CREATING METHODS FOR VALUE-ADDED BOTTLE-GRADE POLY (ETHYLENE TEREPHTHALATE) FROM BLENDS OF BOTTLE-GRADE AND THERMOFORM-GRADE POLY (ETHYLENE TEREPHTHALATE)

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ABSTRACT

One of the widely used plastics in food, consumer goods, beverage, and pharmaceutical industries is poly (ethylene terephthalate) (PET). On a global scale, PET is renowned as the most frequently recycled polymer. Thermoform PET (PET-T) must be separated from bottle-grade PET (PET-B) streams due to variations in their intrinsic viscosity (IV). This research aims to create commercial bottle-grade pellets by blending recycled PET-B and recycled PET-T. Three techniques were used to rebuild PET-B characteristics with 10-20 wt% PET-T: solid-state polymerization (SSP), chain extension, and chain extension combined with SSP. The IV values for PET-B containing 10-20% PET-T were determined. Mechanical parameters like impact strength, tensile modulus, tensile strength, and elongation at break were also tested. Furthermore, thermal characteristics like thermal degradation, crystallinity, glass transition temperature (T_g), and melting temperature (T_m) were studied. The implementation of SSP treatment and a chain extender improves the IV values of rPET blends. The use of SSP treatment and a chain extender also improved the thermo-mechanical behavior of recycled PET blends from PET-B and PET-T. The tensile strengths and Izod impact strengths of blends that had undergone chain extension and SSP were greater than those of untreated PET blends. Meanwhile, the thermal properties, such as the T_g and T_m remained unaffected by adding the chain extender and the SSP treatment.

Keywords: Recycled PET, Solid-State Polymerization, Chain extenders, Reactive extrusion

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CHAPTER 1: INTRODUCTION

1.1 Introduction

PET (Polyethylene terephthalate) is a commonly utilized plastic within the food and beverage industry, where it is used in packaging such as trays, bottles, bottle caps, cups, clamshell containers, and cartons. Every year the utilization of PET in the form of beverage bottles, textiles, and packaging has exceeded 18 billion pounds globally. Nearly 3 million tons out of 51 million tons of recovered PET bottles are recycled. With the increasing demand for PET packaging, it is expected that 63 million pounds of waste will be generated in 2023, with rising yearly consumption to 6.9 million from 5.1 million since 2020 [0-2]. The demand for PET in various applications is driving the growth of the PET market. Conversely, the substantial volume of PET waste underscores the significance of circular economies like mechanical recycling. However, only bottle-grade PET (PET-B) is recycled at a rate of 30%, whereas Thermoform PET (PET-T) is not recycled at all, even though PET-T accounts for roughly 10% of the recycled PET stream [3].

PET-T operates differently from PET-B due to the many fundamental characteristics of the Thermoforming material and other associated components in the stream. The key distinction is that typical PET reclamation processes are designed for bottles and have only recently begun to treat thermoforms. One of the primary reasons thermoforms are only sometimes used is due to the inconsistency of the plastic resins used in their fabrication [4]. Other thermoform manufacturers employ PET-like materials, such as (polylactic acid) (PLA) which is used in thermoform clamshells and trays, and (polyethylene terephthalate glycol) (PETG) which is used in thermoform clamshells and trays [5] The adhesives used on thermoforms are significantly abrasive than the labels used on bottle labels. Because the adhesive covers the whole label in many cases, removing the label from PET-T or PET-G containers (or crushed PET flakes) is frequently more difficult [0].

Furthermore, the aqueous solution used to wash the PET flakes is prone to becoming contaminated with adhesive residue. When PET bottles and clamshells are produced concurrently, problems arise because the intrinsic viscosity (IV), tensile strength, or elasticity of PET-T are frequently lower than those of PET-B. Due to thermal degradation and possible contamination, the mechanical properties and molecular weight frequently diminish over several repeated processing cycles. When PET is reprocessed with extreme temperatures, oxygen, and moisture, the polymer degrades [5]. Because the polymer is made at high temperatures, it contains degradation products such as cyclic oligomers [4,6]. It is a well-established fact that the mechanical, thermal, and rheological characteristics of a polymer are influenced by its molecular weight. The IV range for PET-B and other high-value plastics is 0.72-0.85 dL/g [7-9].

There are several techniques for increasing the IV and molecular weight of PET. First, additives such as chain extenders can be incorporated to generate interlinking bonds between polymer chains and thus enhance the polymer's chain length. The second approach would be to continue the PET chain's melt repolymerization with a chemical recycling process, which would be a costly operation.

The third choice is the Solid-State Polymerization (SSP) method for PET. This involves heating the prepolymer with low molecular weight to temperatures below its T_m but above its T_g. To eliminate byproducts of condensation, a vacuum or inert gas can be employed after the condensation reaction takes place [9]. The polymer becomes more tightly intertwined, and its molecular weight increases. The temperature at which the reaction is done is often lower than the polyester's melting temperature, and thus thermal degradation is dramatically reduced. Side products such as water and ethylene glycol can be eliminated under vacuum or by flushing the polymer with an inert gas.

One of the main issues linked with PET is its elevated melting point, around 250 ºC. The melting points of PET-T and recycled PET-B are lower in contrast to virgin PET-B. All these issues may be addressed by using a chain extender prior to SSP and melting the recycled PET material [9]. The method of chain extensions is widely employed in the process of extending and modifying PET chains, primarily due to its relatively gentle reaction conditions. This approach offers advantages such as minimal energy consumption during flow and a high level of efficiency. Through the utilization of chain extenders, polymers can create covalent chemical bonds, creating the elongation of polymer chains and a subsequent rise in the overall molecular weight of the polymer. [10]. Polymer chains that have undergone degradation can be reconnected through the application of chain extenders. The reactions that occur are impacted by both the functional properties of the selected chain extender and the proportion of the same in relation to the polymer [11].

The characteristics of the utilized chain extender and the quantity of polymer in the mixture determine the formation of branched chains. Joncryl ADR is a family of epoxy-based multifunctional oligomer chain extender that is formulated to react with the terminal group of polyesters [12-13]. Joncryl® ADR 4468 (J) is a multi-functional reactive polymer with high thermal stability that is utilized in food and beverage application involving polycondensation polymers such as PET, PLA, and poly (butylene terephthalate) (PBT).

Many prior studies have shown that adding a chain extender or performing the SSP procedure can increase the IV values and enhance the mechanical characteristics of post-consumer PET. Adding a chain extender to PET raises the molecular weight of the rPET component by simultaneously broadening and lengthening the chains in the polymer [14]. It has been shown that adding J increases the IV and molar mass of recycled PET to greater values than are observed for virgin PET.

Some investigations have investigated whether J may increase the crystallization rate of thermoplastics with sluggish crystallization, such as PET and PLA [15,16].

A few studies have revealed that reactions performed under vacuum conditions improve the IV of PET. As reported by Ma et al., the elimination of water and ethylene glycol using the SSP process enhances the IV of PET [17]. With SSP at 240-245 °C for 3-5 h, the IV may be raised to 0.72 dL/g and the terminal group of PET can be reduced to less than 20 meq/kg [9,18]. Various studies indicate that the IV of PET is influenced by its molecular weight and moisture content. By-products are eliminated during the SSP process, which raises the molecular weight of recovered PET [19-21].

In this work, three techniques were utilized to rebuild the IV characteristics of post-consumer PET-B with 10-20 wt% PET-T to performance matching that of virgin PET. These techniques included SSP, chain extension, and chain extension coupled with SSP. Thermal, rheological, and mechanical characteristics of post-consumer PET-B with 10-20 wt% PET-T were also examined following various treatments.

1.2 Objectives

The objective of the research was to create and develop commercial bottle-grade PET from recycled pellets composed of PET-B and PET-T. To achieve this objective, two specific research tasks were pursued in this investigation.

Firstly, we investigated the consequence of using SSP on the thermomechanical characteristics of an rPET blend created in pellet form from PET-B and PET-T.

Secondly, we evaluated the effect of the chain extender (CE) on rPET pellet blend characterizations like its physical shape, and rheological and thermomechanical properties.

1.3 Thesis Work Scope

The scope of the research is to create commercial bottle-grade pellets from recycled PET-B and PET-T. PET is the most recycled and widely used plastic. Almost 2.91 million tons of PET bottles were recycled in 2022 but that process required the separation of PET-T from bottle streams [0]. This research will help in incorporating PET-T along with PET-B. The research will create thermoform and bottle PET blend pellets from recycled material with the help of SSP and chain extension and enhance the thermal and mechanical characteristics of these rPET blends so that they are equivalent to those of bottles created from virgin pellets. In addition, we can create a consistent recycling stream that includes both bottle-grade and thermoform materials.

1.4 Hypothesis

The **first hypothesi**s is that adding the commercial chain extender Joncryl ADR to a recycled PET blend made of PET-B and PET-T is necessary for bottle making while retaining or improving the desirable thermal and mechanical properties.

The **second hypothesis** is that the combination of chain extension with SSP is likely to increase the intrinsic viscosities necessary for bottle-making purposes while retaining or improving the desirable thermal and mechanical properties.

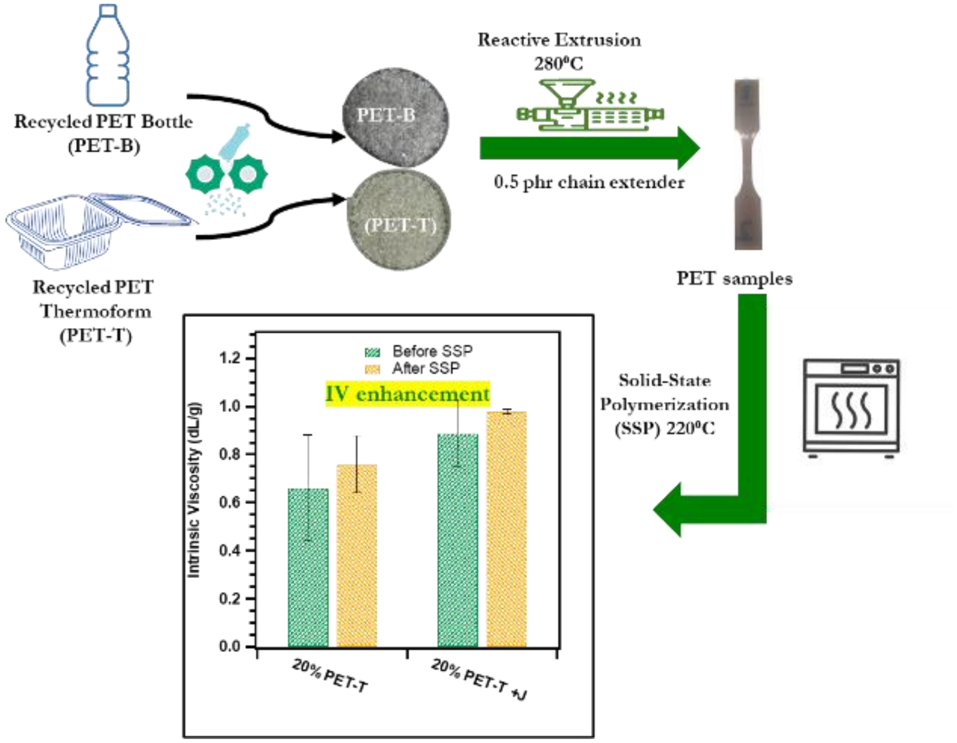

Figure 1.1: Schematic representation of a process for recycled PET-B and PET-T blends using chain extension and SSP to create commercial bottle-grade pellets.

1.5 Structure of the Thesis

This thesis is divided into five chapters, and the contents of these chapters are outlined below:

Chapter 1 introduces the hypothesis, scope, and objectives of this work.

Chapter 2 lays out the literature review on PET recycling techniques, chain extenders, and SSP processes.

Chapter 3 discusses the materials and methodology used in this study.

Chapter 4 provides the results obtained during this research.

Chapter 5 summarizes the overall conclusions and discusses the future scope of the research conducted.

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CHAPTER 2: REVIEW OF LITERATURE

2.1 PET

Polyethylene terephthalate (PET), a type of polycondensation polymer, is synthesized from ethylene glycol (EG) and terephthalic acid (TPA) or terephthalic ester. PET is widely employed in the packaging industry due to its favorable attributes, including strong mechanical properties, impressive optical and thermal characteristics, and effective barrier properties [1].

PET was first created by the USSR and Great Britain in 1941 through the polycondensation process of EG and TPA. In the 1970s, the large-scale production of PET bottles and containers commenced. By 2019, the worldwide yearly manufacturing capacity for polyethylene terephthalate (PET) had reached approximately 30.5 million metric tons. This capacity is projected to rise to 35.3 million metric tons per annum by 2024. PET is the dominant polymer utilized in the production of bottles. [2]. The Global waste generated by PET plastics waste accounts for 12% of global plastic waste produced. 30% of PET bottles are recycled today, while 70% are sent to landfills. There is a strong interest in further increasing PET recycling. However, the rPET (post-consumer recycled or post-consumer resin PET) ends up mostly in fibers and some in bottles, despite there being an interest in bottle-to-bottle PET.

2.1.1 Structure and Properties

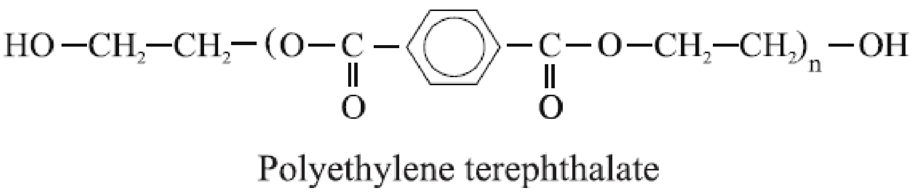


Figure 2.1: Chemical structure of PET.

PET is formed through the polycondensation of dimethyl terephthalate (DMT) or terephthalic acid (TPA) with ethylene glycol (EG). PET possesses ester bonds within its backbone structure and has a melting point ranging between 250-260ºC. The density of PET varies based on its level of crystallinity, with crystal PET exhibiting a density of 1.455 g/cm^3, while amorphous PET has a density of 1.333 g/cm^3 [3].

Bottle-grade PET is often produced in 3 stages: i) transesterification, ii) pre-polymerization, iii) polymerization, and iv) SSP. The esterification of EG and TPA at 180ºC creates BHET bis(hydroxyethyl)terephthalate. Then BHET is further polymerized at 220 ºC under vacuum. Then the melt condensation of the polymer is done at 150-2200ºC up to the degree of polymerization of about 100 [4]. With the help of a catalyst like antimony triacetate in a helical screw reaction, the SSP process is executed at 200-230ºC below melting temperature 240-260ºC where the PET polymer pellets are created. Most of the PET have CEs when the pellets are made. The application of these chain extenders (CEs) accelerates the production rate, thereby raising the molecular weight of PET [5].

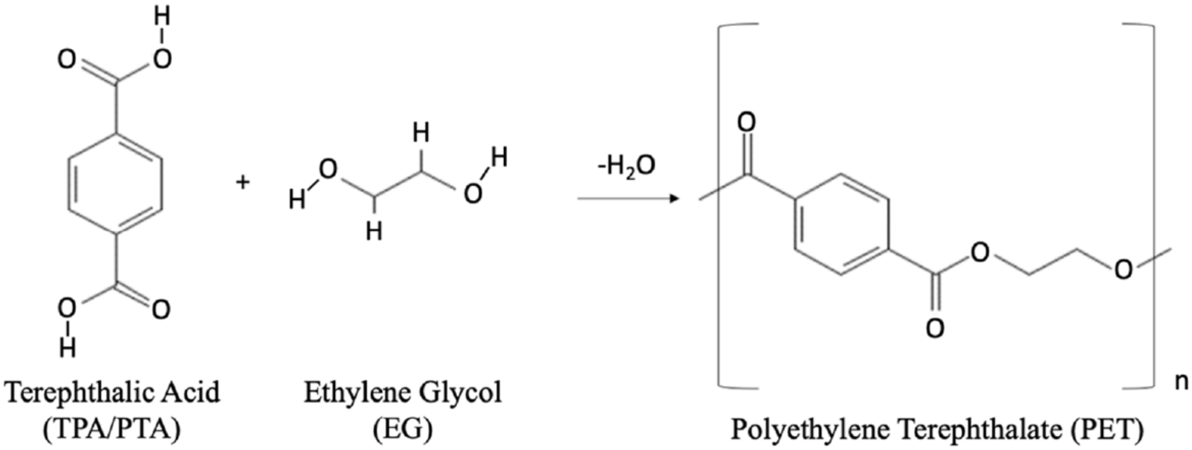
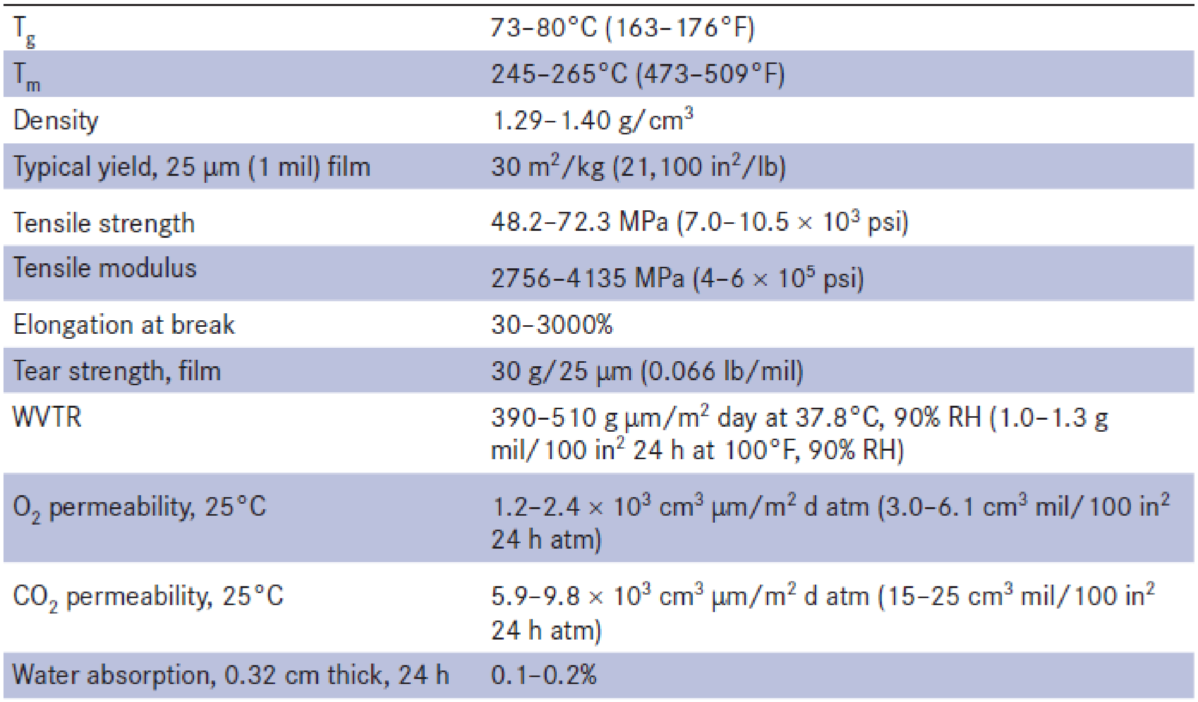


Figure 2.2: PET synthesis from TPA and EG [6].

The benzene ring in the main chain of PET polymer gives stiffness to the polymer. Tg for PET ranges from 67-81ºC depending on its crystallinity and the melting point for PET is 256-260ºC [7,8].



T_g	73–80°C (163–176°F)
T_m	245–265°C (473–509°F)
Density	1.29–1.40 g/cm^3
Typical yield, 25 µm (1 mil) film	30 m^2/kg (21,100 in^2/lb)
Tensile strength	48.2-72.3 MPa (7.0–10.5 × 10^3 psi)
Tensile modulus	2756–4135 MPa (4–6 × 10^5 psi)
Elongation at break	30–3000%
Tear strength, film	30 g/25 µm (0.066 lb/mil)
WVTR	390–510 g µm/m^2 day at 37.8°C, 90% RH (1.0–1.3 g mil/100 in^2 24 h at 100°F, 90% RH)
O_2 permeability, 25°C	1.2–2.4 × 10^3 cm^3 µm/m^2 d atm (3.0–6.1 cm^3 mil/100 in^2 24 h atm)
CO_2 permeability, 25°C	5.9–9.8 × 10^3 cm^3 µm/m^2 d atm (15–25 cm^3 mil/100 in^2 24 h atm)
Water absorption, 0.32 cm thick, 24 h	0.1–0.2%

Figure 2.3: Properties of PET polymer. Table is taken from ref. [3]. Selke Susan E M, J. D. C., Rafael Auras, Muhammad Rabnawaz. Plastics packaging: Properties, processing, applications, and regulations.; Carl Hanser Verlag Munich, 2021.with permission from the publisher.

The above table shows the typical properties of a PET polymer. The tensile strength of the virgin polyethylene terephthalate polymer comes in the range of 48.2-72.3Mpa and the elongation varies from 30-3000% depending on the long chain of PET and the crystals of the PET. The PET polymer has a good O_2 and CO_2 barrier but poor water vapor and water barrier. Most PET containers or bottles are clear and transparent due to high crystallinity but can also be found in a hazy color if the amorphous regions are present in the structure [3].

2.1.2 Different Types of Commercial PET

PET is one of the most utility plastics that is being used globally. Due to its versatility, it can be used as a thermoplastic polymer, or when processed it can be created as strong and as functional as a thermosetting polymer. 5 different types of PET can be seen in use widely Oriented Polyethylene terephthalate (OPET), Polyethylene terephthalate glycol (PETG), Extrudable Polyethylene terephthalate EPET, Cyclohexylenedimethylene Terephthalate (PCTG), and Polyethylene terephthalate (PET) [9].

PETE or PET: It is a semicrystalline PET homopolymer. it can be rigid or semi-rigid. This PET can find utilization in sophisticated applications including industrial components, pharmaceutical and medical device components, automotive parts, and electrical circuit elements.

OPET: Oriented PET is used for high-end applications because of its high tensile properties and stability. OPET is used for fiber and films. OPET is created by heating and stretching the unbalanced chains in the polymer molecules and then arranged in a parallel way in the stretched direction. This helps to increase the clarity and barrier properties of PET [1,3].

EPET: Extrudable PET (EPET) resins have very high melt viscosity and slow crystallization rate, which makes the processing of PET resins easier for extrusion blown film and extruded blow molded bottle applications.

APET: Amorphous PET is the PET resins made so that the polymer remains amorphous using the copolymerization technique. There are two types of amorphous PET. PETG and PCTG. PETG is a copolymer made from EG and TPA in the presence of isophthalic acid and diethylene glycol [10]. The modifier makes sure it reduces the crystallization rate and melting point of the polymer. They also make sure that no orientations in crystals take place. PCTG is a type of PETG made from the copolymerization of TPA and EG by adding a few mol percent of cyclohexane di-methanol in the PET structure to create a copolymer. Both PETG and PCTG have good chemical resistance and clarity. PCTG is known for its excellent impact resistance and is majorly used in cosmetic industries. PETG is used in food industries for trays and in medical sectors for making thermoforms due to its excellent clarity [9-11].

2.1.3 PET Application

Because of its adaptable nature and favorable physical and chemical attributes, PET finds extensive application in sectors like food and beverage, pharmaceuticals and medical fields, automotive manufacturing, electronics, power tools, as well as clothing and textiles. [10]. If we use CPET (crystallized PET) we can use it in applications like packaged frozen food, microwaveable containers, and toiletries. Oriented PET in film and sheet forms can be used for laminations in food packaging, cheese, and meat packaging, creating boil-in-bags. Oriented PET is also used in the medical industry as sterilizable pouches and thermoform trays [3]. PETG is specially used in medical industries as it can be sterilized with gamma radiation and ethylene oxide. Also, due to its semi-crystalline nature and high thermal degradation temperature PETG can be used in 3D printing industries [11-12].

2.2 Recycling

Recycling of plastic is the collecting of plastic material or waste generated from either post-consumer or post-industrial use and using the recovery of the material in use to make the same product or different end-use product. Addressing the environmental repercussions of plastic waste has made polymer waste recycling a vital solution. Recycling can be classified into four distinct categories: primary recycling (mechanical recycling of industrial waste), secondary recycling (mechanical recycling of consumer plastics), tertiary recycling (chemical recycling), and quaternary recycling (energy recovery). [13]. Primary recycling includes recycling and creating similar quality products from post-industrial materials. Mechanical recycling of rPET is secondary recycling, which involves cleaning and reprocessing of the material. Often down-cycling, such as creating textiles from bottle-grade material or creating plastic lumber from the material. Sometimes the polymer or material is depolymerized in monomers and remade again. The last type of recycling is quaternary recycling, where the polymer is converted into energy from the waste generated [14]. Recycling is broadly categorized into two main types: chemical recycling and mechanical recycling. Most of the thermoplastics can be mechanically recycled [13]. The recycling process follows collection, sorting, cleaning, and grinding before melt-reprocessed into pellets (mechanical recycling) [15] or contaminated plastics are converted into flakes and depolymerized into small molecules (chemical recycling).

2.2.1 PET Recycling

As PET is extensively recycled, to boost waste management and reduce the price of PET pellet creation of rPET pellets was started in 1977 [16-17]. PET soft drink bottles were the first post-consumer plastic containers to be recycled on a wide scale in the United States. As previously stated, they benefitted from the existence of bottle deposit legislation in several states. The use of PET in packaging applications has expanded fast. Fiber applications of different sorts have been the greatest end-use market for recovered PET, ranging from fiberfill for ski coats and sleeping bags to face yarn for polyester carpets. Over the last decade, the utilization of rPET in food and beverage bottles has grown considerably [3]. In the last few years, the creation of packaging material from post-consumer recycled material (RPET) has increased dramatically [18-19]. In recent years the utilization of bottle PET for recycling has become significant due to the production accessibility, and purity of PET material in bottle packaging. Furthermore, the recycling of PET from bottles and PET used in food packaging holds significance, as other recycled PET materials tend to contain higher levels of contaminants and are typically limited to non-food contact applications. [16].

2.2.2 Mechanical Recycling

Mechanical Recycling of PET means reprocessing either post-consumer or post-industrial PET by shear force and extreme heating conditions without changing the polymer structure and chemical properties [20]. The steps for mechanical recycling are getting the materials separated according to their polymeric system. Followed by the cleaning process, which involves washing dirt and other contaminants, then grinding and shredding polymeric products into smaller flakes, cleaning the flakes from contaminants, and subsequent extrusion of the flakes into PET pellets, after creating the pellets the pellets are converted into PET products like bottles, textiles, straps and other packaging materials [20]. Currently, mechanical recycling remains the most commercially viable option due to its cost-effectiveness and energy efficiency.

2.2.2.1 Method of Creating Mechanically Recycled Pellets

Mechanical recycling of PET involves collection, flaking, cleaning, drying, and palletization [21]. These pellets are then enhanced into desired pellets for various applications. PET bottle mono-collection systems produce high-purity rPET [22]. The technique and sorting equipment employed are critical to have good quality rPET. The separation process is based on identifying a feature that distinguishes between PET and a specific adulterant or impurities, such as density, melting temperature, and the NIR (near-infrared) spectrum. Based on these distinctions, identification, and separation are performed [23].

The first method is to start manual sorting. The garbage is placed on a conveyor belt before entering the recycling line. Workers are stationed along the conveyor belt to gather and discard things that do not need to be introduced into the recycling process [24].

Automated sorting is considered to be more reliable, efficient, and proficient in handling substantial waste volume compared to manual sorting. In cases where recycling facilities manage larger waste quantities, the initial costly investment can be recovered over time. However, for certain tiny plants, this may not be possible. Various systems, such as machine vision or NIR sorting, can be employed [24-25]. Flotation is a widely used separation method that relies on the principle of density variations. It's a straightforward and cost-effective technique. In this process, the mixed plastic flakes are placed in a tank with a floating medium. Plastics with densities more than the medium sink to the tank's bottom, while those with lower densities float. Typically, water is utilized as the flotation medium. In this setup, PET sinks while the remaining plastics float, allowing for effective separation [26].

For full bottles and powdered PET flakes, NIR sorting technologies are commonly utilized. The reason for this is that near-infrared sensors can identify a series of different materials quickly and consistently, allowing for larger throughputs. NIR, on the other hand, this method struggles to differentiate between different types of packaging waste made from identical polymer (like PET bottles and PET trays), as well as polymers with similar spectral characteristics, such as polyethylene terephthalate glycol (PETG) and polyethylene terephthalate [25-26].

2.2.2.2 Cleaning and Drying Process

Before shredding PET, bottles, or thermoform, they are washed to remove labels and adhesives using hot water, scrubs, and brake cleaning solutions. When all rPET is cleaned, the cap and the safety seal must be removed and then cut into flakes. The incoming flake might be clean or unclean; all reclaimed flakes are cleaned as part of the reclaimer processing procedures. This procedure can be carried out using a caustic wash; however, other recyclers have mentioned the utilization of various washing products like defoamers, surfactants, and wetting agents. [27]. The PET flakes are washed three times in the following order: clean using water for 10 minutes, using 1% aqueous sodium hydroxide solution for five minutes, and again clean using water for 10 minutes.

PET flakes, after washing, are dried in a regular oven at 160 °C for 6 hours or at 80 °C for 12 hours [28]. PET bottles that have been used for non-food purposes, possibly containing hazardous materials, are consistently gathered and introduced into the recycling system. Consequently, these non-food containers could potentially introduce contaminants into the recycled PET (rPET) product. It's essential to keep these non-food PET bottles separate in the collection process. To enhance the decontamination effectiveness of rPET bottles intended for direct food contact packaging, a technique known as super-clean recycling or deep-clean recycling has been adopted. This process involves three main phases: (1) high-temperature cleaning, (2) gas-based cleaning, and (3) chemical cleaning [16,29].

2.2.2.3 Extrusion Process

Shredded and dried PET flakes are fed into an extruder for pelletization/granulation. Extrusion involves the melting of PET flakes for palletization. The extrusion also helps to get rid of leftover contamination (volatiles by venting and pigments/dirt by screening), particularly regarding food-grade rPET [30-31]. Although washing and sorting processes effectively eliminate a substantial portion of contaminants, they are inadequate in addressing organic impurities that may be embedded within the plastic structure. Additionally, PET flakes are transformed into pellets for easier handling during the extrusion phase. Following extrusion, these solid rPET pellets undergo solid-state polymerization (SSP). The pellets are exposed to temperatures ranging from 180 to 220 °C, which is above the glass transition temperature of PET but below its melting point, ensuring the pellets remain in a non-melted state. The prescribed conditions prevent thermal degradation and facilitate polymer condensation. This condensation process leads to the formation of longer PET chains and an increase in intrinsic viscosity (IV) [32].

rPET flakes are heated until they melt in the process at 280 °C. The molten plastic is then forced through a die, resulting in cylindrical pellets. These pellets may be recycled as raw materials in manufacturing operations, lowering raw material prices.

The strand pelletizer forms pellets from molten plastic strands, whereas the underwater pelletizer immerses the plastic melt in water to cool and solidify the pellets. Before cutting the plastic melt into pellets, the water ring pelletizer cools and hardens it in a ring of water [33-34].

2.2.3 Chemical Recycling

The hydrolysis of ester linkages can lead to the breakdown of PET into monomers, oligomers, and various other compounds [35]. Chemical recycling of PET has numerous advantages, including providing a true closed-loop approach (e.g., bottle-to-bottle recycling for an almost infinite cycle of recycling), providing mechanical and thermal properties which is equivalent to virgin polymer, the absence of contaminants, and thus yielding polymer suitable for applications like food contact packaging material. Chemical recycling is the sole method that aligns with the principles of 'sustainability' as it generates new raw materials. Moreover, additional resources for PET production are unnecessary when employing chemical recycling for PET. Multiple techniques are utilized for the chemical recycling of PET, including hydrolysis, glycolysis, and methanolysis [36-37]. PET can also be chemically recycled to feedstock for polyurethane and unsaturated polyester resins. Glycolysis is the most widely employed, as the resulting BHET can be utilized to produce PET. However, the downside of chemical recycling is its elevated cost.

2.3 Recycled PET content

2.3.1 Demand for Recycled PET

The projected value of rPET demand is anticipated to rise from 11 billion USD to 15 billion USD within 5 years. Because of the demand for sustainable packaging materials and products, the people find alternative ways to reduce the use of a virgin polymer that comes from non-renewable resources, as efforts to save the environment the demand for recycling is growing even higher. Also, government regulations and policies focus on the use of recyclable materials and circular economy [38]. However, even with ambitious goals for incorporating recycled materials in the long run, the demand for recycled polyethylene terephthalate (rPET) is forecasted to maintain a relatively modest trend in 2023. This could potentially lead to downward pricing pressures in the United States. Around 80% of the rPET capacity in the United States originates from post-consumer sources, primarily bottles, while the remaining 20% is sourced from post-industrial feedstock [39]. During the forecast period, bottles are predicted to be the most significant and fastest-growing application in the rPET Market.

The momentum behind PET recycling is anticipated to stem from its minimal energy requirements and the straightforward bottle-to-bottle recycling process. Throughout the projected timeframe, the utilization of PET in food, beverage, and bottle applications is predicted to exhibit the highest compound annual growth rate (CAGR). The Asia Pacific region emerged as the global leader in terms of revenue, and this region is projected to sustain a steady CAGR during the forecast period [40].

2.3.2 Effect of Contamination

One of the significant issues with rPET content is the presence of unwanted contamination in it. rPET tends to get moisture content to it faster than virgin PET material, which creates problems of sticking, and clogging, and degradation during the processing. Also, during the drying of rPET, contaminants like vinyl ester are produced [6,41]. During reprocessing and extrusion at high temperatures, acidic compounds are generated from polyethylene vinyl acetate (PVA) lines, adhesives, and labels. Also, by-products like acetaldehyde produce vinyl ester, which affects PET polymer and is volatile and harmful for bottles and food packaging applications [42]. The presence of metal ions also affects the rPET content. Metal ion contaminants affect the melting behavior of polymers [43].

2.3.3 End-use Application

This industry's expansion may be due to the coordinated development of food and beverage, domestic applications, personal care goods, and other consumer packaged goods. rPET flakes are used in fibers to make a variety of apparel items, such as polyester clothing. They are also utilized in the production of automotive seat coverings, furniture textiles, carpets, and so on. The cost-effectiveness of producing clothing from recycled polyethylene terephthalate pellets is anticipated to drive a surge in global usage for rPET pellets. The presence of a robust manufacturing industry, in which rPET is widely employed across a variety of applications, can be attributed to the expansion [3].

The increasing investments in manufacturing facilities focused on recycling, particularly in the Asia Pacific region, are foreseen to boost the demand for recycled polyethylene terephthalate (rPET) flakes, particularly for the production of non-food bottles and containers [38,40]. The establishment of advanced bottled water production plants and the rise in tourism, particularly in Asia Pacific, are projected to stimulate the demand for bottled water, consequently driving the utilization of recycled polyethylene terephthalate flakes for the creation of food and beverage bottles and containers. The United States recovers over 1.5 billion pounds of discarded PET plastic bottles and containers (such as beverage bottles and cosmetic containers) for recycling each year.

Recycled PET (rPET) plastic serves as a versatile material for crafting bottles, clamshell food containers, trays, cups, carpets, garments, and fiberfill, among other items. A notable aspect of PET plastic is its recyclability, as recycling facilities can incorporate additives to enhance the intrinsic viscosity (IV) of rPET during the recycling process. IV signifies the polymer's molecular weight, encompassing its melting point, crystallinity, and tensile strength. Both PET and rPET plastics are secure and practical for food packaging. Nevertheless, obstacles in the bottled water sector's adoption of rPET plastic arise from cost considerations, contamination issues, and supply constraints [40].

2.4 Challenges in Mechanical and Chemical Recycling of PET

The challenge of generating recycled resins from plastic waste stems from the intrinsic immiscibility of most distinct plastic types at the molecular level, coupled with differences in processing requirements on a larger scale. The presence of even a small amount of non-compatible plastic in a PET recycling stream can lead to damage to the recovered PET resin. This occurs due to the generation of by-products at higher temperatures required for melting and reprocessing PET. Incorporating recovered plastic into new polymers often presents physical limitations without compromising certain qualities of virgin plastic, including color, clarity, or mechanical properties like impact strength. The feasibility of substituting recycled plastic for virgin polymer is primarily influenced by the purity of the recycled plastic feed and the specific property demands of the end plastic product. Consequently, contemporary recycling systems for post-consumer waste prioritize the recycling of packaging that can be easily separated, such as PET soft drinks and water bottles. [13,44].

The major difficulty of mechanical recycling of PET is its lower purity. PET is often combined with additives and composite material to enhance its physical and chemical properties. Also, PET can be chemically recycled but currently, chemical recycling is not much done at the commercial level [14-15]. One of the major issues with using recycled content is the degradation of IV during chemical and mechanical recycling. Due to shear force and high heating conditions in chemical and mechanical recycling, the IV of the plastic reduces. Also, sometimes the catalyst used for depolymerization during chemical recycling negatively affects the PET polymer during reprocessing.

2.4.1 The Challenge of Thermoforming in Bottle-Grade PET

The variability of PET resins used in thermoform manufacture is the primary concern, thermoforms are not routinely recycled. Even though PET is the favored material in the recycling sector, thermoforms constructed from OPS (oriented polystyrene) continue to be popular. Furthermore, some thermoform producers employ PET substitutes such as PLA, PVC, and PETG [45].

Another significant technological problem is labels and adhesives. The labels used in clamshell PET containers vary widely, including the ongoing use of recycling with contaminated paper labels. The most favorable label substrates for PET recycling are polyolefin-based, the most often used label is polypropylene. In the reclamation process, the thinness of thermoform trays poses a "bulk density" concern (clogging of the polymer thermoform samples into the recycling stream). Before washing, Plastic bottles and containers are transformed into chips by crushing, and if these chips are too lightweight, they may encounter challenges in smoothly traversing through the washing process. [46].

When bottles and thermoforms are melted together, the intrinsic viscosity of PET thermoforms is often less compared to that of PET bottles, posing complications. Following washing, the intrinsic viscosity of post-consumer thermoforms regrind can be improved through solid-state processing during decontamination and reprocessing. This enhancement is geared towards tailoring the material for specific end-use applications, like PET bottles, which demand a higher intrinsic viscosity compared to the initial sheets used in producing the thermoforms [45-46].

PETG should be omitted from the input materials in the recycling stream of PET bottles due to its incompatibility with PET. However, this situation becomes more complicated. It has been challenging to distinguish PETG from PET as they have similar morphologically and density.

Due to these factors, recycling companies urge PET bottle manufacturers to explore substitute materials. Nevertheless, PET bottle producers are reluctant to relinquish the advantages of this superior material. The inclusion of PETG leads to notable challenges during the granulation process. Additionally, owing to PETG's lower melting point compared to PET, it can result in the formation of an adhesive mass during drying and transfer operations. Furthermore, it can cause blockages of the PETG polymer within the extruder's mandrels before extrusion. Another unfavorable consequence is rPET browning [6,47].

Furthermore, PETG contains glycol. EG is utilized in the chemical recycling of PET (glycolysis) to break polymeric chains. Depending on the circumstances, a similar effect might occur when glycol is eliminated during granulation, influencing the intrinsic viscosity of rPET [48].

2.4.2 Intrinsic Viscosity of PET and its Relevance for Processing

In a cost-efficient manner, Intrinsic Viscosity (IV) serves as a rheological measurement indicating the polymer's average molecular weight. Fundamentally, PET's IV is indicative of its molecular weight. Typically, virgin PET boasts a higher IV than rPET, given that the latter is subjected to degradation processes including elevated temperatures, shear forces, hydrolysis, and the influence of contaminants and moisture [49]. When PET is recycled at a higher temperature than its melting temperature, volatile compounds are generated with a decrease in the IV of the polymers. The IV of a polymer increases with the polymer’s molecular weight and high IV values are essential for better Thermo-mechanical characteristics. The IV of the polymers is directly proportional to the length of the polymer chains. The more chain entanglement, the higher the viscosity. Different applications of PET have different grades of pellets. Each pellet has a different intrinsic viscosity.

The inherent viscosity is impacted by the length of polymer chains. Longer polymer chains lead to increased entanglements between them, resulting in higher viscosity values. PET's intrinsic viscosity is determined by its use and is divided into the following grades.

Table 2.1: IV values of different PET grades [31,49].

Application	IV (dl g^{-1})
Bottle Grade	0.70 – 0.78
Carbonated Drinks	0.78 – 0.85
Film Grade	0.70 – 1.00
Tape Grade	0.60
Fiber Grade	0.40 – 0.70

The critical feature of intrinsic viscosity arises where the properties of the rPET need to be controlled. IV is important for PET to have consistent production of the PET or rPET bottle, pipes, and caps in processing conditions, it is important to maintain and control the quality in the PET manufacturing sector [50].

As PET loses the metallic catalyst used for polymerization during recycling, it leads to a reduction in the intrinsic viscosity of rPET. To increase the intrinsic viscosity various techniques have been used. One approach involves employing thorough drying alongside vacuum degassing to eliminate moisture from the polymer, thereby enhancing the molecular weight of rPET. Another technique is to implement solid-state polymerization, leading to an increase in both Mw (molecular weight) and IV (intrinsic viscosity) of the polymers. A less expensive option for increasing the IV of the polymer for processing is to add a stabilizer or CE to the polymer to increase the M_w thereby increasing the IV of the polymer [50-51].

2.5 Solid-State Polymerization (SSP)

Solid-state Polymerization (SSP) is an approach to increase the molar mass of the polymer by enabling a reaction between the terminal group in a solid state [53-54]. For SSP treatment, PET is heated at temperature below T_m of the plastic and above the (T_g) to increase its molecular weight. SSP is usually done in the presence of inert gases under a vacuum [54]. The SSP process helps the amorphous phase of the polymer mobile enough so that it can react with the terminal group and crystalline phase with restricted mobility [55]. With the process of SSP under vacuum or inert gases, the unwanted by-products are removed, and the molecular weight of the polymer increases. The SSP process can be integrated into the recycling process to enhance the molecular weight of the recycled material, SSP also enhances the properties of rPET which deteriorated during the reprocessing the post-consumer polymer [56].

2.5.1 Types of SSP

The two procedures used for SSP include batch and continuous process. In the continuous process of SSP, the polymer is heated and mechanically agitated in glass tubes, rotating flasks, or vertical reactors. The weight of the reacting mass is continuously checked for water being formed [57]. One process of SSP is to heat the polymer at a temperature higher than 200 ºC under vacuum conditions. SSP under vacuum is less time-consuming to attain a higher molecular weight polymer. SSP under vacuum also helps the polymer create proper orientation amongst the chains. But SSP under vacuum can cause oxidation and discoloration of the PET plastic. Another drawback of SSP under vacuum is low polymerization rates, so it is feasible for large batches to create a good yield of polymer [58].

The other technique of SSP under high temperatures inside an oven is to pass inert gases through the polymeric sample. Nitrogen (N_2), Helium (He), and Carbon Dioxide (CO_2) are used for SSP treatment of PET. The benefit of using SSP under inert gases is, it suppresses deterioration and discoloration. This is also a little quicker [58-59]. When both techniques are combined, it provides proper monomer maintenance in reactors and the removal of unintentional by-products to have an appropriate polymerization.

2.5.2 Effect of SSP on PET

SSP of PET increases crystallinity in a polymer due to monomer cyclization, and undesired reactions are prevented. The process improves the stability of PET under higher heating temperatures which is useful for processing the recycled material under an extruder. Also, SSP helps in improving the linearity in the chain than can prevent ultra cross-linking of the polymer during reactive extrusion and other processing. Another advantage of SSP is that it removes unwanted monomer and volatile byproducts and moisture, and thus improves the processing of PET resin and the quality of rPET [53,60].

2.6 Chain Extenders (CE)

Chain Extenders (CE) are additives that can adjust the rheological properties of the polymer with chemical modifications done in reactive melt processing conditions. CEs are usually used to improve the characteristics of mechanically recycled PET and reduce the amount of chain scission in rPET [61]. The objective of using chain extenders (CEs) is to interact with the terminal groups of polyethylene terephthalate (PET), elongating the PET chains and minimizing the likelihood of material decomposition. This process helps maintain the desired molecular weight [62-63]. CEs are usually used in polymer and recycled contents of PET polyethylene terephthalate (PET), polyamides (PA), polyoxymethylene (POM), thermoplastic polyurethanes (TPU), polybutylene terephthalate (PBT), bisphenol A-based polycarbonates (PC) to reduce the degradation of these polymeric materials. Different CEs have other purposes; some CEs are plasticizers, and some improve melt-processing and dispersion of fillers in plastics [64].

Different types of CE can be found according to the functional group. Epoxy CE which promotes an increase in the chemical resistance and mechanical characteristics. The chain extender have epoxy functional groups which react with polymers terminal groups. Usually, they are used for food contact material and mainly used with PBAT, PET and PLA which react with the carboxyl group of the polymer and increase the number of chains. Isocyanates are used during pre-polymerization process of material like PU, PLA, and PET, it is used to enhance the molecular weight and IV of polymers like PET and PLA and increase the elongation at break from 5-300%. Oxazolines are low toxic and transparent materials. Oxazolines are capable of forming ester-amide bonds by undergoing ring-opening reactions with carboxyl groups. Oxazolines are commonly utilized with oligomers in solution reactions, although melt processing has also been observed to result in higher molecular weight and melt strength. Anhydride has a reactive functional group with a high affinity for PET, which can increase rPET performance [64].

2.6.1 Reactive Extrusion Method

Polycondensation polymer like PET, PBT, PU tend to deteriorate during the extrusion process by acid hydrolysis and thermal degradations. This leads to decrease in the M_w and IV reduction and loss of the mechanical performance of the material [63,65]. To overcome the degradation, reactive extrusion is done where the polymer is extruded along with a CE in a single or twin-screw extruder [65]. For PET, the temperature set during the reactive extrusion is above 260 ºC and the concentration of the CE is kept below 2% wt. of the polymer. If the weight of the CE is increased, it increases the IV and M_w. Still, the polymer degrades inside the extruder due to the torque generated, and the increasing shear force tends to degrade the polymer.

2.6.2 Effect of Chain Extender on the PET- CHEMISTRY

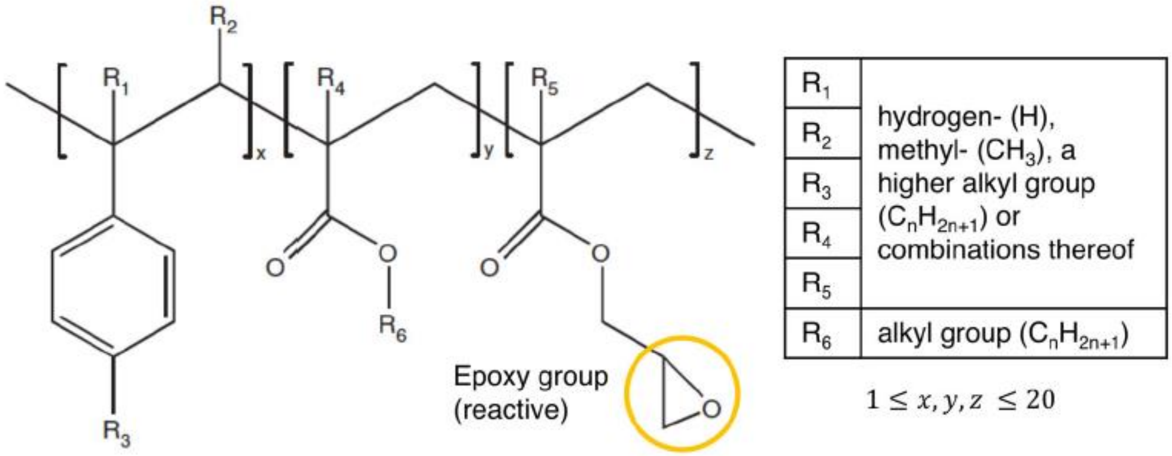


Figure 2.4: Composition of epoxy based Joncryl chain extender taken from source [66] page 2 figure1 with permission from the Taylor francis.

When PET goes through the process of mechanical recycling, the polymer tends to degrade thermo-mechanically during reprocessing in extruder due to shear force and high heating temperature. Thermal degradation decreases the M_w and IV of the polymers, which affects the mechanical properties of the material. The use of CEs like Joncryl® shows an increase in the M_w of the PET polymer. It also tends to increase the mechanical characteristics like tensile strength of the material. In the reactive extrusion of CE and PET, It has been shown that even with increased concentrations, the system can remain reactive after compounding. [66]. Different functional groups of CEs have different effects on PET chemistry. The utilization of epoxy groups can be attributed to their involvement in transesterification reactions with the carboxyl and hydroxyl end groups of PET. This chemical process generates additional hydroxyl groups, which in turn can interact with other epoxy groups [67].

The epoxy groups can react with the terminal groups of PET polymer to form extended chains. The ring-opening reaction of epoxy with PET follows two distinct pathways. The first involves a general interaction between the oxirane ring and PET's carboxyl groups, while the second pathway involves a reaction with hydroxyl groups [68]. Through these chain extension methods, the inclusion of CE with the epoxy functional group to the processing will increase the rPET characteristics. The isocyanate's reactivity with the hydroxyl groups in rPET was observed to be faster compared to its reaction with the carboxyl groups. The initial reaction led to the formation of urethane groups, while the reaction between PET's carboxyl and isocyanate groups resulted in the creation of amide groups. Both of these PET branching reactions occurred within the temperature range of 250 to 280 ºC during processing. When subjected to extrusion temperatures within the range of 250-280 ºC, the OXA interacted with the carboxyl end-groups of the two PETs, resulting in the formation of a by-product known as an ester amide group [69,70]

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CHAPTER 3: EXPERIMENTAL

3.1 Materials

3.1.1 Preparation of PET bottle pellets

Feedstocks of post-consumer and waste bottles, thermoform, and clamshells PET (PET-T) were from the Michigan State University recycling facility (Michigan, USA). The bottles, thermoform, and clamshells PET (PET-T) were first cleaned by rinsing them with warm water and a detergent bath to eliminate labels, impurities, and contaminants from the bottles and vacuum dried at 80°C overnight in a oven. The bottles and thermoforms were then shredded as small flakes using a plastic granulator (polymer machinery B.T.P granulator, Michigan, USA) and washed in a detergent bath again to remove any impurities present. These flakes are then dried and extruded in a twin-screw extruder (Leistritz Extruder, Michigan, USA) at 250°C at 100 rpm to create recycled PET-B pellets [1].

3.1.2 Chain Extender Joncryl® ADR 4468

Joncryl® ADR 4468 was acquired from BASF. It was used to enhance the thermal stability of recycled PET blends and increase melting strength [2].

Table 3.1: Specification data for Joncryl® ADR 4468 {[3-4]}.

Appearance	Solid flakes
Specific gravity, 25° C	1.08
Mw	7250
Tg (°C)	59
Non-volatile by GC (%)	>99
Epoxy equivalent weight (g/mol)	310
Typical dosage (%)	0.1-1.0%
Processing temperature range (°C)	170-330

3.1.3 Preparation of PET Bottle/Thermoform Blends

Both PET-T and PET-B were vacuum dried conditions at 80 ºC for 12 hours to eliminate moisture content to prevent hygroscopic reaction during the extrusion process and reactive extrusion. PET-B and PET-T were manually combined in 90:10 and 80:20 ratios to produce PET-B/10% PET-T and PET-B/20% PET-T. Yielding a total of four distinct Pellet form samples. These pellets were produced in a micro-compounder (DSM Xplore 15 cc, Netherlands) at 280ºC and 100 rpm with a two minute residence duration.

3.1.4 Preparation of the Joncryl ADR (J) blends

The rPET blends with chain extender Joncryl ADR (J) were prepared by taking the blends created in subtopic (3.1.3)and 0.5 phr of Joncryl ADR (J) in a reactive extrusion process. These pellets were produced in a micro-compounder (DSM Xplore 15 cc, Netherlands) at 280ºC and 100 rpm with a two-minute residence duration. Two distinct pellets with chain extenders were created.

Table 3.2: Designation and formulation composition of the neat polymer and the blend.

Samples	PET-B (wt.%)	PET-T (wt.%)	J (phr)
PET-B	100	----	----
PET-T	---	100	---
10%PET-T	90	10	----
20%PET-T	80	20	----
10%PET-T+J	90	10	0.5
20%PET-T+J	80	20	0.5

* PET-B: PET wastewater bottles, PET-T: PET thermoforming clamshells, J: Joncryl ADR4468

3.1.5 Preparation of SSP (Solid State Polymerization Samples)

Each of the compositions in **Table 3.2** was placed and vacuum dried in a oven for a reaction time of 8 h in between 3-4 Pa at 220 ºC and then cooled at room temperature. The resulting samples with the samples before the solid-state polymerization were analyzed for their thermo-mechanical behavior and intrinsic viscosity.

3.1.6 Preparation of Tensile T-bones and Izod Impact Bars

The compositions from **Table 3.2** were melt processed in a micro compounder (DSM Xplore 15 cc, Netherlands) at 280ºC and 100 rpm with a two-minute residence duration. The molten composition from the extruder was then injected into a mold of T-bone and impact bar to create samples for tensile testing and Izod impact testing according to ASTM D638 and ASTM D625 in a micro-Injector at 30 ºC mold temperature and vacuum pressure of 0.8 MPa for 10 secs.

3.2 Methods

3.2.1 Intrinsic Viscosity Analysis and Molecular Weight Determination

The Intrinsic Viscosity (IV) was analyzed by the ASTM standard of D4603. The flow time for different PET blend compositions from **Table 3.2** and in subsection **3.1.6** was determined by using a (1 C Ubbelohde-Type) viscometer (Appx. constant: 0.03mm^2/s, Kinematic viscosity range: 6 to 30 mm^2/s) at 25 ± 0.2 ºC in a solution of 60/40 w/w Phenol/1,1,2,2-tetrachloroethane (Sigma–Aldrich, St. Louis, MO) solution at a polymer concentration of 0.25 g/dl. Six distinct solutions of recycled PET composition were created and tested for their flow rate. Using Bill Meyer's Relationship [5].

$$\eta = 0.25(\eta_r - 1 + 3 \ln \eta_r)/C. \qquad \text{Eq. 1}$$

Where: η = intrinsic viscosity, η_r = relative viscosity = t/t_o, t = average solution flow time (sec), to = average solvent flow time (sec), and C = polymer solution concentration, g/dL.

- All the composition of PET blends and its SSP samples are dried in vacuum condition for 2hrs at 65°C to remove any kind of moisture present in the polymer pellets.
- recycled PET composition of 0.2475 g to 2.2525 g were completely dissolved in the 25 ml solvent at 110°C to create a solution of 50 ml for each blend.
- The solution was filled in the Ubbelholde viscometer.

- The viscometer was positioned within a temperature-controlled bath set at a constant 30°C. After reaching equilibrium pull the solution to the top mark of the Ubbelohde bulb. Measure the flow time. By repeating the steps 3-4 times to get an average range.

3.2.2 Mechanical Properties

3.2.2.1 Tensile Strength Testing

Five Specimens each of T bone tensile were created for the six different compositions and their SSP pellets. Each of the specimens was kept for 48 hours at standard laboratory conditions of 23°C and 50% relative humidity after being processed in the injection molding process. To measure the tensile strength Instron model 5565 (Massachusetts, USA) having tensile grips and a load cell was used with a parameter of testing speed of 30 mm/min. the test was done according to ASTM standards D638-14 (Type V) for rigid plastic specimens. The gauge length for the specimens was 10 mm and the distance between the grip was 25 mm. The specimen is loaded between the grips and tested for the force required by the machine to stretch and break the specimen at the center [6].

3.2.2.2 Izod Impact Testing

Five Specimens each of Izod Impact were created for the Six different compositions and their SSP Pellets. Each of the specimens was kept for 48 hours at standard laboratory conditions of 23°C and 50% Relative Humidity for conditioning after being processed in the injection molding process. A Ray-Ray impact test was used to test the Izod impact for the specimens. The parameter for the hammer impact energy was 5.417J testing according to ASTMD256 standards for notched samples. The notching of 1mm was done using the notch-cutting tool TMI 22-05 (Michigan, USA). The specimen was placed vertically in between the grips in the Ray-Ray impact tester. The specimen was struck with a single swing of the hammer pendulum and the absorbed energy by the specimen was measured. The average of the Five specimens was recorded and reported in KJ/m^2 [7].

3.2.3 Thermal Properties

3.2.3.1 Differential Scanning Calorimetry (DSC)

DSC (Differential Scanning Calorimetry) was performed using a DSC Q100 Analyzer (TA Instruments, DE, USA). 6-12 mg of PET samples were sealed in hermetic aluminum pans. Each specimen was pre-conditioned at 65^{o}C for 12hr prior to testing to remove moisture. Each Recycled PET composition was examined under nitrogen of flow rate of 70 ml/min at a heating rate of 10°C/min and utilizing the heat-cool-heat cycle technique. Two replications were tested for each specimen. All samples were equilibrated at -20°C before being heated to 280 °C. The first heating cycle was performed to eliminate the thermal history of the polymer -20°C to 280°C. the cooling 280°C to -20°C was used to determine the crystallization temperature and the last heating cycle was used to determine the T_g, T_m, ΔH_m, and X_c. The characterization data were collected from the integration of the curve, and the step change formed in the cooling and second heating cycle. TA Instruments Universal Analysis 2000 version 4.5A (TA Instruments) was used to analyze the data [8].

T_m and T_c are the melting and cooling temperatures, respectively; T_g is the glass transition temperature; X_c is the degree of crystallinity; and ΔHm is the melting enthalpy.

The equation used to calculate the degree of crystallinity is given by: -

$$\%Xc = \left(\frac{\Delta \mathrm{Hm}}{(1-\emptyset) * \Delta \mathrm{Hm}^*}\right) * 100 \qquad \text{Eq.3}$$

Where Ø is the chain extender's weight percentage and ΔH_m^* is the expected melting enthalpy of 100% crystalline PET (140 J/g) [9].

3.2.3.2 Thermogravimetric Analysis (TGA)

The thermal stability and degradation analysis of the recycled PET compositions were determined from TA Q50 (TA instruments, DE, USA). Each specimen was pre-conditioned at 65ºC for 12hr prior to testing to remove moisture. All the samples weighed around 6-12 mg were characterized at 10ºC/min up to 600ºC under a nitrogen flow of 40 mL/min. The average value of two TGA is reported. TA Instruments Universal Analysis 2000 version 4.5A (TA Instruments) was used to analyze the data of the thermograms and first-order derivative thermograms curve [10].

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CHAPTER 4: RESULTS AND DISCUSSION

This chapter presents and exhibits the effect of the SSP process and the addition of a chain extender on the recycled polyethylene terephthalate blends. The rheological and thermos-mechanical properties of the recycled PET-B and PET-T blends were investigated before and after the SSP process and reactive extrusion with chain extenders.

4.1 SSP and Reactive Extrusion

The acquired bottle PET and thermoform PET were converted into pellet forms and blended into the different compositions as designated in **Table 3.2**. The blends were then exposed to form ground flakes with SSP. It was observed that due to the SSP process, the recycled polymer was stuck together after 8 h of SSP. The addition of a chain extender to the polymer helped create the non-sticking of the polymer due to SSP. Recycled polymer when processed mechanically tends to degrade and starts melting at lower temperatures and starts sticking to the other pellets of the polymer, this can happen due to the polydispersity of the polycondensation polymer [1]. The reason for caking in recycled PET blends is the chemical compounds found in the thermoform and the blend composition, which is glycol content. If there is the presence of PET-G in the thermoform trays, the glycol content in the polymer increases and decreases the melting point hence creating caking and stickiness [2]. The chain extender is used to prevent the caking and stickiness of the polymer blend pellets.

The temperature needed for the melt extrusion process was 280 ºC and the torque resistance increased when reactive extrusion was done using the chain extender suggesting an increase in the melt viscosity and the molecular weight of the polymer. The chain extender use help in the reduction of degradation during processing for the recycled PET blends and the non-sticking of the polymer blend when the SSP process is performed [3].

4.2 Characterization

4.2.1 Intrinsic Viscosity and Molecular Weight

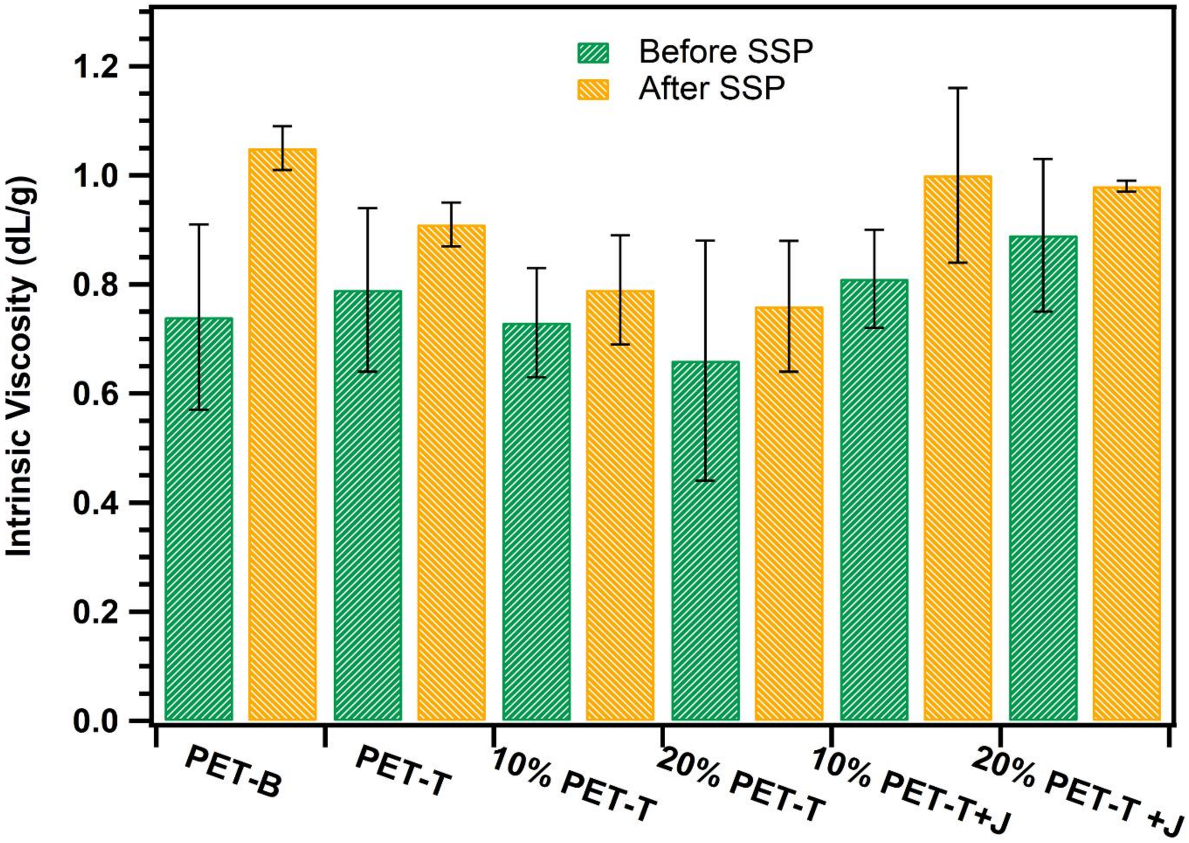

Figure 4.1: Intrinsic Viscosity of PET samples with different composition ratios PET-B and its blends.

Intrinsic Viscosity of the polymer exhibits its physical and rheological characteristics. This IV of the polymers is important for the processing of the polymer at varied temperatures and systems. The bottles and thermoform were recycled and the IV is characterized by Bill-Meyer's relationship in Ubbelohde glass capillary.

Figure 4.1 exhibits the IV of the recycled PET-B and its blends. The IV of PET-B was determined to be 0.74 g/dl. This number is consistent with the literature, which states that the IV of the pellets found in the market for PET water bottles ranges between 0.73 and 0.8 dl/g [2]. Meanwhile, virgin

PET-B exhibits IV values in the range of 0.8-0.85 dl/g, but these values drop to 0.73-0.8 dl/g during bottle manufacture due to hydrolytic degradation of PET during this process. SSP treatment of PET increased the IV to 1.05 dl/g, which was higher than before the bottle forming procedure. Prior to SSP, recycled PET-T had an IV of 0.79 dl/g, and SSP assisted in increasing the IV of PET-T to 0.91 dl/g [4]. In **Figure 4.1**, we can observe that the IV reduces and goes below (<0.73-0.8 dl/g) when the recycled PET-B and PET-T are blended in an extrusion process, this reduction in IV happens due to the thermo-oxidative degradation that takes place in the extruder processing at 280 ^{o}C when the blend pellets are created [5]. Also, the more the presence of thermoform PET in the blend pellet, the more is the reduction in IV which can be observed in 20%PET-T/PET-B, the IV reduces by 11% and reduces up to 0.66 dl/g [1].

Following that, we evaluated the IVs of PET-B samples with PET-T contents of 10 and 20% by weight. Prior to SSP treatment, a sample containing 10% PET-T had an IV of 0.73 dl/g, which was lower than the necessary IV for making PET bottles. The 10 wt %PET-T an IV of 0.79 dl/g after SSP treatment, which was extremely near to the value necessary for bottle manufacture. Similarly, before SSP, the 20 wt% PET-T system had an IV of 0.66 dl/g, which is lower than the needed IV for producing PET bottles. The 20 wt% PET-T system had an IV of 0.76 dl/g after SSP treatment, which was very near to the IV necessary for bottle manufacture (IV 0.8 dl/g) [6-7]. Even after SSP, the IV values for both the 10% and 20% PET-T samples are in the lower range of what is necessary for plastics. As a result, we chose to combine SSP therapy with chain extenders. Both the 10 wt% and 20 wt% PET-T compounds were evaluated first with a chain extender, 0.5 phr Joncryl 4468. Both demonstrated increases in their IVs to values greater than 0.8 dl/g with the addition of chain extenders, and these values rose further after the SSP therapy. For example, the 20 wt% PET-T had an IV of 0.85 after adding the chain extender, and this value climbed to nearly

1.0 after SSP treatment [8]. The findings indicate that SSP treatment may be insufficient for recycled PET with a PET-T concentration of roughly 20% by weight. On the other hand, the chain extender alone is sufficient to raise the IV over 0.8, and following SSP treatment, the values approach 1 dl/g, matching those of SSP-treated 100 wt% PET-B.

Figure 4.1 also exhibits the difference in the intrinsic viscosity before and after the process of solid-state polymerization. There is a significant increase in the IV and molecular weight in the recycled PET blends after the SSP process. It was observed that the IV increased by 10-25% for all the recycled PET compositions. It was observed that after SSP of 8hr at 220 ^{0}C tends to improve the esterification in recycled PET blends which removes the by-products group in the PET and thereby increases the IV and molecular weight. The enhancement occurs due to the crystallization of recycled PET blends at 180-190 ^{0}C for 1-2hr and the inherent viscosity tends to increase from 0.6 to 0.72dL/g after 3-5hrs, This happens due to the reduction of carboxyl content to less than 20meq/kg during SSP [1].

The addition of PET-T to the PET-B blends at a loading of 20% lowered the IV by 11% to 0.66 g/dl. **Figure 4.1** demonstrates that adding 1 phr of chain extender J to the blend increased the IV of the PET-B and its blends somewhat. In comparison to PET-B, the SSP procedure at 220 0C and integration of 0.5 phr of J increased the IV by 10-30%. The insertion of 0.5 phr of J may raise the IV of recycled PET, implying that chain extenders successfully connected various PET chains, increasing their IV (Figure 4.1).[9-11]. As shown in Figure 4.1, there was a significant enhancement in the viscosity properties of the recycled PET-B and its blends. The SSP process caused the IV values to increase by 10-25% in IV. It was observed that SSP at 220 ^{0}C for 8 h improved the esterification in PET-B and its blends and, indeed reduced the by-product groups in the PET-B and its blends and thereby increasing the IV.

4.2.2 Mechanical Properties

We evaluated their mechanical characteristics after generating desirable IV values using the chain extender alone and the chain extender combined with SSP treatment. The mechanical characteristics of PET-B, PET-T, and their mixtures are depicted in **Figure 4.2**

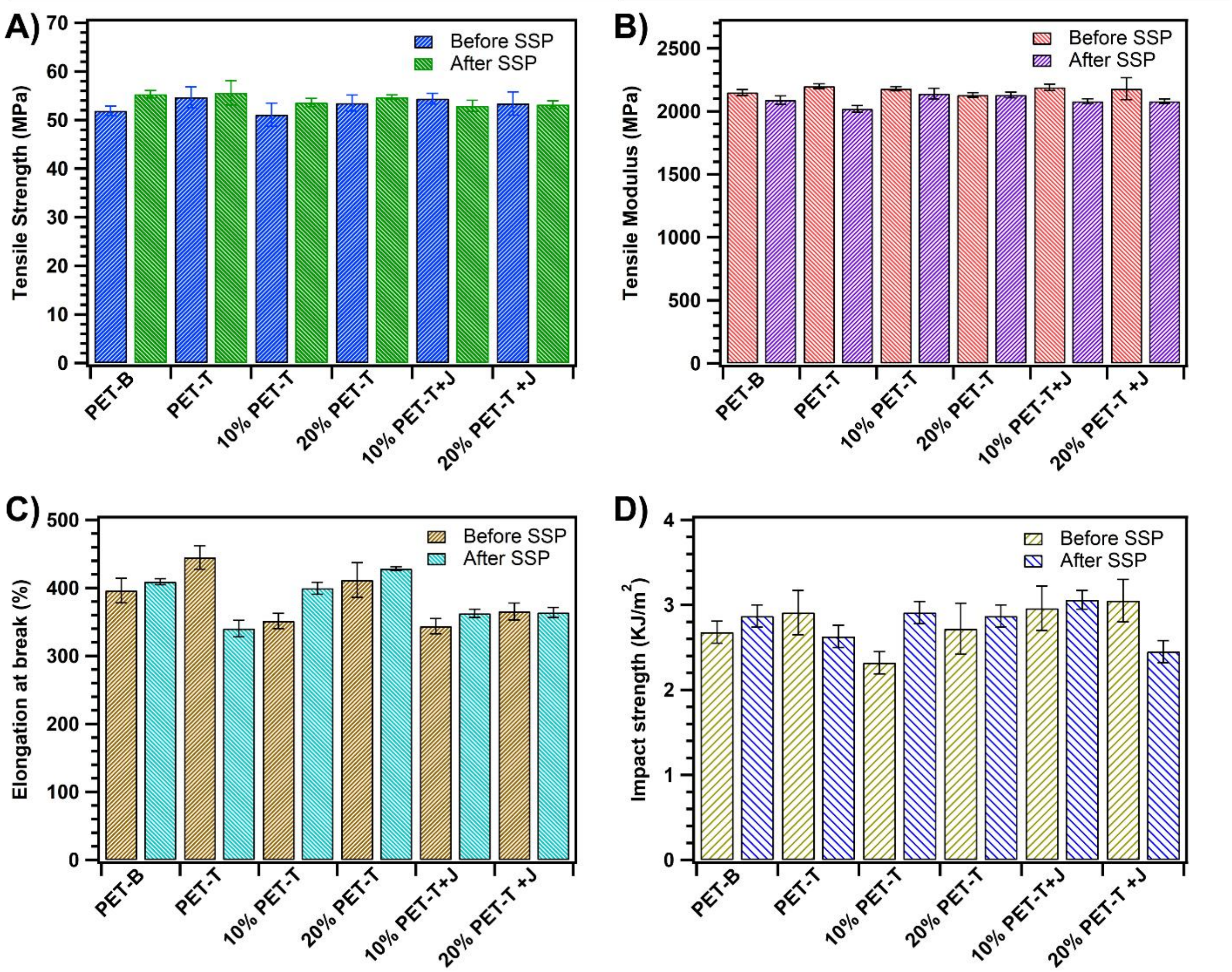

Figure 4.2: Mechanical Properties of neat PET-B, neat-T, and its blends with PET-T before and after SSP including the (A) tensile strength, (B) tensile modulus, (C) elongation at break, and (D) notched impact strength.

4.2.2.1 Tensile Properties

Figure 4.2 exhibits the mechanical characteristics namely young modulus, tensile strength, and elongation at break before the SSP process and addition of chain extender (J) and after the SSP process and reactive extrusion. The tensile properties of PET-B like tensile strength of 52 MPa and tensile modulus of 2150 MPa were observed. It was also observed that the elongation at the break of the recycled PET-B was 396%. The blending of 10% and 20% PET-T with PET-B did not have much effect on the tensile strength and tensile modulus. But it was observed that there was a slight reduction in 10% blends and then an increase in elongation at break at 20% blend. This increase in elongation is due to a reduction in the molecular weight of the polymer during the extrusion process. This can also happen due to the realignment of orientation in the crystals during the extrusion process. The reduction of M_w leads to an increase elongation at break can be observed due to the hydrolysis and transesterification process which reduces and shortens the chains of recycled PET blends during the extrusion process [12-14]. Also, we can observe that tensile strength and tensile modulus are directly proportional to the molecular weight of the polymer, which can be seen in **Figure 4.1** and **Figure 4.2** [13-15].

SSP process and chain extender tend to increase the M_w of recycled PET thereby increasing the tensile strength of recycled PET blends. The process of SSP and chain extension increases the M_w of the rPET blends. The elongation at break can be observed to be much lower after the addition of a chain extender, the reduction in elongation at break is down at least by (50-100%) elongation in 10% and 20% of PET-B/PET-T blends. This can happen due to cross-linking of chains between the chain extender (J) and the functional group of recycled PET blends [16-18].

4.2.2.2 Izod Impact

The Izod Impact test is done to calculate the impact resistance and toughness of recycled PET blends. The Izod impact of PET-B was found to be 2.8 KJ/m^2. It can be observed that with the SSP process there is a 5-10% increase in the impact resistance of the recycled PET blends. Also, the addition of chain extender (J) to 10% and 20% PET-T/PET-B blend shows a significant increase in the impact resistance of the specimens of those PET blends [19]. This can happen due to an increase in the chain length and molecular weight of the recycled PET. There is also increase in the impact resistance of the polymer [19-20]. Some anomalies that can be found in the results on Izod impact from **Figure 4.2** are that reduction of impact resistance for PET-T and 20%PET-T/PET-B added with chain extender (J) post the SSP treatment. This may have occurred due to heavy crosslinking of the polymer chain which is determinantal to the mechanical properties and thermal stability of recycled PET blends [12,20].

4.2.3 Thermal Properties

The thermal properties were determined by DSC and TGA. DSC and TGA were used to investigate the recycled PET blend processing temperature, its crystallization temperature, and its degradation temperature. These properties are extremely important for processing bottles and pellets from an extrusion machine or creating specimens from an injection molding machine.

Table 4.1: Thermal Characteristics Determined by TGA and DSC of ratios PET-B and its blends.

Sample	**TGA**		**DSC**				
	T_{10} (°C)	T_{max} (°C)	T_c (°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PET-B	400.99 (0.028)	429.95 (1.40)	204.44 (2.72)	82.71 (1.95)	244.19 (1.35)	35.68 (0.47)	25.48 (0.33)
PET-T	402.85 (0.36)	430.54 (1.06)	206.07 (0.18)	79.36 (0.23)	250.21 (0.66)	39.09 (0.22)	27.93 (0.15)
PET-B /10% PET-T	401.28 (0.66)	429.21 (0.63)	208.64 (4.67)	80.34 (1.88)	243.85 (1.68)	48.045 (2.66)	34.31 (1.90)
PET-B /20% PET-T	402.91 (1.09)	425.89 (1.58)	213.32 (1.06)	79.92 (0.24)	245.25 (0.25)	39.84 (0.61)	28.46 (0.43)
PET-B /10% PET-T+J	401.35 (1.08)	429.89 (3.12)	209.18 (0.68)	80.15 (0.05)	244.79 (0.07)	39.52 (3.03)	28.37 (2.17)
PET-B /20% PET-T +J	400.94 (1.27)	430.37 (1.12)	204.16 (6.81)	80.89 (1.21)	248.91 (0.06)	35.56 (1.35)	25.52 (0.97)
PET-B(SSP)	400.94 (1.27)	430.37 (1.43)	199.25 (4.74)	79.28 (0.30)	244.18 (1.95)	39.19 (0.72)	27.99 (0.51)
PET-T(SSP)	400.30 (0.44)	429.40 (0.92)	203.82 (1.65)	81.34 (0.52)	249.41 (0.51)	35.34 (2.23)	25.24 (1.60)
PET-B /10% PET-T(SSP)	401.58 (2.44)	429.94 (3.05)	207.85 (1.65)	81.85 (1.49)	245.13 (1.13)	38.75 (3.89)	27.68 (2.79)
PET-B /20% PET-T(SSP)	400.74 (1.66)	428.90 (0.24)	203.86 (1.48)	80.40 (0.05)	246.54 (3.52)	38.38 (3.88)	27.41 (2.76)
PET-B /10% PET-T+J(SSP)	401.85 (2.92)	430.50 (3.48)	202.89 (2.58)	82.42 (0.66)	246.00 (0.43)	37.92 (1.29)	27.22 (0.90)
PET-B /20% PET-T +J(SSP)	400.14 (1.02)	429.01 (1.38)	207.00 (2.46)	80.88 (1.21)	248.29 (1.77)	35.14 (3.27)	25.23 (3.07)

* T_m and T_c are the melting and cooling temperatures, respectively; T_g is the glass transition temperature; X_c is the degree of crystallinity; ΔH_m is the enthalpy of melting. The formula $X_c = [(\Delta H_m)/((1-Ø)\ \Delta H_m^*)]100$ was used to determine X_c, where Ø is the weight percentage of the chain extender and ΔH_m^* is the predicted melting enthalpy of 100% crystalline PET (140J/g). According to TGA measurements, T_{10} and T_{max} are the breakdown temperatures at 10% weight loss and the maximum derivative peaks, respectively.

4.2.3.1 Differential Scanning Calorimetry (DSC)

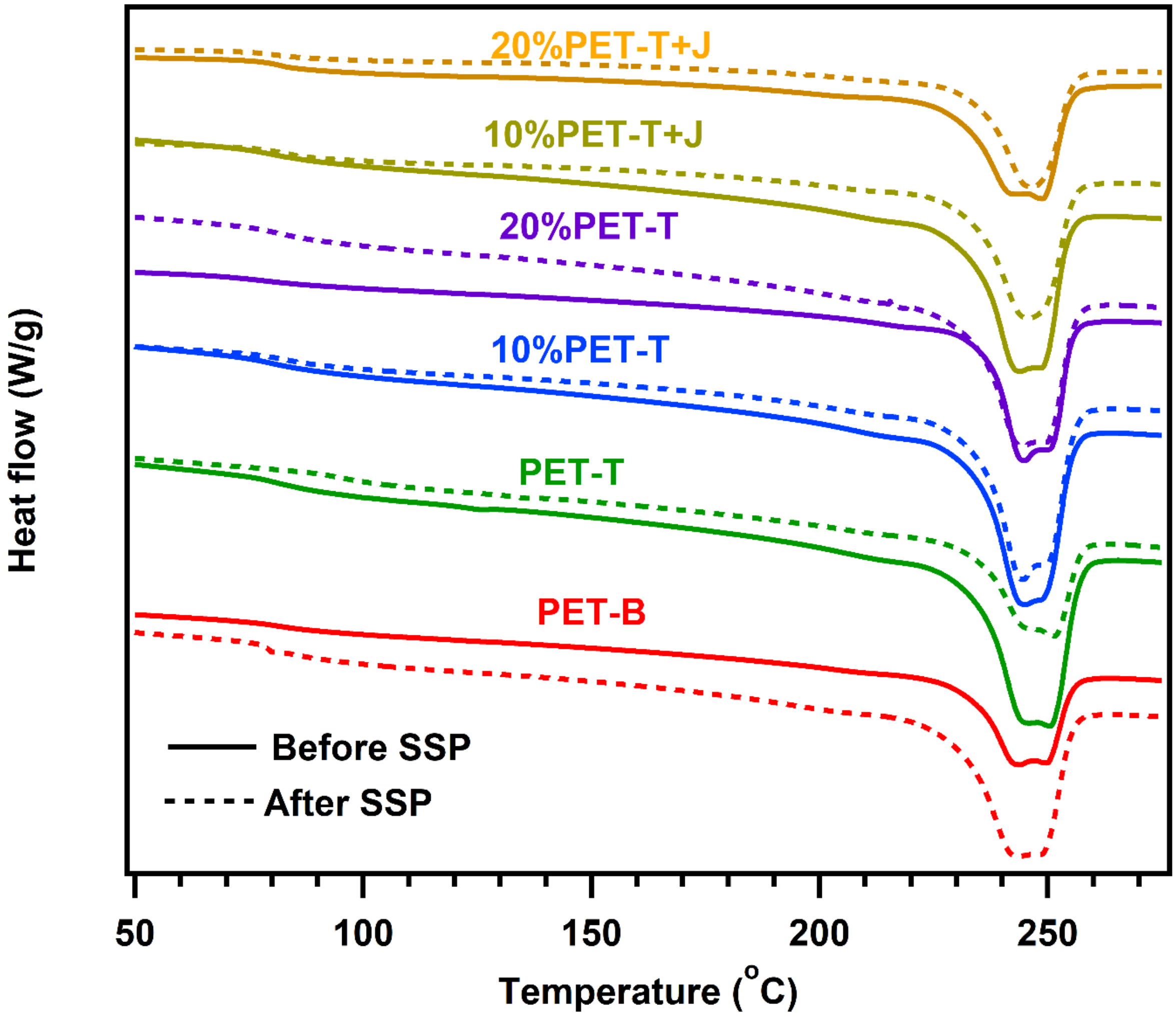

Figure 4.3: DSC 2^{nd} heating curve of PET-B, PET-T and PET-B/PET-T blends.

The glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature. (T_c) of the recycled blend composition were measured and analyzed with DSC. DSC helped in establish the miscibility of the blend. **Figure 4.3** and **Table 4.1** illustrate the second heating cycle and cooling cycle of the recycled PET blends. There was no significant change in the T_g and T_m of the recycled PET blend pellets before and after the SSP process [21-22]. The addition of a chain extender helped reduce the processing temperature by 1°C. We observed that the melting temperature T_m for PET-T is higher than the rest of all recycled PET compositions. The heating cycle was found to be in the range of 244-250°C. The T_g of all the samples was between 79-83°C. **Figure 4.3** showed two melting peaks. This may be due to the restructuring of the crystals during the heating cycle due to the higher molecular weight present due to the addition of a chain extender in the blend samples [23].

We can observe a reduction in the melting temperature of recycled PET blend and its compositions after the SSP process. Which may be due to the SSP process at higher temperatures raising the melting point of the final polymer. But we see a shift towards lower temperature, this may be due to heavy cross-linking of the polymer during SSP and reactive extrusion with chain extender, making the polymer requires less energy and less temperature to break the chain and create a melt flow during extrusion [24-25].

We also observed that the crystallization temperature for PET-B is 204.4°C. The study discovered that employing the SSP procedure requires less heat and takes less time to crystallize PET-B. Furthermore, the heating curve shows that as molecular weight increases, chain-extending PET's crystallinity decreases significantly. This is because, given the same crystallization setting, the molecular weight is more, and the melt viscosity is greater. As a result of the crystallization setting the aligning links often form a highly ordered lattice, which is easier to break. As less energy is required to break the lattice during melting, we observed that the melting peak moves to a lower temperature as crystallinity decreases [26]. Also, it can be observed that during the reactive extrusion, the polymer chains tend to reorganize and form crystals reducing the branching in the chains and increasing the M_w with the addition of a chain extender which decreases the T_c of the polymer [10-11,25].

4.2.3.2 Thermogravimetric analysis (TGA)

The Thermal Stability of the recycled PET blends was measured using TGA and was listed in **Table 4.1**. **Table 4.1** depicts the degradation temperature of the recycled PET blends. As observed, the thermograms for all the recycled PET blends were similar and the thermal stability of all the polymer blends remained intact till the range of (425-430°C). There was no significant variation in the thermal stability of recycled PET blends even after the SSP process and the addition of the chain extender. As the thermal degradation temperature is higher than the degradation temperature of recycled PET-B and recycled PET-T we can say that the polymer will not degrade while processing.

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CHAPTER 5: CONCLUSION AND FUTURE WORK

5.1 Conclusion

In conclusion, we have shown that blends of PET-B with 10-20 wt% PET-T content may be recycled back to bottle-grade PET. Among the three studied techniques, chain extension and the combination of chain extension with SSP completely recovered the desired inherent viscosity values for PET-B blends containing 10-20 wt% PET-T.

The SSP process was used to enhance the intrinsic viscosity (IV) of the polymer blends.

Through the implementation of solid-state polymerization (SSP), the polymer's chain extension was enhanced, leading to a diminished level of degradation during the treatment of PET blends using processes like extrusion and injection molding. The IV of the recycled blends was increased by 0.05-0.3 dl/g. Meanwhile, the tensile strength has increased by 5-10% after SSP and the tensile strength had also increased. The Izod impact strengths of the PET-B/PET-T blends containing 10 and 20 wt% PET-T had increased by 0.5 and 0.2 kJ/m^2, respectively. This increase in overall impact strength can be attributed to the SSP process.

In this study, a chain extender was employed to improve the thermal stability of the polymer and enhance the melt processability of recycled PET in the extrusion procedure. The application of the chain extender Joncryl ADR (J) within the reactive extrusion process mitigated the degradation of recycled PET while elevating molecular weights. The addition of J enhanced the polymer’s viscosity and thermos-mechanical properties. The addition of J to the 10 and 20 wt% PET-B/PET-T blends enhanced the IV by 0.82 and 0.86 dL/g, respectively, which indicates that the M_w of the polymer blend had increased after the implementation of the chain extender. TGA and DSC data showed that the chain extension and SSP treatment did not have much of an impact on the recycled

PET blend's thermal characteristics. The thermal characteristics were like that of a 100% recycled PET material.

The hypothesis was thus proven, demonstrating an elevation in IV, it was shown that the incorporation of the chain extender and subsequent SSP process led to improvements that could be applied for bottle production. This investigation also confirmed our hypothesis that there would be no degradation in the thermomechanical characteristics of the rPET blends made from the reactive extrusion process and via SSP pre-processing. This project will help create a streamlined system in which post-consumer PET bottles and PET thermoforms can be recycled together to create 100% recycled bottles from these blends, thus creating a bottle-bottle recycling system and reducing landfilling and reducing the need for a separate recycling process to handle thermoform PET.

5.2 Future Work

The research provided insight into improving the IV values and thermal characteristics of rPET blends of PET-B and PET-T using chain-extension and a SSP process. There are a few points that can be considered for further research in more depth in characterizing the polymer blend material. UV-visible spectroscopy can be employed to analyze the polymer blend for color presence and assess material transparency, facilitating the potential use of recycled material for producing clear bottles. However, it's important to note that this study didn't verify the material's barrier properties, a crucial factor in practical applications. Hence, evaluating the PET blends for oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) would be valuable. In addition, the performance of the recycled PET blend pellet should be compared with those of commercially available recycled pellets in a future investigation. Also, the homogeneity of the blends can be verified by visual inspection and microscopic analysis.