



HAL
open science

Progress in Polyethylene Terephthalate Recycling

Adel Elamri, Khmais Zdiri, Omar Harzallah, Abdelaziz Lallam

► **To cite this version:**

Adel Elamri, Khmais Zdiri, Omar Harzallah, Abdelaziz Lallam. Progress in Polyethylene Terephthalate Recycling. Polyethylene Terephthalate: Uses, Properties and Degradation, Nova Science Publishers, 2017, 978-1-53611-991-6. hal-02953197

HAL Id: hal-02953197

<https://hal.science/hal-02953197>

Submitted on 29 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chapter

PROGRESS IN POLYETHYLENE TEREPHTHALATE RECYCLING

Adel Elamri¹, Khmais Zdiri¹, Omar Harzallah^{2,}
and Abdelaziz Lallam²*

¹Unité de Recherche Matériaux et Polymères Textiles,
Ecole Nationale d'Ingénieurs de Monastir, Monastir, Tunisie

²Laboratoire de Physique et Mécanique Textiles (EA 4365),
Université de Haute Alsace, Mulhouse, France

ABSTRACT

In the last decade, an increasing interest has been focused on the recycling of plastic wastes, especially on the polyethylene terephthalate (PET). PET polymer is already being recycled and numerous applications for recycled polyesters can be explored depending on the properties of the resin. However, the common problem faced during processing of recycled PET is degradation. Thus, many solutions have been proposed in literature to undermine this problem. This chapter presents a background of the current state of knowledge with respect to PET recycling. In the first section, a brief theoretical background is presented about virgin PET synthesis, thermal transitions, processing and applications. The second section deals with the PET recycling process with a focus on contaminations and ways to increase the molecular weight of recycled PET (RPET). It serves as an introduction to Section Three where our process to improve the RPET properties is described. Finally, Section Four covers the effect of blending virgin PET (VPET) with recycled PET on thermal and rheological behaviors.

Keywords: PET, recycling, blends, thermal and rheological

* Corresponding Author address: Email:omar.harzallah@uha.fr.

1. INTRODUCTION

The production of plastic materials in its various declinations comes mainly from petroleum. However, we know that the depletion of fossil resources is inevitable. The economy of the main material, in this case oil, becomes a goal in itself. This objective can be achieved both through the use of renewable materials, or recycling of materials, if operations are technically and economically feasible.

In this work, the treatment is focused on the technical aspect of thermomechanical recycling of PET waste from mineral water bottles. The thermomechanical recycling presents the advantage of being fast and cheap. In contrast, thermomechanical recycling leads to loss of important mechanical properties by thermal degradation mechanism. It is possible to overcome the loss of these properties, either by recycling under vacuum, which requires heavy and expensive equipment, or by the addition of virgin material to the primary material for recycling. In this chapter, it is the second procedure which is described.

2. VIRGIN PET

Virgin PET has come to be considered as one of the most important engineering polymers in the past two decades. It is regarded as an excellent material for many applications and is widely used for making liquid containers (bottles). It has excellent thermomechanical and chemical properties [1]. Many companies produce virgin PET giving it different trade names [2]. Some of the common trade names of commercially available PET are summarized in Table 1.

Table 1. Trade names of common PET and their manufacturer

Trade name	Manufacturer
Rynite	Du Pont de Nemours & Co.
Diolen	ENKA-Glazstoff
Eastapac	Eastman chemical company
Arnite	DSM Engineering Plastics
Mylar	E. I. Du Pont de Nemours & Co.
Melinex	Imperial Chemical Industries Ltd.

Commercial PET has a wide range of intrinsic viscosity $[\eta]$ that varies from 0.45 to 1.2 dL.g⁻¹ with a polydispersity index generally equal to 2. The PET repeating unit is shown in Figure 1.

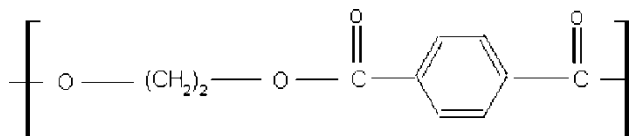


Figure 1. PET repeating unit.

2.1. PET Synthesis

PET production process involves two different starting reactions. The first starting reaction is an esterification reaction (Figure 2a) where terephthalic acid (TPA) reacts with ethylene glycol (EG) at a temperature between 240°C and 260°C and a pressure between 300 and 500 kPa. The second reaction is a trans-esterification reaction (Figure 2b) where dimethyl terephthalate (DMT) reacts with EG at 180 – 210°C and 100 kPa [3]. Trans-esterification is the much preferred process due to easier purification. The output of both these processes is bis(hydroxyethyl) terephthalate (BHET). The pre-polymerisation step follows, in which BHET is polymerised to a degree of polymerization (DP) of up to 30 (Figure 2c). Pre-polymerisation reactions conditions are 250–280°C and 2–3 kPa. The third stage is the polycondensation process where the DP is further increased to 100. The polycondensation process conditions are 280–290°C and 50–100 Pa.

Up to this stage, PET is suitable for applications that do not require high molecular weight (Mw) or intrinsic viscosity $[\eta]$ such as fibers and sheets. A solid state polymerization (SSP) step might be required when a high Mw PET is produced. SSP is used to increase the DP to 150, and also increasing Mw. SSP operating conditions are 200–240°C at 100 kPa and 5–25 h [4]. Bottle grade PET that has an $[\eta]$ of 0.7–0.85 dL.g⁻¹ is normally produced by SSP at 210°C for around 15–20 h [5-6]. Some virgin PET manufacturers have tended in recent years to produce PET co-polymer; such as isophthalic acid modified PET, rather than homopolymer PET. Bottles are then made from co-polymer PET because of its lower crystallinity, improved ductility, better process ability and better clarity [7].

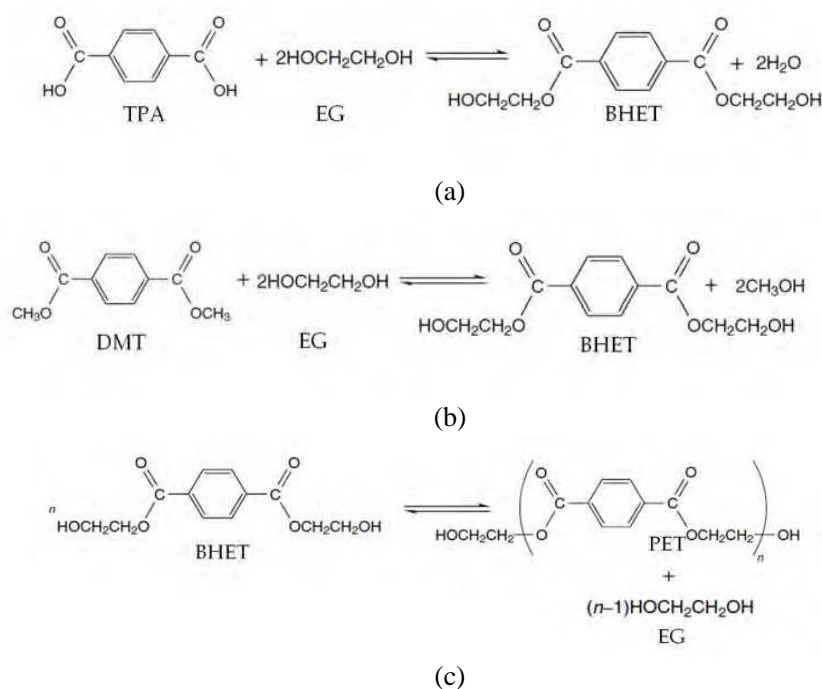


Figure 2. PET synthesis reactions (a) esterification of TPA with EG (b) trans-esterification of DMT with EG and (c) polymerization.

The PET chain is considered to be highly stiff above the glass transition temperature (T_g) unlike many other polymers. The low flexibility of the PET chain is a result of the nature of the short ethylene group and the presence of the p-phenylene group. This chain inflexibility significantly affects PET structure-related property. The standard physical and chemical properties of commercial PET are shown in Table 2.

Table 2. Physical and chemical properties of PET [8]

Property	Test method	Value (Unit)
Molecular weight (of repeating unit)	-	192 (g.mol ⁻¹)
Weight-average M_w	GPC	30,000 – 80,000 (g.mol ⁻¹)
Density	-	1.41 (g.cm ⁻³)
Glass transition temperature	DSC	69-115 (°C)
Melting Temperature	DSC	265 (°C)
Breaking strength	Tensile	50 (MPa)
Tensile strength (Young's modulus)	-	1700 (MPa)
Yield strain	Tensile	4 (%)
Water absorption (after 24h)	-	0.5 (%)

2.2. PET Applications

PET is used broadly in products such as bottles, electrical and electronic instruments, in different sectors of automotive industry, housewares, lighting products, power tools and material handling equipment. PET films and fibers are the oldest applications of PET. Films are produced by biaxial orientation through heat and drawing. PET films are used in photographic applications, x-ray sheets and in food packaging. PET films are also reported to be used in electrical and dielectrics applications due to the severe restriction of the electric dipole orientation at room temperature that is well below the transition temperature [9].

Table 3. Intrinsic viscosity of PET depending on its application [11]

	PET	$[\eta]$ (dL.g ⁻¹)
Fibers	Textiles	0.40 – 0.70
	Techniques	0.72 – 0.98
	bi-oriented	0.60 – 0.70
	Thermoforming	0.70 – 1.00
Bottles	for water	0.70 – 0.78
	for soft drinks	0.78 – 0.85

PET fibers are another important application of PET and are produced by forcing molten PET through small holes in a die. Fiber strength is achieved by applying tension to align the chains through uniaxial stretching. Bottle production requires the use of PET with high molecular weight. This is explained in part by the manufacturing process (bi-stretching, blow - extrusion), and by the need to obtain sufficient barrier properties for this application, often related to beverage packaging. PET chains with high molecular weight will allow a 'mesh' at

most ends of the chains after bi-stretching which will limit the diffusion of gaseous molecules from the outside to the content and vice versa [10].

Virgin PET is produced at different specifications because different applications require various properties. Examples of PET's $[\eta]$ with respect to the required application are shown in Table 3.

2.3. Thermal and Crystallization Behaviors

Commercial PET has a melting temperature (T_m) between 255 and 265°C and for more crystalline PET it is situated between 255 and 270°C [4]. The T_g of virgin PET varies between 67 and 140 C. The thermal transitions and crystallization of virgin PET with a focus on reversing crystallization and melting have been analyzed by several researchers [12, 13]. An interesting phenomenon was reported in which the virgin PET experiences multiple endothermic transitions during thermal analysis [14]. It was reported that this phenomenon is attributable to morphological and structural re-organization. As the temperature increases, better crystal structures are achieved because of the re-organization of the less perfect crystals.

Virgin PET is well known for having a very slow crystallization rate. The highest crystallization rate takes place between 170°C and 190°C. Cooling PET rapidly from the melt to a temperature below T_g can produce an amorphous, transparent PET. Semi-crystalline PET can be obtained by heating the solid amorphous PET to a temperature above T_g where 30% crystallinity can be achieved [15].

The rate of crystallization of virgin PET depends greatly on temperature and reaches its maximum at a temperature of 150–180°C. The rate of crystallization also depends on other factors such as M_w , the presence of nucleating agents, the degree of chain orientation, the nature of the polymerization catalyst used in the original production of PET and the thermal history.

3. RECYCLED PET

Due to its increasing consumption and non-biodegradability, PET waste disposal has created serious environmental and economic concerns. Thus, management of PET waste has become an important social issue. In view of the increasing environmental awareness in the society, recycling remains the most viable option for the treatment of waste PET. On the other hand, as the price of virgin PET remains stable, new and cheaper technologies for recycling PET give an added value to the PET recycling industry by providing industry with relatively cheaper PET.

Many researchers reported that in order to achieve successful PET recycling, PET flakes should meet certain minimum requirements [16, 17]. Examples of the minimum requirements for the post consumer PET (POSTC-PET) flakes are summarized in Table 4.

Table 4. Minimum requirements for POSTC-PET flakes to be reprocessed

Property	Value
Intrinsic viscosity [η]	>0.7 dL.g ⁻¹
Melting temperature T _m	>240 °C
Water content	<0.02 wt.%
Dye content	<10 ppm
Yellowing index	<20
Metal content	<3 ppm
PVC content	<50 ppm
Polyolefin content	<10 ppm

The major factor affecting the suitability of POSTC-PET flake for recycling is the level and nature of contaminants present in the flakes.

3.1. Recycled PET Contamination

Contamination of POSTC-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 quality of recycled PET. POSTC-PET is contaminated with many substances such as:

3.1.1. Acid Generating Contaminants

The most harmful acids to the POSTC-PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, rosin acid and abietic acid that are produced by adhesives and hydrochloric acid that is produced by PVC. The acids act as catalysts for the chain scission reactions during POSTC-PET melt processing [18]. Paci and La Mantia [19] investigated the influence of small amount of PVC during the melt processing of POSTC-PET. They reported that the presence of PVC (as little as 100 ppm) would increase POSTC-PET chain scission due to the catalytic effect of hydrogen chloride evolving during the degradation of PVC. The presence of PVC also results in discoloration of POSTC-PET during processing.

3.1.2. Water

Water reduces Mw during POSTC-PET recycling through a hydrolysis reaction. Moisture contamination should be below 0.02% to avoid the Mw reduction. Most water content comes from the flake washing process but can be reduced substantially by proper drying.

3.1.3. Coloring Contaminants

Fragments of colored bottles and printed ink labels cause undesirable colors during processing. Enhancement of sorting and washing processes in bottle recycling may reduce coloring contaminants.

3.1.4. Acetaldehyde

Acetaldehyde is present in virgin PET and POSTC-PET. It is a by-product of PET degradation reactions. The migration of acetaldehyde into food products from PET containers was a major concern in the early stages of developing the POSTC-PET recycling process. The high volatility of acetaldehyde means that it can be minimized by processing under vacuum or by drying. Stabilizers such as (4-aminobenzoic acid, diphenylamine and 4,5-dihydroxybenzoic acid) are added to PET in order to minimize the amount of the generated acetaldehyde [20].

3.1.5. Other Contaminants

The public use PET bottles for storing other substances such as detergents, fuel, pesticides, etc... The remains of these substances could be a health hazard if traces of these substances remain after POSTC-PET recycling [21]. The increase of people's awareness of the danger of such practices to public health has minimized the amount of these contaminants significantly.

3.2. Recycling Methods

PET recycling has been one of the most successful and widespread among polymer recycling. PET recycling methods can be categorized into three groups namely primary, secondary and tertiary recycling. There is also a so-called 'zero-order' recycling technique, which involves the direct reuse of a PET waste material [22].

3.2.1. Zero-order Recycling

This technique consists in washing of PET bottles in hot water with detergents following the similar procedure of that practiced for glass bottles. The collected bottles are first subjected to hot washing with detergents and then to a control by sensors that detect and eject bottles containing volatile or liquid pollutants. The main disadvantage of this method is that it does not allow to effectively eliminate any contaminants absorbed by the PET [23].

3.2.2. Primary Recycling

Primary recycling, also known as mechanical recycling, was applied for the first time in the 1970s. It involves separating the polymer from its contaminants and reprocessing it to granules via mechanical means. Mechanical recycling steps include sorting and separation of wastes, removal of contaminants, reduction of size by crushing and grinding, extrusion by heat, and reforming. The more complex and contaminated the waste is, the more difficult it is to recycle mechanically. Among the main drawbacks of primary recycling are the heterogeneity of the solid waste, and the degradation of the product properties each time it is recycled. Mechanical recycling of PET includes 4 phases (Figure 3).

3.2.3. Secondary Recycling

Secondary recycling, more commonly known as chemical recycling, involves the transformation of the PET polymer chain. Usually by means of solvolytic chain cleavage, this process can either be a total depolymerization back to its monomers or a partial depolymerization to its oligomers and other industrial chemicals. Since PET is a polyester

with functional ester groups, it can be cleaved by some reagents such as water, alcohols, acids, glycols, and amines. Also, PET is formed through a reversible polycondensation reaction, so it can be transformed back to its monomer or oligomer units by pushing the reaction to the opposite direction through the addition of a condensation product. These low molecular products can then be purified and reused as raw materials to produce high quality chemical products [24].

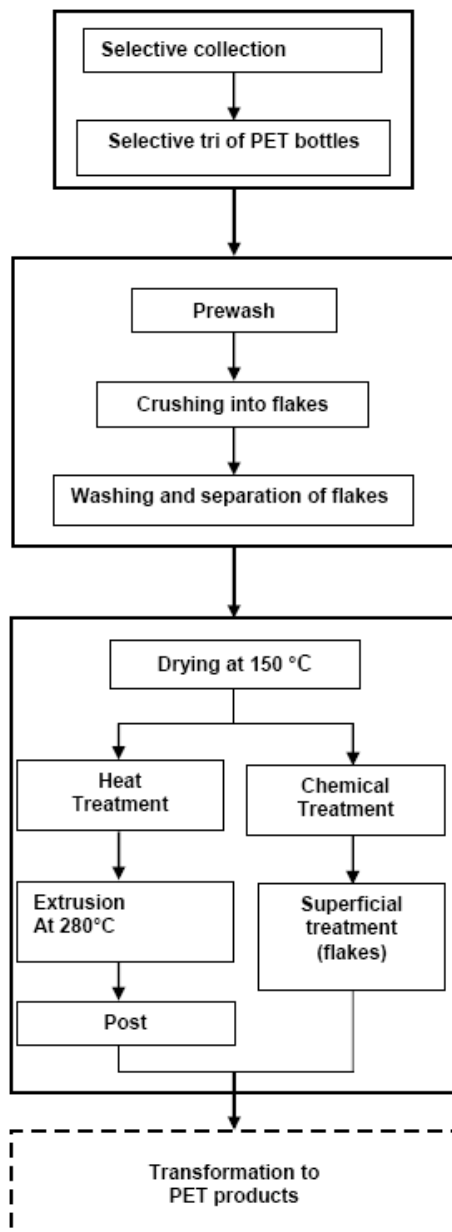


Figure 3. Phases of mechanical recycling of PET bottles.

Among the recycling methods, chemical recycling is the most established and the only one acceptable according to the principles of ‘sustainable development’, defined as development that meets the needs of the present generation without compromising the ability of future generations to meet their needs, because it leads to the formation of the raw materials (monomers) from which the polymer is originally made [25].

As shown in Figure 4, there are three main methods in PET chemical recycling depending on the added hydroxyl bearing molecule: glycol for glycolysis, methanol for methanolysis, and water for hydrolysis. Other methods include aminolysis and ammonolysis. Over the past five decades, since the start of PET chemical recycling research numerous researches have been done in order to fully understand the chemical pathways of the depolymerization methods, and improve desired products yield from these methods.

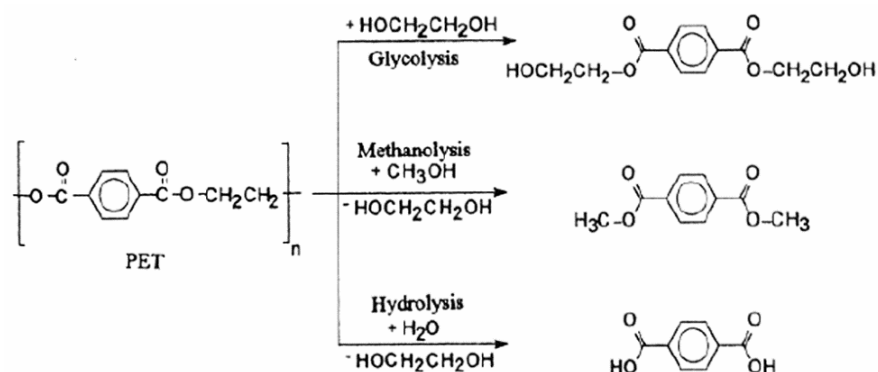


Figure 4. Different solvolysis methods for PET chemical recycling.

3.2.4. Tertiary Recycling

Tertiary recycling represents the recovery of energy content from the plastic waste by incineration. When the collection, sorting and separation of plastics waste are difficult or economically not viable, or the waste is toxic and hazardous to handle, the best waste management option is incineration to recover the chemical energy stored in plastics waste in the form of thermal energy. However, it is thought to be ecologically unacceptable due to potential health risks from the airborne toxic substances.

3.3. Increasing PET Intrinsic Viscosity

During the melt processing of recycled PET at high temperatures, R-PET undergoes a series of thermal and hydrolytic degradation reactions in the presence of water and contaminants, such as adhesives, poly(vinyl chloride) (PVC), etc... This leads to the decrease in intrinsic viscosity (η) by formation of low molecular mass PET with a significant increase of carboxyl and hydroxyl end groups. Oligomers and volatile compounds are produced during PET processing above its melting temperature, which contribute to the depression of Mw [26]. Scheirs [7] reported that cyclic and linear oligomeric compounds are formed during the reprocessing of PET as a result of thermal degradation reactions. He also showed that the oligomers content increased from 0.9 wt.% in virgin PET to 1.8–3.0 wt.% in R-PET. These

products also serve as a catalyst to increase the rate of degradation reactions. Furthermore, as some of the degradation products have carboxyl ends, this increases the overall PET carboxyl content which leads to a decrease in PET thermal stability.

Overcoming the reduction of R-PET's Mw or $[\eta]$ has been the objective of many investigations [27, 28]. Different methods and processes have been reported over the past two decades to restore or maintain R-PET properties during processing, which are outlined below.

3.3.1. Reprocessing Under Vacuum

The most recent PET recycling units are equipped with vacuum systems. All volatile substances present or produced while processing, including water vapor, are removed constantly during processing. Volatile components further promote the degradation reactions and the removal of the volatile compounds during processing has recently been regarded as essential. Currently, intensive drying to remove moisture, as well as vacuum degassing processing, is introduced in plastic recycling systems to minimize the effect of degradation reactions, resulting in higher R-PET intrinsic viscosity in comparison with normally extruded POSTC-PET.

3.3.2. Stabilizers

PET processing stabilizers mainly have the function of reducing the effect of PVC contamination and are also associated with thermal stabilization. The majority of the PET process stabilizers are metal based such as butyl tin mercaptide, antimony mercaptide and lead phthalate. Adding organic phosphate to PET during re-processing helps to stabilize it by decomposing hydroperoxide groups to non-radical products. Scheirs [7] reported that bis(2,4,di-tertbutylphenyl) pentaerythritol diphosphite can prevent Mw loss, inhibit yellowing reactions and reduce the production of acetaldehyde. The major disadvantage of using stabilizers is the significant added cost to the PET recycling process.

3.3.3. Solid State Polymerization

The SSP is a process in which POSTC-PET is heated to above its Tg but below the Tm. Condensation reactions occur at a temperature range of between 200 and 240°C, which is lower than the melt processing temperature (280°C). Degradation reactions have little effect at the low temperature of processing leading to an increase in R-PET Mw. The SSP by-products are removed continuously by vacuum or by applying an inert gas stream [29].

Karayannidis et al. [30] investigated the use of SSP to increase the POSTC-PET's Mw. They investigated the effect of reaction temperature and time on the resulted PET $[\eta]$. They reported that modified PET is produced with improved Mn after solid stating at 230°C for 8 h. However, SSP is considered too slow and expensive to be applied on an industrial scale.

3.3.4. Chain Extension

PET or POSTC-PET chain extension is a process where a di- or poly-functional low Mw material is reacted with PET carboxyl and/or hydroxyl end groups to rejoin the broken chains that result from PET chain scissions during melt processing.

The mechanism of the PET chain extension reaction was introduced by Inata and Matsumura [31]. They suggested that for a 2,2'-bis(2-oxazoline) chain extender there are three types of reactions with PET:

- A blocking reaction where a molecule of chain extender reacts with one chain of PET.
- A coupling reaction where a molecule of chain extender joins two PET chains.
- No reaction where the chain extender molecule fail to react.

Chain extenders can be classified according to the PET functional end group that they react with. The chain extenders that react with carboxyl end groups are effective, in addition to the chain lengthening, by reducing the overall carboxyl content leading to high hydrolytic and thermal stability which in turn maintains Mw during melt processing [32]. The other type of chain extenders is hydroxyl-reactive chain extenders. They are more effective with low Mw PET produced by melt polycondensation because the hydroxyl content predominates over the carboxyl end groups. The hydroxyl-reactive chain extenders will increase $[\eta]$ rapidly when reacting with PET that is produced by melt polycondensation PET [33]. An example of hydroxyl reactive chain extenders are 2,2'-bis(3,1-benzoxazin-4-one). Many researchers reported disadvantages associated with operating with some chain extenders. Cardi et al. [34] reported that undesired side reactions could take place when using bis(2-oxazoline) (BO) to chain extend PET due to the sensitivity of the oxazolinic ring to acidic compounds. Structure of bis(2-oxazoline) is shown on Figure 5.

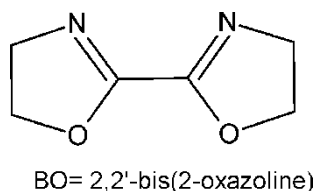


Figure 5. Chemical structure of BO chain extender.

Torres et al. [27] reported that diisocyanates are more effective chain extenders than BO and diepoxides; however, they reported product discoloration when using diisocyanates.

PMDA has previously been reported as an efficient chain extender or branching agent. It is thermally stable, produces no side products on reaction with PET, is tetra functional, commercially available and economical [35].

3.3.5. Reactive Extrusion Process

Reactive extrusion processes facilitate polymer modifications greatly in the sense of providing a modified polymer with better specifications for different applications. Reactive extrusion is basically achieved by using an extruder as a reactor. For the POSTC-PET modification process, reactive extrusion has been attractive because of its advantages of combining a reactor and an extruder in one system. Many researchers used reactive extrusion systems to modify POSTC-PET [36] in order to achieve better chemical and rheological properties. When applying POSTC-PET chain extensions in a reactive extrusion system, process parameters such as the twin-screw extruder performance and stability are closely monitored to ensure successful operation. Awaja et al. [37] investigated a reactive extrusion system with added chain extenders. They obtained lower carboxylic content using different types of chain extenders. For the POSTC-PET reactive extrusion processes, single or twin-screw extruders can be used. Single screw extruders have the advantage over twin-screw

extruders lower capital cost which is the reason why they are used widely in the extrusion industry. Twin-screw extruders are well known for their high mixing ability and are used mainly in compounding and reactive polymer processes.

As described in this section, several efforts have been made by researchers to overcome the problem of intrinsic viscosity loss of POSTC-PET when extruded. Nevertheless, the proposed techniques have two main disadvantages: the high cost of required chemical products and the complication of the process. Indeed, the application of these techniques on the industrial scale is both relatively difficult and costly.

4. ENHANCEMENT OF RECYCLED PET PROPERTIES

Using recycled polymer blends with virgin polymer of the same nature is a common solution for upgrading post-consumer materials. Scarfato and La Mantia [38], have studied blends of recycled PA6 and virgin PA. They found that the blends prepared in specific conditions show rheological and mechanical properties close to those of the virgin polymer. Kukaleva et al. [39], investigated blends of recycled and virgin HDPE polymers. They stated that mechanical properties (modulus and elongation) of the blends have predictable linear behavior. Earlier Wenguang [40], prepared and characterised homopolymer blends of recycled/virgin PVC. He found that the properties of the blends are between those of the pure compounds.

In many cases it is proposed to use blends of recycled PET and virgin PET to maintain the properties of the recycled polymer sufficiently high during the transformation processes.

4.1. Raw Polymers

In this context, the authors of this chapter conducted experiments based on three types of polymers: two PET bottle waste polymers and a virgin one to obtain melt spun yarns. Chips of crushed and cleaned bottles, purchased from an industrial plastic waste collector, were used as the source for recovered PET materials. Recycled PET (PET-A) comes from blue post-consumer bottles and recycled PET (PET-B) arises from heterogeneous deposits of various colored bottles (white, green, etc...). A fiber grade PET (PET-C) was used as the virgin PET resin. The characteristics of these three starting polymers are recapitulated in Table 5:

Table 5. Intrinsic Viscosity, molecular weight and MFI of the three PET polymers

	$[\eta]$ (dL.g ⁻¹)	M_w (g.mol ⁻¹)	M_n (g.mol ⁻¹)	MWD (M_w/M_n)	MFI (g.10')
PET-A	0,67	35500	17700	2,03	26
PET-B	0,63	32300	16100	2,01	30
PET-C	0,74	42100	20200	2,1	20

4.2. Melt Processing

The moisture content of PET should not exceed 0.005%. So, recycled chips and virgin pellets were dried under vacuum during 12H at 90°C in order to eliminate the residual moisture. Then, blends of virgin/recycled PET (PETV/R) were obtained using a Haake-Rheocard twin screw extruder under the following conditions: die temperature 270°C, extrusion speed 40 rpm and residence time of 5mn. The extrudate is cooled in water then passed through a pelletizing unit. We considered the following compositions of blends: 90/10, 70/30, 50/50 and 25/75 (PETV/ PETR w/w).

4.3. Methods of Analysis

Solution viscosity measurements were carried out on a Scött Gerate viscosimeter equipped with Ubbelohde capillary in a solution of phenol and 1,1,2,2-tetrachloroethane (60/40 w/w %) at 25°C. the intrinsic viscosity, $[\eta]$, of polymers was extrapolated using the Huggins equation. The average molecular weights, M_w and M_n , were then computed from the values of $[\eta]$ according to the following relations, Berkowitz [41] and Kokkalas [42]:

$$\bar{M}_w = 6,58.10^4 [\eta]^{1,54} \quad \text{Eq. 1}$$

$$\bar{M}_n = 3,29.10^4 [\eta]^{1,54} \quad \text{Eq. 2}$$

A TA Instruments calorimeter was used to obtain thermograms of virgin, recycled and blended PET polymers. The swept temperature lies between 30 and 280°C under nitrogen atmosphere and an empty capsule as reference. The calorimeter is attached to a thermal analysis data station that calculates glass transition temperature T_g , crystallisation temperature T_c , melting temperature T_m , enthalpy of crystallisation ΔH_c , enthalpy of melting ΔH_m of samples. The percent of crystallinity, χ_c , for all PET samples was calculated from equation 3 whenever a crystallisation exotherm was present during heating:

$$\chi_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} * 100 \quad \text{Eq. 3}$$

where $\Delta H_m^0 = 32,5 \text{ cal/g}$, is the heat of fusion of a 100% crystalline PET [43].

Dynamic and steady shear rheological measurements were carried out on a dynamic rheometer MCR500 from Physica. This operates at both controlled stress and strain modes. The rheological properties of molten materials were determined using parallel plate geometry: 25 mm diameter and a constant gap of 1 mm. Steady shear viscosity measurements were carried out in a shear rate range varying from 0,1 to 300 s^{-1} . For very higher shear rates the data obtained were inconsistent due to the fact that molten polymer ejected outside of measurement gap because of the important centrifuge force that develops at high rotation speed of superior plate.

For dynamic tests, the strain (γ) values are chosen in order to perform the frequency sweeps in the linear viscoelastic range (LVR) i.e., the limiting strain under which the rheological parameters (η^* , G' , G'' ...) remained constant. For this purpose, preliminary strain sweeps were made, at constant frequency (1 Hz) and temperature (270°C), and the LVR was determined for each polymer. The frequency range investigated was 0,1-100 Hz with a constant shear strain of 10% (within the LVR of polymers).

5. RECYCLED/VIRGIN PET BLENDS' BEHAVIOR

5.1. Thermal Analysis of PET-V/R Blends

DSC analysis of PET-V/R blend pellets was carried out following this experimental protocol:

- a heating step from 20 to 280°C at a rate of 10°C.mn⁻¹
- a thermal treatment at 280°C for 3 minutes
- a crystallization step from 280°C down to 20°C at 10°C.mn⁻¹.

The thermograms recorded during heating run of PET-C/A blends are reported on Figure 6:

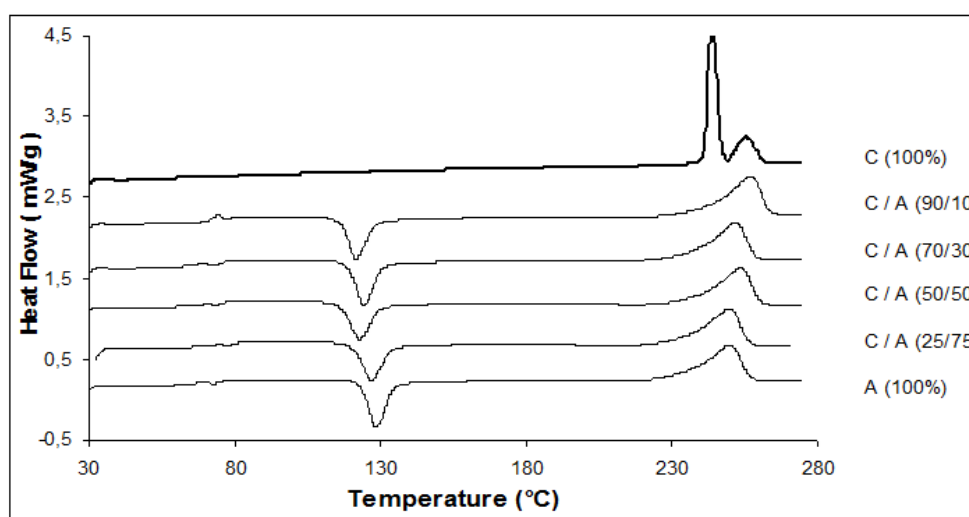


Figure 6. Thermal behavior during crystallization run of PET-C/A blends.

The same behavior was also observed for PET-C/B blends.

It can be deduced from PETV/R thermograms that:

- glass transition temperature (T_g) that remains almost constant for all the PET-V/R blends (between 83 and 84°C).

- an exothermic peak known as “cold crystallisation” [44], corresponding to the crystallisation of amorphous phase. This peak is typical for semicrystalline polymers such as PET or PEEK. The phenomenon of cold crystallisation is explainable. As the frozen chains are heated, a critical mobility for crystallisation is reached and the material organises with an exothermic process. From the Table 6, we observe that the values of the cold crystallisation temperature ($T_{cc, min}$) of our blends increase with increasing recycled PET content.
- an endothermic peak associated with the fusion of the whole crystalline structure. We can see on Figure 5 that the values of melting temperatures ($T_{m, max}$), that correspond to the maximum of the melting peak, of the PET-V/R blends decrease with the PETR concentration and are between those of the starting materials i.e., PETR and PETV. This absence of melting depression or synergy was explained by Fann et al. [45] by the fact that PET/PET blends are crystalline-crystalline isomorphous polymer blends of the same material (PET).

Table 6. Thermal characteristics of the PET-V/R blends

	T_g (°C)	$T_{m, max}$ (°C)	ΔH_m (J.g ⁻¹)	$T_{cc, min}$ (°C)	ΔH_{cc} (J.g ⁻¹)	χ (%)	$T_{c, min}$ (°C)	ΔH_c (J.g ⁻¹)
PET-C (100%)	83	255	55.8	-	0	41	199	36
PET-C/A (90/10)	83	257	39.5	121	26.1	10	211	44.6
PET-C/B (90/10)	83	257,5	38,7	119	23	11,5	212	44
PET-C/A (70/30)	84	255	38.1	124	27.1	8	213	42.9
PET-C/B (70/30)	84	254.5	35.7	122	21.2	10.6	213.5	45.1
PET-C/A (50/50)	84	253.5	40.6	125	25.5	11	213	44.3
PET-C/B (50/50)	84	253	38.2	124	22.1	12	214.5	43.9
PET-C/A (25/75)	84	252	37.5	129	23.8	10	212	43.6
PET-C/B (25/75)	84	255	44.5	127	20.7	17.5	217.5	44.1
PET-A (100%)	85	251	45.5	131	21	18	217	38.6
PET-B (100%)	85	254	44.3	129	22	16	218	37.8

DSC curves obtained from the cooling run of PET-V/R samples are plotted on Figure 7.

Contrary to other samples, PETC exhibits a rather broad temperature range of crystallisation starting at a lower temperature than other materials. However, recycled PET polymers (PETA and PETB) show higher crystallisation temperatures T_c ($\sim + 20^\circ\text{C}$) with a sharper and narrower temperature range of crystallisation than PETV. This is explainable by the lower molecular weight (M_w) of PETR polymers and the physical contaminations that they may contain that will act as nucleation agents for crystallisation kinetics.

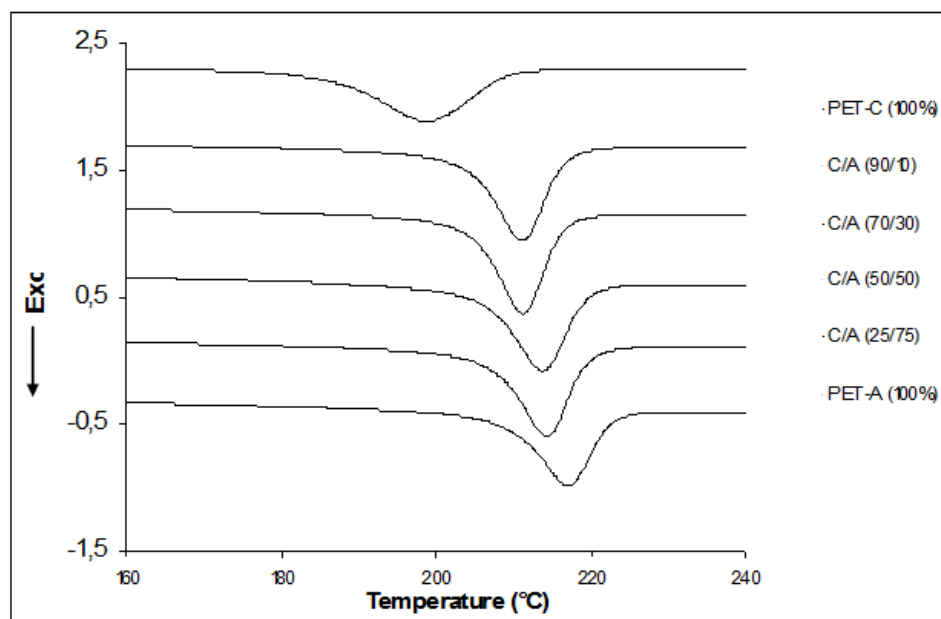


Figure 7. Thermal behavior during crystallization run of PET-C/B blends.

On the other hand, PET-V/R blends show various degrees of improvement of the crystallisation process. Their crystallisation is narrower and sharper than parent polymers. We can also deduce from Table V that minimum crystallisation temperature (T_c , min) of the blends increases with the increase of PETR composition.

5.2. Rheological Behavior of PET-V/R Blends

Steady state rheological properties of virgin/recycled PET blends were determined at shear rates ranging between $0,1-300 \text{ s}^{-1}$ at constant temperature 260°C . The flow curves obtained for different blends are reported on Figure 8. We remark that the apparent viscosity increases with the increase of PETR percentage for the two types of blends PET-C/A and PET-C/B. Also the viscosities of all the blends lie between those of pure PET materials.

Furthermore, it can be noted that the viscosity of the blends PET-C/B is higher than that of the blends PET-C/A. This is probably due to the fact that the PET-A is more likely to degrade than the PET-B. Indeed, during the preparation of the blends the polymers undergo shearing, thermal and mechanical stress (temperature and pressure).

The zero shear viscosity of the PET-C/A blends is plotted against the PETV weight fraction (Figure 9). The experimental curves show a negative deviation (ND) from the logarithmic additivity rule frequently used to model polymer/polymer blends viscosity [46].

Dynamic rheological properties (η^* , $G' = \eta''/\omega$ and $G'' = \eta'/\omega$) for the PETV/R blends and extruded pure polymers (PETR and PETV) were measured with constant strain of 10% at 260°C . As expected the dynamic viscosity (η^*) decreases with frequency (Figure 10). Also, as for steady state shear viscosity, the complex melt viscosity increases with virgin PET concentration.

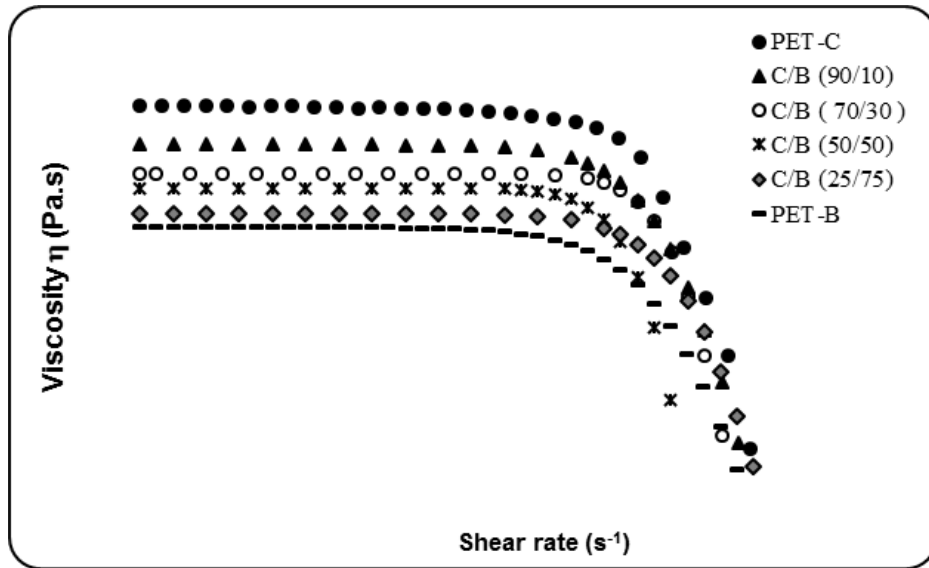


Figure 8. Viscosity η vs shear rate $\dot{\gamma}$ for PET-C/B blends (at 260°C).

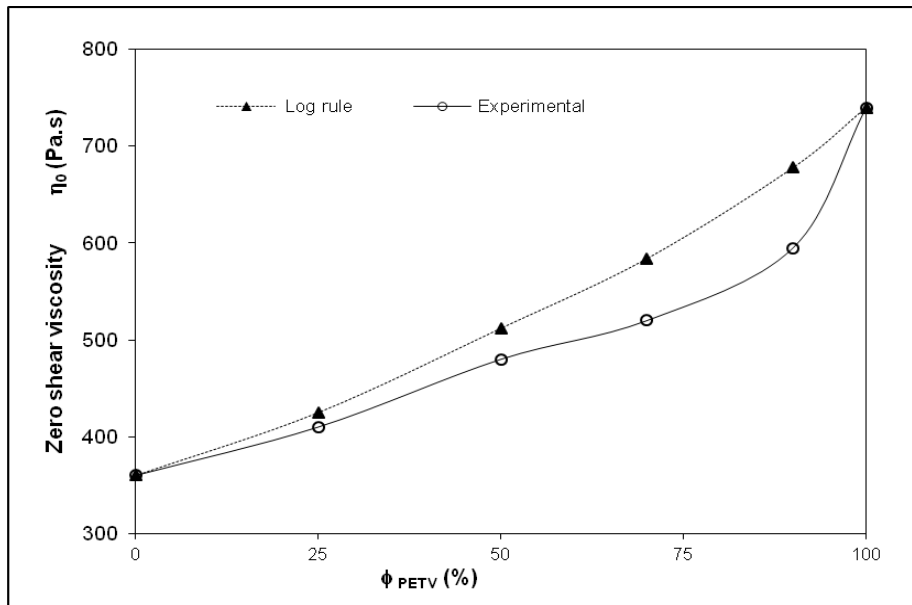


Figure 9. Negative deviation of η_0 vs. composition for PETC/A blends.

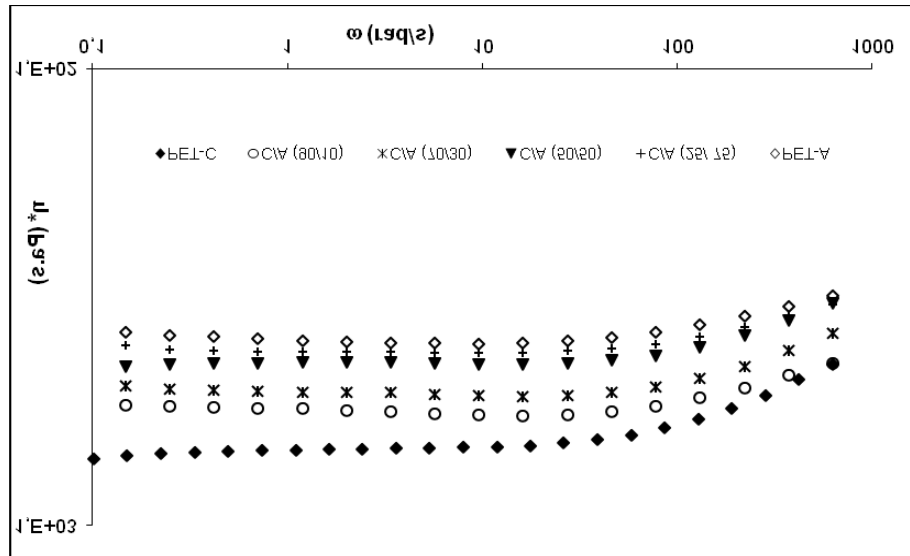


Figure 10. Dynamic viscosity η^* of PET-C/A blends at 260°C.

In order to analyse the dynamic rheological data, the Cole-Cole plot (G' vs. G'') was used. This criterion was developed by Han and Kim [47]. In this method, if a blend is miscible the same slope is observed between the blend compositions and pure components; otherwise it is considered to be immiscible or a phase separated blend. On Figure 11, the plots showed almost the same slope for all the PET-V/R blends which is a good criterion proving the miscibility of recycled and virgin PET polymers. The independence of composition and the absence of phase separation would mean that PETV and PETR are miscible down to the macromolecular level. The PET-V/R blends would thus form an isotropic medium that has no separate domains occupied by the respective constituent components.

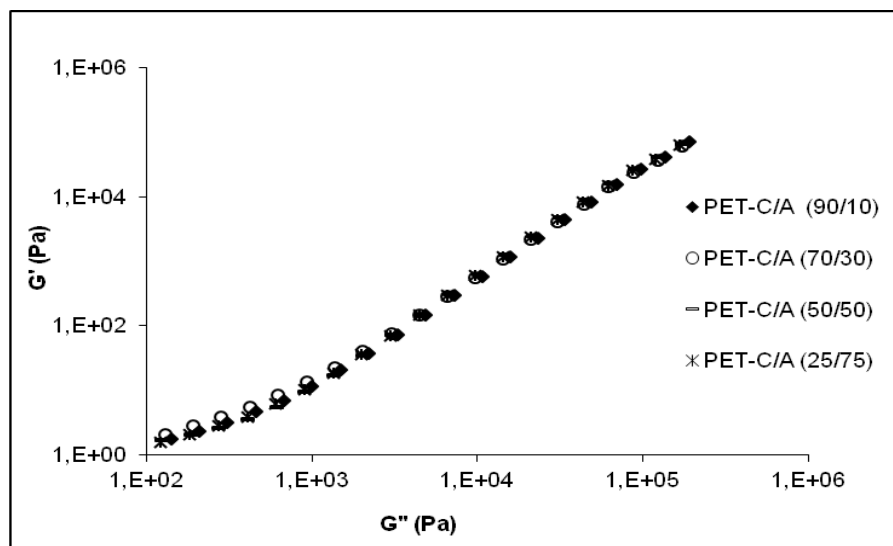


Figure 11. Cole-Cole analysis of viscoelastic modulus of PET-C/A blends.

CONCLUSION

In addition to the environmental incentive, recycling of PET as an industry derives its driving force from the increasing value and applications of virgin and modified PET. As described in the first sections, many scientific findings have been made in the field of PET recycling. Particular focus in this study was given to the methods used to enhance properties of recycled PET.

The study of thermal behavior of virgin/recycled PET blends points out the their good microstructural morphology. The absence of melting depression or synergy was explained by the fact that PETR/PETV blends are crystalline-crystalline isomorphous polymer blends of the same material. This statement was in accordance with rheological measurements. The steady and dynamic tests showed the absence of phase separation that would mean that PETV and PETR are miscible down to the macromolecular level. The PET-V/R blends can be considered as forming an isotropic medium that have no separate fields occupied by the respective constituent components.

Thus, the study reveals that the mechanical blending of recycled PET chips and virgin PET pellets improves the melt processing of recycled PET.

REFERENCES

- [1] Zhang, H., Wen, Z. G., (2014). The consumption and recycling collection system of PET bottles: A case study of Beijing, China. *Waste Management*. 34(6), 987–998.
- [2] Westerhoff, P., Prapaipong, P., Shock, E. and Hillaireau, A., (2008). Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water. *Water Research*. 42(3), 551-556.
- [3] El Toufaily, F. A., (2006). PhD Thesis: Catalytic and mechanistic studies of polyethylene terephthalate synthesis, University of Berlin, Berlin, Deutschland.
- [4] Ravindranath, K., Mashelkar, R. A., (1986). Polyethylene terephthalate-chemistry, thermodynamics and transport properties. *Chemical Engineering Science*. 41(9), 2197–2214.
- [5] Al-Ghatta, H., (1996). Production of foam grade PET. In: Conference Proceedings, SPE ANTEC, Volume (2), 1846-1849, Indianapolis, USA.
- [6] Al-Ghatta, H., Cobror, S., Severini, T., (1997). New technology for solid-state polymerization of polymers: polyethylene terephthalate solid-state polyaddition. *Polymers Advanced Technologies*, 8(4), 161–168.
- [7] Scheirs, J., (1998). *Polymer recycling: Science, Technology and Applications*. Wiley.
- [8] Mark, H. F., (1986). *Encyclopedia of polymer science and engineering*. New York, USA: Wiley.
- [9] Brydson, J. A., (1995). *Plastics materials*. 6th Edition, Oxford, UK: Butterworth-Heinemann.
- [10] Goshel, U., (1996). Thermally stimulated structural changes in highly oriented glassy PET, *Polymer*. 37, n° 18, 4049-4059.

-
- [11] Marechal, E., Geil, P.H., Gupta, V.B, Bashir, Z., (2002). *Handbook of thermoplastic polyesters: Homopolymers and copolymers*, Ed. by Stoyko Fakirov, WILEY-VCH, Allemagne.
- [12] Kong, Y., Hay, J. N., (2003). Multiple melting behavior of poly(ethylene terephthalate). *Polymer*. 44(3), 623–633.
- [13] Wunderlich, B., (2003). Reversible crystallization and the rigid-amorphous phase in semicrystalline macromolecules. *Progress in Polymer Science*, 28(3), 383–450.
- [14] Avila-Orta, C. A., Medellin-Rodriguez, F. J., Wang, Z. G., Navarro-Rodriguez, D., Hsiao, B. S., Yeh, F., (2003). On the nature of multiple melting in poly(ethylene terephthalate) (PET) and its copolymers with cyclohexylene dimethylene terephthalate (PET/CT), *Polymer*. 44, 1527–1535.
- [15] Charrier, J. M., (1990). *Polymeric materials and processing. Plastics, elastomers and composites*, New York, USA: Hanser Publishers.
- [16] Pawlak, A., Pluta, M., Morawiec, J., Galeski, A., Pracella, M., (2000). Characterization of scrap poly(ethylene terephthalate). *European Polymer Journal*. 36(9), 1875–1884.
- [17] Giannotta, G., Po, G., Cardi, N., (1994). Processing effects on poly(ethylene terephthalate) from bottle scraps. *Polym. Eng. & Sci.* 34(15), 1219-1223.
- [18] Fann, D. M., Huang, S. K., and Lee, J. Y., (1997). Processing Characteristics of recycled PET as melt spun fibers, *Textile Research Journal*. 67(12), 891-896.
- [19] Paci, M., La Mantia, F. P., (1999). Influence of small amounts of polyvinylchloride on the recycling of polyethylene terephthalate. *Polymer Degradation and Stability*. 63(1), 11-14.
- [20] Villain, F., Coudane, J., Vert, M., (1995). Thermal degradation of polyethylene terephthalate: study of polymer stabilization. *Polymer Degradation and Stability*. 49(3), 393–397.
- [21] Demertzis, P. G., Johansson, F., Lievens, C., Franz, R., (1997). Studies on the development of a quick inertness test procedure for multi-use PET containers-sorption behavior of bottle wall strips. *Packaging Technology and Science*, 10(1), 45–58.
- [22] Hopewell, J., Dvorak, R., and Kosior, E., (2009). Plastics recycling: challenges and Opportunities. *Philosophical Transactions of the Royal Society B, Biological Sciences*, 364(1526):2115-2126.
- [23] Romão, W., Spinacé, M.A.S. and De Paoli, M.A., (2009). Poly (ethylene terephthalate), PET: A review on the synthesis processes, degradation mechanisms and its recycling. *Polímeros*.19(2), 121-132
- [24] Carta, D., Cao, G., & D'Angeli, C., (2003). Chemical recycling of poly(ethylene terephthalate) (PET) by hydrolysis and glycolysis, *Environmental Science And Pollution Research*,10(6),390-394.
- [25] Karayannidis, G. and Archilias, D., (2007) Chemical Recycling of Poly(ethylene terephthalate). *Macromolecular Materials and Engineering*, 292(2), 128-146.
- [26] Freire, M. A., Damant, A., Castle, L., Reyes, F., (1999). Thermal stability of polyethylene terephthalate (PET): oligomer distribution and formation of volatiles. *Packaging Technology and Science*, 12(1), 29–36.
- [27] Torres, N., Robin, J. J., Boutevin, B., (2001). Chemical modification of virgin and recycled PET by adding of chain extenders during processing. *Journal of Applied Polymer Science*. 79(10), 1816–1824.

- [28] Itim, B., Philip, M., (2015). Effect of multiple extrusions and influence of PP contamination on the thermal characteristics of bottle grade recycled PET. *Polymer Degradation and Stability*. 117, 84-89.
- [29] Gao, Q., Nan-Xun, H., Zhi-Lian, T., Gerking, L., (1997). Modeling of solid state polycondensation of poly(ethylene terephthalate). *Chemical Engineering Science*. 52(3), 371–376.
- [30] Karayannidis, G. P., Kokkalas, D. E., Bikiaris, D. N., (1995). Solid-state polycondensation of PET recycled from postconsumer soft-drink bottles. II. *Journal of Applied Polymer Science*. 56(3), 405–410.
- [31] Inata, H., Matsumura, S., (1987). Chain extenders for polyesters IV. Properties of the polyesters chain extended by 2,2'-bis(2-oxazoline), *Journal of Applied Polymer Science*. 33(8), 3069–3079.
- [32] Haralabakopoulos, A. A., Tsiourvas, D., Paleos, C. M., (1999). Chain extension of poly(ethylene terephthalate) by reactive blending using diepoxides. *Journal of Applied Polymer Science*. 71, 2121–2127.
- [33] Awaja, F., Daver, F., Kosior, E., (2004). Recycled poly(ethylene terephthalate) chain extension by a reactive extrusion process. *Polymer Engineering & Science*. 44(8), 1579–1587.
- [34] Cardi, N., Po, R., Giannotta, G., Occhiello, E., Garbassi, F., Messina, G., (1993). Chain extension of recycled poly(ethylene terephthalate) with 2,2'-Bis(2-oxazoline). *Journal of Applied Polymer Science*. 50(9), 1501–1509.
- [35] Xanthos, M., Wan, C., Dhavalikar, R., Karayannidis, G. P., Bikiaris, D. N., (2004). Identification of rheological and structural characteristics of foamable poly(ethylene terephthalate) by reactive extrusion. *Polymer International*, 53(8), 1161–1168.
- [36] Incornato, L., Scarfato, P., Di Maio, L., Acierno, D., (2000). Structure and rheology of recycled PET modified by reactive extrusion. *Polymer*. 41(18), 6825–6831.
- [37] Awaja, F., Daver, F., Kosior, E., Cser, F., (2004). The effect of chain extension on the thermal behavior and crystallinity of reactive extruded recycled PET. *Journal of Thermal Analysis and Calorimetry*, 78(3), 865–884.
- [38] Scarfato, R. and La Mantia, F. P., (2002). Characterization of monopolymer blend of virgin and recycled polyamide 6, *Polymer Engineering & Science*. 42(12), 2412-2417.
- [39] Kukaleva, N., Simon, G. and Kosior, E., (2001). The Effect of Blending on the Viscosity Reduction of Recycled Milk Bottle Grade HDPE, ANTEC 01 Conference Proceedings, Dallas, USA.
- [40] Wenguang, Ma. and La Mantia, F. P., (1996). Processing and mechanical properties of recycled PVC and of homopolymer blends with virgin PVC, *Journal of Applied Polymer Science*. 59(5), 759-767.
- [41] Berkowitz, S., (1984), Viscosity–molecular weight relationships for poly(ethylene terephthalate) in hexafluoroisopropanol–pentafluorophenol using SEC–LALLS, *Journal of Applied Polymer Science*, 29(12), 4353-4361.
- [42] Kokkalas, D. E., Bikiaris, D. N. and Karayannidis, G. P., (1995). Effect of the Sb₂O₃ catalyst on the solid-state postpolycondensation of poly(ethylene terephthalate), *Journal of Applied Polymer Science*. 55(5), 787-791.
- [43] Starkweather, H. W., Zoller, P. and Jones G. A., (1983). The heat of fusion of poly(ethylene terephthalate), *Journal of Polymer Science/Part B, Polymer Physics*. 21(2), 295-299.

- [44] Groennickx, G., Reynaers, H., Berghmans, H. and Smets, G., (1980). *Journal of Polymer Science/Part B, Polymer Physics*, 18(6), 1311-1324.
- [45] Fann, D. M., Huang, S. K. and Lee, J. Y., (1996). Kinetics and thermal crystallinity of recycled PET. I. Dynamic cooling crystallization studies on blends recycled with engineering PET, *Journal of Applied Polymer Science*. 61(8), 1375-1385.
- [46] Utracki, L. A. and Kaniyal, M. R., (1982). Melt rheology of polymer blends, *Polymer Engineering & Science*. 22(2), 96-114.
- [47] Chang, D. H. and Kim, J., (1987). Rheological technique for determining the order-disorder transition of block copolymers, *Journal of Polymer Science/Part B: Polymer Physics*, 25(8), 1741-1764.

LCH