T.C.
YALOVA UNIVERSITY
INSTITUTE OF GRADUATE STUDIES

POLYMER MATERIALS ENGINEERING DEPARTMENT
POLYMER MATERIALS ENGINEERING PROGRAMME

IMPROVING THE PROPERTIES OF POLYLACTIC ACID BY MELT BLENDING

M.Sc. THESIS

ZEHRA KURU

ADVISOR: Assoc. Prof. Dr Mehmet Arif KAYA

YALOVA
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ETHICAL STATEMENT

In this thesis study, "Improving the Properties of Polylactic Acid by Melt Blending", which I prepared based on Yalova University Institute of Graduate Studies Thesis Writing Rules; the data, information, and documents I have presented in the thesis were obtained with the insight of academic and ethical rules; all the information, documents, evaluations, and results are presented based on scientific ethical and moral rules; all the references used in the thesis were cited; no changes were made in the data presented in the thesis and the study presented in the thesis is original. In the case of proving the contrary, I undertake and declare that I accept any legal responsibility.

Zehra KURU

To my dearest family,

FOREWORD

I would like to thank my valuable advisor Assoc. Prof. Dr. Mehmet Arif KAYA, who supported me throughout my undergraduate and graduate education, was always there for me academically and professionally and showed me the right path.

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January – 2022 Zehra KURU

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

°C	: Celsius
G’	: Storage Modulus
G’’	: Loss Modulus
GPa	: Gigapascal
MPa	: Megapascal
M_w	: Molecular weight
Rad/s	: The radian per second
T_g	: Glass Transition Temperature
T_m	: Melting Tempeature

ABBREVIATIONS

ABS	: Acrylonitrile Butadiene Styrene
BHBT	: Bis-(4-hydroxyethyl) Terephthalate
EBA-g-MAH	: Ethylene butyl acrylate copolymer grafted with maleic anhydride
FTIR	: Fourier-Transform Infrared Spectroscopy
HDPE	: High-Density Polyethylene
HDT	: The Heat Deflection Temperature
LA	: Lactic Acid
MFI	: Melt Flow Index
PBT	: Polybutylene Terephthalate
PCDI	: Polycarbodiimide
PDLA	: Poly-D-Lactic Acid
PET	: Polyethylene Terephthalate
PHA	: Polyhydroxyalkanoates
PLA	: Poly Lactic Acid
PLLA	: Poly (l-lactic acid)
PP	: Polypropylene
PPDI	: Para phenylene Diisocyanate
TNPP	: Tris (nonylphenyl) Phosphite
UV	: Ultraviolet

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IMPROVING THE PROPERTIES OF POLYLACTIC ACID BY MELT BLENDING

ABSTRACT

Poly (lactic acid) (PLA) is part of the aliphatic polyester family and consists of α-hydroxy acids. In addition, it is a biodegradable polymer that can also be used in industrial areas, obtained from the fermentation of renewable resources such as corn, wheat, potatoes, and starch. It is a biodegradable, biocompatible material and is a high-modulus thermoplastic polymer with high strength, available from renewable resources. The biodegradable nature of PLA makes it a sustainable, promising, and popular raw material for many fields from packaging to the textile industry. The wide application areas are due to the processability of PLA. Because PLA is a rigid polymer, its flexibility is low and its elongation at break values is generally low. This is one of the most important problems of PLA-based products. Mechanical properties of PLA, such as tensile strength and elastic modulus, limit its use in applications. It is also brittle below the glass transition temperature (T_g), which is in the range of 50-60 °C. The brittleness of PLA is its biggest and most important disadvantage. PLA has low abrasion resistance and hydrolysis resistance because it is a hard and brittle material. To overcome these questions, it will be blended with different polymers and compatibilizers and compared with both traditional and modern production methods and their use in the industrial field will be examined. In order to modify the thermal, morphological, and mechanical properties of PLA, it is blended with different polymers. To this disadvantage of PLA, it is aimed to eliminate the weak properties by preparing blends with polymers such as PET and PBT. Thus, new raw materials can be provided to many sectors, especially textile, automotive and electronic products, by preparing materials that are biodegradable, environmentally friendly, and with better p, performance properties.

In this study, PLA/PBT and PLA/PET blends prepared to contain 5%, 10%, and 15% PBT by weight and PET in the same proportions, maleic anhydride grafted ethylene (EBA-g-MAH) as a compatibilizer, random ethylene-methyl acrylate-glycidyl methacrylate (Production was carried out in a twin screw extruder using GMA) terpolymer and Joncryl as chain extender. PLA/PBT and PLA/PET blends blended in different ratios were produced without compatibilizer, without compatibilizer and by adding a chain extender, and the rheological, physical, mechanical, and thermal properties of these blends were characterized. For the characterization of the PLA/PBT and PLA/PET blends created, first rheological, physical, mechanical, and thermal analyzes of neat PLA, PBT, and PET polymers and then PLA blends performed time sweep test was performed as a rheological test. Densities of polymers and blends, shore D hardness, tests and mold shrinkage properties were analyzed for physical characterization. For mechanical tests, tensile strength, tensile strength, elastic modulus and Izod impact strength properties were examined. In the thermal analysis part, HDT/VICAT tests of neat polymers were made, and it was observed how the use of a compatibilizer and chain extender affected the thermal properties. It was also observed that blend samples containing 10% PBT, and 10% PET showed the highest mechanical properties. In all analysis test results, the properties of neat PLA, PBT, and

PET polymers and PLA blends change when compatibilizer or chain extender is used were analyzed. It is seen that repeating the extrusion process for the second time in PLA/PBT and PLA/PET blends prepared using compatibilizers increases the mechanical properties positively. For this reason, in the comparison of the mechanical properties of the samples extruded for the second time, the values of the samples produced were compared and it was thought that the samples that were extruded for the second time were blended more efficiently. mostly performance products were used and comments were made on them.

It was concluded that when the double extruder process is performed on samples without compatibilizer, the molecular weight decreases due to repeated heat treatment, the mechanical properties are reduced due to degradation, and yet it is better in the samples without compatibilizer, so the use of compatibilizer and additionally the mechanical properties are further improved.

Keywords: Polylactic acid, Melt blending, Compatibilization, Polyester.

POLİLAKTİK ASİTİN ERİYİK HARMANLAMA YOLUYLA TERMAL ÖZELLİKLERİNİN İYİLEŞTİRİLMESİ

GENİŞLETİLMİŞ ÖZET

Poli (laktik asit) (PLA), alifatik polyester ailesinin bir parçası olup, α-hidroksi asitlerden meydana gelmektedir. Bunlara ek olarak mısır, buğday, patates ve nişasta gibi yenilenebilir kaynakların fermantasyonundan elde edilen endüstriyel alanlarda da kullanılabilen biyobozunur bir polimerdir. Biyolojik olarak parçalanabilen, biyouyumlu bir malzeme olup, yüksek dayanımlı, yenilenebilir kaynaklardan elde edilebilen, yüksek modüle sahip termoplastik bir polimerdir. PLA'nın biyoparçalanabilir yapısı onun ambalajdan tekstil endüstrisine kadar birçok alan için sürdürülebilir, gelecek vaat eden ve popüler bir hammadde yapmaktadır. Geniş uygulama alanlarının olması PLA'nın işlenebilirliğinden kaynaklanmaktadır. PLA rijit bir polimer olduğu için, esnekliği düşüktür ve kopma uzama değerleri genellikle düşüktür. Bu PLA esaslı ürünlerin en önemli problemlerinden birisidir. PLA'nın kopma dayanımı ve elastik modül gibi mekanik özellikleri uygulama alarındaki kullanımını sınırlandırmaktadır. Ayrıca 50-60 °C aralığında olan camsı geçiş sıcaklığının (T_g) altında da kırılgandır. PLA'nın kırılgan özelliği en büyük ve önemli dezavantajıdır. PLA, sert ve kırılgan bir malzeme olduğu için düşük aşınım direncine ve hidroliz direncine sahiptir. Bu soruların üstesinden gelmek için farklı polimerler ve uyumlaştırıcılar ile karıştırılarak hem geleneksel hem de modern üretim yöntemleri ile karşılaştırılması yapılıp endüstriyel alandaki kullanım alanları incelenecektir. PLA'nın ısıl, morfolojik ve mekanik özelliklerinin modifiye edilmesi için farklı polimerlerle karışımları yapılmaktadır. PLA'nın bu dezavantajını ortadan kaldırmak için PET ve PBT gibi polimerler ile blendler hazırlayarak zayıf özelikleri ortadan kaldırmak hedeflenmektedir. Böylece biyobozunur, çevre dostu ve daha iyi performans özelliklerine sahip malzemeler hazırlanarak başta tekstil, otomotiv ve elektronik ürünler olmak üzere birçok sektöre yeni hammaddeler sağlanabilmektedir. PBT (polibütilen tereftalat) yaygın olarak kullanılan bir polyester çeşididir. Yüksek kristalleşme hızı ve yüksek erime sıcaklığına sahiptir. PBT, PLA' dan daha yüksek erime sıcaklığına sahiptir. Bu nedenle PLA ile blend yapılacak ilk polimer PBT seçilmiştir. PLA blendi için seçilen diğer polimer ise PET (Polietilen tereftalat) 'tir. PET iyi termal ve mekanik özelliklere, düşük geçirgenliğe ve kimyasal dirence sahip olan önemli bir ticari mühendislik termoplastiğidir. PLA'nın termal stabilitesini PET'e dahil edilmesiyle incelenmesi hedeflenmektedir.

Bu çalışmada; ağırlıkça %5, %10 ve %15 PBT ve yine aynı oranlarda PET içerecek şekilde hazırlanan PLA/PBT ve PLA/PET karışımları, uyumlaştırıcı olarak maleik anhidrit aşılı etilen (EBA-g-MAH), random etilen-metil akrilat-glisidil metakrilat (GMA) terpolimeri ve zincir uzatıcı olarak da Joncryl kullanılarak çift vidalı bir ekstrüderde üretim gerçekleştirildi. Çift vidalı ekstrüderde üretilen olan PLA/PET ve PLA/PBT blendlerinin granülleri enjeksiyon yöntemi ile test numuneleri olarak kalıplanmış ve tez analiz numunleri hazırlanmıştır. Farklı oranlarda karıştırılmış PLA/PBT ve PLA/PET blendleri uyumlaştırıcısız, uyumlaştırıcısız ve zincir uzatıcı eklenerek üretilmiş ve bu blendlerin reolojik, fiziksel, mekanik ve termal özellikleri karakterize edilmiştir.

Oluşturulan PLA/PBT ve PLA/PET blendlerinin karakterizasyonları için ilk önce saf PLA, PBT ve PET polimerlerinin daha sonrasında da PLA blendlerinin reolojik, fiziksel, mekanik ve termal analizleri yapıldı. Reolojik test olarak time sweep test gerçekleştirildi. Fiziksel karakterizasyon için polimerlerin ve blendlerin yoğunlukları, shore D sertlik testleri ve kalıp çekme özellikleri analiz edilmiştir. Mekanik testler için ise çekme, kopma dayanımları, elastik modülleri ve izod darbe mukavemeti özellikleri incelenmiştir. Ayrıca %10 PBT ve %10 PET içeren harman numunelerinin en yüksek mekanik özellikleri gösterdiği görülmüştür. Termal analiz kısmında ise saf polimerlerin HDT/VICAT testleri yapılmış ve uyumlaştırıcı ve zincir uzatıcı kullanımının termal özellikleri nasıl etkilediği gözlemlenmiştir. Yapılan tüm analiz test sonuçlarında saf PLA, PBT ve PET polimerlerinin özellikleri ile PLA blendlerinin uyumlaştırıcı veya zincir uzatıcı kullanılması halinde nasıl bir değişiklik gösterdiği analiz edilmiştir. Uyumlaştırıcı kullanılarak hazırlanan PLA/PBT ve PLA/PET karışımlarında ekstrüzyon işleminin ikinci kez tekrarlanmasının mekanik özellikleri olumlu yönde artırdığı görülmektedir. Bu nedenle ikinci kez ekstrüde edilen numunelerin mekanik özelliklerinin karşılaştırılmasında, ikinci kez ekstrüde edilen numunelerin daha verimli karıştığının düşünüldüğü ve üretilen numunelerin değerleri karşılaştırılmıştır. daha çok performans ürünleri kullanılmış ve bunlar üzerinden yorumlar yapılmıştır.

Çift ekstrüder işlemi uyumlaştırıcısız numunelerde yapıldığında tekrarlı ısıl işlemden dolayı moleküler ağırlığın azalması, bozunma nedeniyle mekanik özellikler düşer ve buna rağmen uyumlaştırıcısız numunelerde daha iyidir, bu nedenle uyumlaştırıcı kullanılması ve buna ek olarak mekanik özellikler daha da iyileştirilmiştir sonuca varılmıştır.

Bu çalışmanın sonucunda PLA'nın dezavantajlarının üstesinden gelmek amacı ile farklı polimerler ve uyumlaştırıcılar ile karıştırılarak hem geleneksel hem de modern üretim yöntemleri ile karşılaştırılması yapılıp endüstriyel alandaki kullanım alanları incelenmiştir.

Anahtar kelimeler: Polilaktik asit, Eriyik harmanlama, Uyumlaştırma, Poliester.

1. INTRODUCTION

Biodegradable polymers have recently attracted significant interest as a replacement for conventional petroleum-based thermoplastics regarding their effects on the environment because they can be made from various renewable resources and completely decompose via hydrolysis into carbon dioxide and biomass in a short period [1,2]. Lactic acid (LA) or lactide (the cyclic dimer of lactic acid, as an intermediary) are polymerized to produce poly(lactic acid) or polylactide (PLA), respectively [1,3-5]. PLA is a thermoplastic aliphatic polyester that is produced from non-fossil renewable natural resources by fermentation of polysaccharides or sugar, such as those extracted from corn, potato, cane molasses, sugar beet, etc. This enables the biological cycle to come full circle with PLA biodegradation as well as the photosynthesis process [2-6]. Some of the keywords frequently encountered during this study and used while conducting the research are shown in Table 1.1.

Table 1.1. List of critical technical keywords for polymer science with their definitions

Terms	Definition
Biopolymer	Polymers that can degrade naturally. Although polymers are made from biological materials or renewable bioproducts, plastics may or may not be biodegradable.
Bio-based Polymer	The term "bio-based polymer" refers to products that contain at least a fraction of a raw material that is generated sustainably.
Bio-polyester	A microbial polyester known as a bio-polyester is produced by microorganisms from sugar and plant oils, and it degrades naturally in the environment.
Compostability	It is a property of the ability to degrade naturally; any harmful, or noticeable remnants should not leave behind.
Petroleum-Based Polymer	Petroleum-based plastics are synthetic organic polymers made from oil or gas and are widely used in modern civilization in all facets of daily life.
Sustainable Polymer	Materials derived from renewable, recycled, and/or waste carbon sources and their combinations can be recycled, biodegraded, or composted at the end of their life.

The main uses of PLA have historically been confined to medical applications such as implant devices, tissue scaffolds, internal sutures, and others due to the polymer's high cost, limited availability, and low molecular weight [1-3,4]. High molecular weight PLA has gained a lot of interest as a potential substitute for synthetic polymers in recent years due to new manufacturing techniques that make it possible to produce it affordably [3-7].

Poly (lactic acid) or polylactide (PLA) is the most extensively researched and utilized biodegradable and renewable aliphatic polyester. PLA has a proven potential either to replace conventional petrochemical-based polymers for industrial applications or as a leading biomaterial for numerous applications in medicine [8,9]. Environmental, economic, and safety challenges have provoked packaging scientists and producers to partially substitute petrochemical-based polymers with biodegradable ones [10]. PLA as a leading candidate is a thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable resources to yield different components for use in either the industrial packaging field or the biocompatible/ bioabsorbable medical device market. It is easily processable on standard plastic equipment to yield molded parts, film, or fibers [11,12]. As they can be made from a variety of renewable resources and completely decompose into carbon dioxide and biomass in a short period of hydrolysis time, biodegradable polymers have attracted significant attention recently to replace conventional petroleum-based thermoplastics in terms of their environmental impact [13,14].

Poly(lactic acid) is created by polymerizing lactic acid (LA) [13,15-17]. PLA, corn, potatoes, cane molasses, sugar beet, etc. It is a thermoplastic aliphatic polyester made from non-fossil renewable natural resources by the fermentation of polysaccharides like those found in extracted sugar. With PLA biodegradation and the photosynthetic process, the biological cycle can now complete itself [14–18]. Due to the polymer's high cost, limited availability, and low molecular weight [18-21], its principal usage has historically been restricted to medical applications such as implant devices, tissue scaffolds, internal sutures, and others.

Several aromatic polyesters, including poly(ethylene terephthalate), poly(butylene terephthalate), and poly(trimethylene terephthalate), have found extensive use in the packaging and textile industries as well as engineering materials due to their superior thermal and mechanical properties [20,21]. Unfortunately, aromatic polyesters have high levels of stability and resistance to deterioration, which is occasionally undesirable, especially for short-term applications [22]. However, the thermal and mechanical performance of biodegradable aliphatic polyesters is frequently poor [20, 23].

The possibility to combine the mechanical performance of aromatic polyesters with the biodegradability associated with aliphatic ones has drawn a lot of interest to materials combining both aliphatic and aromatic polyesters. Existing aliphatic-aromatic copolymers with good mechanical characteristics are petroleum-based and biodegradable [23,24]. It can be argued that PBT and PLA are immiscible based on theoretical calculations. However, three other kinds of chemical reactions, including alcoholysis, acidolysis, and ester exchange, can occur in a polyester-polyester blend when the temperature is high. As a result of these chemical reactions, block or random copolymers are produced. The chain structure may be impacted by the catalyst concentration, the amount of blending time, and the reaction temperature [25–27].

Ultrahigh molecular weight PLA has attracted a lot of attention in recent years as a potential substitute for synthetic polymers due to improved production techniques that allow it to be produced cheaply.

Blending biodegradable and petroleum-based polymers allows for the synthesis of partially bio-based polymers with enhanced or desired properties at a reasonable cost [28,29]. The work that focuses on adjusting the properties of bio-based PLA blends to improve their performance has recently attracted a lot of attention [30–35]. PBT and PLA are both members of the polyester family, making them great candidates for combining to produce a bio-based polymer.

PBT and PLA are both members of the polyester family, hence they can be considered to be great options for combining to produce a bio-based polymer. The subject of PLA and PBT blends have only been covered in a few studies. The physical interactions between the functional groups of the polyesters allow for compatibility even if the PLA and PBT combination is incompatible [36]. Kim et al. looked at the degradability and crystallization rate of a PLA/PBT blend using a para phenylene diisocyanate (PPDI) chain extender. They reported that the PLA phase's degradation rate had reduced, and the crystallization rate had increased [37]. The transesterification and ring-opening processes used to polymerize PLA-PBT block copolymers have received very little attention [38]. The compatibilizer properties of ethylene-glycidyl methacrylate copolymer added to biodegradable PLA in ratios of around 3 to 10% by weight were covered by Santos et al. in a recent study. This work aimed to enhance t tohe mechanical properties of PLA, a biodegradable aliphatic polyester, in particular. Melt blending was employed to create PLA/PBT blendes with different compositions for this aim, with PLA serving as the major phase and PBT serving as the minor phase. EBA-g-MAH compatibilizer was used to make PLA and PBT blends compatible. The production of PLA/PBT samples devoid of any compatibilizer was also done for comparison studies. Investigations were done on the rheological characteristics of neat PLA and PBT. Following the appropriate standards, the mechanical characteristics of all PLA/PBT blends, including yield strength, elongation at yield, modulus, tensile strength, elongation at break, and izod impact strength, were measured. Additionally, physical characteristics including shrinkage, density, and hardness were exposed. The impact of adding PBT to PLA polymer and using a compatibilizer in the composition on the qualities was investigated in light of the results.

2. LITERATURE REVIEW

2.1. Bio-Based Polymers

Bio-based polymers are materials made from renewable resources. In other words, it is defined as materials whose physical and chemical properties are subject to degradation. They are completely degraded when exposed to microorganisms, carbon dioxide (aerobic) processes, methane (anaerobic processes), and water (aerobic and anaerobic processes). Bio-based polymers make significant contributions by reducing dependency on fossil fuels and, consequently, with positive environmental effects such as reduced carbon dioxide emissions [39].

As a result, there is a worldwide demand to replace petroleum-derived raw materials with renewable resource-based raw materials. They can be natural or synthetic, but due to environmental concerns and the depletion of fossil fuels, intense research is being conducted to develop biodegradable polymers and plastic materials from renewable natural sources such as starch, cellulose, and soy protein. The most important biodegradable polymer derived from renewable resources is polylactic acid. The advantages and disadvantages of PLA are shown in Table 2.1.

2.1.1. Polylactic Acid (PLA)

Most polymeric materials are petroleum-based, and they are non-biodegradable waste products in the environment. Polymer production and disposal from fossil fuels have been condemned by the ecologically concerned globe in recent decades. As a result of this reason, academic and industry research has concentrated on developing an ecologically friendly product made from renewable resources. Furthermore, they are compostable and biodegradable. Poly (Lactic Acid) or Polylactide (PLA) is a well-known example that is manufactured from sugar cane and maize starch. PLA is the most promising bio-based polymer because of its commercial availability, strong mechanical properties, and outstanding processability [40,41]. Polymerization of lactic acid, which is formed by the fermentation of plants and sugar, produces poly(lactic acid), an aliphatic polyester that is 100% biodegradable and natural in origin [42]. Almost all industrial sectors employ petroleum-based synthetic polymers, with the automobile, plastics, and aerospace sectors using them most often. However, during the past ten years, scientists have become increasingly interested in using biodegradable polymers rather than synthetic ones because of ongoing environmental and economic concerns [43-46].

Poly(lactic acid), or PLA, has received the most attention out of all biodegradable polymers due to its distinctive and similar features with other traditional petroleum-based polymers, such as compatibility, resorbability, high strength, high modulus, and transparency [47-49]. Due to its biodegradability, PLA, a promising polyester, is marketed as a "green" polymer and made from renewable resources like sugar beet, starch, corn, etc. [43-44].

Carothers made the discovery of PLA, or poly-lactide, in 1932 (DuPont). Only by heating lactic acid under a vacuum and taking out the condensed water was he able to create a low molecular weight PLA. The challenge at the time was to raise the molecular weight of the products, and in the end, lactide ring-opening polymerization allowed for the synthesis of high-molecular-weight PLA. Wallace Carothers initially developed poly(lactic acid), commonly known as polylactide, in 1932 when he was employed by DuPont. He conducted a condensation process to produce low molecular weight PLA while heating the lactic acid under vacuum and removing the condensed water from the reaction media.

The rheological characteristics of PLA were investigated by Dorgan et al., who asserted that branching has a considerable impact on melt flow properties. In contrast to branching PLA, which deviates from the Cox-Merz rule that connects stable viscosity against shear rate curve to complicated viscosity vs angular frequency curve, the researchers noted that linear PLA obeys the rule. Furthermore, they claimed that when branching in PLA rises, so does zero shear viscosity and the strength of polymer shear [45].

Furthermore, research has been done on PLA's thermal characteristics. The melting temperature of poly (lactic acid) is between 130 and 180 °C, while the glass transition temperature (T_g) is between 60 and 70 °C. Molecular weight decrease begins at low temperatures even if its maximal degradation temperature is rather high because of the synthesis of cyclic monomers during thermal processing [46]. Although PLA has a variety of special qualities, as was already noted, its uses are limited by undesirable qualities including excessive brittleness and poor thermal stability. Different methods are used to enhance the inadequate qualities, including copolymerization, integration of filler materials, plasticization using a biocompatible plasticizer, and blending with other polymers [50,51].

Table 2.1. The most common advantages, and disadvantages of PLA

Polymer	Advantages	Disadvantages
Polylactic Acid (PLA)	%100 Biodegradable. Eco-friendly. Bio-compostable. Good mechanical and physical properties. Gloss and transparency are fine. Non-toxic and safe. Antibacterial and anti-fungal properties. Processing ability. Renewable resources. Blended with petroleum-based polymers. Easy to 3D printing applications.	High cost. A lack of toughness. Low heat resistance. Low melting point. A slow rate of deterioration. Impact resistance and hardness are weak. Permeability to moisture and oxygen is high. Not suitable for high-temperature environments. Not suitable for long-term food storage applications.

The biodegradable linear thermoplastic aliphatic polyester known as PLA is made from lactic acid, which is produced during the fermentation of renewable natural resources like corn, sugar cane, and wheat [52-54]. Because of its environmentally favorable, biocompatibility, and biodegradability characteristics, it has been widely employed in the packaging, disposable products, biomedical, pharmaceutical, and textile industries. Because of their great UV protection, low flammability, and low moisture absorption, PLA fibers can be used in outdoor furniture and sports apparel [55-57]. Because PLA has thermoplastic qualities, it may be processed using common techniques to create fiber, film, and sheets, including extrusion, injection molding, film blowing, thermoforming, and film and fiber applications. The lactic acid used to make PLA is (2-hydroxy propionic acid). Chemical synthesis from petrochemicals or bacterial fermentation of carbohydrates is used to treat lactic acid. L- and D-lactic acid are the two stereoisomers of lactic acid, which is a hydroxyl acid with an asymmetric carbon atom. The direct condensation polymerization method is the least expensive approach to polymerize PLA. Lactic acid is used to make PLA. Due to challenges in getting the water out of the process, low molecular weight PLA with undesirable mechanical traits, such as brittleness, might be produced [54, 56]. Without the use of adjuvants or other additions like chain extenders, azeotropic dehydrative condensation of lactic acid yields high molecular weight PLA [58]. Without any chemicals, large chain lengths are possible. The most typical process is called ring-opening polymerization. This technique can be used to create PLA with a high molecular weight and more intricate macromolecular architectures. During this polymerization, lactide is also used as a material in between.

2.1.1.1. Rheological properties of polylactic acid

Rheology is concerned with the flow and deformation of matter (liquid or soft solid) when a force is applied during a conversion process. A highly developed discipline called polymer rheology has been developed to study a critical feature of polymeric materials like PLA. Because rheological characteristics are highly dependent on molecular weight, temperature, and shear rate, rheological measurement must be taken into consideration during process optimization, tool modeling, and process design and simulation. While PLA with a high molecular weight behaves like a non-Newtonian fluid with h shear thinning characteristic (pseudoplastic), PLA with a low molecular weight behaves more like a Newtonian fluid. Semi-crystalline PLA exhibits a greater shear viscosity under compression than its amorphous counterpart under equal processing circumstances [59,60].

Rheology is the examination of the deformation and flow of a fluid. It is a crucial characteristic of a molten polymer that links the viscosity to temperature and shear rate and, as a result, to a polymer's processability. Many polymer melts are categorized as shear-thinning fluids, in which the polymer molecules orient and the number of entanglements between the polymer chains reduce with greater shear rates. During the polymerization process, these occurrences facilitate the polymer chains' effortless movement past one another and into confined spaces. At high temperatures, the viscosity also falls because of the molecules' increased kinetic energy. To get information on the shear viscosity of polymers, instruments like rotational and capillary rheometers can be used. Low-shear-rate applications are where rotational rheometers excel. These instruments typically have a cone and plate geometry, and by carefully designing the cone angle, it is possible to keep the shear rate constant throughout the investigation. The apparent rheological information of the polymer melt is obtained using capillary rheometers, which employ a pressure-driven flow and monitor the pressure at the entry to a capillary die.

Compared to rotational measurements, these measures need a substantial amount of time and material. Thermal methods like extrusion and injection molding are used to turn poly(lactic acid) (PLA) into usable products. Its rheological characteristics, particularly its shear viscosity, thus, have a significant impact on the thermal processes, including film blowing, paper coating, injection molding, sheet forming, and fiber spinning. To develop a fundamental understanding of the processability of PLA materials, it is essential to research the rheological characteristics of PLA [61].

PLA polymers are typically converted into useful materials using thermal techniques such as injection molding and extrusion. As a result, its rheological properties, particularly shear viscosity, have a considerable impact on thermal processes such as film blowing, paper coating, injection molding, sheet forming, and fiber spinning.

PLA melt, like other plastic polymers, is viscoelastic in nature. That is, the polymer's flow behavior is a combination of irreversible viscous flow caused by chain slippage and reversible elastic deformation caused by molecule blending. PLA melts behave similarly to non-Newtonian fluids. When a non-Newtonian fluid is exposed to shear deformation, the shear stress to strain rate is not constant, unlike Newtonian fluids [62].

2.1.1.2. Mechanical and physical properties of polylactic acid

In general, it can be argued that PLA has strong mechanical properties, including an elastic modulus of around 3500 MPa and a tensile strength of about 50–70 MPa, although its low elongation at break (2–10%) restricts certain of its uses [59]. Notching is a significant factor in how PLA impacts since imperfections on the surface reduce impact strength. The impact strength is also impacted by the notch's radius. Grijpma et al. looked at this issue. They claimed that the strength values of the samples decrease from 2.2 to 1.2 kJ/m² when the radius is decreased from 1.00 to 0.10 mm (by the izod impact test). Impact resistance greatly increases as PLA's crystallinity rises [63].

According to scale H and around 12 on scale L, PLA typically has a Rockwell hardness between 70 and 90. The literature claims that molecular weight and crystallinity have a negligible impact on the Rockwell hardness attribute. However, the impact of Tg on Rockwell hardness is quite strong [64]. In semi-crystalline polymers, crystallization reduces fracture toughness while also causing embrittlement.

The mechanical qualities of lactic acid-based polymers can range from soft and stretchy plastics to rigid and high-strength materials. When greater mechanical qualities are required, semicrystalline PLA is preferable over amorphous polymers. Semicrystalline PLA exhibits a tensile modulus of about 3 GPa, a tensile strength of 50-70 MPa, a flexural modulus of about 5 GPa, a flexural strength of 100 MPa, and an elongation at break of around 4% [65,66].

Mechanical properties and crystallization behavior of PLA, unlike thermal properties, are highly reliant on the Mw and stereochemical makeup of the backbone [67].

Lactic acid-based polymers can have a variety of mechanical properties, from flexible and soft plastics to rigid and strong materials. Semicrystalline PLA is preferred over amorphous polymers when higher mechanical characteristics are needed. The tensile modulus of semicrystalline PLA is around 3 GPa, the tensile strength is 50–70 MPa, the flexural modulus is approximately 5 GPa, the flexural strength is 100 MPa, and the elongation at break is approximately 4% [65,66].

Contrary to thermal characteristics, the Mw and stereochemical composition of the backbone has a significant impact on the mechanical properties and crystallization behavior of PLA [67]. Controlling the stereochemical architecture enables exact control over the material's processing temperatures, mechanical properties, and degree and rate of crystallization.

The crystalline equilibrium temperature of neat PDLA or PLLA is 207 °C, however common T_m is in the range of 170-180 °C [68].

Impurities, mild racemization, and small, imperfect crystallites are to blame for this. The stereo complexation (racemic crystallite) of the two polymers during crystallization or polymerization results in an insoluble gel when neat PLLA and neat PDLA are blended 1:1 ratio [69,70].

Stereo complexation of enantiomeric PLAs led to the development of stereo complex crystallites that provided intermolecular crosslinks, which in turn led to the achievement of superior mechanical characteristics.

Greater mechanical characteristics than either neat polymer can be found in this neat stereo complex, which has a Tm of 230 °C [71-75]. The ultimate tensile strength of the 1:1 stereo complex made of low M_w (molecular weight) PLA was found to be 50 MPa, as opposed to 31 MPa for neat L-PLA similar stereo complexation can be seen in variations like the block and star copolymers of D- and L-lactide [71]. After studying their mechanical properties, Lalla and Chugh, who had previously synthesized D-, L-lactide using 2% (w/v) and 0.1% (w/v) zinc oxide and stannous chloride catalyst systems, respectively, found that the degree of orientation and stereochemical makeup of different PLA samples were to blame for the wide variation in the oriented properties [72].

2.1.1.3. Thermal properties of polylactic acid

Crude oil is nearly exclusively employed in the production of the common plastic items that have become a part of daily life. The amount of oil reserves are estimated in a variety of ways, but it is becoming more and more necessary to employ other resources, preferably renewable ones, to make plastic goods. Though so-called bioplastics/biopolymers plastics made from renewable resources, bio-based, and intrinsically biodegradable are now available on the market, their qualities are not necessarily up to par with those of "regular" petroleum-based plastics, which the bioplastic is intended to replace. Currently, Poly (lactic acid) is one of the most promising bioplastics (PLA).

Although PLA has a big potential to replace engineering plastics made from petroleum, such as Acrylonitrile Butadiene Styrene (ABS), Polypropylene (PP), and others, its intrinsic brittleness, and low Heat Deflection Temperature (HDT) prevent its widespread use. The qualities of PLA have been improved using numerous techniques, but their extensive industrial application is still more of an anomaly than a rule. In 2020, the price of PLA ranged from 2.1 to 4.7 USD/kg, which is slightly more expensive than the average price of traditional polymers [76]. However, PLA's primary flaws are its innate fragility and low Heat Deflection Temperature (HDT) [77].

2.2. Petroleum-Based Polymers

Petroleum-based plastics are artificial or organic polymers derived from natural gas or petroleum and used in a variety of applications. The use of petroleum-based plastic materials in various applications, particularly in the medical, industrial, commercial, and municipal sectors, is increasing, but it also creates a significant environmental problem.

Petroleum-based plastics also can be biodegradable, but due to their high stability, they cannot degrade in a short time. Even biodegradable plastics can last for many years, depending on environmental factors such as temperature, oxygen levels, and ultraviolet (UV) light exposure levels. Additionally, stabilizers and plasticizers are used to improve the properties and effectiveness of petroleum-based plastic materials, and they can leach into the environment during the degradation process. In this work, Polybutylene terephthalate (PBT) and Polyethylene terephthalate (PET) were selected as petroleum-based polymers.

2.2.1. Polybutylene terephthalate (PBT)

Polybutylene terephthalate (PBT) is a semicrystalline engineering thermoplastic that is the commercially second-most important polyester. By 2026, the global PBT market is expected to reach 1.5 million metric tons [78]. PBT is a fast-crystallizing polymer, making it ideal for high-cycle-time extrusion and injection-molding applications [79]. Given its excellent properties, PBT is the preferred material when high strength, good dimensional stability, resistance to various chemicals, and good insulation are required as well as when bearing and wear characteristics play a role in material selection. As a result, PBT can be used to make valves, food processing machinery parts, wheels, and gears. PBT has excellent electrical insulating qualities, including good contact and surface resistance, high dielectric strength, and good tracking current resistance, all of which are stable across a broad temperature and humidity range. For the construction of electrical and electronic equipment, PBT is a dependable and superior material [79]. The advantages and disadvantages of petrochemical PBT are shown in Table 2.2.

Table 2.2. The most common advantages, and disadvantages of PBT

Polymer	Advantages	Disadvantages
Polybutylene Terephthalate (PBT)	High continuous use temperature up to 150 °C.	Notch impact strength is low.
	Very good creep resistance even at higher temperatures.	The forming shortening rate is large.
	High rigidity.	Poor resistance to hydrolysis
	Good friction properties and wear resistance.	Susceptible to halogenated hydrocarbon corrosion.
	High dimensional and UV stability.	Tendency to warp when reinforced with glass.
	Good weather resistance.	
	Resistant to cracking from environmental stress.	Not resistant to stronger acids and bases.
	Low water absorption, Dyeability at low temperatures	Lower glass transition temperature compared to other high-grade plastics.
	Moldability, Resistant to solvents.	Poor resistance to hydrolysis

The condensation polymerization method is used to create polybutylene terephthalate (PBT), a crucial semicrystalline commercial thermoplastic, from 1,4-butanediol (BDO), terephthalic acid (TPA), or dimethyl terephthalate (DMT), in the presence of a polyesterification catalyst [79–82]. Tetraalkyl titanates are the catalysts most frequently employed for PBT polymerization [79,80]. The traditional method for polymerizing PBT involves first transesterifying BDO with DMT to produce the diester, bis (4-hydroxy butyl-terephthalate) (BHBT), or ester oligomers with hydroxy butyl ester end groups [80, 83]. Due to the flexible butylene groups that make up part of its molecular structure, PBT crystallizes at a relatively rapid rate, and the melting and crystallization characteristics of the substance are affected by its temperature history. The glass transition temperature (T_g) range for fully crystalline PBT homopolymer is 30 to 50 °C, while the typical melting temperature (T_m) is from 222°C to 232 °C. By annealing PBT for a long time, the crystallinity of the material allows for a shift in the glass transition temperature and melting temperature to higher values. Furthermore, annealing can increase the crystallinity of PBT to 60% from its typical range of 35 to 40%. Several melting peaks may appear on the DSC curve for PBT because it often contains crystals of various sizes [79, 83-84].

PBT exhibits excellent electrical properties, low creep at elevated temperatures, great dimensional stability, low coefficient of friction, outstanding chemical, grease, oil, and solvent resistance, and good tensile strength due to the presence of its crystalline phase [80-85]. The mechanical properties of PBT are significantly influenced by the crystallinity level. The resin's solvent resistance and mechanical strength are provided by the crystalline PBT regions. It can be said that the elongation characteristics of a material are provided by the amorphous area. PBT's quick crystallization and low melt strength features make processing simple [79, 84].

PBT is a viscoelastic polymer, and its melt has a low viscosity and very fast crystallization, allowing for easier processing when compared to PET. Spinning, extrusion, injection molding, and gas-assisted injection molding can all be used to process PBT resins [79, 82]. PBT has good electrical insulating properties (contact and surface resistance) as well as high dielectric strength and tracking current resistance that is stable over a wide temperature and humidity range. As a result, PBT is a dependable and superior building material for electrical and electronic equipment. It is used as an insulator in plugboards, contact strips, and plug connections [79]. Polybutylene terephthalate (PBT) is an important commercial polymer with applications in a variety of industries including automotive parts, electrical, electronic, and textile. It has similar thermal, chemical, and mechanical properties to PET, but slightly better impact strength and PBT crystallizes at a faster rate than PET [79, 80].

2.2.2. Polyethylene terephthalate (PET)

Engineering grades of PETs, which are part of the polyester polymers family and have high-performance mechanical and electrical qualities, are readily available. PET is a semi-aromatic thermoplastic polyester that is widely used in a variety of industrial applications [86-88]. For most of these applications PET as an effective packaging material for food and beverage products, also plays important role in textile fibers, automotive components, and biomedical applications [89,90]. This widespread application is due primarily to its superior mechanical properties, high chemical resistance, good barrier properties against oxygen and water vapor, and thermal stability, as well as its low production cost, processability, and recyclability [91-94]. As a result of such widespread PET use, primarily in soft drink containers, global production exceeded 56 million tons in 2016 and is expected to exceed 70 million tons by 2020 [90]. The advantages and disadvantages of PET are shown in Table 5.

PET is produced in two steps: pre-polymerization and melt polycondensation. Pre-polymerization occurs via two reactions: direct esterification of terephthalic acid (TPA) with ethylene glycol (EG) or transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) [83].

PET's thermal properties, which in turn rely on the degree and kind of crystallinity, are a key factor in how processable it is. PET has a low crystallization rate because of the short ethylene chain that separates the aromatic rings. PET samples also frequently display multiple melting endotherms, which depend on the wide temperature range in which crystallization occurs and result in crystals of various sizes and perfections [95, 96]. Depending on PET processing and thermal history, PET samples may be in an amorphous, semicrystalline, or completely orientated condition [97]. PET has a T_g of 67 °C in the amorphous state, and it is possible to produce amorphous, transparent PET by rapidly cooling from the melt to a temperature below T_g.

Table 2.3. The most common advantages, and disadvantages of PET

Polymer	Advantages	Disadvantages
Polyethylene Terephthalate (PET)	Easily available and inexpensive Highly resistant to moisture and chemically resistant to organic matter and water. High strength-to-weight ratio. High transparent and shatterproof. Easily recycled. Very strong and lightweight. Easy and efficient to transport.	Lower heat resistance Resins are susceptible to oxidation. Partially derived from crude oils. PET resins are even susceptible to oxidation. Not biodegradable.

Semi-crystalline PET, which has a T_g of 81°C in the semi-crystalline state, can be created by heating solid amorphous PET over T_g. While PET's fully annealed melting point is 280 °C, its melting temperature ranges from 250 to 265 °C. The final polymer's processability and thermal characteristics are significantly influenced by the degree of crystallinity and shape [98]. The molecular weight of the polymer may have an important bearing on the crystallinity of PET. Low-molecular-weight grades could provide more crystallinity because, in contrast to greater molecular weights, they make it easier for the chain to align. Combinations of crystallinity and molecular weight can have an impact on the final mechanical characteristics [83, 96, 99-101]. It has a range of high tensile strengths and flexural modulus between 55 and 75 MPa and 2412-3102 MPa respectively. It is also nearly impermeable to most of gases and liquids, and its properties could be further enhanced by increasing crystallinity. Moreover, it shows resistance to being dissolved by ordinary solvents. The low melt strength and slow rate of crystallization of PET, which is primarily brought on by the presence of ethylene units in its structure, make processing it is challenging [102,103]. The most widely used PET has a narrow molecular weight distribution, comparatively low molecular weight, and weak melt strength and viscosity by nature. For applications like foaming or extrusion blow molding, these properties are not appropriate. By raising the molecular weight and expanding the molecular weight distribution, it will be feasible to improve the attributes of PET, such as die swell, melt strength, and melt flow index [100,101]. Since diverse applications call for different features, PET can be produced through modification such as chain extension, grafting, branching, blending, controlled cross-linking, or controlled degradation [100].

2.3. Bio-Based PLA/Polyester Blends

The neat bio-based polymers are typically pricy and underwhelming. But, if the bioplastics, which contain both fossil and renewable carbon, can be synergistically adjusted for creating the blends, higher performance can be reached. Hence, these cannot be used as-is, and it is necessary to achieve a balance between performance and cost while blending the polymers because combining thermodynamics does not help the blending process and is not a simple task. One of the promising approaches for attaining durability is by formulating PLA blends or synthesizing PLA composites because of the distinctive properties and cost competitiveness of PLA. Hence, work needs to be done to fabricate PLA-based blends. However, preparing a good miscible blend or composite of PLA with other polymers is a challenging task that should not hamper the toughness of the PLA. Also, the environmentally beneficial properties of the synthetic PLA blend must be considered. Hence, choosing the right antecedents is crucial and demands careful consideration when PLA is modified. The mechanical properties, biodegradability, biocompatibility, simplicity of manufacture, and non-toxicity of the bio-based polymer polylactic acid (PLA) make it stand out. Because of this, PLA is a desired polymer for use in technical and biological applications and is a wonderful alternative to polymers based on petroleum in a variety of goods. The drawbacks of PLA, on the other hand, prevent it from being used in a wide range of applications. These drawbacks include low melting strength, poor processability, high brittleness, a slow rate of crystallization, and low toughness. To remedy these shortcomings, blending PLA with other polymers is a practical way to increase the polymer's compatibility with the properties of PLA-based products [75].

To understand PLA/polyester blends well, their pure chemical structures are shown in Figure 2.1.

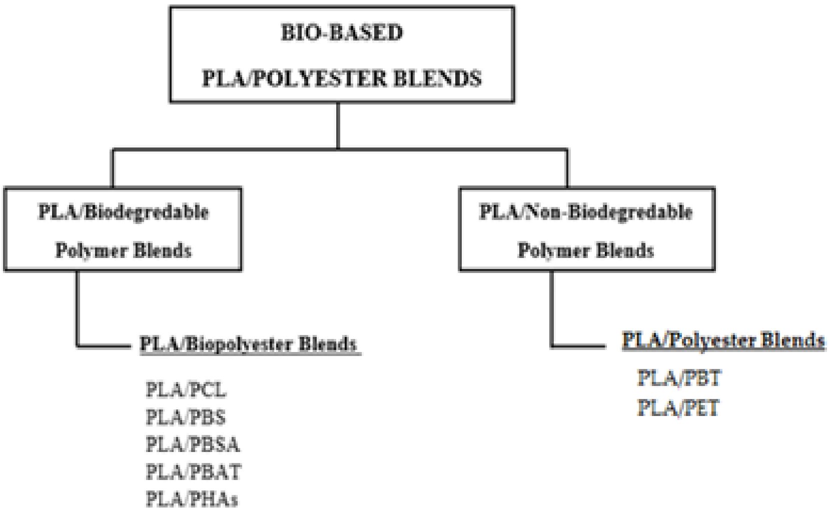


Figure 2.1. Schematic representation of bio-based PLA blends

2.3.1. PLA-PBT blends

Butylene terephthalate, or PBT, a commonly used polyester, crystallizes quickly and has a high melting point for crystals (higher than the PLA melting temperature). Hence, when utilizing PBT spherulites, PLA might function as a crystal-nucleating agent. Although having high compatibility, blends of PLA and PBT are believed to be immiscible due to interactions between their functional groups. Widely used polyester Poly (butylene terephthalate, or PBT), has a rapid rate of crystallization and a high melting point for crystals (higher than the PLA melting temperature). As a result, PLA might act as a crystal-nucleating agent when using PBT spherulites. PLA and PBT blendtures are said to be immiscible despite having excellent compatibility because of interactions between their functional groups.

Good phase adhesion and dispersion arise from this. When PLA/PBT was made utilizing reactive extrusion and para phenylene diisocyanate (PPDI) as a chain extender, Kim et al. looked at the crystallization behavior. PBT promoted the crystallization of PLA, although PLA had the opposite impact on PBT [105].

PPDI reduced the crystallinity of the PLA and PBT phases alone, while the PLA crystallization rate was enhanced when PLA, PBT, and PPDI were combined. The rate of PLA degradation was slowed down by the PPDI-generated high interfacial adhesion between PLA and PBT. The effects of PBT droplet size and shape on the morphology and porosity structure of the biaxially stretched PLA blend films were also investigated by Samthong et al. [38,105]. Due to the interfacial debonding, the stretched films made up of PBT droplets showed ellipsoidal microvoids, and the void size matched the size of the PBT droplets. They asserted that the void content of the stretched films was unaffected by the PBT droplet size. Furthermore, blends of PLA and highly crystalline polyesters, specifically PBT, have been thoroughly researched since the dispersed rapid crystallizing phase may operate as a nucleating agent for PLA, improving its crystallization kinetics. In the physical blends phase-separated systems, an additional compatibilizer is needed to improve interfacial adhesion and compatibility between individual phases [27,48,106]. This is true even though desirable combinations of properties can be obtained by simply and economically blending two or more polymers.

However, it was discovered from the previous literature study that extended two-step polymerization at high reaction temperature causes thermal degradation of poly (L-lactic acid) (PLLA) and generation of copolymers with random distribution throughout the copolymer chain. Only the copolymers examined by Olewnik et al. and possessing an equimolar terephthalate/lactate ratio demonstrated some block copolymer characteristics. Furthermore, by ring-opening polymerizing LA with bis-(4-hydroxyethyl) terephthalate (BHBT) in solution, copolymers comprising PBT and PLLA as a primary component (PLA-b-PBT-b-PLA) with the somewhat defined blocky structure were created [38,47].

Though the produced product had a relatively small number of average molecular weights (Mn) with a maximum value of 81.1 g/mol, the approach succeeded in promoting the organization into a blocky structure. To create polymers with unique features, the latter process has shown promise [105-108].

The immiscibility of the polymer pair and the existence of groups that can react during melt blending are the two prerequisites that must be satisfied to use this approach in the synthesis of copolymers [109]. In their system, both requirements have been fulfilled. Theoretical studies have shown that PBT and PLA are incompatible, and high temperatures in a polyester-polyester blend can lead to three different chemical reactions, including alcoholysis, acidolysis, and ester exchange [26,27]. Copolymers that are either block or random are created because of these chemical processes. The temperature of the reaction, the quantity of catalyst, and the blending time can all affect the chain structure. The production of two PBT/PLA systems physical blends and reactive blends and their ensuing morphologies have been compared in the current work. On the based Hoy and Van Krevelen group contribution techniques, the thermodynamic compatibility of the PBT-PLA polymer pair was evaluated.

2.3.2. PLA-PET blends

Polyethylene terephthalate (PET) is a thermoplastic engineering material with superior thermal, mechanical, low permeability, and chemical resistance that is widely used in industry. PET also exhibits exceptional clarity and effective moisture and oxygen barriers in contrast to alternative packaging polymers. Water and soft drink bottles, it has grown to be the most widely used packaging material globally [110–112]. However, this polymer's extraordinarily high resistance to breakdown by atmospheric and biological agents, which restricts its use and makes chemical recycling challenging is one of its primary drawbacks [113,114].

In recent years, polymers produced from renewable resources, notably biomass, have drawn considerable attention because of their favorable effects on the environment [115]. A biodegradable polyester with high strength and high modulus, polylactide (PLA) is made from renewable materials including maize and starch [116]. Recently, especially with the rise in oil costs, PLA bottles have become extensively utilized and have begun to challenge PET bottles' hegemony. The usage of PLA bottles is, however, constrained since it is challenging for PLA to replace the widely used commodity packaging material due to its high cost and inherent permeability qualities [117]. To create goods with desirable qualities that aren't necessary by any one component polymer, several polymers have been blended extensively. The compatibility or miscibility of polymer pairings is typically a crucial aspect in determining the qualities of blends.

The blending of PET and PLA has been studied by Cebe et al., who contend that the PET/PLA blends produced by solution casting are miscible in the melt across the full composition range [118]. Even if they are precise, the experimental techniques take a lot of time and money. Due to their ability to provide microscopic images of underlying mechanisms that would otherwise be difficult or impossible to obtain experimentally, molecular simulations have become more and more important in materials modeling and the development of subsequent technologies because of the ever-increasing computational power and resources [119–123]. One of the most used polymers in the packaging industry is polyethylene terephthalate (PET), which has high mechanical qualities and low permeability [124-126].

For a biodegradable material for packaging and bottle manufacture with suitable barrier qualities, PET is a promising choice for blending with PLA. Focusing on decreasing the temperature at which PET/PLA blends degrade, Xia et al. discovered that the PLA content significantly affects the material's mechanical and thermal stability [127].

The nonisothermal crystallization of PET/PLA blends has been studied by Chen et al. They found that PLA may crystallize in both amorphous and crystalline forms [118]. With PLA loading, however, the level of PET crystallinity declines. PET is a significant engineering thermoplastic used in commerce that has strong thermal and mechanical characteristics as well as low permeability and chemical resistance. Girija et al. examined the thermal and mechanical properties of blends of PLA and PET [130]. The integration of PET improved the thermal stability of PLA, but PET's impact and tensile strengths and elongation at break were reduced because of the increased stiffness of PLA. Chen et al. have thoroughly investigated the crystallization behavior of PLA/PET blends created using solution casting [118]. The blends of PLA and PET were discovered to be miscible over the whole composition range. As the quantity of either crystalline or amorphous PLAs increased, the PET's crystallinity dropped. The PLA crystallinity, however, was only reduced when the PET crystallized.

Moreover, Fu et al. and Huerta et al. validated the miscibility of PLA/PET blends across the board of blend content [118,130]. Huerta and colleagues investigated the miscibility of PET/PLA blendes and contrasted their compatibility with PET/chitosan blends [130]. The saturation level of PLA in the polymer matrix could be increased to 10 weight percent, and researchers discovered that PLA is more miscible than chitosan.

Despite the results of all this research, Li et al. showed that cold crystallized electrospun PLA/PET (70/30 and 50/50) blends were immiscible and had two unique glass transition temperatures [131]. They verified that during electrospinning, cold crystallization, and blends of 70/30 and 50/50 PET/PLA, phase separation occurred. The crystallization of both PLA and PET was hampered in these immiscible blends. The ability to combine the two polymers is restricted by the considerable gap between the melting temperature of PLA (160–180 °C) and the processing temperature of PET (260–300 °C) [132]. Torres-Huerta et al. investigated how miscible PET/PLA blends were. Weak interactions in the blends point to electrostatic contact and hydrogen bridges between the constituents [130].

McLauchlin et al. have investigated the impact of adding PLA (0.5–20%) to PET [72]. The investigation was done to see how the mechanical and thermal behavior of PLA in recycled PET (rPET) process streams would be affected. The polymers were co-processed in an injection molding machine over a brief (4 s) residence time. To improve the compatibility of the two polymers, no additive was utilized in the procedure. The addition of more than 2% of PLA to PET resulted in a significant loss in mechanical strength. The larger and more numerous PLA tiny beads were blamed for the behavior.

Using epoxide compatibilizers, You et al. have made PLA/PET blends compatible. As a chain extender and toughening agent, respectively, EBA-GMA and SA-GMA were employed. The epoxy group on EBA-GMA interacted with the carboxylic and hydroxyl groups of PLA [132]. Furthermore, SA-GMA (Joncryl) reduced the rate of PLA thermal degradation in the blend. The epoxide reaction stopped PLA from degrading. Two compatibilizers were added, but it was found that this did not appreciably improve the characteristics. EBA-GMA, on the other hand, produced micelles and had little adherence to the PLA phase. Just SA-GMA was added, and it concurrently served as a chain extender and compatibilizer. The impact strength increased by 292% because of the toughening agent's inclusion, however, the modulus dropped to 25%.

Moreover, McLauchlin et al. have demonstrated the immiscibility of PLA/PET blends with a maximum of 20 wt.% PLA in injection molding tests [131]. The addition of PLA considerably decreased the impact and tensile strength of the blends. With a maximum PLA content of 7.5 wt.%, partial miscibility of PLA/PET blends was reported using single-screw extrusion [133].

Jiang et al. have examined blends including PLA-g-MA as a compatibilizer and 20% PET glycol-modified (PETG) and 80% PLA by weight [134]. They also claimed that the blends had an immiscible, droplet-like shape. They demonstrated that the use of 3 wt.% PLA-g-MA greatly decreased the interfacial tension between PLA and PET using rheological data and emulsion models, such as the Palierne model. By maintaining the tensile strength and modulus, the droplet size was decreased, and the size distribution was improved. The addition of PLA (up to wt. 5%) had a detrimental effect on the rheological characteristics of PET made from recycled bottles [133].

PET is a significant engineering thermoplastic used in commerce that has strong thermal and mechanical characteristics as well as low permeability and chemical resistance. It is meant to evaluate the thermal stability of PLA by adding it to PET.

2.3. Compatibilizer Used in PLA Blends

The major plastics companies have invested much in research and development of partially or wholly bio-based polymers to completely replace plastics made from petroleum feedstock. There are a variety of bio-based plastics on the market, including bio-PET, bio-PP, poly (lactic acid), polyhydroxyalkanoate (PHA), bio-HDPE, bio-LDPE, and others. As a result of its excellent qualities, including its high mechanical strength and modulus, transparency, and non-toxic byproducts, PLA appears to be one of the biodegradable polymers that many academics and businesses are researching the most. Combining biodegradable and petroleum-based polymers enables the production of partially bio-based polymers with improved or desired properties at an affordable price [135,136].

There has been a lot of interest in recent years in the work being done to improve the performance of bio-based PLA blends by modifying their properties. PLA is a good candidate to combine with PBT to create a bio-based polymer because they are both members of the polyester family [137,141]. Nevertheless, the two polymers are incompatible and immiscible with one another. [131] Direct blending won't make the attributes of this blend better. In addition, PBT is processed at a temperature of roughly 240–260 °C, whereas PLA is processed at a temperature between 170-190 °C. The processing temperature must be raised to 240–260 °C to melt and blend these two polymers together.

Random main-chain scission, depolymerization, and oxidative degradation in an oxygen environment during melt processing exceeding 180 °C are examples of thermal degradation processes [132]. Cyclic oligomers arise and transesterification degrades at processing temperatures higher than 200 °C [133]. The mechanical performance of PLA significantly deteriorates. As a result, a significant obstacle to the industrial sector's ability to produce this bio-based realistically is the breakdown of PLA when blending with engineering polymers at higher processing temperatures.

With the idea of reconnecting the broken chains of PLA and so causing recovery and prevention in the molecular weight drop of PLA, several studies have shown the effectiveness of chain extenders in minimizing the degradation problem of PLA when processing at high temperatures. Some of the chain extenders that have been studied and shown to help reduce PLA breakdown include poly carbodiimides (TNPP), an epoxy-functionalized styrene-acrylate copolymer [124,134–136]. Najafi et al. claim that styrene-acrylate copolymer with reactive epoxy is more effective and efficient than PCDI and TNPP in improving the thermal stability of PLA-clay nanocomposites under the experimental conditions [137].

PLA's multi-functional epoxy component may easily react with polyester's hydroxyl and carboxyl end groups [138,139].

Therefore, it functions efficiently as a chain extender and PBT compatibilizer. Only a few articles have so far examined the bio-based combination of PLA and PBT. Although the PLA/PBT blend is immiscible, there is some compatibility due to physical interactions between the polyester functional groups [140]. Kim et al. studied the degradability and crystallization rate of a PLA/PBT blend using a para-phenylene diisocyanate (PPDI) chain extender [141]. The crystallization and degradation rates of the PLA phase, respectively, were observed to have risen and slowed down, respectively. The transesterification and ring-opening processes used to polymerize PLA-PBT block copolymers have not been extensively studied [142]. In a recent study, Santos et al. described the properties of biodegradable PLA combined with PBT concentrations of 3, 5, and 10 %wt., along with ethylene-glycidyl methacrylate copolymer added as a compatibilizer [26]. They said that adding a PBT dispersion phase with a nanometer-sized size to the blend enhanced the PLA's mechanical properties. All the research previously stated and covered uses PLA (biodegradable-based polymer) as the main matrix component and PBT (petroleum-based polymer) as the minor blend component to improve the properties and crystallization behavior of PLA.

3. EXPERIMENTAL PROCEDURE

3.1. Materials

Industrial-grade polymers PLA, PBT, and PET were used in the studies. In addition to these, two different compatibilizers and a chain extender were selected.

A commercial grade polylactic acid (PLA) from Ingeo™ 2003D (NatureWorks) with a melt flow rate of 2.66 g/10 min. was used.

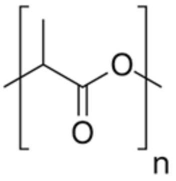
A commercial grade of polybutylene terephthalate (PBT) (TH6095 coded), provided by Xinjiang Blueridge Tunhe Chemical Industry Co. Ltd. with a melt flow rate of 36 g/10 min. was selected.

PET was selected from Köksan PET with the grade name PET K. 076 having a density of 1.3345 g/cm^3 and intrinsic viscosity (IV) = 0.76 ml/g.

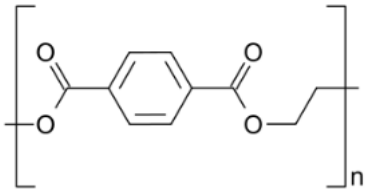
A chemically modified ethylene butyl acrylate copolymer grafted with maleic anhydride (EBA-g-MAH) Lucofin 1492M HG (LUC) provided by Lucobit (Wesseling, Germany) with a melt flow rate of 5 g/10 min was used as compatibilizer agent.

Lotader AX8900 random terpolymer of ethylene acrylic ester-glycidyl methacrylate was obtained commercially from Arkema Functional Polyolefins, Istanbul, Turkey.

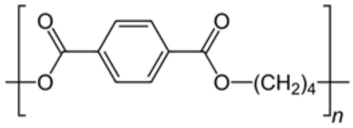
A commercial chain extender with the brand name Joncryl ADR 4468 was provided by BASF. Joncryl is a multifunctional styrene acrylic oligomer with epoxy reactive groups. Joncryl ADR 4468 also acts as an epoxy-based chain extender for PC, PBT, and PET.



PLA

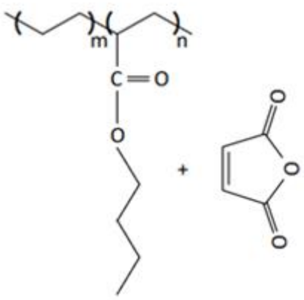


PET

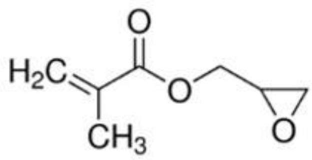


PBT

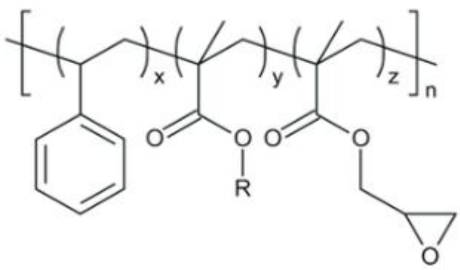
Figure 3.1. Chemical structures of PLA, PBT, and PET



EBA-g-MAH



GMA



Jonhcrl ADR 4468

Figure 3.2. Chemical structures of compatibilizers and chain extender

Table 3.1. Mechanicals and physical properties of PLA and PBT polymers

Property	Standard	PLA	PBT	PET	Unit
Density	ISO 1183	1.25	1.30	1.345	g/cm³
MFI (190°C /2.16 kg)	ISO 1133	2.66	-	-	gr/10’
MFI (250°C /2.16 kg)	ISO 1133	-	36	-	gr/10’
MFI (265°C /2.16 kg)	ISO 1133	-	-	17.88	gr/10’
Impact Test	ISO 180/1A	3.81	5.52	2.00	kJ/m^2
Molding Shrinkage	ISO 294-4	0.42	0.8	0.6	%
Tensile Strength	ISO 527-2	75	36	58.4	MPa
Elongation at Break	ISO 527-2	2.36	2	4.2	%
Yield Strength	ISO 527-2	79.25	58.4	32	MPa
Elongation at Yield	ISO 527-2	2.21	4	40	%
Young Modulus	ISO 527-2	3000	2380	2240	MPa
Hardness	ISO 868	73	75	80	Shore D

Table 3.2. Properties of EBA-g-MAH compatibilizer

Typical Analysis	Standard	EBA-g-MAH	Unit
Density	ISO 1183	0.94	g/cm³
MFI (190°C /2.16 kg)	ISO 1183	2.01	gr/10’
Grafting level - Maleic anhydride	FTIR	0.76	%
Methyl Acrylate Content	FTIR	24	%
Glycidyl Methacrylate Content	FTIR	8	%

Table 3.3. Properties of Lotader GMA AX8900 compatibilizer

Typical Analysis	Standard	GMA	Unit
MFI (190°C /2.16 kg)	ISO 1183	5.96	gr/10’
Methyl Acrylate Content	FTIR	23.72	%

Table 3.4. Properties of Joncryl ADR 4468 chain extender

Typical Analysis	Standard	Joncryl	Unit
Density	ISO 1183	1.16	g/cm³
Glycidyl Methacrylate	FTIR	0.300	%

3.2. Methods

PLA blends were produced by melt blending by using an interlocking, co-rotating twin screw extruder with a screw diameter of 30 mm and an L/D ratio of 36.

For PLA/PBT blends;

Melt blending was performed using an interlocking, co-rotating twin screw extruder with a screw diameter of 30 mm and an L/D ratio of 36.

PLA/PBT blends were prepared with 5%, 10%, and 15% PBT by weight. 3 phr EBA-g-MAH and GMA compatibilizers were added to the PLA/PBT blends created.

Samples without compatibilizer were also prepared to compare the properties of the blends.

The extruder zone temperatures were chosen as 220-230°C, the feeding speed was 30 kg/h and the screw speed was 260 rpm.

Table 3.5. The compositions of the PLA, PBT, compatibilizers, and chain extender

Samples	PLA (%)	PBT (%)	EBA-g-MAH (phr)	GMA (phr)	Joncryl (phr)
PLA/PBT (95:5)	95	5	0	0	0
PLA/PBT (90:10)	90	10	0	0	0
PLA/PBT (85:15)	85	15	0	0	0
PLA/PBT-E (95:5)	95	5	3	0	0
PLA/PBT-E (90:10)	90	10	3	0	0
PLA/PBT-E (85:15)	85	15	3	0	0
PLA/PBT-G (95:5)	95	5	0	3	0
PLA/PBT-G (90:10)	90	10	0	3	0
PLA/PBT-G (85:15)	85	15	0	3	0
PLA/PBT-J (95:5)	95	5	0	0	0.5
PLA/PBT-J (90:10)	90	10	0	0	0.5
PLA/PBT-J (85:15)	85	15	0	0	0.5

Samples were categorized based on the component weight percentage and compatibilizer content. The predominant and minor phases of the prepared PLA/PBT blends were found to be PLA and PBT, respectively. It is abbreviated as EBA-g-MAH compatibilizer (E) and GMA compatibilizer (G), respectively. In the examples marked with a J, it stands in for Joncryl, the extender. For instance, the blend code PLA/PBT (95:5) denotes a composition of 95% PLA and 5% PBT with no compatibilizers or chain extenders. Another illustration shows that the sample with the PLA/PBT-E code (90:10) contains 90% PLA, 10% PBT, and 3 phr EBA-g-MAH. The Table 3.5. shows that the composition is 85% PLA, 15% PBT, and 0.5 phr chain extender. According to Table 3.5, the sample designated as PLA/PBT-G included 85% PLA, 15% PBT, and 0.5 phr chain extender Joncryl.

<u>For PLA/PET blends;</u>

For PLA/PET blends; 5%, 10%, and 15% by weight PET was used for PLA/PET blends.

In the prepared blends, 3 phr EBA-g-MAH and GMA were used as a compatibilizers and blend samples were prepared by using 0.5 phr Joncryl as a chain extender.

Temperatures for the extruder zone were set at 230-210°C, 30 kg/h for feed, and 300 rpm for the screw.

After being acquired in granule form during the melt blending process, all PLA/PBT and PLA/PET polymer blend samples were formed into test samples using the injection method.

A 110 metric ton/70cm^3 INAN injection machine was utilized for the test samples that were used in the characterizations.

Injection temperatures for PLA/PBT blends vary from 190 to 170 °C.

The temperature range for PLA/PBT blend injection is between 170°C and 160°C.

Table 3.6. The compositions of the PLA, PET, compatibilizers, and chain extender

Samples	PLA (%)	PET (%)	EBA-g-MAH (phr)	GMA (phr)	Joncryl (phr)
PLA/PET (95:5)	95	5	0	0	0
PLA/PET (90:10)	90	10	0	0	0
PLA/PET (85:15)	85	15	0	0	0
PLA/PET-E (95:5)	95	5	3	0	0
PLA/PET-E (90:10)	90	10	3	0	0
PLA/PET-E (85:15)	85	15	3	0	0
PLA/PET-G (95:5)	95	5	0	3	0
PLA/PET-G (90:10)	90	10	0	3	0
PLA/PET-G (85:15)	85	15	0	3	0
PLA/PET-J (95:5)	95	5	0	0	0.5
PLA/PET-J (90:10)	90	10	0	0	0.5
PLA/PET-J (85:15)	85	15	0	0	0.5

Similar to PLA/PBT blends, PLA/PET blend samples were coded during preparation based on the component weight percentage and if compatibilizers were included. The major phase of the created PLA/PET blends were found to be PLA, and the minor phase to be PET. It is abbreviated as EBA-g-MAH compatibilizer (represented by the letter E) and GMA compatibilizer (represented by the letter G). It stands for Joncrly, the extender, in the examples marked with the letter J. For instance, the blend coded PLA/PET (95:5) indicates that 5% PET and 95% PLA were used, with no compatibilizers or chain extenders. Another illustration shows that 90% PLA, 10% PET, and 3 phr EBA are utilized in the sample with the code PLA/PET-E (90:10).

According to Table 3.6, the sample designated as PLA/PET-G (85:15) contained 85% PLA, 15% PET, and 0.5 phr chain extender Joncryl.

3.3. Characterizations

3.3.1. Rheological examinations

Melt flow index (MFI) values of PLA, PBT, PET polymers, EBA-g-MAH, and GMA compatibilizer and PLA/PBT and PLA/PET blends were determined using Zwick/Roell type BMF-001 plastometer according to ISO 1133 standard.

Figure 3.3. Melt flow index (MFI) tester

All measurements were performed under the same weight (2.16 kg) but various temperature values proper to the polymer type, 190 °C for PLA, EBA-g-MAH, and GMA, 220 °C for PLA/PBT and PLA/PET blends, 250 °C for PBT, and 265°C for PET were chosen.

Figure 3.4. Controlled rate rheometer

A controlled strain rheometer (AR-G2, TA Instruments) equipped with a 25 mm diameter parallel plate geometry was used for rheology examinations of neat PLA, PBT and PET polymers. Samples were loaded directly between the plates and molded. In the time sweep test, viscoelastic properties of neat PLA, PBT, and PET have been followed at constant strain amplitude (1%) and frequency (1 rad/s) for 15 minutes at 240 °C for PBT and 260 °C for PLA and PET.

3.3.2. Physical examinations

The density values of neat PLA, PBT, and PET polymers, and PLA/PBT and PLA/PET blends have followed with ISO 1183 standard test method. For measurement of the density of the polymers and blends, HR-250 AZ analytical balance was used. Three samples were used for each material and the mean value of the density has been reported.

Figure 3.5. Density meter

The hardness values of three specimens were evaluated using a Shore D hardness tester (Bareiss PRÜFGERTEBA-G-MAHU) according to ISO 868 standard and the mean value has been given.

Figure 3.6. Shore D hardness tester

The molding shrinkage measurement (parallel to the melt flow direction) was realized according to ISO 294-4 standard after injection molding of samples.

Figure 3.7. Caliper thickness gauge

3.3.3. Mechanical Analysis

3.3.3.1. Tensile test

Mechanical tensile tests were performed at room temperature according to ISO 527-2, using a Zwick Roell Z030. The tensile tests of three specimens were conducted at 50.0 mm/min speed and the results were given as average.

Figure 3.8. Tensile tester machine

3.3.3.2. Izod impact test

Izod impact values were determined by Zwick-Roell HIT 5.5P Impact Tester Pendulum apparatus according to ISO 180/1A standard. Three specimens were tested for all materials at room temperature and 50 % ± 10 relative humidity and the results were given as average.

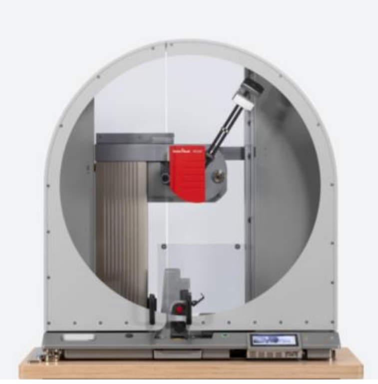


Figure 3.9. Impact tester

3.3.4. Thermal analysis

3.3.4.1. HDT/VICAT test

The procedure of figuring out the temperature resistance point of plastic materials that flex under constant load uses a thermal distortion temperature test. Vicat's softening temperature test is used to figure out where plastic materials under steady strain begin to soften. The device was a Zwick Roell HDT/VICAT 6300 STD brand.

These are the experiments done to determine the deformation rates under continuous load to gauge how well polymers and polymer composite materials withstand heat. It is done in accordance with ISO 75 to apply these tests. The test instrument consists of an oil bath with a constant temperature and an immersion arm with a curved needle in that bath. These are the application steps of the thermal distortion test, commonly known as the HDT test. Three test samples with dimensions of 120x10x4 mm were put within the apparatus in line with the regulations. The gadget was designed with 100 mm between the supports on which the samples are mounted. The sample was subjected to a total load of 137 g during the experiment. Micrometer printing accounts for 70 grams of total weight, with the print head making up the last 67 grams. The point when it deflects 0.35 mm is measured at what is known as HDT temperature. Vicat softening temperature testing is done to figure out the maximal softening temperature resistance of plastic materials while they are continuously loaded in an oil bath. A straight needle-equipped immersion arm and an oil bath with a fixed temperature make up the test apparatus. According to ISO 306 specifications, the Vicat softening temperature test is carried out by inserting three test specimens into the device with measurements of 120x10x4 mm and loading each one with 5000 g. The print head, the micrometer pressure spring, and the weight discs total 67 grams, 70 grams, and 863 grams, respectively, of the applied loads. The temperature used in the test is created by gradually raising the temperature of an oil bath that has been heated to 50 °C (often at a pace of 50 °C per hour) as per the requirements. The temperature used in this experiment is referred to as the Vicat temperature since it determines when a needle with a 1 kg weight enters 1 mm of a 1 mm^2 surface. Vicat softening temperature is a crucial factor in figuring out how hard a polymer's surface is since it relies on it.

Figure 3.10. HDT/VICAT test machine

4. RESULT AND DISCUSSION

4.1. Rheological Examinations

Melt Flow Index values of neat PLA (190 °C / 2.16 kg), neat PBT (250 °C / 2.16 kg) and neat PET (265 °C / 2.16 kg) were determined as 2.66 g/10 min., 36 g/10 min., and 17.88 g/min respectively (Table 4.1). Since PLA is the major phase in the PLA/PBT blends, the MFI values of the prepared PLA/PBT blends were examined at 220°C at 2.16 kg.

MFI values of PLA/PBT blends have shown lower viscosity characteristics compared to their constituent components (Table 4.2). Thus, PLA/PBT blends can be used more easily and successfully in applications requiring low viscosity such as injection molding and 3D printing, instead of using PLA or PBT alone.

Table 4.1. MFI values of neat PLA, PBT, and PET

Samples	**MFI (220 °C/ 2.16 kg) gr/10 min.**	**MFI (250 °C/ 2.16 kg) gr/10 min.**	**MFI (265 °C/ 2.16 kg) gr/10 min.**
Neat PLA	2.66		
Neat PBT		36	
Neat PET			17.88

While Table 4.2 is examined, MFI value of PLA/PBT (95:5) blend which prepared without using compatibilizer is seen as 17.2 gr/10 min. Besides when EBA-g-MAH was added to this blend as a compatibilizer, it was observed that the MFI value decreased to 13.99 gr/10 min.

On the other hand, when GMA was used as a compatibilizer, the MFI value decreased further and reached 7.57 g/10 min. It has been observed that as the MFI value decreases, the fluidity of the material decreases proportionally. A PLA/PBT (85:15) blend prepared without the use of a compatibilizer contains 85% PLA and 5% PBT, and when Table 4.2 is examined, the MFI value of this blend was determined to be 13.99 g/10 min.

When 3 phr EBA-g-MAH was added as compatibilizer, the MFI value decreased to 9.94 g/10 min.

Similarly, when GMA was used (3 phr) as compatibilizer, the MFI value decreased further and reached 8.41 g/10 min.

Table 4.2. MFI values of PLA/PBT blends prepared with and without compatibilizer

Samples	MFI (220 °C/ 2.16 kg) g/10 min.
PLA/PBT (95:5)	17.2
PLA/PBT (90:10)	8.31
PLA/PBT (85:15)	13.99
PLA/PBT-E (95:5)	11.67
PLA/PBT-E (90:10)	10.36
PLA/PBT-E (85:15)	9.94
PLA/PBT-G (95:5)	7.57
PLA/PBT-G (90:10)	8.12
PLA/PBT-G (85:15)	8.41

In Figure 4.1, it was observed that the MFI values of PLA/PBT blends containing 95%, 90% and 5% PBT in PLA/PBT blends prepared without using compatibilizers were between neat PLA and neat PBT values. In general, as the molecular weight of PLA/PBT blends increases, their fluidity decreases. In other words, it can be interpreted as an increase in its viscosity, that is, its resistance to flow.

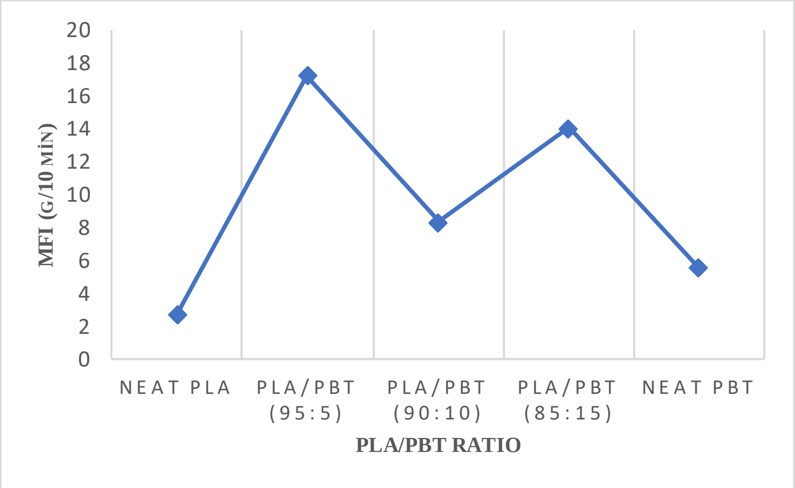


Figure 4.1. MFI values of neat PLA, neat PBT and PLA/PBT blends

Figure 4.2 shows the effects of compatibilizer using on PLA/PBT blends. In this graph, a linear change was observed in the MFI values of the EBA-g-MAH and GMA compatibilizers, while an uneven distribution was observed from the PLA/PBT blends prepared without compatibilizers. It is noticed that PLA/PBT blends without compatibilizers do not exhibit very good blending properties and therefore irregularities occur in MFI values. PLA/PBT blends appear to be in better compatibility and exhibit good blending properties when compatibilizer is added.

For example, In figure 4.2, a decrease in the MFI value of the PLA/PBT (90:10) blend was observed in PLA/PBT blends prepared without using compatibilizer. From this, it can be concluded that the viscosity increases with the decrease of the MFI value.

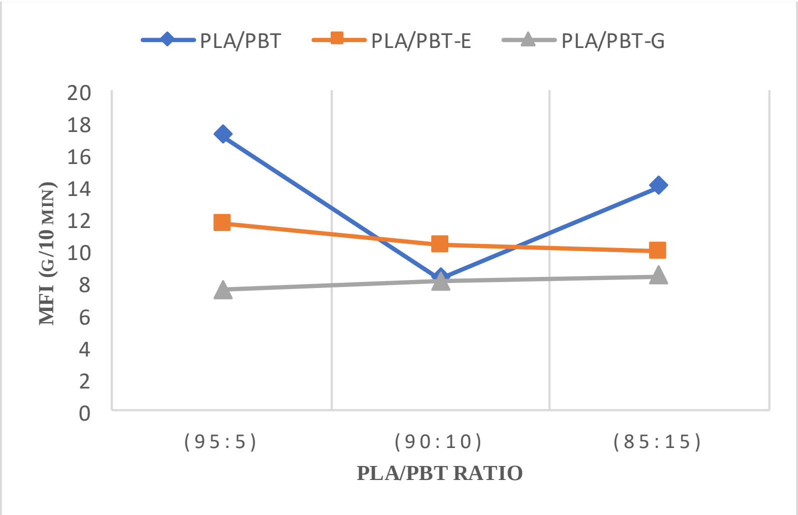


Figure 4.2. Effect of compatibilizer use on MFI values in PLA/PBT blends

When PLA/PBT blends prepared without using compatibilizers in PLA/PBT blends are examined in Table 4.2, the MFI value of the PLA/PBT blend containing 5% PBT is 13.3 g/10 min., the MFI value of the PLA/PBT blend containing 10% PBT is 11.9 g/10 min., and it is seen that the MFI value of the PLA/PBT blend containing 15% PBT is 8.44 g/10 min. The result from here is the MFI value decreased depending on the increasing amount of PBT.

When MFI measurement analysis in PLA/PBT blends using EBA-g-MAH as a compatibilizer is examined in Table 4.2, it is seen that the MFI value decreases with increasing PBT amount.

The MFI value of PLA/PBT (95:5) blends is 17.2 g/10 min. when the MFI values of PLA/PBT blends are analyzed in Table 4.3. However, when 0.5 phr Joncryl is added as a chain extender, the MFI value decreases to 6.12 g/10 min. Like this, using a chain extender caused the MFI value of the PLA/PBT (90:10) blend to decrease from 8.31 g/10 min. to 5.90 g/10 min. An increase in the molecular weight of blends including chain extender can be used to explain MFI results in PLA/PBT blends. It can be claimed that PLA/PBT show shear thinning behavior that their viscosity increases with chain extender concentration.

Table 4.3. Chain extender effect in PLA/PBT blends

Samples	**MFI (220 °C/ 2.16 kg) g/10 min.**
PLA/PBT (95:5)	17.2
PLA/PBT (90:10)	8.31
PLA/PBT (85:15)	13.99
PLA/PBT-J (95:5)	6.12
PLA/PBT-J (90:10)	5.90
PLA/PBT-J (85:15)	3.1

Figure 4.3, which was created using the information in Table 4.3, shows how using a chain extender affects PLA/PBT blends. The MFI results of the PLA/PBT blend

prepared without the chain extender showed a non - uniform distribution, as seen in the graph, whereas the addition of Joncryl as a chain extender at 0.5 phr shows a linear increase in the MFI values.

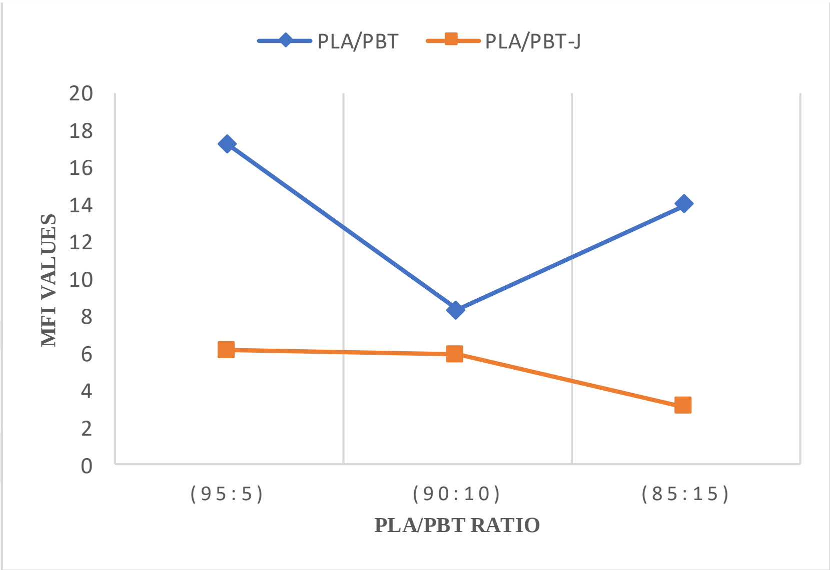


Figure 4.3. The effect of chain extender use on MFI values in PLA/PBT blends.

In Table 4.4, the MFI test results for PLA/PET blends without and with compatibilizers are presented. The MFI value of PLA/PET blends without compatibilizers, such as PLA/PET (95:5) blend, was 17.60 g/10 min. in this case, but the MFI value of PLA/PET-E (95:5) blend was 14.7 g/10 min. The MFI value in the PLA/PET (90:10) blend also decreased from 18.5 g/10 min. to 14.7 g/10 min. and 6.05 g/10 min. according to using compatibilizer types.

Table 4.4. MFI values of PLA/PET blends prepared with and without compatibilizer

Samples	**MFI (220 °C/ 2.16 kg) g/10 min.**
PLA/PET (95:5)	17.60
PLA/PET (90:10)	18.5
PLA/PET (85:15)	16.28
PLA/PET-E (95:5)	14.7
PLA/PET-E (90:10)	10.47
PLA/PET-E (85:15)	11.64
PLA/PET-G (95:5)	11.8
PLA/PET-G (90:10)	6.05
PLA/PET-G (85:15)	7.24

The graph in Figure 4.4, which was derived using Table 4.4, clearly shows the effects of compatibilizers on PLA/PET blends. In this graph, the MFI value increased in the PLA/PET blend containing 10% PBT when the PLA/PET blends were prepared without compatibilizer, however it reduced in the PLA/PET blend including 10% PBT and 3 phr compatibilizer. When the PET component is increased by 5% to 10% in PLA/PET-E and PLA/PET-G blends, the MFI value decreases. As PLA/PET-E and PLA/PET-G blends with 10% PBT to blends with 15% PBT are seen, there is a linear increase in MFI.

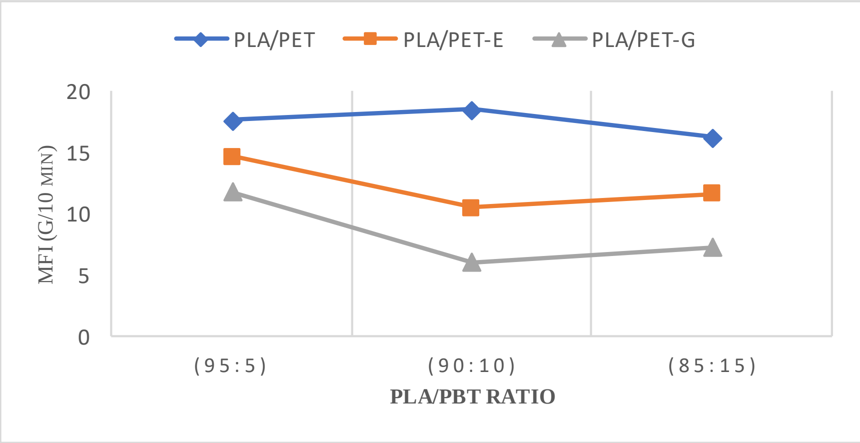


Figure 4.4. The effect of compatibilizers use on MFI values in PLA/PET blends

The results obtained by using 0.5 phr Joncryl as a chain extender in PLA/PET blends is given in Table 4.5.

While the MFI values of the blends prepared without the use of chain extender are in the range of 16-18 g/10 min., the MFI values of PLA/PET blends containing 5%, 10% and 15% PET prepared with the use of 0.5 phr Joncryl are between 5 and 8 g/10 min. is coming. As an example of these blends prepared using chain extender, for example, PLA/PET-J (85:15) can be considered because of molecular degradation of the chain, which prevents the reduction of melt flow. The possibility of using these blends as a filament for 3D printing can also be considered.

Table 4.5. Chain extender effect in PLA/PET blends

Samples	MFI (220 °C/ 2.16 kg) g/10 min.
PLA/PET (95:5)	17,6
PLA/PET (90:10)	18,5
PLA/PET (85:15)	16,28
PLA/PET-J (95:5)	6,06
PLA/PET-J (90:10)	8,39
PLA/PET-J (85:15)	5,49

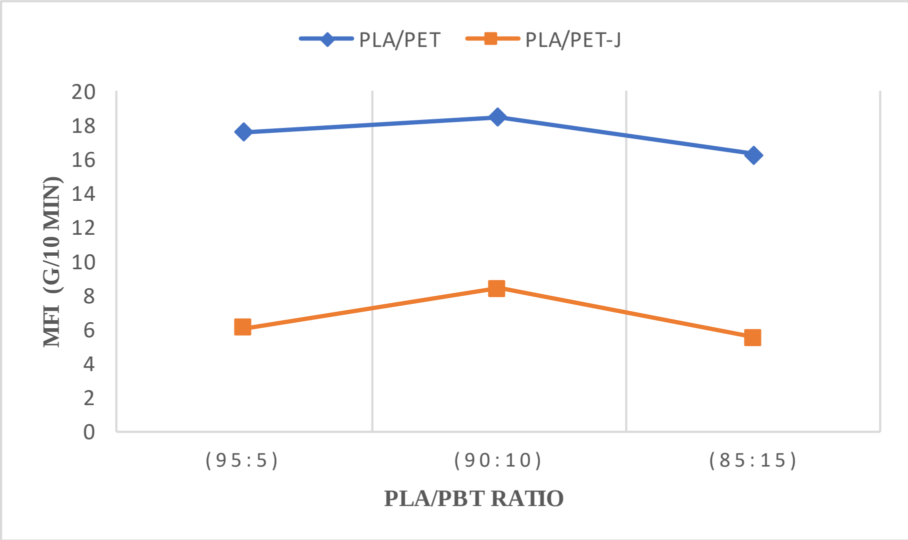


Figure 4.5. The effect of chain extender use on MFI values in PLA/PET blends

In Figure 4.5, the effect graphs of the MFI values of the blends prepared at different rates without compatibilizer and using 0.5 phr Jocnryl are given. For example, the MFI value of PLA/PET (90:10) blend is 18.5 g/10 min., while the MFI value of PLA/PET-E (90:10) blend is 8.39 g/10 min.

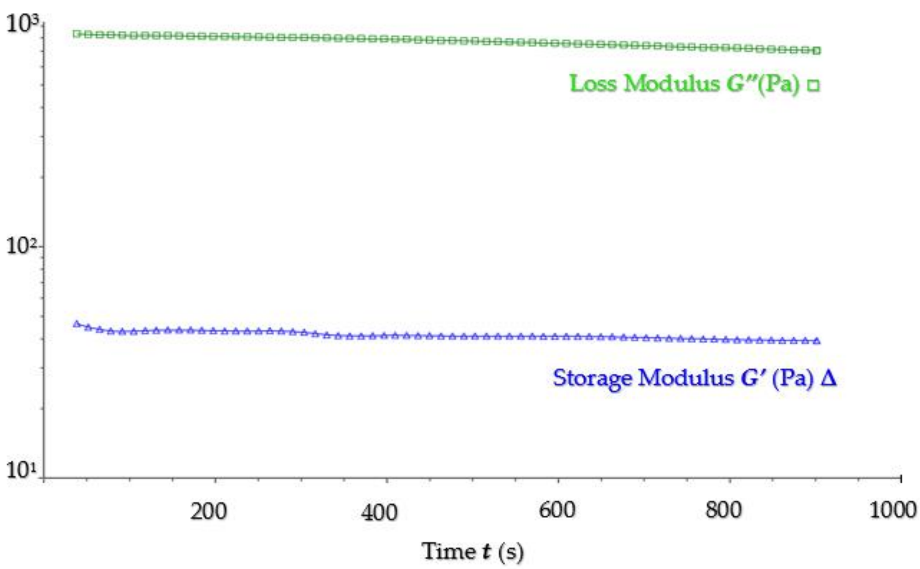


Figure 4.6. PBT's time sweep test graphic

At 240 °C for 15 minutes, it was found that the PLA polymer material's G' and G" values showed a lowering trend, as shown in the following information in Figure 4.7.

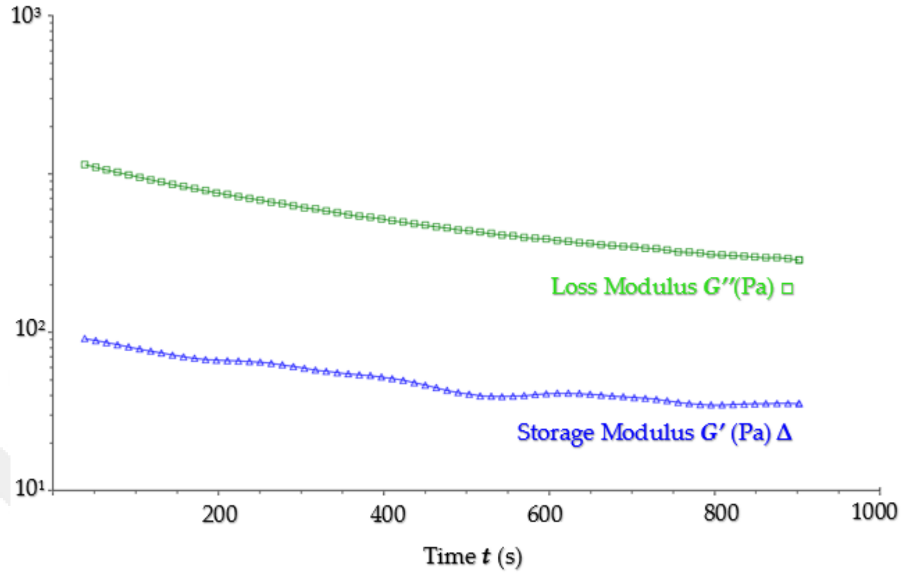


Figure 4.7. PLA's time sweep test graphic

When the corresponding graph is studied, it can be seen that the G' and G" values of PLA have begun to decline after 200 seconds. Therefore, it is anticipated that a processing time of 3 minutes for the PLA polymer can be advantageous without causing any damaging effects, such as chain degradation or cross-linking on the structure of the material.

This material withstood the temperature of 260 °C for 15 minutes and its modulus was low.

Decreases in viscoelastic properties (modulus and/or viscosity) over time indicate property losses due to thermal degradation and chain splits, while an increase indicates composition changes such as the opposite bonding between polymer chains or loss of solvent or plasticizer. It can be interpreted as a material that may have bubbles or moisture.

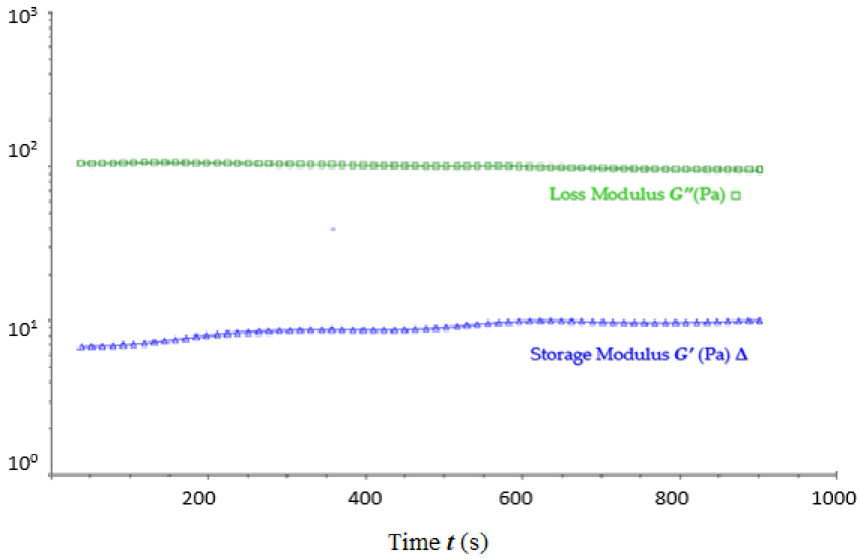


Figure 4.8. PET's time sweep test graphic

4.2. Physical Properties of the Samples

As shown in Table 4.6 there are slightly differences in the physical properties of the blend codes created depending on whether 5%, 10%, and 15% PBT including compatibilizer and chain extender are utilized or not. There was a condition that resembled an increase and reduction in units when the blends' densities were utilized as a chain extender and compatibilizer. It is a result of the blends' polymer extrusion machine's polymer blend. Examining the findings of the Shore D (hardness) test study on PLA/PBT blends reveals that they typically range between 75 and 76 on average.

The physical properties of the prepared blends are shown in Table 4.6. First, density, hardness, and molding shrinkage values of PLA/PBT blends prepared without using compatibilizers were carried out. Afterward, mentioned physical properties of blends prepared by using 3 phr EBA-g-MAH and GMA compatibilizers and 0.5 phr chain extender Joncryl were also investigated. The results of the obtained values are given in Table 4.6.

Table 4.6. Effect of use of compatibilizers and chain extender on physical properties in PLA/PBT blends

Samples	**Density (g/cm^3)**	**Hardness (Shore D)**	**Molding Shrinkage (%)**
PLA/PBT (95:5)	1.26	76	0.40
PLA/PBT (90:10)	1.26	75	0.40
PLA/PBT (85:15)	1.27	76	0.70
PLA/PBT-E (95:5)	1.25	75	0.51
PLA/PBT-E (90:10)	1.26	75	0.45
PLA/PBT-E (85:15)	1.25	74	0.51
PLA/PBT-G (95:5)	1.25	75	0.42
PLA/PBT-G (90:10)	1.26	75	0.52
PLA/PBT-G (85:15)	1.25	75	0.50
PLA/PBT-J (95:5)	1.26	76	0.48
PLA/PBT-J (90:10)	1.26	74	0.44
PLA/PBT-J (95:5)	1.26	75	0.59

According to the results of the analysis of the physical properties of neat PLA and neat PBT in Table 3.1, the density of neat PLA was 1.25 g/cm^3; The density of neat PBT was measured as 1.30 g/cm^3. As seen in Table 4.6, the density of PLA/PBT blends containing 5%, 10%, and 15% PBT also varies between 1.25-1.26 on average, so the density of the blends is not affected much.

For instance, the densities of PLA/PBT (95:5) and PLA/PBT (90:10) blends are 1.26 g/cm^3, while 1.27 g/cm^3 is the density of PLA/PBT (85:15) blends that contain 15% PBT. It can be claimed that the screw draws more polymer material from the hopper in the extruder's feeding area, increasing density as a result.

Table 4.6 shows the density variation between 1.25-1.26 g/cm^3 when using EBA-g-MAH and GMA as compatibilizers in PLA/PBT blends.

The reason for the decrease in the density here is that the PLA/PBT blends containing the compatibilizer produced in the injection affected the density of the printing samples due to the inability to print properly due to the temperatures during the injection.

The effect graph of the use of compatibilizer on PLA/PBT blends, inspired by Table 4.6, is shown in Figure 4.9. As seen here, it is seen that the incoming density of 1.26 g/cm3 in 5% and 10% blends of PLA/PBT blend prepared without compatibilizer increased by 1 unit in 15% blend. In PLA/PBT-E blends, the density was 1.25 g/cm^3 in the 5% and 15% blends, while the density increased by 1 unit in the 10% PLA/PBT blend.

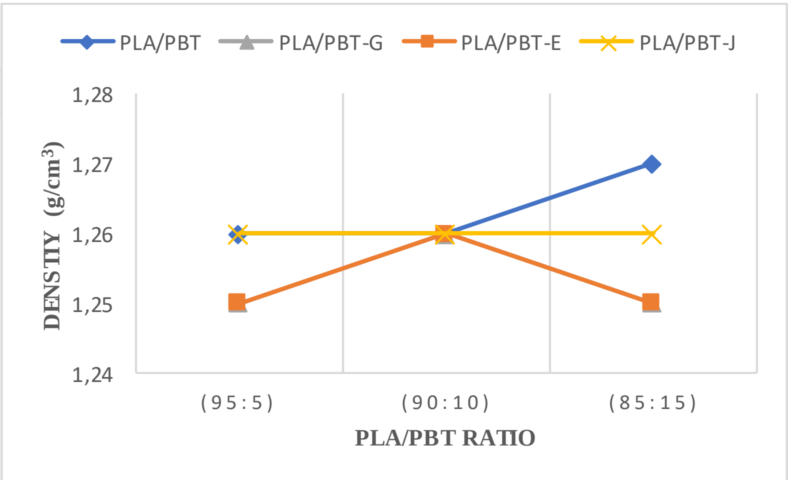


Figure 4.9. Effect of compatibilizers and chain extender use on density values in PLA/PBT blends

On the other hand, the density values had remained stable when Joncryl was used. The extruder fed 5%, 10% and 15% PLA/PBT blends properly, and densities were determined as 1.26 g/cm^3. As seen in Figure 4.9, the density curve of PLAPBT-J blend progresses linearly as 1.26 g/cm^3.

Before preparing PLA/PBT blends, shore D test results of neat PLA and neat PBT are given in Table 3.1. Neat PLA has a Shore D of 73, while neat PBT has a Shore D of 75. Based on these results, it can be expected that Shore D results of PLA/PBT blends without compatibilizers will come in a close range to their neat form. As seen in Table 4.6, the hardness test results of 5%, 10% and 15% PLA/PBT blends are between 75-76.

Figure 4.10 shows the graph based on the results obtained when using compatibilizers in PLA/PBT blends. Although a definite interpretation cannot be made, shore D results can be interpreted as giving results between 74-76 on average.

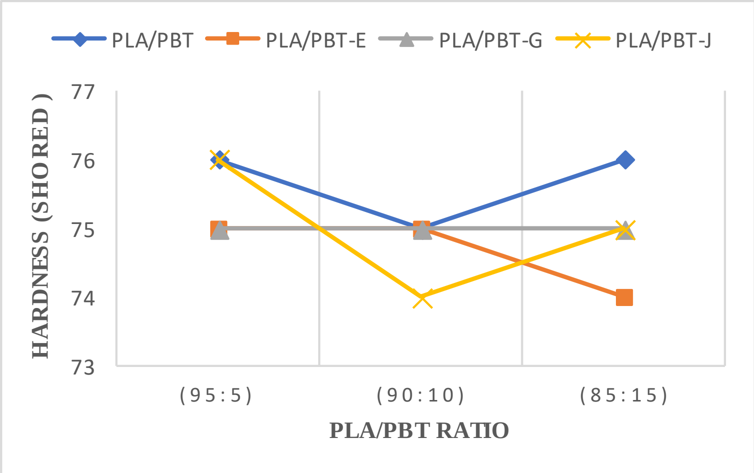


Figure 4.10. Effect of compatibilizers and chain extender use on hardness values in PLA/PBT blends

The mold tensile test, which is one of the most important tests in terms of determining the physical properties, is important in terms of determining the suitability of the material for the usage area. The extrusion results of all PLA/PBT blends prepared are shown in Table 4.6. In Figure 4.10 we see the effect of casting on PLA/PBT blends of compatibilizers and chain extender. Previously, the mold shrinkage value of neat PLA was 0.42%, while the mold shrinkage value of neat PBT was recorded as 0.8% in Table 3.1. When the mold shrinkage values of PLA/PBT blends prepared in Table 4.6 are examined, it is seen that the average is in the range of 0.40-0.70%.

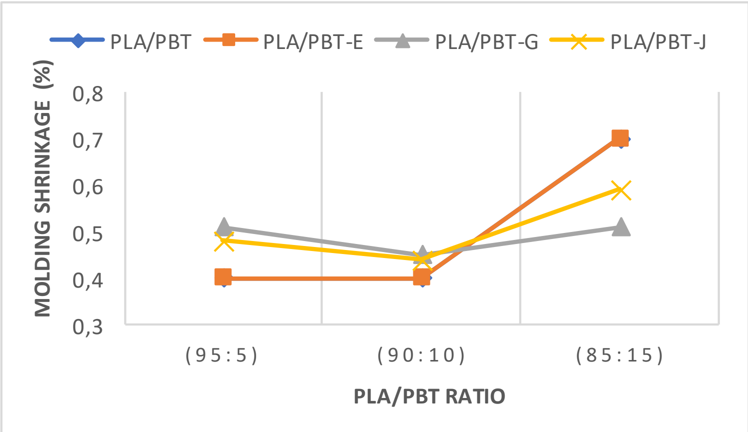


Figure 4.11. Effect of compatibilizers and chain extender use on molding shrinkage values in PLA/PBT blends

When Figure 4.11 is examined in general, it is seen that the molding shrinkage value of PLA/PBT blend containing 15% PBT is higher in percentage than the others. There may be several reasons why the data obtained in mold shrinkage differ from each other.

The smaller the unequal shrinkage in extrusion, the more stresses occur in parts made of PLA/PBT blends. It may depend on the set of parts, which can cause deformation or deformation of the part formed at these stresses. This can cause cracks in PLA/PBT parts in long-term use. Mold shrinkage characteristics of molded plastic parts is very important for these reasons.

Finally, the molding shrinkage value of neat PLA was 0.42%, while the molding shrinkage value of neat PBT was 0.80 in Table 3.1. Molding shrinkage values of PLA/PBT blends created in Table 4.6 also show average values by taking values between 0.40 % and 0.50 %.

Table 4.7. Effect of use of compatibilizer and chain extender on physical properties in PLA/PET blends

Samples	Density (g/cm^3)	Hardness (Shore D)	Molding Shrinkage (%)
PLA/PET (95:5)	1.26	76	0.49
PLA/PET (90:10)	1.26	75	1.51
PLA/PET (85:15)	1.26	75	1.46
PLA/PET-E (95:5)	1.25	76	1.47
PLA/PET-E (90:10)	1.25	75	1.50
PLA/PET-E (85:15)	1.26	75	1.50
PLA/PET-G (95:5)	1.25	75	0.56
PLA/PET-G (90:10)	1.26	75	1.41
PLA/PET-G (85:15)	1.26	75	1.55
PLA/PET-J (95:5)	1.25	75	0.74
PLA/PET-J (90:10)	1.26	75	1.81
PLA/PET-J (85:15)	1.26	76	1.8

The physical properties of the prepared PLA/PET blends are shown in Table 4.7. First of all, the density, hardness and mold shrinkage values of PLA/PET blends prepared without using compatibilizers were carried out, and then the physical properties of the blends prepared using 3 phr EBA-g-MAH, GMA compatibilizers and Joncryl as 0.5 phr extender were examined. The results of the obtained values are given in Table 4.7.

For example, the densities of PLA/PET (95:5), PLA/PET (90:10) and PLA/PET (85:15) blends are 1.26 g/cm^3. This shows that the polymers are fed properly in the injection. In Table 3.1, the density of neat PLA was expressed as 1.25 g/cm3 and the density of neat PET as 1.345 g/cm^3.

Table 4.7 shows the density variation between 1.25-1.26 g/cm^3 when EBA-g-MAH and GMA are used as compatibilizers in PLA/PBT blends. The reason for 1 unit increases and decreases in density may be due to process parameters during production.

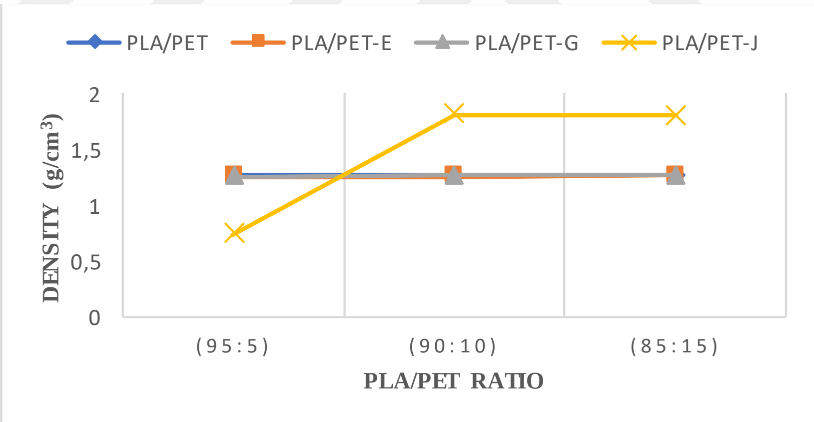


Figure 4.12. Effect of compatibilizers and chain extender use on density values in PLA/PET blends

Figure 4.12 shows the effect graph of the use of the compatibilizer, prepared based on the data in Table 4.7, on PLA/PET blends. Here, we see that EBA-g-MAH and GMA used as compatibilizers and intensities progress stably in the same direction. However, we see that Joncryl, which is used as an extender, first increases, and then continues steadily, depending on the amount of PET.

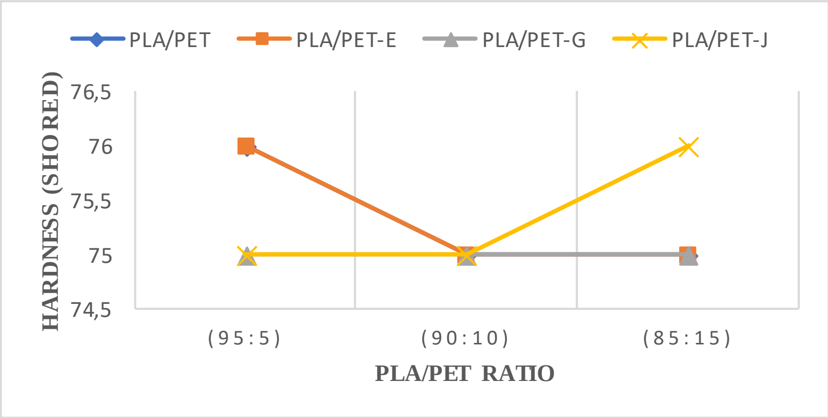


Figure 4.13. Effect of compatibilizers and chain extender use on hardness values in PLA/PET blends

Before preparing PLA/PET blends, shore D test results of neat PLA and neat PET are given in Table 3.1, neat PLA has a Shore D of 73, while neat PET has a Shore D of 80. Based on these results, it can be expected that Shore D results of PLA/PET blends without compatibilizers will come in a close range to their neat form. As seen in Table 4.7, the hardness test results of 5%, 10% and 15% PLA/PBT blends were between 75-76. In addition the major phase is PLA and the minor phase is PET, it has been observed that there is not much change in the density and hardness values and the values are close to the physical values of neat PLA.

The graph created from the hardness test results obtained when using compatibilizers in PLA/PET blends is shown in Figure 4.13. Shore D test results of PLA/PET blends averaged between 74-76.

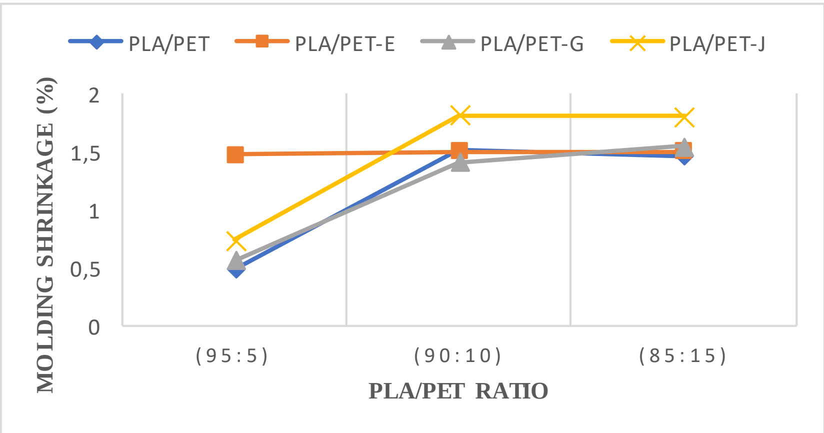


Figure 4.14. Effect of use of compatibilizers and chain extender on molding shrinkage of PLA/PET blends

The molding shrinkage results of all PLA/PET blends prepared are shown in Table 4.6.

Figure 4.10 shows the effect of casting on PLA/PBT blends of compatibilizers and chain extender. Previously, the molding shrinkage value of neat PLA was 0.42%, while the mold shrinkage value of neat PBT was recorded as 0.8% in Table 3.1. When the mold shrinkage values of PLA/PET blends prepared in Table 4.7 are examined, it is seen that the average is in the range of 0.5-1.8%.

When we examine Figure 4.14, it is seen that the increase in the amount of PET and the mold drawing ratios increased in all blends, except for the EBA compatibilizer, and it continued to be stable afterwards. It is seen that there is no big difference in mold drawing ratios in PLA/PET-E blends prepared at 5%, 10% and 15%.

Percent shrinkage that occurs in PLA/PET blends refers to the volume shrinkage of polymer blends. This occurs during the cooling stage of processing the polymers. The shrinkage is partly due to the difference in density of the polymers in the molten state and in the cooled, hard state.

4.3. Mechanical Analysis of the Samples

4.3.1. Tensile properties

When the compatibilizer-free PLA/PBT blends were prepared with different compositions, the first thing that stood out was that the mechanical values of these blends showed a distribution between neat PLA and neat PBT.

It is concluded that the use of two different compatibilizers such as EBA-g-MAH and GMA takes the mechanical properties to the next level, in this sense, it is necessary to use a compatibilizer for PLA/PBT blends.

It is seen that repeating the extrusion process for the second time in PLA/PBT blends prepared using a compatibilizer increases the mechanical properties positively. For this reason, the values of the samples that were extruded for the second time were compared in the comparison of the mechanical properties, based on the conclusion that the samples, which were extruded for the second time, were thought to blend more efficiently and produced more performance products, and the interpretations were made on these.

Mechanical properties of PLA/PBT blends prepared in 3 different ratios are shown in Table 4.8. It is seen that Young Modulus and Yield Strength values increase depending on the decrease in the amount of PBT. It is seen that the elongation at yield and elongation at break values of PLA/PBT blends prepared without compatibilizers decreased with increasing PBT amount. For example, as shown in Table 4.8, while the tensile strength value in PLA/PBT (95:5) blend is 65.8 MPa, the tensile strength value in PLA/PBT (90:10) blend increases to 67.3 MPa.

Without using any compatibilizer, the highest modulus value in PLA/PBT blends is recorded as 3360 MPa in PLA/PBT (95:5) blend with the lowest PBT amount.

Based on all these results, the slight increase in tensile strength in PLA/PBT blends shows that these two polymers interact well in blends with increased PLA content. In terms of modulus, the Young Modulus value shows an increasing slope with increasing PLA content in PLA/PBT blends. This can be attributed to the high modulus inherent in PLA.

Table 4.8. Mechanical properties of PLA/PBT blends with and without compatibilizers

Samples	Young Modulus (MPa)	Yield Strength (MPa)	Elongation at Yield (%)	Tensile Strength (MPa)	Elongation at Break (%)
PLA/PBT (95:5)	3360	65.8	2.4	65.8	2.4
PLA/PBT (90:10)	2990	63.7	2.6	67.3	2.6
PLA/PBT (85:15)	3140	56.2	2.0	56.2	2.0
PLA/PBT-E (95:5)	3440	68.3	2.3	53.9	6.4
PLA/PBT-E (90:10)	3240	66.5	2.4	66.5	2.4
PLA/PBT-E (85:15)	3030	60.1	2.5	60.1	2.5
PLA/PBT-G (95:5)	3340	68.1	4.9	67.2	5.1
PLA/PBT-G (90:10)	3280	63.5	2.5	63.5	4.8
PLA/PBT-G (85:15)	3020	57.3	2.2	57.3	2.2

Considering PLA/PBT blends in terms of compatibilizer usage in Table 4.8, PLA/PBT-E (95:5) blend using 3 phr EBA-g-MAH has higher mechanical properties than other 10% and 15% PLA/PBT blends prepared. As seen in Figure 4.20, the modulus values of PLA/PBT blends using EBA-g-MAH show an increase depending on the increasing amount of PBT. While the modulus value of PLA/PBT-E (95:5) blend is 3440 MPa, the modulus value of PLA/PBT-E (85:15) blend is 3030 MPa. In other words, Young Modulus values increased depending on the decreasing amount of PBT. Similarly, the yield strength of the PLA/PBT-E (95:5) blend was 68.3 MPa, while the yield strength of the PLA/PBT-E (85:15) blend decreased to 66.5 MPa.

Figure 4.15 shows how PLA/PBT blends prepared in 3 different ratios are related to neat PLA and neat PBT in terms of tensile strength.

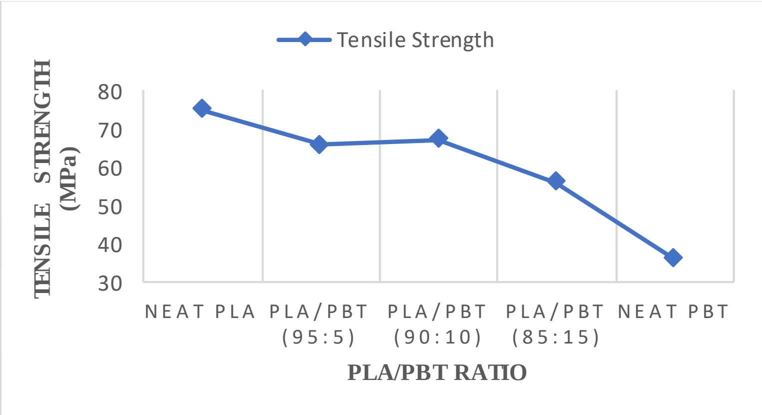


Figure 4.15. Tensile Strength values of neat PLA, neat PBT and, PLA/PBT blends

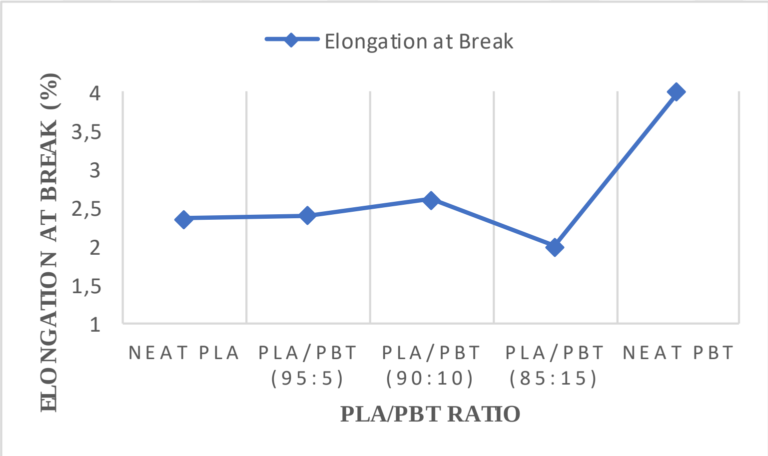


Figure 4.16. Elongation at Break values of neat PLA, neat PBT and, PLA/PBT blends

The graph of the change in the elongation at break values of PLA/PBT blends prepared without compatibilizer and neat PLA and neat PBT blends is shown in Figure 4.16. As can be seen here, the elongation at break of neat PBT is quite high. We observe that the 5% and 10% PBT added to the neat PLA increase the elongation at break values of the blends.

An important point to note in this graph is that the elongation at break in the PLA/PBT (85:15) blend significantly decreases after PLA is incorporated into the PBT. This is due to the low ductility of PLA behavior and the interruption of the continuous phase of PBT after blending. Therefore, the percentage elongation at break of PLA/PBT blends remained low.

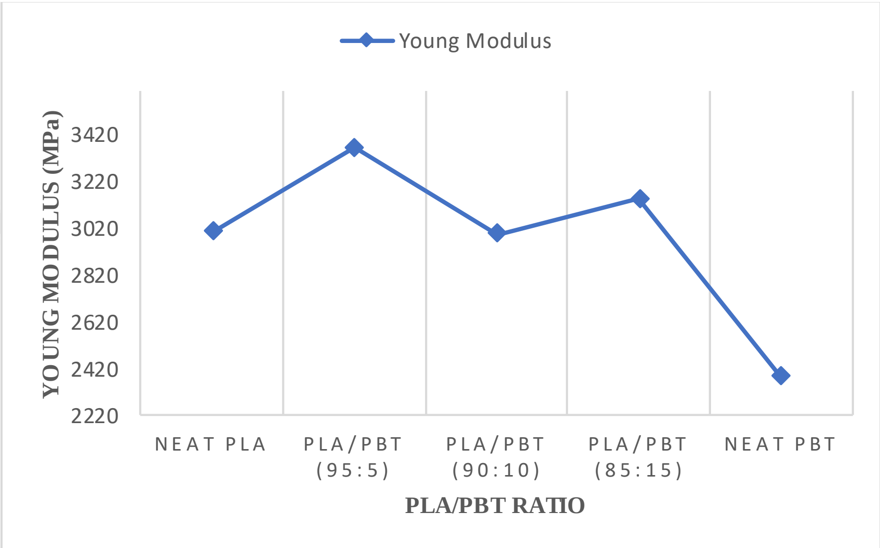


Figure 4.17. Young Modulus values of neat PLA, neat PBT and, PLA/PBT blends

Before beginning the blend preparations, as indicated in Table 3.1, the Young's modulus value of neat PLA was recorded as 3000 MPa and the Young's Modulus value of neat PBT was recorded as 2380 MPa. PLA is inherently high modulus. As seen in Figure 4.17, the modulus of PLA/PBT blends generally increases with increasing PLA addition.

The effect of EBA-g-MAH and GMA compatibilizers on the mechanical properties of PLA/PBT blends is shown in Figure 4.18. It is seen that the tensile strength values of EBA-g-MAH and GMA compatibilizers are higher due to the increasing PLA ratio. It can be concluded that the use of compatibilizer significantly increases the Tensile strength values. Here, the branching effect of EBA also caused the PLA/PBT-G blend to harden with the increase in the entanglement density of the chains.

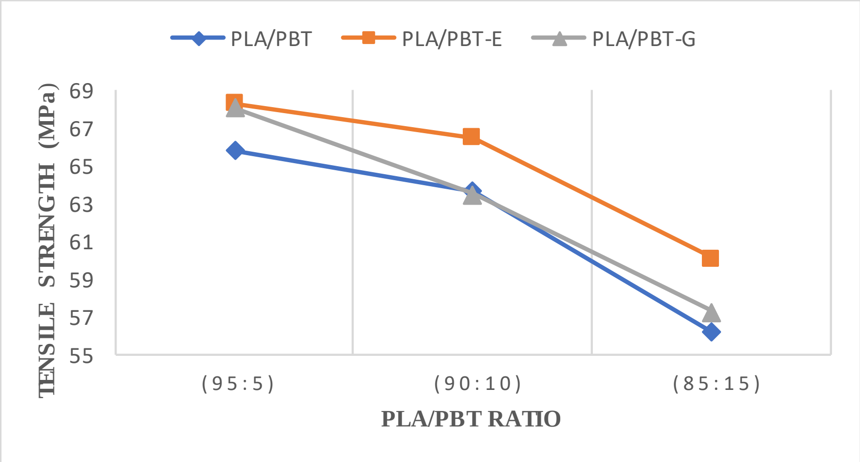


Figure 4.18. Effect of compatibilizers use on Tensile Strength values in PLA/PBT blends

While the elongation at break values of the compatibilizers used in PLA/PBT blends varied between 2-2.5% when examined in Figure 4.19, the elongation at break value increased by 4.9% in the PLA/PBT-G (95:5) blend. Here, the elongation at break value of the PLA/PBT-G (85:15) blend, which has a high content of PLA, is 2.2%, while the elongation at break value of the PLA/PBT-G (95:5) blend is 4.9% has risen.

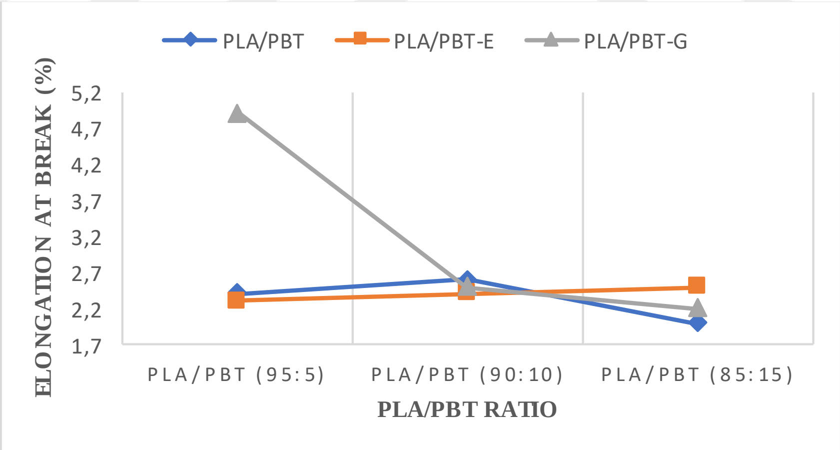


Figure 4.19. Effect of compatibilizers use on Elongation at Break values in PLA/PBT blends

Figure 4.20 shows the effect of compatibilizer usage on Young Modulus values. Here, while Young Modulus values remain stable in PLA/PBT blends containing 10% PBT, when the PBT ratio increases to 15%, PLA/PBT prepared without compatibilizer using PA/PBT (85:15) blend and using 3 phr EBA-g-MAH compatibilizer. While the Young

Modulus values of the PLA/PBT-E (85:15) blend increased, a 9.58% loss was observed in the PLA/PBT-G (85:15) blend prepared using 3 phr GMA.

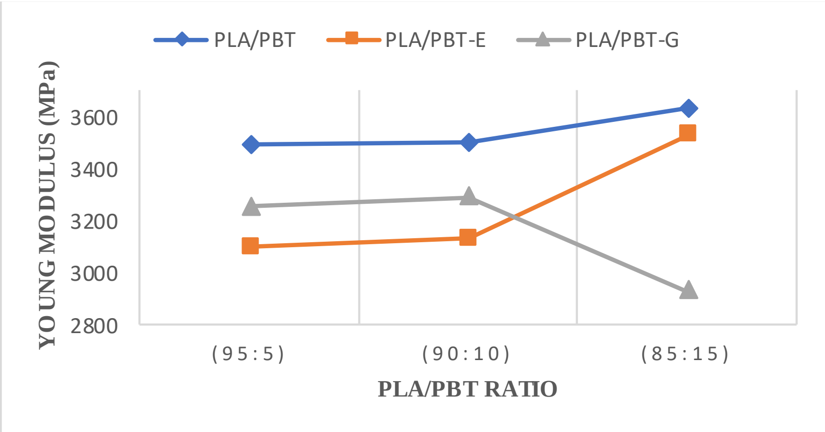


Figure 4.20. Effect of compatibilizer usage on Young Modulus of PLA/PBT blends

The brittleness of PLA can be improved by blending it with PBT, but their compatibility is poor due to their immiscibility. To increase compatibility, two chain extenders with epoxy groups were applied in this study.

Table 4.9. Mechanical properties of chain extender on PLA/PBT blends

Samples	Young Modulus (MPa)	Yield Strength (MPa)	Elongation at Yield (%)	Tensile Strength (MPa)	Elongation at Break (%)
PLA/PBT (95:5)	3360	65,8	2,4	65,8	2,4
PLA/PBT (90:10)	2990	63,7	2,6	67,3	2,6
PLA/PBT (85:15)	3140	56,2	2	56,2	2
PLA/PBT (95:15)	3660	67,9	2,3	65,2	2,8
PLA/PBT (90:10)	3060	67,9	2,5	67,9	2,5
PLA/PBT (85:15)	3150	61	2,3	69,4	2,3

By adding a chain extender into PBT blends; A greater increase was observed in blends created with 5% PBT, that is, in blends with less PBT. From this, it improved the molecular weight of PLA and had a greater effect in blends with higher PLA content.

Looking at the results in Table 4.9, when the mechanical properties of PLA/PBT blends without Joncryl ADR 4468 and PLA/PBT blends containing Joncryl are examined, it is seen that the major phase PLA, the chain extender used, is more effective on increasing the molecular properties of PLA rather than PBT.

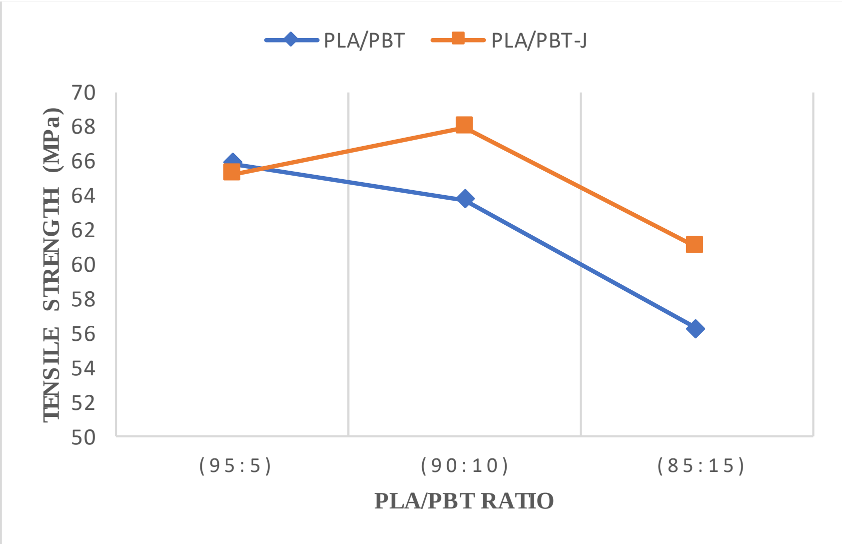


Figure 4.21. Effect of chain extender use on tensile strength values in PLA/PBT blends

Figure 4.21 shows how the use of 0.5 phr Joncryl as a chain extender affects the tensile strength values. As seen in this graph, the highest values are seen in PLA/PBT-J (90:10) blends. While the tensile strength of PLA/PBT (90:10) blend was 63.7 MPa, this value increased to 67.9 MPa with an increase of 6.59% when 0.5 phr Joncryl was used.

In terms of elongation at break, we observe the Joncryl effect in Figure 4.22. Here, it is seen that the elongation at break in PLA/PBT blends prepared without the use of chain extender is in the range of 2.4-2%, while it increases to the range of 2.3-2.8% with the use of 0.5 phr Joncryl. The best elongation at break result was measured as 2.8% in PLA/PBT-J (95:5) blend. For example; While the elongation at break was 2.4% in PLA/PBT (95:5) blend prepared without compatibilizer, the elongation at break value of PLA/PBT-J (95:5) blend increased by 16.66% and reached 2.8%.

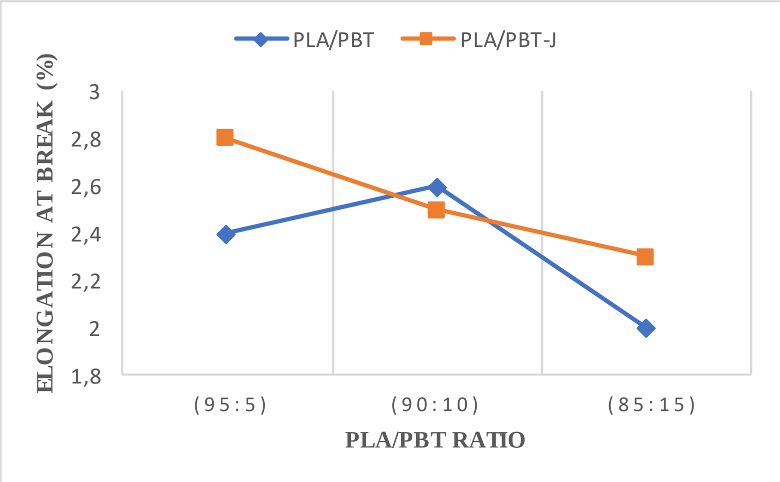


Figure 4.22. Effect of chain extender use on elongation at break values in PLA/PBT blends

The effect of Joncrly, which is used as a chain extender, on Young Modulus values can be seen in Figure 4.22. It was observed that the tensile strength and modulus values increased with the chain extender concentration in PLA/PBT blends.

For example, in Table 4.9, the Young Modulus value of the PLA/PBT (95:5) blend was 3360 MPa, while the Young Modulus value of the PLA/PBT-J (95:5) blend increased to 3660 MPa.

Similarly, it is seen that the Young Modulus value of 2990 MPa in the PLA/PBT (90:10) blend and 3060 MPa Young Modulus in the PLA/PBT-J (90:10) blend.

It can be said that the use of 0.5 phr Joncryl as a chain extender in the PLA/PBT melt blending method improves the mechanical properties.

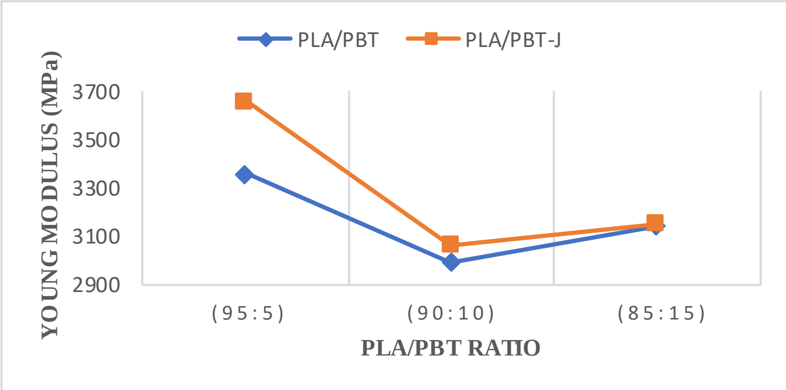


Figure 4.22. Effect of chain extender use on Young Modulus values in PLA/PBT blends

As the amount of PET increases, the modulus of elasticity increases, therefore the impact strength decreases. Therefore, the elongation becomes shorter, but there is no significant change in strength. When PLA/PET blends prepared without using compatibilizers are examined in Table 4.10, it is seen that blends containing low PET amounts give better results than others.

Table 4.10. Mechanical properties of PLA/PET blends with and without compatibilizers

Samples	Young Modulus (MPa)	Yield Strength (MPa)	Elongation at Yield (%)	Tensile Strength (MPa)	Elongation at Break (%)
PLA/PET (95:5)	3490	64.7	2.6	64.7	2.2
PLA/PET (90:10)	3500	61	2	61	2
PLA/PET (85:15)	3630	60.4	2	60.4	2
PLA/PET-E (95:5)	3100	62.4	2.5	62.4	2,.5
PLA/PET-E (90:10)	3130	65.7	2.2	65.7	2.2
PLA/PET-E (85:15)	3530	64.6	1.9	64.6	1.9
PLA/PET-G (95:15)	3256	66.6	2.6	66.6	2.6
PLA/PET-G (90:10)	3290	65.9	2.4	65.9	2.4
PLA/PET-G (85:15)	2930	64.1	2.8	64.1	2.8

The effect graph of neat PLA, PET and PLA/PET blends prepared at 5%, 10% and 15% PET ratios on tensile strength values is shown in Figure 4.23. Here, it is seen that the module values of the PLA/PET (95:5) blend are higher than the other 10% and 15% PLA/PET blends. Among PLA/PET blends, PLA/PET (95:5), which contains 5% of the highest Tensile Modulus value, is also examined as 64.7 MPa. When the amount of PET was used at the rate of 15%, a decrease of 6.64% was observed in the tensile strength value.

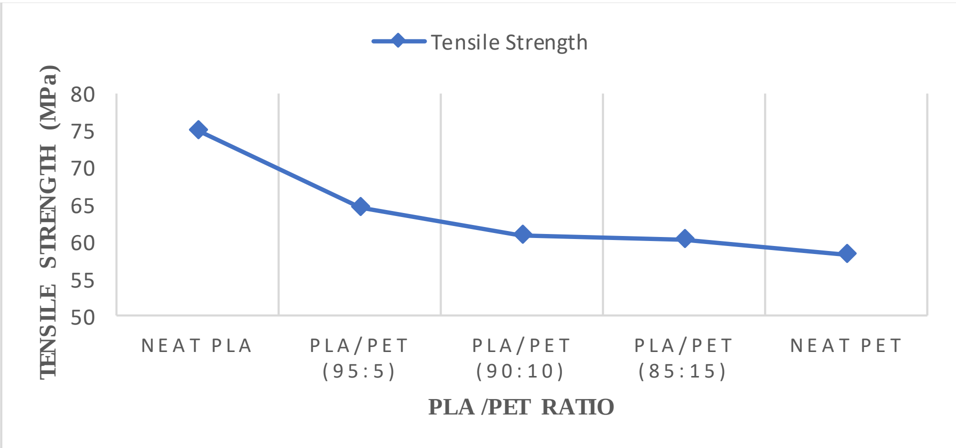


Figure 4.23. Tensile strength values of neat PLA, neat PET and, PLA/PET blends

Figure 4.24 shows the effect graph of neat PLA, neat PET and PLA/PET blends prepared in 3 different ratios on elongation at break values. As stated in Table 3.1, the elongation at break value of neat PET was recorded as 4.2% and this value is quite high compared to the others. As can be seen from the graph, there is a general change between 2% and 2.8% in elongation at break values.

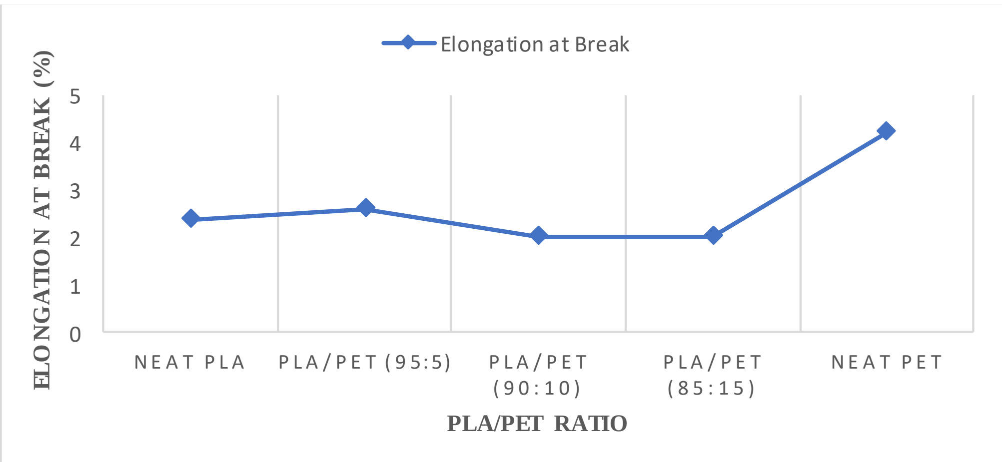


Figure 4.24. Tensile strength values of neat PLA, neat PET and, PLA/PET blends

Figure 4.25 shows the effect graph of neat PLA, neat PET and PLA/PET blends prepared in 3 different ratios on elongation at break values. Here, Young Modulus values of PLA/PET blends are between the Young Modulus values of neat PLA and neat PET.

Young Modulus values were found to be high in blends with high PET content. For example, PLA/PET (95:5) blend has a Young Modulus value of 3490 MPa, while the reading value in PLA/PET (85:15) blend increases to 3630 MPa.

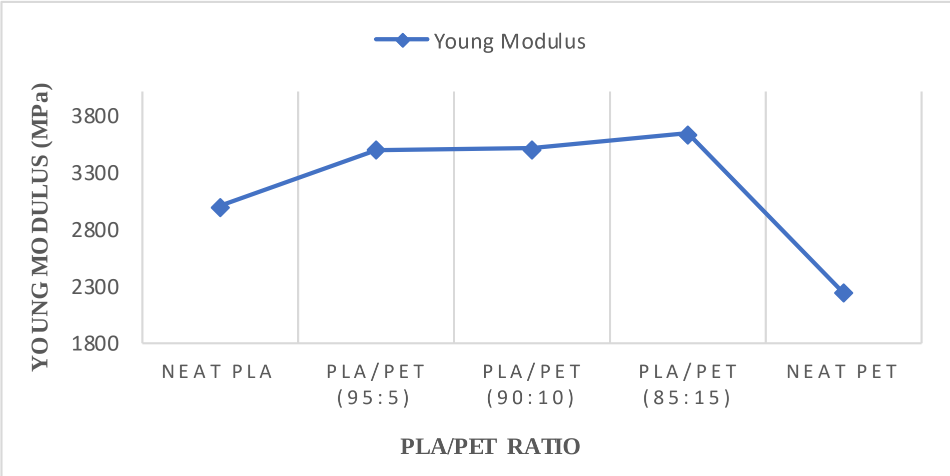


Figure 4.25. Young Modulus values of neat PLA, neat PET and, PLA/PET blends.

The effect of 3 phr EBA-g-MAH compatibilizer on the mechanical properties of PLA/PBT blends is shown in Figure 4.26. It is observed that EBA-g-MAH compatibilizer increases tensile strength values in PLA/PET-E blends containing 10% PET. It can be concluded that the use of compatibilizer significantly increases the Tensile strength values.

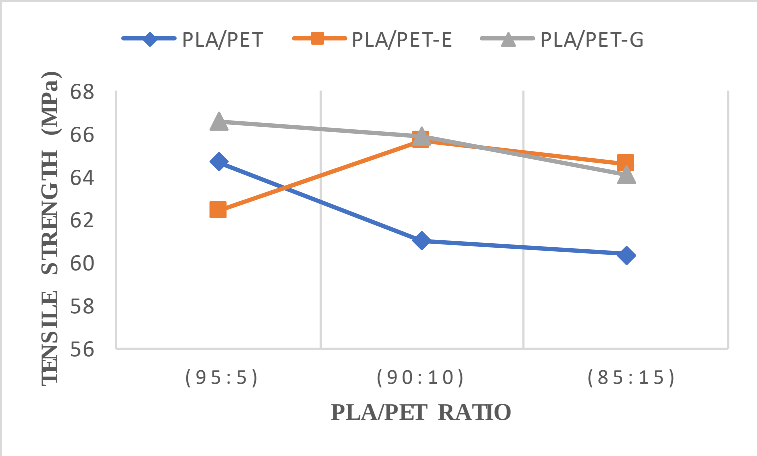


Figure 4.26. Effect of compatibilizers use on tensile strength values in PLA/PET blends

When the elongation at break values of compatibilizers used in PLA/PET blends are examined in Figure 4.27, the elongation at break value in PLA/PET-G (95:5) blends increased by 4.9%. Here, the elongation at break value of the PLA/PBT-G (95:5) blend, which has a high content of PLA, is 2.6%, while the elongation at break value of the PLA/PET-G (85:15) blend is 2.8% has risen.

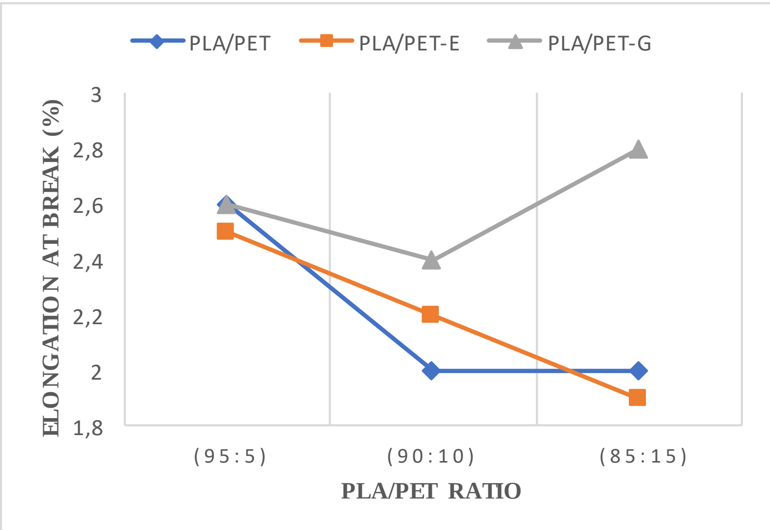


Figure 4.27. Effect of compatibilizers use on tensile strength values in PLA/PET blends

Figure 4.28 shows the effect of compatibilizer use on Young Modulus values. For example, the Young Modulus value of the prepared PLA/PET-E (95:5) blend was 3100

MPa, while the Young Modulus value of the PLA/PET-E (85:15) blend increased to 3530 MPa.

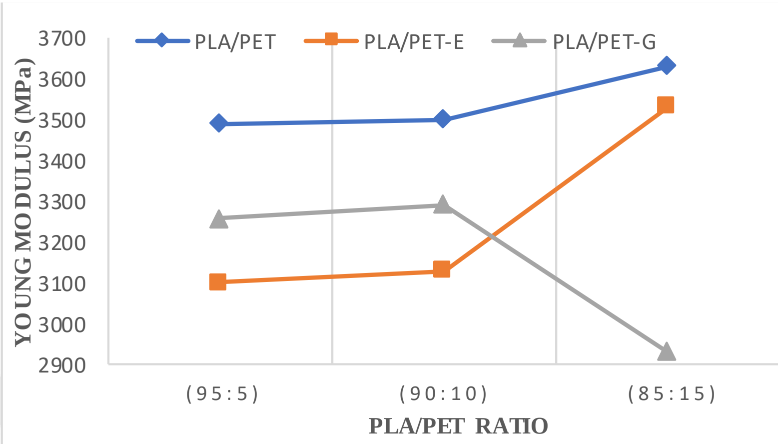


Figure 4.28. Effect of compatibilizers use on mechanical properties of PLA/PET blends

Table 4.11. Mechanical properties of chain extender on PLA/PET blends

Samples	Young Modulus (MPa)	Yield Strength (MPa)	Elongation at Yield (%)	Tensile Strength (MPa)	Elongation at Break (%)
PLA/PET (95:5)	3490	64,7	2,6	64,7	2,6
PLA/PET (90:10)	3500	61	2	61	2
PLA/PET (85:15)	3630	60,4	2	60,4	2
PLA/PET-J (95:5)	3420	68,2	2,6	68,2	2,6
PLA/PET-J (90:10)	3230	70,6	2,6	70,6	2,6
PLA/PET-J (85:15)	3255	60,3	2,1	6,3	2,1

As seen in Table 4.11, it is seen that mechanical values increase in PLA/PET blends prepared when 0.5 phr Joncryl is used as a chain extender. For example, PLA/PET (95:5) while the Young modulus value in its blend was 3490 MPa, it decreased to 3420 MPa when 0.5 phr Joncryl was used as a chain extender. Yield strength increased from 64.7 MPa to 68.2 MPa.

Figure 4.29 shows how the use of 0.5 phr Joncryl as a chain extender affects tensile strength values. As seen in this graph, the highest values are seen in PLA/PET-J (90:10) blends. While the tensile strength of PLA/PET (90:10) blend was 61 MPa, this value increased to 70.6 MPa when 0.5 phr Joncryl was used.

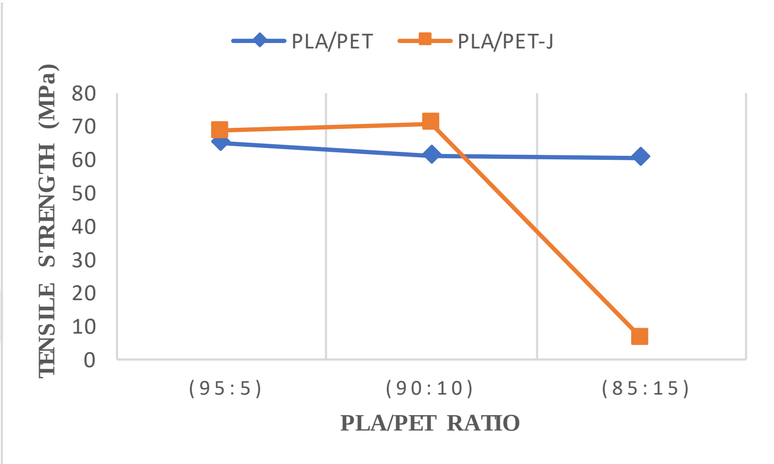


Figure 4.29. Effect of chain extender use on tensile strength values in PLA/PET blends

The Joncryl effect in terms of elongation at break is observed in Figure 4.30. For example; While the elongation at break was 2% in the PLA/PET (90:10) blend prepared without compatibilizer, the elongation at break value of the PLA/PET-J (95:5) blend increased to 2.6%.

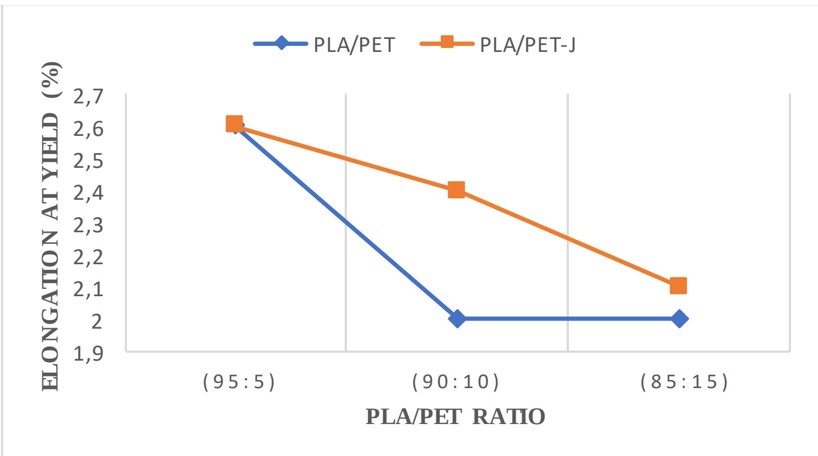


Figure 4.30. Effect of chain extender use on elongation at yield values in PLA/PET blends

The effect of Joncrly, which is used as a chain extender, on Young Modulus values can be seen in Figure 4.31. The use of 0.5 phr Joncyl in PLA/PET blends did not increase the value. This may be due to the problems caused by the temperature parameters experienced during the injection production of PLA/PET-J blends.

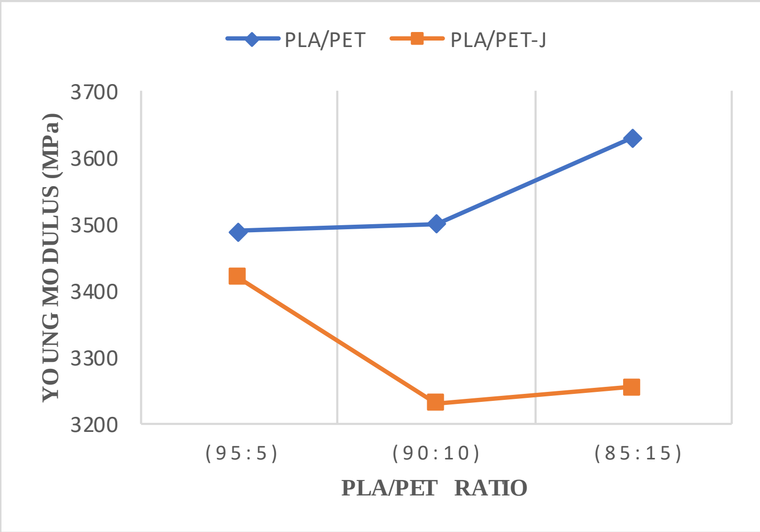


Figure 4.31. Effect of chain extender use on young modulus values in PLA/PET blends

4.3.2. Izod impact properties

As seen in Table 4.12, when the izod values of PLA/PBT blends are examined before using the compatibilizer, it is seen that the Izod values of the blends containing 5% PBT are higher than the others. Likewise, PLA/PBT (95:5) from PLA/PBT blends containing 5% PBT.

The highest value of PLA/PBT blends using 3 phr EBA-g-MAH as compatibilizer is PLA/PBT-E (95:5), ıt is observed as 3,51 kJ/m² in the blend coded as. As a result, the results obtained from the blends obtained with and without compatibilizer are between the izod values of neat PLA and neat PBT.

Figure 4.32 shows the graphical result of the impact resistance effect of neat PLA, neat PBT and PLA/PBT blends prepared in certain proportions. The impact resistance values of the prepared PLA/PBT blends are between the impact resistance values of neat polymers.

Table 4.12. Izod impact values of PLA/PBT blends with and without compatibilizers

Samples	Notched Izod Impact Test (kJ/m^2)
Neat PLA	3,98
Neat PBT	5,52
PLA/PBT (95:5)	2,93
PLA/ PBT (90:10)	3,15
PLA/PBT (85:15)	2,2
PLA/PBT-E (95:5)	3,51
PLA/PBT-E (90:10)	3,24
PLA/PBT-E (85:5)	2,63
PLA/PBT-G (95:5)	2,5
PLA/PBT-G (90:10)	3,17
PLA/PBT-G (85:15)	3,85

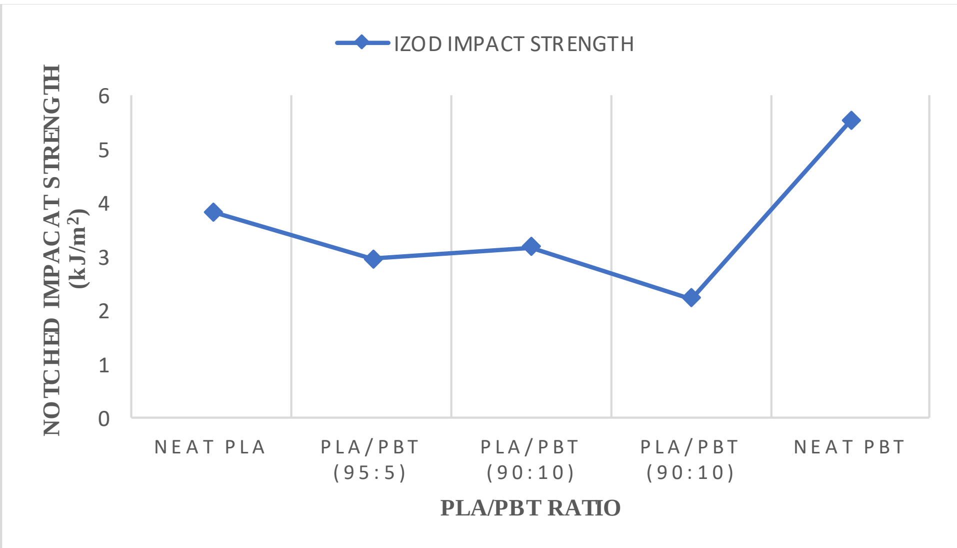


Figure 4.32. Notched impact strength values of neat PLA, neat PBT and PLA/PBT blends

Figure 4.33 shows the effect of compatibilizer use on PLA/PBT blends. In Table 4.12, the impact strength of the notched izod blend of PLA/PBT-E (95:5) is 2.93 kJ/m², while the impact strength of 3 phr EBA-g-MAH PLA/PBT-E (90:10) blend as compatibilizer 3 increased to 51 kJ/m². As another example, the impact strength of PLA/PBT (85:15) blend was 2.2 kJ/m², while the impact strength of PLA/PBT-G (85:15) blend was recorded as 3.85 kJ/m².

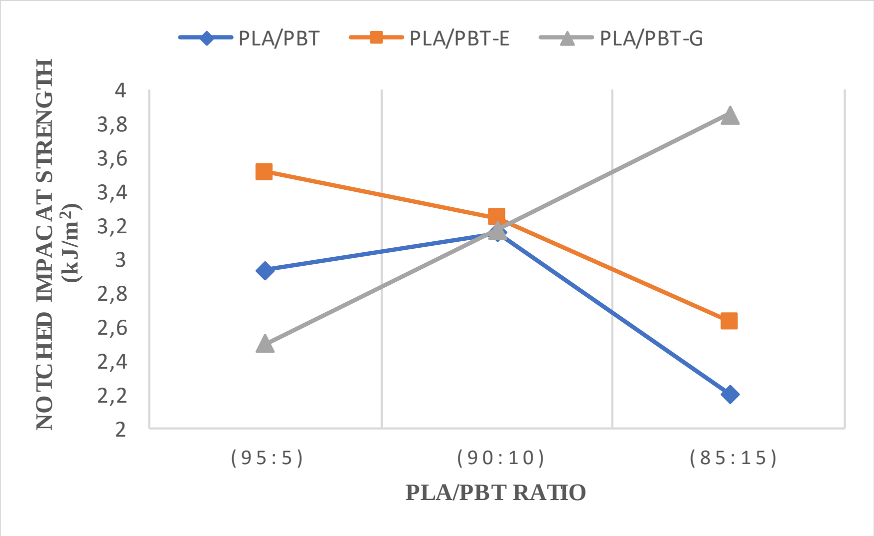


Figure 4.33. Effect of compatibilizers use on notched impact strength values in PLA/PBT blends

Table 4.13. The effect of chain extender on izod impact values in PLA/PBT blends

Samples	**Notched Izod Impact Test (kJ/m²)**
Neat PLA	3.98
Neat PBT	5.52
PLA/PBT (95:5)	2.93
PLA/PBT (90:10)	3.15
PLA/PBT (85:15)	2.2
PLA/PBT-J (95:5)	4.62
PLA/PBT-J (90:10)	5.90
PLA/PBT-J (85:15)	6.25

Table 4.13 shows the effects of Joncryl, which is 0.5 phr used as a chain extender, in PLA/PBT blends.

For example, PLA/PBT (95:5) as seen in Table 4.13. While the izod value of the PLA/PBT blend coded as, was 2.57 kJ/m^2, when it was passed through the extruder for the second time, the izod value increased to 2.93 kJ/m^2.

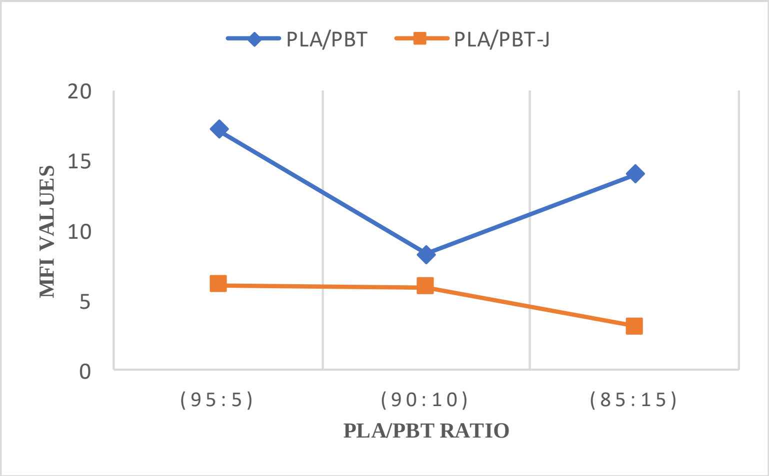


Figure 4.34. Effect of chain extender use on notched impact strength values in PLA/PBT blends

Figure 4.34 shows the effect of using 0.5 phr Joncryl as a chain extender on PLA/PBT blends. In Table 4.13, the notched izod impact strength of PLA/PBT (90:10) blend is 3.15 kJ/m^2, while the impact strength of PLA/PBT-J (90:10) blend with 0.5 phr chain extender as compatibilizer is increased to 5.90 kJm^2. As another example, the impact strength of PLA/PBT (85:15) blend is 2.2 kJ/m^2, while the notched izod impact test result of PLA/PBT-J (85:15) blend is 6.25 kJ/m^2.

Table 4.14. Izod values of PLA/PET blends with and without compatibilizers

Samples	Notched Izod Impact Test (kJ/m^2)
Neat PLA	3.98
Neat PET	2.00
PLA/PET (95:5)	4.80
PLA/PET (90:10)	3.47
PLA/PBT (85:15)	2.60
PLA/PET-E (95:5)	5.07
PLA/PET-E (90:10)	4.86
PLA/PET-E (85:15)	3.55
PLA/PET-G (95:5)	4.71
PLA/PBT-G (90:10)	4.78
PLA/PBT-G (85:15)	4.15

In Figure 4.35, the graphic result of the impact resistance effect of neat PLA, neat PET and PLA/PET blends prepared in certain proportions is shown. The impact strength values of the prepared PLA/PET blends are between the impact strength values of neat polymers and the highest impact strength among all values is shown as 4.80 kJ/m^2 in the PLA/PET (95:5) blend.

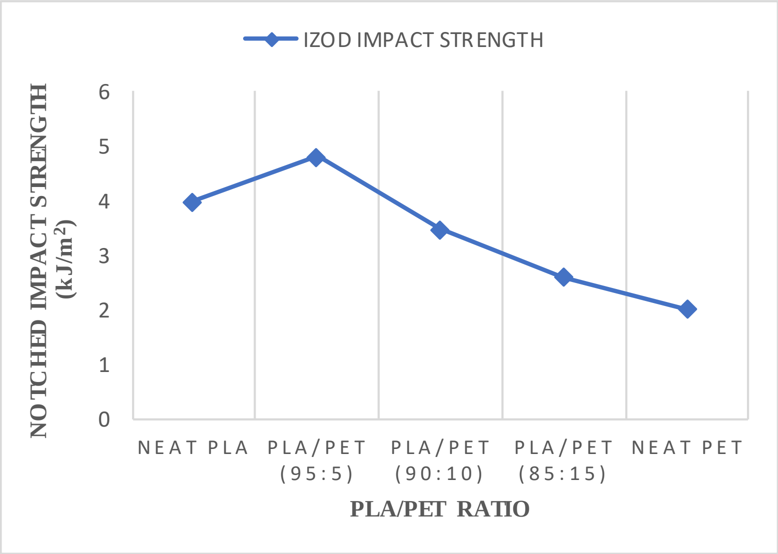


Figure 4.35. Notched impact strength values of neat PLA, neat PET and PLA/PET blends

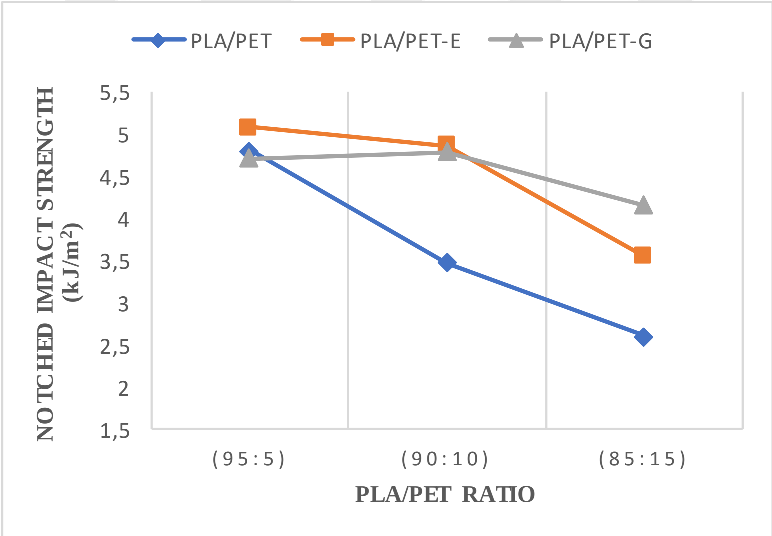


Figure 4.36. Effect of compatibilizers use on notched impact strength values in PLA/PET blends

Figure 4.36 shows the effect of compatibilizer use on PLA/PET blends. In Table 4.14, the impact strength of notched izod of PLA/PET-E (95:5) blend is 4.80 kJ/m^2, while EBA-g-MAH was using the impact strength values of PLA/PET-E (95:5) blend is 5 increased to 5.07 kJ/m^2. As another example, the impact strength of PLA/PET (85:15) blend was 2.60 kJ/m^2, while the impact strength of PLA/PET-G (85:15) blend was recorded as 4.15 kJ/m^2.

Table 4.15. The effect of chain extender on izod impact values in PLA/PBT blends

Samples	Notched Izod Impact Test (kJ/m^2)
Neat PLA	3.98
Neat PET	2.00
PLA/PET (95:5)	4.8
PLA/PET (90:10)	2
PLA/PET (85:15)	2
PLA/PET-J (95:5)	4.98
PLA/PET-J (90:10)	5.3
PLA/PET-J (85:15)	5.49

In Table 4.15, while the notched izod impact strength of PLA/PET (90:10) blend is 2 kJ/m^2, the impact strength of PLA/PBT-J (90:10) blend with 0.5 phr chain extender as compatibilizer is 5.3 kJ/m^2. It has risen to. As another example, the impact strength of the PLA/PET (85:15) blend is 2 kJ/m^2, while the notched izod impact test result of the PLA/PET-J (85:15) blend is 5.49 kJ/m^2. Figure 4.37 shows the effect of using 0.5 phr Joncryl as a chain extender on PLA/PET blends.

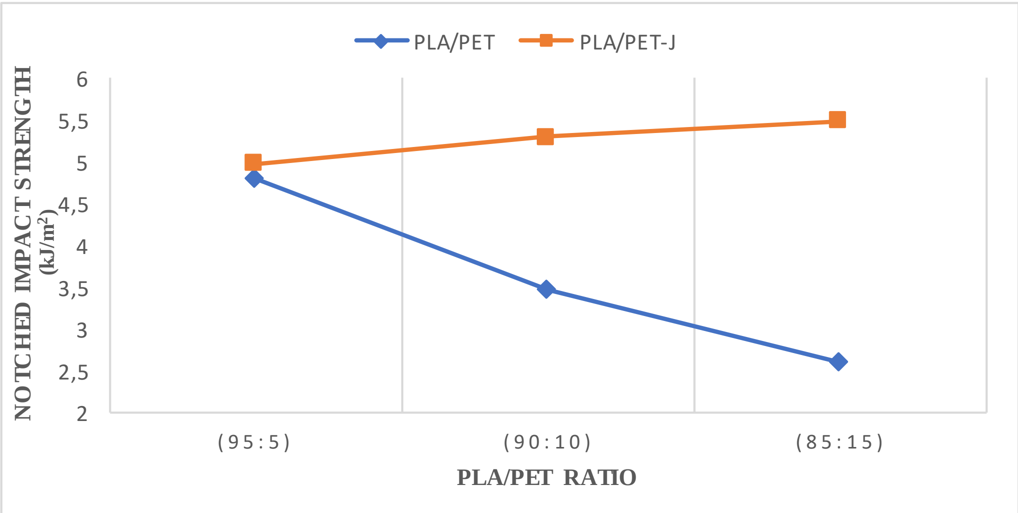


Figure 4.37. Effect of chain extender use on notched impact strength values in PLA/PET blends

4.4. Thermal Analysis of the Samples

In the mechanical properties' examination, it was seen that the samples passed through the extruder for the 2nd time had better mechanical properties due to the effective blending of the samples. Therefore, in the subsequent examinations, the measurements were taken only on the sample that was passed for the 2nd time.

At the same time, it was deemed appropriate to measure the blend samples containing 5% PBT in the thermal self-examination in the HDT VICAT test, since the samples containing 5 % PBT showed the highest mechanical properties.

The results obtained from these measurements are given in table 4.16. When we look at the values given in Table 4.16, when we look at the Vicat values; As expected, the values of the blends were close to the PLA values forming the major phase, however, due to the higher softening value of the neat PBT depending on the PBT content, the Vicat values of the blends increased compared to the neat PLA.

Table 4.16 shows the analysis results of HDT/VICAT tests of PLA/PBT blends containing 5% PBT. Here, the Vicat value of PLA was recorded as 61.23 °C. Thanks to the prepared PLA/PBT (95:5) blend, the vicat value increased to 65,35 °C. Similarly, HDT A and HDT B values are also observed to increase.

In HDT A analysis, which is one of the thermal tests, the HDT A value of neat PLA was 58.3°C, while the HDT A value of PLA/PBT-E (95:5) blend prepared using 3 phr EBA compatibilizer was recorded as 62.47°C. When neat PLA and PLA/PBT-E (95:5) blend with 3 phr EBA compatibilizer are compared, it is seen that the Vicat value increased from 61.23 °C to 62.57 °C. In another way, while the HDT B value of PLA is 55.62°C, the HDT B value of PLA/PBT-G (95:5) blend prepared using 3 phr GMA is observed as 58.83°C. To give another example, while the HDT B value of neat PLA was 55.62°C, the HDT B value of PLA/PBT-J (95:5) blend prepared by using 0.5 phr Joncryl increased to 62.47°C.

Table 4.16. HDT/VICAT test analysis of PLA/PBT blends containing 5% PBT

Samples	**VICAT B (ISO 306) °C**	**HDT A (ISO 75) °C**	**HDT B (ISO 75) °C**
Neat PLA	61.23	58.3	55.62
Neat PBT	183.97	78.1	92.84
PLA/PBT (95:5)	65.34	62.89	58.52
PLA/PBT-E (95:5)	62.57	62.47	58.85
PLA/PBT-G (95:5)	64.96	58.8	58.83
PLA/PBT-J (95:5)	62.25	60.41	62.47

Table 4.17 shows the analysis results of HDT/VICAT tests of PLA/PBT blends containing 10% PBT. The Vicat value of PLA was recorded as 61.23 °C. Vicat value of PLA/PBT (90:10) blend, rises to 65.97 °C, showing an increase of 9.37%. While the HDT A value of neat PLA was 58.3°C, the HDT A value of PLA/PBT-E (90:10) blend prepared using 3 phr EBA compatibilizer was recorded as 59.07°C. When neat PLA and PLA/PBT-E (90:10) blend with 3 phr EBA compatibilizer are compared, it is seen that the Vicat value increased from 61.23 °C to 67.28 °C. To give another example, the HDT B value of PLA is 55.62°C, while the HDT B value of PLA/PBT-G (95:5) blend prepared using 3 phr GMA is 58.64°C.

While the HDT B value of neat PLA was 55.62°C, it was recorded that the HDT B value of PLA/PBT-J (90:10) blend prepared by using 0.5 phr Joncryl increased to 60.23°C.

Table 4.17. HDT/VICAT test analysis of PLA/PBT blends containing 10% PBT

Samples	VICAT (ISO 306) °C	HDT A (ISO 75) °C	HDT B (ISO 75) °C
Neat PLA	61.23	58.3	55.62
Neat PBT	183.97	78.1	92.84
PLA/PBT (90:10)	66.97	63.17	62.90
PLA/PBT-E (90:10)	67.28	59.07	59.65
PLA/PBT-G (90:10)	64.67	57.86	58.64
PLA/PBT-J (90:10)	63.28	62.18	60.23

Table 4.17 shows the analysis results of HDT/VICAT tests of PLA/PBT blends containing 10% PBT. The Vicat value of PLA was recorded as 61.23 °C. Vicat value PLA/PBT (90:10) blend of rises to 65.97 °C, showing an increase of 9.37%.

While the HDT A value of neat PLA was 58.3°C, the HDT A value of PLA/PBT-E (90:10) blend prepared using 3 phr EBA compatibilizer was recorded as 59.07°C.

When neat PLA and PLA/PBT-E (90:10) blend with 3 phr EBA compatibilizer are compared, it is seen that the Vicat value increased from 61.23 °C to 67.28 °C. To give another example, the HDT B value of PLA is 55.62°C, while the HDT B value of PLA/PBT-G (90:10) blend prepared using 3 phr GMA is 58.64°C.

While the HDT B value of neat PLA was 55.62°C, it was recorded that the HDT B value of PLA/PBT-J (90:10) blend prepared by using 0.5 phr Joncryl increased to 60.23°C.

Table 4.17 shows the analysis results of HDT/VICAT tests of PLA/PBT blends containing 15% PBT. The Vicat value of PLA was recorded as 61.23 °C. Thanks to the prepared PLA/PBT (85:15) blend, the Vicat value rises to 63.12 °C, showing an increase of 3.08%.

While the HDT A value of neat PLA was 58.3°C, the HDT A value of PLA/PBT-E (85:15) blend prepared using 3 phr EBA compatibilizer was recorded as 63.14°C.

When neat PLA and PLA/PBT-E (85:15) blend with 3 phr EBA compatibilizer are compared, it is seen that the Vicat value increased from 61.23 °C to 64.07 °C. Another example is that while the HDT B value of PLA is 55.62°C, the HDT B value of PLA/PBT-G (85:15) blend prepared using 3 phr GMA is observed as 58.81°C.

While the HDT B value of neat PLA was 55.62°C, it was recorded that the HDT B value of PLA/PBT-J (90:10) blend prepared by using 0.5 phr Joncryl increased to 60.00°C.

Table 4.18. HDT/VICAT test analysis of PLA/PBT blends containing 15% PBT

Samples	**VICAT (ISO 306) °C**	**HDT A (ISO 75) °C**	**HDT B (ISO 75) °C**
Neat PLA	61.23	58.3	55.62
Neat PBT	183.97	78.1	92.84
PLA/PBT (85:15)	63.12	63.14	60.09
PLA/PBT-E (85:15)	64.07	57.58	58.90
PLA/PBT-G (85:15)	63.45	57.73	58.81
PLA/PBT-J (85:5)	62.46	61.52	60.00

Figure 4.38 shows neat PLA, neat PBT, and Figure 4.38 shows HDT/VICAT values of neat PLA, neat PBT and PLA/PBT blends without compatibilizers. The graph showing HDT/VICAT values of PLA/PBT blends without compatibilizer is given.

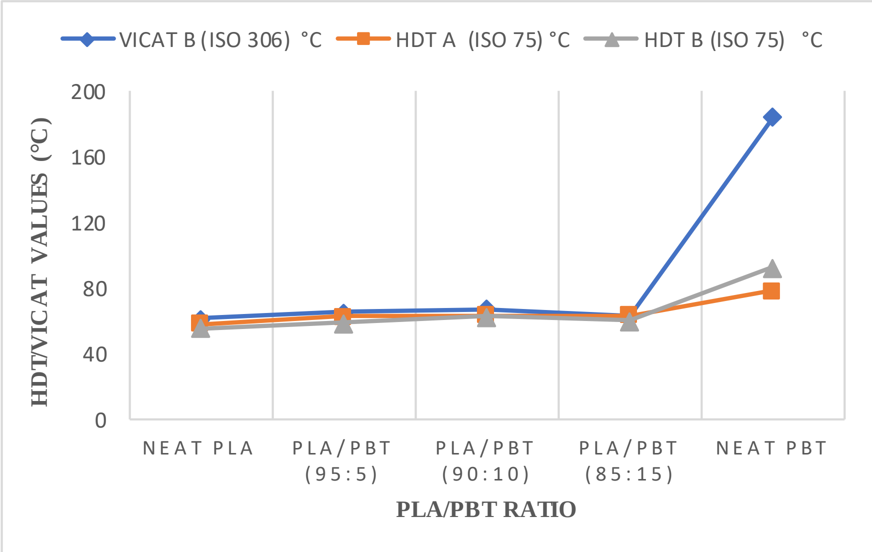


Figure 4.38. HDT/VICAT values of neat PLA, neat PBT and, PLA/PBT blends

Figure 4.39 shows how the effect of compatibilizer and chain effect on the Vicat B values of PLA/PBT blends is shown. When the graph is examined in general, the PLA/PBT (90:10) blend without compatibilizer, PLA/PBT (90:10) blends with compatibilizer and chain extender have higher Vicat B values than 5% and 15% PLA/PBT blends appears to yield results. For example, as recorded in Table 4.16, the Vicat B value of PLA/PBT-E (95:5) blend is 62.57°C, while the Vicat B value of PLA/PBT-E (90:10) blend is 67.23, as seen in Table 4.17. increased to °C.

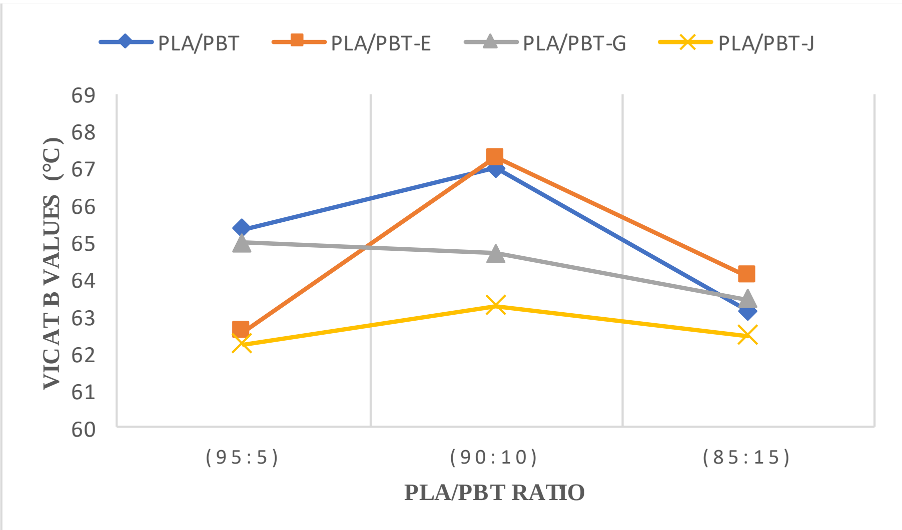


Figure 4.39. Effect of compatibilizers and chain extender use on VICAT B values in PLA/PBT blends

Figure 4.40 shows how the effect of compatibilizer and chain effect on HDT A values of PLA/PBT blends is shown. Here, it is seen that the highest HDT A values are in PLA-rich blends. For example, the HDT A value of PLA/PBT-E (90:10) blend with 3 phr EBA-g-MAH compatibilizer is 59.07 °C, while the HDT A value of PLA/PBT-E (95:5) blend is 62.47 It is recorded in °C. Similarly, HDT A value of PLA/PBT-G (85:15) blend prepared using 3 phr GMA was 57.73 °C, while HDT A value of PLA/PBT-G (95:5) blend increased to 58.8 °C.

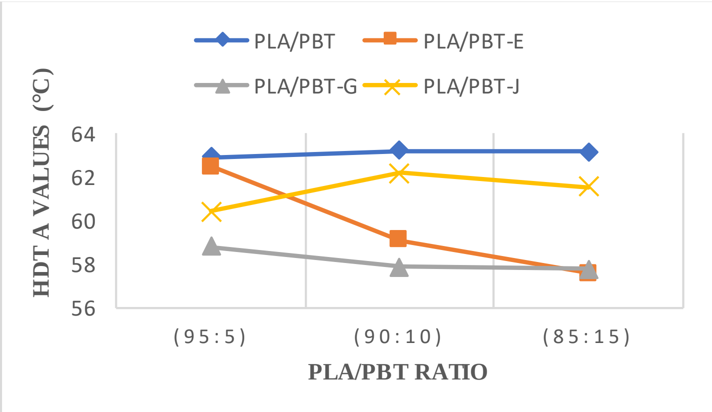


Figure 4.40. Effect of compatibilizers and chain extender use on HDT A values in PLA/PBT blends

Figure 4.41 shows the effect of compatibilizer and chain effect on HDT B values of PLA/PBT blends. Here, the highest HDT B value was measured as 62.47 °C in PLA/PBT-J (95:5) blend created with Joncryl used as 0.5 phr chain extender. HDT B values in PLA/PBT blends formed with 3 phr EBA-g-MAH and GMA compatibilizers are around 58.83-58.88 °C.

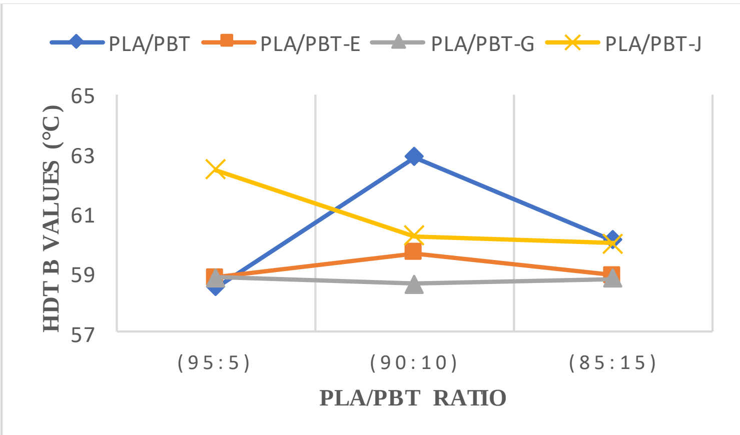


Figure 4.41. Effect of compatibilizers and chain extender use on HDT B values in PLA/PBT blends

Table 4.19. HDT/VICAT test analysis of PLA/PET blends containing 5% PET

Samples	VICAT (ISO 306) °C	HDT A (ISO 75) °C	HDT B (ISO 75) °C
Neat PLA	61.23	58.3	55.62
Neat PET	92.37	68.46	72.25
PLA/PET (95:5)	63.18	59.56	57.82
PLA/PET-E (95:5)	64.34	61.6	57.16
PLA/PET-G (95:5)	63.67	53.87	57.21
PLA/PET-J (95:5)	62.52	53	56.6

Table 4.19 shows the analysis results of HDT/VICAT tests of PLA/PET blends containing 5% PET. Here, the Vicat value of PLA was recorded as 61.23 °C. Thanks to the prepared PLA/PET (95:5) blend, the vicat value increased to 63.18 °C.

In HDT A analysis, the HDT A value of neat PLA was 59.56°C, while the HDT A value of PLA/PET-E (95:5) blend prepared using 3 phr EBA compatibilizer was recorded as 61.6°C. When neat PLA and PLA/PET-E (95:5) blend with 3 phr EBA compatibilizer are compared, it is seen that the Vicat value increased from 61.23 °C to 64.34 °C. While the HDT B value of PLA is 57.62°C, the HDT B value of the PLA/PET-G (95:5) blend prepared using 3 phr GMA is observed as 57.21°C. For example, while the HDT B value of neat PLA was 55.62°C, the HDT B value of PLA/PET-J (95:5) blend prepared by using 0.5 phr Joncryl increased to 56.60°C.

Table 4.20. HDT/VICAT test analysis of PLA/PET blends containing 10% PET

Samples	VICAT (ISO 306) °C	HDT A (ISO 75) °C	HDT B (ISO 75) °C
Neat PLA	61.23	58.3	55.62
Neat PET	92.37	68.46	72.25
PLA/PET (90:10)	62.57	58.67	59.15
PLA/PET-E (90:10)	64.80	55.92	56.73
PLA/PET-G (90:10)	64.73	56.11	56.65
PLA/PET-J (90:10)	64.65	54.15	57.15

Table 4.19 shows the analysis results of HDT/VICAT tests of PLA/PET blends containing 10% PET. The Vicat value of PLA was recorded as 61.23 °C and the Vicat value of PET was recorded as 92.37 °C. Thanks to the prepared PLA/PET (90:10) blend, it was observed that the Vicat value of PLA increased from 61.23 °C to 62.57 °C. While the HDT A value of neat PLA was 58.3°C, the HDT A value of PLA/PBT-E (90:10) blend prepared using 3 phr EBA compatibilizer was recorded as 59.07°C. While the HDT B value of PLA was 55.62°C, it was recorded that the HDT B value of PLA/PET-J (90:10) blend prepared by using 0.5 phr Joncryl increased to 57.15°C.

Table 4.21. HDT/VICAT test analysis of PLA/PET blends containing 15% PET

Samples	**VICAT (ISO 306) °C**	**HDT A (ISO 75) °C**	**HDT B (ISO 75) °C**
Nat PLA	61.23	60.39	55.62
Neat PET	92.37	68.46	77.8
PLA/PET (85:15)	60.11	57.7	55.11
PLA/PET-E (85:15)	64.92	55.80	56.64
PLA/PET-G (85:15)	65.54	58.05	58.11
PLA/PET-J (85:15)	65.24	55.31	58.32

Figure 4.42 shows the graph showing HDT/VICAT values of neat PLA, neat PET and PLA/PET blends without compatibilizers.

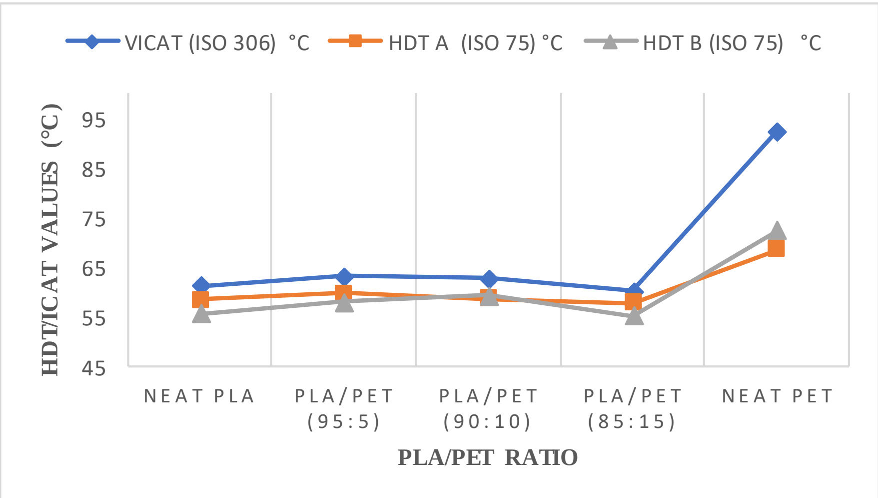


Figure 4.42. HDT/VICAT values of neat PLA, neat PET and, PLA/PET blends

Figure 4.43 shows the graph showing how compatibilizer and chain effect affect the Vicat B values of PLA/PET blends. For example, as recorded in Table 4.19, the Vicat B value of PLA/PET-E (95:5) blend is 64.34°C, while the Vicat B value of PLA/PET-E (90:10) blend is 64.80, as seen in Table 4.20. increased to °C.

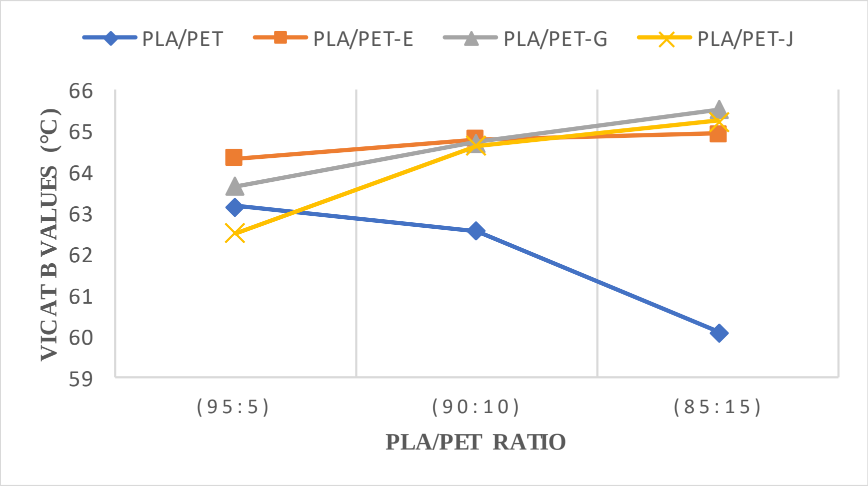


Figure 4.43. Effect of compatibilizers and chain extender use on VICAT B values in PLA/PET blends

Figure 4.44 shows the graph showing how the compatibilizer and chain effect affect the HDT A values of PLA/PBT blends. For example, the HDT A value of PLA/PET-E (90:10) blend with 3 phr EBA-g-MAH compatibilizer is 55,92 °C, while the HDT A value of PLA/PET-E (95:5) blend is 61,6 It is recorded in °C. It was observed that HDT A value increased with increasing PLA ratio in 3 phr EBA-g-MAH compatibilizer.

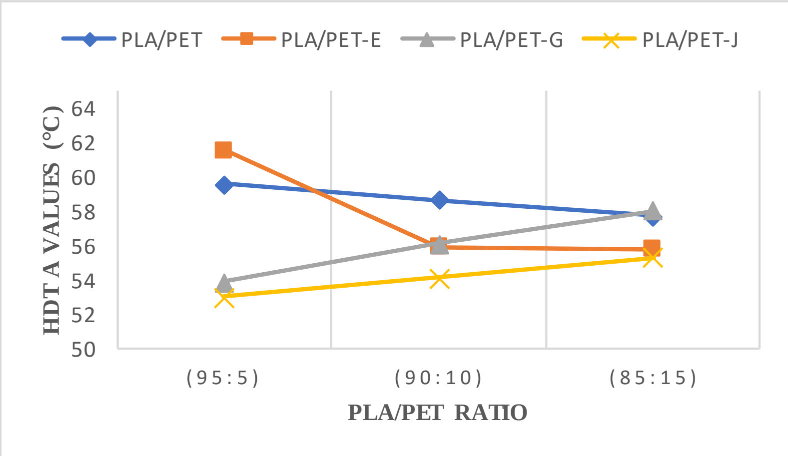


Figure 4.44. Effect of compatibilizers and chain extender use on HDT A values in PLA/PBT blends

However, with the use of 3 phr GMA as a compatibilizer, an increase in HDT values was observed in PLA/PET blends due to the decreased amount of PLA. For example, the HDT A value of the PLA/PET-G (95:5) blend is 53,87 °C, while the HDT A value of the PLA/PET-G (90:10) blend is 56.11 °C and finally PLA/PET-G (85:15) blend's HDT A value of 58,05 °C was observed by making a continuous shot.

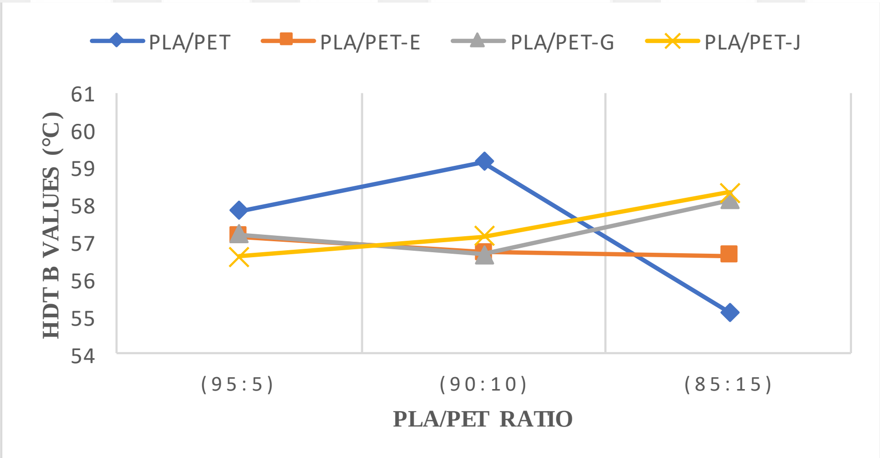


Figure 4.45. Effect of compatibilizers and chain extender use on HDT B values in PLA/PBT blends

Figure 4.45 shows the effect of compatibilizer and chain effect on HDT B values of PLA/PBT blends. For example, HDT B value was measured as 57.15 °C in PLA/PBT-J (90:10) blend created with Joncryl used as 0.5 phr chain extender. HDT B values in PLA/PBT blends formed with 3 phr EBA-g-MAH and GMA compatibilizers are around 56.73-56.65 °C.

5. CONCLUSION

Poly (lactic acid) (PLA) is a promising polymer with its value and potential due to its sustainability, low carbon footprint and being a superior bio-based polymer compared to other bioplastics. In the thesis study, the properties of PLA, which is a bio-based, biodegradable and compostable, renewable polymer, were developed by forming blends with traditional petrochemical-based polymers, especially polyesters such as PBT and PET.

It is extremely important that the applications of PLA/Polyester blends ensure that the materials developed are not only economical and sustainable, but also able to meet current and suitable needs in the future. PLA-based materials have disadvantages such as slow biodegradation, high cost and low toughness, and generally blends with petroleum-based polymers are prepared to eliminate these disadvantages. Therefore, physical, mechanical, and thermal properties of PLA were tried to be improved by using different compatibilities to PLA/PBT and PLA/PET blends. In this thesis, blends of 5%, 10%, and 15% were prepared in such a way that PLA, which is one of the biodegradable polymers, will be a major phase and PBT and PET, which are polyesters, will be a minor phase.When preparing PLA/PBT and PLA/PET blends, 3 phr EBA-g-MAH by using MAH and GMA compatibilizers and Joncryl as a 0.5 phr chain extender, it is aimed to improve the properties of the blends and to improve the rheological, mechanical and thermal properties compared to neat PLA. When using 3 phr EBA-g-MAH, PLA/PBT blends were able to outperform the uncoupler PLA/PBT blend in terms of notched izod impact strength. The tensile strength, tensile modulus, and elongation at the break of the blend were improved with the addition of the EBA-g-MAH compatibilizer. In PLA and PBT combinations, it was determined that among the 15%, 10%, and 15% samples, the best samples were suitable at 5% in terms of strength values. These blends were subjected to heat treatment and separated. For this reason, its durability has been increased by adding 3 phr EBA-g-MAH as a compatibilizer in PLA/PBT blends. So, the purpose of these studies was to investigate its use in terms of sustainability and reusability. In addition, it was observed that the mechanical and notched izod impact strengths of PLA/PBT blends containing 5% PBT were improved. The notched izod impact test results show that the addition of compatibilizer, the addition of PLA/PBT increases the impact resistance of the blends by 16%. The significant increase in the notched izod impact strength of the blends can be attributed to the interface compatibility of the EBA-g-MAH compatibilizers. The interface compatibility of the EBA-g-MAH compatibilizers is the reason for the remarkable increase in the notched Izod impact strength of the blends. The tensile modulus values of PLA/PBT blends with 3 phr EBA-g-MAH compatibilizer were reduced by approximately 2%. According to these studies, PLA varies from brittle to ductile behavior for compatibilized blends. It is thought that the use of chain extender in PLA/PET blends increases isod values and can be an alternative in 3D printing applications. It was observed that while the isod value was 2 kJ/m^2 in PLA/PET blends containing 15% PET, it increased to 5.49 kJ/m^2 when 0.5% chain extender was used. In application areas where impact resistance is important, a PLA/PET blend can be a good option.

Consequently, in this thesis, blending of polymers was also requested to provide high performance polymer materials for new uses. It is aimed to produce sustainable materials with biodegradable, sustainable and improved performance properties and alternative raw materials for many industries including automotive, electrical and electronic devices. In addition to all this, it aimed to minimize dependence on petroleum-based resources and promote more sustainable development by creating durable and sustainable bio-based PLA/polyester blends.

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RESUME

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