ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

CITRIC ACID AND DIMER DIOL-BASED POLYESTER MEMBRANES FOR FOOD PACKAGING APPLICATIONS

M.Sc. THESIS

Sara AGHAEINEJAD AJBISHEH

Department of Material and Metallurgy Engineering

Material Engineering Program

DECEMBER 2023

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

CITRIC ACID AND DIMER DIOL-BASED POLYESTER MEMBRANES FOR FOOD PACKAGING APPLICATIONS

M.Sc. THESIS

SARA AGHAEINEJAD AJBISHEH
(506191424)

Department of Material and Metallurgy Engineering

Material Engineering Program

Thesis Advisor: Assoc. Prof. Dr. Bihter ZEYTUNCU GÖKOĞLU

DECEMBER 2023

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

GIDA PAKETLEME UYGULAMALARI İÇİN SİTRİK ASİT VE DİMER DİOL BAZLI POLYESTER MEMBRANLAR

YÜKSEK LİSANS TEZİ

Sara AGHAEINEJAD AJBISHEH
(506191424)

Metalurji ve Malzeme Mühendisliği Anabilim Dalı
Malzeme Mühendisliği Programı

Tez Danışmanı: Doç. Dr. Bihter ZEYTUNCU GÖKOĞLU

ARALIK 2023

SARA AGHAEINEJAD AJBISHEH, a M.Sc. student of ITU Graduate School, student ID 506191424, successfully defended the thesis entitled “CITRIC ACID AND DIMER DIOL-BASED POLYESTER MEMBRANES FOR FOOD PACKAGING APPLICATIONS”, which she prepared after fulfilling the requirements specified in

Thesis Advisor: Assoc. Prof. Bihter ZEYTUNCU GÖKOĞLU ....
Istanbul Technical University

Thesis Co- Advisor: Prof. Emrah ÇAKMAKÇI ....
Marmara University

Jury Members: Prof. Dr. H. Funda KARBANCIOĞLU GÜLER ....
Istanbul Technical University

Prof. Dr. Memet VEZIR KAHRAMAN ....
Marmara University

Assoc. Prof. Mohammadreza NOFAR ....
Istanbul Technical University

Date of Submission: 5 DECEMBER 2023
Date of Defense: 8 DECEMBER 2023

To my family,

FOREWORD

I am sincerely grateful to convey my deep appreciation to my esteemed advisor, Assoc. Prof. Dr. Bihter Zeytuncu Gökoğlu, for her unwavering encouragement, remarkable patience, and immense support throughout my journey, significantly shaping my understanding of the subject matter. In conclusion, I extend my gratitude to Prof. Dr. EMRAH ÇAKMAKÇI for his support, encouragement, and assistance during my thesis. Special thanks go to Sevde Korkut and Dilara Nur Dikmetaş for their invaluable help and guidance with lab experiments.

Lastly, I express my heartfelt regards and blessings to my beloved family, especially my mother, and to all those who supported me in every aspect, culminating in the successful completion of my thesis.

December 2023

SARA AGHAEINEJAD
AJBISHEH
(Material Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

SEM	: Scanning Electron Microscopy
FTIR	: Fourier-Transform Infrared Spectroscopy
CA	: Contact Angle
TS	: Tensile Strength
TGA	: Thermo Gravimetric Analysis
OTR	: Oxygen Gas Permeability Test
CNF	: Cellulose Nanofiber
NFC	: Nanocellulose Films
FP	: Fluoropolymer
PE	: Polyethylene
PP	: Polypropylene
PA	: Polyamide
EVOH	: Ethylene Vinyl Alcohol
TOCNF	: Templated Oxidized Cellulose Nanofiber
USD	: United States Dollar
CAGR	: Compound Annual Growth Rate
PPE	: Personal Protective Equipment
PLA	: Polylactic Acid
NPG	: Neopentyl glycol
NS	: Neopentyl glycol and Citric acid
NSSe	: Neopentyl glycol, citric acid, Sebacic acid
NSSeD0.5	: Neopentyl glycol, citric acid, Sebacic acid ,dimer diol
NSSeD1.0	**:** Neopentyl glycol, citric acid, Sebacic acid ,dimer diol
PTSA	: P-Toluenesulfonic
ITU	: Istanbul Technical University

SYMBOLS

Mw : Molar Weight

C : Carbon

OH : Hydroxide

O : Oxygen

-OH : Hydroxyl

C : Celsius

LIST OF TABLES

Page

LIST OF FIGURES

Page

CITRIC ACID- AND DIMER DIOL-BASED POLYESTER MEMBRANES FOR FOOD PACKAGING APPLICATIONS

SUMMARY

In recent years, the environmental concerns regarding the use of fossil-based materials have gained more attention than ever before. petroleum-based materials, such as plastics derived from petrochemicals, contribute to greenhouse gas emissions and climate change. The extraction, refining, and production processes of fossil fuels release large amounts of carbon dioxide and other greenhouse gases into the atmosphere. This has led to increasing global temperatures, disrupted ecosystems, and other adverse effects on the environment. Carbon-based plastics are a major contributor to plastic pollution, especially in the marine environment. Improper disposal and inefficient recycling systems have resulted in large quantities of plastic waste ending up in oceans, rivers, and landfills. This not only harms marine life but also poses risks to human health through the consumption of contaminated seafood and the leaching of harmful chemicals from plastics. Additionally, increasing consumer awareness and concern about environmental issues have influenced purchasing decisions. Consumers are now more likely to choose products with eco-friendly and sustainable packaging options. As a result, there has been a significant shift towards the use of renewable sources, and intensive academic and industry research is being carried out to find new and improved polymers, production methods, sources, and properties. Biopolymers, in particular, polysaccharides, have been proposed as potential alternatives to conventional synthetic and non-biodegradable ones as packaging materials to passively protect food products against environmental factors, and inhibit or retard microbial growth on food, extending food shelf life of different food groups such as fruits, vegetables, grains, protein foods, and dairy products. Biobased polymers and polyesters which are derived from renewable resources such as plant-based feedstocks, agricultural waste, or bio-based monomers. Feedstocks are often rich in carbohydrates and can be processed to extract or produce various materials. For example, corn, sugarcane, and wheat can be used to produce bio-based polymers like polylactic acid (PLA) or bio-based polyethylene (PE), which are widely used in food packaging. These raw materials offer advantages such as renewability, reduced dependence on fossil fuels, and potential carbon neutrality. Agricultural waste such as corn stalks, wheat straw, rice husks, and bagasse (sugarcane waste) can undergo processes like enzymatic hydrolysis or fermentation to extract valuable components like cellulose, hemicellulose, or lignin. These components can then be used as Inputs for the production of bio-based polymers or as additives to enhance the properties of existing packaging materials. Bio-based monomers are building blocks derived from renewable resources, such as plant oils or sugars. These monomers can be polymerized to produce bio-based polymers used in food packaging. For instance, bio-based monomers like glycolic acid, succinic acid, or 1,4-butanediol can be used to produce polyesters like polyethylene terephthalate (PET).

Compared to traditional petroleum-based plastics contribute significantly less to greenhouse gas emissions, fossil fuel consumption, and depletion of natural resources. By using Bio-sourced materials, we can reduce our dependence on finite fossil fuel reserves and move towards a more sustainable and circular economy. Moreover, there will be a lower carbon footprint compared to conventional plastics. The production of renewable materials generally requires less energy and generates fewer greenhouse gas emissions. The utilization of plant-based polymers and polyesters in food packaging stimulates research and innovation in the development of new materials and technologies. Ongoing research aims to improve the performance and functionality of green packaging, such as enhancing barrier properties, mechanical strength, and shelf life extension capabilities.

In this study, we aimed to prepare bio-derived polyesters for food packaging applications using citric acid and dimer diol. The improvement of existing membranes, particularly regarding their mechanical properties, resistance to liquid water, and permeability to water vapor, is crucial for enhancing the shelf life of packaged foods. Therefore, we preferred to use vegetable oil-based dimer diol, which is known to create a tighter and denser polymer matrix, reducing the permeability of gases such as oxygen and moisture and enhancing barrier capability to extend the shelf life of food products by protecting them from external factors that can lead to spoilage or degradation. In addition, citric acid is also a naturally occurring organic acid that is biodegradable. When incorporated into polyester membranes, it enhances their biodegradability. This means that the membranes can break down into natural components over time, reducing their environmental impact and contributing to a more sustainable packaging solution.

Different stoichiometric ratios of Citric acid, dimer diol, NPG, and Sebacic acid are chosen as the monomers for polyester membrane synthesis , a catalyst, such as p-Toluenesulfonic acid (PTSA), was added to the reaction mixture to promote the esterification reaction and the mixture was heated under a vacuum , typically at elevated temperatures ranging from 80 to 220 °C, to facilitate the formation of ester linkages between the carboxylic acid groups of citric acid and sebacic acid and the hydroxyl groups of dimer diol and NPG.

As the esterification reaction progresses, the polymer chains grow in length. The reaction mixture was maintained at the elevated temperature for a sufficient time to achieve the desired molecular weight and viscosity. The resulting polyester polymer was casted onto a teflon substrate to form thin films or membranes and the effect of this monomers on the thermal, physical and mechanical properties of the resulting polyesters was investigated.

Polyester membranes were characterized using various techniques such as scanning electron microscopy (SEM) to analyze the morphology, surface roughness, fiber distribution, and overall microstructure of the membranes. Tensile Strength Test (TS) to measures the mechanical strength and properties of polyester membranes. It determines the ability of the membranes to resist deformation, stretching, or breaking under tension. Fourier-transform infrared spectroscopy (FTIR) to analyze the chemical composition and molecular structure of polyester membranes and provide information about the functional groups present in the membranes and allows for identification of specific chemical bonds.

Contact angle test (CA) to determine the hydrophobic or hydrophilic nature of the membrane and provide insights into its surface energy, wettability, and interaction with liquids. Thermogravimetric analysis (TGA) for measuring the weight changes of polyester membranes as a function of temperature. It helps in evaluating the thermal stability, decomposition temperature, and degradation behavior of the membranes. And OTR testing is employed to assess the barrier properties of packaging materials. Determining how effectively Cellulose films prevents the permeation of oxygen, which is crucial for preserving the freshness and quality of food products. Packaging with low OTR is essential for extending the shelf life of perishable goods.

Our findings suggest that the use of dimer diol in the preparation of citric acid-based polyester membranes for food packaging applications can significantly enhance the mechanical properties, water resistance, and thermal stability of the resulting polyesters. The results obtained in this study provide valuable insights into the development of biobased materials for food packaging applications, which can ultimately contribute to sustainable food preservation practices.

GIDA PAKETLEME UYGULAMALARI İÇİN SİTRİK ASİT VE DİMER DİOL ESASLI POLYESTER MEMBRANLAR

ÖZET

Son yıllarda, fosil bazlı malzemelerin kullanımına ilişkin çevresel kaygılar her zamankinden daha fazla dikkat çekmiştir. Petrokimyasallardan türetilen plastikler gibi petrol bazlı malzemeler, sera gazı emisyonlarına ve iklim değişikliğine katkıda bulunur. Fosil yakıtların çıkarılması, rafine edilmesi ve üretim süreçleri atmosfere büyük miktarlarda karbondioksit ve diğer sera gazları salmaktadır. Bu, artan küresel sıcaklıklara, bozulan ekosistemlere ve çevre üzerinde diğer olumsuz etkilere yol açmıştır. Karbon bazlı plastikler, özellikle deniz ortamında plastik kirliliğine önemli bir katkıda bulunuyor. Uygun olmayan imha ve verimsiz geri dönüşüm sistemleri, büyük miktarlarda plastik atığın okyanuslara, nehirlere ve çöplüklere gitmesine neden olmaktadır. Bu sadece deniz yaşamına zarar vermekle kalmıyor, aynı zamanda kontamine deniz ürünlerinin tüketimi ve plastiklerden zararlı kimyasalların sızması yoluyla insan sağlığına da risk oluşturuyor. Ek olarak, artan tüketici bilinci ve çevresel konularla ilgili endişeler satın alma kararlarını etkilemektedir. Tüketicilerin artık çevre dostu ve sürdürülebilir ambalaj seçenekleri olan ürünleri seçme olasılığı daha yüksek olmaktadır. Sonuç olarak, yenilenebilir kaynakların kullanımına doğru önemli bir kayma olmuştur ve yeni ve geliştirilmiş polimerler, üretim yöntemleri, kaynakları ve özellikleri bulmak için yoğun akademik ve endüstriyel araştırmalar yürütülmektedir. Biyopolimerler, özellikle polisakkaritler, gıda ürünlerini çevresel faktörlere karşı pasif olarak korumak ve gıda üzerindeki mikrobiyal büyümeyi engellemek veya geciktirmek, meyveler, sebzeler, tahıllar, proteinli gıdalar ve süt ürünleri gibi farklı gıda gruplarının gıda raf ömrünü uzatmak için bitki bazlı hammaddeler, tarımsal atıklar veya biyo bazlı monomerler gibi yenilenebilir kaynaklardan türetilen biyo bazlı polimerler ve polyesterler ambalaj malzemeleri olarak geleneksel sentetik ve biyolojik olarak parçalanamayanlara potansiyel alternatifler olarak önerilmiştir. Besleme stokları genellikle karbonhidrat açısından zengindir ve çeşitli malzemeleri çıkarmak veya üretmek için işlenebilirler. Örneğin mısır, şeker kamışı ve buğday, gıda ambalajlarında yaygın olarak kullanılan polilaktik asit (PLA) veya biyo-bazlı polietilen (PE) gibi biyo-bazlı polimerleri üretmek için kullanılabilir. Bu ham maddeler, yenilenebilirlik, fosil yakıtlara bağımlılığın azalması ve potansiyel karbon nötrlüğü gibi avantajlar sunar. Mısır sapları, buğday samanı, pirinç kabuğu ve küspe (şeker kamışı atığı) gibi tarımsal atıklar, selüloz, hemiselüloz veya lignin gibi değerli bileşenleri çıkarmak için enzimatik hidroliz veya fermantasyon gibi işlemlerden geçebilir. Bu bileşenler daha sonra biyo-bazlı polimerlerin üretimi için girdiler olarak veya mevcut ambalaj malzemelerinin özelliklerini geliştirmek için katkı maddeleri olarak kullanılabilir. Biyo bazlı monomerler, bitki yağları veya şekerler gibi yenilenebilir kaynaklardan elde edilen yapı taşlarıdır. Bu monomerler, gıda paketlemede kullanılan biyo-bazlı polimerleri üretmek için polimerize edilebilir.

Örneğin, glikolik asit, süksinik asit veya 1,4-butandiol gibi biyo-bazlı monomerler, polietilen tereftalat (PET) gibi polyesterler üretmek için kullanılabilir.
Geleneksel petrol bazlı plastiklerle karşılaştırıldığında, sera gazı emisyonlarına, fosil yakıt tüketimine ve doğal kaynakların tükenmesine önemli ölçüde daha az katkıda bulunur. Biyo-kaynaklı malzemeleri kullanarak, sınırlı fosil yakıt rezervlerine olan bağımlılığımızı azaltabilir ve daha sürdürülebilir ve döngüsel bir ekonomiye doğru ilerleyebiliriz. Ayrıca, geleneksel plastiklere kıyasla daha düşük bir karbon ayak izi olacaktır. Yenilenebilir malzemelerin üretimi genellikle daha az enerji gerektirir ve daha az sera gazı emisyonu üretir. Bitki bazlı polimerlerin ve polyesterlerin gıda ambalajlarında kullanılması, yeni malzeme ve teknolojilerin geliştirilmesinde araştırma ve yeniliği teşvik eder. Devam eden araştırmalar, bariyer özelliklerini, mekanik mukavemeti ve raf ömrü uzatma yeteneklerini geliştirmek gibi yeşil ambalajın performansını ve işlevselliğini iyileştirmeyi amaçlamaktadır.
Bu çalışmada, sitrik asit ve dimer diol kullanarak gıda paketleme uygulamaları için biyo-türevli polyesterler hazırlamayı amaçladık. Mevcut membranların özellikle mekanik özellikleri, sıvı suya karşı direnci ve su buharı geçirgenliği açısından iyileştirilmesi, ambalajlı gıdaların raf ömrünün artırılması için çok önemlidir. Bu nedenle, daha sıkı ve yoğun bir polimer matris oluşturduğu, oksijen ve nem gibi gazların geçirgenliğini azalttığı ve gıda ürünlerini bozulmaya veya bozulmaya yol açabilecek dış etkenlerden koruyarak raf ömrünü uzatmak için bariyer kabiliyetini arttırdığı bilinen bitkisel yağ bazlı dimer diol kullanmayı tercih edilmiştir. Ek olarak, sitrik asit ayrıca biyolojik olarak parçalanabilen doğal olarak oluşan bir organik asittir. Polyester membranlara dahil edildiğinde, biyolojik olarak parçalanabilirliğini artırır. Bu, membranların zamanla doğal bileşenlere ayrılarak çevresel etkilerini azaltabileceği ve daha sürdürülebilir bir paketleme çözümüne katkıda bulunabileceği anlamına gelir.
Poliester membran sentezi için monomerler olarak Sitrik asit, dimer diol, NPG ve sebasik asidin farklı stokiyometrik oranları seçildi, esterleşme reaksiyonunu desteklemek için reaksiyon karışımına p-toluensülfonik asit (PTSA) gibi bir katalizör eklendi ve karışım, sitrik asit ve sebasik asidin karboksilik asit grupları ve dimer diol ve NPG'nin hidroksil grupları arasında ester bağlantılarının oluşumunu kolaylaştırmak için, tipik olarak 80 ila 220 °C arasında değişen yüksek sıcaklıklarda bir vakum altında ısıtıldı.
Esterleşme reaksiyonu ilerledikçe polimer zincirlerinin boyu uzarmaktadır. Reaksiyon karışımı, istenen moleküler ağırlık ve viskoziteyi elde etmek için yeterli bir süre boyunca yükseltilmiş sıcaklıkta tutuldu. Ortaya çıkan polyester polimer, ince filmler veya zarlar oluşturmak için bir teflon substrat üzerine döküldü ve bu monomerlerin, elde edilen polyesterlerin termal, fiziksel ve mekanik özellikleri üzerindeki etkisi araştırıldı.
Polyester membranlar, membranların morfolojisini, yüzey pürüzlülüğünü, lif dağılımını ve genel mikro yapısını analiz etmek için taramalı elektron mikroskobu (SEM) gibi çeşitli teknikler kullanılarak karakterize edildi. Polyester membranların mekanik mukavemetini ve özelliklerini ölçmek, membranların gerilim altında deformasyona, esnemeye veya kırılmaya karşı direncini belirlemek için Çekme Mukavemeti Testi (TS) uygulandı. Fourier dönüşümü kızılötesi spektroskopisi (FTIR), polyester membranların kimyasal bileşimini ve moleküler yapısını analiz etmek ve membranlarda bulunan fonksiyonel gruplar hakkında bilgi sağlamak ve belirli kimyasal bağların tanımlanmasına izin vermek için kullanıldı. Membranın hidrofobik veya hidrofilik doğasını belirlemek ve yüzey enerjisi, ıslanabilirliği ve sıvılarla etkileşimi hakkında bilgi sağlamak için temas açısı testi (CA) ve sıcaklığın

bir fonksiyonu olarak polyester membranların ağırlık değişimlerini ölçmek için Termogravimetrik analizi (TGA) yapıldı. Membranların termal stabilitesini, ayrışma sıcaklığını ve bozunma davranışını değerlendirmede yardımcı olmuştur. Ambalaj malzemelerinin bariyer özelliklerini değerlendirmek için OTR testi kullanılır. Selüloz filmlerin, gıda ürünlerinin tazeliğini ve kalitesini korumak için hayati önem taşıyan oksijenin nüfuzunu ne kadar etkili bir şekilde engellediğinin belirlenmesi. Bozulabilir malların raf ömrünü uzatmak için düşük OTR'ye sahip ambalajlar şarttır.

Bulgularımız, gıda paketleme uygulamaları için sitrik asit bazlı polyester membranların hazırlanmasında dimer diol kullanımının, elde edilen polyesterlerin mekanik özelliklerini, su direncini ve termal stabilitesini önemli ölçüde artırabileceğini göstermektedir. Bu çalışmada elde edilen sonuçlar, nihai olarak sürdürülebilir gıda koruma uygulamalarına katkıda bulunabilecek gıda paketleme uygulamaları için biyobazlı malzemelerin geliştirilmesine ilişkin değerli bilgiler sunmaktadır.

1. INTRODUCTION

1.1 Purpose of Thesis

Food packaging is an essential aspect of the food industry, as it plays a vital role in protecting food products from contamination, spoilage, and other external factors that could compromise their quality and safety. Synthetic polymers, such as polyester membranes, have become increasingly popular in the food packaging industry due to their excellent physical and chemical properties, which include barrier properties, mechanical strength, and resistance to moisture and gases. However, concerns have been raised about the environmental impact of traditional synthetic polymers, including the use of non-renewable resources and the accumulation of non-biodegradable waste in landfills and oceans (Zhao et al., 2020).

As a result, there has been a growing interest in developing more sustainable and eco-friendly alternatives to traditional synthetic polymers in food packaging. Biobased materials, derived from renewable resources such as plants and agricultural waste, have emerged as a promising alternative to traditional synthetic polymers. One such biobased material is citric acid, a natural organic acid found in citrus fruits such as lemons and oranges. Citric acid is widely used in the food industry as a natural preservative, acidulant, and flavor enhancer (Rajak et al., 2020; Senthil Muthu Kumar et al., 2019; Tian et al., 2018).

In recent years, citric acid has also been used in the production of polyester membranes for food packaging applications. Citric acid can be used as a monomer in the synthesis of polyesters, resulting in citric acid-based polyester membranes that offer excellent barrier properties, thermal stability, and mechanical strength. Additionally, citric acid-based polyester membranes have been shown to be biodegradable and compostable, making them a more sustainable and environmentally friendly alternative to traditional synthetic polymers. Another biobased material that has shown promise in the production of polyester membranes for food packaging applications is dimer diol, specifically Dimer diol Priplast 3186. Dimer diol is a type of diol that is derived from natural oils and fats and has a unique molecular structure that offers superior physical and chemical properties compared to traditional diols. Dimer diol-based polyester membranes have excellent barrier properties, flexibility, and adhesion to substrates, making them an ideal material for food packaging applications. This study will explore the properties and potential benefits of citric acid and dimer diol-based polyester membranes by incorporation of sebacic acid agent and Neopentyl glycol as a low molecular weight polyol that enhances the tensile strength and improves the thermal stability of the polyester membranes for flexible food packaging applications (Alkan Tas et al., 2019; Bonnin et al., 2020; Costa et al., 2015; De Azeredo, 2013; Reinikuinen et al., 1982).

1.2 Literature Review

The global demand for sustainable and biobased packaging including biobased alternatives, has been gaining significant attention worldwide due to growing environmental concerns and increased consumer awareness of the impact of packaging waste. The market is experiencing continued growth as more food and beverage products are being packaged using sustainable materials. This expansion is primarily driven by the introduction of environmentally-friendly packaging materials, which significantly minimize their environmental impact. Active food packaging refers to the incorporation of functional properties in packaging materials to enhance food quality, safety, and shelf-life. And biobased polyester membranes have gained enormous attention as potential materials for active food packaging due to their unique properties and environmental advantages. According to a report by Grand View Research, in 2021, the global market size for bioplastic packaging was roughly USD 12.4 billion. It is projected to experience a compound annual growth rate (CAGR) of 16.9% from 2022 to 2030. Several factors contribute to the expansion of this market, including a rise in the consumption of renewable and bio-based products, increased demand from the flexible packaging industry, and the advantageous properties of bioplastics, such as their lower carbon footprint and faster decomposition compared to traditional plastics. However, the price competitiveness of bioplastic packaging in relation to conventional plastics poses a slight constraint on market growth (Hu et al., 2019; Yasa et al., 2017; Y. Zhang et al., 2019).

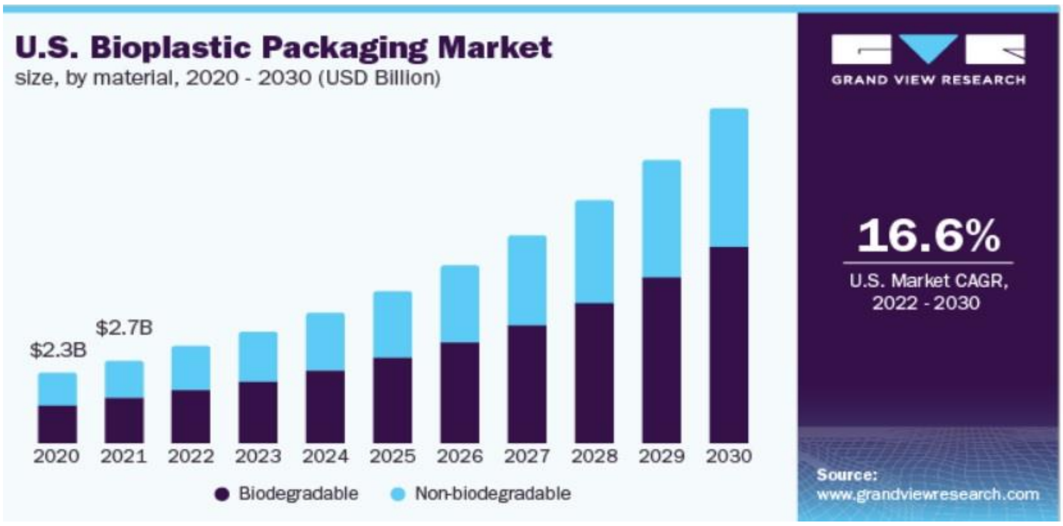


Figure 1.1: Demonstrates a growing need from the flexible packaging sector.

This indicates a growing need and demand for biobased packaging solutions, including those used in the food industry, driven by factors such as increasing environmental concerns, stricter regulations, and consumer preference for sustainable packaging options. Even though, Following the global spread of COVID-19, the attention towards sustainability has unfortunately diminished in favor of addressing the virus and its consequences and has resulted in an increase in plastic waste. Another report published by Research and Markets in 2021 titled "Sustainable Packaging Market - Growth, Trends, COVID-19 Impact, and Forecasts (2021 - 2026)" highlights the increasing demand for sustainable packaging solutions, including biobased options (Ferreira et al., 2016; Malhotra et al., n.d.; Ratnayake et al., 2007; Rose & Palkovits, 2012). The report emphasizes factors such as government regulations promoting sustainability, consumer preference for eco-friendly products, and the growing need for reducing plastic waste as drivers for the adoption of biobased food packaging.

Careless disposal of personal protective equipment (PPE) has been observed, despite ongoing efforts to restrict the use of single-use plastics. The demand for items such as bottled water, plastic bags, disposable wipes, and sanitizers continues to rise, posing challenges to the reduction of plastic waste. Growing consumer awareness about environmental issues has sparked increased interest in sustainable packaging and processing operations. In line with sustainability initiatives, manufacturers have adopted various strategies such as downsizing, using thinner and lighter materials, and minimizing waste in their packaging. Modern consumers now prioritize eco-friendliness, ethical practices, product quality, safety, and cost when making purchasing decisions. Additionally, legislative regulations pertaining to packaging address many of these concerns, contributing to the overall growth of the global green packaging market (Carrillo et al., 2017; Dussenne et al., 2017; Koroma et al., 2018; Peinemann et al., 2010).

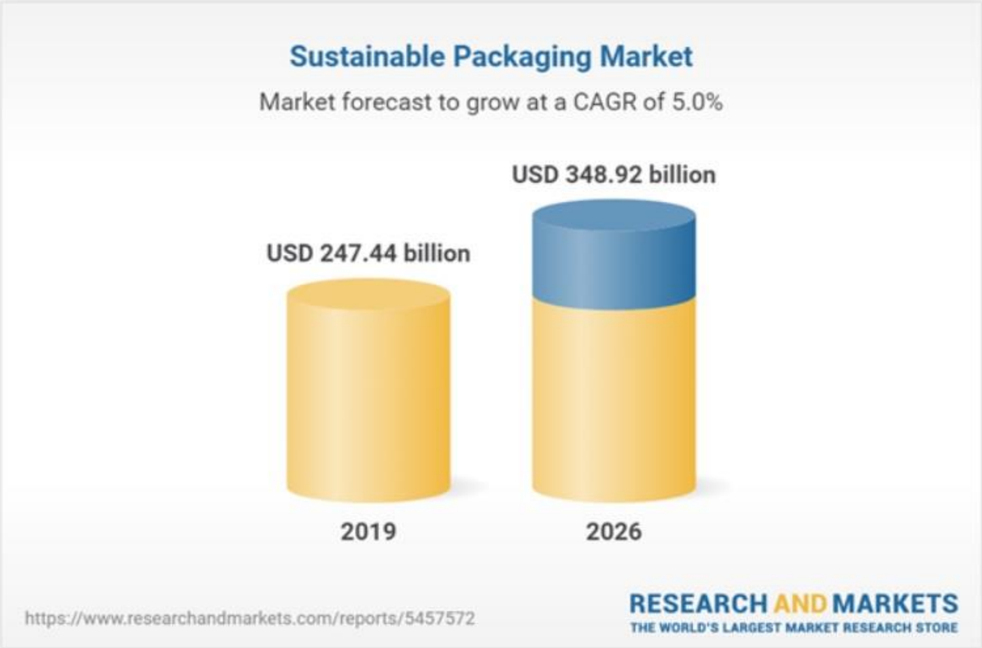


Figure 1.2: Underlines the growing need for environmentally-friendly packaging alternatives.

Moreover, the recent developments in smart food packaging have showcased a shift towards more sustainable solutions by utilizing biobased and biodegradable polymers. These advancements aim to improve the environmental footprint of food packaging while ensuring food safety, quality, and longer shelf life. These materials offer advantages such as reduced environmental impact and improved sustainability compared to traditional petroleum-based polymers (Aricò et al., n.d.; Bonjour et al., 2020; Prabha et al., 2014; Wrzecionek et al., 2021).

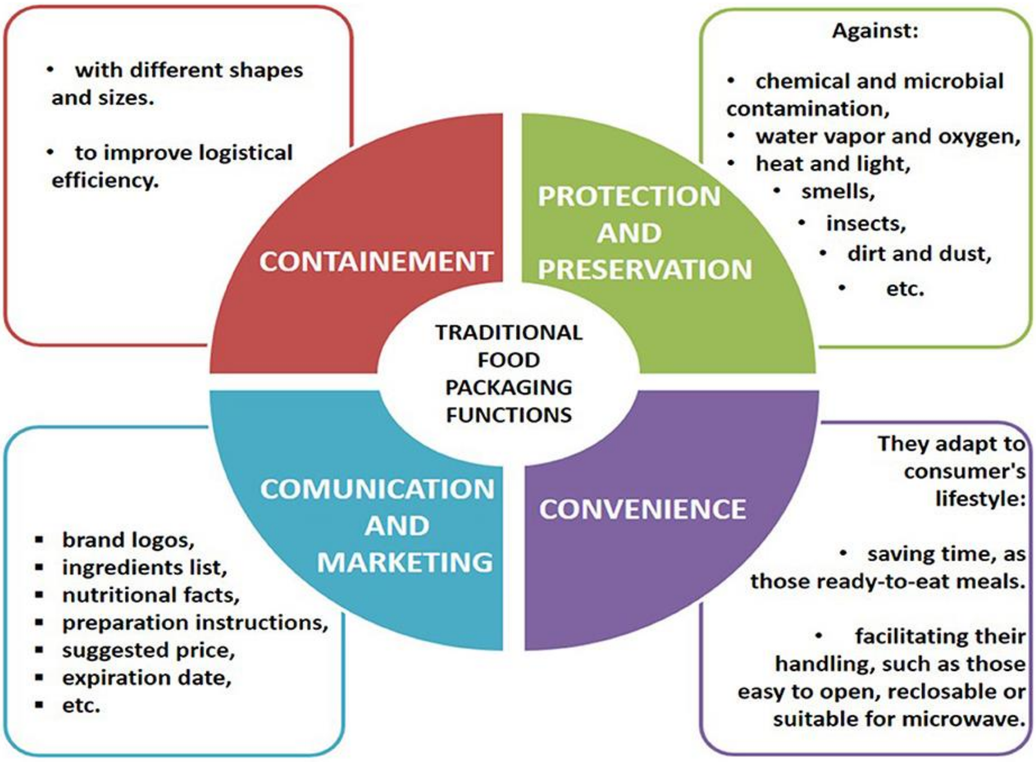


Figure 1.3: Illustrates recent smart food packaging developments on biobased and biodegradable polymers, promoting sustainability and reduced environmental impact.

1.2.1 Biomaterials

Biobased materials refer to materials that are derived from renewable biological sources such as plants, animals, and microorganisms. These materials can be used to replace traditional petroleum-based materials in various food packaging applications. Biobased materials have become increasingly popular in food Packaging applications due to their potential environmental benefits. They can be biodegradable, compostable, and have a lower carbon footprint compared to petroleum-based materials. Additionally, they can be sourced from local and sustainable agricultural sources, which can help support local economies and reduce transportation-related emissions. Examples of biobased materials used in food engineering include bioplastics made from starch, cellulose, and other plant-based materials, as well as biodegradable coatings made from proteins such as casein and soy protein. These materials can be used to produce food packaging films, containers, and other products that can help extend the shelf life of food, reduce food waste, and minimize the environmental impact of food packaging (Daniele et al., 2022; Dhaliwal, 2019; Thomas & Nair, 2011).

Overall, these biodegradable materials offer a sustainable alternative to traditional petroleum-based materials. Using bio-based materials in polyester membranes can provide several benefits, including reduced environmental impact, improved sustainability, and potential cost savings. However, it is important to ensure that the bio-based materials used in the production of polyester membranes are safe for food contact and meet regulatory requirements for food packaging applications (Chon et al., 2017; Djuric et al., n.d.; Dworakowska et al., n.d.; Indira R et al., 2012).

1.2.2 Bio-Based Materials in Polyester Membranes

There are several possible bio-based materials that can be used in the production of polyester membranes for food packaging applications. Some examples include: Polylactic Acid (PLA) which is a biodegradable polymer made from renewable resources such as corn starch or sugarcane. It can be used to produce polyester membranes with good barrier properties and low gas permeability. Another instance would be Starch-based polymers that are made from natural starches, such as corn or potato starch. They are biodegradable and can be used to produce polyester membranes with good mechanical properties (Djordjevic et al., 2009; C. Zhang et al., 2020). There are also Cellulose-based polymers which is a renewable and biodegradable polymer that can be derived from wood or other plant materials. Cellulose-based polymers can be used to produce polyester membranes with good barrier properties and low gas permeability. And last example includes the bio-based polyesters that can be made from renewable resources, such as vegetable oils or bio-based monomers. They can be used to produce polyester membranes with good mechanical properties and thermal stability. Using bio-based materials in polyester membranes can provide several benefits, including reduced environmental impact, improved sustainability, and potential cost savings. However, it is important to ensure that the bio-based materials used in the production of polyester membranes are safe for food contact and meet regulatory requirements for food packaging applications (Forghani et al., 2021; Torres-Giner, 2011; Zhao et al., 2020).

Figure 1.4: Bio-based polyesters from bio-based monomers are gaining prominence in the fast-growing bio-based industry.

1.2.3 Polyester Membranes

Polyester membranes are thin films made from polyester polymers that have a wide range of applications, including in the field of food packaging. They can be produced using various methods, including solution casting, melt extrusion, and electrospinning. Polyester membranes are known for their excellent mechanical properties, thermal stability, and barrier properties, which make them ideal for food packaging applications.

Polyester membranes used in food packaging are typically composed of a blend of different polyester polymers, as well as other materials such as plasticizers and processing aids. The specific composition of the polyester membranes can vary depending on the desired properties and performance requirements. For example, citric acid and dimer diol-based polyester membranes have been developed for food packaging applications, which can provide good mechanical and barrier properties. Polyester membranes used in food packaging must be safe for food contact and meet regulatory requirements for food packaging materials. This includes complying with regulations for the use of additives and processing aids in food packaging materials, as well as requirements for migration testing and overall safety of the packaging material.

1.2.3.1 Citric Acid in Polyester Membranes

Citric acid is a weak organic acid that is naturally present in citrus fruits such as lemons, limes, and oranges. It is a colorless, odorless crystalline powder with a tart taste and is widely used in food, beverage, and pharmaceutical industries. One of the main uses of citric acid is as a flavor enhancer and preservative in food and beverage products. It is used to add a sour or acidic taste to foods such as candies, soft drinks, and jams. Citric acid can also be used to prevent spoilage by inhibiting the growth of bacteria and fungi in food products.

Citric acid is typically included in polyester membranes as a crosslinking agent. Crosslinking agents are used to create a more stable and durable polyester membrane by linking individual polymer chains together. In the case of citric acid, it reacts with the hydroxyl groups on the polyester chains to form ester linkages, which can improve the mechanical and barrier properties of the membrane. Additionally, citric acid can also act as a plasticizer in polyester membranes, which can improve their flexibility and toughness. By incorporating citric acid into the polyester resin, the resulting membrane had improved thermal stability, mechanical strength, and barrier properties. In addition, citric acid can also act as an antimicrobial agent in polyester membranes for food packaging applications. It has been shown to have inhibitory effects against a variety of microorganisms, including bacteria and fungi, which can help to extend the shelf life of packaged foods and reduce the risk of foodborne illness (De Azeredo, 2013; Senthil Muthu Kumar et al., 2019).

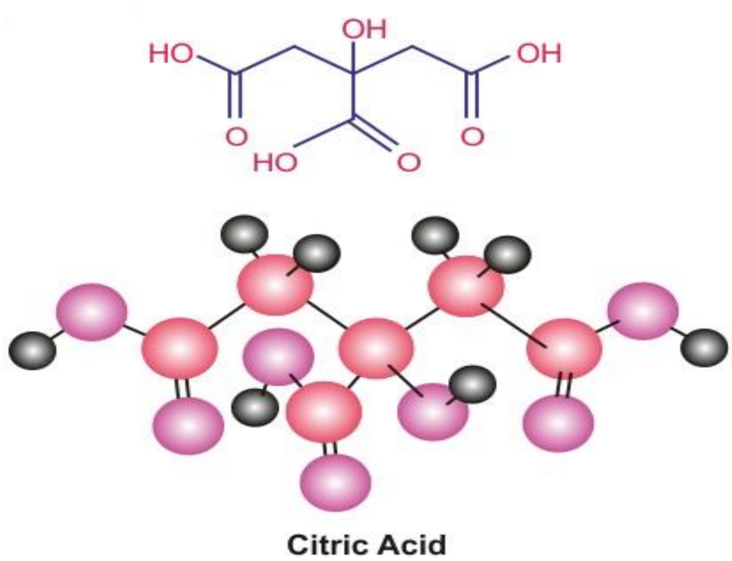


Figure 1.5: This image depicts the structure of citric acid, with the connections indicating its Carbon (C) bonds with other C (carbon), OH (hydroxide), and O (oxygen) atoms.

1.2.3.2 Dimer Diol in Polyester Membranes

Dimer diol is a type of diol, which is a chemical compound that contains two hydroxyl (-OH) groups. It is synthesized through the dimerization process of unsaturated fatty acids, which are naturally occurring compounds found in vegetable oils and animal fats. In the dimerization process, two unsaturated fatty acid molecules react with each other under high temperature and pressure to form a dimer acid, which is then converted to dimer diol by hydrogenation with the use of a catalyst. The resulting dimer diol has a branched molecular structure with a high degree of purity and consistent quality (Chon et al., 2017).

Dimer diol Priplast 3186 is a specific type of diol used in the production of polyester membranes for food packaging. Diols are one of the monomers used to create the polyester polymer, and they react with dicarboxylic acids such as sebacic acid to form ester linkages. It has a dimeric structure, meaning it has two identical monomers linked together.

It is commonly used in the production of polyurethanes, which is used as a raw material for the production of polyesters in different applications including food packaging, textiles, and engineering plastics. The addition of Dimer diol Priplast 3186 to polyester resins can improve the thermal stability of the material, making it more resistant to high temperatures during processing and sterilization (Rajak et al., 2020). This can help to ensure that the packaging material maintains its integrity and does not degrade or deform during use (Koroma et al., 2018). It can also improve the chemical resistance of the material, making it more resistant to degradation from exposure to acids, alkalis, and other chemicals commonly found in food products. Additionally, it can improve the mechanical properties of the polyester membrane, making it more resistant to tearing, puncturing, and other forms of physical stress.

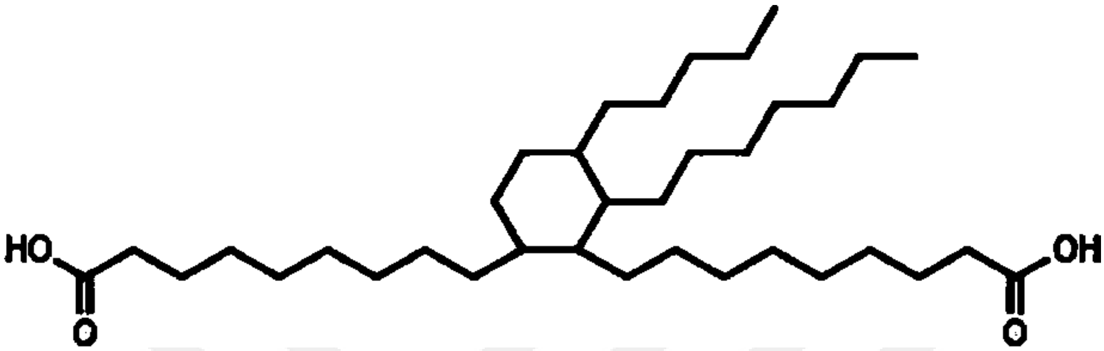


Figure 1.6: Represents the Chemical structure of Dimer Diacid.

1.2.3.3 Sebacic acid in Polyester Membranes

Sebacic acid is a white crystalline powder that is soluble in water and used as a co-monomer in the production of polyester resins. It can also improve the mechanical properties of the polyester membrane, making it more resistant to tearing, puncturing, and other forms of physical stress. Additionally, sebacic acid can act as a plasticizer, improving the flexibility and toughness of the material. Furthermore, sebacic acid has been shown to have antimicrobial properties, making it useful in food packaging applications. It can inhibit the growth of bacteria and other microorganisms, helping to extend the shelf life of packaged foods and reduce the risk of foodborne illness. sebacic acid is one of the building blocks used to create the polyester polymer. Specifically, sebacic acid is a dicarboxylic acid, meaning it has two carboxyl groups that can react with alcohol molecules to form ester linkages. In combination with diols such as dimer diol Priplast 3186, sebacic acid can be used to create a polyester polymer that has desirable properties for food packaging applications, such as high tensile strength, barrier properties, and thermal stability. It can also improve the flexibility of the polyester membrane, making it more resistant to cracking or breaking during handling or transport (Bonjour et al., 2020; Ferreira et al., 2016).

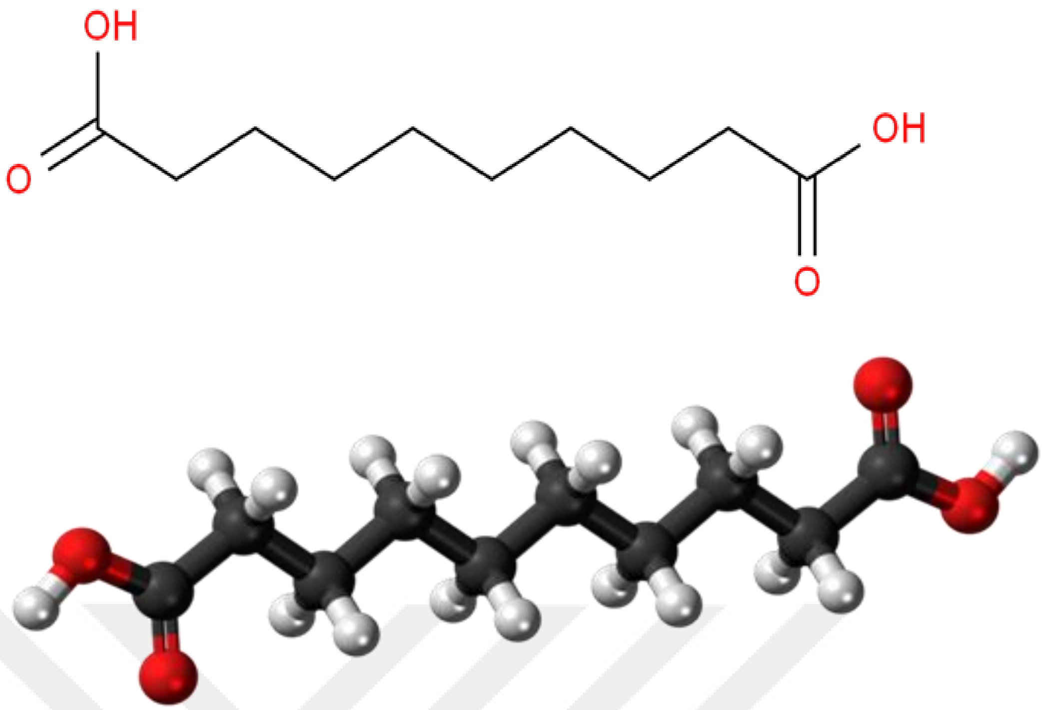


Figure 1.7: Illustrates the Chemical structure of Sebacic acid.

1.2.3.4 Neopentyl glycol (NPG) in Polyester Membranes

Neopentyl glycol (NPG) is a synthetic organic compound that is derived from formaldehyde and isobutyraldehyde. It was first developed in the 1950s and is now widely used in various industrial applications, including in the production of polyester resins and coatings.

In the food packaging industry, NPG is used as a key ingredient in the production of polyester membranes, which are commonly used as packaging materials for various food products. NPG helps to improve the strength, durability, and chemical resistance of the polyester membranes, making them ideal for use in food packaging applications. NPG-based polyester membranes have several advantages over other packaging materials, including excellent oxygen and moisture barrier properties, high tensile strength, and good flexibility. They are also resistant to temperature changes and have good printability, making them suitable for a wide range of food packaging applications, including packaging for meat, dairy, and baked goods. Additionally, NPG-based polyester membranes are eco-friendly and can be easily recycled, making them a sustainable option for food packaging (Dussenne et al., 2017; Ratnayake et al., 2007; Rose & Palkovits, 2012).

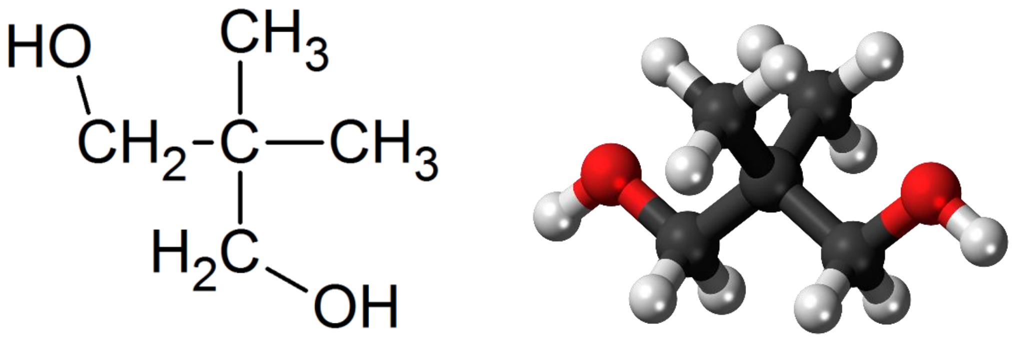


Figure 1.8: Shows the Chemical structure of Neopentyl glycol (NPG).

2. MATERIALS AND METHODOLOGY

2.1 Materials

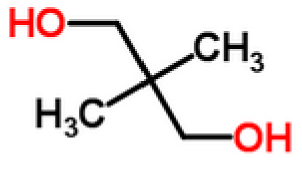
During the thesis study, the following chemicals were used in the experiments. During the analysis phase, no purification was done to the chemical substances. The name of the chemical substances, the chemical formula, the company of the products are given below.

Neopentyl glycol (NPG): A chemical compound with chemical formula ($C_5H_{12}O_2$, M_w= 104.148 g/mol) purchased from sigma-aldrich/USA as a cross-linking agent to improve the mechanical properties and chemical resistance of the material.

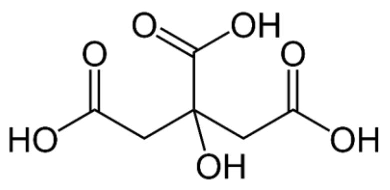
Dimer diol Priplast 3186 :(Polyester polyol, M_w = 1700), a type of polyol, high molecular weight, linear diol with a unique structure that provides enhanced thermal stability, chemical resistance, and mechanical properties was used in the production of polyester resins were gifted by Croda International Plc, a global specialty chemical company.

Citric acid :($C_6H_8O_7$ M_w 192.12 g/mol) is a multifunctional organic acid was utilized as a cross-linking agent to improve the properties of the material and as a plasticizer to help improving the flexibility and toughness of the material, making it more resistant to cracking and other forms of physical stress was prepared by Sigma Aldrich/USA.

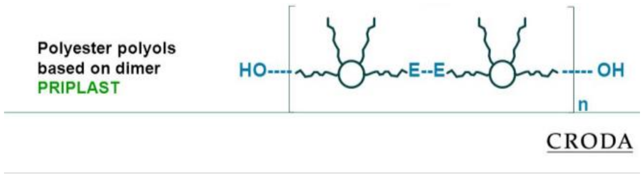
Sebacic acid :($C_{10}H_{18}O_4$ M_w = 202.25 g/mol) is a naturally occurring dicarboxylic acid that was applied in the production of polyester membranes was obtained from Sigma-Aldrich CO., Ltd. The addition of sebacic acid to polyester resins can improve the thermal stability and chemical resistance of the material. This helped to ensure that the packaging material maintains its integrity and does not degrade or deform during use, even when exposed to high temperatures or harsh chemicals.



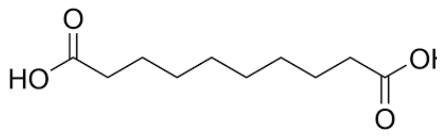
(a) NPG: Neopentyl glycol



(b) Citric acid



(c) DDİOL: Priplast 3186



(d) Sebacic acid

Figure 2.1: Structure images of a) NPG: Neopentyl glycol, b) Citric acid, c) DDİOL: Priplast 3186, d) Sebacic acid.

2.2 Polyester Membranes Preparation

At first, the monomers| citric acid and amorphous polyester polyol based on dimer (Priplast), neopentyl glycol and sebacic acid as a co-monomer were mixed into a beaker according to the ratios given in Table 2.1. Four different formulations were prepared with a 1:1 ratio of OH groups to COOH groups. The tertiary OH group of citric acid has been neglected in the calculations. For the calculation of the formulations, the mole ratio of NPG was kept constant at ~0.05 moles. ~0.032 moles of Citric acid was added for the first formulation. 50 percent by mole of total OH was met by sebacic acid and the other half by citric acid for the rest of the formulations. 10% and 20% of dimer diol-based polyester was added with respect to the weight of the NPG to the third and the forth formulations.

Table 2.1: Each sample is denoted according to the monomer feed ratio.

No	Sample	Neopentyl glycol (NPG) (gram)	Citric acid (gram)	Sebacic acid (gram)	Dimer diol (gram)
1	NS	5	6.15	0	0
2	NSSe	5	3,0943	4.854	0
3	NSSeD0.5	5	3,0943	4.886	0.5
4	NSSeD1.0	5	3,1145	4.918	1.0

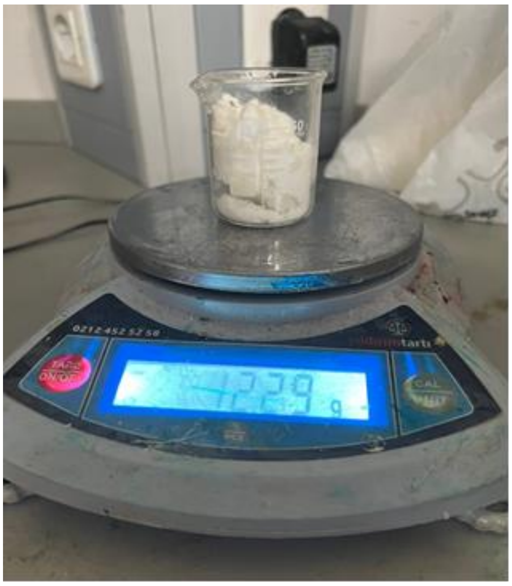
-NS: Neopentyl glycol and citric acid.

-NSSe: Neopentyl glycol, citric acid and Sebacic acid.

-NSSeD0.5 or NCSeD1.0: Neopentyl glycol, citric acid, Sebacic acid,dimer diol.

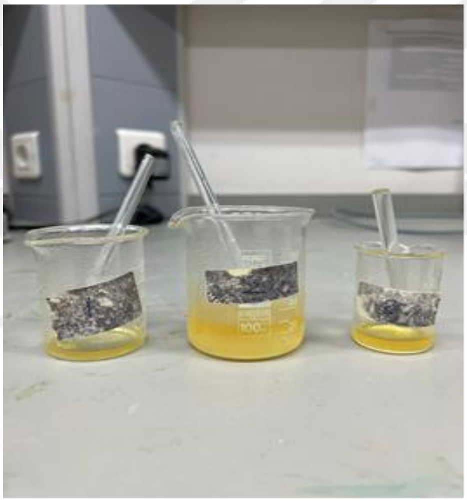
2.3 Esterification Method

We conducted a feasible, easier and faster esterification method. We placed beakers directly into a vacuum oven at 160°C for 15 minutes. Afterwards, the catalyst p-Toluenesulfonic (PTSA, 0.5%) was added to the reaction mixture to catalyze the esterification reaction between the monomers and polyols and promote the reaction between the carboxylic acid groups of the monomers and the hydroxyl groups of the polyols, which results in the formation of ester bonds and the polymerization of material.



(a)

(b)



(c)

Figure 2.2: a) Weighing sample b) Mixtures under vacuum c) After 15 minutes under heating.

The reaction then was continued under vacuum for about 1 hour at 140°C then the beakers were taken out to be stirred for gaining a homogenous melt prepolymer. Then, we lowered the reaction temperature to 110°C and kept the beakers for another 1 hour at this temperature. Finally, they were cast into Teflon molds and kept for 1 day at 80°C.Next, we left the films at room temperature for 2 days to obtain the polyester films. All the films were produced under same reaction conditions and the samples were stored in a desiccator for subsequent tests.

a) b)

Figure 2.3: a) Casting the films to the Teflon Molds b) Polyester films under Vacuum.

3. CHARACTERIZATION

3.1 Fourier-Transform Infrared Spectroscopy FTIR Analysis

To gain insight into the chemical composition, molecular structure, quality control and performance, the Perkin Elmer model of the FTIR-ATR Spectroscopy device was applied during the experiments. FTIR-ATR enables the examination of molecular bonds and functional groups present in the polyester membranes. By analyzing the specific absorption peaks and bands in the spectrum, it is possible to determine the types of chemical bonds (e.g., C-O, C=O) and functional groups (e.g., hydroxyl groups) present in the membranes. This information helps us in understanding the molecular structure and properties of the membranes. By comparing the FTIR-ATR spectra of different membrane samples, it is possible to assess batch-to-batch variations, detect any potential contaminants or impurities, and ensure the overall quality of the membranes.

compatibility and interaction between the polyester membranes and food products is another function of this test which makes us possible to assess polyester membranes suitability for specific food packaging applications, such as barrier properties, food compatibility, and shelf-life preservation.

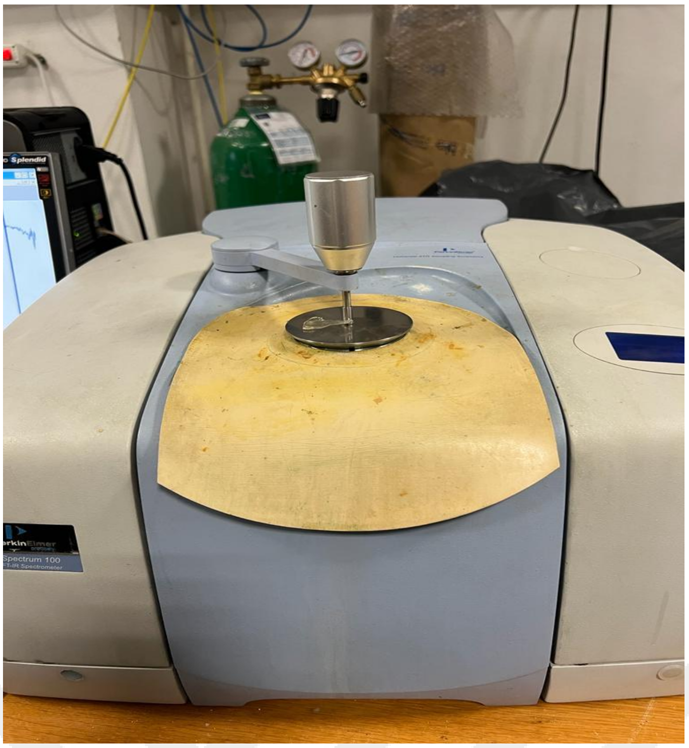


Figure 3.1: Fourier Transform Infrared (FTIR) spectroscopy.

3.2 Contact Angle Measurement

The contact angle test was used to evaluate the hydrophilicity or hydrophobicity of polyester membranes surfaces. It is important to understand the wettability of the packaging material. This is because the wettability of a surface affects the ability of the packaging to repel or absorb moisture, which can have a significant impact on the quality and shelf life of food products, in this research an accurate optical tensiometer Attension® Theta Lite was utilized. The contact angle of the fabricated membranes was measured by placing a droplet from a syringe with a volume of 2-5 ml onto the surface of the membrane, and then the angle between the surface of the membrane and the droplet was measured. The contact angle was calculated at several points on each membrane, and the average value was reported. According to several studies, by measuring the contact angle of a liquid droplet on a polyester membrane surface, we determined the degree of hydrophilicity or hydrophobicity of the membrane. This information is used to optimize the surface properties of the membrane and ensure that it is suitable for use in food packaging applications.

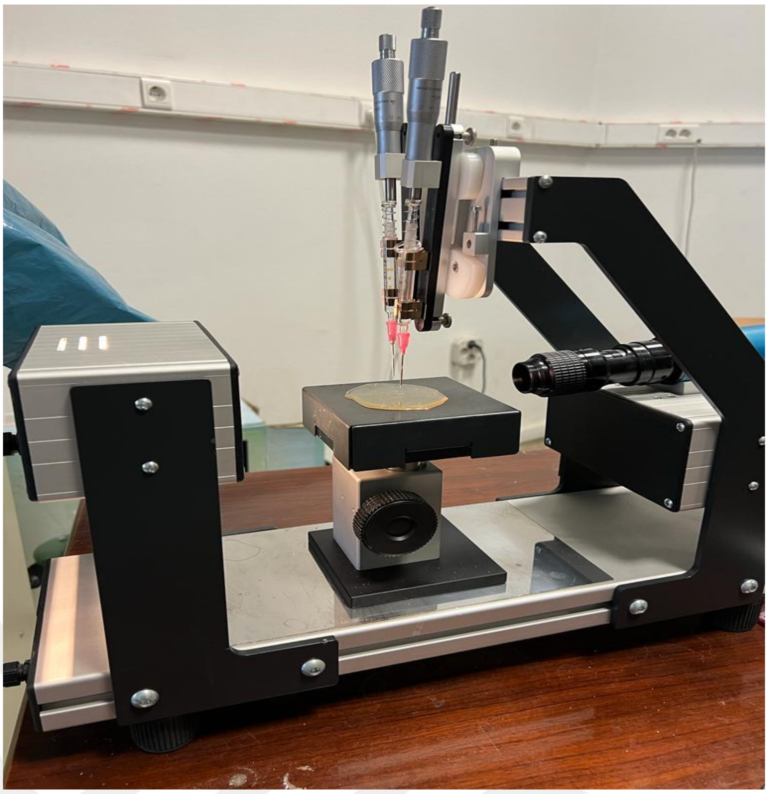


Figure 3.2: Contact angle measurement device.

3.3 The Thermogravimetric Analyzer (TGA) Test

Thermogravimetric analysis (TGA) was utilized to analyze the thermal stability and degradation behavior of polymer samples, including polyester membranes.

First, we cut the polyester membrane samples into small pieces (around 10-20 mg) and dry them under vacuum to remove any residual moisture. Then we set up the heating rate, temperature range, and atmosphere (usually nitrogen or air). And Place the dried polyester membrane samples in the sample pan, and record the initial weight. Then, start the TGA test and record the weight change of the sample as it is heated over the specified temperature range. The weight loss of the sample provided us information on the thermal stability and degradation behavior of the polymer.

In this test we aim to analyze the TGA data to determine the degradation temperature and the percentage of weight loss at different temperature ranges. The onset temperature of degradation can be determined from the derivative of the TGA curve. The percentage of weight loss can provide information on the amount of volatile components and the decomposition products of the polymer. TGA analysis can provide important information on the thermal stability and degradation behavior of the polyester membranes, which can be useful for understanding their performance and properties in food packaging applications.

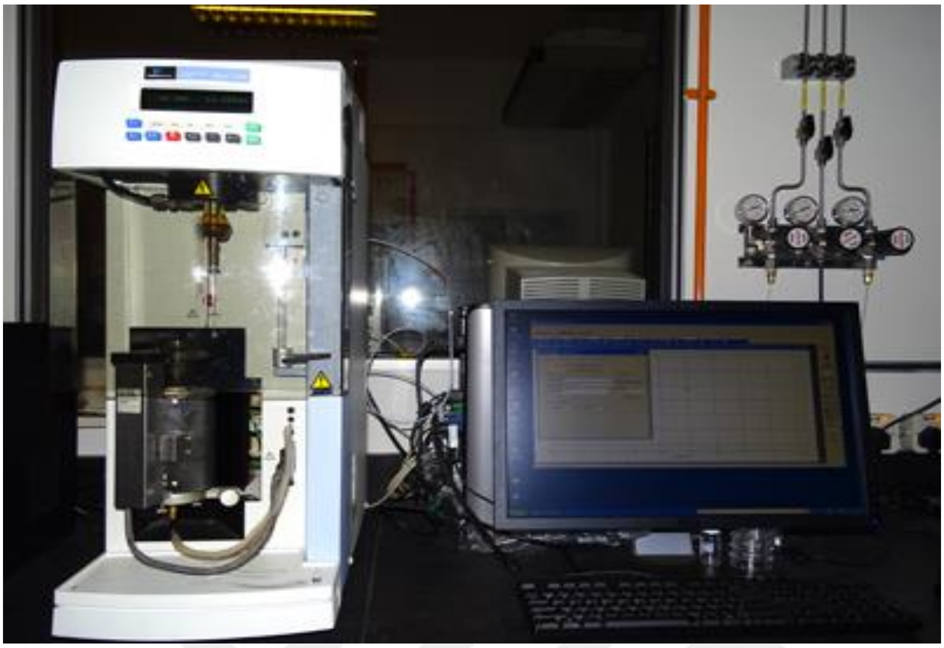


Figure 3.3: Thermogravimetric Analysis (TGA) Test Device.

3.4 Scanning Electron Microscope (SEM) Test

The surface morphology and cross-sections of the Diol-Citric-acid polyester membranes were visualized using the FEI Quanta FEG 250 model of SEM (Scanning Electron Microscope) equipment. The aim of conducting SEM test is to examine the surface morphology and cross-sectional structure of the membranes at a high resolution. This analysis provides valuable information about the membrane's physical characteristics, such as surface texture, porosity, and uniformity, which are important considerations for their performance in food packaging applications. This test helps to assess the quality, integrity, and overall suitability of the membranes for effectively packaging and protecting food products. Additionally, it can aid in optimizing the manufacturing process and evaluating any potential changes in the membrane structure due to various factors, including composition, processing parameters, and environmental conditions.

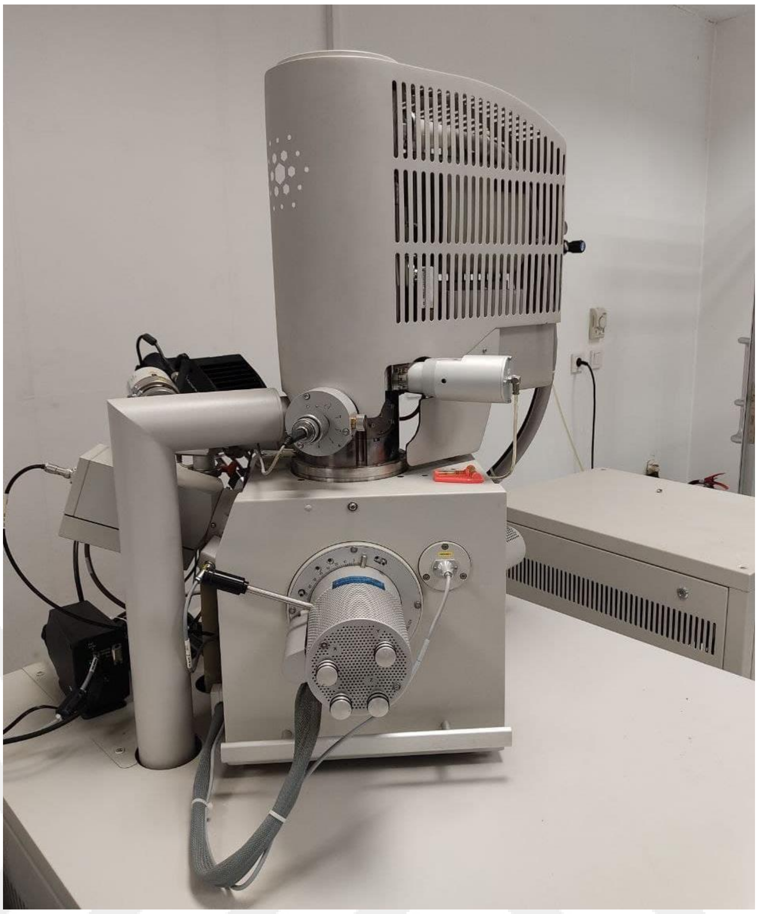


Figure 3.4: Scanning electron microscope (SEM) equipment.

To start examining, first we cut samples into appropriate sizes for analysis. Then, Fixed the membrane samples onto a sample holder or stub using a conductive adhesive or carbon tape. Moreover, a thin layer of conductive material (gold-palladium alloy) using a sputter coater was applied to enhance the sample's conductivity and prevent charging effects during SEM imaging, then, we Placed the sample holder with the mounted membrane into the SEM's vacuum chamber. It is important to adjust the beam current and spot size to optimize the image quality and minimize damage to the sample. We Captured images at different magnifications to observe the surface morphology, texture, and any specific features of interest.

3.5 Tensile Strength (TS) Test

To assess the mechanical properties and performance of the membranes Tensile testing is required. Important parameters such as tensile strength, elongation at break, Young's modulus, and yield strength is provided by this test. These parameters provide insights into the material's strength, flexibility, and ability to withstand deformation and stress.

In the context of food packaging, it is crucial to ensure that the polymer membranes possess sufficient mechanical strength to withstand handling, transportation, and storage processes without experiencing failure or compromising the integrity of the packaged food. The tensile tester helps evaluate the membrane's ability to withstand applied forces and elongation, which are essential for maintaining the packaging's structural integrity.

By subjecting the polymer membrane samples to controlled tension until they break or reach a specified elongation point, the Zwick Roell tensile tester enables the measurement and characterization of the membrane's mechanical behavior. This information is used to assess the suitability of the membranes for specific food packaging applications, such as determining the appropriate material thickness or evaluating the impact of different formulation variations on mechanical properties.

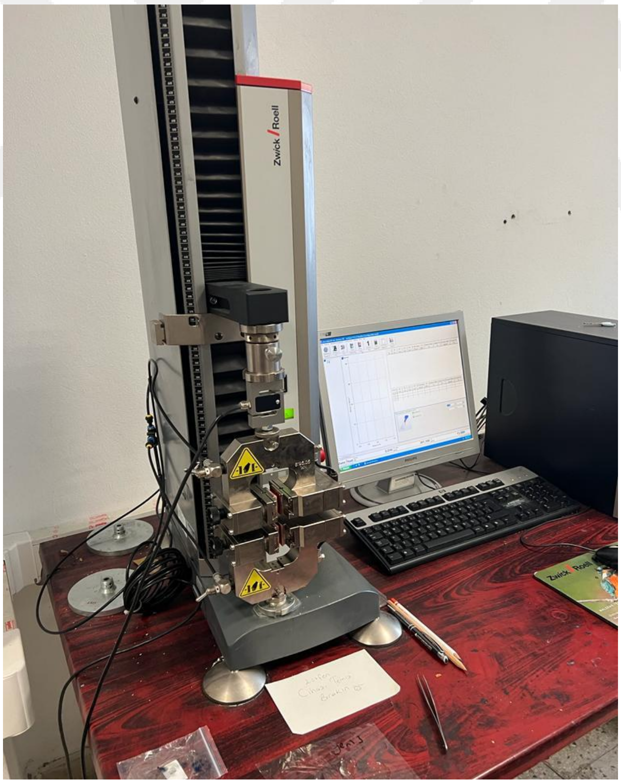


Figure 3.5:Zwick Roell tensile tester device.

3.6 O_2 Gas Permeability Test

The oxygen gas permeability (OTR) was determined at 23 °C with a Brugger Feinmechanik brand GDP-C model gas permeability device according to the ASTM D1434-82 standard monomeric method (American Society for Testing and Materials, 1998). Measurements were made on a circular film area of 10 cm diameter.

Figure 3.6: Brugger Feinmechanik brand GDP-C equipment.

4. RESULT AND DISCUSSION

4.1 The Chemical Structure of Polyester Membranes

The chemical structure of a polyester membrane formed by mixing dimer diol, citric acid, sebacic acid, and NPG can be described as follows:

Polyesters are formed through a condensation reaction between carboxylic acid (or acid anhydride) and alcohol. In this case, citric acid and sebacic acid act as the carboxylic acids, while Neopentyl glycol and dimer diol act as the alcohols. The condensation reaction involves the loss of water molecules. The chemical structure of the polyester membrane can be represented as a repeating unit of the following sequence:

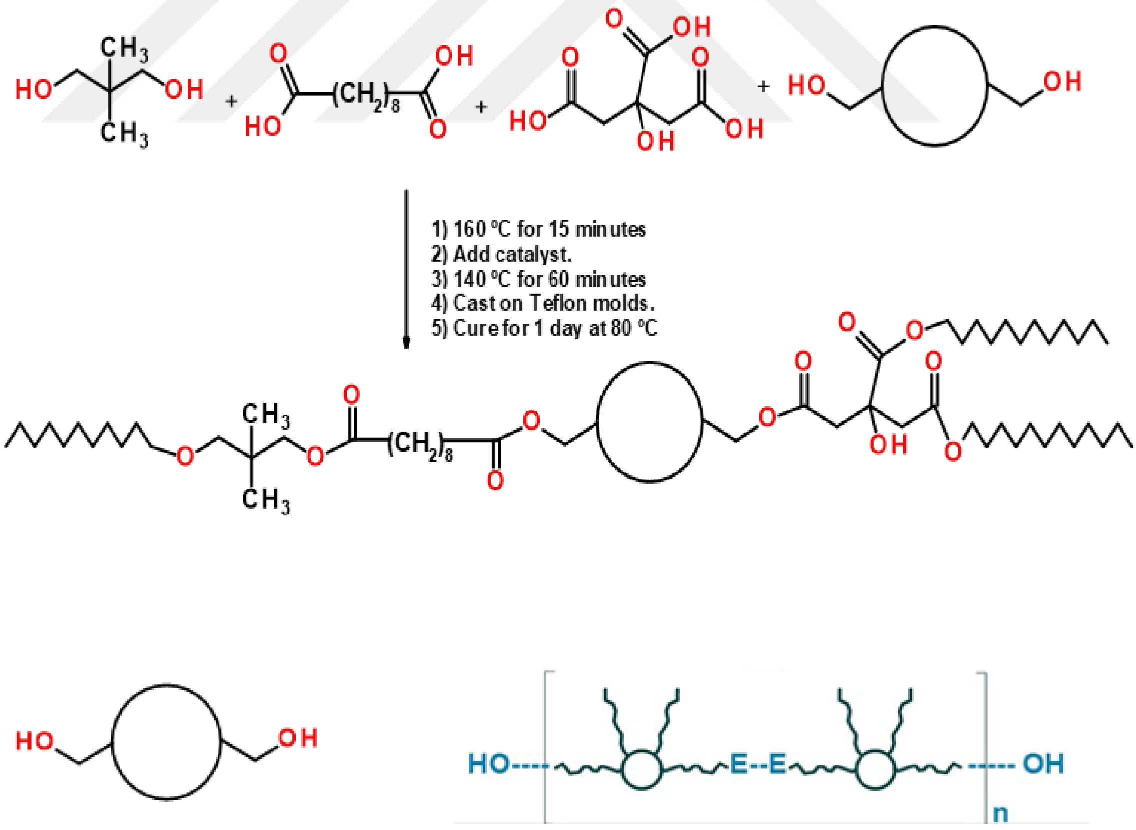


Figure 4.1: Schematic representation of the transesterification reaction.

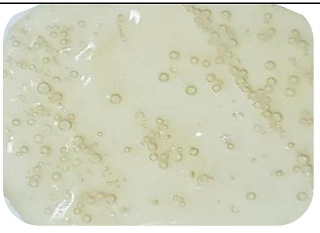
The dimer diol contributes to the formation of a flexible, branched polymer structure, enhancing the mechanical properties and water resistance of the polyester membrane.

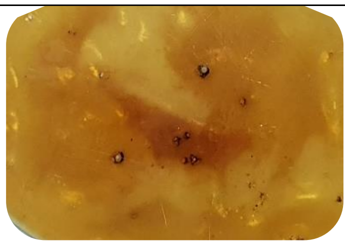
Overall, the combination of these materials results in a complex polymer structure with varying segments of different lengths and compositions, providing a balance of properties suitable for polyester membranes in food packaging applications.

4.2 The Physical Characteristic of Polyester Membranes

However, the specific effect on the physical properties depend on the combination of all components in the polyester membrane and the processing conditions used to produce the material. It is shown that according to the formulations presented in Table 4.1, mixing only Neopentyl glycol and citric acid in sample NS leads to a very hard and brittle, translucent film, so by reducing citric acid ratio and with addition of sebacis acid in sample NSSe we reached to a slight Flexible-opaque film. In samples NSSeD0.5 and NSSeD1.0, by increasing Sebacic acid and adding Dimer diol we improved the flexibility, durability, toughness, and thermal stability of the membranes.

Table 4.1: Photographs of a 45 μm thick film of cast from different ratio solutions.

Sample Names	Physical Properties	pictures
NS	Hard and brittle-transparent	
NSSe	Flexible-opaque	
NSSeD0.5	Flexible-Yellow	

NSSeD1.0	Flexible-Light Brown	

4.3 FTIR-ATR Spectroscopy

All samples displayed similar FTIR spectra. The bands at around 2900-2800 cm^{-1} belong to the $–CH_2$, $-CH_3$ stretching vibration bands. The characteristic ester carbonyl bands were observed at around 1720 cm^{-1}.

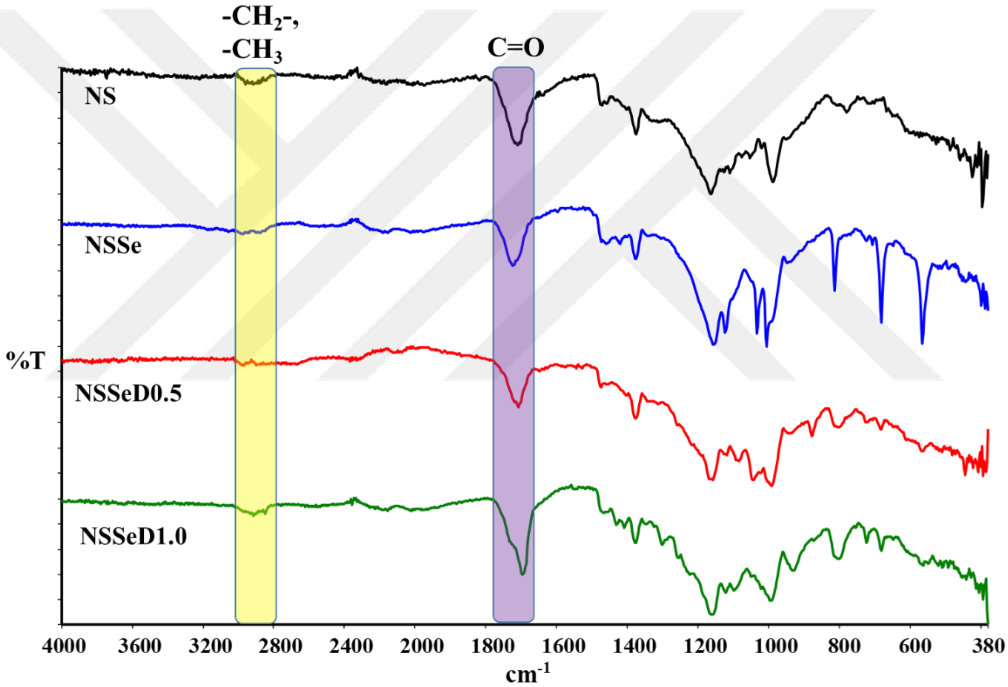


Figure 4.2 : FTIR spectra of Ddiol-Citric acid synthesized polyester membranes.

4.4 Contact Angle Test

To ensure desirable barrier properties, moisture resistance, and compatibility with specific food products, the contact angle test was provided to access the valuable information about the surface characteristics and wetting behavior of polymer membranes. It helps us in selecting appropriate materials and optimizing the design of packaging membranes. As shown in Figure 4.3, Ns has a hydrophilic structure and the average contact angle is 34°. With the addition of sebacic acid as a hydrophobic co-monomer, and reducing the amount of citric acid which is a hydrophilic monomer hydrophilicity has been decreased (NSSe). Dimer diol based polyester increased hydrophobicity and contact angle increased as expected (NSSeD1.0 contact angle 82°). This is especially important in terms of decreasing water adsorption.

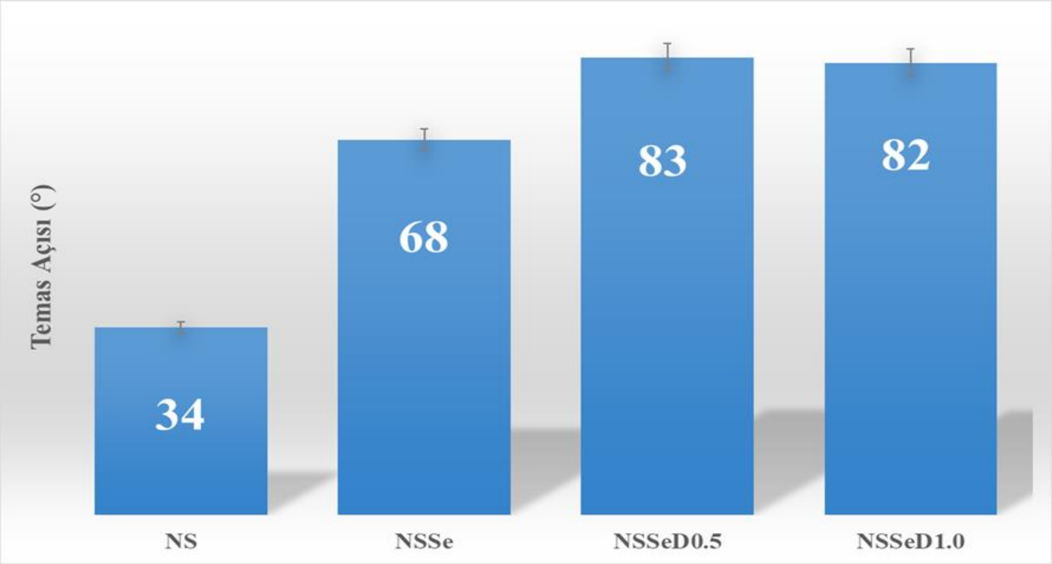
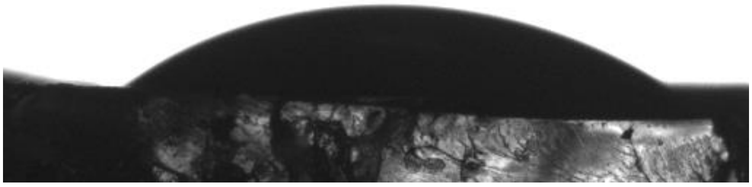
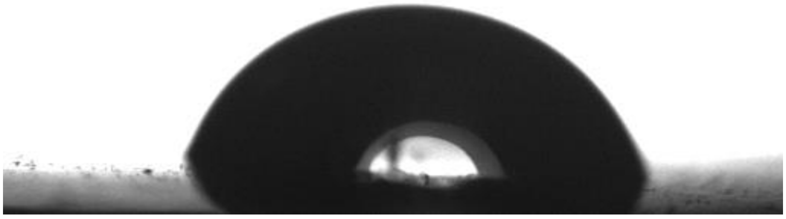
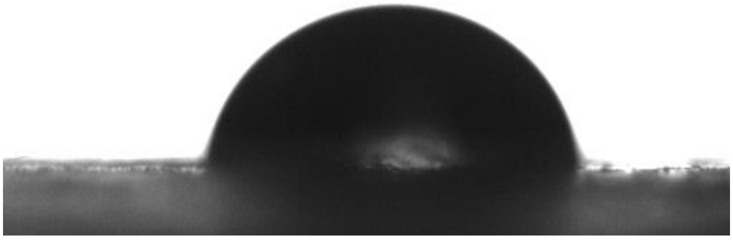
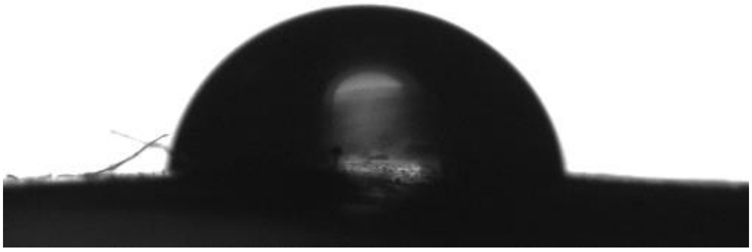


Figure 4.3:Illustrates hydrophilicity and contact angle feature of polyester membranes.

Table 4.2 : Depicts contact angle feature of polyester membranes.

Sample names	**Representative images of contact angle measurements**
NS	
NSSe	

NSSeD0.5	
NSSeD1.0	

4.5 The TGA (Thermogravimetric Analysis) Test

All samples showed in 2-step and similar thermal degradation. Since the NS crosslink density was higher, it left higher residue compared to the other samples. However, 5 percent (T5) mass loss and 10 percent (T10) mass loss temperatures are lower than other samples. The addition of sebacic acid decreased the crosslink density, but increased the T5 and T10 degradation temperatures. Maximum decomposition temperatures (Tmax1 and Tmax2) also increased with the addition of sebacic acid.

Table 4.3: TGA result of dimer diol / citric acid base polyester membranes.

Sample	T5 (°C)	T10 (°C)	Tmax1 (°C)	Tmax2 (°C)	Residue at (%)
NS	255	280	295	362	9.5
NSSe	285	313	350	453	2.9
NSSeD0.5	347	358	360	468	4,15
NSSeD1.0	369	378	352	463	6.4

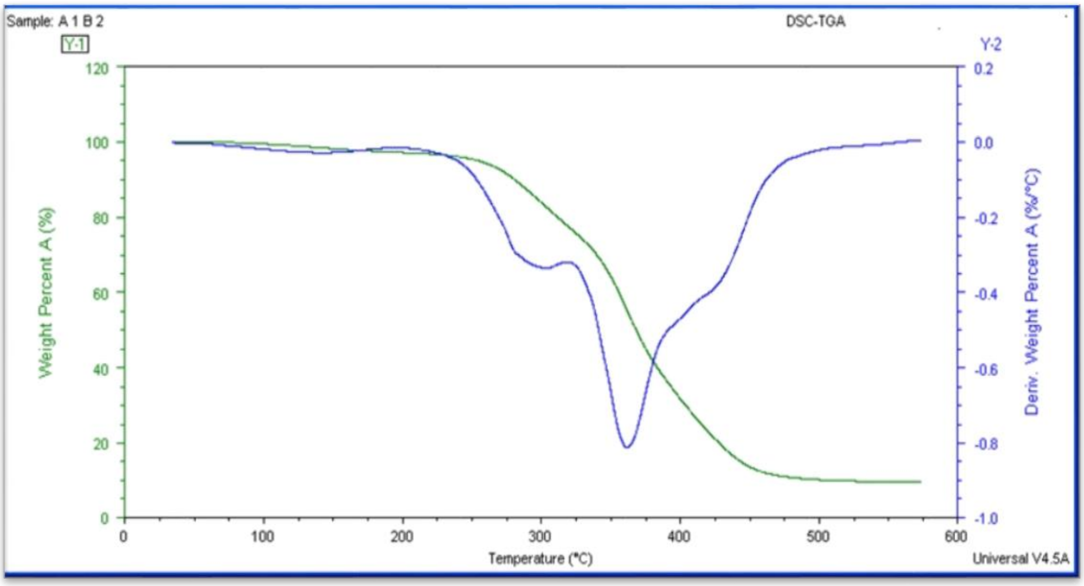


Figure 4.4 : TGA curve of 5 % (T5) and 10% (T10) of polyester Membranes NS samples showing the continuous weight loss before ca. 450 °C.

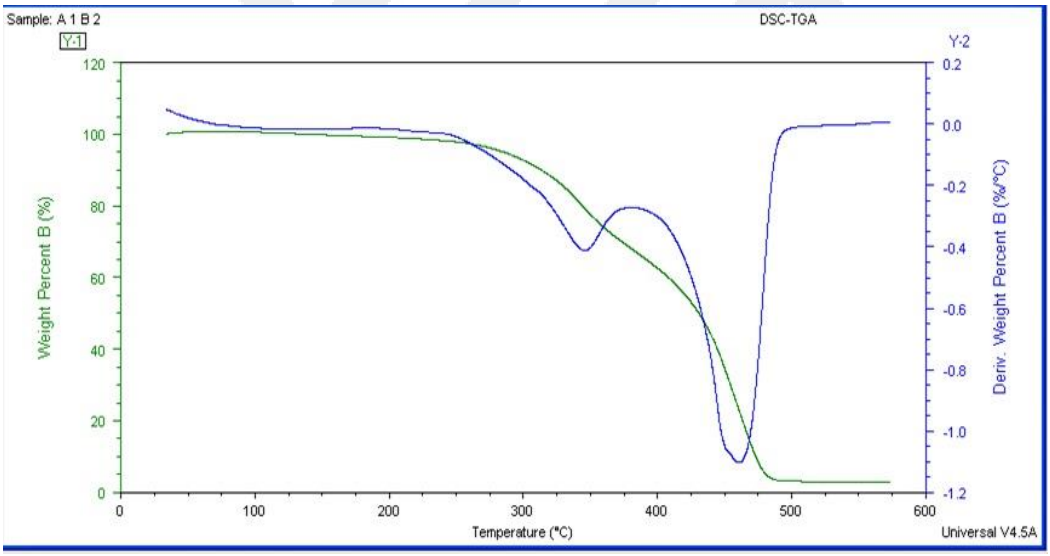


Figure 4.5: TGA curve of 5 % (T5) and 10% (T10) of polyester Membranes NSSe samples showing the continuous weight loss before ca. 500 °C.

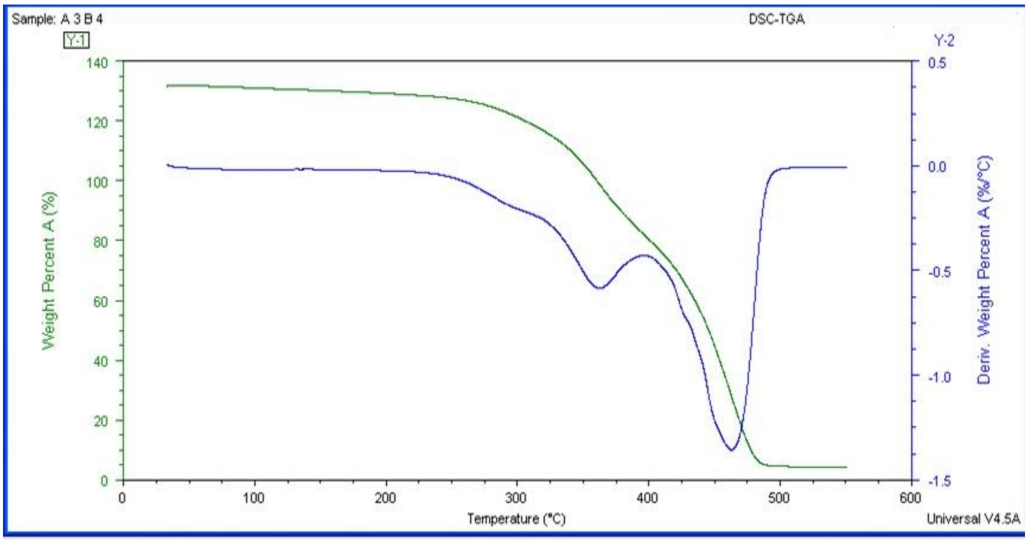


Figure 4.6: TGA curve of 5 % (T5) and 10% (T10) of polyester Membranes NSSeD0.5 samples showing the continuous weight loss before ca. 500 °C.

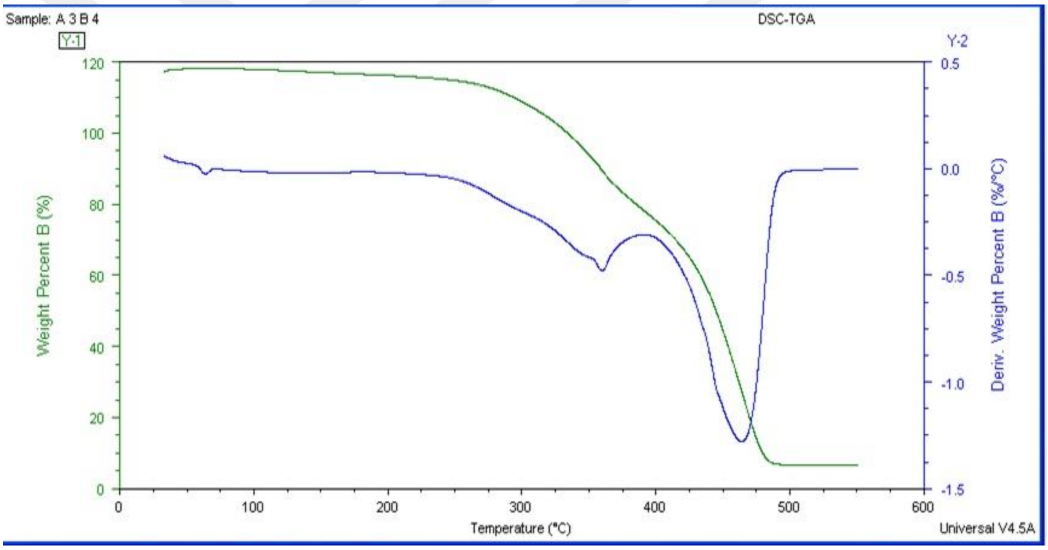
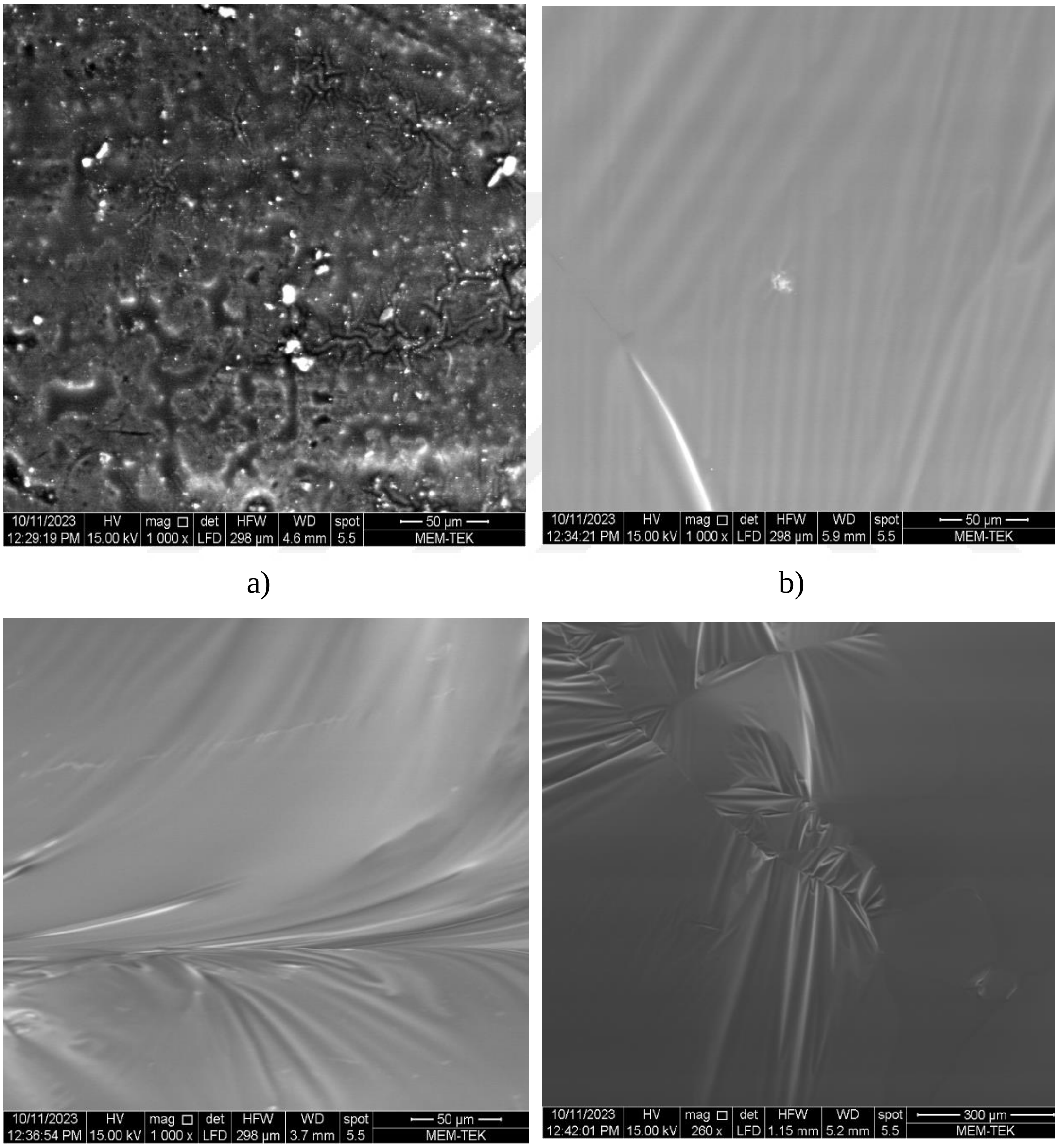


Figure 4.7: TGA curve of 5 % (T5) and 10% (T10) of polyester Membranes NSSeD1.0 samples showing the continuous weight loss before ca. 500 °C.

4.6 SEM Test

Morphology of the membranes was investigated by SEM. SEM micrographs of the membranes can be seen at different magnifications in Figure 4.8. As can be displayed from picture (a, Sample NS has a smooth surface without any cracks or defects. When the formula of the membranes was changed, by addition of Sebacic acid and lowering the ratio of citric acid in NSSe sample high miscibility between all three materials is confirmed but some cracks or defects can be seen on the surface of the membranes. In samples NSSeD0.5 and NSSeD1.0 contributing dimer diol as a co-monomer in polyester synthesis, outer surface morphology illustrated the good miscibility between citric acid/dimer diol/sebacic acid enabling the formation of flexible and hydrophobic polyester chains and enhancing the thermal stability and elasticity of the membrane. It leaded us to the smoother surfaces. In general, we are expecting, a uniform, smooth, homogenous and compact outer surface morphology which can illustrate the good miscibility between polymers.



a) b) c) d)

Figure 4.8: SEM images of a) NS b) NSSe c) NSSeD0.5 and d) NSSeD1.0

4.7 Tesnsile Strenght Test

The importance of tensile strength in the context of food packaging lies in its role in ensuring the packaging material's ability to endure the pressures associated with transportation, storage, and distribution. This, in turn, contributes to prolonging the shelf life of the enclosed food items and enhancing overall quality. Notably, in samples NS and NSSe, a decrease in tensile strength is expected when compared to those incorporating dimer diol. The introduction of sebacic acid and dimer diol, should impact not only on tensile strength but also penetration resistance, seal strength, gas permeability, and the thermal and mechanical properties of the membranes. However, Samples were either too brittle or too flexible to be tested for mechanical properties. We could not be able to get reliable results.

4.8 O_2 Gas Permeability Test

The oxygen and water permeability of packing materials are key features for their use in food preservation. Because oxygen and water migration aid in the oxidation of food, resulting in food quality issues (Yi et al., 2023). Poor barrier characteristics of packing materials have a significant negative influence not only on the freshness of packed food, but also on the development of germs, resulting in quick food decomposition and a shortened shelf-life of food (Shi et al., 2022). According to Hult et al. (Hult et al., 2010) if oxygen barrier properties less than 75 cm3/m2dayatm a material is considered "high oxygen barrier". Cellulose films are a transparent, high barrier, bio-polymeric packaging material that lowers oxygen permeability. The packaging of foods that are susceptible to oxygen has recently been significantly improved using polymeric and flexible cellulose materials. OTR values of the membrane shown in Table 4.4. Souza et al. (de Souza et al., 2022) that produced modified nanocellulose films with the combination of mixture of NFC suspension and an emulsion of blocked isocyanates by the casting method and found OTR values as 15 (cm3/m2dbar), similar to our results. A wide range of different polymers with a variety of physical qualities are commercially available and may be utilized to produce flexible films. Nonpolar polymers, such as PE and PP, have strong oxygen permeabilities, but polar compounds, such as ethylene vinyl alcohol (EVOH), polyamide (PA), are hydrophilic and absorb moisture, lowering their oxygen barrier characteristics (Sonar et al., 2022). In addition, A TOCNF-based barrier coating on PET film, demonstrated an oxygen transmission rate (OTR) of 0.08 cc/m2·day·atm at 0% relative humidity (Rodionova et al., 2012). Yang et al. (Yang et al., 2011) demonstrated a notable outcome wherein they created a free-standing film of cellulose nanofiber (CNF) from LiOH/urea/H2O solution. At 0% RH, the film had an OTR value of 3.34 cc/m2·day·atm. Kim et al. (Kim et al., 2020) modified a high oxygen barrier film, OTR value reduced to 0.15 cc/m2·day·atm from a 1.28 cc/m2·day·atm with the addition of fluoropolymer (FP) to cellulose nanofiber (CNF). By the way, Zhu et al. (Zhu et al., 2024) reported OTR of pure pineapple peel cellulose film nearly 88 cm3/m2day0.1MPa, which was lower than our results. Additionally, as oxygen molecules cannot pass through the crystalline zone, films strong crystallinity also contributed to its exceptional barrier qualities. The barrier qualities of the cellulose films made in this work were generally better.

Table 4.4 : Oxygen barrier properties of membrane.

Membrane	**Unit**
12.1	OTR (cm^3/m^2dbar)

5. CONCLUSION

In this study, our objective was to create bio-based polyesters suitable for food packaging by employing citric acid and dimer diol. We aimed to enhance the mechanical properties, barrier properties, compatibility with food constituents, resistance to liquid water, and water vapor permeability of existing membranes to prolong the shelf life of packaged foods. To achieve this, we utilized dimer diol derived from vegetable oil, known for reducing water absorption in polymers. Through varying ratios of dimer diol, we examined four different formulations and their impact on the thermal and mechanical characteristics of the resulting polyesters. The polyester membranes underwent comprehensive characterization using techniques such as Scanning electron microscopy (SEM), Tensile testing, Fourier-transform infrared spectroscopy (FTIR), Contact angle measurements, Thermogravimetric analysis (TGA) and, Oxygen Permeability (OTR) test. And the following results were obtained: In FTIR analysis, Bands at 2900-2800 cm^{-1} are attributed to the stretching vibrations of the $-CH_2$ and $-CH_3$ groups. The presence of these bands suggests the presence of aliphatic hydrocarbon chains in the samples. And bands at around 1720 cm^{-1} correspond to the ester carbonyl stretching vibrations. The presence of these bands indicates the presence of ester groups, which are typically associated with polyester materials. The obtained information was instrumental in gaining insights into the molecular structure and properties of the membranes. This test enabled us to assess the compatibility and interaction between the polyester membranes and food products, allowing us to evaluate their suitability for specific food packaging applications.

Contact angle test: Ns sample, with its hydrophilic structure, exhibits an average contact angle of 34°. In four distinct formulations, hydrophilicity has been reduced by incorporating sebacic acid as a hydrophobic co-monomer and decreasing the amount of citric acid, a hydrophilic monomer (resulting in NSSe). Furthermore, the inclusion of dimer diol in polyester has led to increased hydrophobicity, as evidenced by an increased contact angle as expected (NSSeD1.0 with a contact angle of 82°). This enhancement is particularly significant in terms of reducing water adsorption.

In TGA test, the crosslink density has increased by adding the sebacic acid and led us to an improved thermal stability because the presence of crosslinks restricts molecular mobility and enhances the polymer's resistance to thermal degradation. So, this is expected to exhibit a higher onset temperature and slower weight loss during the TGA test. These results contribute to evaluating the suitability and performance of the membranes in maintaining food quality and safety during packaging processes.

In SEM Test, the morphology demonstrated a controlled and uniform distribution of pores, ensuring effective gas and moisture barrier properties while allowing for the necessary gas and moisture permeability for food preservation.

In the Tensile strength test, NS and NSSe samples are anticipated to exhibit decreased tensile strength in the absence of dimer diol. The inclusion of sebacic acid and dimer diol affects not only tensile strength but also penetration resistance, seal strength, gas permeability, and the thermal and mechanical properties of the membrane. Regrettably, mechanical property testing was hindered by samples being either too brittle or flexible, leading to unreliable results.

In OTR Test, the findings reveal that cellulose films effectively reduce oxygen permeability, thereby significantly improving the packaging of oxygen-sensitive foods. A comparison with existing literature emphasizes the favorable oxygen transmission rate (OTR) observed in the developed cellulose films. The study demonstrates that films with robust crystallinity display exceptional barrier qualities, thereby contributing to the enhancement of packaging materials. In essence, these results highlight the potential of cellulose films with enhanced oxygen barrier properties, presenting promising solutions for advancing food packaging technologies.

The studies have revealed that the synthesized membranes are suitable for utilization in food packaging applications.

References

Alkan Tas, B., Sehit, E., Erdinc Tas, C., Unal, S., Cebeci, F. C., Menceloglu, Y. Z., & Unal, H. (2019). Carvacrol loaded halloysite coatings for antimicrobial food packaging applications. *Food Packaging and Shelf Life*, *20*. https://doi.org/10.1016/j.fpsl.2019.01.004

American Society for Testing and Materials. (1998). *Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting*.

Aricò, F., Aldoshin, A. S., & Tundo, P. (n.d.). *COMMUNICATION One-pot Preparation of Dimethyl Isosorbide from D-Sorbitol via Dimethyl carbonate Chemistry*.

Bonjour, O., Liblikas, I., Pehk, T., Khai-Nghi, T., Rissanen, K., Vares, L., Jannasch, P., & Jannasch, P. (2020). Rigid biobased polycarbonates with good processability based on a spirocyclic diol derived from citric acid. *Green Chemistry*, *22*(12), 3940–3951. https://doi.org/10.1039/d0gc00849d

Bonnin, I., Mereau, R., Tassaing, T., & de Oliveira Vigier, K. (2020). One-pot synthesis of isosorbide from cellulose or lignocellulosic biomass: a challenge? In *Beilstein Journal of Organic Chemistry* (Vol. 16, pp. 1713–1721). Beilstein-Institut Zur Forderung der Chemischen Wissenschaften. https://doi.org/10.3762/BJOC.16.143

Carrillo, W., Carpio, C., Morales, D., Vilcacundo, E., Álvarez, M., & Silva, M. (2017). Content of fatty acids in corn (Zea mays L.) oil from Ecuador. *Asian Journal of Pharmaceutical and Clinical Research*, *10*(8), 150–153. https://doi.org/10.22159/ajpcr.2017.v10i8.18786

Chon, Y. J., Koo, J. M., Park, Y. J., Hwang, S. Y., Jung, Y. M., & Im, S. S. (2017). Synthesis of a high-performance citric acid-based polyester elastomer by a hot-pressing technique. *Polymer*, *125*, 283–291. https://doi.org/10.1016/j.polymer.2017.08.013

Costa, L. A. S., Assis, D. de J., Gomes, G. V. P., Da Silva, J. B. A., Fonsêca, A. F., & Druzian, J. I. (2015). Extraction and Characterization of Nanocellulose from Corn

Stover. *Materials Today: Proceedings*, *2*(1), 287–294. https://doi.org/10.1016/j.matpr.2015.04.045

Daniele, M., Turner, B., Twiddy, J., Wilkins, M., Ramesh, S., Kilgour, K., Domingos, E., Nasrallah, O., Menegatti, S., Turner, B. L., Wilkins, M. D., Kilgour, K. M., & Daniele, M. A. (2022). *Biodegradable Elastomeric Circuit Boards from Citric Acid-based Polyesters*. https://doi.org/10.21203/rs.3.rs-1945950/v1

De Azeredo, H. M. C. (2013). Antimicrobial nanostructures in food packaging. In *Trends in Food Science and Technology* (Vol. 30, Issue 1, pp. 56–69). https://doi.org/10.1016/j.tifs.2012.11.006

de Souza, G., Belgacem, M. N., Gandini, A., & Carvalho, A. J. F. (2022). Synthesis and characterization of nanofibrilated cellulose films modified with blocked isocyanates in aqueous media and their barrier properties to water vapor and oxygen. *Carbohydrate Polymer Technologies and Applications*, *4*, 100249. https://doi.org/10.1016/j.carpta.2022.100249

Dhaliwal, K. (2019). The Development of in-Situ, Photo Crosslinked, Citric Acid Based Polymeric Delivery Systems. *Biomedical Journal of Scientific & Technical Research*, *13*(4). https://doi.org/10.26717/bjstr.2019.13.002441

Djordjevic, I., Choudhury, N. R., Dutta, N. K., & Kumar, S. (2009). Synthesis and characterization of novel citric acid-based polyester elastomers. *Polymer*, *50*(7), 1682–1691. https://doi.org/10.1016/j.polymer.2009.01.045

Djuric, D., Haberecht, M., Kolter, K., Bruchmann, B., & Assignee, F. (n.d.). *CITRICACID, THEIR PREPARATION AND USE Inventors*.

Dussenne, C., Delaunay, T., Wiatz, V., Wyart, H., Suisse, I., & Sauthier, M. (2017). Synthesis of isosorbide: An overview of challenging reactions. *Green Chemistry*, *19*(22), 5332–5344. https://doi.org/10.1039/c7gc01912b

Dworakowska, S., Kasprzyk, W., Bednarz, S., & Bogdał, D. (n.d.). *Polyesters from renewable sources*.

Ferreira, A. R. V., Alves, V. D., & Coelhoso, I. M. (2016). Polysaccharide-based membranes in food packaging applications. In *Membranes* (Vol. 6, Issue 2). MDPI AG. https://doi.org/10.3390/membranes6020022

Forghani, S., Almasi, H., & Moradi, M. (2021). Electrospun nanofibers as food freshness and time-temperature indicators: A new approach in food intelligent packaging. In *Innovative Food Science and Emerging Technologies* (Vol. 73). Elsevier Ltd. https://doi.org/10.1016/j.ifset.2021.102804

Hu, L., Du, H., Liu, C., Zhang, Y., Yu, G., Zhang, X., Si, C., Li, B., & Peng, H. (2019). Comparative Evaluation of the Efficient Conversion of Corn Husk Filament and Corn Husk Powder to Valuable Materials via a Sustainable and Clean Biorefinery Process. *ACS Sustainable Chemistry and Engineering*, *7*(1), 1327–1336. https://doi.org/10.1021/acssuschemeng.8b05017

Hult, E.-L., Iotti, M., & Lenes, M. (2010). Efficient approach to high barrier packaging using microfibrillar cellulose and shellac. *Cellulose*, *17*(3), 575–586. https://doi.org/10.1007/s10570-010-9408-8

Indira R, I. R., Sivakumar E. K .T, S. E. K. . ., Hariharapriya G, H. G., & Jaisankar V, J. V. (2012). Synthesis and Characterisation of Citric Acid Based Polyester - Hydroxyapatite Nanocomposites. *Global Journal For Research Analysis*, *3*(7), 20–24. https://doi.org/10.15373/22778160/July2014/7

Kim, J.-K., Choi, B., & Jin, J. (2020). Transparent, water-stable, cellulose nanofiber-based packaging film with a low oxygen permeability. *Carbohydrate Polymers*, *249*, 116823. https://doi.org/10.1016/j.carbpol.2020.116823

Koroma, L., Yormah, T. B. R., Kamara, L. M., Robert, G. M. T., & Leone, S. (2018). Extraction and Characterization of Linoleic Acid from the Leaves of the Traditional Medicinal Plant Caloncoba Echinata in Sierra Leone. *Technology, and Sciences (ASRJETS) American Scientific Research Journal for Engineering*, *45*(1), 185–206.

Malhotra, S. V, Kumar, V., East, A., & Jaffe, M. (n.d.). *Corn-Based Chemistry and its Applications*.

Peinemann, K. V. (Klaus-V., Nunes, S. P. (Suzana P., & Giorno, L. (2010). *Membranes for food applications*. Wiley-VCH.

Prabha, G. S., Malar[1], L., & David[2], S. B. (2014). Development of Novel Citric Acid Based Biodegradable Polyesters from Sesame Oil. In *International Journal of Chemistry and Applications* (Vol. 6, Issue 2).

Rajak, A., Hapidin, D. A., Iskandar, F., Munir, M. M., & Khairurrijal, K. (2020). Electrospun nanofiber from various source of expanded polystyrene (EPS) waste and their characterization as potential air filter media. *Waste Management*, *103*, 76–86. https://doi.org/10.1016/j.wasman.2019.12.017

Ratnayake, W. S., Wassinger, A. B., & Jackson, D. S. (2007). Extraction and characterization of starch from alkaline cooked corn masa. *Cereal Chemistry*, *84*(4), 415–422. https://doi.org/10.1094/CCHEM-84-4-0415

Reinikuinen, P., Suortti, T., Olkku, J., Malkki, Y., Linko, P., Olkku, of J., Flec, B. G., & Huchette, M. (1982). Food Processing Systems. In *12] Miles Laboratories Inc.: Technical Bulletin* (Vol. 20). Applied Science Publishers.

Rodionova, G., Saito, T., Lenes, M., Eriksen, Ø., Gregersen, Ø., Fukuzumi, H., & Isogai, A. (2012). Mechanical and oxygen barrier properties of films prepared from fibrillated dispersions of TEMPO-oxidized Norway spruce and Eucalyptus pulps. *Cellulose, 19*(3), 705–711. https://doi.org/10.1007/s10570-012-9664-x

Rose, M., & Palkovits, R. (2012). Isosorbide as a renewable platform chemical for versatile applications-quo vadis? *ChemSusChem*, *5*(1), 167–176. https://doi.org/10.1002/cssc.201100580

Senthil Muthu Kumar, T., Senthil Kumar, K., Rajini, N., Siengchin, S., Ayrilmis, N., & Varada Rajulu, A. (2019). A comprehensive review of electrospun nanofibers: Food and packaging perspective. In *Composites Part B: Engineering* (Vol. 175). Elsevier Ltd. https://doi.org/10.1016/j.compositesb.2019.107074

Shi, H., Wu, L., Luo, Y., Yu, F., & Li, H. (2022). A facile method to prepare cellulose fiber-based food packaging papers with improved mechanical strength, enhanced barrier, and antibacterial properties. *Food Bioscience*, *48,* 101729. https://doi.org/10.1016/j.fbio.2022.101729

Sonar, C. R., Tang, J., & Sablani, S. S. (2022). Polymer packaging for in-pack thermal pasteurization technologies. In *Food Engineering Innovations Across the Food Supply Chain* (pp. 307–322). Elsevier. https://doi.org/10.1016/B978-0-12-821292-9.00020-0

Thomas, L. V., & Nair, P. D. (2011). (Citric acid-co-polycaprolactone triol) polyester: a biodegradable elastomer for soft tissue engineering. *Biomatter, 1*(1), 81–90. https://doi.org/10.4161/biom.1.1.17301

Tian, J., Deng, H., Huang, M., Liu, R., Yi, Y., & Dong, X. (2018). Electrospun nanofibers for food and food packaging technology. In *Electrospinning: Nanofabrication and Applications* (pp. 455–516). Elsevier. https://doi.org/10.1016/B978-0-323-51270-1.00015-7

Torres-Giner, S. (2011). Electrospun nanofibers for food packaging applications. In *Multifunctional and Nanoreinforced Polymers for Food Packaging* (pp. 108–125). Elsevier. https://doi.org/10.1533/9780857092786.1.108

Wrzecionek, M., Matyszczak, G., Bandzerewicz, A., Ruśkowski, P., & Gadomska-Gajadhur, A. (2021). Kinetics of Polycondensation of Citric Acid with Glycerol

Based on a Genetic Algorithm. *Organic Process Research and Development*, *25*(2), 271–281. https://doi.org/10.1021/acs.oprd.0c00492

Yang, Q., Fukuzumi, H., Saito, T., Isogai, A., & Zhang, L. (2011). Transparent Cellulose Films with High Gas Barrier Properties Fabricated from Aqueous Alkali/Urea Solutions. *Biomacromolecules*, *12*(7), 2766–2771. https://doi.org/10.1021/bm200766v

Yasa, S. R., Cheguru, S., Krishnasamy, S., Korlipara, P. V., Rajak, A. K., & Penumarthy, V. (2017). Synthesis of 10-undecenoic acid based C22-dimer acid esters and their evaluation as potential lubricant basestocks. *Industrial Crops and Products*, *103*, 141–151. https://doi.org/10.1016/j.indcrop.2017.04.005

Yi, C., Yuan, T., Xiao, H., Ren, H., & Zhai, H. (2023). Hydrophobic-modified cellulose nanofibrils (CNFs)/chitosan/zein coating for enhancing multi-barrier properties of heat-sealable food packaging materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *666*, 131245. https://doi.org/10.1016/j.colsurfa.2023.131245

Zhang, C., Li, Y., Wang, P., & Zhang, H. (2020). Electrospinning of nanofibers: Potentials and perspectives for active food packaging. In *Comprehensive Reviews in Food Science and Food Safety* (Vol. 19, Issue 2, pp. 479–502). Blackwell Publishing Inc. https://doi.org/10.1111/1541-4337.12536

Zhang, Y., Chen, T., Zhang, G., Wang, G., & Zhang, H. (2019). Efficient production of isosorbide from sorbitol dehydration over mesoporous carbon-based acid catalyst. *Applied Catalysis A: General*, *575*, 38–47. https://doi.org/10.1016/j.apcata.2019.01.014

Zhao, L., Duan, G., Zhang, G., Yang, H., Jiang, S., & He, S. (2020). Electrospun functional materials toward food packaging applications: A review. In *Nanomaterials* (Vol. 10, Issue 1). MDPI AG. https://doi.org/10.3390/nano10010150

Zhu, H., Cheng, J.-H., & Han, Z. (2024). Construction of a sustainable and hydrophobic high-performance all-green pineapple peel cellulose nanocomposite film for food packaging. *International Journal of Biological Macromolecules*, *256*, 128396. https://doi.org/10.1016/j.ijbiomac.2023.128396

CURRICULUM VITAE

Name Surname **: SARA AGHAEINEJAD AJBISHEH**

EDUCATION **:**

- **B.Sc.** **:** 2010 – 2015 Bachelor of Science, Industrial Engineering.
  University of Mehrastan in Iran GPA: 16.80/20
- **M.Sc.** **:** 2019 – 2023 MSc in Material Engineering, Material and Metallurgy Faculty Istanbul Technical University GPA: 3.63 out of 4

PROFESSIONAL EXPERIENCE AND REWARDS:

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

17-19 October 2023 **Published Paper Presentation**

- Paper **''Citric acid- and dimer diol-based polyester membranes for food packaging applications''** selected for poster presentation at "7th MEMTEK International Symposium on Membrane Technologies and Applications (MEMTEK 2023)

OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

January 2023 to April 2023 **Internship**

- **SCIENTIFIC RESEARCH PROJECTS COORDINATION DEPARTMENT OF ISTANBUL TECHNICAL UNIVERSITY**
  Involved in the Research and Development (R&D), in which the Production and Application of Polymer Containing Membranes for the Recovery of Precious Metals from Industrial Wastewaters are tested.
  Review scientific and technical literature to prepare for experiments

July 2023 **Chapter Review**

- Engage in **''Polymeric membranes for food packaging''** chapter on book **'Academic Analysis and Discussions in the Field of Engineering review'** published by **IMPERIAL Publishing.**
  Research in Natural and synthesized Polymers, Sustainability and Environmental Considerations
  Smart Solutions for Safer Food:Exploring Advanced Packaging Technologies
  Enhancing Food Monitoring: Intelligent Packages