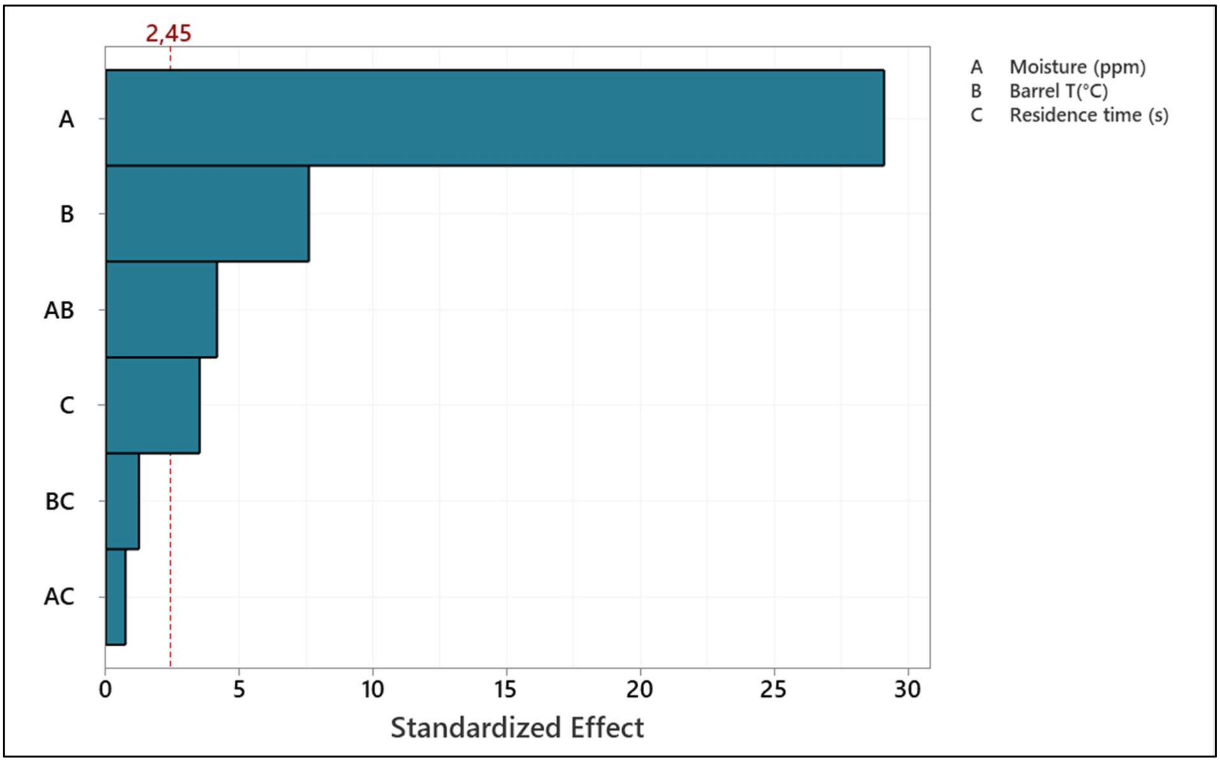


Figure 44 - Pareto chart of rPET2

The bars that cross the reference line (2,45) are statistically significant and have an influence and impact in the response, where in this case, IV drop. As expected, moisture pays the most significant role in destroying the intrinsic viscosity, followed by barrel temperature, in both materials.

In the case of rPET1, even a combination of moisture and barrel temperature (AB), and moisture and residence time (AC) has an influence in this property.

Residence time has the less significant effect in the IV drop.

Table 11 summarizes the IV drop values for all references in both materials

Table 11 – IV drop values in rPET1 and rPET2

	References	Drying T(°C)	Drying time (h)	Barrel T(°C)	Residence time (s)	**rPET1** IV drop (dL/g)	**rPET2** IV drop (dL/g)
	A	120	5	265	21,37	0,064	0,080
	B	120	5	265	31,37	0,077	0,085
	C	120	5	285	21,37	0,087	0,092
	D	120	5	285	31,37	0,099	0,101
	Middle point	150	4	275	26,37	0,062	0,062
	E	180	3	265	21,37	0,051	0,058
	F	180	3	265	31,37	0,049	0,070
	G	180	3	285	21,37	0,054	0,070
	H	180	3	285	31,37	0,059	0,072
100 ppm of moisture	Extra 1	150	1	265	21,37	0,126	0,123
	Extra 2	150	1	265	31,37	0,154	0,140
	Extra 3	150	1	285	21,37	0,173	0,160
	Extra 4	150	1	285	31,37	0,210	0,165

The rPET2, produced under the same conditions, suffers a higher degradation in the IV than rPET1. Although, for the references with a high level of moisture, the opposite behaviour can be attained. This means that rPET2 has a higher resistance to hydrolysis that rPET1.

The lower IV drop value for rPET1 was achieved in reference F, under an aggressive drying procedure, lower barrel temperature and high residence time. This can be explained by measurement accuracy, since 0,051 and 0,049 dL/g are very close values.

In the case of rPET2, the lower value is achieve in samples dried to a very low moisture content and injected under the mildest conditions. This material follows the expected behaviour.

4.3 Colour

4.3.1 Colour analysis of resin and preforms

Part of PET’s appeal to the food and beverage industry is the combination of its excellent clarity and lack of colour. This makes studying colour generation in PET a vital step.

All of the data from the colour measurements, for both materials, resin and preform samples, are shown in figure 45 and table 12, in terms of the b value that measures the yellowing of PET.

The contour plot in the right shows the results for rPET1, while the one on the left shows the results for rPET2.

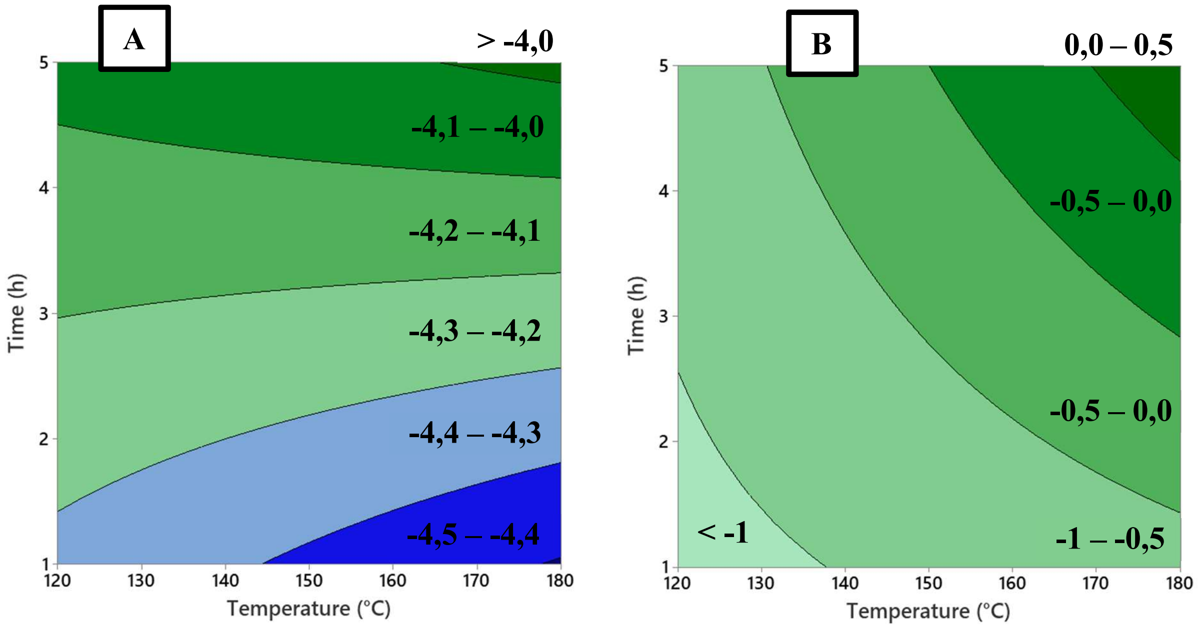


Figure 45 - Drying DOE: contour plots of b value for rPET1 (A) and rPET2 (B)

Regarding rPET1 resin, the results are inconclusive. This could be explained by a very small range of values from the apparatus, where it is difficult and not recommendable to draw conclusions.

Although, rPET2 follows the expected behaviour. Longer the time that the material spends inside the drier, an oxidation phenomena of the pellets may occur. Therefore, the pellets start to suffer from over-drying and show some yellowness.

Drying rPET2 at 180°C for 5 hours transforms an initial b value of -0,76 into ≈ 0,5. Even though, an increase of 1 does not translates itself into a visible colour degradation. In fact there was no yellowing of the resin detected by the naked eye.

From the injection DOE, colour degradation, namely yellowing of rPET preforms, increases with increasing barrel temperature and residence time. Barrel temperature has the most detrimental effect and impact in colour. Table 12 shows the b values of both materials.

Table 12 - Injection DOE: b value results for both rPET materials

	References	Drying T(°C)	Drying time (h)	Barrel T(°C)	Residence time (s)	**rPET1** b value	**rPET2** b value
	A	120	5	265	21,37	9,94	11,87
	B	120	5	265	31,37	10,57	12,12
	C	120	5	285	21,37	10,62	12,08
	D	120	5	285	31,37	11,04	12,64
	Middle point	150	4	275	26,37	10,64	12,22
	E	180	3	265	21,37	10,73	12,81
	F	180	3	265	31,37	10,95	13,58
	G	180	3	285	21,37	11,52	13,76
	H	180	3	285	31,37	11,9	14,57
100 ppm of moisture	Extra 1	150	1	265	21,37	9,58	10,25
	Extra 2	150	1	265	31,37	10,48	10,15
	Extra 3	150	1	285	21,37	10,3	10,32
	Extra 4	150	1	285	31,37	10,76	11,08

The highest indication of a yellow preform is obtained in reference H in both materials, as expected. Results from the references of the extra exercise show a significant influence of moisture reducing the yellowing of PET when it's processed through any condition.

4.3.2 Colour analysis of preforms with a high level of moisture

To quantify how much degradation in colour during processing with a high moisture level present within the matrix of PET, the b values of each sample were established in the following contour plots of figures 46 and 47.

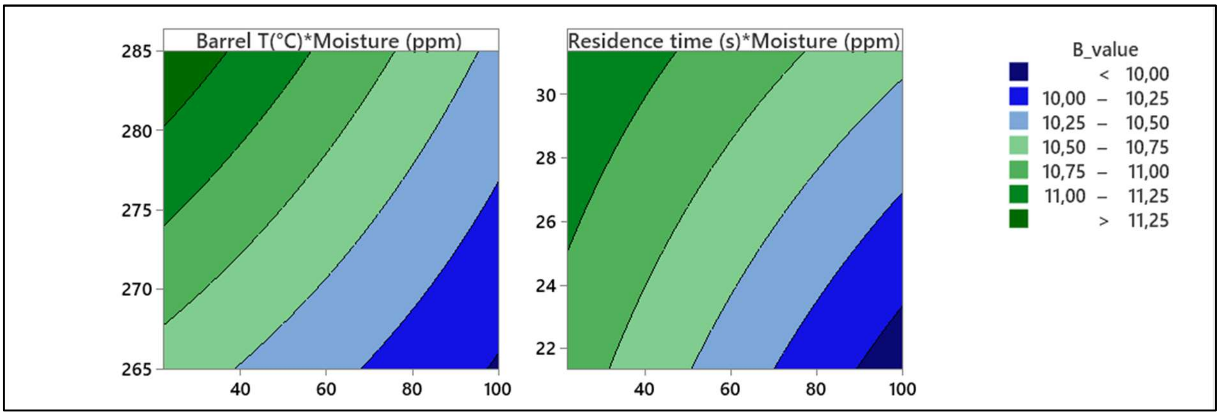


Figure 46 - rPET1 contour plots of (b) value in function of moisture vs. injection conditions

Moisture indeed helps reducing the yellowing of the material, and consequently, the b value of rPET1 decreases with increasing moisture content. The same can be attained for rPET2.

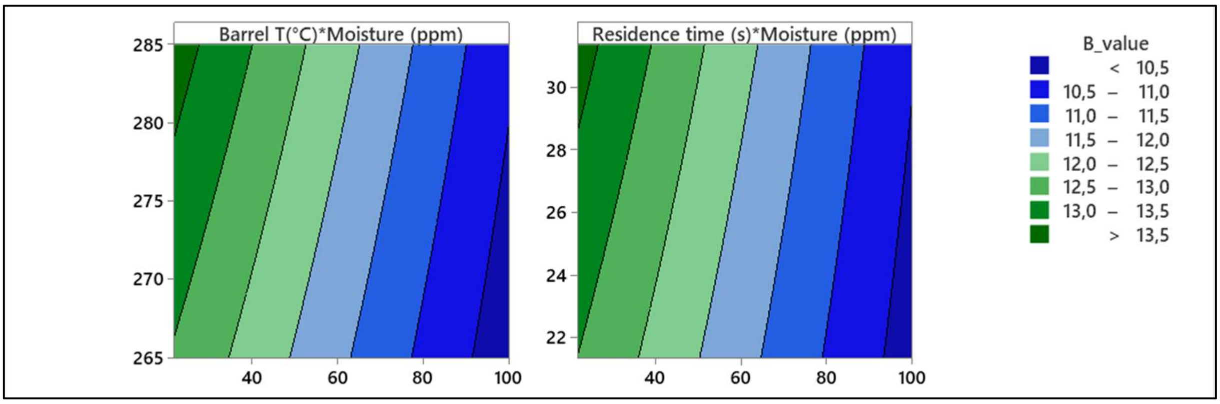


Figure 47 – rPET2 contour plots of (b) value in function of moisture vs. injection conditions

In fact, the curves are almost vertical, indicating that, as long as a high moisture content is present (above 80 ppm), barrel temperature and residence time can be raised until their maximum that there is barely no influence in colour degradation.

4.4 Modeling

4.4.1 Model optimization to minimize AA generation, IV drop and colour degradation

From the previous references and data collection, a statistical model based on a response surface design was built in order to achieve the optimal conditions for drying and injection moulding of recycled PET material, provided by two different recycling technologies, that minimizes the generation of acetaldehyde, the drop in the intrinsic viscosity and the impact of the drying and processing in the colour of the preforms.

The solution given is shown in table 13.

Table 13 - Optimized solution that minimizes AA, IV drop and colour degradation, obtained from the built statistical model

	Drying T(°C)	Drying time (h)	Barrel T(°C)	Residence time (s)
rPET1	180	5	265	21,37
rPET2	165	5	283	21,37

As it could be attained from the previous results, in order to minimize simultaneously AA generation, IV drop and colour degradation, a compromise must be found. The results from the software exposed in table 13 are obtained with a 95% of significance level and correspond to a compromise between the behaviour of each response and what it takes to minimize all of them, with the same pondered weight.

The next step of this work was conducted in order to check if the solution provided above was in fact worse, better or even close to the reality of the Company's current drying and injection parameters. The lowest values achieved for AA, IVdrop and colour were set-up as targets and the data collected is shown in table 14.

Table 14 – Final comparative results between the samples produced under the optimal given conditions and the Company's current processing conditions

	Reference	Injection conditions	Drying conditions	**Response**		
				AA (ppm)	IV_{drop} (dL/g)	ΔE
			Target	**1,04**	**0,049**	**< 3**
rPET1	**(A) realistic**	Temperature profile (°C): 270/272/275/278/280 Residence time (s): 21,04	100°C overnight 160°C before injection 100°C during injection	2,35	0,095	1,12
	(B) optimal	Temperature profile (°C): 265/265/265/265/265 Residence time (s): 21,4	180°C for 5h 100°C during injection	2,06	0,053	
			Target	**2,00**	**0,058**	**< 3**
rPET2	**(C) realistic**	Temperature profile (°C): 270/272/275/278/280 Residence time (s): 21,03	100°C overnight 160°C before injection 100°C during injection	5,40	0,104	1,39
	(D) optimal	Temperature profile (°C): 283/283/283/283/283 Residence time (s): 21,4	165°C for 5h 100°C during injection	6,67	0,104	

Samples from references A and C were produced under the normal drying and injection conditions currently used in the Company by the process engineers.

It is important to enhance the fact that the targets consider the minimal value that it is possible to achieve individually each response. As explained, the solution given is a compromise that minimizes all the responses with the same weight.

AA generated and IV drop values of rPET1 were not only very close to the targets but also lower than the realistic conditions normally used internally, with no impact in colour. This reflects a good selection and approach of the optimal conditions given by the model.

On the other hand, with rPET2, these values were far from the targets, but there was no impact in colour degradation when the optimal conditions are used. This results rely on the need of repeating the procedure with rPET2 to increase the accuracy of those values.

Another extra study focusing on the drop in the intrinsic viscosity was conducted, externally to DOE procedures. In this particular case, in each injection exercise with rPET1, the inlet temperature, i.e, the temperature of the pellets at the feeding area, before entering the extruder barrel, was kept at the settled drying temperature, as described in table 15.

Table 15 - Final results of the extra intrinsic viscosity drop exercise

	Reference	Injection conditions	Drying conditions	**IV_{drop} (dL/g)**
rPET1	**(A) realistic**	Temperature profile (°C): 270/272/275/278/280 Residence time (s): 21,04	100°C overnight 160°C before injection 100°C during injection	0,095
	Inlet realistic	Temperature profile (°C): 270/272/275/278/280 Residence time (s): 21,04	Dryer temperature kept at 160°C during whole injection exercise	0,056
	(B) optimal	Temperature profile (°C): 265/265/265/265/265 Residence time (s): 21,4	180°C for 5h 100°C during injection	0,053
	Inlet optimal	Temperature profile (°C): 265/265/265/265/265 Residence time (s): 21,04	Dryer temperature kept at 180°C during whole injection exercise	0,038

A significant and important result was achieved. With the optimal conditions given by the statistical model and by keeping the inlet temperature at the temperature in which the material is dried, the preforms produced with rPET1 suffer the minimal IV drop.

The resin is normally kept at 100°C during the injection moulding to preserve and prevent the over-drying of the material. Although, from a thermal and mechanical thermoplastic behaviour point of view, and considering that the material enters the barrel, gets plasticized and by the time it is ready to be injected into the mould cavity, it goes through just a few seconds (even less than the whole cycle time) to make PET resin going from a temperature of 100°C to 265°C. With the inlet optimal injection and drying conditions, the material goes from 180°C to 265°C, resulting in a less thermomechanical shock, a lower shear-heating phenomena because the material is at a higher temperature and, therefore, a lower IV drop value.

This could open a field of possibilities to improve the preservation of PET's intrinsic viscosity.

5. CONCLUSIONS

In the present work, the optimal design for a drying and injection moulding process has been developed using the DOEs procedure. All experiments were designed to be able to consider two-way interactions between various factors as well as main effects of individual factors.

The proposed approach has been applied to the drying and injection moulding process of resin and preforms containing 100% of two different recycled PET. The optimal drying and injection process conditions were determined by analysing the DOE results statistically. Then experiments were performed for those optimal conditions and the current conditions that are used in the Company.

As a result, acetaldehyde generation and the drop in the intrinsic viscosity of the materials were minimized with the optimal conditions built by the statistical model plotted by Minitab, with no visible impact in colour. Keeping the same resin inlet temperature as the set for the drying produces a huge improvement in preservation of PET's intrinsic viscosity.

It is thus concluded that the proposed approach can be successfully reflected in the design procedures of industrial injection moulding processes of Plastipak.

6. RECOMMENDATIONS

While this work provided a broad investigation toward understanding the overall effects of drying temperature and time, barrel temperature and residence time in AA generation, IV drop and colour impact in preforms containing 100% of recycled PET, further work should be conducted to expand upon this information and improve the fundamental understanding of this responses sequestering systems for PET. For this, 3 recommendations are proposed:

- Extending the study to the effect of more injection parameters such as backpressure and screw speed. This should provide a larger window for the screening DOEs and a minor error associated with the mathematical and statistical configurations of DOE methodology;

- Repeat the study with rPET2. The goal would be to improve upon the initial model and consequently advance the accuracy of its results relative to experimental data;

- Explore different temperature profiles instead of specifying the same temperature for the different zones of the extruder barrel.

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