

ALTERNATIVE METHODS OF USING GLYCIDOL-FREE AS FOOD-SAFE CHAIN
EXTENDERS FOR POST-CONSUMER PET BOTTLES AND PET THERMOFORM BLENDS

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ABSTRACT

The accumulation of plastics such as poly (ethylene terephthalate) (PET) in landfills and oceans poses a significant environmental threat. Chain extenders can help to divert post-consumer PET from landfills to manufacturing. However, the current chain extenders are glycidol-based with toxicity concerns. This thesis work aims to develop non-toxic, glycidol-free chain extenders for post-consumer mixed bottle-grade PET (PET-B) and thermoform PET (PET-T). In one project, a new chain extender, mono epoxy styrene (MES), is used to enhance the rPET characteristics such as rheological, mechanical, and thermal. The incorporation of chain extenders in varying proportions showed significant improvement in intrinsic viscosity, along with an improvement in impact properties. In another project, glycidol- and styrene-free epoxy acrylate chain extenders with terminal (PEAT-BA) and internal (PEAI-BA) epoxy groups were tested in PET-B/PET-T blends, and improvements in the mechanical, rheological, and thermal properties better than the commercial chain extender Joncryn ADR (J) were observed. This research will promote the utilization of recycled PET, potentially reducing greenhouse gas emissions by 50%, decreasing landfilling, and protecting the environment from microplastic pollution.

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LIST OF ABBREVIATIONS

PET	Polyethylene terephthalate
PET-B	Bottle grade Polyethylene terephthalate
PET-T	Thermoform grade Polyethylene terephthalate
CE	Chain Extender
IV	Intrinsic Viscosity
PES	Mono-epoxy styrene
PEAT	Epoxy acrylate-based terminal chain extender
PEAI	Epoxy acrylate-based internal chain extender
rPET	Recycled Polyethylene Terephthalate
APET	Amorphous Polyethylene Terephthalate
BPET	Biaxially Oriented Polyethylene Terephthalate
CPET	Crystalline Polyethylene Terephthalate
OPET	Oriented Polyethylene Terephthalate
BA	Butyl Acrylate
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
T _g	Glass transition temperature
T _m	Melting temperature

CHAPTER 1: INTRODUCTION

1.1 Introduction

Polyethylene terephthalate (PET) is a widely used plastic because it offers desirable characteristics such as optical properties, mechanical strength, and good moisture and gas barrier properties¹. Additionally, PET offers a high strength-to-weight ratio and is widely applicable in various fields, including packaging, engineering, and biomedical applications². As a result, PET accounts for 60 percent of the global plastics market. According to a study published in the Journal of Cleaner Production, PET recycling rates have seen a steady increase, with global recycling rates reaching approximately 31% in recent years. Another report in Polymer Chemistry Material advances³ (2022) highlighted that over 60 million tons of PET waste are produced annually⁴.

PET-B bottles are differently processed as compared to thermoform PET (PET-T). PET-B bottles have lower viscosity and more suitable for the injection molding to make parison and then blown stretched to make bottle⁵. While PET-T thermoforms have high viscosity, less crystalline materials are shaped into packing structures via thermoforming process. This process involves use of sheet of PET subjected to temperature to shape in or around a mold. Hence it can be said that PET-B bottles have lower intrinsic viscosity and crystallinity as compared to the PET-T thermoform containers.

The label adhesives used on thermoform containers made of PET-T are found to be more abrasive in nature than as compared to bottle surface due to adhesive content in release liner of the label substrate. This creates complexity while removing the label from the thermoform substrate and is finally prone to be contaminated because of incomplete removal of adhesive residue from the substrate of PET-T container.

A key challenge with PET (PET-T, PET-B) recycling is that these are made of ester linkages, which are prone to hydrolysis. Due to this hydrolytic degradation, PET loses its desired properties, such as a decrease in IV and mechanical properties, an increase in melt-flow and crystallinity is observed.⁶ To overcome this challenge, mechanical recycling (secondary recycling) relies on various strategies such as chain extenders, solid-state polymerization (SSP), and/or blending with virgin PET. For example, Ma et al. reported an increase in PET Mw via SSP (solid state polymerization process), which leads to direct enhancement of the intrinsic viscosity of PET. Solid state polymerization boosts the molecular weight of PET by facilitating additional polymerization reactions at reduced temperatures, thereby reducing thermal degradation and promoting the formation of longer polymer chains⁷.

This thesis focuses on the use of chain extenders for increasing the molecular weights and IV of PET-B and PET-T. Here, two broad categories of novel chain extenders were incorporated in the reference blend, namely glycidol-free chain extender (PES) (mono-epoxy styrene-based chain extender) another chain extender free of glycidol and styrene content, namely PEAT (terminal epoxy acrylate) and PEAI (Internal epoxy acrylate). Chain extension technique was used to enhance the rheological, mechanical and thermal properties of the reference blend (PET-B/20%PET-T) which were examined⁸.

1.2 Objectives

The prime objective of this research is focused on developing food-safe glycidol-free chain extenders for PET-B and PET-T blends.

This research comprises two main PET aspects.

Objective 1: Investigate the impact of novel mono-epoxy styrene-based, a glycidol-free chain extender, in post-consumer PET-B and PET-T blends on their rheological, mechanical, and thermal properties.

Objective 2: Investigate the effect of novel glycidol and styrene-free novel chain extenders in post-consumer PET-B and PET-T blends on their rheological, mechanical, and thermal properties.

1.3 Scope of Research

- Creation of PET-B and PET-T blends were formed from post-consumer feedstock
- Several glycidol-free chain extenders are investigated in PET-T and PET-B blends
- ADR is used as a commercial benchmark
- The effect of new chain extenders on the rheological, mechanical, and thermal properties of PET-T and PET-B blends are tested.

1.4 Overview of Research Projects

This section represents a pictorial overview of my research project. First objective represents incorporation of glycidol free chain extender in reference blend of PET (as below): To understand the effect and implications of newly prepared chain extender in recycled PET blend was studied on three different types of weight% proportions of PES (mono-epoxy styrene) chain extender such as 5%, 10% and 20% weight respectively. Addition of 5% weight of PES (i.e., PES5-BA) led to enhancements in mechanical properties such as tensile strength by 4.66%, 20% increase in %elongational properties of blend and 30% increase in impact strength of the reference sample, even surpassing the Joncryl ADR chain extender. The addition of PES10-BA (10% weight) led to enhancement by 7.65% in tensile strength and 10.75% increase in % elongation. All the thermal

graph of respective proportions showed the same trend without any variations which confirms it to be thermally stable chain extender blended samples.

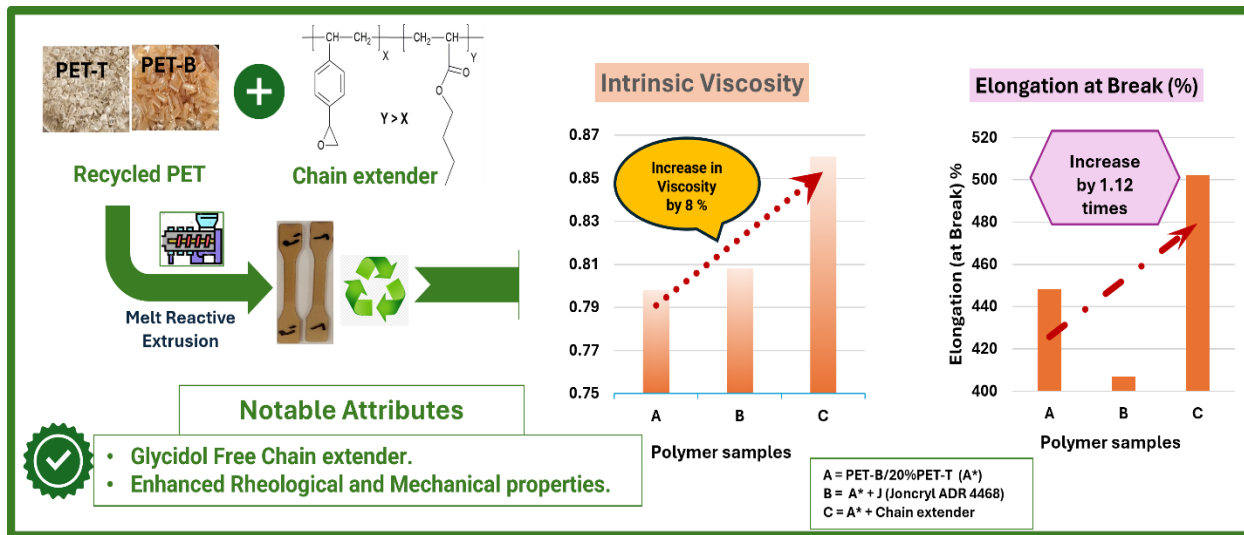


Figure 1.1: Graphical and Pictorial representation of Objective 1.

Second objective represents incorporation of glycidol and styrene free chain extender in reference blend of PET (as below):

Incorporation of glycidol and styrene free chain extender namely PEAT and PEAI in reference blend PET-B/20%PET-T led to enhancement in rheological, Mechanical and thermal properties as depicted in pictorial representation in **Figure 1.2** below. Addition of PEAI20-BA chain extender enhanced the molecular weight of the reference blend by 6.04% (59.70 k Da) as compared to reference blend having 56.30 k Da. Increase in molecular weight has much more significant value when it comes down to processing of the blend for manufacturing of final consumer-end products, while along with minimal increase of tensile strength by 2.88% and drastic increase in impact strength by 32.42%. Furthermore, incorporation of PEAT20-BA terminal chain extender has surpassed PEAI20-BA in tensile strength leading to 8.8% increase along with 9.45% in modulus

of elasticity and 25.4% increase in impact strength than reference blend. PEAT20-BA terminal chain extender has also surpassed commercially available joncryl ADR leading to 12.6% increase in impact strength and 6.4% increase in tensile strength. Hence making it a preferred choice for it improving the recycled PET blend.

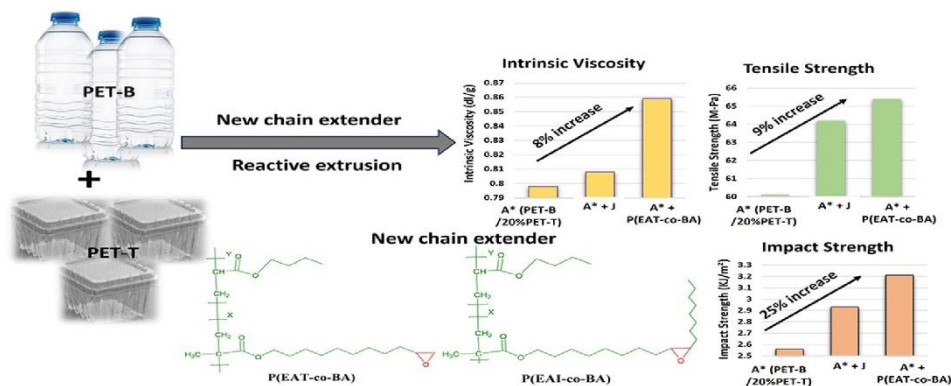


Figure 1.2: Graphical and Pictorial representation of Objective 2.

1.5 Structure of Thesis Project

This thesis is mainly divided into Five main chapters as designated below:

Chapter 1 - Introduction, objectives, scope of research, and overview of research projects.

Chapter 2 - Literature review on PET, its application in packaging industry, types of recycling techniques, processing techniques, chain extenders and its implications in PET polymer.

Chapter 3 - Materials and Methodology used in this research.

Chapter 4 - Results and Discussions from this research

Chapter 5 – Summary and Future Outlook

CHAPTER 2: REVIEW OF LITERATURE

2.1 Polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is a versatile polymer widely used in various applications due to its excellent physical and chemical properties. As a type of polyester, PET is known for its high strength, durability, and resistance to moisture and chemicals⁹. These characteristics make it suitable for packaging materials, especially in the food and beverage industry where it is commonly used to produce bottles and containers. The recyclability of PET makes it a favored choice, contributing to environmental sustainability efforts. Its optical clarity and ability to mold into different shapes also make it a popular choice in the textile industry, where it is spun into fibers for clothing and other fabrics. The combination of these attributes has established PET as a crucial material in modern manufacturing and everyday products.

Polyethylene terephthalate (PET) polymer has a rich history that dates to the early 20th century. The development of PET began in 1941 when British chemists John Rex Whinfield and James Tennant Dickson, working for the Calico Printers' Association, patented the polymer¹⁰. They discovered PET while attempting to create new synthetic fibers, and their invention marked a significant advancement in polymer chemistry. Initially, PET was used to produce synthetic fibers, which quickly gained popularity due to their strength, durability, and resistance to shrinking and stretching.

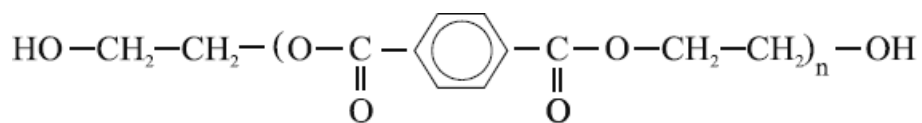
In the 1970s, the use of PET expanded significantly with the advent of PET bottles. The American company DuPont played a crucial role in this development by introducing PET as a material for beverage containers¹¹. The introduction of PET bottles revolutionized the beverage industry, providing a lightweight, shatter-resistant alternative to glass. This innovation not only improved

safety and convenience for consumers but also reduced transportation costs for manufacturers due to the lighter weight of PET bottles compared to glass.

The widespread adoption of PET in packaging led to further innovations and applications. In the 1980s and 1990s, advancements in PET recycling technology emerged, allowing for the reuse of PET materials and promoting environmental sustainability. Recycled PET (rPET) began to be used in various applications, including clothing, carpeting, and new packaging materials. This recycling capability significantly enhanced the appeal of PET as a sustainable choice, aligning with growing environmental awareness and regulatory pressures¹².

Today, PET remains one of the most widely used and versatile polymers in the world. Its applications extend beyond packaging and textiles, including parts in the automotive and electronics industries. Ongoing research and development efforts continue to enhance PET's properties and processing techniques, ensuring its relevance and utility in a wide array of modern applications. PET's history is a testament to its adaptability and enduring value in both consumer and industrial markets.

2.2 Chemical Structure and Properties of PET



Polyethylene terephthalate

Figure 2.1: Chemical structure of PET.

PET is made of ethylene glycol and terephthalic acid/ester repeating units as shown in Fig. 2.1. Its structure is characterized by its ester linkages, formed through a condensation/transesterification reaction between these monomers. Each repeating unit in the PET chain consists of one glycol unit

and one terephthalic acid unit, creating a long linear chain¹³. This linear structure contributes to the polymer's strength and crystallinity, making it highly durable and deformation resistant.

PET exhibits a semi-crystalline nature, which means it contains both amorphous (non-crystalline) and crystalline regions. The crystalline regions are responsible for their high tensile strength and thermal stability, while the amorphous regions provide flexibility and impact resistance. This unique combination of properties allows PET to be easily processed into various forms, including fibers, films, bottles and containers^{11, 13}, while maintaining its desirable mechanical and chemical characteristics. The arrangement of the polymer chains and the degree of crystallinity can be controlled during the manufacturing process to tailor the material's properties for specific applications in packaging.

Polyethylene terephthalate (PET) is renowned for its impressive array of properties, making it one of the most versatile and widely used polymers today. One of its key attributes is its high tensile strength, which ensures durability and resistance to breaking under tension. This strength is complemented by its excellent dimensional stability, meaning PET maintains its shape and size under various conditions, including exposure to heat and mechanical stress. Its toughness and resilience make it ideal for applications requiring robust material.

Another significant property of PET is its resistance to moisture and most chemicals, including acids, alkalis, and organic solvents¹⁴. This chemical resistance makes it particularly suitable for packaging applications, especially in the food and beverage industry, where it effectively protects contents from contamination and spoilage. PET's low permeability to gases and liquids further enhances its suitability for packaging, ensuring long shelf life for perishable products. Additionally, PET is known for its excellent optical properties, including clarity and transparency, which make it an attractive choice for products where visibility of the contents is important.

The recyclability of PET makes it a favored choice, contributing to environmental sustainability efforts. It can be efficiently recycled into new PET products or repurposed for other uses, such as fibers for textiles and carpeting. The recyclability of PET helps reduce waste and the demand for raw materials, contributing to a circular economy. Moreover, PET's lightweight nature reduces transportation costs and energy consumption, adding to its environmental benefits. These properties collectively highlight PET's versatility and importance across various industries, from packaging and textiles to automotive and electronics.

2.3 Types of PET used in the packaging industry

In the packaging industry, several types of PET polymers are employed, tailored to meet specific requirements. Amorphous PET (APET) is commonly used for its clarity and excellent barrier properties, making it ideal for packaging fresh produce, bakery items, and other food products that benefit from visible presentation. Crystalline PET (CPET) is heat-resistant and often used in microwaveable and oven-able trays due to its ability to withstand high temperatures without deforming. Additionally, biaxially oriented PET (BOPET) offers high strength, gas and moisture barrier, chemical resistance, and excellent optical properties, making it suitable for a wide range of applications including flexible food packaging, labels, and protective films. Each type of PET provides unique advantages that cater to the diverse needs of the packaging industry, emphasizing both functionality and sustainability. Detailed types of PET polymer as below:

Amorphous PET (APET):

Amorphous Polyethylene Terephthalate (APET) is a type of PET characterized by its non-crystalline transparent structure. Unlike its crystalline counterpart, APET does not have a rigid organized molecular arrangement, which grants it exceptional clarity and gloss. This transparency is a significant advantage in packaging applications where product visibility is essential, such as in food containers, clamshell

packaging, and display trays. The amorphous nature of APET also provides good barrier properties against gases and moisture which helps to extend the shelf life of perishable products. Additionally, APET is known for its excellent impact resistance and toughness, to ensure that packaged goods are well-protected during handling and transportation¹⁵.

APET's versatility extends to its ease of processing and thermoforming capabilities. It can be efficiently molded into various shaped packaging containers of different sizes, making it ideal for creating custom packaging solutions tailored to specific product dimensions and designs. The material's ability to maintain structural integrity under different temperature conditions adds to its appeal, as it can endure the demands of both refrigerated and ambient storage. Moreover, APET is fully recyclable, aligning with increasing consumer and industry demand for sustainable packaging options. Its recyclability does not only help in reducing plastic waste but also conserve resources by enabling the production of new APET products from recycled materials. Overall, APET's combination of clarity, durability, and recyclability makes it a preferred choice in the packaging industry.

Crystalline PET (CPET):

Crystalline Polyethylene Terephthalate (CPET) is a form of PET that is partially crystallized giving it unique properties suitable for specific applications. Unlike Amorphous PET (APET), CPET has a semi-crystalline structure that provides it with higher thermal stability and the ability to withstand elevated temperatures¹⁶. This makes CPET particularly well-suited for applications such as microwaveable food trays, where the material is needed to maintain its shape and structural integrity under high temperatures. The crystalline regions within CPET contribute to its rigidity and strength, while also providing excellent barrier properties against gases and moisture, which ensures the preservation and protection of food products during storage and heating.

The production of CPET involves a process like that of other PET materials but includes a critical annealing step that promotes crystallization. During this process, the PET polymer is heated to a specific temperature range between 250°C to 280°C that encourages the alignment of its molecular chains into a crystalline structure. This controlled crystallization process is essential to achieving the desired thermal and mechanical properties of CPET^{16, 17}. Additionally, the material's ability to be thermoformed allows manufacturers to produce a variety of shapes and sizes, which caters to diverse packaging needs. CPET's recyclability further adds to its appeal, as it can be reprocessed and used in new products that support environmental sustainability efforts. Overall, CPET's enhanced thermal resistance, strength, and versatility make it an invaluable material in the packaging industry, particularly for applications requiring durable and heat-resistant containers¹⁸.

Oriented Polyethylene Terephthalate (OPET):

Oriented Polyethylene Terephthalate (OPET) is produced by stretching PET in both the machine and transverse directions and aligns the polymer chains to enhance its strength and clarity¹⁹. This biaxial orientation process significantly improves OPET's tensile strength and dimensional stability, making it suitable for applications requiring durable and high-performance materials. OPET exhibits excellent barrier properties against gases and moisture, which is crucial for food packaging, maintaining product freshness and extending shelf life¹⁹. Additionally, its superior optical properties, including high transparency and gloss, make OPET a preferred choice for packaging that showcases the product inside. The material's versatility and enhanced performance characteristics have made it a staple in the packaging industry²⁰.

Recycled PET (rPET):

Recycled Polyethylene Terephthalate (rPET) is produced by processing used PET materials, such as bottles and packaging in new PET products. The recycling process involves collecting, cleaning,

and shredding the waste PET into small flakes, which are then melted and reformed into rPET pellets²¹. These pellets can be used to manufacture a wide range of products, including new bottles, containers, and textile fibers. rPET retains the desirable properties of virgin PET, such as strength, clarity, and chemical resistance, while significantly reducing the environmental impact by lowering the demand for raw materials and minimizing plastic waste. The use of rPET supports sustainability initiatives and contributes to a circular economy by enabling continuous reuse of PET materials.

Biaxially oriented PET (BOPET):

Biaxially Oriented Polyethylene Terephthalate (BOPET) is manufactured by stretching PET film in both the machine and transverse directions, which aligns the polymer chains and enhances its strength, clarity, and barrier properties²². This orientation process results in a material that is highly resistant to stretching and tearing makes an ideal for applications which requires durable and reliable packaging. BOPET's excellent gas and moisture barrier capabilities are crucial for preserving the freshness and quality of food products²³. Additionally, its superior optical properties, such as high transparency and gloss, make it an attractive choice for packaging and labeling. BOPET's versatility extends to its use in various industries, including electronics, where it serves as an insulating material, and in solar panels, where it enhances efficiency.

2.4 Plastic Recycling

Plastics are recycled using one of four methods: primary recycling, secondary recycling, tertiary recycling, and quaternary recycling. Primary recycling refers to the mechanical recycling of post-industrial plastics, while secondary recycling refers to the mechanical recycling of post-consumer plastics, and the latter involves washing and cleaning steps. After cleaning, plastic is shredded and melted to form pellets. Chemical recycling/tertiary recycling, which breaks down polymers into

their monomers such that these monomers can be reused for new plastics; and quaternary recycling/energy recovery wherein plastics are incinerated to produce energy. Each recycling method has its advantages. For example, mechanical recycling is straightforward and cost-and energy-effective, while chemical recycling can handle a wider range of plastics and improve material purity. These recycling methods collectively contribute to reducing plastic waste, conserving resources, and minimizing environmental impact.

2.4.1 Recycling of PET

Recycling of PET is done using both chemical and mechanical methods, which are described below:

2.4.2 Mechanical Recycling

Mechanical recycling of PET involves the process of collecting, sorting, and reprocessing post-consumer PET materials, such as bottles and packaging, to produce new PET products. The first step in this process is the collection of used PET items from recycling bins and collection centers. These items are then sorted to remove any contaminants or other ancillary materials such as labels, tamper-bands, caps etc. if any. Once they are sorted, then the PET is cleaned to ensure that all residues, labels, and impurities are removed. The cleaned PET is then shredded into small flakes. These flakes undergo further washing and drying to prepare them for reprocessing²⁴. The dried flakes are melted and extruded into pellets, which serve as the raw material for manufacturing new PET products. This process helps reduce the reliance on virgin PET and conserves resources.

The quality of the recycled PET (rPET) depends largely on the thoroughness of sorting and cleaning stages. Mechanical recycling of PET is advantageous because it maintains the material's intrinsic properties, such as strength and clarity which makes rPET suitable for a wide range of applications, including new bottles, fibers for textiles, and packaging materials^{12, 25}. One of the

significant benefits of mechanical recycling is its contribution to environmental sustainability by diverting plastic waste from landfills and reducing the carbon footprint associated with producing virgin PET. However, repeated recycling can degrade the quality of PET, which is why mechanical recycling is often combined with chemical recycling techniques to enhance the overall efficiency and sustainability of PET recycling.

A. Ancillary Process

The cleaning process in the mechanical recycling of PET is crucial for ensuring the quality and purity of the recycled material. After the PET is collected and sorted, it undergoes an initial wash to remove surface dirt and residues. This is followed by a more thorough cleaning process, which typically involves several stages. The PET flakes are placed in hot water baths combined with detergents and friction washing to eliminate any remaining labels, adhesives, and contaminants. The use of high temperatures helps dissolve and remove oils and residues that may be clinging to the plastic. In addition, advanced washing systems may employ ultrasonic waves or chemical solvents to ensure that even the smallest particles of contamination are removed from the PET flakes²⁶.

Once the PET flakes are thoroughly cleaned, they are dried to remove any remaining moisture, which is essential for maintaining the integrity of the material during the melting and extrusion phases. The drying process usually involves the use of dehumidifying dryers that reduce the moisture content of the PET flakes to a very low level. This is achieved by passing the flakes through a series of heated air streams or vacuum systems that effectively evaporate and extract the water. Ensuring the flakes are completely dry prevents hydrolytic degradation during reprocessing, which can weaken the polymer chains and affect the quality of the recycled PET. This meticulous

cleaning and drying process is vital to produce high-quality rPET that meets industry standards for use in new products⁸.

B. Pelletization using Extrusion process

In the mechanical recycling of PET, the extrusion process begins once the PET flakes are thoroughly cleaned and dried. The dried flakes are fed into an extruder, which is a machine consisting of a long barrel with a rotating screw inside. As the screw turns, it moves the PET flakes forward through the barrel. The barrel is heated, causing the PET flakes to melt as they progress. The temperature and speed are carefully controlled to ensure the PET melts uniformly without degrading. As the molten PET moves through the extruder, it is filtered to remove any remaining impurities to ensure a high-quality product²⁷.

After filtering, the molten PET exits the extruder through a die, shaping it into long, continuous strands. These strands are then cooled, typically in a water bath, to solidify the PET. Once cooled, the strands are cut into small pellets, which are known as rPET pellets. These pellets can be used as raw material for manufacturing new PET products which includes bottles, packaging, and fibers. The extrusion process is crucial for transforming recycled PET flakes into a form that can be easily processed and utilized in various applications, contributing to a more sustainable cycle of PET usage.

C. Introduction to Chain extender (CE)

Polyethylene terephthalate (PET) is a widely utilized polymer, known for its application in fibers, bottles, and various packaging materials due to its strength, thermal stability, and clarity. However, during polymer processing, PET can undergo degradation, leading to reduced molecular weight and mechanical properties. To address this issue, chain extenders are introduced. These additives react with the end groups of degraded PET chains, effectively rebuilding the polymer network and

restoring its properties. By reconnecting the broken chains, chain extenders play a crucial role in maintaining the integrity and performance of PET products.

The use of chain extenders in PET not only helps in recovering its mechanical ²⁸and thermal properties, but also enhances its processability. Common chain extenders for PET include multifunctional epoxy compounds, carbodiimides, and Poly carbodiimides. These substances react with the hydroxyl and carboxyl end groups in the polymer, forming strong covalent bonds that increase the molecular weight and viscosity of PET. This chemical reinforcement allows PET to be reused and recycled more efficiently contributes to sustainability in plastic manufacturing and reducing environmental impact²⁹.

In practical applications, the selection of a suitable chain extender depends on the specific requirements of the PET product, such as desired mechanical strength, thermal resistance, and processing conditions³⁰. For instance, epoxy-based chain extenders are preferred for their compatibility and efficiency in various processing environments, whereas carbodiimide-based extenders are favored for their superior performance in high-temperature applications. The correct application of chain extenders thus ensures that PET retains its desirable attributes, which makes it a versatile and reliable material for a wide range of industrial applications.

D. Introduction to commercial chain extender Joncryl (J)

Joncryl ADR is a widely recognized commercial chain extender used in the polymer industry to enhance the properties of various thermoplastics, including polyethylene terephthalate (PET). This multifunctional epoxy-based additive is specifically designed to react with the terminal functional groups of degraded polymers, thereby increasing their molecular weight and improving their mechanical and thermal properties. Joncryl ADR is particularly effective in restoring the

performance of recycled PET which makes it a valuable component in the sustainable production and recycling of plastic materials.

Table 2.1 Technical Specification data of Joncryl® ADR 4468.

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

One of the key advantages of Joncryl ADR is its ability to efficiently react with both hydroxyl and carboxyl end groups in PET. This reactivity allows it to form stable covalent bonds, effectively "healing" the polymer chains that have been broken down during processing. As a result, the use of Joncryl ADR leads to a significant increase in the melt viscosity and strength of PET and enables manufacturers to produce higher quality products with enhanced durability and performance.

In addition to its reactivity, Joncryl ADR offers excellent processability and makes it suitable for a wide range of industrial applications. It can be easily incorporated into standard extrusion and injection molding processes without requiring significant modifications to existing equipment. This flexibility is particularly beneficial for manufacturers looking to improve the properties of recycled PET, as it allows them to seamlessly integrate Joncryl ADR into their production lines and achieve consistent results.

The use of Joncryl ADR also supports environmental sustainability by facilitating the recycling of PET. By restoring the mechanical and thermal properties of degraded PET, Joncryl ADR enables

the production of high-quality recycled materials that can compete with virgin PET. This not only reduces the need for new plastic produce but also helps minimize plastic waste and its impact on the environment. Thus, Joncryl ADR plays a crucial role in promoting a circular economy in the plastics industry, where materials are continuously reused and recycled to create new products.

E. Effect of Commercial Joncryl ADR on PET in general

The addition of commercial Joncryl ADR to PET significantly enhances the material's properties. By acting as a chain extender, Joncryl ADR reacts with the terminal end groups of the PET molecules which leads to increased molecular weight and improved polymer chain integrity. This results in enhanced mechanical properties, such as greater tensile strength and impact resistance. Additionally, the thermal stability of PET is improved, making it more suitable for high-temperature applications. The overall processability of PET is also enhanced, as the increased viscosity allows for better flow during extrusion and molding. Consequently, incorporating Joncryl ADR into PET not only restores degraded polymers, but also extends the lifespan and performance of recycled PET materials and contributes towards more sustainable manufacturing practices.

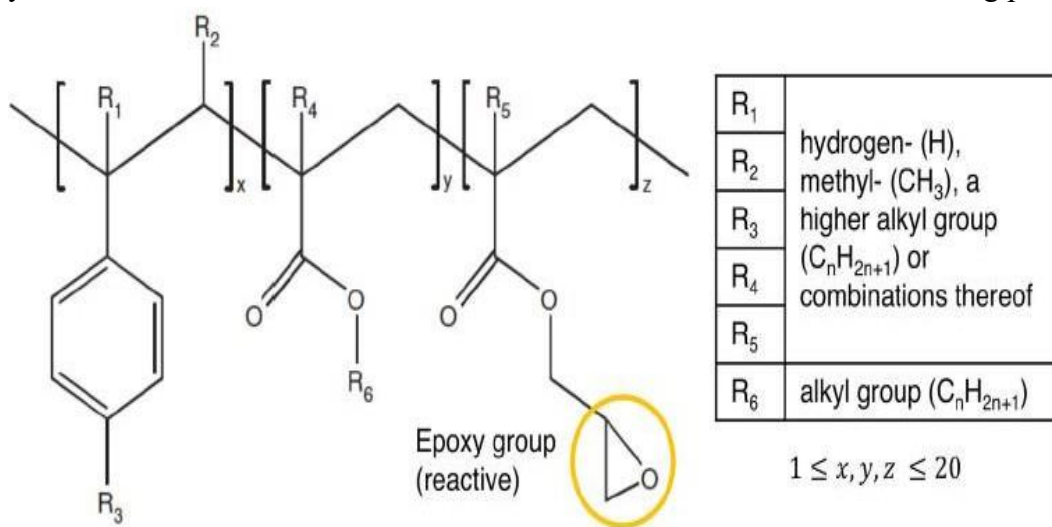


Figure 2.2: Epoxy based Joncryl ADR chain extender diagram³¹.

F. Some disadvantages associated with Joncryl ADR

While Joncryl (J) ADR is effective in enhancing the properties of degraded polymers, it does come with some disadvantages. One notable issue is the potential for increased brittleness in the polymer, which can occur if the chain extender is not evenly distributed or is used in excessive amounts. Additionally, the cost of Joncryl ADR can be relatively high compared to other chain extenders, which may be a limiting factor for some manufacturers. There is also a possibility of compatibility issues with certain polymers or additives, leading to suboptimal performance or processing difficulties. Furthermore, the handling and incorporation of Joncryl ADR requires careful control and expertise to avoid unwanted side reactions and ensure consistent results.

Some additional health disadvantages associated with Joncryl ADR include its content of glycidol and styrene. Although styrene units generally contribute to the overall strength and stability of the polymer matrix, enhancing its mechanical properties, they pose a threat to humans. Products containing styrene in the polymer matrix can directly affect the central nervous system. The glycidol content found in Joncryl ADR is also associated with toxic effects when the product packaged in such type of packaging structure containing glycidol traces in polymer matrix directly results to toxic effects on human body.

2.4.3 Chemical Recycling

Chemical recycling of PET involves breaking down the polymer into its original monomers or other useful chemicals through various chemical processes³². One common method is glycolysis, where PET is reacted with ethylene glycol at high temperatures in the presence of a catalyst. This reaction depolymerizes the PET, converting it back into bis(2-hydroxyethyl) terephthalate (BHET). Another method is methanolysis, where PET is treated with methanol to produce dimethyl terephthalate (DMT) and ethylene glycol. Both BHET and DMT can be purified and

polymerized again to form a new PET which ensures that the recycled material retains properties equivalent to virgin PET.

Additionally, hydrolysis is used, which involves breaking down PET with water, either in acidic or alkaline conditions, to yield terephthalic acid (TPA) and ethylene glycol. These monomers are then purified and used to synthesize new PET. Chemical recycling offers the advantage of dealing with mixed or contaminated PET waste, as the processes can effectively separate and remove impurities. This method contributes significantly to sustainability by enabling the production of high-quality PET from recycled materials and reduces reliance on fossil resources and minimizing environmental impact.

2.5 Market Demand for Recycled PET

The market demand for rPET has been growing significantly, driven by increasing environmental awareness and regulatory pressures for sustainable practices³³. Consumers and companies alike are seeking eco-friendly alternatives which leads to a higher demand for products made from recycled materials. The packaging industry is a major driver of this demand, as brands strive to meet sustainability goals and reduce their carbon footprint. Additionally, legislation in many regions mandates the use of recycled content in packaging, further boosting the demand for rPET. This rising demand is also fueled by advancements in recycling technology, which improve the quality and availability of rPET makes it a viable option for a broader range of applications beyond packaging, such as textiles and automotive components. The combination of consumer preference, regulatory requirements, and technological improvements is expected to sustain and increase the market demand for rPET in the coming years.

2.6 Current market end use applications of rPET

rPET is widely utilized across various industries due to its versatility and environmental benefits. In the packaging sector, rPET is extensively used to produce beverage bottles, food containers, and packaging films which offers a sustainable alternative to virgin PET. The textile industry also benefits significantly from rPET, where it is spun into fibers for making clothing, carpets, and upholstery. Additionally, the automotive industry incorporates rPET in manufacturing seat fabrics, insulation materials, and interior components which contributes to lighter and more eco-friendly vehicles. The construction industry utilizes rPET in products like insulation materials and panels, while consumer goods such as electronics and household items increasingly feature components made from rPET. These diverse applications highlight the material's adaptability and its role in promoting a circular economy by reducing plastic waste and conserving resources.

2.7 Challenges Involved in Mechanical and Chemical Recycling

Mechanical and chemical recycling of PET face several challenges that impact their efficiency and viability. In mechanical recycling, the primary issues are contamination and degradation. Contaminants such as food residues, labels, and non-PET materials can compromise the quality of the recycled PET to make it less suitable for high-quality applications³⁴. Additionally, repeated recycling can cause polymer chains to break down and results in lower mechanical properties and limited recyclability over multiple cycles.

Chemical recycling, while offering the potential to produce high-quality PET, is often hindered by its complexity and cost. The processes involved, such as glycolysis and methanolysis, require significant energy and advanced technologies and make them more expensive than mechanical recycling^{34, 35}. Furthermore, the need for precise control of reaction conditions and purification of the resulting monomers adds to the operational costs and technical difficulties. Both recycling

methods also face logistical challenges, such as efficient collection and sorting of PET waste, which are crucial for maintaining a steady supply of material for recycling processes³⁵. These challenges must be addressed to improve the sustainability and economic feasibility of PET recycling.

2.8 Role of Intrinsic Viscosity of PET for Packaging related applications

Intrinsic viscosity (IV) is related to the molar mass of polymers by the well-known Mark-Houwink equation. A higher IV values correspond to longer polymer chains, which generally result in better mechanical strength and toughness³⁶. IV plays a pivotal role in polymer processing because it affects the melt-flow characteristics during melting and extrusion. For instance, PET with a higher IV is preferred for applications requiring robust mechanical performance, such as in the manufacture of bottles and industrial fibers, these values are mentioned in **Table 2.1**. Conversely, lower IV PET is easier to process and mold as mold can easily be filled with molten plastic. Therefore, ensuring desirable IV is essential for achieving the required balance between processability and performance of final plastic article.

Table 2.2: IV values of different PET grades.

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

CHAPTER 3: EXPERIMENTAL

A part of this chapter has been published in reference link below⁸:

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A part of this chapter has been under review in a peer-reviewed journal.

3.1 Materials

3.1.1 Recycled PET-B and PET-T samples preparation

PET beverage bottles (PET-B) and PET thermoform containers (PET-T) were obtained from the Michigan State University (MSU) Surplus Store in Michigan, USA. These items were then sorted, with the labels set aside and the tamper band rings and caps removed from the bottles. The containers and bottles were washed in a detergent solution to eliminate any label residue. After washing, the PET materials were dried in a vacuum oven at 80°C for 24 hours to remove moisture, which was 0.021 wt% before processing. The dried samples were then crushed into a coarse powder using a BTP Granulator grinder (Berlin, CT 06037). To ensure they were moisture-free, the ground plastics were placed back in the oven for an additional 24 hours before extrusion processing.

3.1.2 Fabrication of PET-B and PET-T blended samples

To ensure uniformity among all recycled materials, the dried polymers, neat PET-B and neat PET-T, were processed through an extrusion process. This was performed using a co-rotating twin-screw extruder (Leistritz, USA) with a 48:1 L/D ratio and a 27 mm screw diameter. The extruder operated at temperatures between 210 and 245 °C across the feeding, compression, and metering zones, with a screw speed of 100 rpm and a melt temperature of 230 °C, maintaining an extruder torque of 40 Nm.

The extruded samples were then dried in an oven at 80 °C for 24 hours to ensure they were free of

moisture before further testing (with a moisture content of 0.021 wt% before processing). Neat PET-B and neat PET-T were blended using a vertical barrel housing with a two-screw co-rotating micro-compounder DSM extrusion machine (Xplore Instruments BV), which has an L/D ratio of 150:18 and a barrel volume of 15 cc. This process was conducted at 280 °C and 100 rpm for 2 minutes. The extruded samples were then transferred to a portable system for injection molding using DSM Xplore Instruments BV, with the mold temperature set at 32 °C and the injection machine temperature set at 280 °C. The injection-molded samples were stored at room temperature for 48 hours before their mechanical, thermal (DSC and TGA), and rheological properties (such as intrinsic viscosity) were evaluated.

3.1.3 Compounding of PET-B/20%PET-T with Novel Glycidol free Chain extender (PES)

The dried PET-B (bottle-grade) and PET-T (thermoform-grade) samples were processed by extrusion process using a twin screw co-rotating extruder (Leistritz, USA). To ensure uniform heat distribution, the processing temperature was maintained between 210 and 250 °C across the feeding, compression, and metering zones. The extruder operated at a twin screw speed of 100 rpm with a torque of 40 Nm.

After extruding the samples from the extrusion machine, they were dried in an oven at 80 °C to remove any residual moisture to prevent hydrolytic degradation if any. A moisture analyzer confirmed that the moisture content was 0.02 wt.%. The PET-B and PET-T samples were then blended with and without chain extenders in a DSM micro-compounder (Xplore instruments BV) with a 12-gram capacity. The blending was conducted at 280 °C, a screw speed of 100 rpm, and a 2-minute residence time for each sample. The inclusion of up to 20 wt.% PET-T in the PET-B blends is justified by data from the National Association for PET Container Resources (NAPCOR), which indicates that approximately 7% of thermoforms are found in the PET recycling stream

alongside PET bottles.

The DSM Xplore instruments BV device is connected to a portable system that maintains the extruded samples at the same temperature as the extruder. This system is used to transfer samples to the injection molding machine, set at 280 °C, with a mold temperature of 30 °C. The processed PET-B and PET-T blends were stored at room temperature for 48 hours before undergoing mechanical tests (tensile and impact), thermal properties tests (DSC and TGA), and intrinsic viscosity evaluations, all in compliance with ASTM standards.

Table 3.1 Composition, codes of neat PET and chain extender with glycidol free blended samples.

Compositions	PET-B (wt.%)	PET-T (wt.%)	J (phr)	PES-BA (phr)
Neat PET-B	100	0	0	0
Neat PET-T	0	100	0	0
A* (PET-B/20%PET-T)	80	20	0	0
A* + Joncryl ADR	80	20	1	0
A* + PES5-BA	80	20	0	1
A* + PES10-BA	80	20	0	1
A* + PES20-BA	80	20	0	1

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PES denotes mono

epoxy (styrene and glycidol free chain extender), while 5,10,20 stands for their respective weight % of PES.

Table 3.2 Composition, codes of neat PET polymer along with Styrene and Glycidol free Chain extender blended samples.

Compositions	PET-B (wt.%)	PET-T (wt.%)	J (phr)	PEAI-BA (phr)	PEAT-BA (phr)
Neat PET-B	100	0	0	0	0
Neat PET-T	0	100	0	0	0
A* (PET-B/20%PET-T)	80	20	0	0	0
A* + Joncryl ADR	80	20	1	0	0
A* + PEA120-BA #	80	20	0	1	0
A* + PEAT20-BA #	80	20	0	0	1

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PEAT (Terminal) and PEA1 (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight %of PEAT and PEA1.

3.2 Methods

3.2.1 Rheological properties determination

To determine the rheological properties of the polymer, Intrinsic viscosity (IV) was performed as per ASTM standard of D4603-03 using glass capillary viscometer also known as Ubbelohde viscometer. A total of 7 variations as mentioned in **Table 3.2** and 6 variations as mentioned **Table**

3.3 of polymer flow were tested with respect to time, each of 3 replicates of polymer samples viscosities were conducted to determine and confirm with accurate values.

Following steps were followed for each sample while conducting the intrinsic viscosity test:

Step 1: A solid sample weighing approximately 0.25grams was measured on the weighing scale, and then dissolved in a 25mL solvent comprising of 60:40 ratio containing 60% of phenol and 40% of Tetrachloroethane by volumes. This sample was allowed to dissolve in the solvent and exposed to a temperature of 115 °C for 15 mins in an arrangement of silicon bath and carefully observed until all the polymer sample was miscible or dissolved completely.

Step 2: The fully dissolved sample containing solvent was cooled down for approximately 15 mins before passing it through the capillary tube for viscosity measurements.

Step 3: After cooling the solution was then passed through the capillary tube and the flow rate was measured with respect to time to determine the viscosity.

Step 4: Following equations were then used to calculate the relative viscosity, inherent viscosity and intrinsic viscosity:

Relative viscosity (t/t₀): The initial time (t/t₀) refers to the duration it takes for a phenol/tetrachloroethane solution with a 60/40 volume ratio to pass through the capillary viscometer tube. In contrast, t is the time required for the solution, which contains 0.25 g of dissolved polymer mixed in 25 mL of the phenol/tetrachloroethane solution, to flow through the tube.

Intrinsic Viscosity:
$$\frac{0.25[\eta r - 1 + 3 \ln(\frac{t}{t_0})]}{c}$$

wherein C denotes concentration which is weight of the polymer / quantity of solution in deciliters (grams/dL). Molecular weights are also determined based on the intrinsic viscosity values of solution. As per Mark-Houwink's equation every polymer grade material has a dedicated constant

value. Wherein constants K and a change based on the polymer product grades. Here for bottle grade polymer as per Farahetal., the equation, ³⁷ $\eta = KM^a = 4.68 * 10^{-4} (M_w)^{0.68}$.

3.2.2 Mechanical properties determination

Using an injection molding machine, samples were prepared, and their mechanical properties were assessed with an Instron 5655 Universal Testing Machine, following the ASTM D638 standard protocol. The tests were conducted at a rate of 100 mm/min. Impact bars were notched using a precision notch cutter, ensuring the remaining plastic material under the notch was 10.16 ± 0.05 mm. This was verified with a tapered blade near the notch machine. The samples were then subjected to Izod Impact tests using a Ray Ran Impact Tester, adhering to ASTM D256 standards. Prior to testing, the samples were conditioned at room temperature for 48 hours.

3.2.2.1 Tensile Strength Test (ASTM D638-14)

A total of 5 samples were prepared from injection molding as per the ASTM standard, these T bones type V samples were created for each of 7 variants of neat polymer and mono epoxy styrene grades polymer along with 6 other variants of neat and epoxy acylate terminal and internal polymer samples. These samples were majorly kept for 48 hours at room conditioning temperature at 23°C conditions. The tensile equipment named Instron model 5565 (Massachusetts, USA) was used to test all the mentioned samples for their mechanical strength namely tensile strength, elongation at break, elongation %, modulus of elasticity. These samples were tested as per complying with ASTM D638-14 (Type V) for formed rigid injection molded samples.

3.2.2.2 Izod Impact Test (ASTMD256)

A total of 5 replicates of each variant were prepared from injection molding as per the ASTM standard. These impact bars were then kept at room temperature at 23°C for duration of 48 hours. The equipment used for determination of impact strength was Ray-Ran Impact tester. The

specimens were notched before subjecting it/ or performing the impact test. The notch cutting tool machine named TMI 22-05 (Michigan, USA) was used for notching all the specimens. The hammer was calibrated and had 5.417J energy as per the ASTM D256 compliance. The samples to be tested were gripped and then struck with a pendulum of single swing pattern. The absorbed energy was recorded as displayed on the digital screen of Ray-Ran impact tester reported in KJ/m².

3.2.3 Thermal properties determination

3.2.3.1 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) technique, utilizing a DSC100 Analyzer from TA Instruments, was employed to ascertain the glass transition temperature, melting temperature, cold crystallization temperature, and heat flow values of the polymer. These measurements were conducted with a nitrogen gas flow rate of 70 mL/min over three cycles. Each sample, weighing between 5 and 10 mg, was initially heated to 280 °C to eliminate the sample's thermal history. The sample was then cooled to -20 °C at a rate of 10 °C/min to identify the cold crystallization temperature peak, and subsequently reheated to 280 °C at the same rate to acquire the melting curve. In DSC studies, the degree of crystallinity is important because it is linked to heat flow and crystalline transitions. By examining the endothermic and exothermic peaks, DSC characterization enables the estimation of the polymer's percent crystallinity.

Degree of crystallinity can also be determined using the following crystallinity equation

$$x_c = \frac{\Delta H_m}{\Delta H^0_{mw} \cdot PET} \times 100$$

Wherein, enthalpy of 100% PET crystallinity (ΔH^0_m) is 140 J/g as indicated in NG Karsli ³⁸

3.2.3.2 Thermogravimetric Analysis (TGA)

All the polymer sample variants were also tested using thermogravimetric analysis to understand the thermal stability of a polymer when exposed to a temperature condition at 600 °C in this case.

The instrument used for the conduction of this experiment was TGA Q50 thermogravimetric analyzer. The polymer sample to be tested was weighed to ensure it was between 5 to 10mg. Nitrogen flow rate set was 40mL/min and heating ranged from 10°C to 600°C.

CHAPTER 4: RESULTS AND DISCUSSIONS

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A part of this chapter has been under review in a peer-review journal.

4.1 Rheological effect of novel chain-extenders in PET-B/PET-T blend

In PES (Glycidol free) blended samples, the Intrinsic viscosity measurements were performed for neat PET-B, PET-T, and PET-B/PET-T with and without chain extenders. These values were determined using glass capillary viscometer also known as Ubbelohde viscometer. The neat bottle grade polymer PET-B intrinsic viscosity was found out to be 0.76 dL/g and each polymer sample either neat or with chain extender were performed three times so as to get the confirmed/exact intrinsic viscosity value, while thermoform grade PET-T was found out to be 0.89 dL/g which was 17% higher than the neat PET bottle grade.

Furthermore, the intrinsic viscosity of reference blend i.e., PET-B/20%PET-T was found out to be 0.80dL/g which was found to be approximately 5% higher than the neat PET-B polymer. To understand the rheological behavior of the sample containing commercial Joncryl ADR it was found out to be 1.25% higher than the reference blend. To improve the viscosity characteristic of the reference blend, this sample was then blended with novel glycidol free chain extender mono-epoxy styrene (PES) in various proportions namely 5, 10 and 20 weight% to understand the rheological effect on the reference blend by altering or increasing the % quantity in the blend. It was found out that sample with PES5-BA (5 wt% of PES) showed 3.5% enhancement. In 10wt% i.e., PES10-BA when incorporated was found out to increase the viscosity property by approximately 6% than the reference blend, due to its reaction of COOH group with the epoxy group of P(MES-co-BA), leading to an increase in the overall molecular weight of the sample,

which directly results to an enhancement in the mechanical property of the polymer, the resultant data is presented in below table:

Table 4.1 Rheological properties of various PET samples – comprising blended with PES (Glycidol free chain extender) as well as neat polymers.

Samples	PET-B (wt%)	PET-T (wt%)	J (phr)	PES-BA (phr)	Intrinsic viscosity (dL/g)	Molecular Weight (M_w) (kDa)
Neat PET-B	100	0	0	0	0.76± 0.02	52.42 ± 0.03
Neat PET-T	0	100	0	0	0.89± 0.02	65.79 ± 0.02
20%PET-T	80	20	0	0	0.80± 0.02	56.33 ± 0.08
20%PET-T + J	80	20	1	0	0.81± 0.04	57.36 ± 0.05
20%PET-T + PES5-BA	80	20	0	1	0.83 ± 0.01	59.78 ± 0.04
20%PET-T + PES10-BA	80	20	0	1	0.86 ± 0.06	62.87 ± 0.05
20%PET-T + PES20-BA	80	20	0	1	0.80 ± 0.02	56.74 ± 0.07

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PES denotes mono epoxy styrene (glycidol free chain extender), while 5,10,20 stands for their respective weight % of

PES.

In PEAT and PEAI chain extender with glycidol and styrene free properties, were too blended with the reference sample to understand the rheological behavior of the blend. It was found that adding Internal chain extender PEAI20-BA led to an enhancement in intrinsic viscosity by 4.7% while adding terminal chain extender PEAT20-BA led to more enhancement in the IV by 7.6% more than the reference blend and surpassing PEAI20-BA too. The reason for the highest enhancement while incorporating PEAT20-BA is since terminal groups have higher tendency to react with the functional groups of PET than the internal groups resulting in to a greater values. This leads to direct enhancement of the molecular weight of the sample blended with terminal chain extender. The results obtained are depicted in the below table:

Table 4.2 Rheological properties of various PET samples – comprising blended with PEAT and PEAI (Glycidol and styrene free chain extender) as well as neat polymers.

Samples	PET-B (wt%)	PET-T (wt%)	J (phr)	PEAI-BA (phr)	PEAT-BA (phr)	Intrinsic viscosity (dL/g)	Molecular Weight (M_w) (kDa)
Neat PET-B	100	0	0	0	0	0.70± 0.02	52.40 ± 0.03
Neat PET-T	0	100	0	0	0	0.90± 0.02	65.80 ± 0.02
20%PET-T	80	20	0	0	0	0.80± 0.02	56.30 ± 0.08
20%PET-T + J	80	20	1	0	0	0.80± 0.04	57.40 ± 0.05
20%PET-T + PEAI20-BA	80	20	0	1	0	0.80 ± 0.08	59.70 ± 0.04
20%PET-T + PEAT20-BA	80	20	0	0	1	0.90 ± 0.05	62.80 ± 0.04

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryn ADR, PEAT (Terminal) and PEAI (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight %of PEAT and PEAI.

4.2 Mechanical effect of novel chain-extenders in PET-B/PET-T blend

Mechanical strength of polymer samples in neat and glycidol chain extender (PES) blended sample prepared from injection molding after conditioning were then subjected to the tensile stress to

understand their mechanical behavior during the exposure (for values please see **Table 4.3** and **figure 4.1**). It was found that reference sample blend (PET-B/20%PET-T) was found to have tensile strength of 60.1 MPa which was found to have 7.32% less as compared to neat PET-B sample. To enhance its properties, this reference sample was further blended with Joncryl ADR 4468 (J) 1 phr to understand its mechanical behavior. It was found that addition of 1 phr J led to enhancement in mechanical properties by 6.82 % in tensile strength, 1.49% in modulus of elasticity and approximately 15% by impact strength. It was found slight reduction in elongational properties by 9.5% approximately, the reason for such reduction is due to increased cross linking inside the polymer matrix³⁹.

Furthermore, newly prepared epoxy styrene-based chain extender was introduced to understand its mechanical property when introduced in the reference blend in 1 phr. To study in detail three weight% proportions of PES (chain extender) were added in the reference in 1 phr. It was found that incorporation of PES5-BA (5 weight%) when added in the reference blend led to slight enhancement in tensile strength by 4.7% as compared to reference blend. While it led to a minor decrease in modulus of elasticity by less than 0.5% approximately, further it led to exceptional enhancement in elongation and impact strength by 20% and 34% respectively.

Incorporation of PES10-BA (10% weight) in reference blend led to total enhancement in all the properties be it in tensile strength, modulus of elasticity, %elongational properties at break as well as impact strength. Compared to commercially viable Joncryl ADR 4468 (J), addition of PES10-BA led to 7.6% increase in tensile strength, 2% increase in modulus of elasticity, 12% increase in elongation at break% as well as 22.5% increase in impact strength. The reason for such an exceptional enhancement is due to reaction of epoxy based chain extender with the functional groups of PET polymer matrix which led to creation of newer covalent bonds and hence directly

resulted in the total enhancement in molecular chain lengths and increase in chain entanglements which led to such an increase⁴⁰.

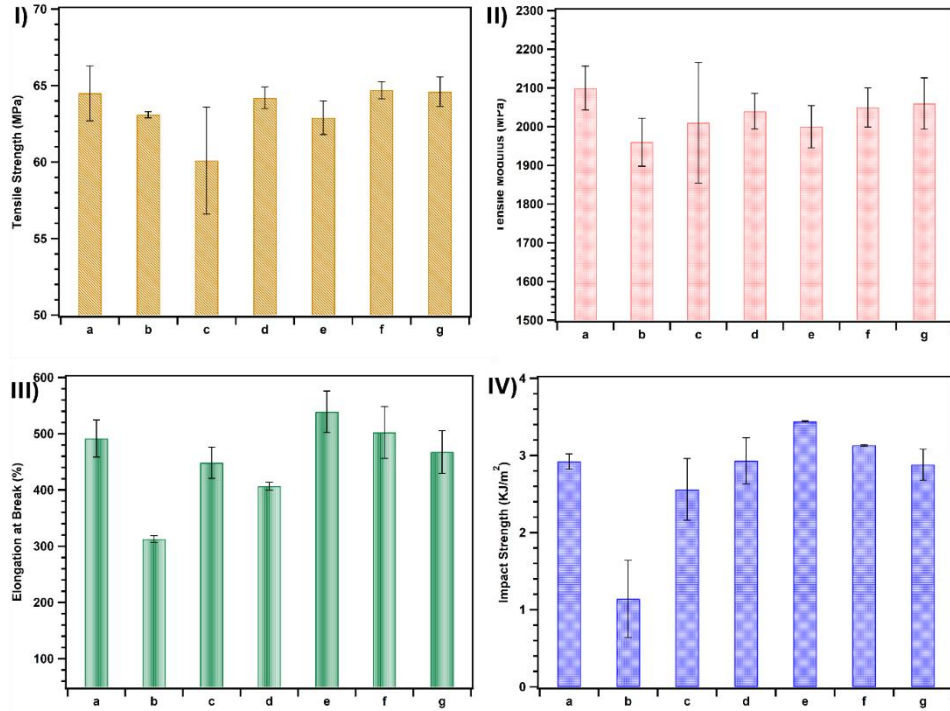


Figure 4.1: Graphical representation of Mechanical properties of Neat polymers and polymers blended with PES (glycidol free chain extender).

In figure: (a) Neat PET-B, (b) Neat PET-T, (c) 20%PET-T (reference blend), (d) 20%PET-T + J, (e) 20%PET-T + PES5-BA, (f) 20%PET-T + PES10-BA, (g) 20%PET-T + PES20-BA. Wherein Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, 20%PET-T stands for reference blend, J stands for Joncryl ADR, PES denotes mono epoxy styrene (glycidol free chain extender), while 5,10,20 stands for their respective weight % of PES.

Table 4.3 Mechanical properties of various PET samples – comprising blended with PES (Glycidol free chain extender) as well as neat polymers.

Sample	Tensile Strength (MPa)	Modulus of Elasticity (MPa)	%Elongation at break	Izod Impact Strength (kJ/m ²)
Neat PET-B	64.5 ± 1.8	2100 ± 57	492 ± 33	2.9 ± 0.1
Neat PET-T	63.1 ± 0.2	1960 ± 62	313 ± 6	1.1 ± 0.5
PET-B/20% PET-T (A*)	60.1 ± 3.5	2010 ± 156	448 ± 28	2.6 ± 0.4
A* + 1 phr J	64.2 ± 0.7	2040 ± 46	407 ± 7	2.9 ± 0.3
A* + 1 phr PES5-BA	62.9 ± 1.1	2000 ± 55	539 ± 37	3.4 ± 0.0
A* + 1 phr PES10-BA	64.7 ± 0.6	2050 ± 51	502 ± 46	3.1 ± 0.0
A* + 1 phr PES20-BA	64.6 ± 1.0	2060 ± 66	468 ± 38	2.9 ± 0.2

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PES denotes mono epoxy styrene (glycidol free chain extender), while 5,10,20 stands for their respective weight % of PES.

Mechanical properties of glycidol and styrene free epoxy acrylate-based chain extender namely PEAI and PEAT blended samples in reference were also subjected to tensile stress to understand its mechanical nature of the blended polymer (for values please see **Table 4.4** and **figure 4.2**). In reference sample comprising of PEAI20-BA led to a slight increase in some mechanical properties namely tensile strength by 2.8% more than reference sample as well as 33% enhancement in impact strength. The reference sample blended with terminal chain extender i.e., PEAT20-BA (20% wt.,) led to exceptional increase in elongation at break by 453% and total tensile strength by 8.8% surpassing the internally chain extender blended reference sample, and an impact strength by 25.4% which is slightly lower than PEAI20-BA observed. To compare with commercially viable chain extender J, it was incorporated in reference blend to understand its mechanical characteristic

and result after blending it with reference sample which resulted to a very slight increase in tensile strength by 6.8%, modulus of elasticity by 1.5%, impact strength by 14.4% all these values obtained were far less than the PEAT20-BA sample blended with reference sample. The ultimate reason for such enhancement is since the increase in molecular weight along with the formations of crosslinked structure in polymer matrix during the chain extension reaction which directly shows a gradual increase in its mechanical properties or aspects⁴¹.

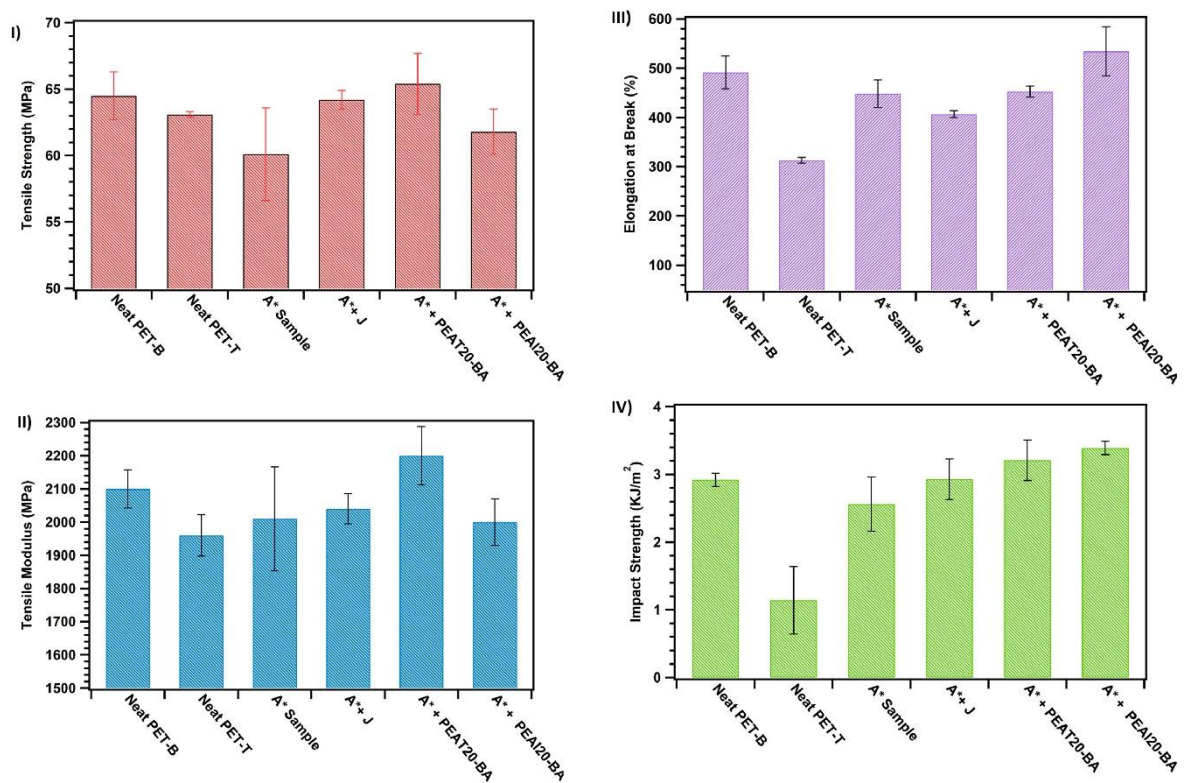


Figure 4.2: Graphical representation of Mechanical properties of Neat polymers and polymers blended with PEAI and PEAT (glycidol and styrene free chain extender).

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PEAT (Terminal) and PEAI (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight %of PEAT and PEAI.

Table 4.4 Mechanical properties of various PET samples – comprising blended with PEAT and PEAI (Glycidol and styrene free chain extender) as well as neat polymers.

Sample	Tensile Strength (MPa)	Modulus of Elasticity (MPa)	% Elongation at Yield	%Elongation at break	Izod Impact Strength (kJ/m ²)
Neat PET-B	64.5 ± 1.8	2100 ± 57	4.4 ± 0.1	491.6 ± 33	2.92 ± 0.1
Neat PET-T	63.1 ± 0.2	1960 ± 62	3.5 ± 0.2	312.7 ± 6	1.14 ± 0.5
PET-B/20% PET-T (A*)	60.1 ± 3.5	2010 ± 156	4.6 ± 0.2	448.4 ± 28	2.56 ± 0.4
A* + 1 phr J	64.2 ± 0.7	2040 ± 46	4.7 ± 0.2	406.9 ± 7	2.93 ± 0.3
A* + 1 phr PEAT20-BA	65.4 ± 2.3	2200 ± 88	4.6 ± 0.3	452.6 ± 11	3.21 ± 0.3
A* + 1 phr PEAI20-BA	61.8 ± 1.7	2000 ± 70	4.4 ± 0.1	534.5 ± 50	3.39 ± 0.1

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PEAT (Terminal) and PEAI (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight %of PEAT and PEAI.

4.3 Thermal effect of chain-extendors on PET-B/PET-T blend

Thermal effect or thermal properties of polymer samples on neat as well as reference samples blended with chain extendors were studied by using two thermal equipment's namely DSC and TGA. Thermal values or data for the neat sample as well as samples blended with glycidol free chain extender (PES) are represented in tabular form in **Table 4.5** and represented graphically to understand the heat flow in **Figure 4.3**. Neat PET samples were studied and found out that Tg (glass transition) value for PET-B sample is 79.5 °C while that for PET-T is 86.6 °C. This clearly

denotes that the T_g value for PET-T was found on a higher side which depicts higher crystalline regions in PET-T matrix. Higher crystalline depicts more packing molecules in the structure which eventually results to more of heat or adequate heat required to create mobility in the polymer matrix⁴².

Incorporating the newly chain extender PES10-BA in reference blend led to decrease in T_g of the blended reference sample. This decrease is due to the presence of butyl acrylate which tends to enhance the free volumes leading to flexibility in the polymeric chains which directly relates to reduction in T_g due to less packing molecules in the structure⁴³. This decrease in T_g directly relates to the % crystalline regions in the polymer structure of the chain extender blended reference. Which exhibits 3.5% reduction in crystallinity as compared to the reference sample as shown in the **Table 4.5** under X_c column.

Table 4.5 Thermal properties of various PET samples – comprising blended with PES (Glycidol free chain extender) as well as neat polymers.

Name	DSC						TGA
	T_c (°C)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)	T_{10} (°C)
Neat PET-B	205.7 ± 0.3	79.5 ± 0.2	243.3 ± 0.7	249.0 ± 0.3	40.7 ± 1.1	29.2 ± 1.1	406 ± 1
Neat PET-T	213.3 ± 0.7	86.6 ± 0.3	240.8 ± 0.6	250.5 ± 0.6	41.9 ± 1.5	30.1 ± 1.5	399 ± 1
PET-B/20%PET-T (A*)	214.8 ± 0.5	82.8 ± 0.3	243.5 ± 0.8	251.3 ± 0.9	39.4 ± 1.2	28.2 ± 1.5	404 ± 1
A* + 1 phr PES10-BA	209.0 ± 0.6	79.6 ± 0.5	233.5 ± 0.5	248.6 ± 0.4	38.1 ± 1.0	27.2 ± 1.7	405 ± 2

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET,

A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PES denotes mono epoxy styrene (glycidol free chain extender), while 5,10,20 stands for their respective weight % of PES.

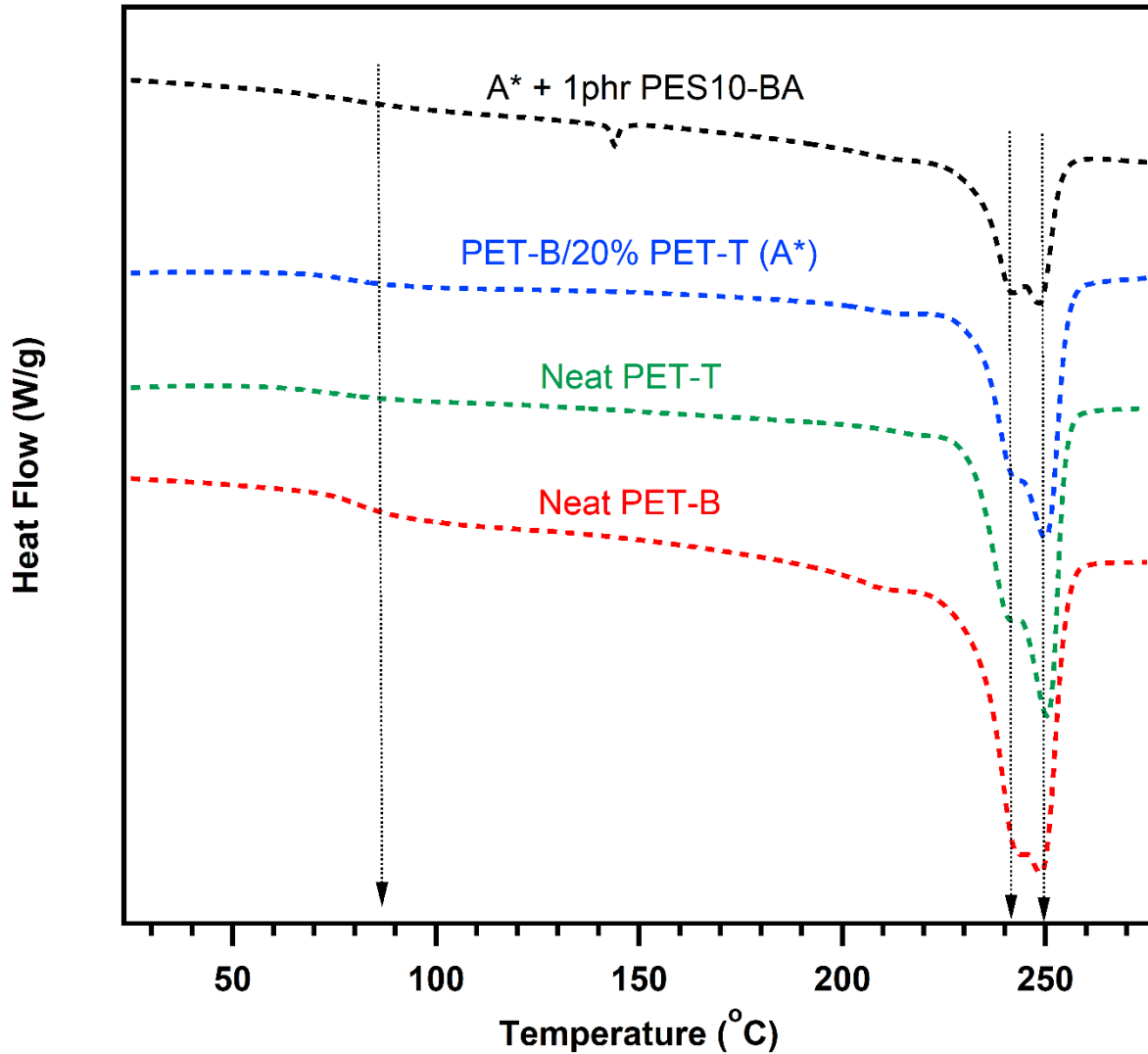


Figure 4.3: Graphical representation of Mechanical properties of neat polymers and polymers blended with PES (glycidol free chain extender).

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET, A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PES denotes mono

epoxy styrene (glycidol free chain extender), while 5,10,20 stands for their respective weight % of PES.

Furthermore, DSC analysis was conducted for the reference sample blended with newly prepared chain extender with glycidol and styrene free properties namely PEAI and PEAI, to understand the thermal behavior of the samples. It was found that incorporation of chain extenders namely PEAT20-BA and PEAI20-BA led to an increase in T_g value by 15% as compared to reference sample. In this all polymers depicted a two melting peaks in the third cycle, this denotes there were imperfect crystals present which have occurred during the cooling stage⁴⁴. To understand more in detail the reference samples blended with J were also analyzed since they are very reactive in nature due to its reactions between the hydroxyl and epoxy groups⁴⁵.

Table 4.6 Thermal properties of various PET samples – comprising blended with PEAT and PEAI (Glycidol and styrene free chain extender) as well as neat polymers.

Name	DSC						TGA
	T_c (°C)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)	T_{10} (°C)
Neat PET-B	205.7 ± 0.3	79 ± 0.2	243.3 ± 0.7	249.0 ± 0.3	40.7 ± 1.1	29.2 ± 1.1	405.6 ± 0.8
Neat PET-T	213.3 ± 0.7	86 ± 0.3	240.8 ± 0.6	250.5 ± 0.6	41.9 ± 1.5	30.1 ± 1.5	398.5 ± 0.7
PET-B/20% PET-T (A*)	214.8 ± 0.5	69 ± 0.6	243.5 ± 0.8	251.3 ± 0.9	39.4 ± 1.2	28.2 ± 1.6	403.8 ± 1.0
A*+ 1 phr J	208.4 ± 0.3	75 ± 0.2	241 ± 0.7	249 ± 0.4	39.8 ± 1.3	28.5 ± 1.1	409 ± 0.2
A*+ 1 phr PEAT20-BA	208.9 ± 0.5	79 ± 0.4	242.5 ± 0.8	249.4 ± 0.7	38.4 ± 1.1	27.6 ± 1.0	401.9 ± 0.4
A*+ 1 phr PEAI20-BA	204.0 ± 0.4	75 ± 0.2	239.7 ± 0.7	248.2 ± 0.6	37.8 ± 1.3	28.0 ± 0.1	389.5 ± 1.5

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET,

A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PEAT (Terminal) and PEAI (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight % of PEAT and PEAI.

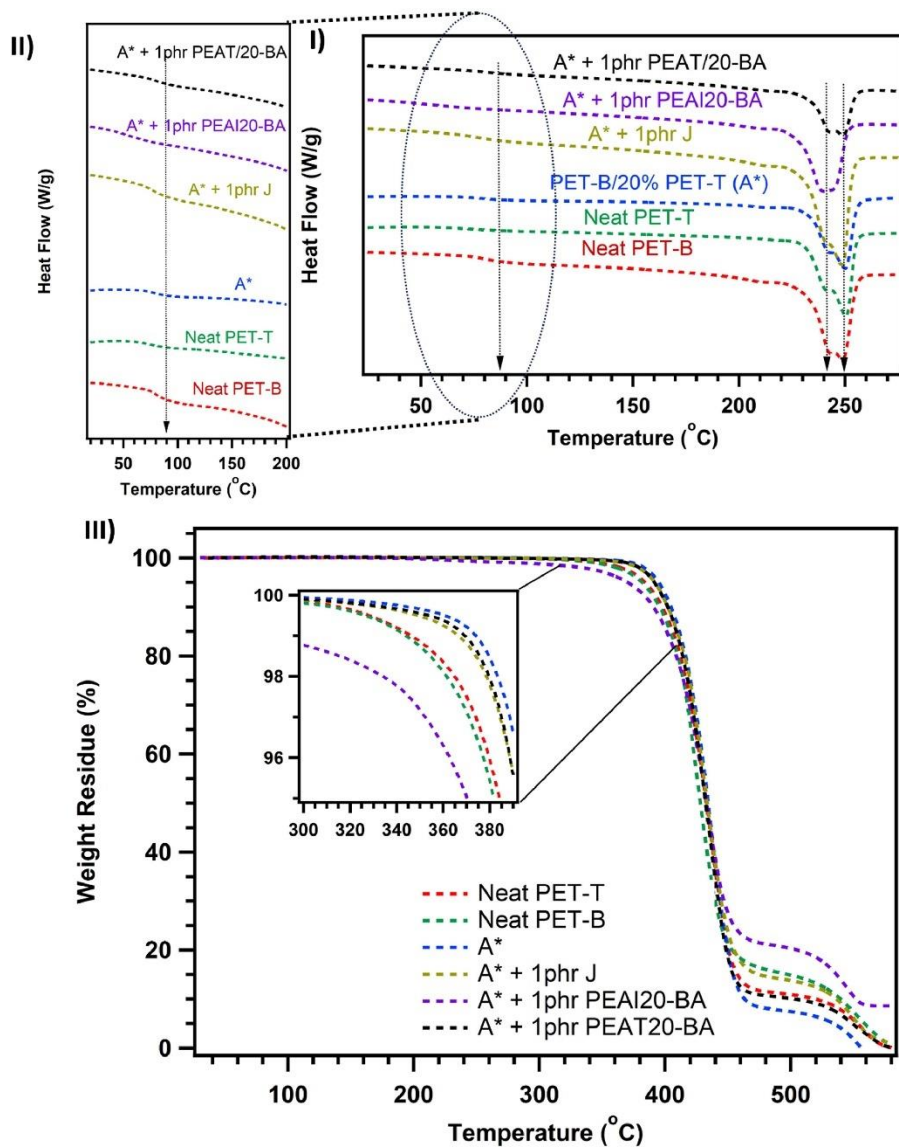


Figure 4.4: Thermal graph representation of neat polymers and polymers blended with PEAI and PEAT (glycidol and styrene free chain extender).

Here, Neat PET-B stands for Bottle grade PET and Neat PET-T stands for thermoform grade PET,

A* stands for reference blend of PET-B/20%PET-T, J stands for Joncryl ADR, PEAT (Terminal) and PEAI (Internal) are styrene and glycidol free chain extenders, BA stands for Butyl Acrylate while 20 stands for weight %of PEAT and PEAI.

Thermogravimetric analysis (TGA) was also conducted for the neat samples as well as samples blended with chain extenders. It was found that samples blended with PES with reference did not show any effect on thermal stability which can be observed in **Figure 4.3**. Furthermore, samples blended with terminal and internal chain extenders namely PEAT20-BA and PEAI20-BA did not show any variations in the thermal curve indicating to be stable at high temperatures which can be observed from **Figure 4.4** above.

CHAPTER 5: CONCLUSION AND FUTURE WORK

5.1 Conclusion

In conclusion, we have demonstrated the synthesis of food-safe, glycidol-free chain extenders. These extenders were used in PET-B and PET-T blends with promising results. We observed an increase of IV values by 4.7% for PEAI20-BA and 7.6% for PEAT20-BA compared with PET-B/20%PET-T without any chain extenders. PEAT20-BA as a chain extender offered an improvement in tensile strength by 8.8%, an improvement in Young's modulus of 9.4%, and an improvement in impact strength of 25.4%, better than those of a commercial chain extender. Thermal properties determined via TGA and DSC remained almost unchanged. These findings indicate that our new chain extender additives improve the properties of recycled PET blends.

The use of epoxy styrene-based chain extenders, such as PES10-BA in PET-B/PET-T blends, showed an IV increase of 7.5% for 20%PET-T with 1 phr PES10-BA. The use of PES10-BA as a chain extender resulted in an enhancement in the mechanical properties, such as a 7.65% increase in tensile strength, a 12% increase in elongation at break, and a 22.3% rise in impact strength relative to the reference PET-B/20%PET-T. The commercial ADR showed a slight enhancement in the mechanical properties (a 1.3% increase in elongational properties, a 6.4% increase in tensile strength, and a 12.6% enhancement in impact strength). Data with epoxy styrene-based PES10-BA as a chain extender demonstrates that PES10-BA led to an enhancement in all thermal and mechanical properties, even better than commercial benchmark chain extenders.

5.2 Future Scope of work

This research provided new chain extenders that improved key technical parameters of rPET-B and r-PET-T blends. Moving ahead, there are three aspects of research that need to be explored. First, the formation and properties assessment bottles from the glycidol- and styrene-free chain

extended PET-B and PET-T blend. To understand the formed bottle from this improvised blend by subjecting and analyzing it to ASTM test procedures for a bottle to comply with the technical and regulatory standards. The second major area to explore is to test the chain-extended PET-B and PET-T blends for migration and leaching. The third major aspect that needs to be explored is the techno economic analysis for these new chain extenders.

REFERENCES

- (1) Sonnendecker, C.; Oeser, J.; Richter, P. K.; Hille, P.; Zhao, Z.; Fischer, C.; Lippold, H.; Blázquez-Sánchez, P.; Engelberger, F.; Ramírez-Sarmiento, C. A. Low carbon footprint recycling of post-consumer PET plastic with a metagenomic polyester hydrolase. *ChemSusChem* **2022**, *15* (9), e202101062.
- (2) Jang, J. Y.; Sadeghi, K.; Seo, J. Chain-extending modification for value-added recycled PET: a review. *Polymer Reviews* **2022**, *62* (4), 860-889.
- (3) Ghosal, K.; Nayak, C. Recent advances in chemical recycling of polyethylene terephthalate waste into value added products for sustainable coating solutions—hope vs. hype. *Materials Advances* **2022**, *3* (4), 1974-1992.
- (4) Chu, J.; Zhou, Y.; Cai, Y.; Wang, X.; Li, C.; Liu, Q. A life-cycle perspective for analyzing carbon neutrality potential of polyethylene terephthalate (PET) plastics in China. *Journal of Cleaner Production* **2022**, *330*, 129872.
- (5) Selke, S. E.; Culter, J. D.; Auras, R. A.; Rabnawaz, M. *Plastics packaging: properties, processing, applications, and regulations*; Carl Hanser Verlag GmbH Co KG, 2021.
- (6) Abdelwahab, M. A.; Khan, A.; Matuana, L. M.; Auras, R.; Rabnawaz, M. Polystyrene-Free Chain Extenders for Recycled Poly(ethylene terephthalate). *ACS Applied Polymer Materials* **2022**, *4* (12), 9272–9283. DOI: 10.1021/acsapm.2c01544.
- (7) Ma, Y.; Agarwal, U.; Sikkema, D.; Lemstra, P. Solid-state polymerization of PET: influence of nitrogen sweep and high vacuum. *Polymer* **2003**, *44* (15), 4085-4096.
- (8) Mestry, J.; Abdelwahab, M. A.; Elkholy, H. M.; Rabnawaz, M. Superior glycidol-free chain extenders for post-consumer PET bottles and PET thermoform blends. *Resources, Conservation and Recycling* **2024**, *203*, 107420.
- (9) Sulyman, M.; Haponiuk, J.; Formela, K. Utilization of recycled polyethylene terephthalate (PET) in engineering materials: A review. *International Journal of Environmental Science and Development* **2016**, *7* (2), 100.
- (10) Sorrentino, L.; D’Auria, M.; Amendola, E. Poly (ethylene terephthalate)—PET and Poly (ethylene naphthalate)—PEN. *High Performance Polymers and Their Nanocomposites* **2018**, *30*, 255-314.
- (11) Beswick, R.; Dunn, D. *Plastics in Packaging: Western Europe and North America*; iSmithers Rapra Publishing, 2002.
- (12) Nisticò, R. Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing* **2020**, *90*, 106707.
- (13) Lepoittevin, B.; Roger, P. Poly (ethylene terephthalate). *Handbook of engineering and speciality thermoplastics* **2011**, *3*, 97-126.

- (14) Karayannidis, G. P.; Achilias, D. S. Chemical recycling of poly (ethylene terephthalate). *Macromolecular Materials and Engineering* **2007**, *292* (2), 128-146.
- (15) Lee, S.; Miyaji, H.; Geil, P. Morphology of amorphous polyethylene terephthalate. *Journal of Macromolecular Science, Part B: Physics* **1983**, *22* (3), 489-496.
- (16) Jog, J. Crystallization of polyethyleneterephthalate. *Journal of Macromolecular Science, Part C: Polymer Reviews* **1995**, *35* (3), 531-553.
- (17) Jabarin, S. Crystallization kinetics of polyethylene terephthalate. I. Isothermal crystallization from the melt. *Journal of Applied Polymer Science* **1987**, *34* (1), 85-96.
- (18) Cobbs Jr, W.; Burton, R. Crystallization of polyethylene terephthalate. *Journal of Polymer Science* **1953**, *10* (3), 275-290.
- (19) McLellan, M.; Lind, L.; Kime, R. A shelflife evaluation of an oriented Polyethylene Terephthalate package for use with hot filled apple juice. *Journal of Food Science* **1987**, *52* (2), 365-368.
- (20) Korycki, A.; Garnier, C.; Irusta, S.; Chabert, F. Evaluation of fatigue life of recycled opaque PET from household milk bottle wastes. *Polymers* **2022**, *14* (17), 3466.
- (21) Salminen, P. Using recycled polyethylene terephthalate (PET) in the production of bottle trays. **2013**.
- (22) Hashemi, S.; Xu, Y. Thermal effects on fracture of biaxial-oriented poly (ethylene terephthalate)(BOPET) film. *Journal of materials science* **2007**, *42*, 6197-6204.
- (23) Breil, J. Future trends for biaxially oriented films and orienting lines. In *Biaxial Stretching of Film*, Elsevier, 2011; pp 240-273.
- (24) Navarro, R.; Ferrándiz, S.; López, J.; Seguí, V. J. The influence of polyethylene in the mechanical recycling of polyethylene terephthalate. *Journal of Materials Processing Technology* **2008**, *195* (1-3), 110-116.
- (25) Benyathiar, P.; Kumar, P.; Carpenter, G.; Brace, J.; Mishra, D. K. Polyethylene terephthalate (PET) bottle-to-bottle recycling for the beverage industry: A Review. *Polymers* **2022**, *14* (12), 2366.
- (26) Mancini, S. D.; Zanin, M. Consecutive steps of PET recycling by injection: evaluation of the procedure and of the mechanical properties. *Journal of applied polymer science* **2000**, *76* (2), 266-275.
- (27) Mohsin, M. A.; Abdulrehman, T.; Haik, Y. Reactive extrusion of polyethylene terephthalate waste and investigation of its thermal and mechanical properties after treatment. *International Journal of Chemical Engineering* **2017**, *2017* (1), 5361251.

- (28) Vozniak, A.; Hosseinneshad, R.; Vozniak, I.; Galeski, A. PET mechanical recycling. A new principle for chain extender introduction. *Sustainable Materials and Technologies* **2024**, *40*, e00886.
- (29) Nofar, M.; Oğuz, H. Development of PBT/recycled-PET blends and the influence of using chain extender. *Journal of Polymers and the Environment* **2019**, *27*, 1404-1417.
- (30) Awaja, F.; Pavel, D. Recycling of PET. *European polymer journal* **2005**, *41* (7), 1453-1477.
- (31) Villalobos, M.; Awojulu, A.; Greeley, T.; Turco, G.; Deeter, G. Oligomeric chain extenders for economic reprocessing and recycling of condensation plastics. *Energy* **2006**, *31* (15), 3227-3234.
- (32) Rabnawaz, M.; Khan, A.; Aayanifard, Z.; Naveed, M. Methods for chemical recycling of condensation polymers. Google Patents: 2024.
- (33) Alders, D. Impacts of Participating in an Environmental Voluntary Agreement. A Case Study of Plastics Pact NL. 2020.
- (34) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste management* **2017**, *69*, 24-58.
- (35) Smith, R. L.; Takkellapati, S.; Riegerix, R. C. Recycling of plastics in the United States: plastic material flows and polyethylene terephthalate (PET) recycling processes. *ACS sustainable chemistry & engineering* **2022**, *10* (6), 2084-2096.
- (36) Yilmazer, U.; Xanthos, M.; Bayram, G.; Tan, V. Viscoelastic characteristics of chain extended/branched and linear polyethylene terephthalate resins. *Journal of applied polymer science* **2000**, *75* (11), 1371-1377.
- (37) Farah, S.; Kunduru, K. R.; Basu, A.; Domb, A. J. Molecular weight determination of polyethylene terephthalate. In *Poly (ethylene terephthalate) based blends, composites and nanocomposites*, Elsevier, 2015; pp 143-165.
- (38) Karsli, N. G. A study on the fracture, mechanical and thermal properties of chain extended recycled poly (ethylene terephthalate). *Journal of Thermoplastic Composite Materials* **2017**, *30* (8), 1157-1172.
- (39) Maitra, J.; Shukla, V. K. Cross-linking in hydrogels-a review. *Am. J. Polym. Sci* **2014**, *4* (2), 25-31.
- (40) Chen, C.-W.; Liu, P.-H.; Lin, F.-J.; Cho, C.-J.; Wang, L.-Y.; Mao, H.-I.; Chiu, Y.-C.; Chang, S.-H.; Rwei, S.-P.; Kuo, C.-C. Influence of different molecular weights and concentrations of poly (glycidyl methacrylate) on recycled poly (ethylene terephthalate): a thermal, mechanical, and rheological study. *Journal of Polymers and the Environment* **2020**, *28*, 2880-2892.

- (41) Wang, K.; Qian, J.; Lou, F.; Yan, W.; Wu, G.; Guo, W. The effects of two-step reactive processing on the properties of recycled poly (ethylene terephthalate). *Polymer Bulletin* **2017**, *74*, 2479-2496.
- (42) Demirel, B.; Yaraş, A.; Elcicek, H. Crystallization behavior of PET materials. **2011**.
- (43) Rahman, M.; Brazel, C. S. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Progress in polymer science* **2004**, *29* (12), 1223-1248.
- (44) Zhao, Z.; Wu, Y.; Wang, K.; Xia, Y.; Gao, H.; Luo, K.; Cao, Z.; Qi, J. Effect of the trifunctional chain extender on intrinsic viscosity, crystallization behavior, and mechanical properties of poly (ethylene terephthalate). *ACS omega* **2020**, *5* (30), 19247-19254.
- (45) Standau, T.; Nofar, M.; Dörr, D.; Ruckdäschel, H.; Altstädt, V. A review on multifunctional epoxy-based Joncryl® ADR chain extended thermoplastics. *Polymer Reviews* **2022**, *62* (2), 296-350.