

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**ATTEMPTS TO RE-EVALUATE WASTE THERMOPLASTIC
POLYURETHANE (TPU)**



M.Sc. THESIS

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Department of Metallurgical and Materials Engineering

Materials Science and Engineering Programme

JANUARY 2025

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**TERMOPLASTİK POLİÜRETAN (TPU) ATIKLARININ YENİDEN
DEĞERLENDİRİLMESİNE YÖNELİK GİRİŞİMLER**

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In memory of my father,



FOREWORD

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January 2025

Simay YANIK
(Metallurgical and Materials Engineer)



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ABBREVIATIONS

DMF	: Dimethyl Formaldehyde
DSC	: Differential Scanning Calorimetry
EMA	: Ethylene-Co-Methyl Acrylate
ENR	: Epoxidized Natural Rubber
EPDM	: Ethylene Propylene Diene Rubber
EVA	: Ethylene Vinyl Acetate
GHS	: Globally Harmonized System of Classification and Labelling of Chemicals
GPC	: Gel Permeation Chromatography
HDI	: Hexamethylene Diisocyanate
IM	: Injection Molding
mm	: Milimeter
MPa	: Megapascal
M_n	: Number-Average Molecular Weight
M_w	: Weight-Average Molecular Weight
PA	: Polyamide
PET	: Polyethylene Terephthalate
PBT	: Polybutylene Terephthalate
PDMS	: Polydimethylsiloxane Rubber
POSS	: Polyhedral Oligomeric Silsesquioxanes
POM	: Polyoxymethylene
PLA	: Polylactic acid
PMDI	: Polymerized-Methylene Diphenyl Diisocyanate
PMMA	: Polymethyl Methacrylate
PVC	: Polyvinyl Chloride
PVDF	: Poly (Vinylidene Fluoride)
rpm	: Revolutions per minute
s	: second
SAOS	: Small Amplitude Oscillatory Shear
SEM	: Scanning Electron Microscopy

PMDA	: Pyromellitic Dianhydride
TDI	: Toluene Diisocyanate
TGA	: Thermogravimetric Analysis
TPU	: Thermoplastic Polyurethane
TSE	: Twin Screw Extruder
wt.	: Weight



SYMBOLS

-OH	: Hydroxyl Group
-COOH	: Carboxyl Group
N-H	: Amino Group
C=O	: Carbonyl Group
T	: Temperature
T_c	: Crystallization Temperature
T_m	: Melting Temperature
T_g	: Glass Transition Temperature
°C	: Degrees Celsius
G'	: Storage Modulus
G''	: Loss Modulus



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ATTEMPTS TO RE-EVALUATE WASTE THERMOPLASTIC POLYURETHANE (TPU)

SUMMARY

Polymers' excellent mechanical and thermal qualities, lightweight nature, and economical manufacturing have made them essential materials in many different sectors. However, there are major environmental issues with waste management and large-scale polymer production, which highlights the need for sustainable recycling solutions. Thermoplastic polyurethanes (TPUs), which are widely used in industries including consumer goods, automotive, and medicine, are known for their flexibility, toughness, and chemical resistance. In order to encourage sustainable material development, this study aims to enhance the revaluation of TPU waste through chemical modification and blending procedures. The environmental problems caused by polymeric waste are highlighted in this study of the literature, especially in the case of TPU, which has been widely used in the consumer goods, automotive, and medical sectors. TPU is a good option for recycling because of its thermoplastic characteristics, mechanical strength, and durability. However, the process is made more difficult by its structural complexity and the presence of additives.

Studies have investigated polymer blending and chemical modification as approaches to enhance the properties of TPU and make recycling less challenging. The rheological, mechanical, and thermal properties of TPU are enhanced via chemical modification. Through a variety of processes, additives such as diisocyanates (polymerized-methylene diphenyl diisocyanate (PMDI), and hexamethylene diisocyanate (HDI)), Joncryl ADR 4468, pyromellitic dianhydride (PMDA), and other different additives have an impact on the properties of TPU. Waste of TPU could also have effectively be revalued through blending it with polymers including polylactic acid (PLA), polyamide (PA), polymethyl methacrylate (PMMA), and polybutylene terephthalate (PBT). This method improves mechanical properties including toughness, flexibility, and impact resistance while addressing PLA's shortcomings, such as brittleness, low melt strength, and slow degradation. However, compatibility problems with PLA/TPU blends can result in phase separation as well as limitations. Compatibilizers such as Joncryl optimize mechanical and thermal qualities by enhancing phase compatibility and blend morphology.

The objective of this thesis is to develop sustainable materials with improved mechanical, thermal, morphological, and rheological properties by improving the reutilization of TPU waste through chemical modification and blending techniques. Due to TPU's great resistance to degradation and growing environmental concerns about its recycling and disposal, improved methods are required to increase its reusability. Through the chemical modification of TPU with different additives and also blending the waste TPU with biodegradable polymers like PLA, this work aims to address these problems. The experimental process has been divided into two parts: the chemical modification and blending. TPU wastes have been melt processed with

additives (PMDI, HDI, Joncryl ADR 4468, and PMDA) at 0.5% and 1% by weight for five minutes at 200°C and 100 rpm in an internal melt mixer. Rheological, mechanical, thermal, and properties of the samples were determined using small amplitude oscillatory shear (SAOS) rheometer, tensile and hardness tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). PLA/TPU blends were made with 20% waste TPU and 80% PLA in a twin screw extruder. Joncryl was utilized as a compatibilizer in certain samples. Mechanical, thermal, and morphological properties of the samples were investigated using tensile, impact, and hardness tests, DSC, TGA, and scanning electron microscopy (SEM).

Chemical modification study findings shown significant increases in TPU properties depending on the type and concentration of additions. particularly when diisocyanates are incorporated, resulting in improved mechanical performance (tensile strength and elongation at break) and melt strength (complex viscosity) while preserving thermal stability. However, PMDA-modified TPU resulted in lower mechanical performance because to hydrolysis-induced degradation. This finding highlights the potential of the modifications to enhance material performance without compromising its fundamental characteristics. Experiments carried out in the second stage of the study indicated that, the use of waste TPU contributed to improving the disadvantageous properties of PLA. Based on the results of various mechanical analyses, the structure obtained by blending PLA and TPU exhibited a decrease in tensile strength due to the immiscibility between PLA and TPU. However, the presence of TPU led to a more ductile structure, reflected by an increase in elongation at break values, while hardness values decreased. Additionally, TPU enhanced the impact resistance properties of PLA. The incorporation of Joncryl ADR 4468 as a compatibilizer improved phase compatibility, thereby enhancing the mechanical properties. Blend structure created by pre-blending TPU with Joncryl (PLA/(TPU/J)*) resulted in only a slight increase in tensile strength and modulus values. SEM analysis revealed that phase separation occurred due to the immiscibility of PLA and TPU, with TPU appearing as droplets inside the PLA matrix. The addition of Joncryl increased phase compatibility, resulting in finer and more uniform microstructures by interacting with PLA and TPU to lower interfacial tension and increase viscosity by branching in the PLA matrix. Stronger interphase bonding and a more stable structure were confirmed in PLA/(TPU/J)* blends. The microstructure was further improved by pre-blending TPU with Joncryl, which improved its dispersion inside the blend. The presence of TPU improved PLA's thermal stability and processability by increasing the degree of crystallization while decreasing its total crystallinity, according to thermal analysis. T_g of PLA was lowered by TPU's plasticizing effect, which may reduce brittleness. Joncryl enhances the overall performance of the blend and increases the maximum degradation temperatures, especially when blended with TPU before that, which greatly increases thermal stability.

This study emphasizes the possibilities of chemical modification and blending methods for tackling TPU waste recycling concerns. While the incorporation of additives enhances the rheological and mechanical property of TPU, blending it with PLA tackles PLA's limitations, and the two methods promote the revaluation of waste TPU. The findings emphasize the importance of optimizing process parameters, selecting suitable materials, and evaluating alternating additives for enhanced performance. These efforts contribute to the development of sustainable materials, reduction of polymer waste, and promotion of a circular economy.

TERMOPLASTİK POLİÜRETAN (TPU) ATIKLARININ YENİDEN DEĞERLENDİRİLMESİNE YÖNELİK GİRİŞİMLER

ÖZET

Polimerler, üstün mekanik ve termal özellikleri, hafif yapıları ve ekonomik üretim süreçleri sayesinde birçok endüstride vazgeçilmez malzemeler haline gelmiştir. Ancak, geniş ölçekli polimer üretimi ve atık yönetiminin çevresel etkileri, geri dönüşüm ve sürdürülebilirlik odaklı bir dönüşümü zorunlu kılmaktadır. Esneklik, dayanıklılık ve kimyasal direnç gibi özellikleriyle öne çıkan termoplastik poliüretanlar (TPU'lar), otomotiv, medikal ve tüketici ürünleri gibi farklı sektörlerde yaygın olarak kullanılmaktadır. Bu çalışma, TPU atığının yeniden kullanılabilirliğini artırmak amacıyla kimyasal modifikasyon ve karıştırma teknikleri kullanarak sürdürülebilir malzeme üretimini hedeflemektedir.

Literatür taraması, polimerik atıkların çevresel zorluklarını, özellikle otomotiv, medikal ve tüketim malları gibi endüstrilerde yaygın olarak kullanılan termoplastik poliüretan (TPU) bağlamında vurgulamaktadır. TPU, mekanik mukavemeti, dayanıklılığı ve termoplastik özellikleri sayesinde geri dönüşüm için cazip bir aday olarak öne çıkmaktadır. Ancak, yapısal karmaşıklığı ve katkı maddelerinin varlığı, bu süreci karmaşıklştırmaktadır.

Çalışmalar, TPU'nun geri dönüşümünü kolaylaştırmak ve özelliklerini iyileştirmek amacıyla kimyasal modifikasyon ve polimer harmanlama yöntemlerini incelemiştir. Kimyasal modifikasyon, TPU'nun reolojik, mekanik ve termal performansını artırmada etkili bir yöntem olarak öne çıkmaktadır. Örneğin, diizosiyanatlar (HDI ve PMDI), Joncryl ADR 4468 ve Piromellitik Anhidrit (PMDA) gibi katkı maddeleri, TPU'nun özelliklerini farklı mekanizmalarla geliştirmektedir. Diizosiyanatlar, TPU'nun zincir yapısını uzatarak ve dallandırarak viskoziteyi, mekanik dayanımı ve termal kararlılığı artırmaktadır. Joncryl ise TPU'nun sert segmentleriyle reaksiyona girerek moleküler ağırlığını ve elastikiyetini yükseltmektedir. Ancak, PMDA'nın işleme sırasında hidrolize bağlı bozulmaya neden olabileceği belirtilmiştir. TPU'nun Polilaktik Asit (PLA), Poliamid (PA), Polimetil Metakrilat (PMMA) ve Polibütilen Tereftalat (PBT) gibi farklı polimerlerle harmanlanması, TPU atıklarını yeniden değerlendirmede etkili bir strateji sunmaktadır. Bu harmanlama işlemi, PLA'nın kırılgenlik, düşük eriyik mukavemeti ve yavaş bozunma gibi dezavantajlarını gidermekte, aynı zamanda gelişmiş mekanik dayanıklılık, esneklik ve darbe direnci sağlamaktadır. Ancak, PLA/TPU karışımlarındaki uyumsuzluk, faz ayrımına yol açarak performansı sınırlayabilmektedir. Joncryl gibi uyumlulaştırıcıların kullanımı, faz uyumluluğunu ve karışım morfolojisini geliştirerek mekanik ve termal özellikleri optimize etmektedir. Bu çalışma, TPU'nun geri dönüşüm zorluklarını aşmak, yenilikçi malzemeler geliştirmek ve sürdürülebilir atık yönetimine katkı sağlamak için kimyasal modifikasyon ve harmanlama yaklaşımlarının önemini vurgulamaktadır.

Bu tez çalışması, gelişmiş mekanik, termal, morfolojik ve reolojik özelliklere sahip sürdürülebilir malzemeler yaratmayı hedefleyen yenilikçi kimyasal modifikasyon ve

harmanlama yaklaşımları aracılığıyla termoplastik TPU atıklarının yeniden kullanımının geliştirilmesini amaçlamaktadır. TPU atıklarının bertarafı ve geri dönüşümüne ilişkin artan çevresel kaygılar, malzemenin bozunmaya karşı yüksek direnciyle birleştiğinde, yeniden kullanılabilirliğini artırmaya yönelik daha gelişmiş yöntemlerin geliştirilmesini zorunlu kılmaktadır. Bu çalışma, TPU'nun çeşitli katkı malzemeleri kullanılarak kimyasal modifikasyonu ve PLA gibi biyobozunur polimerlerle harmanlanması yoluyla bu zorlukların ele alınmasına odaklanmaktadır.

Tez çalışması kimyasal modifikasyon ve harmanlama yöntemiyle TPU'nun değerlendirilmesi olmak üzere iki aşamadan oluşmaktadır. Kimyasal modifikasyon deneylerinde, atık TPU malzemeler bir eriyik iç karıştırıcı yardımıyla, 200 °C, 100 rpm ve 5 dakika süre ile kontrollü koşullar altında eriyik proses gerçekleştirilmiştir. Ağırlıkça 0,5 % ve 1,0 % oranlarında dört farklı katkı malzemesi (PMDI, HDI, Joncryl ADR 44668 ve PMDA) kullanılarak gerçekleştirilen proseste, katkı malzemelerinin etkisinin gözlemlenmesi adına atık TPU herhangi bir katkı malzemesi içermeksizin de proses edilmiştir. Kimyasal modifikasyon yöntemiyle gerçekleştirilen deneylerde, bahsi geçen bu katkı malzemelerinin TPU kimyasal yapısı ile etkileşimi ile beraber TPU'nun moleküler yapısında değişikliklere sebep olarak ve mekanik, termal ve reolojik özelliklerini iyileştirmek amaçlanmıştır. İkinci deneysel aşama kapsamında gerçekleştirilen harmanlama deneylerinde, atık TPU'ların biyobozunur biyoyumlu PLA ile eriyik proses sonucu harman yapısının oluşturulması hedeflenmiştir. Elde edilen numuneler, eriyik reolojik davranışlarının incelenmesi için düşük genlikli salınımlı kayma (SAOS) reoloji analizine, mekanik özelliklerinin incelenmesi adına çekme ve sertlik testlerine, termal özelliklerinin irdelenmesi için diferansiyel taramalı kalorimetre (DSC) ve termogravimetrik analizlerine (TGA) ve yapısal analiz için jel geçirgenlik kromatografisi (GPC) testine tabi tutulmuştur.

Harmanlama deneyleri kapsamında atık TPU malzemeler ağırlıkça 20 % oranında kullanılırken, ana faz olarak ağırlıkça 80 % oranında PLA 4043D tercih edilmiştir. PLA ve TPU'yu harman yapısı oluşturulmasında birbirleriyle karışmayan bir morfolojik yapı sergiledikleri için bu karışmazlık oranını düşürebilmek adına uyumlaştırıcı olarak ağırlıkça 0.5 % oranında Joncryl ADR 4468 kullanılmıştır. Deneyler kapsamında beş farklı harman hazırlanmış olup, bunlar ağırlıkça 80/20 oranında karıştırılmış PLA/TPU harmanı, aynı oranlarda harman içerisine ağırlıkça 0.5 % oranında Joncryl ilave edilmiş PLA/TPU/J harmanı ve aynı oranlarda ağırlıkça 2.5 % oranında Joncryl ilave edilmiş TPU/J harmanı üretilip bu harmanın PLA matriks içerisine karıştırılması ile elde edilen PLA/(TPU/J)* harman yapısıdır. Kendi içinde de iki aşamalı gerçekleşen harmanlama deneylerinde, numuneler öncelikli olarak çift vidalı ekstrüder kullanarak baştan sona 185, 195, 200, 200, 200, 110, 50 °C proses sıcaklıkları ile karıştırılmış ve sudan geçirilip peletize edilmiştir. Bu numuneler ardından aynı sıcaklık değerleri ile enjeksiyon kalıplama makinesinde de eriyik işleminden geçirilmiş ve gerçekleştirilecek testlere uygun kalıplara basılmıştır. Elde edilen numuneler mekanik özelliklerinin incelenmesi adına çekme, darbe ve sertlik testlerine, morfolojik analiz için taramalı elektron mikroskop (SEM) görüntüleri alınmış ve termal özelliklerinin irdelenmesi için diferansiyel taramalı kalorimetre (DSC) ve termogravimetrik analizlerine (TGA) tabi tutulmuştur.

Kimyasal modifikasyon deneylerinde, kullanılan katkı malzemelerinin türüne ve konsantrasyonuna bağlı olarak, birçoğuna TPU'nun özelliklerinde önemli iyileştirmeler sağladığı söylenebilir. Eriyik reolojik analizler, özellikle HDI ve PMDI gibi diizosiyanatların, TPU'ların kompleks viskozitesini belirgin bir şekilde artırdığını ortaya koymuştur. Bu davranış, artan moleküler ağırlığı gösteren Jel Geçirgenlik

Kromatografisi (GPC) sonuçlarıyla doğrulanan zincir uzaması ve dallanma reaksiyonları nedeniyle iyileştirilmiş eriyik mukavemetini işaret ettiği düşünülmektedir. Ek olarak, mekanik testler, çekme mukavemetinin, kopma uzamasının ve sertliğin diizosiyanatların kullanımıyla artırıldığını ve malzemenin yeniden kullanım için mekanik açıdan gelişmiş özellikler elde edildiğini göstermektedir. PMDA ile modifiye edilmiş TPU malzemeler ise olası hidroliz reaksiyonu sonucundaki bozunma sebebiyle, atık TPU'lara göre daha düşük mekanik performans göstermişlerdir. Termal analizler, yapılan değişikliklere rağmen, katkı malzemelerinin hiçbirinin TPU'nun erime veya kristalleşme sıcaklıklarında kayda değer bir değişikliğe yol açmadığını ortaya koymuş, bu da malzemenin temel termal özelliklerinin korunduğunu göstermektedir. Bu bulgu, yapılan çalışmanın temel özelliklerden ödün vermeksizin malzeme performansını artırma potansiyelini ortaya koymaktadır.

Çalışmanın ikinci aşamasında gerçekleştirilen deneyler sonucunda, atık TPU'nun PLA ile harmanlanarak gelişmiş özelliklere sahip malzemeler üretilmesi potansiyelini net bir şekilde ortaya koymuştur. Çevre dostu ve biyoyumlu bir malzeme olarak bilinen PLA, kırılganlık, düşük tokluk ve yavaş bozunma gibi sınırlamalara sahiptir ve TPU ile PLA'nın harmanlanması bu dezavantajların etkili bir şekilde hafifletilmesini sağlamıştır. Gerçekleştirilen çeşitli mekanik analizler sonucunda, PLA ve TPU'nun ağırlıkça 80/20 oranında harmanlanmasıyla elde edilen ilk yapı (PLA/TPU), PLA ve TPU arasındaki karışmazlıktan ötürü azalan bir çekme mukavemeti değeri göstermiştir. Ayrıca bu yapı, TPU'nun etkisiyle daha sünek bir yapı sergileyerek % uzama değerleri artmış ancak sertlik değerleri azalmıştır. Yine TPU'nun etkisiyle PLA'nın darbe dayanımı özellikleri de artış göstermiştir. Joncryl ADR 4468'in uyumlaştırıcı olarak eklenmesi ile ise faz uyumluluğunun artıp, faz ayrımı azalmış ve harman içinde daha homojen bir dağılım sağlayarak mekanik özelliklerin iyileşmesini sağlanmıştır. TPU'nun Joncryl ile önden harmanlanması sonucunda ise sadece çekme mukavemetinde çok az ve modül değerinde artış göstermiştir. Sonuç olarak hedeflendiği şekilde, atık TPU'lar kullanılarak, PLA'nın dezavantajlı özelliklerinin geliştiği analiz sonuçlarında görülmektedir. Morfolojik analizler sonucunda elde edilen SEM görüntüleri incelendiğinde, tüm görüntülerde, PLA ve TPU'nun birbirleriyle karışmaz yapısından ötürü, fazların ayrılarak TPU PLA matrisi içerisinde damlacık şeklinde görülmektedir. SEM incelemeleri, uyumlu hale getirilmiş harmanların azaltılmış faz ayrımıyla daha homojen bir yapı sergilediğini ortaya koymuştur. Ayrıca Joncryl ilavesi, PLA/TPU harman yapısında fazlar arası uyumu artırarak daha ince ve homojen bir mikro yapı elde edilmesini sağladığı görülmektedir. Bunun sebebinin, Joncryl'in PLA ve TPU ile reaksiyona girerek arayüz gerilimini azaltması ve PLA matrisinde dallanma etkisiyle viskoziteyi artırarak damlacık boyutunun küçülmesine neden olmasıyla ilişkili olabileceği düşünülmektedir. PLA/(TPU/J)* harmanında ise fazlar arası bağlanmanın güçlendiği ve daha stabil bir yapı olduğu SEM görüntüleriyle doğrulanmıştır. TPU ve Joncryl'in önceden harmanlanması, Joncryl'in TPU içinde daha iyi dağılmasını sağlayarak harmanın mikro yapısını iyileştirmektedir. Termal analizler, karışımların performansı hakkında ek bilgi sağlamıştır. DSC sonuçları, TPU ilavesinin PLA'nın kristalleşme hızını artırırken genel kristallliğini azalttığını göstermiştir. Bu değişim, malzemenin termal kararlılığını ve işlenebilirliğini iyileştirerek yüksek sıcaklık uygulamalarında daha üstün performans sunmasını sağlamıştır. TPU'nun plastikleştirici etkisi, PLA'nın T_g değerini düşürdüğü ve bunun kırılganlığı azaltacağı düşünülmüştür. PLA/TPU harmanında PLA ve TPU'nun erime pikleri korunmuş, ancak Joncryl ilavesi PLA/TPU/J ve PLA/(TPU/J)* harmanlarında, bu piklerin şiddetini azaltmış ve

kristaliniteyi düşürmüştür. TGA sonuçlarına göre PLA, TPU'ya kıyasla daha yüksek termal stabilite göstermektedir; ancak TPU ilavesi, PLA'nın dekompozisyon sıcaklığını düşürmüştür. Joncryl, PLA ve TPU harmanlarında bir uyumlaştırıcı olarak davranarak daha iyi bir karışım sağlamış ve maksimum bozunma sıcaklıklarını artırmıştır. Özellikle Joncryl'in önce TPU ile karıştırılması, termal stabiliteyi daha belirgin şekilde artırmıştır.

Sonuç olarak, bu çalışma, gelişmiş kimyasal modifikasyon ve harmanlama yöntemleri aracılığıyla TPU atıklarının yeniden kullanılabilirliğini ve özelliklerinin geliştirilebileceğini göstererek, TPU atık geri dönüşümünün zorluklarını ele almada hem kimyasal modifikasyon hem de harmanlama yöntemlerinin etkisini vurgulamaktadır. Kimyasal modifikasyonda özellikle diizosiyanatların dahil edilmesi, TPU'nun yapısal ve mekanik bütünlüğünü önemli ölçüde iyileştirirken; PLA ile harmanlama, PLA'nın dezavantajlı özelliklerini geliştirmeyi ele almış ve uygulama potansiyelini genişletmiştir. Çalışma, proses koşullarını optimize etmenin, uygun malzeme seçiminin ve malzeme performansını daha da artırmak için alternatif katkı malzemelerini belirlemenin önemini vurgulamaktadır. Bu kapsamda gerçekleştirilen çalışma, sürdürülebilir malzemelerin geliştirilmesine, polimer atıklarının azaltılmasına ve döngüsel bir ekonominin teşvik edilmesine katkıda bulunmaktadır.

1. INTRODUCTION

Polymers are widely used in a variety of industries, including automotive, construction, textiles, electronics, medical, and packaging, due to their superior mechanical and thermal qualities, lightweight nature, and low-cost production techniques. However, the environmental consequences of large-scale polymer manufacture and use make recycling and sustainability more important than ever. The waste generated by the manufacturing, frequent use, and disposal of thermoplastic polymers, in particular, presents substantial issues for both natural resource conservation and trash management [1].

Furthermore, during production and reprocessing, many polymers, including TPU, are exposed to high temperatures and mechanical strains, which causes structural degradation. This degradation causes a loss of mechanical and thermal properties during recycling procedures, impeding the effective reuse of polymeric waste. Polyurethanes, on the other hand, rank fifth in Europe and seventh internationally, with an estimated three million tons in use. The global rankings and consumption quantities of plastics, together with the European Union's objectives to encourage plastic recycling by 2050, highlight the need of controlling and recycling polymer waste [2]. In this setting, novel technologies are required to improve recycling processes and improve polymer waste properties.

TPUs are a kind of thermoplastic elastomer with unique qualities such as flexibility, durability, chemical resistance, and biocompatibility. The mechanical characteristics of TPU are derived from the balance of soft and hard segments in its structure. While the hard segments give strength and stiffness, the soft segments gives elasticity and flexibility at low temperatures. The chemical modification and blending processes of TPU provide possible solutions to the underlying difficulties. Specifically, enhancing the features of TPU waste through various chemical modification processes or blending it with other polymers to increase their properties or make them suitable for certain applications has a high potential. These methods can improve the qualities of recycled TPU, making it more valuable and versatile in the reprocessed form. Studies

on the recycling and improvement of TPUs have grown in importance as a means of increasing the material's sustainability and assuring its more efficient usage in a variety of applications. TPU's block copolymer structure, consisting of soft and hard segments, is responsible for its remarkable characteristics like as elasticity, strength, and chemical resistance.

In the literature, various chemical modification and blending methods have been emphasized to enhance the properties of TPU. Studies on chemical modifications have demonstrated that additives such as diisocyanates (PMDI and HDI), Joncryl ADR 4468, and PMDA improve the mechanical and rheological behavior of TPU. Diisocyanate-based compounds enhance mechanical strength and thermal stability by extending and branching the chain structure of TPU [3]. It is frequently highlighted in the literature that compounds like PMDI and HDI react with the hard segments of TPU, increasing the viscosity and strength of the material [4]. Additionally, epoxy-based additives like Joncryl ADR 4468 have also been reported to increase the molecular weight of TPU, creating a more stable structure and improving the material's elasticity [5-6].

In blending studies, TPU has shown significant potential for optimization when combined with biodegradable polymers such as PLA. While PLA is an environmentally friendly and biocompatible polymer, it has disadvantages such as low toughness and brittleness [7]. Blending TPU with PLA not only addresses these shortcomings but also enhances the mechanical durability and flexibility of the blend. However, the typically immiscible nature of PLA/TPU blends often results in phase separation, which reduces mechanical performance. The literature frequently references studies showing that the use of compatibilizers like Joncryl improves phase compatibility and optimizes blend morphology. These compatibilizers contribute to achieving a more homogeneous structure by promoting hydrogen bonding between PLA and TPU [8-9]. Within blending studies, factors such as the PLA/TPU ratio, the amount of compatibilizers, and processing parameters have been extensively investigated for their effects on the properties of the blend.

The aim of this study is to enable the reuse of TPU waste through various processes and to examine the properties of the materials obtained by optimizing these processes. In the first phase of the two-stage study, the focus will be on enhancing the reprocessability and performance of TPU through chemical modification methods. In

the chemical modification experiments, the effects of TPU and various additives, such as diisocyanates (PMDI (polymerized-MDI) and HDI), Joncryl ADR 4468, and PMDA, on the rheological, mechanical, and thermal properties of TPU will be investigated using melt processing. To examine the rheological behavior of the modified structures, frequency and time sweep rheology analyses will be conducted. Tensile and hardness tests will evaluate the mechanical properties, while DSC and TGA analyses will assess the thermal behavior of the modified and unmodified samples. Structural analysis will be performed using GPC.

In the second part of the study, blend structures consisting of PLA 4043D and TPU waste will be produced. The goal is to address the disadvantages of PLA, such as slow degradation rate, low melt strength, and slow crystallization rate, by enhancing its properties and re-evaluating the TPU waste. Blending experiments will utilize a composition of 80 % PLA and 20 % TPU by weight. Joncryl ADR 4468 will also be employed as a compatibilizer to assess its effect on the blend structure. In this context, all materials (PLA, TPU, and Joncryl) will be mixed and processed in one blend, while in another blend, TPU and Joncryl will be mixed and melt-processed first, followed by blending the prepared masterbatch with PLA. This approach will observe differences in the structure caused by processing Joncryl, which is known to have greater interaction with PLA, either together with TPU first or simultaneously with all materials. The produced blends will undergo frequency sweep rheology analysis to examine tensile, impact, and hardness tests to determine mechanical properties, DSC and TGA for thermal behavior evaluation, and SEM analysis for structural analysis. This study aims to enhance the reuse potential of TPU waste, creating a sustainable material cycle and reducing its environmental impact.



2. LITERATURE REVIEW

Polymeric wastes, including TPU, pose significant environmental challenges due to their resistance to degradation and recycling inefficiencies. These wastes can disrupt ecosystems, harm biodiversity, and contribute to climate change through greenhouse gas emissions during production and disposal. Addressing these impacts requires innovative recycling technologies and sustainable management strategies [1]. Figure 2.1 shows annual plastic waste production (Figure 2.1a) and consumption (Figure 2.1b).

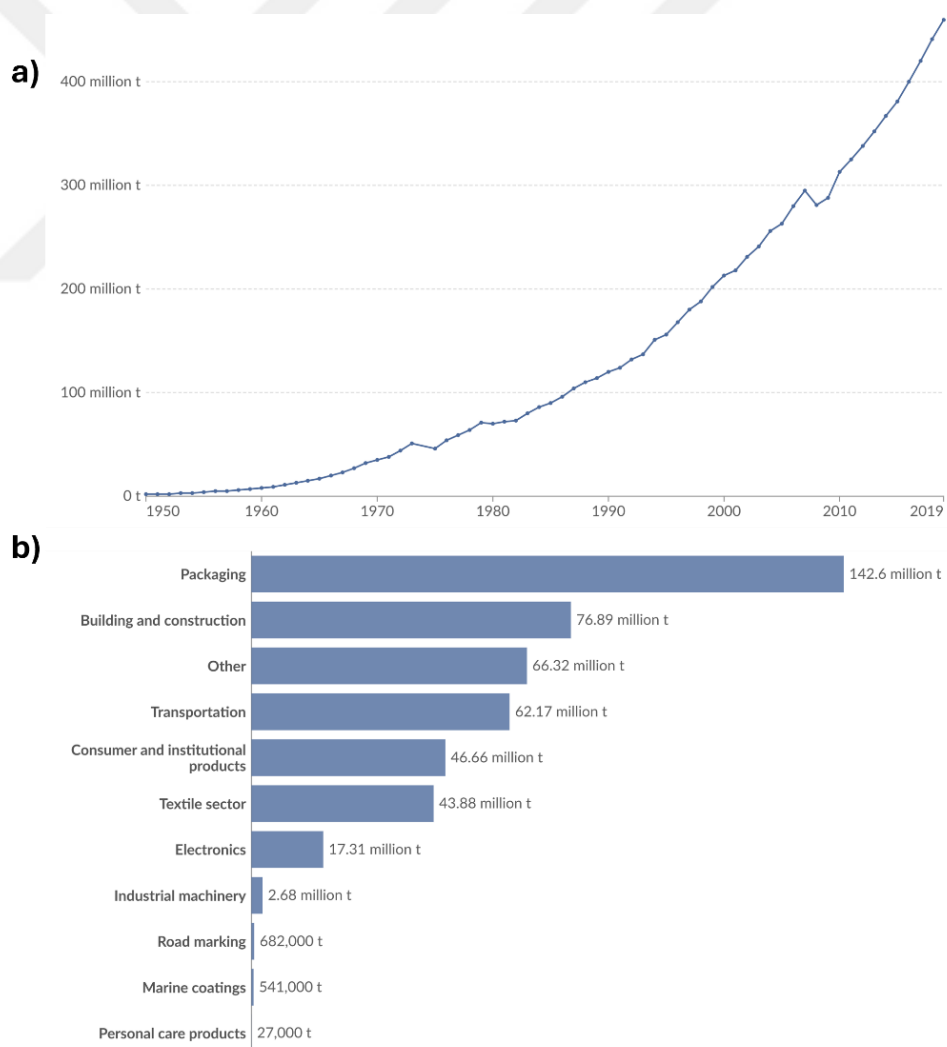


Figure 2.1 : (a) Annual global plastic production of polymer resin and fibers and (b) annual global plastic consumption tonnes per year [11].

TPU, a versatile material widely used in automotive, footwear, and medical devices, contributes to the polymeric waste stream. Despite its mechanical strength and durability, TPU wastes pose recycling challenges due to their structural complexity and the additives used in production [10]. However, TPU's thermoplastic nature allows for potential recycling through reprocessing techniques, making it a candidate for circular economic strategies [1]. The reuse of TPU wastes involves either mechanical recycling, where TPU is melted and reprocessed, or chemical recycling, which breaks down polymers into their monomeric forms. TPU waste can be converted into secondary raw materials for manufacturing new products, such as footwear soles or automotive parts.

Advanced technologies are essential for maintaining the mechanical and thermal properties of recycled TPU, ensuring their usability in demanding applications. Advancements in recycling methods aim to enhance the quality and applicability of recycled TPU, reduce TPU's environmental footprint, bridge the performance gap with virgin polymers and leveraging its potential for sustainable reuse [1, 10].

2.1 Thermoplastic Polyurethane (TPU)

TPUs are a versatile class of polymers that balance biocompatibility and biodegradability with exceptional mechanical, thermal, and rheological properties [4]. These unique properties making them ideal for a wide range of applications. The synthesis of TPUs typically involves the reaction of polyols with diisocyanates, resulting in a segmented structure composed of soft and hard segments (Figure 2.2). Soft segments, typically originating from polyether or polyester diols, contribute to elasticity, whereas hard segments, created from diisocyanates, enhance strength and rigidity [12, 13]. Additionally, the synthesis process can be customized by altering the chemical composition and molecular weight of the components to achieve specific properties. [14, 15].

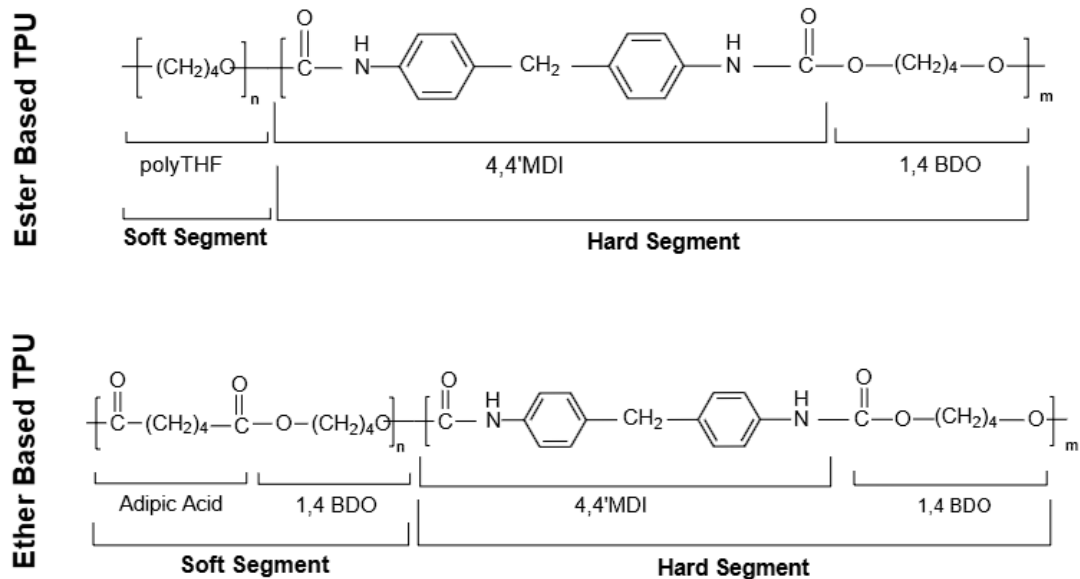


Figure 2.2 : Chemical Structure of Ester Based and Ether Based TPU [8].

The thermal properties of TPU materials, such as glass transition temperature (T_g) and melting temperature (T_m), are influenced by their chemical structure and, in particular, by the ratio of soft and hard segments within their composition (e.g., the molecular weight of the soft segment and the type of diisocyanate used) [14, 16]. The low melting temperature and high decomposition temperature of TPU enable to across a broad range of application area [4]. However, the incorporation of additives such as polyhedral oligomeric silsesquioxanes (POSS) into the structure can enhance TPU for use in even higher-temperature applications [16]. Additionally, the phase-separated microdomain structure present in TPUs contributes to the enhancement of their thermal behavior by allowing tunable properties based on composition [13]. This phase separation characteristic is widely recognized as a key factor influencing the engineering properties of (A–B)_n type thermoplastic elastomers [17].

The mechanical properties of TPUs, known for their excellent tensile strength, wear resistance, and flexibility, are a critical aspect of their performance. These properties can be significantly enhanced by optimizing the ratio of soft to hard segments and incorporating bio-based materials [18-20]. Mechanical characteristics, including tensile strength, elongation at break, and hardness, are essential for the application of TPUs across various industries. For instance, Esclapez et al. highlighted that the customizable mechanical properties of TPUs have led to their growing use in diverse industrial applications, such as automotive and biomedical fields [21]. Moreover, integrating renewable resources into TPU synthesis not only improves mechanical

performance but also addresses environmental concerns associated with petrochemical-based materials [15, 22].

The rheological properties of TPUs play a vital role, particularly in processing and application contexts. Their flow behavior can be customized by selecting specific polyols and diisocyanates and adjusting processing conditions during synthesis [23, 24]. Silva et al. investigated the rheological behavior of TPUs under uniaxial extensional flow, shedding light on flow characteristics essential for manufacturing techniques like extrusion and injection molding [6]. Controlling the viscosity and flow properties of TPUs is crucial for applications requiring precise material handling, such as 3D printing and injection molding [23, 25]. A thorough understanding of rheology is key to optimizing processing conditions and ensuring the production of high-quality TPU materials. Moreover, incorporating nanofillers like cellulose nanocrystals can further refine the rheological properties of TPU nanocomposites, enhancing their performance in various applications [24].

TPUs find applications across numerous industries, including automotive, medical, and consumer goods. Their exceptional wear resistance, flexibility, and durability make them ideal for use in coatings, adhesives, foams, and various molded components [26]. In the medical applications like catheters and prosthetics, TPUs are increasingly utilized because of their biocompatibility and excellent mechanical properties [14, 27]. Additionally, their adaptability to diverse processing techniques, such as extrusion and injection molding, further enhances their application potential across various sectors [23, 26]. In summary, thermoplastic polyurethanes are a prominent focus of research and development, thanks to their customizable properties and versatility across various applications. The incorporation of advanced materials and novel processing methods holds great potential to further improve their performance and broaden their application scope, solidifying TPUs as a critical area of study in materials science.

Each process involving exposure to heat and shearing induces irreversible thermal and mechanical degradation in the polymeric material, leading to physical and/or chemical changes. As a result, the material exhibits weaker properties compared to its virgin form, as originally synthesized or supplied by any manufacturer [2]. In a study conducted by Lee et al. [28], a decrease in M_n^a , M_w^b , tensile strength, elongation at break, and modulus values of TPU materials was observed after each thermal

processing step (o-TPU represents the virgin TPU, TPU-0 refers to TPU subjected to a hot press process, and TPU-1, TPU-2, and TPU-3 indicate the number of melt mixing cycles applied to the TPU-0 material) [Table 2.1].

Table 2.1: Number average and weight average molecular weight, tensile strength, elongation at break and modulus values of TPU materials exposed to repeated thermal processes [28].

Sample Name	Treatment	M_n^a	M_w^b	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)
o-TPU	-	54,400	112,200	-	-	
TPU-0	Hot Pressing (H)	59,400	110,300	36.9±1.8	1,442±22.3	8.7±1.0
TPU-1	H/One Times Melt Mixing	43,700	137,400	32.1±3.1	1,217±34.6	12.1±1.3
TPU-2	H/Two Times Melt Mixing	42,600	127,500	30.8±1.6	1,204±45.6	11.0±1.5
TPU-3	H/Three Times Melt Mixing	40,300	118,700	25.1±2.5	1,097±40.7	11.0±1.4

TPU materials possess a recyclable structure that responds to temperature changes. They consist of macromolecular chains lightly cross-linked by intermolecular hydrogen bonds. When the material is in a molten state, these bonds weaken; however, upon cooling, strong intermolecular forces re-establish, allowing the material to regain the performance of its original solid state. This characteristic enables waste TPU to be mechanically decomposed and reused in melt-processing applications [29].

In many manufacturing fields where polymeric materials are used, a significant amount of waste can be generated, either dependent on or independent of process conditions [30]. Specifically for TPU materials, their elastomeric properties enable them to be processed through various industrial techniques, making them suitable for a wide range of engineering applications [28]. Consequently, in many industrial, medical, and everyday applications where TPU is utilized, non-recyclable waste materials are generated, posing a significant challenge in waste management [31, 32].

The secondary utilization of waste TPU materials is a crucial necessity, as it not only ensures better use of limited resources for humanity but also compels the plastics industry to contribute to the "recycling economy" [29].

2.2 Methods for Improving the Properties of Waste TPU

The primary challenge in recycling plastic waste lies in the degradation of materials after undergoing various processes. During these processes, the formation of oxygenated groups, the breaking of polymer chains, and the weakening of properties, coupled with the release of potentially toxic compounds (e.g., isocyanates in TPU materials) during chain scissions, make these materials problematic as waste [30, 33]. While many of the polymeric materials used today are biodegradable, waiting for their natural decomposition is less favorable. Instead, reprocessing these polymers and finding suitable application areas has become a more preferred approach [32].

Various methods have been developed to enhance and transform these products, which have become waste after undergoing various processes, enabling their reintegration into production lines or reuse in applications. The most fundamental of these methods are (1) chemical modification using modifiers and (2) blending [33].

2.2.1 Chemical modification

Chemical modification methods serve as a means to alter the properties of polymeric materials by inducing changes in their chemical structure, thereby enhancing their performance in various applications. By employing chemical modification, the versatile structure of TPUs—characterized by a balanced mechanical properties combining elasticity, durability, and processability—can be further improved. This allows for modifications and enhancements in their mechanical, thermal, and chemical properties, making these materials more suitable for a broader range of applications, including biomedical devices, automotive components, and consumer goods [34].

One of the primary methods for modifying polymers involves incorporating chain extenders, which can significantly alter the mechanical properties and phase behavior of the polymer. For instance, Tripathi et al. demonstrated that the length of the chain extender in polyurea formulations influences material properties, particularly the hydrogen bonding interactions and phase separation within the polymer matrix [35].

This study highlights the critical role of chain extenders in tuning the physical properties of polyureas, a concept that can also be extended to TPUs.

Chemical modifications is also another method that can significantly effect the thermal and mechanical properties of polymers. Boroğlu & Gürkaynak reported that the incorporating silica to polyimide membranes increases both rigidity and T_g due to reduced local segmental motion [36]. This modification not only improves the polymers' thermal stability but also enhances its mechanical properties, making it suitable for high-temperature applications.

Furhermore, the addition of nanoparticles into polymer matrices through chemical modification has attracted significant interest for enhancing mechanical and thermal properties. For instance, Jagtap et al. examined the impact of dicarboxylic acid salt-based modifiers on poly(ethylene oxide)-multiwall carbon nanotube composites, and found that these modifiers improved the dispersion and conductivity of nanotubes within the polymer matrix [37]. This highlights the critical role of chemical modifications in developing advanced composite materials with tailored properties. Additionally, chemical modifications have been investigated to enhance the adsorption properties of polymers. Ali et al. demonstrated that modified polyvinyl chloride (PVC) effectively removed thionine dye from aqueous solutions, highlighting the potential of chemical modifications to improve polymer adsorption capabilities for environmental applications [38]. This strategy plays a crucial role in developing materials to tackle pollution and waste management challenges.

Similarly, Standau et al. examined the impact of chain extenders on the crystallinity of expanded polybutylene terephthalate foams. Their study revealed that the incorporation of chain extenders reduced crystallinity by disrupting chain linearity, providing valuable insights into how structural modifications can affect polymer properties [39]. This finding is particularly relevant for TPUs, where maintaining a balance between hard and soft segments is critical for optimizing mechanical performance. The chemical modification techniques, including the incorporation of various modifiers such as chain extenders, diisocyanates, or polyols into the structure of TPU, along with modifications to its chain architecture through branching and extension, has a profound impact on its chemical and mechanical properties, thermal stability, rheological behavior, and overall performance.

Sun's study highlighted that the incorporation of modified nanoparticles into TPU composites nearly doubled their maximum stress compared to pure TPU films, primarily due to strong chemical crosslinking that restricted molecular chain mobility [40]. Similarly, the addition of boron nitride nanosheets not only improved mechanical properties but also enhanced thermal stability, demonstrating the effectiveness of nanoadditives in optimizing TPU performance [41]. These enhancements also contributed to flame retardancy, a crucial attribute for various applications [41, 42].

Furthermore, modifying TPU through techniques such as polymer grafting or the inclusion of nanofillers has shown significant improvements in interfacial adhesion and material properties. For instance, grafting TPU onto microfibrillated cellulose covalently resulted in superior mechanical properties and thermal stability, attributed to robust interfacial interactions [43]. These findings underscore the importance of interfacial chemistry and nanoadditives in advancing the performance of TPU composites across diverse applications.

2.2.1.1 Diisocyanates

Diisocyanates are a group of compounds composed of low molecular weight aromatic and aliphatic structures, widely used in polyurethane production [44]. Among the most commonly utilized diisocyanates are toluene diisocyanate (TDI), MDI, and HDI (Figure 2.3). Both MDI and HDI are bifunctional chain extenders with two isocyanate terminal groups, making them some of the most frequently employed diisocyanates in TPU synthesis, polymer modifications, and polymer composites. They serve as effective compatibilizers, cross-linking, and modification agents [3, 45]. In polyurethane synthesis, HDI is particularly preferred due to its lower toxicity compared to other diisocyanates, such as TDI and MDI [46].

However, most diisocyanates are classified as toxic, irritant, and hazardous to health and the environment under the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) and the NFPA 704 system. This classification is primarily due to the high reactivity of free isocyanate groups, which has led to concerns regarding the use of diisocyanates in various applications [47, 48]. Nevertheless, following chemical reactions, these groups can react with other functional groups to form stable covalent bonds, eliminating their toxicity as a concern [47].

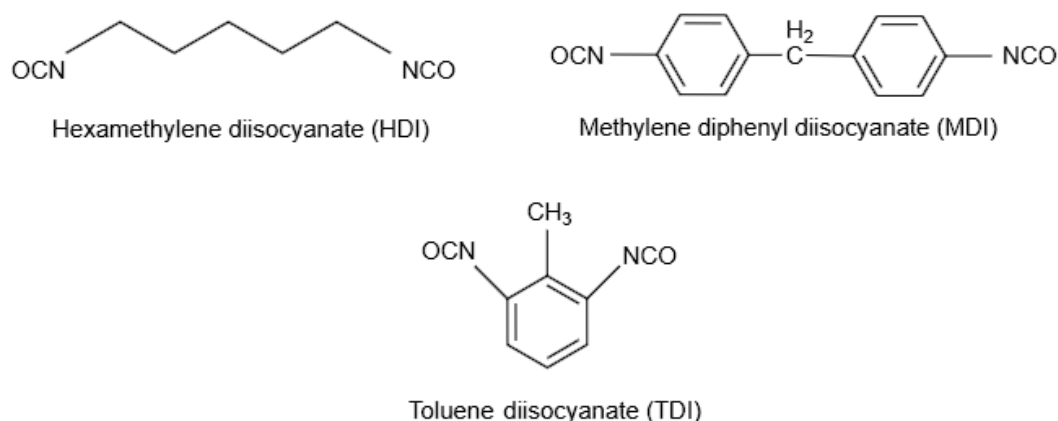


Figure 2.3 : Chemical Structure of various diisocyanates [49].

The utilization of diisocyanates as modifiers in the TPUs has been extensively studied due to their significant impact on the mechanical, thermal, and morphological properties of these materials. The literature also includes studies indicating that the interaction of diisocyanate group materials such as PDI and MDI with TPU leads to improvements in properties such as melt strength, impact resistance, and ductility in blend structures like PLA/TPU, PA/TPU, ethylene vinyl acetate (EVA)/TPU, and polyoxymethylene (POM)/TPU [4, 8, 50-52].

When diisocyanates react with TPU for the purpose of chemical modification, different reactions may occur depending on the type of diisocyanate groups, their concentration, and processing temperature. Diisocyanates preferentially undergo extension-type reactions with hydroxyl groups on the TPU chain, forming urethane linkages within the TPU structure (Figure 2.4a). Less frequently, they react with carboxyl groups to form amide linkages, resulting in a chain-extended TPU structure (Figure 2.4b) [4]. At higher isocyanate concentrations, less favorable reactions may occur, such as the reaction of urethane or amide groups with an isocyanate, leading to the formation of allophanates or ureas, respectively. This can result in a network or cross-linked structure containing branched chains [53, 54]. Consequently, an increase in isocyanate content provides more bond sites for potential reactions, leading to progressively extended, branched, and ultimately cross-linked TPU structures [3, 52].

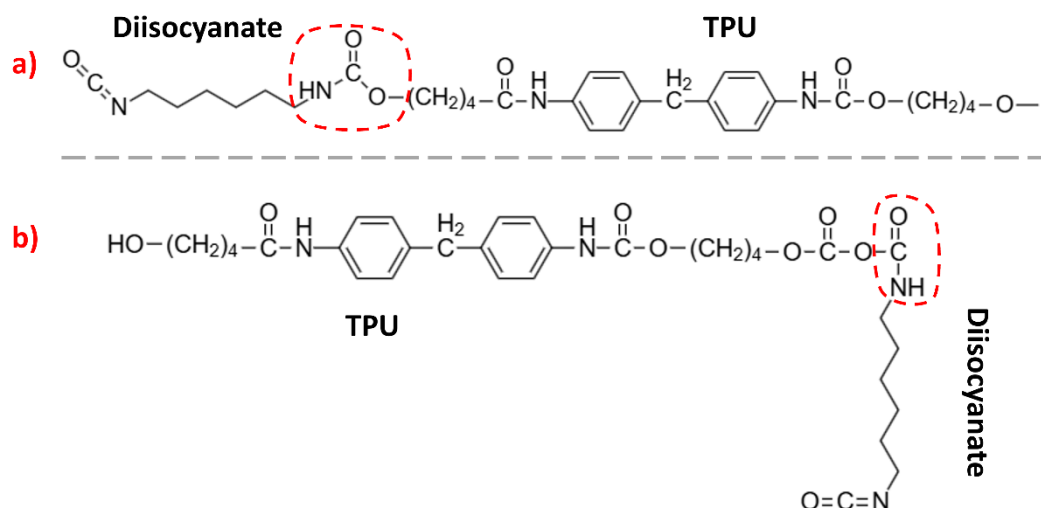


Figure 2.4 : Possible reactions between diisocyanates and TPU (a) urethane formation reactions (b) amide formation reactions [4].

The ability to use MDI and HDI not only for TPU synthesis but also for enhancing TPU structures stems from the reaction between the isocyanate groups in MDI and HDI and the urethane groups in TPU, resulting in the formation of a network structure [50]. One of the primary mechanisms for branching and chain extension in TPUs involves the reaction of diisocyanates with polyols and chain extenders.

The addition of diisocyanates such as MDI to TPU formulations enhances melt viscosity and promotes the development of branched structures. This occurs as the isocyanate groups react with hydroxyl groups in the polyol, forming longer polymer chains and crosslinked networks [3, 4]. The resulting increase in viscosity and mechanical properties is linked to the formation of higher molecular weight polymers and TPU-g-PLA structures in blends with PLA [4]. Zhao et al. showed that incorporating MDI into biodegradable PLA/TPU blends improves toughness by creating a branched structure that enhances energy absorption [3]. These modifications not only strengthen the mechanical properties but also refine the TPU's microstructure, leading to better crack resistance.

2.2.1.2 Joncryn

Joncryn, a commercially available multi-epoxy-functionalized styrene-acrylic oligomer (Figure 2.5), has become an important chemical modifier and chain extender for various polymers, including TPU. Its effectiveness in enhancing interfacial adhesion, increasing molecular weight, and improving thermal stability makes it a vital additive for creating high-performance polymer materials.

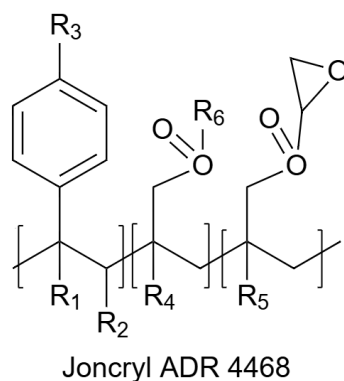


Figure 2.5 : Chemical Structure of Joncryl ADR 4468 [9].

In addition to diisocyanates and chain extenders, the incorporation of multifunctional epoxies, though less commonly used, has been investigated as a strategy for achieving chain extension and branching in TPUs. These epoxies react with the hydroxyl groups of polyols (Figure 2.6), leading to increased molecular weight and modifications in crystallinity, which enhance the thermal and mechanical properties of the TPU [9, 55]. Extensive research has also been conducted on reactive modifiers such as Joncryl. For example, Iqbal et al. analyzed the hydrogen bonding patterns in aromatic versus aliphatic chain-extended polyureas, demonstrating that the type of chain extender plays a crucial role in determining the thermal properties and phase segregation of the polymer [5]. These findings provide valuable insights for designing TPUs with improved thermal stability and mechanical performance.

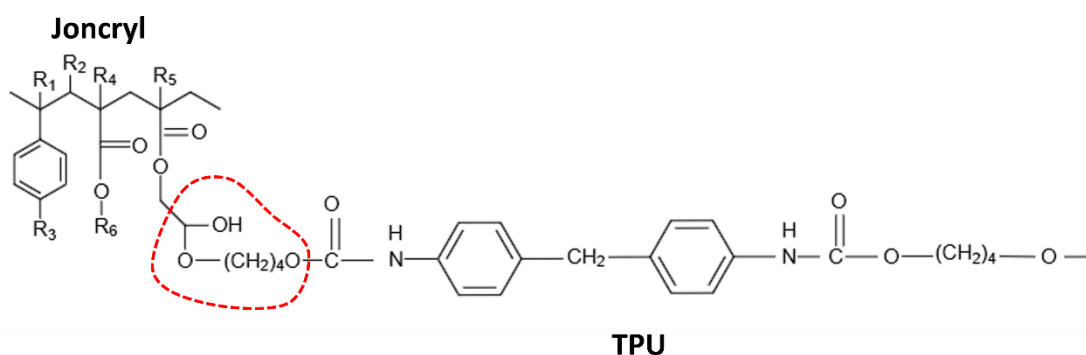
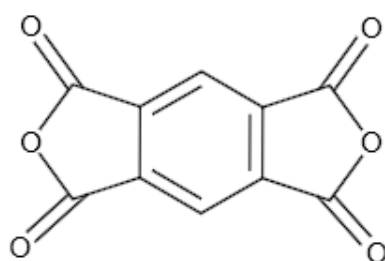


Figure 2.6 : Possible reaction between Joncryl ADR 4468 and TPU [9].

In another study, it was observed that the reactive sites of Joncryl ADR 4468, known for its strong interaction with PLA, also interact with the terminal groups of TPU in a PLA/TPU blend structure [9]. Notably, the addition of 0.5 wt.% Joncryl to a 75/25 PLA/TPU blend resulted in finer TPU droplets, leading to significant improvements in the rheological and mechanical properties of the blend.

2.2.1.3 PMDA

Pyromellitic dianhydride (PMDA), a tetra-functional dianhydride (Figure 2.7), has garnered significant interest in polymer science due to its capability to modify and enhance the properties of various polymers, including TPUs. Known for its high reactivity, exceptional dimensional stability, and cross-linking ability, PMDA can substantially improve the mechanical, thermal, and flame-retardant properties of polymer matrices. These attributes make it suitable for applications such as high-performance structural materials and packaging in printed electronic circuitry [56].



Pyromellitic dianhydride (PMDA)

Figure 2.7 : Chemical structure of Pyromellitic dianhydride (PMDA) [57].

PMDA contains two anhydride structures, which act as functional groups capable of reacting with -OH groups (Figure 2.8) [58]. For example, the anhydride functional groups of PMDA can react with the -OH terminal groups of polyethylene terephthalate (PET), forming two carboxyl groups. These newly formed carboxyl groups can subsequently react with PET, leading to additional coupling and/or branching reactions [59].

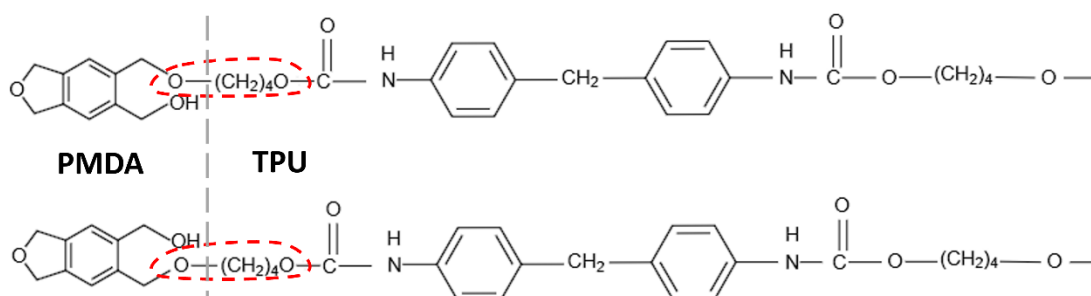


Figure 2.8 : Possible reactions between PMDA and TPU [56].

Although PMDA is used as a chain extender in the synthesis of various polymers, there are not many studies in the literature on TPU for chemical modification purposes [60-62]. Jiao et al. investigated the application of PMDA as a fire safety agent for TPU

[56]. Isocyanate and polyol in TPU structure are chemicals that can be employed as a carbon source in flame retardant areas, and if the isocyanate and polyol can be carbonized into char residue during combustion, TPU fire safety can be considerably enhanced. It has been stated in the relevant study, if the isocyanates in the structure of TPU react with the anhydrides in the structure of PMDA, a polyimide structure with good charring properties can be formed. If this reaction takes place during the TPU's combustion and the decomposition processes, TPU materials with high fire safety can be produced [56].

2.2.2 Blending

Polymer blending involves combining two or more polymers to create materials with enhanced properties that cannot be achieved using a single polymer type. While advanced material synthesis can involve methods like copolymerization, where polymer segments are chemically bonded to form block or graft copolymer structures, blending stands out as a more practical and cost-efficient approach compared to these methods [63]. Blending also offers a pathway for repurposing recycled plastics by combining them with other polymers to produce new materials suitable for both engineering and commodity applications. The underlying theory of polymer blending is based on the principles of miscibility and phase separation, which govern the morphology and subsequently influence the mechanical and thermal properties of the blend.

Miscibility, determined by thermodynamic factors such as temperature and molecular structure, dictates whether the polymers mix at a molecular level or remain as distinct phases [63]. Miscible blends typically feature a single-phase morphology with a homogeneous structure, where the properties of the two polymers are averaged. This results in enhanced mechanical properties due to improved interfacial adhesion between the components. However, most polymer blends are immiscible, meaning the molecules do not mix with each other. Immiscible blends typically exhibit phase-separated structures due to weak interfacial interactions between the phases. While these structures can lead to unique properties, they may also pose challenges in achieving optimal mechanical performance [64-66]. The phase separation phenomena in polymer blends are governed by several factors, such as molecular weight, temperature, and the presence of additives or fillers. For instance, the incorporation of

nanoparticles has been demonstrated to improve the miscibility of certain polymer blends by altering the critical point of phase separation [67]. This improvement arises from the nanoparticles' capacity to modify the local thermodynamic environment, promoting enhanced interactions between polymer chains. There are also blend structures known as partially-miscible or compatible miscible blends. These structures exhibit characteristics that lie between fully immiscible and miscible blends, featuring a certain degree of chemical or physical interaction. Such interactions can lead to improvements in the overall properties of the blend [63]. Theoretical frameworks, such as the Flory-Huggins theory, play a crucial role in understanding the thermodynamics of polymer blend miscibility. According to this theory, the free energy of mixing is influenced by the interaction parameter (χ) between polymer components, which determines phase separation and compatibility [68, 69]. The Flory-Huggins theory has been widely used to predict the miscibility of various polymer blends, particularly those involving polyolefins and other linear homopolymers. For instance, Economou's study on high-density polyethylene and branched polyolefin blends highlights how conformational asymmetry can impact miscibility, demonstrating the practical relevance of theoretical models in polymer science [70].

The morphology of polymer blends (Figure 2.9), identified by miscibility and polymers' concentration, is a critical factor in determining their properties. Tailored morphologies, such as droplets, fibers, laminar structures, or co-continuous phases, can enhance specific characteristics like toughness, strength, or electrical conductivity. Factors such as processing methods, blending ratios, and the viscoelastic properties of the polymers significantly influence the final morphology, offering opportunities to optimize polymer blends for targeted applications.

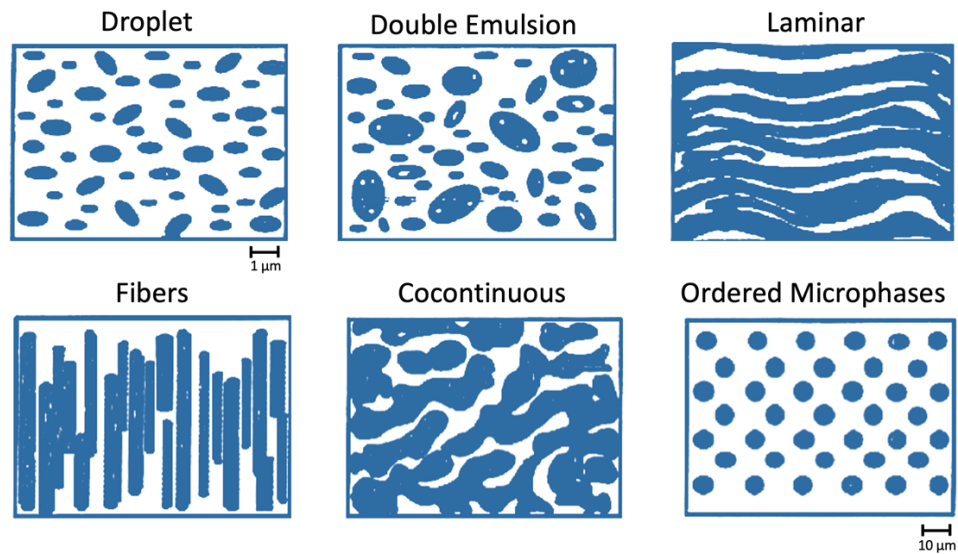


Figure 2.9 : Schematics possible morphologies in immiscible blends [63].

The mechanical performance of polymer blends can be significantly optimized by controlling the microstructure of the film, which is strongly influenced by polymer concentration and miscibility [71]. Additionally, the dynamic mechanical properties of these blends are affected by temperature and deformation rate, underscoring their viscoelastic nature [72]. The incorporation of compatibilizers plays a crucial role in improving interfacial adhesion between immiscible polymers, thereby enhancing the mechanical properties of the blend [66, 73]. The phase behavior of polymer blends is particularly critical in applications such as membrane transport processes, where the morphology of phase-separated blends can significantly influence their transport properties. Understanding this behavior is essential for tailoring materials for specific applications [65, 74]. Compatibilizers are often employed to stabilize immiscible blends by reducing interfacial tension and preventing coalescence of dispersed phases, which is especially important in applications requiring mechanical integrity, such as gas separation membranes and composite materials [64, 65, 74]. Recent research has increasingly focused on biodegradable and bio-based polymer blends, driven by environmental concerns and the need for sustainable materials. Blending biodegradable polymers has been shown to improve mechanical properties and processability, making them suitable for applications like packaging and biomedical devices [75, 76]. Strategies such as the use of block copolymers or functionalized additives have been explored to enhance compatibility and miscibility in these blends [76, 77]. Processing methods also play a vital role in determining the final properties of polymer blends. Techniques such as melt blending, solution blending, and reactive

blending significantly influence blend morphology and mechanical performance [78, 79]. Melt processing, for instance, can produce varying dispersion states, affecting thermal stability and mechanical properties [78, 80]. Furthermore, the addition of fillers and additives during processing can modify the blends' properties, tailoring them for specific applications [66, 81]. Extensive research on polymer blending has highlighted the benefits of incorporating fillers, which enhance compatibility in immiscible blends and improve mechanical properties [82]. Nanocomposites in blends further boost mechanical strength and thermal stability, making them ideal for advanced applications [83, 84]. Ongoing exploration of new compatibilization techniques and novel polymer blends holds promise for creating materials with tailored properties for specific uses [66, 81]. The molecular architecture of polymer blend components, such as starlike and linear polymers, significantly influences rheological properties through entanglement dynamics. Variations in entanglement density and chain architecture result in distinct relaxation dynamics, critical for applications requiring precise control of flow behavior during processing and manufacturing [85, 86]. This knowledge is fundamental for optimizing the performance of polymer blends across diverse industrial applications.

In summary, polymer blending serves as a versatile and cost-effective approach to developing materials with tailored properties. A crucial factor influencing the final properties of a blend is the weight ratio of its components, as this determines the balance of characteristics contributed by each polymer. While miscible blends provide homogeneous structures, the challenges of immiscibility can be mitigated through the use of compatibilizers or by utilizing partial miscibility. By carefully controlling processing conditions and blend compositions, manufacturers can achieve diverse morphologies and unique features, establishing polymer blending as a cornerstone of modern material development.

In recent decades, blending thermoplastics and elastomers has gained significant technological and commercial importance due to its ability to combine complementary properties and create innovative products through the synergistic interactions of compatible blend components [49]. Given the high cost of TPU, products made solely from it are often expensive. To address this, recent efforts have focused on blending TPU with other polymers, resulting in materials with enhanced, distinctive, and application-specific properties [49].

Researchers have investigated a range of TPU-based blends, including TPU/ethylene propylene diene (EPDM) rubber [9], TPU/polydimethylsiloxane rubber (PDMS) [7], PLA/TPU [10,11], poly(vinylidene fluoride) (PVDF)/TPU [12], PA/TPU [51], PMMA/TPU [14], epoxidized natural rubber (ENR)/TPU [15], PBT/TPU [16], EVA/TPU [49], POM/TPU [50], and TPU/poly(ethylene-co-methyl acrylate) (poly-EMA) blends [87]. In many of these studies, the various properties of TPU contribute to forming a balanced composition when blended with other polymers. For instance polyacetals, like PA, POM exhibit toughness but are prone to notch sensitivity. While they resist the initiation of cracks well, they perform poorly in preventing crack propagation [88]. So the impact strength of these polymers can be enhanced by blending with rubbery type polymers like TPU [50]. Another example is blending TPU, known for its excellent tensile modulus, abrasion resistance, low-temperature flexibility, and good chemical and solvent resistance, with materials like EVA, which offers superior mechanical properties, weather resistance, and electrical insulation. This approach aims to enhance TPU's weaker mechanical properties and expand its applicability in specific applications [49]. These structures blend the high strength and stiffness of the hard component with characteristics like flexibility, impact strength and vibration-damping of the soft component. [51].

Among all polymer types, PLA is the most frequently studied in blending research and, consequently, there is extensive literature on its blending with TPU [3, 4, 8, 9, 34, 89-95]. PLA has several disadvantages that negatively impact its use in various applications. Its brittleness, resulting from an elongation at break of less than 10%, low melt strength, and slow crystallization rate, poor processability and foamability, low service temperature and as well as its chemical inertness due to the absence of reactive sites, limit its applicability in many fields [8, 9, 95-105]. However, PLA also offers numerous advantages, such as being eco-friendly and biocompatible, easily processable through various manufacturing techniques like injection molding, film extrusion, and blow molding, and requiring less energy for production compared to many petroleum-based polymers [63, 95, 98-107]. Particularly, PLA's biocompatibility makes it suitable for replacing many metal-based medical devices, and it is increasingly in demand for biomedical applications. To overcome disadvantages such as low crystallization rate, melt strength, thermal stability, and brittleness, blending PLA with other materials emerges as both an economical and

practical approach. This process addresses its limitations while catering to the growing demand for biomedical applications [108].

Polymers suitable for blending with PLA like TPU offer greater ductility, toughness, impact resistance, enhanced melt strength, and better processability than PLA [95]. However, PLA/TPU blends are inherently immiscible, with their physical properties closely tied to their morphological structure. The final morphology of these blends is governed by the balance between droplet breakup and coalescence within the dispersed phase. Enhancing phase compatibility and stabilizing the morphology of the minor phase are critical to achieving optimal performance [9].

Recent findings highlight that, the phase separation caused by the soft and hard segments in TPU results in the formation of microdomains by the hard segments. This phase structure significantly influences the compatibility of the hard segments within TPU with PLA, leading to substantial variations in the rheological and mechanical properties of the blends. [8, 63].

Nevertheless, studies have shown that TPU, composed of polyester or polyether soft segments, is miscible with PLA and has a proven effect on enhancing PLA's properties, particularly its ductility [63]. In a study by Li et al. [91], PLA and TPU demonstrated a two-phase morphology, indicating partial miscibility. This partial miscibility resulted in increased ductility and impact strength of the blend with higher TPU content. Although TPU reduced the total crystallinity in the structure, it accelerated the crystallization of PLA, suggesting an improvement in PLA's inherent limitations. PLA/TPU blends have been shown to achieve significant enhancements in impact strength and elongation at break, thereby expanding PLA's potential applications [10-13]. Notably, both PLA and TPU possess excellent biocompatibility, making their blends suitable for use in biomedical applications [3, 23]. Kahraman et al. [9] studied PLA/TPU blend systems by adding epoxy-based Joncryl as a chain extender for compatibility and different proportions of nanoclay as a stabilizer to improve droplet morphology. The inclusion of nanoclay resulted in finer morphology, which increased storage modulus and complex viscosity, thereby influencing the viscoelastic properties of the blend. While this finer morphology improved tensile strength and modulus, the ductility and impact strength enhanced by the chain extender were diminished due to the nanoclay addition. Another application of PLA/TPU blends is meltblown nonwoven production, as investigated by Rahman et al. [93]. In these

systems, Joncryl ADR 4400 was used to enhance compatibility between PLA and TPU. The addition of TPU to PLA increased the crystallization rate of PLA while reducing its overall crystallinity. At an optimized TPU ratio, the strength and elongation at maximum strength of PLA/TPU blends improved compared to neat PLA. Kemaloğlu et al. [4] advanced PLA/TPU systems by using PDI as a compatibilizer for the first time, examining its effects on the blend. The blending of PLA with TPU transformed PLA's brittle behavior into a more ductile one. Additionally, the bonding potential of diisocyanates with -OH/-COOH terminal groups improved the compatibilization of the two polymers and enhanced the tensile properties of the resulting blend.

Despite the immiscible nature of PLA/TPU blend systems, successful PLA/TPU blends have been produced even without the use of compatibilizers. In a study by Nofar et al. [95], amorphous and semi-crystalline PLA types were blended with TPU containing three different hard segment ratios at an 85/15 ratio. The thermal, morphological, rheological, and mechanical properties of these blends were examined. The findings indicated that using semi-crystalline PLA instead of amorphous PLA resulted in improved mechanical properties due to increased crystallinity. While higher hard segment content TPUs, driven by increased MDI content, showed better compatibility with PLA, they were less effective for improving ductility, toughness, and impact properties. Jayswal and Adanur [23] aimed to develop flexible composite filaments suitable for 3D printing. PLA/TPU blends with varying TPU ratios were prepared using twin-screw and single-screw extruders. DSC and DMA analyses suggested partial miscibility between PLA and TPU. As TPU content increased, compatibility between PLA and TPU improved; however, due to the flexibility provided by the soft segments in TPU, storage modulus decreased. Mechanically, higher TPU ratios reduced tensile stress and modulus values but significantly increased elongation at break. The potential of 3D printing PLA/TPU blends for producing shape-memory polymers suitable for soft actuators was explored by Shin et al. [94]. Using a single-screw extruder, PLA/TPU blends were prepared and analyzed. The addition of TPU transformed PLA's fracture behavior from brittle failure to ductile fracture. With increasing TPU content, the tensile modulus decreased, yet the material exhibited enhanced deformability without significant reduction in tensile strength at an optimized TPU ratio.

FTIR analysis revealed that increasing TPU content facilitated the formation of new hydrogen bonds, indicating improved interaction between PLA and TPU. These findings confirm that blending PLA with TPU, especially at optimized TPU ratios, enhances the material's ductility and toughness without severely compromising tensile strength, offering promising applications in advanced material development.



3. EXPERIMENTAL PROCEDURE

3.1 Materials

Within the scope of chemical modification experiments of the study, waste TPU materials released during production were used and they were supplied by Ravago Petrochemicals Inc. Four different modifiers will be used in this context: Joncryl ADR 4468, PMDA, HDI and PMDI. HDI and PMDI are supplied by Ravago Petrochemicals Inc.

NatureWorks Ingeo Biopolymer PLA 4043D was used as the main matrix for the blending experiments of the study. The second phase was waste TPU used in chemical modification experiments, and Joncryl ADR 4468 was used as the compatibilizer.

3.2 Experimental Design

3.2.1 Chemical modification experiments

In chemical modification experiments, Kökbir RTX-M40 Internal Melt Mixer device was used, as seen in Figure 3.1. All experiments were carried out at 200 °C, 100 rpm, for 5 minutes.



Figure 3.1 : Kökbir RTX-M40 Internal Melt Mixer.

In order to understand the effect of the modifiers used in these experiments, each modifier was used at 0.5 wt.% and 1.0 wt.% amount and neat TPU were processed at the specified parameters. Before the process, TPUs were dried at 60 °C for 6 hours. Dry mixing was applied to the modifiers and TPUs to be used during the process and fed to the device. The list of processes performed is given in Table 3.1.

Table 3.1: Chemical modification experiment list.

Sample Name	Modifier Amount (wt. %)	Process Parameters
TPU - neat	0	
TPU/0.5 Joncryl	0.5	
TPU/1.0 Joncryl	1.0	
TPU/0.5 PMDA	0.5	200°C
TPU/1.0 PMDA	1.0	100 rpm screw speed
TPU/0.5 HDI	0.5	5 minutes
TPU/1.0 HDI	1.0	
TPU/0.5 PMDI	0.5	
TPU/1.0 PMDI	1.0	

All samples were compressed for 5 minutes at process temperature (200 °C) using compression molding in molds suitable for rheological and mechanical analysis. After pressing, the materials were allowed to cool at their own cooling speed. Before molding, pellets were dried under vacuum overnight at 60 °C.

3.2.2 Blending experiments

Blending experiments were carried out in two stages. In the first stage, twin screw extruder (TSE) (Gülnar GM Twin 16mm L/D 30:1) (Figure 3.2) was used and in the second stage, injection molding (IM) (ENGEL victory 50) (Figure 3.3) at Ravago Petrochemicals Inc. was used.



Figure 3.2 : Gülnar GM Twin 16mm L/D 30:1 Twin Screw Extruder.



Figure 3.3 : ENGEL victory 50 Injection Molding.

PLA/TPU blend ratios were determined as 80/20 by weight according to literature research. Joncryn ADR 4468 was used at a rate of 0.5 wt.%. In order to determine the reaction that Joncryn will perform; two different experiments will be carried out in which PLA, TPU and Joncryn are processed by dry mixing (PLA/TPU/J) and in which TPU and Joncryn are first mixed to prepare a masterbatch (TPU/J) and then mixed with PLA to prepare (PLA/(TPU/J))* blend. In order to compare the analysis results of all prepared blends, waste TPU and PLA 4043D were also processed. The list of performed processes and parameters are given in Table 3.2.

Table 3.2: Blending experiment list.

Sample Name	TSE Process Parameter	IM Process Parameter
TPU – neat	185, 195, 200, 200, 200, 110, 50 °C head-to-zone temperatures 100 rpm screw speed	190, 185, 185, 180, 45 °C head-to-zone temperatures 100 rpm screw speed
TPU/J (97.5/2.5)		-
PLA - neat	195, 195, 200, 200, 200, 110, 50 °C	200, 200, 195, 195, 45 °C
PLA/TPU (80/20)	head-to-zone temperatures	head-to-zone temperatures
PLA/TPU/J (80/20/0.5)	100 rpm screw speed	100 rpm screw speed
PLA/(TPU/J)*		

Before the process, waste TPU and PLA 4043D were dried in a vacuum oven at 60 °C for 6 hours. Within the scope of the processes, the samples in Table 3.2 were first produced in a twin screw extruder, temperatures were head to barrel 180, 190, 200, 200, 200, 110, 50 °C, screw speed was 100 rpm. The samples coming out of the extruder were passed through a water pool and fed to the granulator to turn them into pellets. After the process, all samples were dried in a vacuum oven at 60 °C for 12 hours. Then, these samples were dried in the dryer in the injection molding device for 30 minutes before the process.

3.3. Characterizations

3.3.1 Rheological analysis

In order to analyze the melt rheological behaviors of the samples produced with chemical modification experiments, frequency and time sweep rheology analyzes were performed with Anton Paar MCR302 rheometer device. Frequency sweep analyzes were first performed at 190, 200, 210 and 220 °C in order to investigate the effect of temperature, then the following experiments were performed at 220 °C, in the frequency range decreasing from 10^2 rad/s to 10^{-1} rad/s, for 10 minutes, and complex viscosity, storage modulus (G') and loss modulus (G'') behaviors were investigated. Time sweep experiments were performed at 220 °C for 10 minutes.

3.3.2 Mechanical analysis

In the mechanical analyses carried out within the scope of chemical modification and blending experiments, tensile tests were performed with INSTRON 68TM-30 device and tensile strength, elongation at break, stiffness and toughness behaviors were

examined. Within the scope of chemical modification experiments, hardness tests Shore A and Shore D analyses were performed with GIBITRE Instruments device. Within the scope of blending experiments, impact tests were performed with Zwick Roell HIT25P device.

3.3.3 Structural analysis

Within the scope of chemical modification experiments, Gel Permeation Chromatography (GPC) analyzes were performed in order to determine molecular weight distributions in the TOSOH EcoSEC device. Dimethyl formaldehyde (DMF) was used as the solvent.

3.3.4 Morphological analysis

JEOL JSM-6390LV scanning electron microscope (SEM) was used for the analysis of blend morphologies.

3.3.5 Thermal analysis

Within the scope of thermal analysis of all experiments, METTLER TOLEDO differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used. DSC analyses were performed from -50 °C to 250 °C at a speed of 10°C/min., as heat-cool-heat. TGA analyses were performed by heating from -50 °C to 800 °C.



4. RESULTS & DISCUSSION

4.1. Results of Chemical Modification Experiment

4.1.1 Rheological analysis

The biggest problem in understanding the melt rheological behavior of TPU is that the melting temperature of TPU varies depending on the hard segment content and is around 200 °C. Therefore, high temperatures above 200 °C can cause behavior like polycondensation and thermal degradation in TPU. The melt rheological behaviors of processed-waste TPUs have been investigated at several temperatures (Figure 4.1), including 190, 200, 210, and 220 °C, both below and above the process temperature, in order to determine the appropriate analysis temperature.

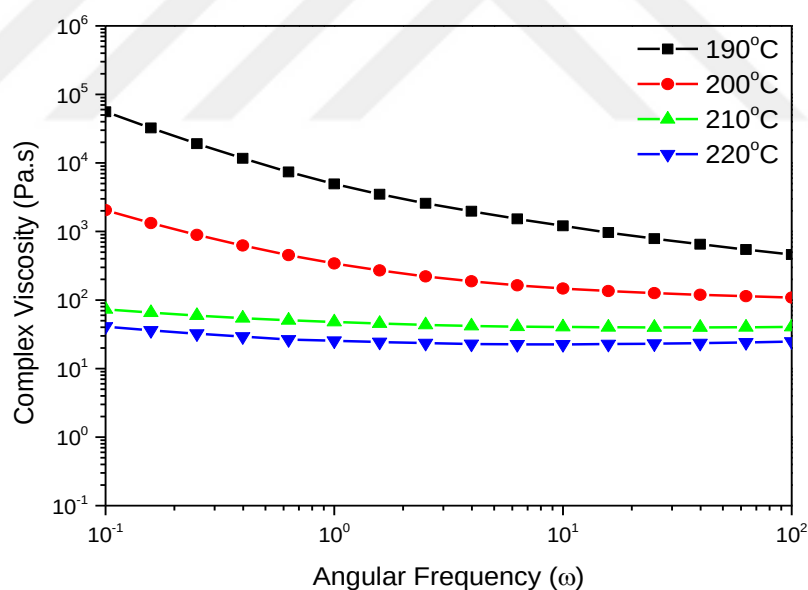


Figure 4.1 : Frequency sweep analysis complex viscosity results performed at 190°C, 200°C, 210°C, 220°C for 10 minutes.

In contrast to the complex viscosity lines at 210 and 220 °C, a larger increase can be observed at 190 and 200 °C. When the DSC second heating graph of the Processed TPU in Figure 4.16 is examined, it shows that the T_m range ends around 185 °C. As a result, at the temperatures used in the analysis (190 and 200 °C), there is a high probability that unmelted crystals are present in the structure, and these unmelted

crystals can act as crystal nucleating agent regions, re-crystallizing and suppressing molecular mobility, resulting in an increase in complex viscosity [109]. Consequently, it is found that increasing the temperature from 190 to 220 °C, lowers the complex viscosity value.

Examining the G' and G'' graphs of the rheology analysis, which included four different temperature scans, reveals that the material's flow point is represented by the G' and G'' cross points at 190 and 200 °C. At the same time, it is observed that solid-like behavior starts to take prominence as the impacts of viscous behavior reduce with decreasing frequency. Similar to the increase in complex viscosity, this situation can be explained by the formation of solid networks and can be recognized as the crystals that have not yet melted acting as crystal nucleating agents. At 210 and 220 °C, there are no cross points in the measured frequency range, and solid-like behavior dominates over elastic behavior. Although cross points are not seen at these temperatures, network formation or recrystallization is most likely the cause of the slight increase in complex viscosity values; polycondensation and/or degradation caused by high temperatures may also be responsible for it [109].

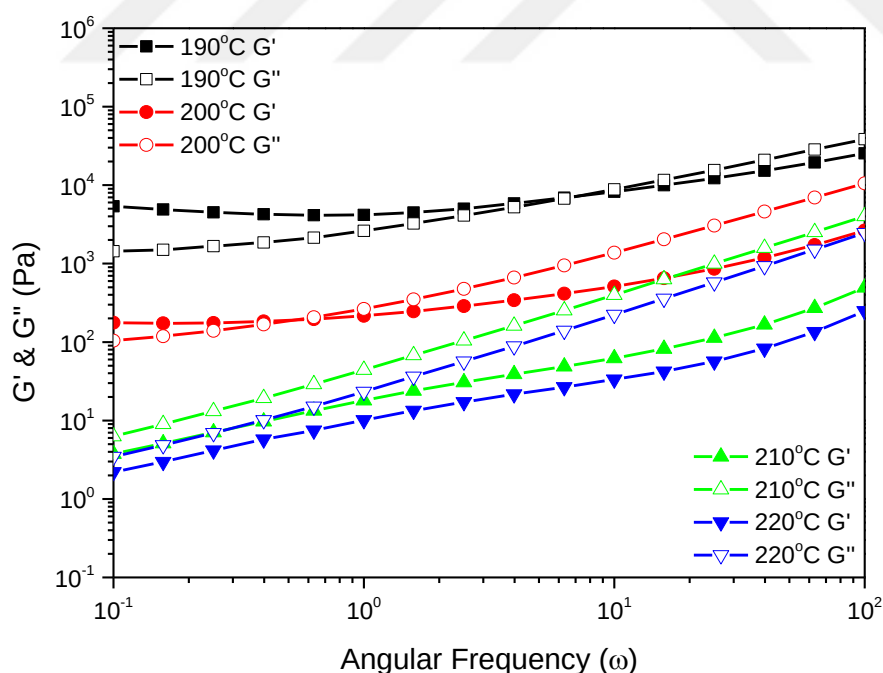


Figure 4.2 : Frequency sweep analysis G' and G'' results performed at 190, 200, 210, 220 °C for 10 minutes.

The following frequency sweep and time sweep analyses were carried out at 220 °C for 10 minutes. A comparison of the as-received and processed samples shows that the

complex viscosity in the processed sample reduces, and it is possible that this decrease happens after the heating process (Figure 4.3). When the processed and received samples are compared to all samples that have 0.5 wt.% modifier applied, it is observed that the complex viscosity increases with decreasing frequency. However, the complex viscosity shows lower values than the processed sample with the addition of all other modifiers, except the sample that contained Joncryl ADR 4468. In particular, compared to the other modifiers, the addition of PMDA to the structure resulted in a larger decrease.

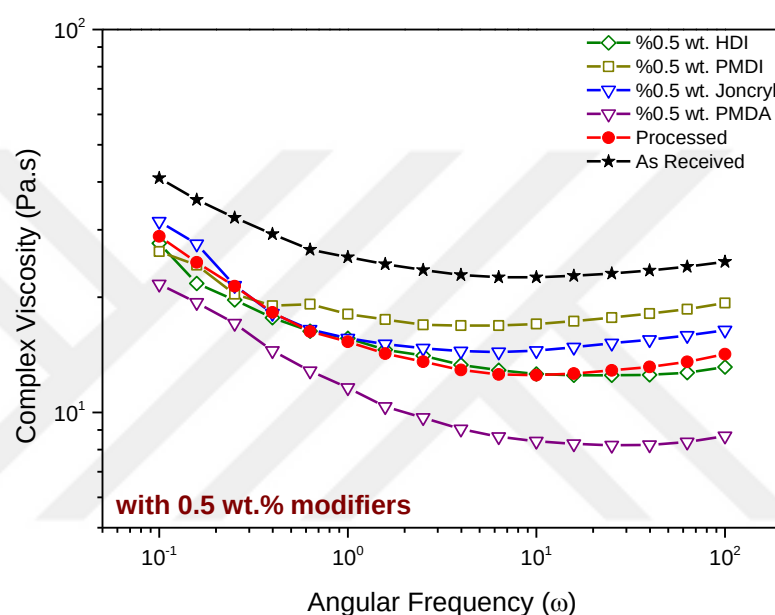


Figure 4.3 : Frequency sweep analysis complex viscosity results with the addition of 0.5 wt.% modifiers performed at 220 °C for 10 minutes.

In Figure 4.4, when the samples with 1.0 wt.% modifier added are compared to the processed and as received samples, no significant difference can be observed between the samples with Joncryl and PMDA added and the ones with 0.5 wt.%. In contrast to both processed and as-received TPUs, the complex viscosity increases substantially with the addition of 1.0 weight percent HDI and PMDI. When complex viscosity values are analyzed, it is shown that HDI, a form of diisocyanate group, interacts better with TPU and hence shows increasing complex viscosity behavior when added at higher amounts.

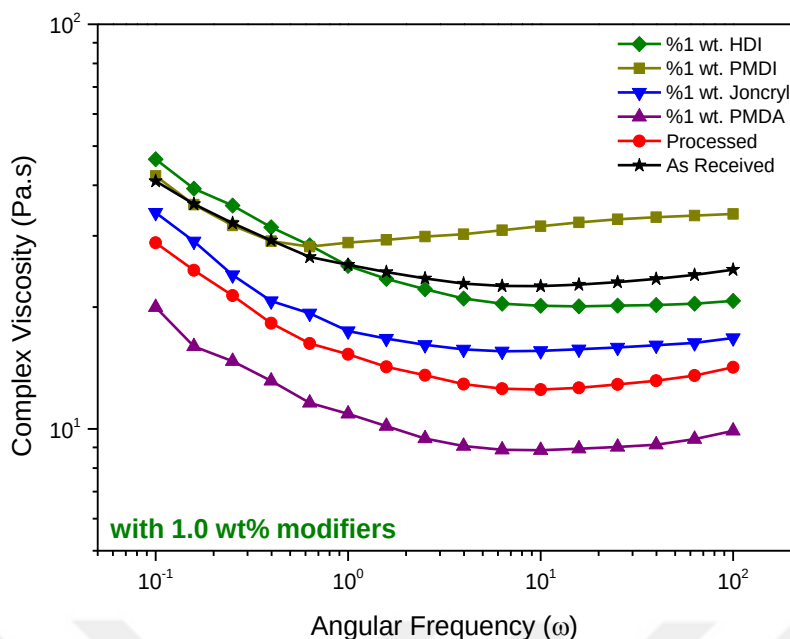


Figure 4.4 : Frequency sweep analysis complex viscosity results with the addition of 1.0 wt.% modifiers performed at 220 °C for 10 minutes.

As seen in Figure 4.5, the G' values of the samples show results that are compatible with the complex viscosity values. While the TPU with 0.5 wt.% Joncryl added shows similar values to the processed sample, a lower G' value is observed with all other modifier additions. With the addition of 0.5 wt.% of modifiers, Joncryl shows the highest G' at the low frequencies. PMDI and HDI show comparable G' values but lower than the Joncryl. PMDA shows the lowest effect on the TPU according to the other additives. No additives were able to increase the elastic properties of the processed TPU with the addition of 0.5% by weight. However, with the increasing frequency, starts to show higher G' , elastic behavior, than processed TPU.

With the addition of 1.0 wt.% of modifiers, in Figure 4.6, all samples exhibit higher G' values, demonstrating a stronger influence of the modifiers on the TPU structure than that observed with the addition of 0.5 wt.% modifiers. PMDI shows the highest G' values reflecting its ability to improve the elasticity of TPU structure, likely through crosslinking and/or enhanced molecular interactions. HDI shows moderate ability to interact with TPU chains, though its effects are less pronounced than PMDI but still enhances elasticity compared to the Processed TPU. Joncryl exhibits lower G' and because of Joncryl's tendency to extend chains by generating new covalent bonds rather than by crosslinking or branching, its effectiveness here is thought to be to act as a chain extender, reducing entanglement and improving flow behavior rather than elasticity. PMDA is seen to exhibit the lowest G' value this time, even lower than

processed TPU. As can be understood from Figure 4.6, while the G' values of TPU increase with the addition of 1 % by weight in all other modifiers, they decrease with PMDA. In an example study for this case conducted by Awaj and Daver [59], it was investigated that the anhydride groups of PMDA reacted with the hydroxyl groups of PET and released water as a by-product. When the same reaction is considered on TPU and PMDA, it is expected that the water by-product will be formed when the hydroxyl groups (-OH) of TPU react with the anhydride groups of PMDA. The ester groups in TPU are particularly sensitive to hydrolysis, which leads to the formation of acidic carboxyl groups (-COOH), which can further accelerate the hydrolysis of the polyester segments in the polymer [110]. This degradation process is critical because it can compromise the mechanical integrity of TPU and lead to brittleness and loss of functionality over time [111]. The presence of water can also cause swelling in TPU, a common phenomenon in hydrophilic polymers. This swelling occurs due to the absorption of water into the polymer matrix, which can disrupt the physical structure and lead to changes in mechanical properties [112]. For example, although polyadipate-based TPUs exhibit good mechanical properties, they are known to degrade when exposed to water due to hydrolysis of ester groups [111]. In a study by Zdrahala et al. [113, 114], they investigated the mechanism behind the softening of TPU by water and heat and concluded that the softening is attributed to the plasticization of the interface regime between the hard and soft areas of TPU, with the placement of water molecules in the original hydrogen bond between the amino group (N-H) and the carbonyl group (C=O) in TPU. Therefore, the presence of free water molecules in the system may lead to the degradation of TPU over time, which is thought to cause a decrease in mechanical, thermal and especially rheological properties.

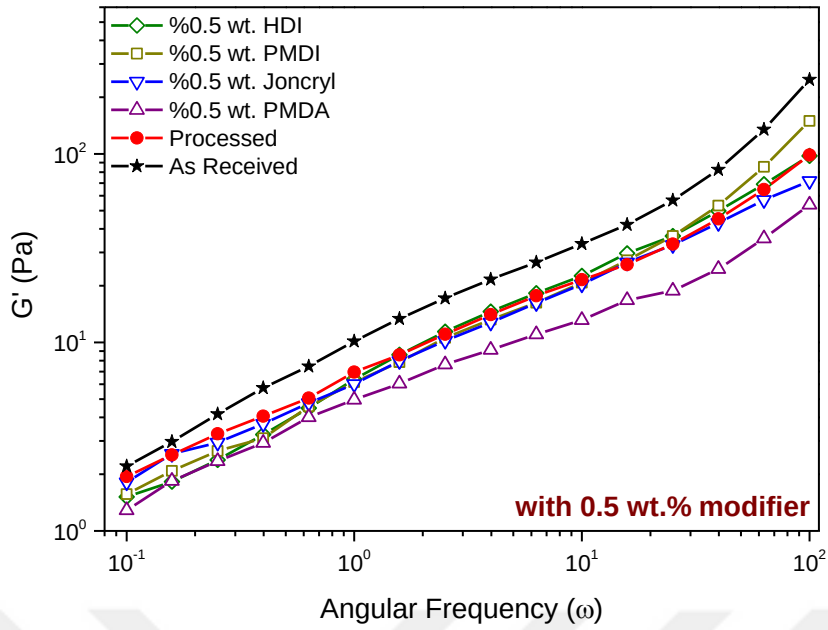


Figure 4.5 : Frequency sweep analysis G' results with the addition of 0.5 wt.% modifiers performed at 220 °C for 10 minutes.

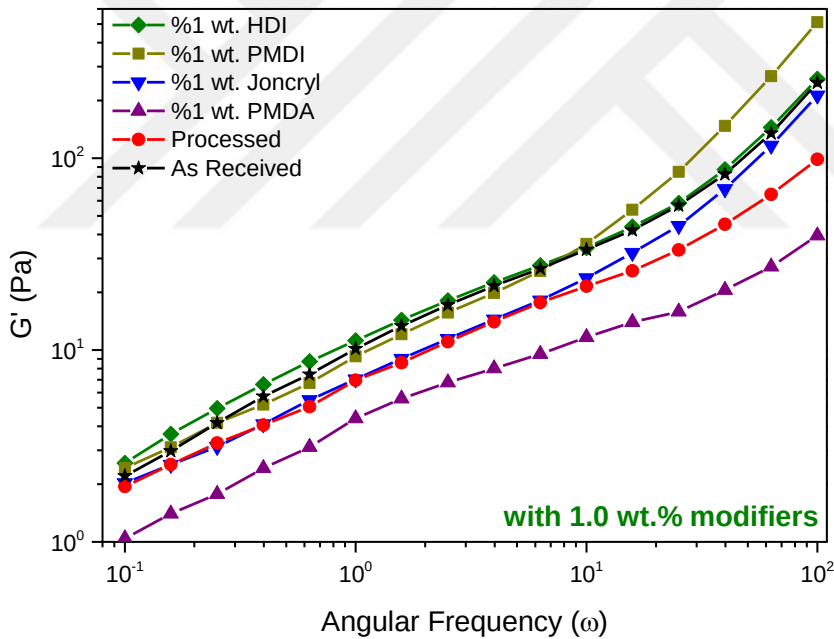


Figure 4.6 : Frequency sweep analysis G' results with the addition of 1.0 wt.% modifiers performed at 220 °C for 10 minutes.

Figure 4.7 shows the time sweep rheological analysis results of processed TPUs with 1.0 wt.% and without modifier addition. In this graph, the increase in complex viscosity can be associated with the formation of a network between TPU and modifiers or with the increase in molecular weight. Joncryl is the modifier that shows the highest increase in time. However, the sample with the highest complex viscosity value is TPU added with PMDI. This increase is consistent with the frequency sweep

analysis results. At the same time, in a study conducted by Brauer et al. [52] an increase is also observed in the complex viscosity values of TPU with increasing MDI value. As stated in Section 2.2.1.1, HDI, another diisocyanate group, is expected to exhibit behavior akin to the rise in MDI because of the reaction between the isocyanate groups and TPU.

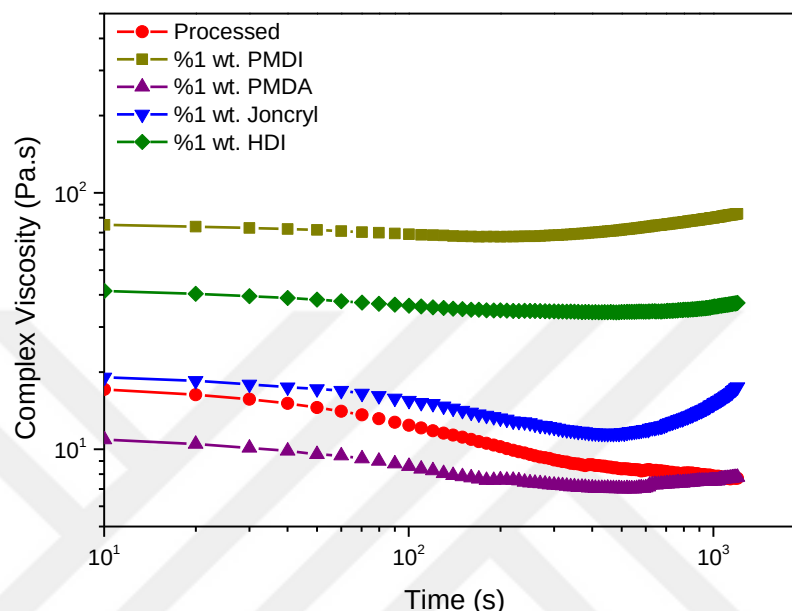


Figure 4.7 : Time sweep analysis complex viscosity results with the addition of 1.0 wt.% modifiers performed at 220 °C for 10 minutes.

PMDA showed the lowest complex viscosity value compared to other modifiers in time sweep analysis as well as in frequency sweep analysis. In the explanation given in Section 4.1.1 regarding the effect of PMDA on TPU, it has been explained by various studies that the water molecule formed as a result of the reaction can lead to degradation [113, 114]. The effect of this degradation is also seen here in the time sweep analysis, with a negative effect.

When the behavior of melt rheological properties is examined with the addition of different types and ratios of modifiers to the structure; the most increase is seen in PMDI and HDI, which are members of the diisocyanate group, with the addition of 1.0 wt.%. This situation is associated with the fact that the diisocyanate group is already present in the TPU structure.

4.1.2 Mechanical analysis

4.1.2.1 Tensile test results

The mechanical properties of the material were investigated by examining the tensile strength, elongation, stiffness, and toughness values that were obtained from the tensile test in individual graphs. TPU's mechanical properties vary significantly depending on its hardness levels and chemical structure. Accordingly, tensile strength values range from 25 to 80 MPa, and elongation ranges from 400 to 800% when TPU's mechanical properties are studied in the literature [2, 115-117].

Evaluating the processed TPU's tensile strength values with various modifier types and amounts in Figure 4.8 reveals that all modifier types and amounts lead to an increase in tensile strength. In this case, it can be determined that modifiers enhance TPU's tensile strength property. When PMDA, HDI, and Joncryl are included, the increasing tensile strength starts to decrease as the modifier amounts increases from 0.5 wt.% to 1.0 wt.%. But when PMDI is incorporated, the tensile strength value increases as the modifier ratio increases. With the addition of 1.0 wt.%, PMDI achieves the maximum tensile strength values.

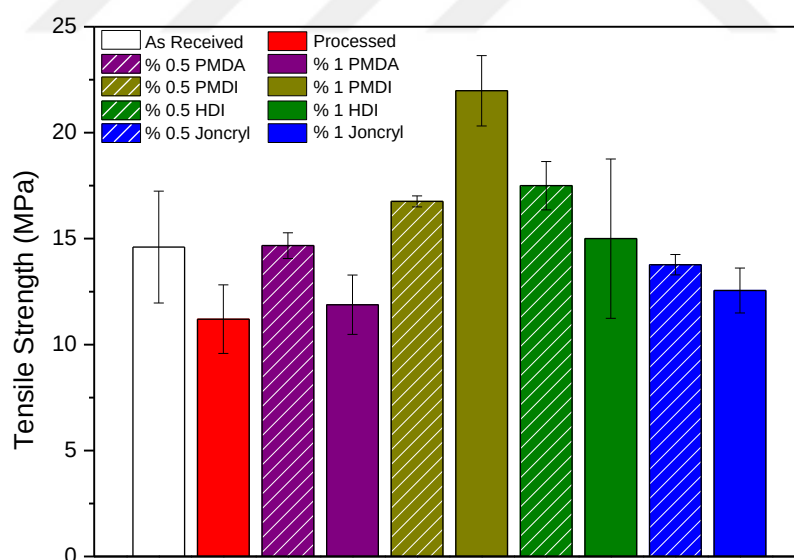


Figure 4.8 : Tensile strength results of chemical modification samples.

Figure 4.9 shows that elongation at break values increase with each modifier type, consistent with tensile strength results. However, at this point in all modifier types, the elongation at break value decreased as the amount of modifiers increased from 0.5 to 1.0 wt.%. Within the scope of these results, diisocyanate groups again showed higher

results than the others and the highest elongation at break value belongs to 0.5 wt.% HDI.

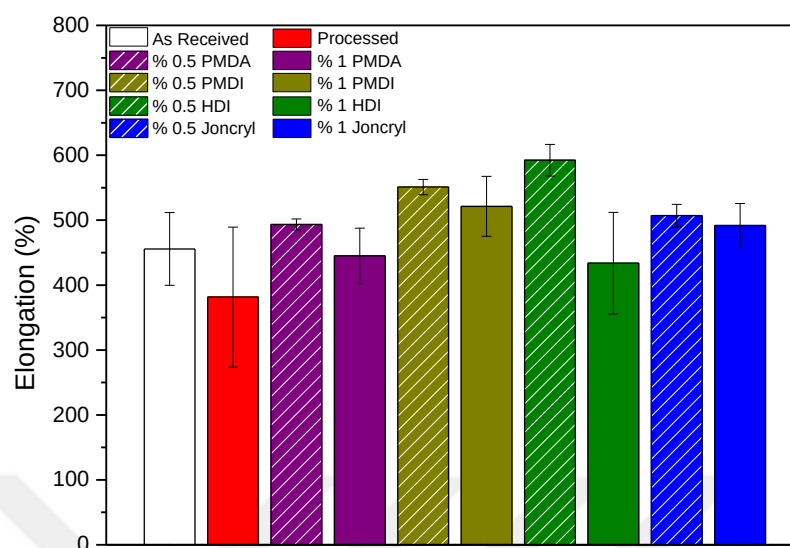


Figure 4.9 : % Elongation results of chemical modification samples.

Figure 4.10 shows that all modifier additions, except PMDA and PMDI, cause stiffness values to increase. Modulus values for Joncryl and PMDI increase with increasing modifier ratio, whereas for PMDA and HDI, they decrease significantly. However, consistent with the elongation at break results, incorporating 0.5 wt.% HDI resulted in the highest young modulus value.

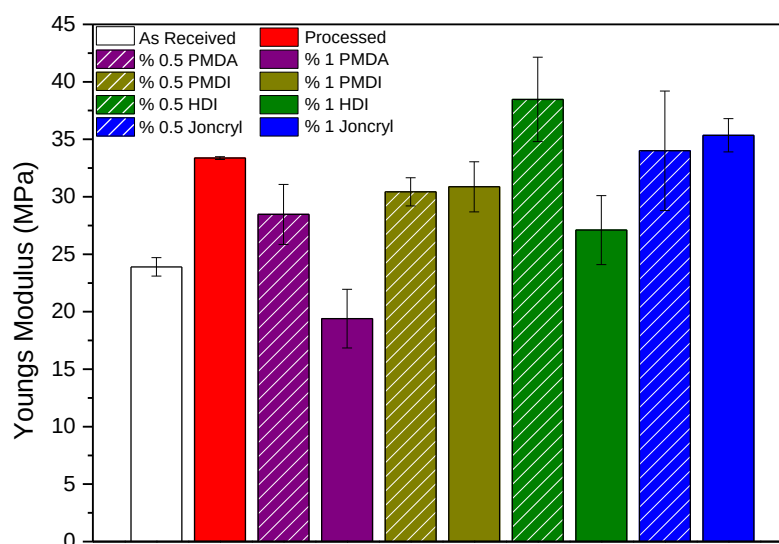


Figure 4.10 : Modulus results of chemical modification samples.

With the addition of all modifiers, the increasing behavior continues when examining the energy at break results in Figure 4.11. Except for PMDI, a higher amount of modifiers resulted in a reduction in toughness values. PMDI has the highest toughness

values after incorporating 1.0 wt.%. Mechanical analyses revealed the highest results for diisocyanate types PMDI and HDI. Several research in the literature support these findings. Brauer et al. found that adding MDI to the TPU structure increased the breaking stress and elastic modulus, but elongation remained constant [51]. The breaking stress increased steadily from 38 to 50 MPa with 0% to 5% MDI addition, while the elastic modulus increased from 0.16 GPa to 0.25 GPa. Although there was no apparent change in the elongation value, a high of 300% was noted. When MDI was added to a blend structure composed of EVA and TPU in a study, the blend structure's tensile properties significantly improved as the amount of MDI in the structure increased [49]. It was stated that higher tensile strength values were observed in structures with more TPU in the blend structure and that the increase in mechanical properties was due to the reaction between MDI and TPU.

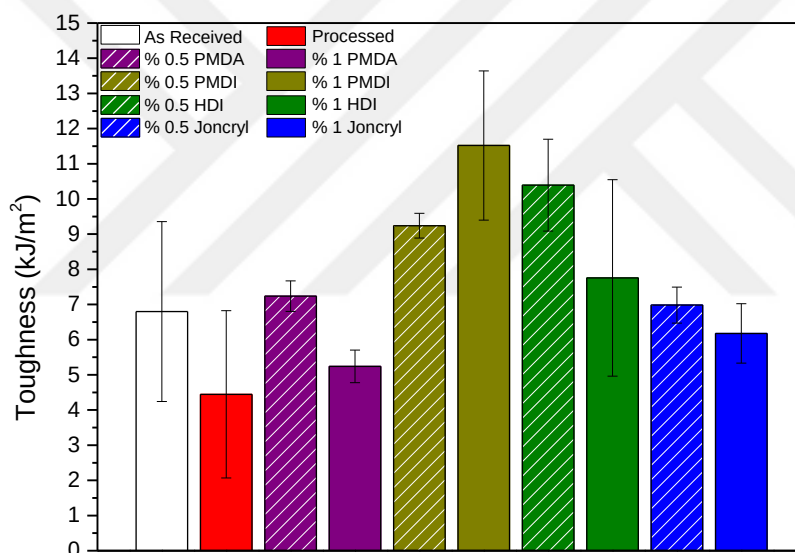


Figure 4.11 : Toughness Results of chemical modification samples.

In the rheology analysis results in Section 4.1.1, it is seen that the effects observed in the TPU structure as a result of PMDA addition are also reflected in the mechanical properties of TPU. According to related research, water acts as a plasticizer, decreasing the modulus E value and the strength of the structure's original hydrogen bonds [113, 116, 118]. As seen in this case study, in all mechanical analysis evaluations, tensile strength, % elongation, young modulus and energy at break values are lower than other additives with PMDA addition. In particular, a significant decrease is observed in young modulus values with increasing PMDA addition. However, these values are still lower than the tensile properties of neat TPU in the literature mentioned earlier. This

can be associated with the fact that the TPUs used have already undergone structural damage during the production process.

4.1.2.2 Hardness test results

For all samples, Shore D hardness test results are given in Figure 4.12 and Shore A hardness test results are given in Figure 4.13. Due to the block copolymer structure of TPU, hardness values vary greatly depending on the changing hard segment and soft segment ratios. However, in the literature, it usually varies between Shore 70A and Shore 80D [115].

When Shore D hardness test results are examined, it is observed that the hardness increase is observed in the samples to which 1.0% modifier is added by weight, compared to the processed sample. While this increase can be considered within the error range for HDI, some increase is observed in Joncryl and HDI and mostly in PMDA. Polyimides formed by the reaction of anhydrides and isocyanates in the structure of PMDA are known to exhibit excellent thermal and mechanical properties, so this increase in PMDA can be associated with the polyimide structure that may be formed as a result of the reaction [119]. A decrease in Shore D values of samples to which 0.5% modifier was added by weight was observed compared to the processed sample.

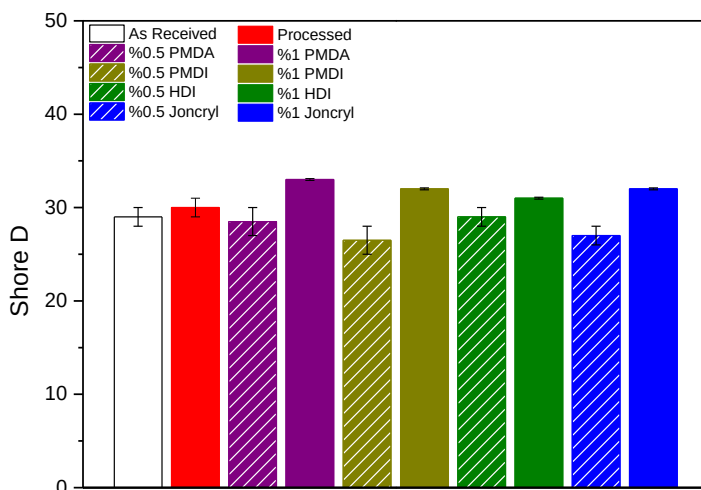


Figure 4.12 : Shore D hardness test results of chemical modification samples.

When Shore A hardness results were examined, the hardness values of TPU materials did not change compared to the processed sample with both 0.5 wt.% and 1.0 wt.% modifier addition. All of the results obtained are values that can be accepted within the error range.

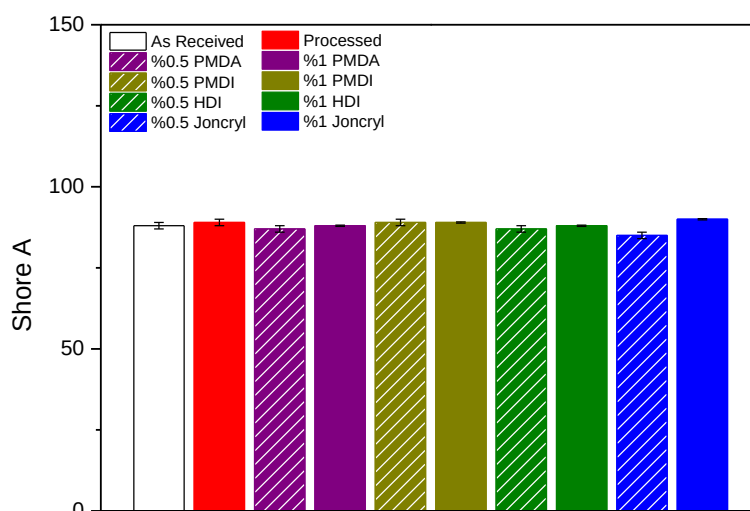


Figure 4.13 : Shore A hardness test results of chemical modification samples.

4.1.3 Structural analysis

Molecular weight is one of the factors that may be adversely influenced by the physical and/or chemical changes that may occur in the structure of the polymeric material following a process that involves heating and/or shearing [28]. The graph in Figure 4.14 below shows the change in M_n and M_w values based on the results of the GPC analysis. When this graph is analyzed, it can be observed that when the TPU undergoes thermal processing, the M_n and M_w values decrease. Then, by incorporating various modifiers into the structure by melt mixing process, an increase in the molecular weight of processed TPU is observed. When these changes are compared, no significant change is observed in the molecular weight with 0.5 wt.% and slight increase is observed with 1.0 wt.% Joncryl addition to the structure. The highest increase compared to all modifiers was achieved with 1.0 wt.% HDI and then PMDI addition. This situation shows a result compatible with rheological and mechanical analyses. However, PMDA shows higher values than Joncryl in GPC analysis, contrary to rheological and mechanical analyses. This situation can be explained as follows: As mentioned in Sections 2.1 and 2.2, the reaction of TPU's hydroxyl groups with PMDA's anhydride group may cause a decrease in rheological and mechanical properties due to the release of water as a by-product, but since TPU and PMDA react at the same time, an increase in M_n and M_w is possible. At the same time, when all modifiers were compared, 1.0 wt.% modifier addition caused higher increases in M_n and M_w values than 0.5 wt.% modifier addition. Therefore, more increase in molecular weight occurred with the increase in modifier ratio.

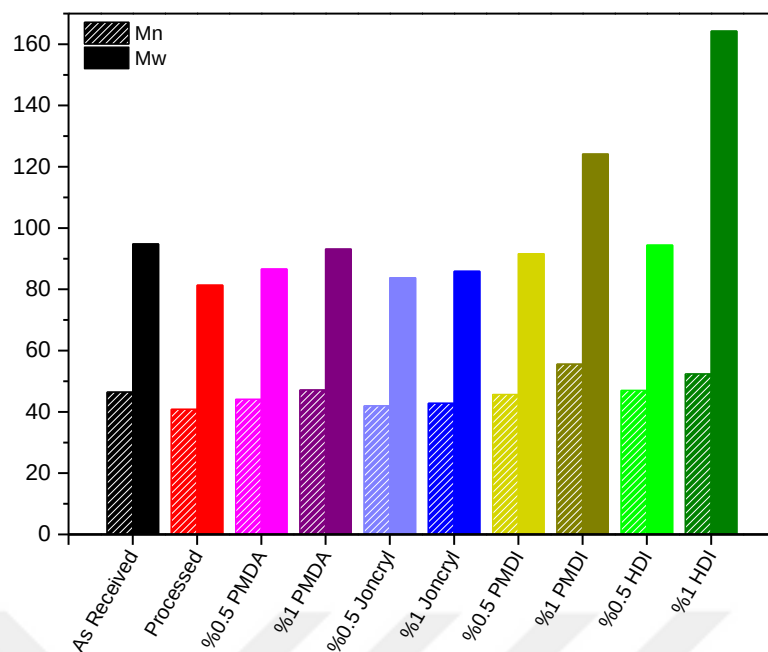


Figure 4.14 : M_n and M_w results of GPC analysis.

When the PDI values in Figure 4.15 are examined, a slight decrease in the PDI value of the Processed sample after the melt process was observed, consistent with the M_n and M_w values. Although the molecular weight values increased in the sample to which PMDA was incorporated, PMDA reactions may selectively reduce lower molecular weight species, potentially narrowing the molecular weight distribution. With the addition of Joncryl to the structure, a very small increase in the PDI values is observed due to the possible chain extension. The PDI results are directly proportional to the molecular weight results, and a wider molecular weight distribution is observed compared to the large molecules formed due to the reactions such as potential branching, crosslinking and/or chain extension given by the TPU members of the diisocyanate group with PMDI and HDI and other modifiers. The highest PDI value is observed with the addition of 1.0 wt.% HDI to the TPU structure. A wider molecular weight distribution is observed with the increase in the modifier amount in all samples.

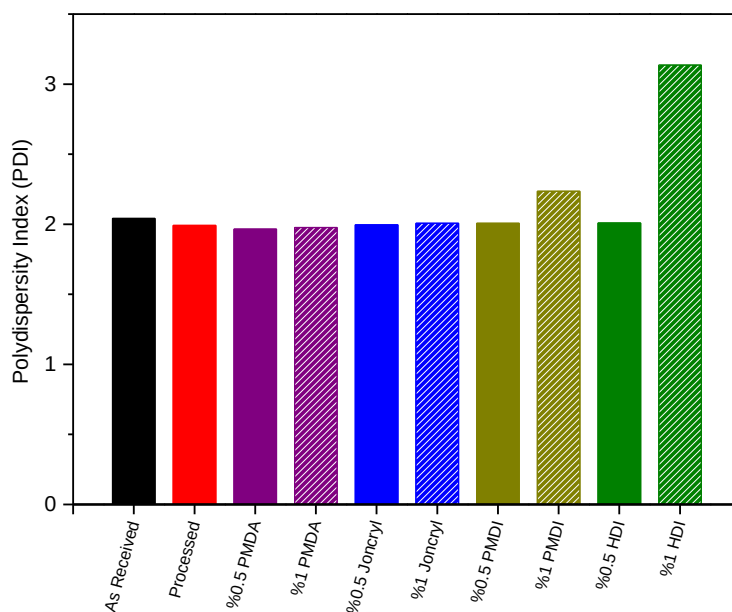


Figure 4.15 : PDI results of GPC analysis.

4.1.4 Thermal analysis

4.1.4.1 Differential scanning calorimetry (DSC) analysis

When the second heating and cooling graphs of the DSC analysis results are examined, only a slight change is observed between the as received and processed TPU wastes in terms of both T_m (Figure 4.16) and T_c (Figure 4.17) temperatures. However, no significant change is observed in the T_m and T_c values with both 0.5 wt.% and 1.0 wt.% modifier additions within the TPU structure. This situation can be concluded that no modifier added to the structure by the melt mixing process causes any change in the thermal properties of the TPU.

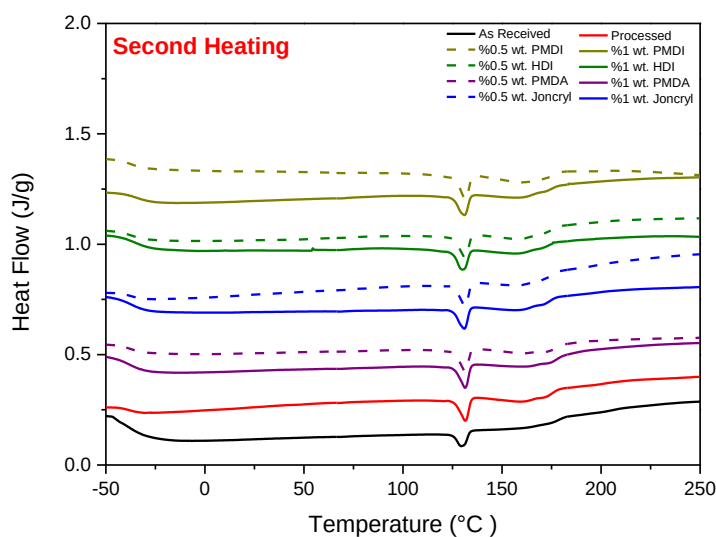


Figure 4.16 : Second heating DSC graph of chemical modification samples.

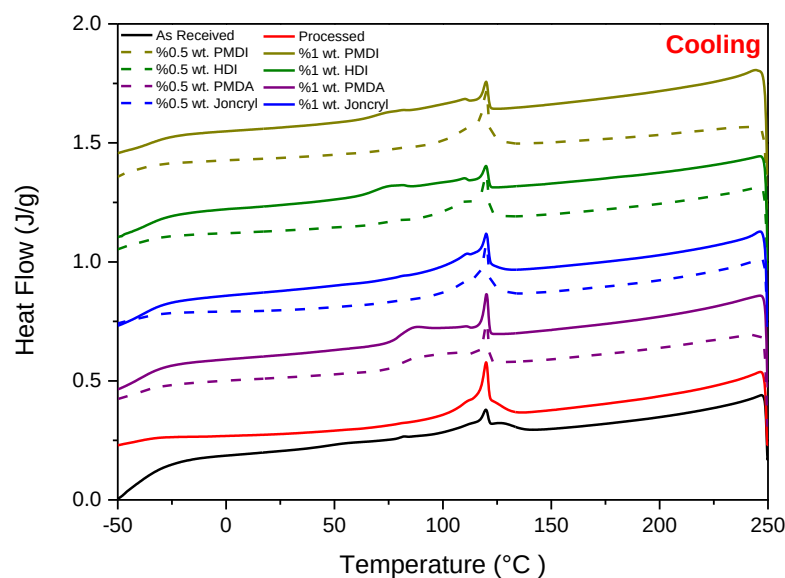


Figure 4.17 : Cooling DSC graph of chemical modification samples.

4.1.4.2 Thermogravimetric analysis (TGA)

Examining the TGA graph in Figure 4.18 shows a degradation that takes place across several stages, which may be related to the degradation of the TPU's hard and soft segments [109]. It demonstrates how easily TPU materials can degrade at temperatures higher than 250°C. Degradation temperatures remain unchanged when compared to neat and processed TPUs with both 0.5 weight percent and 1.0 weight percent modifier additions to the structure. In the later degradation stages, samples containing PMDI, 1.0 weight percent Joncryl ADR 4468, and HDI additives exhibit more mass loss.

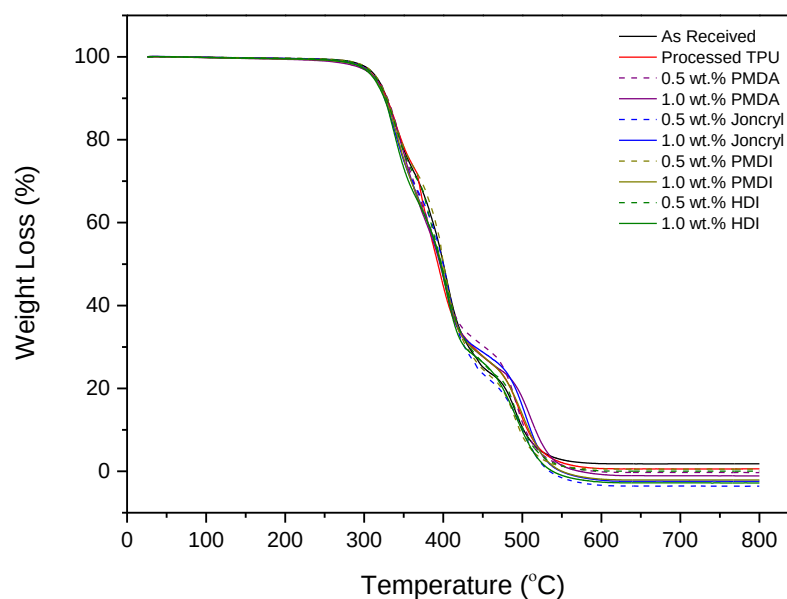


Figure 4.18 : TGA graphs of chemical modification samples.

4.2. Results of Blending Experiment

4.2.1. Mechanical analysis

In order to examine the mechanical properties of the blended samples, tensile and Izod impact strength tests were performed. With these tests, tensile strength, elongation at break, modulus, toughness and impact strength properties of PLA and waste TPU and different blend structures were analyzed.

4.2.1.1. Tensile test results

When Figure 4.19 is examined according to the tensile test results, it is seen that with the addition of 20% waste TPU into the PLA structure, the tensile strength of PLA, which is 60.09 MPa, decreases to 19.82 MPa in the PLA/TPU (80/20) blend structure, approaching the tensile strength of TPU (13.67 MPa). With the addition of Joncryl to the structure, the tensile strength values in both blend structures (PLA/TPU/J and PLA/(TPU/J)*) decreased to 10.44 and 10.84 MPa, respectively. Despite improved phase compatibility, the addition of Joncryl leads to a slight reduction in tensile strength due to reduced crystallinity. There are many studies in the literature on reducing the interfacial tension between PLA and TPU by adding Joncryl as a compatibilizer to PLA blend structures [8, 9, 93, 95]. As before, Kahraman et al. investigated the effect of two distinct types of Joncryl applied to PLA/TPU blend structures [8, 9]. If the interfacial tension between PLA and TPU lowers with the addition of Joncryl to the structure, or if the interaction increases, the strength and modulus are expected to decrease even more [95]. Pre-blending results in a almost similar tensile strength as PLA/TPU/J, reflecting comparable interfacial bonding.

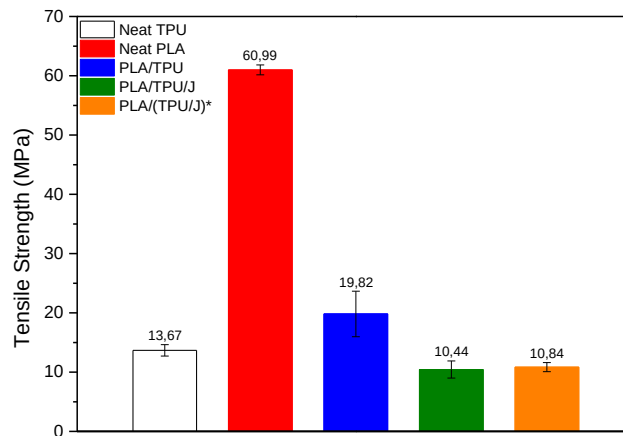


Figure 4.19 : Tensile strength values of blend samples.

Figure 4.20 shows that the modulus value of PLA lowers to 2652.39 MPa after creating a PLA/TPU blend structure. Blending ductile TPU with tougher PLA results in a decrease in modulus values. With the addition of Joncryl to this blend structure, this value lowers even further, reaching 2308.25 MPa. Joncryl further reduces modulus by improving miscibility and reducing stiff surfaces. This is also in line with the relevant studies in the literature [95]. The PLA/(TPU/J)* blend structure, which was formed by pre-blending TPU and Joncryl, showed an increase in modulus. The reason for the slight increase in Young modulus value is that Joncryl, which has a more compatible structure with PLA, can first react with TPU and then blend with PLA, forming a stronger bond between TPU and PLA, resulting in a higher tensile strength and modulus value than the PLA/TPU/J structure. Nevertheless, this result is insufficient for confirming a meaningful change.

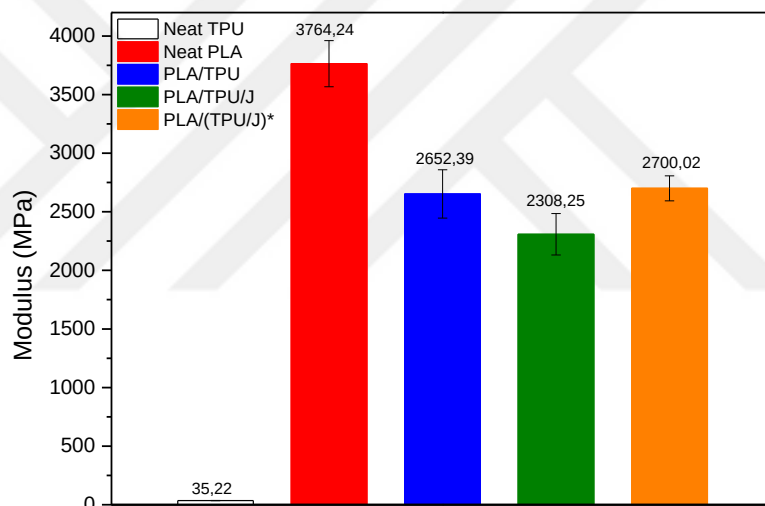


Figure 4.20 : Modulus results of blend samples.

Joncryl, which is more reactive than PLA and TPU, is expected to react directly with PLA, resulting in higher branching in the PLA/TPU/J blend structure. In this case, it is possible that the modulus value will decrease in this blend structure. Pre-blending of TPU and Joncryl may improve modulus and tensile strength due to TPU's higher stiffness compared to PLA/TPU/J structures. However, because TPU and Joncryl have low reactivity, the time required for them to react may be not enough to produce materials with more advanced mechanical properties, and the production method may be inefficient.

When Figure 4.21 is examined, it is seen that TPU, which has very high elongation values, is blended with PLA, resulting in strain at break values that are much lower

than TPU and higher than PLA. With the addition of TPU to the structure, an increase in PLA's strain at break value, or plastic deformation property, can be attributed to the soft segment that provides elasticity to TPU [120]. In terms of elastic properties, PLA and TPU are relatively harder and softer, respectively, which may cause stress to be concentrated within the TPU structure when an external force is applied to the structure, resulting in elastic deformation and storage of deformation energy within the TPU, as well as plastic deformation in the PLA structure [94]. The addition of Joncryl decreased the elongation value of the PLA/TPU blend structure to 38.70%, whereas the PLA/TPU/J and PLA/(TPU/J)* blend structures had values of 36.37% and 31.11%, respectively.

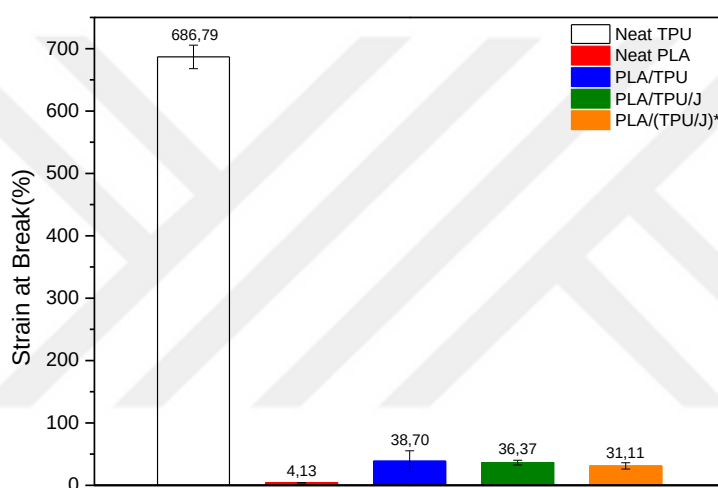


Figure 4.21 : Strain at break results of blend samples.

4.2.1.2. Izod charpy impact results

The notched Izod impact strength analyses (Figure 4.22) reveal that the blend structures produced have values between neat TPU and neat PLA. The incorporation of TPU increases the impact strength of PLA, indicating a synergistic effect in which TPU acts as a toughening agent. The addition of TPU to the PLA structure improves the material's impact strength, which is consistent with the literature [122]. The addition of Joncryl resulted in decreased impact strength values due to the blend structure generated by blending TPU and Joncryl.

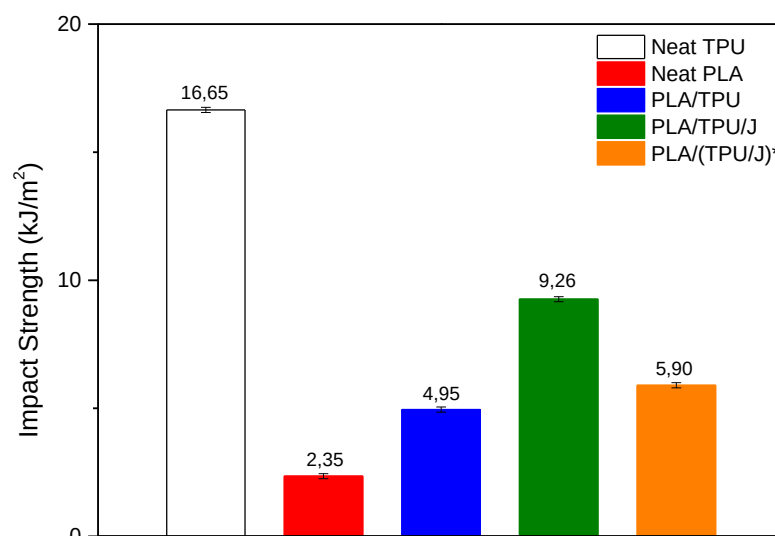


Figure 4.22 : Impact strenght results of blend samples.

4.2.1.3. Hardness test results

When the Shore A and Shore D analysis results are compared in Figures 4.23 and 4.24, it is clear that, notably in the Shore A analysis, when the PLA/TPU blend structure is formed, the hardness value reduces significantly, but this value increases again with the addition of Joncryn. There is no substantial difference in hardness values between the PLA/TPU/J and PLA/(TPU/J)* blend structures. Joncryn can interact with PLA, leading to chain extension and branching, perhaps increasing the toughness of the blend structure. Adding Joncryn may lead to higher hardness levels.

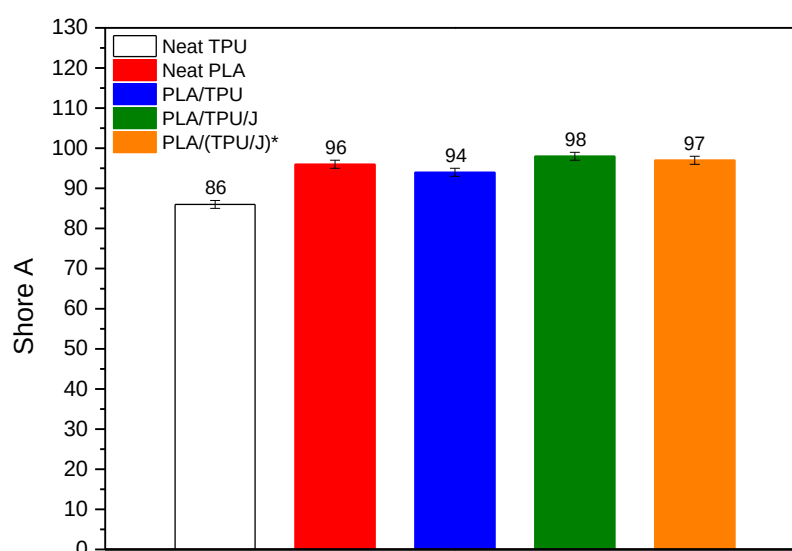


Figure 4.23 : Shore A hardness results of blend samples.

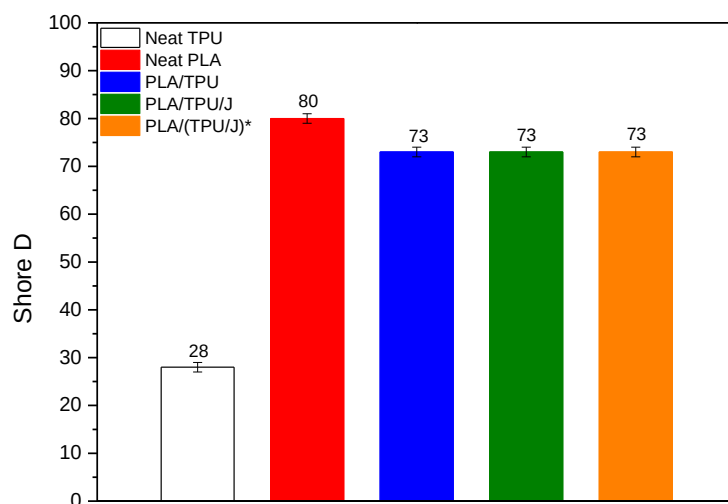


Figure 4.24 : Shore D hardness results of blend samples.

The results obtained as a result of the tensile test show results that are consistent with the literature. In many studies, especially the two studies conducted by Kahraman et al. on PLA/TPU blends, the inclusion of TPU in the structure decreases the tensile strength and modulus values, while the stiffness and toughness values increase [8, 9, 37, 90, 93-95, 120, 121].

4.2.2. Morphological analysis

When Figure 4.25 is examined, an inhomogeneous morphology between PLA and TPU is seen in all SEM images. The thermodynamic immiscibility between hard and soft segments resulted in a microphase separation and consequently a multiphase structure. PLA was completely immiscible with the strongly polar hard segments of TPU, it may be partially miscible with the soft segment [90]. At the same time, many studies in the literature point to the incompatible blend structure between TPU and PLA and the resulting droplet morphology formation [8, 9, 89, 90, 95, 120]. With the addition of Joncryl to the blend structure, finer droplet sizes are observed compared to the PLA/TPU blend structure and this can be associated with the addition of CE refined the TPU droplet size and improved the uniformity of the blend morphology since the CE could behave as a compatibilizer between the phases, finer and more uniform blend structure could be expected [8]. This is because during melt processing, Joncryl reacts with PLA and TPU, which are normally incompatible, to decrease interfacial tension. Additionally, because of the branching effect of Joncryl on PLA, which causes droplet breakage, it enhances matrix viscosity [9, 95].

If examined specifically, it is seen that in the PLA/TPU/J blend structure, with the addition of Joncryl, the bonding between the phases in the blend structure increases and a more homogeneous structure is formed (Figure 4.25b). When the SEM image of the PLA/(TPU/J)* blend structure is examined, a finer microstructure is observed as a result of the pre-blending of TPU and Joncryl (Figure 4.25c). It is thought that better dispersion of Joncryl in TPU provides a more stable structure when mixed with PLA.

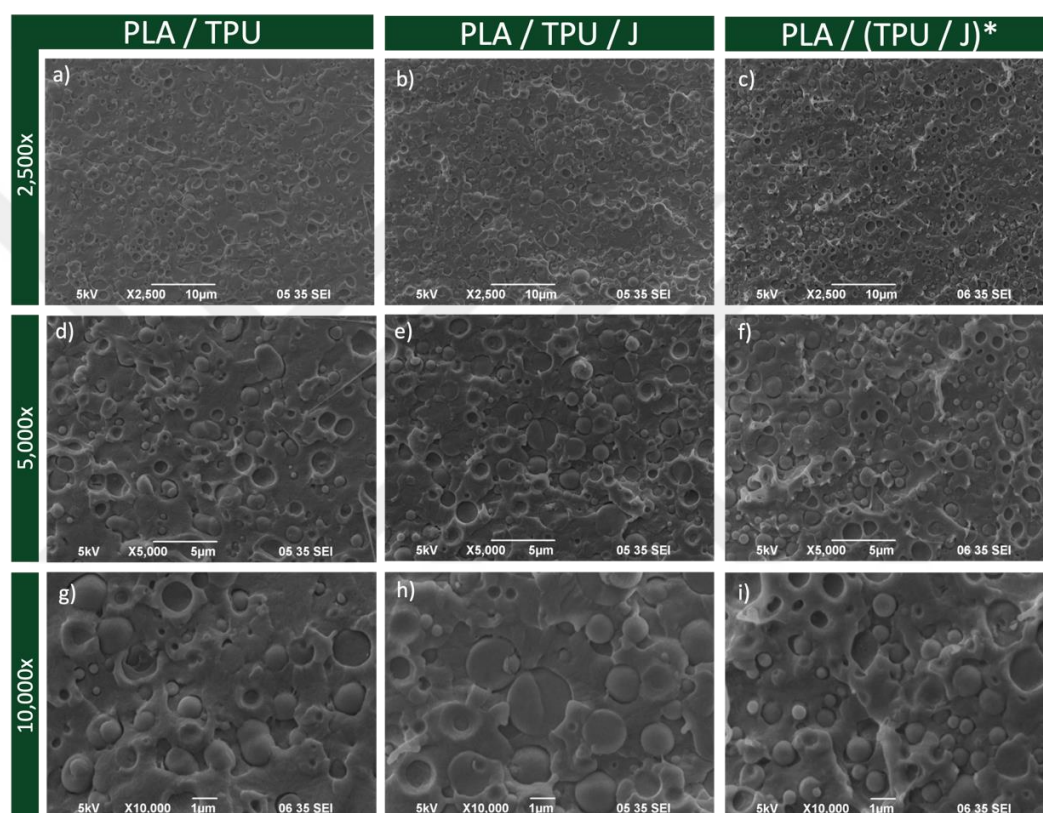


Figure 4.25 : SEM images of blends of PLA/TPU, PLA/TPU/J, and PLA/(TPU/J)* at 2,500x, 5,000x, and 10,000x magnification.

4.2.3. Thermal analysis

4.2.3.1. Differential scanning calorimetry (DSC) analysis

According to the DSC analysis, the plasticizer effect of TPU causes the T_g value of PLA to decrease when it blends with it, as can be seen by looking at the secondary heating graph in Figure 4.26. This decrease in T_g can be interpreted as making the molecular chains in the blend structure more flexible and making a positive contribution to the brittleness of PLA [90].

When the melting peaks of the blend structures are examined, it is seen that while there is no major change in temperature in the PLA/TPU blend, the melting peak becomes narrower, and this can be associated with formation of more uniform crystalline structure. Both PLA and TPU are observed to maintain their peaks in their neat forms in this blend structure. The formation of an immiscible blend structure between PLA and TPU can be explained by this situation. It can be observed that the intensity of these peaks drops in both blend structures when Joncryl is incorporated. This situation can be attributed to Joncryl acting as a compatibilizer in certain blend compositions [9]. When the melting peaks in these blend structures are examined, it is clearly seen that their intensity decreases. This is thought to be due to Joncryl creating a branching effect on PLA and preventing its crystallization, thus reducing the crystallinity [8, 66-68]. When PLA/TPU/J and PLA/(TPU/J)* samples are compared with each other, the PLA/TPU/J sample has a smaller melting peak than the PLA/(TPU/J)* sample. It can be assumed that Joncryl reacts with more reactive ends in this structure, resulting in a more branched structure that prevents crystal formation. The impact strength and strain at break values determined by mechanical tests are consistent with the more ductile or TPU-like structure that is produced by the reduced crystalline region. No significant change was observed in the cooling graphs in Figure 4.27.

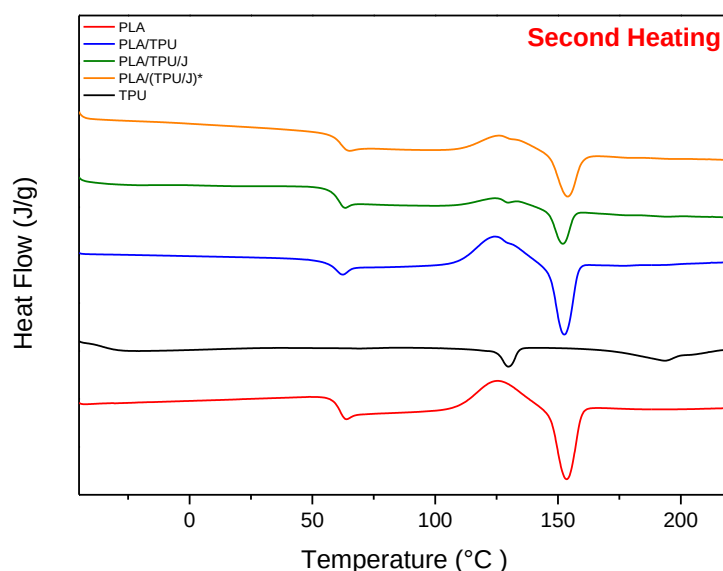


Figure 4.26 : Second heating DSC graph of blending samples.

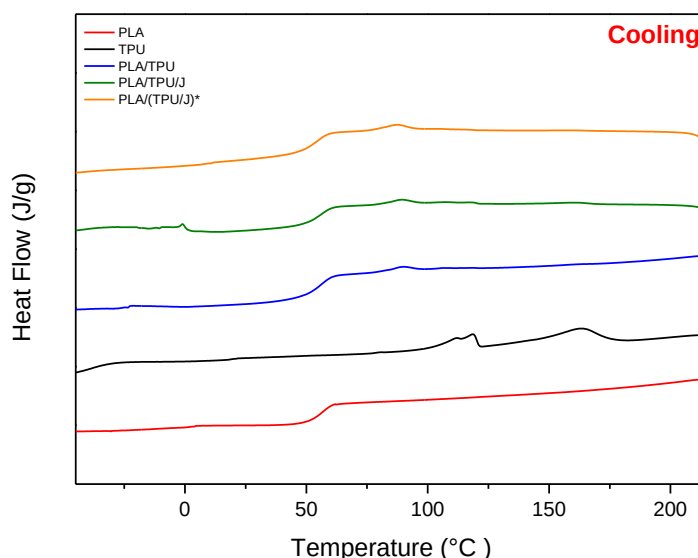


Figure 4.27 : Cooling DSC graph of blending samples.

4.2.3.2. Thermogravimetric analysis (TGA)

When Figure 4.28 is examined, it is seen that the thermal stability of PLA (Onset temperature ~ 350 °C) is higher than TPU (Onset temperature ~ 310 °C). At the same time, due to the different functional groups of TPU, its degradation occurs in more than one stage, i.e. at more than one temperature (310 and 420 °C), and these are generally associated with the hard segment and soft segments in the structure [94, 123]. In the PLA/TPU blend, it is observed that the thermal stability of PLA decreases with the inclusion of TPU in the structure and the weight loss starts to be approximately 300-310 °C. This decrease in the decomposition temperature with the addition of TPU compared to PLA can be interpreted as due to the early decomposition of TPU within the PLA matrix [120]. With the addition of Joncryl to the structure, no significant change is observed between PLA/TPU/J and PLA/TPU blends. However, a significant increase in thermal stability is observed in the PLA/(TPU/J)* blend formed by first mixing Joncryl with TPU and then blending it with PLA. This shows that the bonding of Joncryl with TPU is more effective.

When the temperatures at which thermal degradation is most intense are examined; this temperature is approximately 370 °C for PLA and this temperature is increased to around 380 °C for PLA/TPU blend. The addition of Joncryl to the structure provides a better blend between PLA and TPU in PLA/TPU/J and PLA/(TPU/J)* blends, increasing the maximum degradation temperatures to approximately 385 °C.

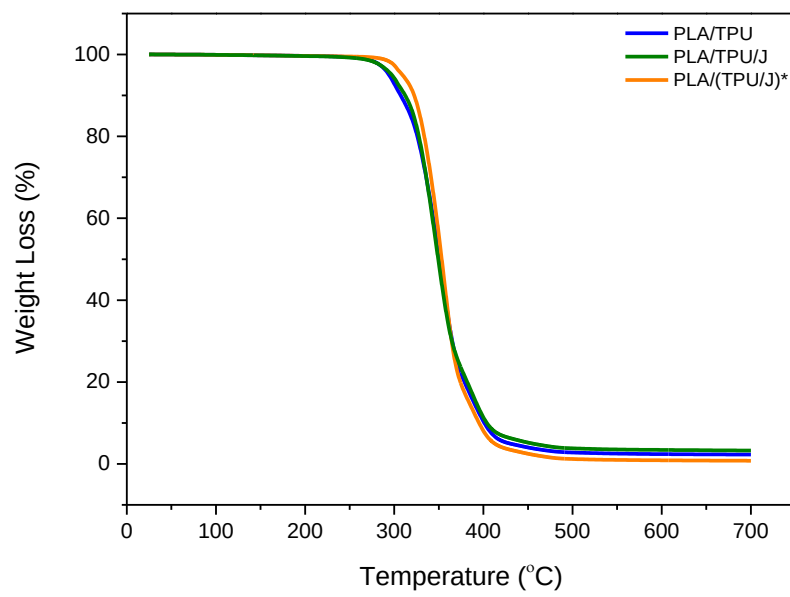


Figure 4.28 : TGA graph of blending samples.

5. CONCLUSION

This study aimed to address the environmental and economic challenges associated with the recycling and re-use of waste TPU through chemical modification and blending methods. The experimental results demonstrated that both approaches effectively enhanced the mechanical, thermal, and morphological properties of waste TPU and its blends, contributing to the development of sustainable materials and a circular economy.

In the chemical modification experiments, the incorporation of additives such as diisocyanates (HDI and PMDI), Joncryl ADR 4468, and PMDA significantly influenced the properties of TPU. Specifically, diisocyanates improved the melt strength, tensile properties, and elongation at break due to chain extension and branching mechanisms. However, PMDA exhibited limited success in enhancing mechanical properties, likely due to degradation effects during processing. Importantly, none of the chemical modifications changed TPU's fundamental thermal stability property, indicating the possibility of improving TPU's re-usability without negatively impacting its important properties.

Blending experiments with waste TPU and PLA 4043D highlighted the potential for addressing PLA's inherent drawbacks, such as brittleness and slow degradation, while providing a re-use of TPU waste. The addition of TPU enhanced PLA's toughness and ductility, while compatibilization with Joncryl significantly improved phase compatibility and mechanical performance. Morphological analysis confirmed that Joncryl reduced phase separation, leading to more uniform and stable microstructures. Moreover, thermal analyses revealed that TPU enhanced PLA's crystallization behavior and processability, further confirming the potential of PLA/TPU blends for diverse applications.

The study's findings highlight the importance of process optimization, choosing appropriate compatibilizers, and carefully modifying material compositions to obtain optimal performance. By incorporating waste TPU into polymer matrices, this study

not only provides a sustainable route for TPU recycling, but it also tackles more diverse issues in polymer waste management and eco-friendly material development.

Future studies can focus on exploring alternative compatibilizers, optimizing processing conditions, and expanding the scope of blends with other biodegradable or high-performance polymers. In conclusion, this study is an important step toward sustainable materials, highlighting the potential of new recycling solutions to reduce environmental effect while developing a circular economy.



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- Yanik, S., İlhan, İ.C., Türkan, B., Arslan Kaba, M., Kartal Sireli, G. “Improvement of Mechanical Properties of Soda-Lime Glass by Ion Exchange Method”, 26th International Congress on Glass(ICG 2022), Berlin, Germany, 2022
- Yanik, S., Nofar, M., “Re-evaluation and Upgrading The Second-Quality Thermoplastic Polyurethane”, RheoSamos, Samos, Greece, 2024
- Yanik, S., Nofar, M. “Effectiveness of different chain modifiers in upgrading the thermoplastic polyurethane waste materials”, 9th International Polymer Science and Technology Congress, Ankara, Turkey, Sep 16-18, 2024

