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EGE UNIVERSITY

Graduate School of Applied and Natural Science

DEVELOPMENT AND CHARACTERIZATION OF POLYLACTIC ACID BASED COMPOSITE MATERIALS WITH ANTIMICROBIAL PROPERTIES

MSc Thesis

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EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

ETİK KURALLARA UYGUNLUK BEYANI

EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "**Antimikrobiyal Özelliklere Sahip Polikaktik Asit Bazlı Kompozit Malzemelerin Geliştirilmesi ve Karakterizasyonu**" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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Melike TUNÇALP

ÖZET

ANTİMİKROBİYAL ÖZELLİKLERE SAHİP POLİKAKTİK ASİT BAZLI KOMPOZİT MALZEMELERİN GELİŞTİRİLMESİ VE KARAKTERİZASYONU

TUNÇALP, Melike

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Yeşil polimer olarak adlandırılan ve kompostlanabilme/biyobozunma özelliğine sahip polilaktik asit (PLA) son yıllarda birçok akademik araştırmaya konu olmuştur. Özellikle biyouyumlu ve degrede olabilen bir malzeme olmasından kaynaklı medikal ve gıda uygulamalarında kendine yer edinerek, geniş uygulama yelpazesi, hammaddelere ucuz erişimi ve mükemmel üretim bilgisi sayesinde küresel biyobozunur polimer üretim kapasitesinde en büyük paya sahiptir. Antimikrobiyal maddeler sağlık, ısıtma ve havalandırma sistemlerinde, paketleme, ambalaj, otomotiv vb sektörlerde, mikropların varlığını ve hayatta kalmasını engellemek için polimerlere ve kaplamalara katılarak son yıllarda kullanılmaya başlanmıştır. Plastiklerin özellikle PLA'nın antimikrobiyel yapılmasında yaygın olarak kullanılan malzemeleri (gümüş - çinko oksit, gümüş kaynaklı inorganik zeomic, titanyum dioksit vb) biyobazlı değildir, ayrıca bu katkı maddelerinin gıda ile temas kısmında bazı soru işaretleri bulunmaktadır. Bu çalışmada biyolojik olarak parçalanabilirliğini ve biyo yapısını korumak için antimikrobiyal etkiye sahip doğal nar kabuğu (POP) tozu kullanılmıştır.

PLA ile farklı oranlarda (%5, %10, %15, %20) POP tozu karıştırılarak ekstrüzyon yöntemiyle kompozit malzemeler üretilmiştir. Ekstrüzyonda farklı POP tozu oranına sahip numune üretiminde 400-500-600 rpm vida dönüş hızları kullanılarak karakterizasyon parametreleri üzerine etkileri araştırılmıştır. POP tozu takviyeli PLA kompozitlerle ilgili literatürdeki çalışma sayısı az olup hepsi solvent döküm yöntemi ile üretilmiştir. Bu yöntem, kullanılan solvent miktarı ve sonrasında bu solventin uzaklaştırılması için gereken ısı miktarından ötürü pahalı ve seri üretimde kullanılmayan bir yöntemdir.. POP tozunun PLA'nın içine doğrudan katılarak seri üretime uygun ekstrüzyon yöntemi ile üretilmesi çalışmanın özgün yönünü oluşturmaktadır.

Tez çalışmasında üretilen kompozit malzemelerin karakterizasyonu mekanik, termal ve antimikrobiyellik olarak üç grup olarak özetlenebilir. Termal karakterizasyon için DSC (Diferansiyel Taramalı Kalorimetri), TGA (Termogravimetrik Analiz) ve TMA (Termomekanik Analiz) yöntemleri kullanılırken, mekanik karakterizasyon için çekme, eğilme ve dayanım testleri yapılmıştır. Antimikrobiyellik testleri ile PLA ve kompozitlerinin Staphylococcus aureus (S.aureus) ve Escherichia coli (E.coli)'ye karşı inhibisyon yüzdesi hesaplanmıştır.

Elde edilen sonuçlara göre atık olarak ziyan edilen POP tozu iyi bir takviye malzemesi olarak pek çok alanda kullanılabilir. Daha düşük POP tozu konsantrasyonlarında daha iyi antimikrobiyal performansın elde edilmesi ve mekanik dayanımının arttırılması daha ileri projelerin kapsamı olabilir.

Anahtar Kelimeler: Kompozit, PLA, antimikrobiyal, nar kabuğu, gıda paketi, dikiş ipi

ABSTRACT

DEVELOPMENT AND CHARACTERIZATION OF POLYLACTIC ACID BASED COMPOSITE MATERIALS WITH ANTIMICROBIAL PROPERTIES

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Polylactic acid (PLA), which is called green polymer and has compostable/biodegradable property, has been the subject of many academic studies in recent years. It has the largest share in the global biodegradable polymer production capacity, own to its wide range of applications, cheap access to raw materials and excellent production know-how, by gaining a place in medical and food applications, especially due to its biocompatible and degradable properties. Antimicrobial substances have been used in health, heating and ventilation systems, packaging, and automotive etc. sectors in recent years by adding them to polymers and coatings to prevent the presence and survival of microbes. Composites formed with materials (silver - zinc oxide, silver-derived inorganic zeomic, titanium dioxide, etc.) commonly used in the plastics with antimicrobial activity, especially in PLA. And these additives are not biobased besides there are some question marks on food contact side of these additives. In order to preserve its biodegradability and biobased formulation natural additive pomegranate peel (POP) powder with antimicrobial effect was used in this study.

Composite materials were produced by extrusion method by mixing PLA and POP powder at different weight fractions w/w (5%, 10%, 15%, 20%). The effects on the characterization parameters were investigated by using different screw rotation speeds of 400-500-600 rpm in the production of each samples have different POP powder concentrations in extrusion. The number of studies in the literature on PLA composites reinforced with POP powder is few, and all of them were produced by solvent casting method. This method is an expensive method that is not used in mass production due to the amount of solvent used and the amount of heat required to remove this solvent afterwards. The production of POP powder by directly adding it into PLA by extrusion method suitable for mass production constitutes the original aspect of the study.

The characterization of the composite materials produced in the thesis study can be summarized in three groups as mechanical, thermal and antimicrobial. While DSC (Differential Scanning Calorimetry), TGA (Thermogravimetric Analysis) and TMA (Thermomechanical Analysis) analyzes were used for thermal characterization, on the other hand tensile, bending and impact tests were performed for mechanical characterization. The percent inhibition of PLA and its composites against Staphylococcus aureus (S.aureus) and Escherichia coli (E.coli) was calculated by antimicrobial tests to evaluate the antimicrobial activity of POP powder.

According to the results obtained, POP powder, which is waste, can be used as a good reinforcement material in many areas. Achieving better antimicrobial performance at lower POP powder concentrations and increasing mechanical strength of POP powder loaded composites can be the scope of further projects.

Keywords: Composite, PLA, antimicrobial, pomegranate peel, food packaging, sewing thread

ÖNSÖZ

Polietilen (PE), polipropilen (PP), polistiren (PS) ve poli tereftalat (PET), dünya çapında ciddi çevre sorunlarına neden olan, biyolojik olarak parçalanamayan petrol bazlı ticari polimerlerdir. Yaygın olarak kullanılan bu plastikleri geri dönüştürmek ve çöplük atıklarını azaltmak için yapılan büyük girişimlere rağmen, birçok paydaş içermesinden dolayı sürecin karmaşık ve maliyetli olması geridönüşümü istenilen noktaya gelmesini engellemiştir. Özellikle ülkemizde ‘0 Atık’ projesi yeni uygulanmaya başlanmış ve proje kültür olarak daha yerleşememiştir. Birçok ülkede geridönüşüm için ayrışım merkezi ve teknolojisi de yer almamaktadır. Sonuç olarak, geri dönüşümün yetersizliğinden ötürü doğada zararlı veya toksik kalıntı bırakmadan ayrışan yenilenebilir kaynaklardan üretilen alternatifler araştırılmaktadır. Onlarca yıllık araştırmaların sonucunda çeşitli özelliklere sahip biyolojik olarak parçalanabilen birçok polimer keşfedilmiştir. PLA yaygın olarak kullanılan yeşil polimerlerden biri yukarıda özetlenen faydaları nedeniyle bu tez kapsamında seçilmiştir. Bu polimerlere antimikrobiyellik, mekanik dayanım arttırılması gibi fonksiyonellik kazandırmak amacıyla kullanılan sentetik katkılar bu plastiklerin degredasyonunu kötü yönde etkilemektedir. Bu tezde seçilen nar kabuğu tozu, Türkiye’de bolca üretilen ve nar meyvesinin 2/3’ünü oluşturan bir atıktır. Bu değerli atığın takviye malzemesi olarak değerlendirilmesi sürdürülebilirliğe ve mikroplastik oluşumunun azaltılmasına katkı sağlayacaktır.

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NOMENCLATURE

Symbol	Explanation
D	Diameter of Screws
L	Length of Screws
°C	Celcius
M_n	Molecular Number
M_w	Molecular Weight
ΔH_m	Entalphy of Melting, J/g
ΔH_c	Entalphy of Crystalization, J/g
T_m	Melting Temperature, ºC
T_g	Glass Transition Temperature, ºC
T_c	Crystallization Temperature, ºC
X_c	Crystallinity, %
ΔHm°	Melting entalphy of 100 % crystalline polymer, J/g
P_{PLA}	Weight fraction of polylactic acid in the composite
N_1	Number of bacteria before the addition of the sample
N_2	Number of bacteria recovered after contact to the sample
w/w	Weigth to weight percentage

NOMENCLATURE (Continoued)

Abbreviations	Explanation
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PET	Polyterephthalate
PLA	Polylactic acid
POP	Pomegranate peel
SCM	Solvent casting method
LA	Lactic acid
HDPE	High density polyethylene
PA6	Polyamide
PLLA	Isomer of PLA, poly(L-lactic acid)
PDLA	Isomer of PLA, poly(D-lactic acid)
PDLLA	Isomer of PLA, poly(DL-lactic acid)
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
HDT	Heat distortion temperature

NOMENCLATURE (Continoued)

Abbreviations	Explanation
TMA	Thermomechanical analyses
CTE	Thermal expansion coefficients
C.R	Compression ratio of extruder
CFU	Colony forming unit
S.Aureus	Staphylococcus aureus
E.Coli	Escherichia coli

1. INTRODUCTION

In this study, polylactic acid is filled with pomegranate peel powder (POP powder) which is a natural antimicrobial additive.

Polyethylene (PE), polypropylene (PP), polystyrene (PS), and poly terephthalate (PET) are non-biodegradable petroleum-based commercial polymers that have produced severe environmental issues around the world. Despite massive attempts to recycle commodity plastics and decrease landfill waste, it is still not cost-effective. As a result, alternatives that are manufactured from renewable resources that decompose in nature without leaving harmful or toxic residues are being investigated. Many biodegradable polymers with various characteristics have been discovered as a result of decades of research. PLA is widely used one of the green polymer is chose as a scope of this thesis due to its benefits summarized above.

Engineering plastics have been developed using a variety of organic and inorganic compounds with antibacterial characteristics. Organic acids, bacteriocins, plant extracts, natural polymers, enzymes, nanoclays, and metallic oxides are among the most common. Various antimicrobial compounds, such as silver, copper, zinc oxide, and zinc rod, have been studied in order to generate starch-based antimicrobial products. However, due to their toxicological impacts on human health and environmental conditions, many compounds are not commercially viable. In the EU, for example, commercial usage of silver nanoparticles is prohibited (Ali et al., 2019).

On the other hand demand to antimicrobial plastics is growing in day today. Antimicrobial compounds derived from natural sources are becoming increasingly popular in food preservation and the development of antimicrobial food packaging materials. Because of their antibacterial action and safety, natural antimicrobial compounds such as essential oils, spice extracts, and fruit extracts have recently sparked a lot of attention. However, because the processing temperature of most biodegradable polymers (150–200 °C) is higher than the decomposition temperature of naturally occurring active compounds (100 °C). Hence most natural antimicrobial compounds are not proper for commercial applications due to their low decomposition temperature and high prices. Because of that problem in many researches solvent casting method (SCM) is used for preparing natural sourced filled green polymers' composites. But in industrial scale using of SCM method is not applicable high amount of solvent usage. It requires extra process for eliminating solvent means cost up. In our investigation extrusion method is used which is the most common method for plastic part manufacturing.

To prevent decomposition of natural sourced active compound during processing, other methods such as plasticization of polymers, microencapsulation or development of inclusion complexes and nanocomposites are tried. However, similar techniques have not found commercial success because to high processing costs (for example, microencapsulation), safety concerns (for example, nanocomposites), or the migration of packing materials (for example, plasticized polymers). In this context, commercial applications will benefit greatly from the development of low-cost natural based green polymers.

In this study production and characterization of commercial, low-costed and eco-friendly pomegranate peel powder filled PLA composites is aimed due to problems mentioned above.

Pomegranate peel has been demonstrated to have antimicrobial properties. However, there is no proof that pomegranate peel can be employed as a filler in antimicrobial films made from starch, The poor mechanical properties of starch-based films, as well as their high water affinity, are well-known drawbacks. It has been combined with various mineral or natural fillers to improve the mechanical qualities of starch-based films. Biocompatibility and biodegradability are exceptional advantages of starch-based films reinforced with natural fillers for packaging, agricultural, medical and pharmaceutical applications.

By transferring matrix stress to the filler, these fillers operate as a reinforcing agent and improve the mechanical properties of the matrix. Pomegranate peel (POP) was used as a functionalized filler in a starch matrix in this study. POP's influence on the microstructure, mechanical, thermal, and antibacterial properties of starch-based films was studied. The new material has a lot of potential in the food industry as edible and antibacterial packaging, in the medical areas as suture, covering of some devices etc.

2. LITERATURE REVIEW

2.1 Polylactic Acid (PLA)

Conventional plastics' (polypropylene, polyethylene, polyamide, polyethylene terephthalate etc.) wastes take over long time to be broken down into harmless substances compared with organic material which is called as degradability of biomass. So background of biodegradable polymers is started with environmental concerns, As a result, petroleum based polymers can be partially degraded by bacteria, but the leftover from biomass, known as polymer skeleton, has the opposite effect on the environment, such as being toxic (Doppalapudi et al., 2014).

There are now three primary methods for dealing with plastic waste: landfill disposal, incineration, and recycling. Recycling process, on the other hand, are relatively expensive and ineffective, whereas landfill and incineration are sources of secondary environmental pollutants and result in the formation of a number of hazardous compounds, the majority of which are released into the atmosphere. As a result, biodegradation offers a compelling alternative to present waste disposal procedures, as it is generally a less expensive, potentially more efficient process that does not produce secondary pollutants like those associated with incineration and landfill (Jafarzadeh et al., 2020). Therefore the demand for biodegradable polymers is increasing day to day.

Biodegradable polymers can be generally categorized according to their source that made. They can be sourced from biomass, microorganisms, biotechnology and petroleum. Classification is explained at Figure 2.1.

Except petroleum based biodegradable polymers are composed from renewable sources, so their significance is major for environment due to running out of petroleum. That thesis focuses on PLA that has the largest share in production as a renewable sourced and biodegradable polymer.

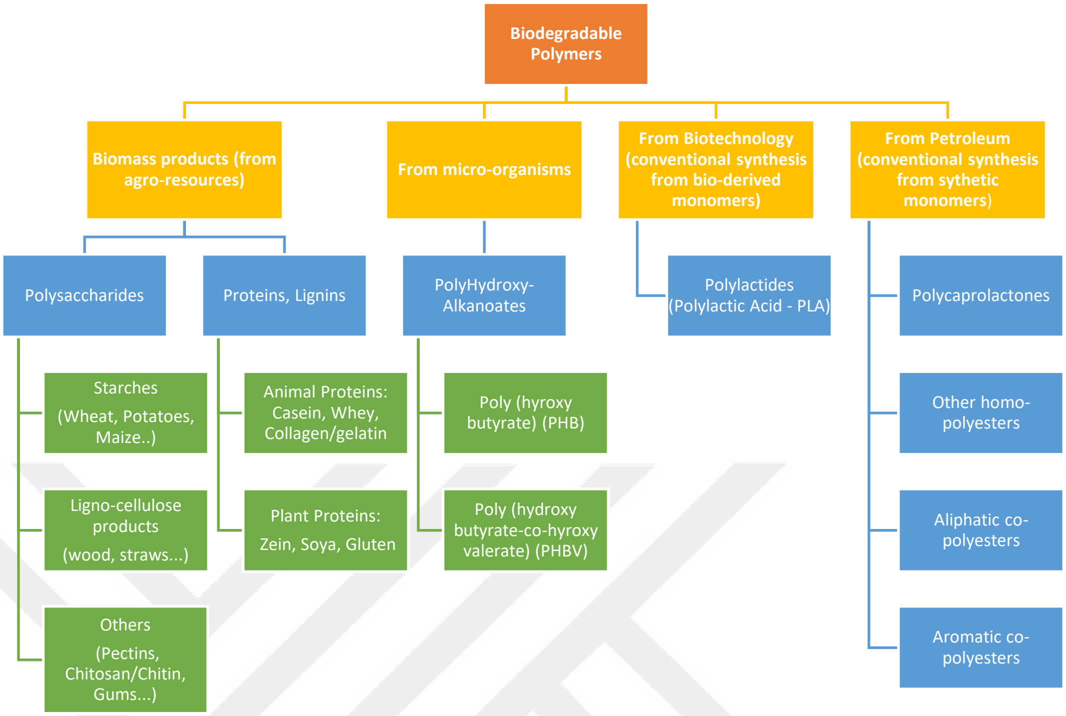


Figure 2.1. Classification of biodegradable polymers (Avérous et al., 2012)

2.1.1 Properties of PLA

2.1.1.1 General Properties

Polylactic acid (PLA) is a biodegradable, biocompatible and aliphatic thermoplastic polymer which is produced from lactic acid (LA). Source of LA is commonly based on plants and animals as a by-product or intermediate product of metabolism (Hagen, 2012).

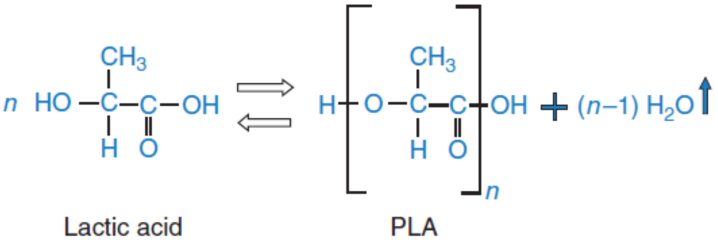
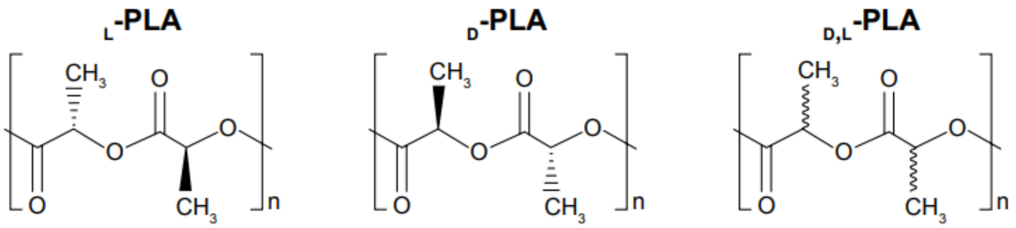


Figure 2.2. Polylactic acid from lactic acid (Hagen, 2012)

There are two stereoisomers of PLA; designated as D and L, and racemic combination of them as DL (Figure 2.3). Structure of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) exist as semicrystalline, whereas structure of poly (DL-lactic acid) (PDLLA) exists as amorphous. PDLLA has been using as a coating for medical due to its biocompatibility and high mechanical stability. Additionally, PDLLA has a low molecular weight that leads to make it proper for drug systems (Sin et al., 2019).



Figuer 2.3. Structure of PLA’s isomers; PLLA, PDLA and PDLLA

respectively (Song et al., 2018).

PLA is derived from renewable sources such as corn starch, potato starch, and sugar beets. There is no fossil raw material in its content. So it is called biobased/bioplastic (Song et al., 2018). PLA are also recognized as a solution to environmental concerns due to its biobased and low CO_2 emissions during production (Figure 2.4). Plastic manufacture requires the usage of fossil fuels as an energy source. Energy requirement for PLA production is less than energy requirement for production petroleum based polymers such as polyamide (PA6), high density polyethylene (HDPE), polyethylene terephthalate (PET). Besides fossil raw materials are input for PA6, HDPE and PET production. It leads to greater total fossil energy requirement for petroleum based polymers (Figure 2.5).

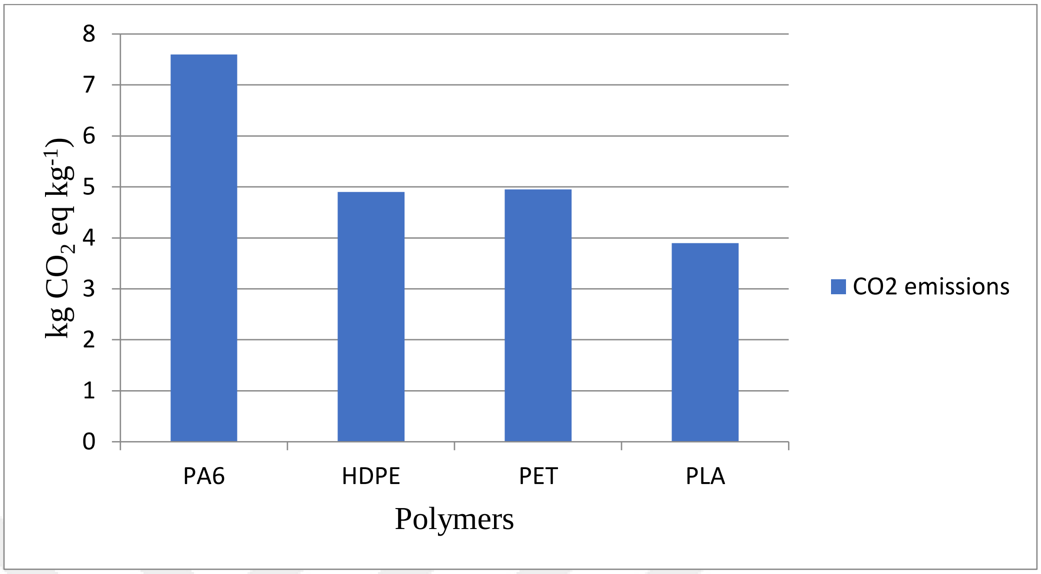


Figure 2.4. CO$_2$ emissions by PLA vs. petroleum based polymers ‘cradle to gate’ (Hagen, 2012).

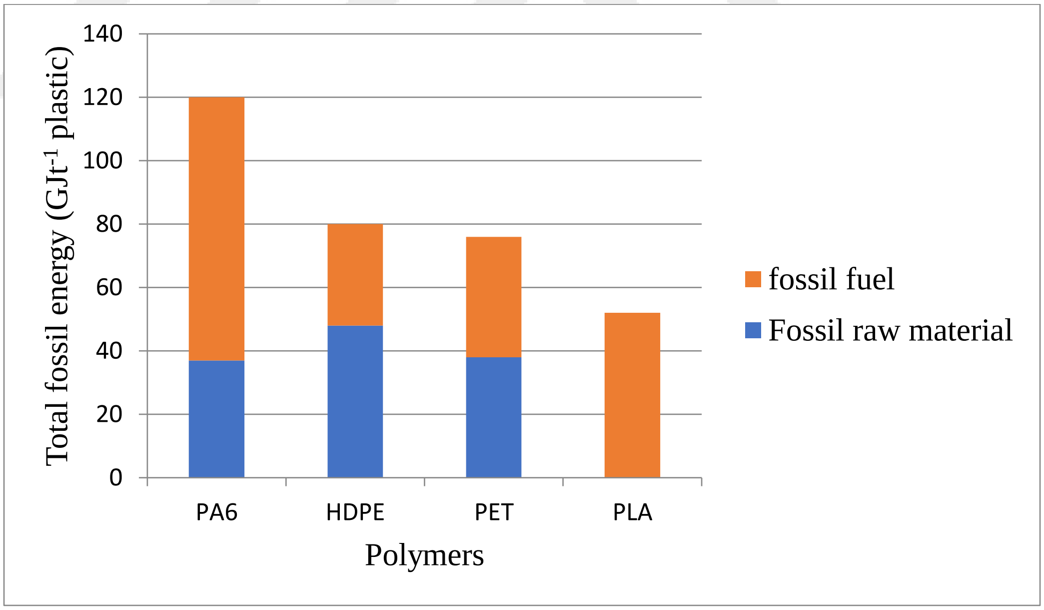


Figure 2.5. Consumption of fossil resources by PLA vs. petroleum based polymers ‘cradle to gate’ (Hagen, 2012).

2.1.1.2 Mechanical Properties

For mechanical properties of PLA, it can be mentioned as range. Since mechanical properties of PLA vary, ranging from soft, elastic materials to stiff, high-strength materials by the reason of parameters that affect. These parameters are polymer structure, molecular weight, crystallinity, material formulation (additives during production, blends, etc.) and orientation. For example crystallinity regarding polymer structure affects tensile strength and stiffness of the polymer.

Structure of polymers can be divided in two categories as: semicrystalline and amorphous. Semicrystalline polymers contain dense regions formed by folding crystallites, which are regular repeating units. These act as crosslinks lead to higher tensile strengths and higher modulus (stiffness) as compared to an amorphous structure. Semicrystalline polymers still have amorphous portions, hence any polymer cannot be totally arranged into a fully crystalline structure. Effects of stereochemistry and crystallinity on mechanical properties is listed at Table 2.3. PLLA, annealed PLLA, and PDLA are compared. After annealing, it is seen that tensile strength increases due to stereo regularity of the chain, likewise impact resistance is increased due to the crosslinking effects of the crystalline structure.

PLA is a brittle polymer like polystyrene (PS) due to low impact strength and low elongation at break. However, its tensile modulus and strength are close to polyethylene terephthalate (PET) and better than PS. Average values of tensile strength, young’s modulus, elongation at break end notched izod for that three polymers mentioned above are listed at Table 2.1. The main problem is PLA has poor toughness leads to plastic deformation at low stresses. For enhancing toughness of PLA, many modifications are applied (Sin et al., 2019).

Table 2.1. Comparison of Poly(L-Lactide) (PLLA) With Polystyrene (PS) and Polyethylene Terephthalate (PET) (Sin et al., 2019)

Materials	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)	Notched Izod (J/m)
PLLA	59	3.8	4 - 7	26
PS	45	3.2	3	21
PET	57	2.8 – 4.1	300	59

Table 2.2. Mechanical properties of a commercial amorphous PLA, injection mold grade (96:4 L:D ratio content produced by NatureWorks Co.) (Farah et al., 2016)

Property	Unit	Value
Tensile Strength	Mpa	59
Elognation at break	%	7
Elastic Modulus	Mpa	3500
Shear Modulus	MPa	1287
Poisson's ratio	-	0.36
Yield strength	MPa	0.70
Flexural strength	MPa	106
Unnotched izod	J/m	195
Notch izod impact	J/m	26
Rocwell hardness	HR	88
Ultimate tensile strength	MPa	73
Percent of elognation	%	11.3
Youngs'modulus	MPa	1280

Table 2.3. Mechanical characteristics as a function of stereochemistry and crystallinity (Farah et al., 2016)

Properties	**Unit**	**PLLA**	**Annealed PLLA**	**PDLA**
Tensile Strength	MPa	59	66	44
Elognation at break	%	7	4	5.4
Modulus of elasticity	MPa	3750	4150	3900
Yield strength	MPa	70	70	53
Flexural strength	MPa	106	119	88
Unnotched izod	J/m	195	350	150
Notch izod impact	J/m	26	66	18
Rocwell hardness	HR	88	88	76

2.1.1.3 Thermal Properties

Thermal properties such melting point (T_m), glass transition temperature (T_g), and crystallization temperature (T_c) are varied according to polymer molecular weight, polymerization conditions, thermal history, purity, etc (Sin et al., 2019).

Understanding of thermal properties of PLA requires quantitative thermal analysis with measuring devices such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis.

Isomers of PLA have different thermal properties, for instance PDLA and PDLA have semicrystalline structure with Tm about 180°C. Other isomer PDLLA is an amorphous material with Tm about 160°C (Sin et al., 2019). Effect of isomers, accordingly molecular number (M_n) and molecular weight (M_w) onto thermal properties are briefly explained at Table 2.2.

Table 2.4. Thermal properties of PLA regarding isomers (Sin et al., 2019)

Isomer Type	**Mn×10^3**	**M_w/M_n**	**T_g (°C)**	**T_m (°C)**	**ΔH_m (J/g)**	**T_c (°C)**	**ΔH_c (J/g)**
L	4.7	1.09	45.6	157.8	55.5	98.3	47.8
DL	4.3	1.90	44.7	-	-	-	-
L	7.0	1.09	67.9	159.9	58.8	108.3	48.3
DL	7.3	1.16	44.1	-	-	-	-
D	13.8	1.19	65.7	170.3	67.0	107.6	52.4
L	14.0	1.12	66.8	173.3	61.0	110.3	48.1
D	16.5	1.20	69.1	173.5	64.6	109.0	51.6
L	16.8	1.32	58.6	173.4	61.4	105.0	38.1

It is obvious that semi-crystalline PLA(L,D) has a larger T_g than amorphous PLA(DL) at roughly the same Mn. Additionally, higher T_g is observed at higher Mn. However, the melting and crystallization of copolymers of Detaching Tm and Tc of PDLLA are not possible even at high molecular weight. The reason of it, microstructure rearranges during cooling down and that microstructure is effected by the formation of an atactic structure (Ahmed et al., 2008).

Tg is a very important thermal property for polymers. Under Tg, polymer is so brittle because it is frozen, glass state. The softness of polymer above Tg is referred to as rubbery like. Molding of polymer is occurred at temperature above Tm, processing (cutting, reshaping, rolling etc.) of polymer is occurred at temperature between Tg and Tm. That’s why 200-210°C temperature range is set to ensure the melting of all crystalline phases during extrusion (Sin et al., 2019).

2.1.1.4 Physical Properties

For desired product some information must know such as dimensions, size and weight requirement, so physical properties are very important. If the material will be used by surgeon, it is so significant to material be light enough to handle. Also density is important for transportation cost.

Table 2.5. Physical properties of a commercial amorphous PLA, injection mold grade (96:4 L:D ratio content produced by NatureWorks Co.) (Farah et al., 2016)

Characteristics	**Unit**	**Amount**
M_w	g/mol	66000
Specific gravity	-	1.27
Solid density	g/cm^3	1.252
Melt density	g/cm^3	1.073
T_g	℃	55
T_m	℃	165
Specific heat (Cp)		
190 ℃	J/kg℃	2060
100 ℃		1955
55 ℃		1590
Thermal conductivity		
190 ℃	W/m℃	0.195
100 ℃		0.197
48 ℃		0.111

2.1.2 Degradation and Stability of PLA

Degradation is a kind of depolymerisation process. This process converts polymers to small molecular weight fragments that lead to further degradation to carbon dioxide and water. PLA is a completely degradable material (Figure 2.6) and the method to polymerize lactic acid during formation of PLA is not a significant parameter for degradation of PLA. Hence ester bond between lactic acid can be broken under many conditions, there are many ways for PLA degradation such as hydrolysis degradation, microorganism degradation and UV (ultra-violet) degradation (Yu et al., 2020).

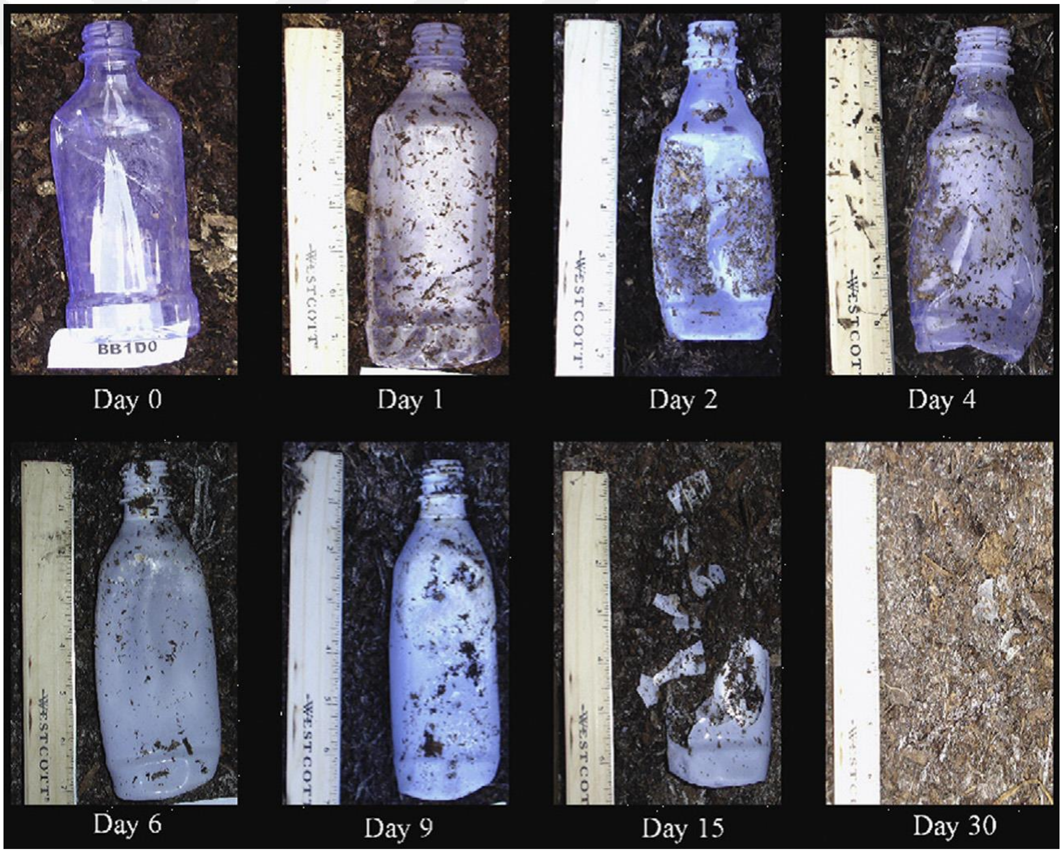


Figure 2.6. Biodegradability of PLA bottles in real and simulated composting conditions. (Sin et al., 2019) p.247

Biodegradation of polymers such as PLA, PCL and PHB occurs in the presence of enzymes by some microorganisms. These enzymes attack polymer chain’s main functional chain and end groups, and oxidise or hydrolyse them. After that process, long polymer chain converts to carbon dioxide and water. Many methods can be used to measure the biodegradation of biopolymers, such as the consumption of oxygen, weight losses, biogas generation, and carbon dioxide production (Miraftab, 2016).

Table 2.6. Degradation Time of Biopolymers (Sin et al., 2019) pp.231

Polymer Type	**Approximate Degradation Time (Months)**
Polylactide (PLA)	12
Polyglycolide (PGA)	>24
Polycaprolactone (PCL)	>24

PLA has a shorter half life than PGA and PCL, as seen in Table 2.6. Its excellent biodegradability and biocompatibility properties mean that it has wide applications comparing with other biodegradable polymers.

Material properties such as stereocomplexity, weight and crystallinity affect the biodegradation characteristics of PLA. Besides external conditions (moisture, sunlight, temperature, presence of a solvent, and oxygen supply) are also significant parameters on influence biodegradation rate of PLA.

From the stand point of the crystallinity property of PLA, higher crystallinity and molecular stereoregularity are less likely it is to degrade. Because the hydrolytic degradation process starts from amorphous to crystalline region. Reason of that water molecules easily diffuse into amorphous regions, and these regions are also easily assimilated by microorganisms. It means how amorphous region is larger, it makes to degrade PLA easier. At Table 2.7 rates of hydrolysis of PLLA, PDLA, PDLLA are summarized. It is seen that amorphous PDLLA has higher rate than semi-crystalline PLLA and PDLA due to mechanisms explained above.

Table 2.7. Rate of Hydrolysis of PLLA, PDLA, PDLLA (Sin et al., 2019) p.238

Polymer Type	**Value *k***
Homopolymer PLLA	$3.49\times10^{-3}\text{day}^{-1}$
Homopolymer PDLA	$3.88\times10^{-3}\text{day}^{-1}$
Copolymer PDLLA	$7.22\times10^{-3}\text{day}^{-1}$

Temperature is the most important factor for degradation. If the temperature is higher than the glass transition temperature (T_g), degradation rate of PLA will be considerably increased. Because flexibility of the polymer chain is increases due to higher temperature. As a result, PLA enables the hydrolysis reaction and the adhesion of microbes/enzymes much easier. At the temperature higher than melting temperature (T_m), degradation mechanism of PLA will change, and the PLA crystal zone melts and disappears, and homogeneous hydrolysis easily occurs in the molten zone. (Yu et al., 2020)

In literature biodegradation performance of PLA is investigated under different environmental conditions; wastewater treatment, landfill, composting plant, and controlled composting conditions. According to research, noticeable white marks on PLA sheets are occurred after 1 month, in wastewater. But, degradation rate is found as higher under composting plant conditions (50℃-60℃ and with 60% relative humidity) as expected (Rudeekit et al., 2008). Hence, the temperature of composting plant is higher than the temperature of wastewater and Tg of PLA leads to chain movement and water diffusion. After 8 days, PLA sheets became brittle and divided into small pieces. The PLA sheets were buried at 1 m depth from the landfill surface, the results are more promising than wastewater treatment. It last 6 months for fragmentation, and 15 months for disappearance accruing. On the contrary, it last only 30 days for disappearance accruing under composting plant conditions. To summarize, PLA degradability is linked to the hydrolysis and cleavage of ester links in the polymer backbone, resulting in the formation of oligomers (Rudeekit et al., 2008).

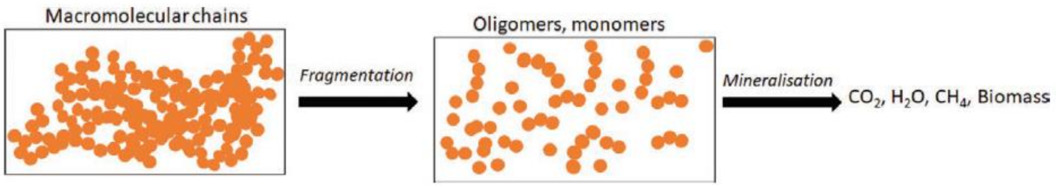


Figure 2.7. Two-step process of biodegradation; first step is fragmentation and the second step is the mineralization by microorganisms. (Agarwal, 2020)

2.1.3 Market Potentials and Application Areas of PLA

Many countries have taken steps to address environmental issues, beginning with rules that limit or prohibit the use of non-biodegradable plastics. Major supermarkets have started to sell plastic bags instead of providing them free. Use of plastic bag is banned in China, the largest polymer-consuming country and with a population of 1.3 billion. Own to these actions, at least 37 million barrels of crude oil per year is saved. But humans are aware of that plastics is not entirely avoidable in modern life. So the production of reusable plastics made of a compostable material is recommended, so that disposal will not burden the environment. These regulations and directions are increased for demand of biodegradable plastics.

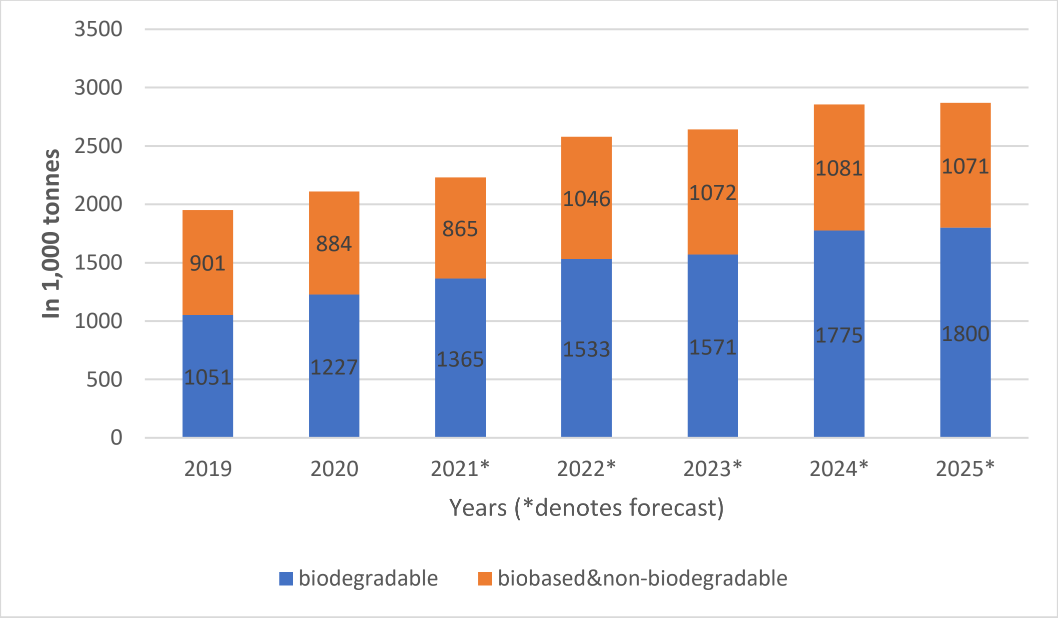


Figure 2.8. Global bioplastic production and forecast from 2019 to 2025 (European Bioplastic, 2020).

Manufacturing capacities for biodegradable plastics (PHA, PLA, starch blends, and others) have reached 60% of total bioplastic production capacities. Also production rates are continuing to rise according to forecast. Own to PHA's considerable growth rates and new researches / investment for PLA production, the production of biodegradable plastics is expected to increase 1.8 million in 2025. (European Bioplastic, 2020).

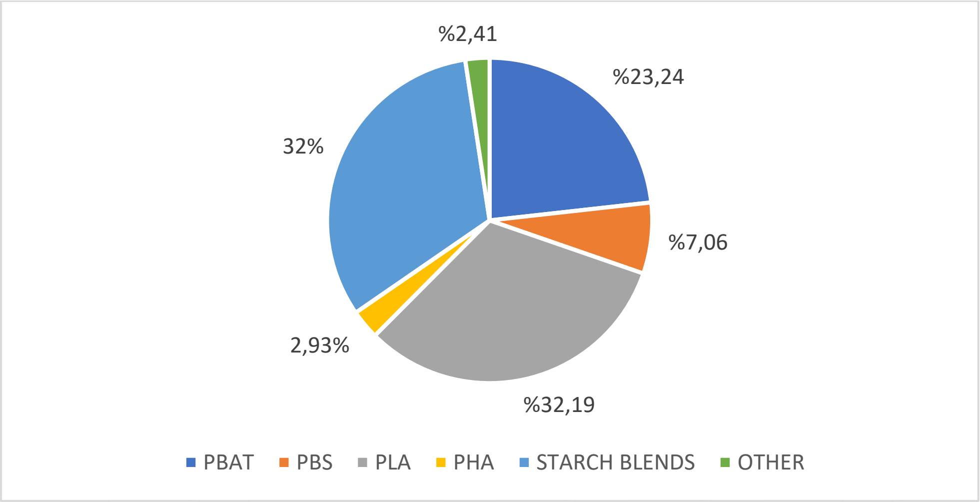


Figure 2.9. Global production capacities (in percentages) of biodegradable polymers by material type (European Bioplastic, 2020).

PLA has the largest proportion of global biodegradable polymer manufacturing capacities, as shown in Figure 2.9, because to its extensive application area (Figure 2.10), easy raw material availability, and strong production know-how.

Figure 2.10 Application Areas of PLA

Table 2.8. Commercial Applications of PLA (Sin et al., 2013)

APPLICATION	MANUFACTURER /PRODUCT	PICTURE
TEXTILE	Mill Direct Apparel is a brand of clothing made (jackets, caps, polo shirts) Codiceasbarre is used to shirts Gattinoni is used for wedding dresses Descente is used for sportswear	  
BOTTLES	Shiseido-Urara is a Japanese cosmetics company , that used PLA in shampoo bottles LAS Polenghi uses lemon juice bottles Sant'Anna is a Italien manufacturer that uses PLA for mineral water bottles	 
AUTOMOTIVES	Toyota is a Japanese automobile manufacturer (floor mat of Toyota Prius and spare tire cover) Toray is a Japanese word that means to (fiber for car mat)	 
SURGIAL IMPLANTS	Zimmer (Bio -Statak® suture anchor and bone cement plug) Ethicon (Vicryl suture and Vicryl mesh) Sulzer (Sysorb® screw)	  
DRUG CARRIER	Abbott (Lupron Depot® for palliative treatment of advanced prostate cancer) AstraZeneca UK Limited (Zoladex, an injectable hormo®al treatment for men with certain types of prostate cancer) Janssen Pharmaceuticals (Risperdal® Consta®, for treatment of schizophrenia and for the long-term treatment of bipolar I disorder)	 

PLGA (polylactide-co-glycolide) is a copolymer of PLA, and PLGA is a biocompatible like PLA. But biocomtibilty of PLA ia limited to L stereoisomer (PLLA) because the enzyme that breaks the PLLA is produced only mammalian metabolism. Hence other isomers of PLA and PLGA are commanly used in screws, pins, scaffolds, etc (Sin et al., 2013). They stand for a while in body to allow tissue growth and after a certain period they degrade naturally in the body. Controlling the rate of degradation by the way of modification of crystallization is the reason of copolymerizing with glycolide. PLA is also used for artificial bones, joints and in decades it is used for surgical suture for decades. Other usage are of PLA is drug carrying. PLA has a high crystall structure that leads to longer degradation time which is not a proper mechanism for active drugs (for treatment of cancer and fibroids) . Hence PLA drug carriers are existed in the copolymer form on the market, and commonly copolymerized with polyglycolic acid (PGA) (Sin et al., 2013).

2.1.4 Processing of PLA

PLA processing is basicly based on thermal treatment that is starting with melting PLA at melting temperature. In that step, material can be shaped as desired. The final process, cooling, secures the product's size. Physical properties are significant to enhance the production performance, hence they influence its behavior (crystallinityi rheology, etc.). Own to PLA’s hygroscopicity property, it is easily effected by humidity and temperature. In that reason, drying (reaching a water content less than 0.01% w/w) must be done carefully to avoid hydrolysis and the relative molecular weight lowering. That’s why drying process must be applied as a first step before melting process through melt extrusion technique (Barletta et al.,2020).

Processing methods of PLA can be categorized as; extrusion, injection molding, injection stretch blow molding, cast film, 3D printing and sheet and thermoforming. Extrusion is the most widely used method and in that thesis that process will be used (Barletta et al.,2020).

Extrusion is a melting and compounding process before the shaping processes (blow molding, injection molding, thermoforming, etc). There are three main steps of the extrusion process of PLA; continous melting of PLA, conveying and discharging of PLA compound thruouh die (Barletta et al.,2020).

There is a screw in extruder that rotates along the barrel continously, that is why it is called infinite screw. General components of the extruder is shown at Figure 2.11.

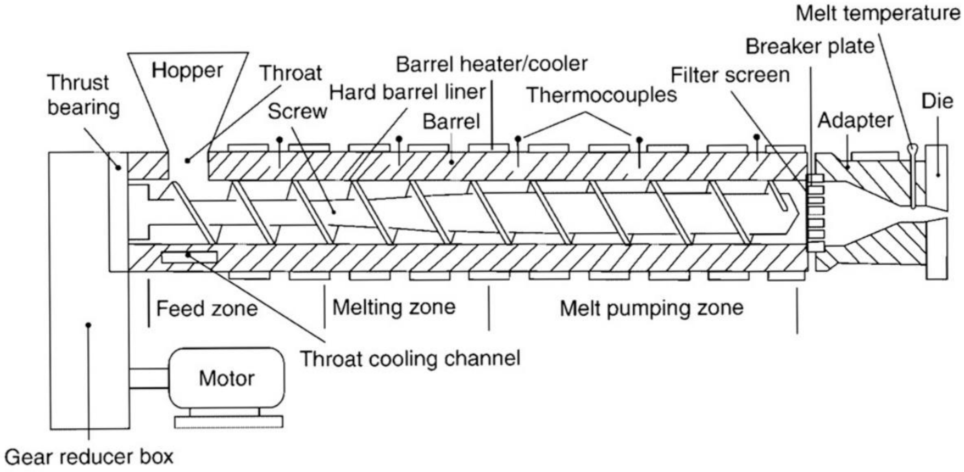


Figure 2.11. General components of the extruder (Barletta et al.,2020)

- The gearbox rotates the **screw** as it slides down the extruder barrel. The gearbox is rotated directly by the DC or AC drive motor coupled via pulleys.

- **A throat** section connected to the gearbox. The vertical channel between the hopper and the barrel is known as the feed throat.

- **Gear reducer** box with a constant reduction ratio of 4: 1–25: 1 depending on the desired application.

- **Hopper** is over the opening in the feed end of the bucket. Material entry into the barrel is made from this feeding chamber.

- **A main control panel** containing all necessary electronic controls for temperature, process monitoring, recording and motor controls.

A typical screw extruder is divided into three main sections which are the feed section, transition section, and metering section, as shown Figure 2.12.

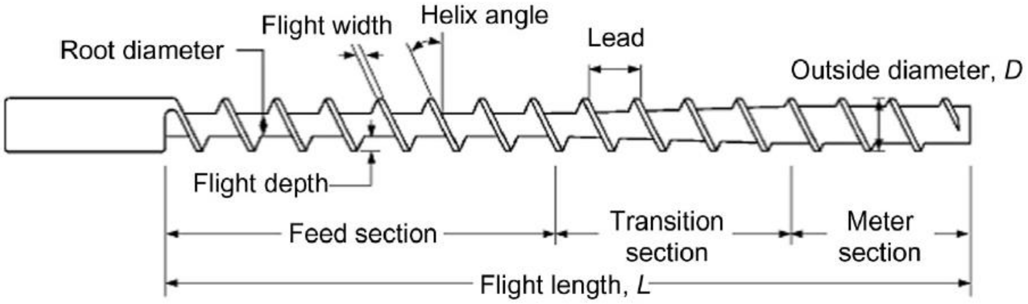


Figure 2.12. Sections of the screw (Sin et al., 2019).

Feed Section, root diameter in the feeding area is constant and the task of this region is to provide proper feeding forward (Sin et al., 2019).

Transition section, the root diameter is getting greater through the section. As a result, the heat transferred from the cylinder is distributed homogeneously due to the reduced material thickness (Sin et al., 2019).

Metering section, It is the region where the material has a homogeneous temperature and pressure distribution due to its constant and greater root diameter (Sin et al., 2019).

The ratio of the screw flight length (L) to the screw outer diameter(D) is called as L/D ratio which is a paramater to see shear and residence time for PLA compound. Greater L/D ratio provides better mixing, shear heating and a longer residence melting time. Another significant term in extrusion is compression ratio (C.R.) which is a ratio flight depth at the feed section (h_f) to the flight depth at the metering section (h_m). It shows us shear heating provided by screw. For example, If greater shear heating is needed for PLA compound, higher C.R. must be designed (Sin et al., 2019).

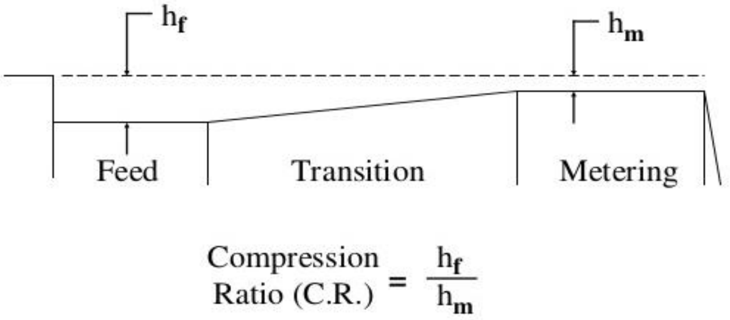


Figure 2.13. Compression ratio definition (Sin et al., 2019)

2.2 Pomegranate Peel (POP)

2.2.1 Properties and Antimicrobial Activity of POP

Pomegranate (Punicagranatum L.) is the fruit which contains outer red hard structure and inner juicy arils. It is one of humanity's first fruits to be cultivated. It can be consumed as fresh or processed (as oil, juice, and vinegar etc.). In today’s world, beside the health benefits of pomegranate fruit, POP is used in many areas. Especially pomegranate production in Turkey is very large, including Antalya, Izmir, Adana and Mersin. Pomegranate cultivation area of the province while also encompasses the southern coast of the country. Also pomegranate; Due to the fact that it is not selective for growing conditions such as development conditions and soil demand, it has started to be grown in larger areas in recent years (Akarca et al., 2019). Pomegranate fruit are reported to reduce the risk of disease due to its rich phenolic content, in recent years, production of is increased five-fold in Turkey (Demir et al.,2019).

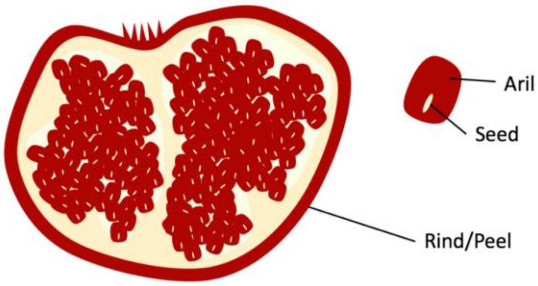


Figure 2.14. Main components of Pomegranate Fruit (Ko et al., 2021)

The arils are comprised 46% w/w of pomegranate which are used as a juice in industry, and residue is considered to be waste. The pomegranate peel (POP) is too valuable to be wasted component and it has 43% w/w mass percentage in the fruit (Ko et al., 2021). POP is one of the most valuable by-product of the food industry due to its content. It is also a waste can be reused as a very valuable additive. 78% of peel is collected during the processing pomegranate juice as a residue (Ali et al., 2018).

Chemical composition of POP is showed at Figure 2.14. POP also is reported as an excellent source of phytochemicals, mainly including phenolic acids, flavonoids, and hydrolysable tannins. Also antioxidant, antimicrobial, anticancer, antiulcer, and anti-inflammatory activities of POP are proved. It has been stated by many studies that pomegranate is rich in phenolic compounds. In studies, it was also found that phenolic substances in the peel were higher than the fruit. It means that POP were more effective than pulp in terms of antioxidant activity (Demir et al., 2019). Also antimicrobial activity of POP is higher than other parts of pomegranate (Chen et al., 2020).

Antimicrobial activity of POP is established against bacterial and fungal pathogens. Pomegranate's antioxidant, antibacterial, and antifungal effects are linked to phytochemicals, particularly total flavonoids (mainly punicalagin), and tannin concentration, as seen in Figure 2.15 (Chen et al., 2020) and Table 2.9. Variability in the concentration of active compounds of pomegranate, including phytochemicals and biological properties important to human health; It varies with the type of fruit, anatomical part, maturity period, extraction type and phenolic extraction type.

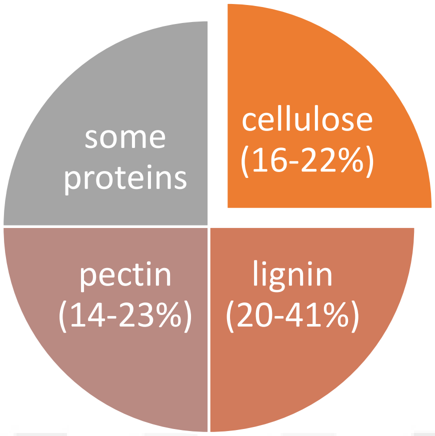


Figure 2.15. Pomegranate peel's composition (Ali et al., 2018)

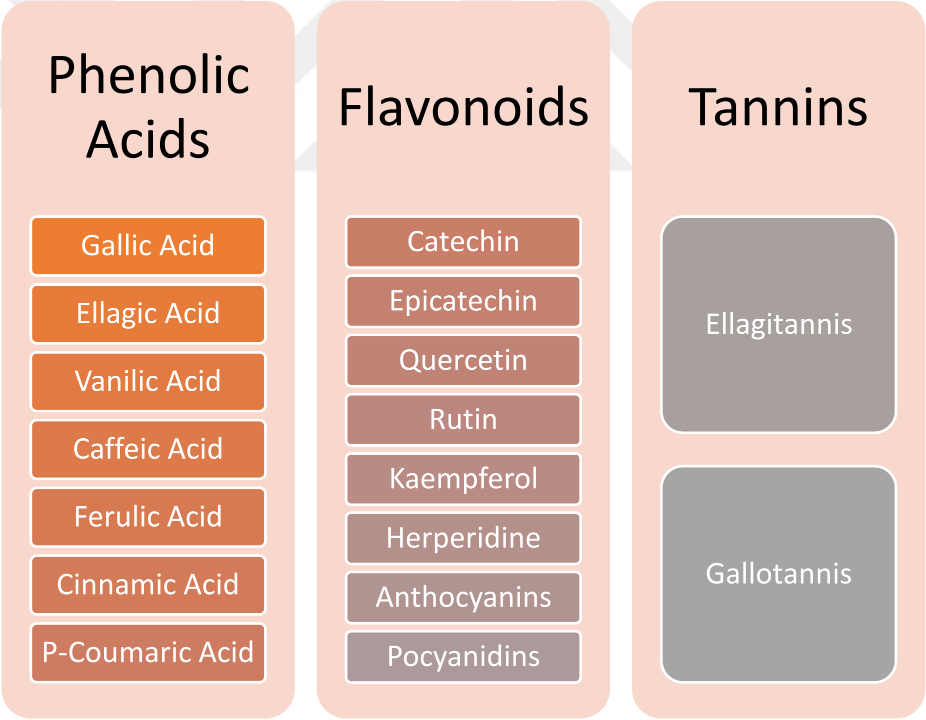


Figure 2.16. Pomegranate peel's phytochemical contents (Gullón et al., 2020)

Table 2.9. Active constituents and their biological activity of POP (Middha et al., 2013)

Compound Bioactivity	**Compound Bioactivity**
Major tannins of pomegranate peel	
Casuarinin	Antiviral, antioxidant
Corilagin	Antihypertensive, antineoplastic
Ellagic acid	Antineoplastic, skin whitening
Gallic acid	Antimutagenic, anti-inflammatory, antiviral, antioxidant
Methyl gallate	Antioxidant
Granatin A	Antioxidant, anti-inflammatory
Granatin B	Antioxidant, anti-inflammatory
Pedunculagin	Antineoplastic, antioxidant
Punicalagin	Antioxidant, antihypertensive, anti-hyperglycemic
Punicalin	Antioxidant, anti HIV, anti-hyperglycemic
Major flavonoids of pomegranate peel	
Catechin	Antineoplastic, antioxidant
Cyanidin	Antioxidant
Epicatechin	Antineoplastic
Epigallocatechin 3-gallate	Antineoplastic
Flavan-3-ol	Antineoplastic
Kaempferol	Antioxidant, anti-inflammatory
Kaempferol-3-0-glucoside	Antioxidant
Kaempferol-3-0-rhamnoglycoside	Antihypertensive
Luteolin	Antioxidant
Luteolin-7-0-glucoside	Antioxidant
Naringin	Antiviral, antibacterial
Pelargonidin	Antiviral, antibacterial
Quercetin	Antiviral, antioxidant, antineoplastic
Rutin	Antiviral, antioxidant, antineoplastic
Major alkaloids of pomegranate peel	
Pelletierine	Antioxidant
Valoneic acid dilactone	Antidiabetic

Antibacterial effects of POP particularly on various foodborne pathogens such as Escherichia coli, Penicillium italicum, Bacillus subtilis and Fusarium sambucinum are approved by researchers due to study results. In one of these extensive studies, the antimicrobial activity of pomegranate parts (peel, seeds, arils, juice and whole fruits) are investigated by extraction of these parts. Tests are carried on seven bacteria (Bacillus coagulans, Bacillus cereus, B. subtilis, Staphylococcus aureus, E. coli, Klebsiella pneumoniae, and Pseudomonas aeruginosa) and maximum inhibitory effect of all bacteria is observed in POP part (Chen et al., 2020).

In another study antimicrobial effect of POP and pomegranate seed extract is investigated on clinical isolates of P. aeruginosa , S. aureus bacteria. According to results the minimum inhibitory concentrations (MICs) of POP and seed extracts were 12.5 and 25.0 mg/mL, respectively. Values indicates that the antibacterial activity of pomegranate seed extract has lower potent effect on P. aeruginosa and S. aureus bacteria compared with POP extract. Also inhibition zones of POP is promising for usage of it in antimicrobial effect (Nozohour et al., 2018)

Antimicrobial effect of POP powder investigated in compostable active films made from fish gelatin. POP powders are carried on with concentrations from 1% to 5% w/w. Bacterial strains (Escherichia coli, Staphylococcus aureus and Listeria monocytes) are used for antimicrobial activity test. According to results no inhibition occurred in control film and 1% POP powder films. Antimicrobial activities are increased at higher concentrations (2% - 5%) significantly. Additionally highest antimicrobial activity is obtained against S. aureus, and in this case the film with 5% POP power with inhibition zone 7.00 mm in diameter. (Hanani et al., 2019)

2.2.2 Application Areas of POP

There are many application areas of pomegranate peels or skin or rind (POP). Due to its exceptionally rich ethnomedical applications, astringent properties (Middha et al., 2013) and other properties is underestimated as an agricultural waste. The application areas of POP can be categorized as food, cosmetic, animal feed, waste water treatment, health and food packaging.

In health category POP is widely used own to its therapeutic effects as shown as Figure 2.17. POP is wide-ranging and include treatment and prevention for cancer, cardiovascular disease, diabetes, dental conditions, and erectile dysfunction, protection from ultraviolet (UV) radiation, and antimicrobial as mention previous chapter. Infant brain ischemia, Alzheimer's illness, male infertility, arthritis, cutaneous wounds, and obesity are all possible applications. For example, POP powder is a form of dietary fiber that can be used as a food additive.

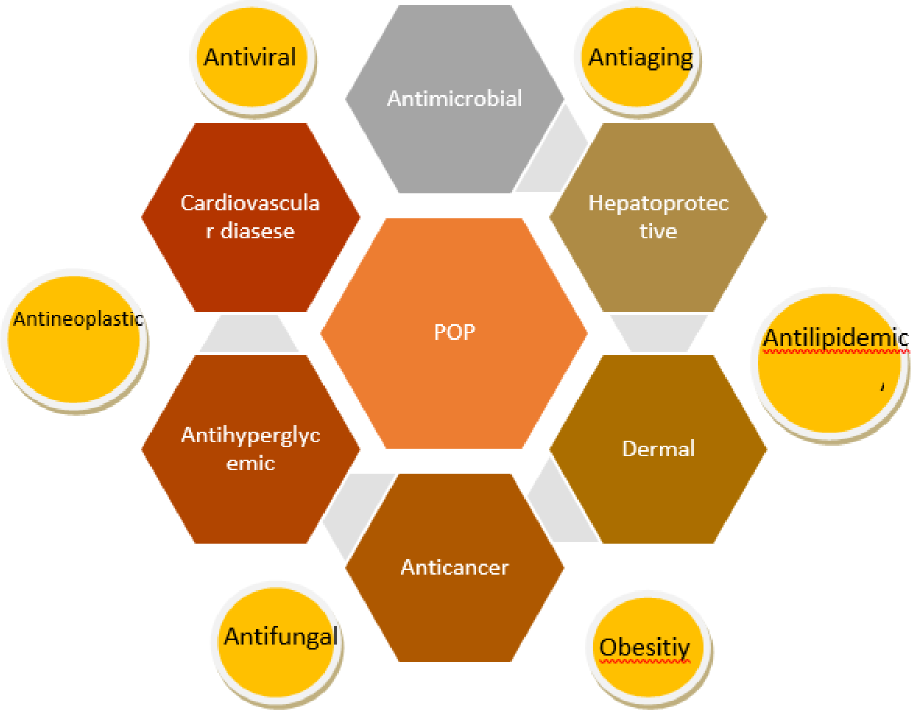


Figure 2.17. Principal therapeutic effects of pomegranate peel (Middha et al., 2013)

POP is used for ecofriendly solutions such as reducing agent in making silver nanoparticles, cattle feed and extraction of natural dyes.

POP is also preferred in food and food packaging industry as food additive, fiber, packaging color and active packaging agent. For example, POP is a good food additive with its antioxidant effct. In food industry oxidation is a huge problem because it leads to deterioration in food’s sensory properties (flavor, odor, texture, and color) and decreases their shelf life. To prevent the oxidation some commercial antioxidants BHT and butylated hydroxyanisole (BHA) are used but they are synthetic and not proper for green label concept (Ko et al., 2021).

Pomegranate rind can be integrated into skin health products own to its ellagic acid and punicalagin content which are both bioactive compounds of POP that promote skin health by inhibiting tyrosinase and initiating anti-inflammatory and anti-fungal effects. Additionaly punicic acid which is highly contented and provides protection and anti-inflammatory characteristics against to UV-induced radiation. Other significant issue in cosmetic sector is decreased skin elasticity that leads to skin wrinkling. The main process for skin elasticity loss is aging-induced glycation, and POP is a natural inhibitor of that process (Ko et al., 2021).

2.2.3 Researches On Antimicrobial Plastics with POP

POP is used in various plastics because of its antibacterial properties. The scope of these thesis is green polymers so researches are limited by in that manner.

In many researches, it is seen that, for processing of polymers with POP SCM method is used. The reason of that technique preferred is low thermal stability of POP due to its organic and volatile structure. Solvent-casting is technique that based on suspended or dissolved in a solution of polymers, plasticizers, and any other substances dissolved in a volatile solvent, such as water or ethanol. To remove the solvents, the coated media is run through a drying apparatus, such as an oven or a convection chamber. These method is not suitable for mass production due to high amount of solvent requirement and energy requirement for drying process. Besides this POP usually was not introduced directly into the polymer matrix, without any active compound from the fruit rind being extracted or encapsulated as an antibacterial ingredient. These processes are cost up for finished products and also increases the carbon footprint.

In contrast to many researches, in one research the extrusion process was used to make the PCL-based antimicrobial films. Hybrids of polycaprolactone (PCL), starch, and POP have been created for antimicrobial packaging. POP was ground in a herbal medicine disintegrator before being sieved through a 180 mesh sieve. Sieved POP and dried at 37 °C in an air dryer for 10–12 hours before being surface treated with stearic acid in a lab scale high speed mixer at 1200 rpm for 3 minutes. POP was employed as an antibacterial ingredient and was introduced directly into the PCL matrix, without any active compound from the fruit rind being extracted. PCL, starch, and POP were carefully combined with different concentrations of POP , PCL and starch. POP is add as 5%, 10%, 15%, 20%, 30% and 40% concentrations. An 80 rpm screw speed is used and the maximum temperature of the barrel was set at 80 °C, while the temperature of the die was fixed at 75 °C. At greater concentrations of active chemical, PCL/POP films were found to have reasonable antibacterial activity. The use of starch not only reduced the cost of the PCL matrix, but it also enhanced its rigidity. Furthermore, by weakening the connections between PCL and POP, starch increased POP's antibacterial activity and provided a release channel for polyphenol transport. Because it is found that specimen includes 60% PCL + %20 POP + %20 Starch has higher inhibition zone

In another study POP was used as an antibacterial and reinforcing ingredient in the development of starch-based films. The POP was frozen to 80°C in the presence of liquid nitrogen and then dried for 24 hours in a freeze dryer with 45pa vacuum pressure and 88°C condenser temperature. The dried POP was then crushed into a fine powder and sieved using a 180 mesh sieve size using a herbal medicine disintegrator. Solution-casting (8 percent w/w) was used to make starch films in a conical flask, with 20 percent polyethylene glycol mixed in on a dry weight basis of starch. The solution was premixed before being heated to 99 °C and kept at that temperature for 1 hour while being regularly shook. The solution was then allowed to cool to 55 °C before being added to at varied concentrations of pomegranate peel powder (0, 2, 4, 6, 8, 10, 12, and 14 % w) depending on dry starch content. After that, the films were dried in an oven at around 35 °C for 10–12 hours to get a consistent weight. The thickness of the films was controlled by putting the same amount of suspensions in the same-sized dish. Zone inhibition was maximum when 12% and 14% POP reinforced films were used against both bacteria. According to the findings, POP inhibited the growth of both gram-positive (S. aureus) and gram-negative (Salmonella) bacteria. Meanwhile, POP improved the starch-based films' Young's modulus, tensile strength, and stiffness. Also it is emphasized that own to choosing all components as food, the produced substance is expected to be safe (Ali et al., 2019).

2.3 Antimicrobial Additives for Plastics

Foodborne infections are a leading cause of human fatalities, hospitalizations, and diseases. The cost of foodborne disease in the United States in 2009 was estimated to be around 152 billion dollars for long-term health and emergency medical care. According to the Centers for Disease Control and Prevention (CDCP), food contamination by bacteria causes 3000 deaths and 48 million illnesses in the United States alone. Toxoplasma gondii, Staphylococcus aureus, Campylobacter spp, Listeria monocytogenes, and Salmonella spp are some of the most common infections that cause death and foodborne illness (Al-Tayyar et al., 2020).

Also some physical and chemical changes such as foul odors, polymer degradation and discoloration by attack of various microbes such as algae, fungi, bacteria and yeast into to the plastics. There are many technologies and additives in the market that block/kill microbial growth on plasticts.

In general, antimicrobial compounds are made of of inorganic and organic components. Enzymes, polymers, and organic acids are examples of organic materials; on the other hand, inorganic materials include metal oxides such as ZnO, MgO, CaO or metal nanoparticles. The main difference between the two types of antimicrobial materials is that inorganic antimicrobial materials have a higher thermal stability than antimicrobial organic materials. As a result, metal oxide and metal nanoparticles are better able to withstand harsh processing conditions (Al-Tayyar et al., 2020).

For many years, biocides are used to prevent microbial colonization on plastics. Usually, technologies are focused on additives to interrupt biofilm formation with the purpose of reducing reduce diminished aesthetic or structural integrity (biodeterioration). However, in order to limit infection transmission, the attention has switched to technologies that provide either a contact-killing surface or a surface that prevents microbial colonization to a level below the threshold for significant pathogen survival. Both inorganic and organic/natural based additives are used for this purpose (Greenhalgh et al., 2017).

Common applications of antimicrobial plastics are medical devices, toys, sports equipment, appliances, food processing machinery, kitchen utensils, bathroom products, garbage bins, and electronic devices. FDA regulates the antimicrobials for medical devices.

2.3.1 Inorganic Additives

Ionics metals are the most common types of polymer incorporated inorganic antimicrobial agents such as ionic silver (Ag+), copper (Cu2+) and zinc (Zn2+). Mechanism of these ions carries on with controlled/constant release system. Silver ions are hypothesized to impair bacterial cells in a variety of ways, resulting in a significant biocidal effect. The ions bind to the cell membrane in the primary mode, influencing the cell's capacity to regulate the diffusion and transport of molecules in and out of the cell. Similarly, once within the cell, the ions seek for thiol groups on proteins that serve as enzymes in the cell's important metabolic pathways. This causes the enzymes to lose their functional abilities, resulting in cell death (Jones, 2009).

However, there are some concerns about the long-term durability of coatings containing ionic metals, which can result in a rapid and significant reduction in effectiveness in the event of a heavy fall with high feet and regularly cleaned areas. Furthermore, any substrate (eg dirt, liquids) deposited on the surface has the potential to act as a physical barrier between metal ions and organisms and could significantly reduce their effectiveness. Biological debris also has the potential to deactivate surface ions, as evidenced by the ability of simple proteins to deactivate metal (silver) ions incorporated into indwelling catheters, potentially reducing effectiveness. This implies that appropriate and rigorous cleaning protocols must also be applied to maintain surface function as intended (Greenhalgh et al., 2017).

Ag-substituted zeolite is the most widely used antimicrobial agent in food packaging plastics. The purpose of zeolite is to allow the slow release of antimicrobial metal ions on the surface of food products. The antimicrobial activity of metals is based on the formation of small amounts of ions. Agricultural zeolite is made from synthetic zeolite by replacing some of its natural sodium with silver ions (Greenhalgh et al., 2017).

Some inorganic antimicrobial agents that are scope of recently researches are summarized at Table 2.10.

Table 2.10. Recent articles summarizing the state of the art based on solution/solvent film casting of antimicrobial agent (Mlalila et al., 2018)

Inorganic Antimicrobials	Polymer	Target Organism	Observations
Silver nanoparticles (AgNPs)	Starch	E. coli, S. Aureus, Bacillus cereus, Salmonella typhi, Pseudomonas aeruginosa, Mycobacterium megmatis	• Component release was within legal limits • AgNPs efficiently inhibited the development of gram positive and gram negative bacteria rather than acidfast bacteria
	PLGA	S. aureus, Staphylococcus, E. Coli, Enterococcus faecalis, C. Albicans, Klebsiella pneumoniae	• Because of the increased surface hydrophilicity of films treated with oxygen and AgNPs, they have better antibacterial characteristics. • Up to 6% w/w AgNPs, no cell toxicity was detected.
Netilmicin	PLGA	P. aeruginosa	• Antimicrobial agent using PLGA nanoparticles has proved to be more effective than free netilmicin.
Zinc oxide nanoparticles	Starch	S. aureus	• Nanoparticles enhanced the viscosity of the starch matrix while lowering water vapor permeability. • In the presence of nanoparticles, the solubility of films reduced.
	PHB	S. aureus, E. coli	• Antimicrobial agent release kinetics were reduced • Nanoparticles improved film mechanical properties • Crystallinity and thermal stability and barrier characteristics improved.
Gold nanoparticles	Starch	S. aureus, E. coli	• E. coli growth was inhibited by 99 percent, while S. aureus growth was inhibited by 98 percent.

Aluminum silicate, copper or silver hydroxyapatite, zeolite of silver or copper or manganese or nickel, magnesium oxide and phosphoric acid are the other inorganic metallic and ions/salts that became scope of some researches (Baldevraj et al., 2011).

Table 2.11 Packaging materials with inorganic antibacterial agents in commercial side (Baldevraj et al., 2011)

Company/institution	**Application**
SongSing Nano Technology Co., Ltd	Nano zinc oxide-treated cling wrap
Sharper Image	Nano silver-treated plastic storage bags
BlueMoonGoods, A-DO Global Quan Zhou Hu Zheng Nano Technology Co., Ltd and Sharper Image	Nano silver is used to treat storage containers.
Daewoo, Samsung and LG	Nano silver-treated refrigerators
Baby Dream©Co., Ltd	Nano silver treatment applied to a baby cup
A-DO Global	Nano silver-treated chopping board
SongSing Nano Technology Co	Teapot with nano silver treatment
Nano Care Technology Ltd	Nano silver-treated kitchenware

2.3.2 Organic Additives

Synthetic/inorganic antimicrobial chemicals are typically included into the biopolymer texture in antimicrobial packaging technologies. Though this pathway has several advantages, such as maintaining high concentrations of antimicrobial agents during storage and preventing these synthetic materials from entering the food matrix and cross-reacting with other food components such as lipids and proteins, it also has several drawbacks, including (a) synthetic additive side effects, (b) uncontrolled distribution of synthetic additives for control of bacteria, and (c) uncontrolled distribution of synthetic additives for control of bacteria.

Also, inorganic antimicrobial additives eliminates the biodegrability property of green polymers due to their toxic effects and no biodegradable properties. In contrast, adding natural fibers enhances PLA biodegradability somewhat, according to biodegradability statistics (Ashothaman et al., 2021).

Antimicrobial substances derived from natural sources, such as plants, essential oils (Eos), have been shown to be a safe and effective way to address these inadequacies. As a result, organic antimicrobial compounds are gaining popularity among consumers due to their lack of toxicity in the majority of cases.

At Table 2.12 some plant based organic antimicrobial additives and their studies are summarized.

Almost in all researches for applying organic antimicrobial compounds into the polymer matrix solving casting method is used. There no any example of using mass production polymer processing method such as extrusion, injection etc. The possible reasons of that organic compounds have lower thermal stability and during conventional plastic processing techniques, high temperatures are used for increased polymer flow rate.

Additionally it is proven that to guarantee the maximum efficiency of EOs as an active ingredient in polymers, it is vital to protect and conserve the volatile constituents of the EOs. Direct incorporation of EOs into the polymer, whether by casting or thermo-processing, does not ensure appropriate antimicrobial especially over extended periods of time. To eliminate that, usually encapsulation by freeze drying and spray drying method is used (Varghese et al., 2020).

Table 2.12. Antibacterial activity of biopolymer films with EO on various pathogens. (Varghese et al., 2020)

EO	**Matrix**	**Pathogens tested**	**Minimum oil: Time until maximum activity shown**
Coriander	PLA	E. coli , B. subtilis	9% (w/w)
Ginger	Chitosan	E. coli, S. aureus	0.1%
Lemon grass	PLA	E. coli , B. subtilis	9% (w/w)
Lavender	Potato starch, furcellaran, and gelatin	E. coli, S. aureus	2% (w/w)
Rosemary	PLA	E. coli , B. subtilis	9% (w/w)
Peppermint	Gelatin	E. coli, S. aureus	10%
Cinnamon and soyabean	Alginate	L. monocytogenes , S. enterica , E. coli	1%
Banana leaf	Gelatin	E. coli, S. aureus	1% (v/v)
Black cumin	Starch	S. typhimurium , E. Coli, L. monocytogenes	No inhibition observed
Bergamot	Chitosan	Penicillium italicum	0.3%
Clove	Chitosan	E. coli, S. aureus	5%

2.4 Investigation for Antimicrobial PLA

PLA is a type of biopolymer that is made from biobased materials like maize or starch and is 100% biorenewable and biodegradable as mentioned before. PLA is became so popular in the plastic industry due to its excellent mechanical strength, transparency, water resistance, melt processability, and low market pricing compared to other biopolymers. Furthermore, due of their biodegradability, biocompatibility, and ease of production, PLA and its copolymers are the most extensively utilized plastics for controlled drug delivery systems. As a result, the use of PLA with antimicrobial properties in biomedical and active packaging applications is a promising area of research.

Antimicrobial compounds were included into PLA matrix so that they could be released in a controlled manner, enhancing their efficiency against bacteria. Some antimicrobial chemicals embedded in the PLA coating layer provide a hydrophilic surface that prevents germs from adhering to the film's surface. Different methods for surface modification of PLA have been developed to suit unique criteria for biomedical applications, such as the surface modification of PLA with silver nanoparticles to form antimicrobial nanocomposite films.

2.4.1 Synthetic Filled Antimicrobial PLA

Similar as in other polymers, antimicrobial activity of PLA mostly tried to be achieved by metals. Many of these research include silver into PLA blends with other suitable materials in order to improve the mechanical or barrier properties of the intrinsically brittle PLA while also providing antibacterial capabilities to the materials. The use of cellulose nanocrystals (CNC) as PLA reinforcement is a common example. Several research have demonstrated that incorporating silver nanoparticles (AgNPs) into PLA-CNC matrices not only does not compromise the materials' high mechanical and barrier performance, but also improves it slightly, which is in addition to their good antibacterial efficiency (Castro-Mayorga et al., 2016). In today, AgNPs have long been utilized in food packaging as an antibacterial agent but the dangers of their possible migration into foods, on the other hand, are a serious issue. The use of AgNPs in food packaging and supplements is not permitted without prior authorization, as suggested by the European Food Safety Authority (EFSA) (Istiqola et al., 2020).

Also in other researches ZnO nanoparticles and aluminum doped ZnO nanoparticles are investigated for antimicrobial activity of PLA. According to results inhibitions of microorganisms (E. coli / S. aureus) are observed (Al-Tayyar et al., 2020). Researches on PLA/nanocellulose composite with different types of synthetic antimicrobial agents are summarized at Table 2.13.

Table 2.13. PLA/nanocellulose composite with different types of synthetic antimicrobial agents (Gan and Chow, 2018)

Antimicrobial Agent	**Microorganism**	**Results**
AgNPs (1 wt%)	Staphylococcus aureus and Escherichia coli	Regardless of incubation duration or temperature, the composite's antibacterial activity was stronger on E. coli than on S. aureus.
AgNPs (1 wt %)	Staphylococcus aureus and Escherichia coli	Antibacterial activity against Staphylococcus aureus and Escherichia coli cells was determined using tertiary techniques.
AgNPs (0.5–1.0 wt%)	Escherichia coli and Staphylococcus aureus	CNC and silver were added to the films to boost their barrier properties. The migration levels of the nano-biocomposites films were not below the allowed limits.
ZnO nanoparticle (0.5–1.0 wt%)	Escherichia coli and Listeria innocua	CNC and ZnO were used to increase mechanical properties and water vapour permeability. However, no significant antibacterial activity was discovere
AgNPs (2, 4, 6 & 8 ml)	Staphylococcus aureus and Escherichia coli	AgNPs and CNF have increased mechanical, thermal, barrier, and antibacterial properties. The ternary nanocomposite film's migration level did not exceed the allowed limits.
rGO (0.5, 0.6, 0.7 wt %)	Staphylococcus aureus and Escherichia coli	Both E. coli and S. aureus were found to have antibacterial properties.

2.4.2 Natural Filled Antimicrobial PLA

In one study biodegradable active films made from PLA and PHB. This polymer was combined with carvacrol as an active ingredient and lactic acid oligomers (OLA) as a plasticizer, then extruded and thoroughly tested for antimicrobial active packaging. Furthermore, the presence of carvacrol improved the antibacterial and antioxidant properties of the proposed formulations, as well as boosted inhibitory activity against Staphylococcus aureus when compared to Escherichia coli at both short and long incubation durations (Zhong et al., 2020).

Another study looked at the possibility of pectin/PLA composites in antimicrobial packaging, and the results showed that incorporating pectin into PLA inhibited the growth of L. plantarum. For the control of foodborne microorganism's researchers employed PLA sheets containing nisin. PLA/nisin had more antimicrobial action against gram-positive L. monocytogenes than against gram-negative E. coli or Salmonella enteritidis (García Ibarra et al., 2016).

In other study antimicrobial PLA is produced with carvacrol or allyl isothiocyanate (AITC), and found that PLA-based materials containing AITC were effective at inhibiting non-Botrytis cinerea growth. However, during 10 days at 22 °C PLA-based materials treated with carvacrol were ineffective in inhibiting B. cinerea growth (Raouche et al., 2011).

Additionally lemon extract, thymol, lysozyme and olive leaf extract are investigated for antimicrobial PLA (García Ibarra et al., 2016). Other studies with natural filled antimicrobial PLA are summarized at Table 2.14.

Table 2.14. PLA composites with various natural antibacterial additives (Sivakanthan et al., 2020)

Antimicrobial Agent	**Main Effects**
Mentha piperita essential oil (MPO), Bunium persicum essential oil (BPO), nanocellulose	Antibacterial activity was shown in MPO and BPO against Staphylococcus aureus, Enterobacteriaceae, and Pseudomonas. In comparison to the control, adding 1% (v/v) of both essential oils to the active film increased the product's shelf life from 4 to 7 days.
Oregano essential oil (OEO)	Staphylococcus aureus, Yersinia enterocolitica, Listeria monocytogenes, Enterococcus faecalis, and Staphylococcus carnosus all showed antibacterial activity in vitro.
Cinnamaldehyde	Cinnamaldehyde was impregnated into PLA sheets using supercritical carbon dioxide, with impregnation yields ranging from 8 to 13 percent (w/w) against E. coli and S. aureus.
Curcumin	PLA packaging with the antibacterial action against Escherichia coli and Bacillus cereus was created with the addition of curcumin (0.5 percent concentration).
Lignin nanoparticle (1 and 3 wt%)	The resulted film showed an effective antibacterial activities against both Xanthomonas axonopodis pv. vesicatoria and Xanthomonas arboricola pv. Pruni.

3. MATERIALS AND METHODS

3.1 Materials

PLA with the trade name Luminy® L105 supplied by Total S.A is used as a matrix polymer. Pomegranate peel (POP) powder is used as fillers to manufacture compostable and antimicrobial PLA based composite materials. POP powder with an average size of 250 µm was purchased from Kurucum Gıda, Turkey.

POP powder is dried 2 hours at 80°C to eliminate water content.

3.2 Methods

3.2.1 Preparation of PLA Based Composites

A co-rotating twin-screw extruder (Leistritz ZSE 27 MAXX) was used to melt-compound POP powder filled PLA composites. PLA composites were filled with 5, 10, 15 and 20 wt% of POP powder (5POP, 10POP, 15POP, and 20POP). The screw rotation speed was set to 400, 500 and 600 rev min−1 for each specimens. The temperature profile of barrel sections from hopper to die was 45-175-185°C. Test specimens were manufactured from POP powder filled PLA composite granules using injection molding machine (Bole, model BL90EK, China). Injection molding method was carried with temperature range of 205 to 220°C and a mold temperature of 50°C.

Table 3.1. Produced PLA composites denomination according to %w/w POP powder content and used screw rotational speed

Composite Name	**%wt of POP Powder in Composite (%)**	**Used Screw Rotation Speed in Composite Production (rpm)**
05POP-4	5	400
05POP-5	5	500
05POP-6	5	600
10POP-4	10	400
10POP-5	10	500
10POP-6	10	600
15POP-4	15	400
15POP-5	15	500
15POP-6	15	600
20POP-4	20	400
20POP-5	20	500
20POP-6	20	600

3.2.2 Characterization Methods

3.2.2.1 Density

The density of the specimens was determined using a Densimeter MD-200S in accordance with ISO1183 standards. The average density of three specimens was used to calculate the density of each composite.

3.2.2.2 Thermogravimetric analysis (TGA)

TGA data of POP powder filled PLA composites were obtained using a TGA Instrument (TA Instruments Inc., TGA-Q50) in the range of 30–800°C under nitrogen atmosphere at a heating rate of 10° C min-1. The samples were around 2 mg in weight each test.

3.2.2.3 Differential scanning calorimeter (DSC) analysis

Under flowing nitrogen, modulated DSC analyses were performed in a differential scanning calorimeter (DSC-Q20, TA Instruments Inc.). Specimens were heated with rate 1°C min-1 from 50 to 200°C and hold for 10 minutes to eliminate any residual nuclei before cooling back with the same rate, 1°C min-1.

3.2.2.4 Thermomechanical analyses (TMA)

A thermo-mechanical analyzer (TA Instruments, Inc., TMA 400) was used to test the thermal expansion coefficients (CTE) of POP powder filled PLA composites in expansion mode. Specimens (10 x 35 x 33 mm) were heated at a rate of 5°C min-1 from -10°C to 120°C.

3.2.2.5 Heat distortion temperature (HDT) testing

Under a particular load of 1.8 MPa, HDT values of PLA and its composites with dimensions of 80x10x4 mm were obtained using the HDT-Vicat Testing Instrument (Coesfeld) according to ISO 75 standard.

3.2.2.6 Mechanical Tests: Tensile and Flexural

Tensile strength (MPa) and modulus (MPa) for each specimen were measured at room temperature using a Hegewald&Peschke Inspect 20 universal testing machine equipped with a video extensometer system (Hegewald&Peschke Inspect 20 Non-contact Video Extensometer). The specimens were tested using the strain rates described in the ISO 527 standard for each specimen type (5 mm/min for Type I and IV). The sample size for each test condition was n = 5.

On a Hegewald & Peschke Inspect 20 universal testing machine, flexural strength and modulus are evaluated using a three-point bending test in compliance with ISO 178 standard at a span-to-depth ratio of roughly 40 at a 1 mm min-1 deformation rate. For ISO527 and ISO178, the specimen dimensions were 150 × 10 × 5 mm and 80 × 10 × 4 mm, respectively.

3.2.2.7 Impact Test

Notched samples and un-notched samples were used in impact tests that followed the ISO 180 standard for Izod test method. The amount of energy absorbed by the specimen for the break is measured in kJ/m2 during this test. For the impact strength, the average value of five tests was recorded.

3.2.3 Antimicrobial Activity

Samples were prepared as (1×1) cm2 plates for antimicrobial activity and they were sterilized in an autoclave at 121°C for 30 minutes at 103 kPa.

Antimicrobial testing were carried out using conventional procedures regarding ASTM E2149-10 test method. Antimicrobial activity against E. coli and S. aureus was tested using this experimental procedure. Each culture solution (1 mL) was injected into 9 mL of saline, resulting in a colony forming unit (CFU) concentration of $3x10^5$–$5x10^5$ CFUs/mL. The antibacterial tests were conducted using bacterial with that solution. For 20 hours, the conical flask was shaken at 25°C with a speed of 300 rpm incubator shaker (Suzhou Peiying Experimental Equipment Co., Ltd., HZQ-F160, Suzhou, China). Then all bacteria were cultured for 24 hours at 37 °C. To assess the antibacterial property, the percent of the inhibition was measured. Percentage of inhibition is calculated as;

$$\text{Inhibition (\%)} = (N_2-N_1)/ N_1 * 100 \qquad (3.1)$$

• N_1 : Number of bacteria before the addition of the sample (at time 0 of h)

• N_2: Number of bacteria recovered after dynamic contact of to the sample (at time of 24 h)

Antibacterial effectiveness - R, was validated with the equation :

$$R = U_t - A_t \tag{3.2}$$

Where Ut is the average of logarithm numbers of viable bacteria after inoculation on control (additive free) sample after 24 h and At is the average logarithm numbers of viable bacteria after inoculation in antibacterial samples after 24 h. To be considered effective, R must be ≥ 2.0 (Pittol et al., 2017).

3.2.4 Scanning Electron Microscopy (SEM) Analysis

A scanning electron microscope (Carl Zeiss 300VP, Germany) was used to capture SEM micrographs of PLA -based composites at a voltage of 7.5 kV. Gold was placed on the composite surface using a plasma sputtering equipment to improve conductivity.

4. RESULTS AND DISCUSSION

4.1 Density Results

The density values of PLA and its composites as a function of filler and reinforcement ratios are shown in Figure 4.1. According to the findings, POP powder has a density as 1.48g/cm^3 that is similar to that of neat PLA, faintly higher.

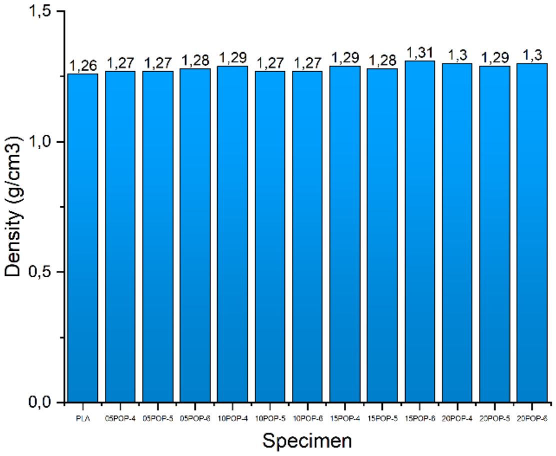


Figure 4.1. Density values of PLA and its composites

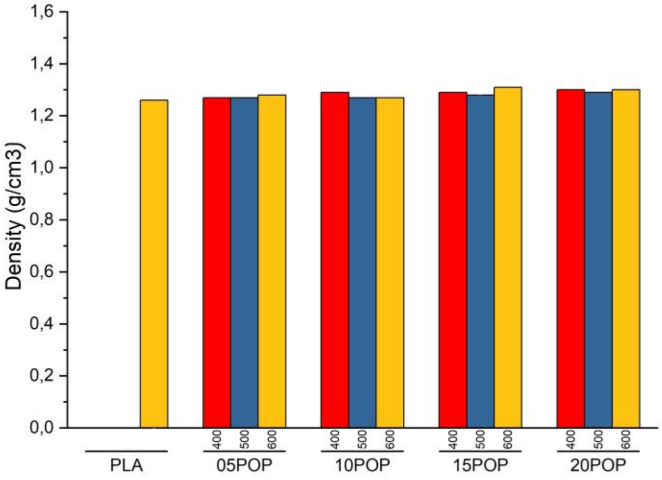


Figure 4.2. Density values of PLA and its composites for comparison

4.2 TGA Results

PLA is a biodegradable and renewable polymer that is susceptible to degradation by moisture and heat. The TGA curves of the PLA and its blended composite samples heated from room temperature to 800 °C in a N_2 environment are shown in Figure 4.3, Figure 4.4 and Figure 4.5.

Table 4.1 shows results of thermogravimetric studies. Due to filler's organic structure degradation temperatures of PLA and its composites are investigated at 5% and 10% weight loss points for the polymers.

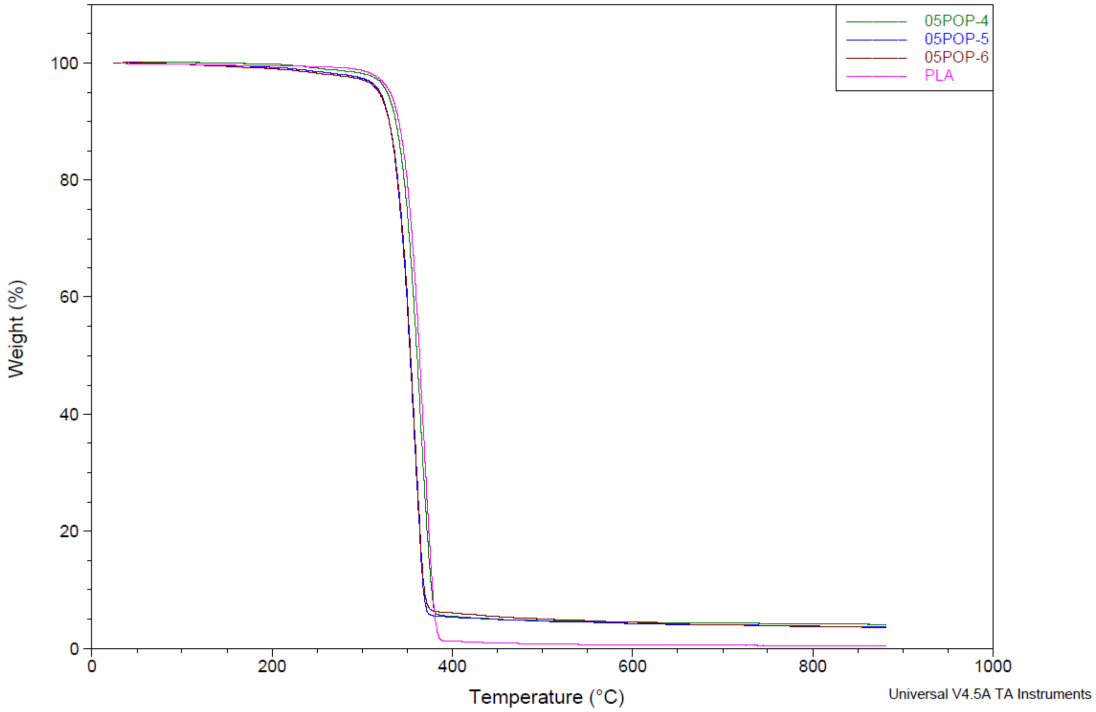


Figure 4.3. TGA curves for PLA and 5% POP powder filled PLA composites

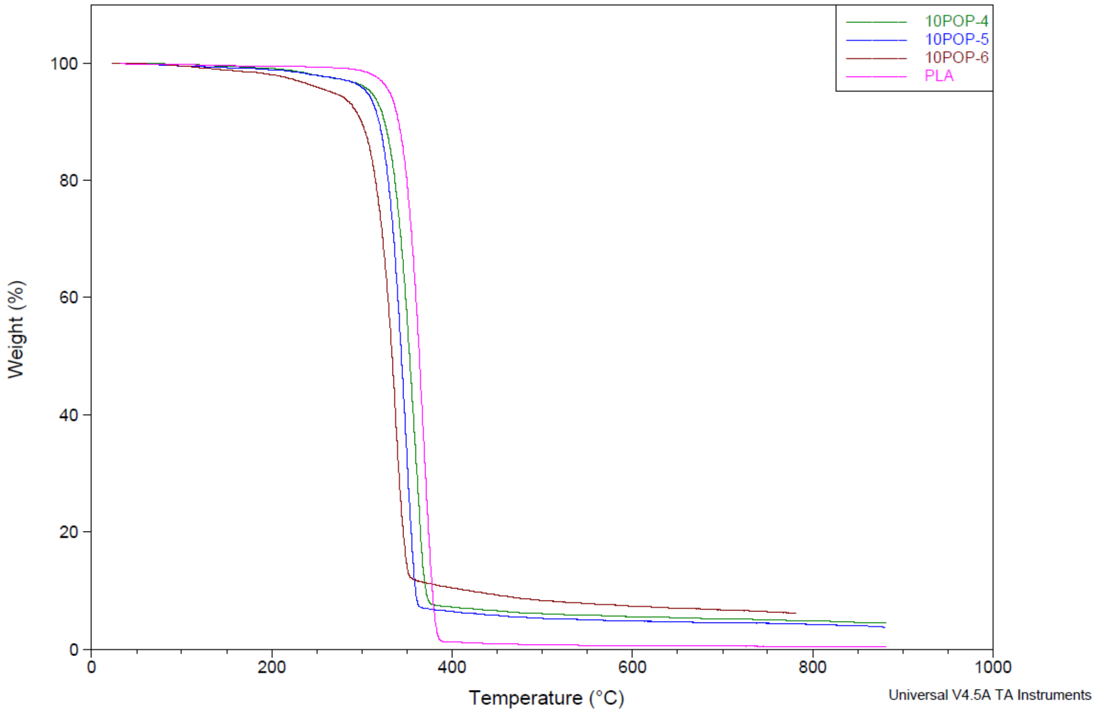


Figure 4.4. TGA curves for PLA and 10% POP powder filled PLA composites

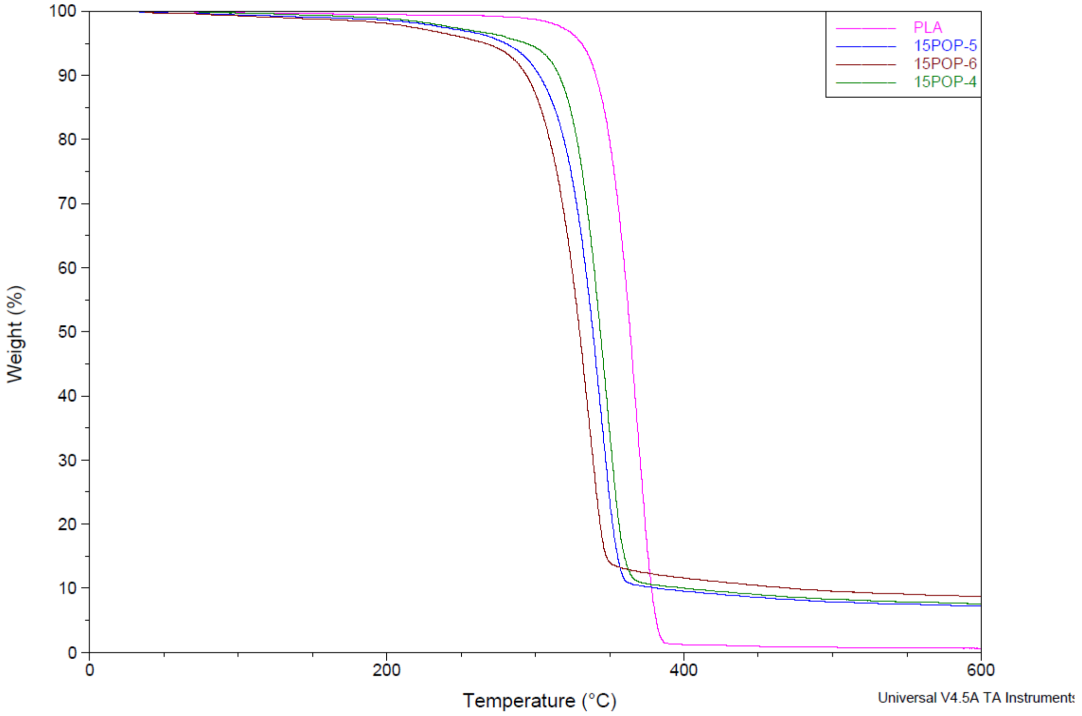


Figure 4.5. TGA curves for PLA and 15% POP powder filled PLA composites

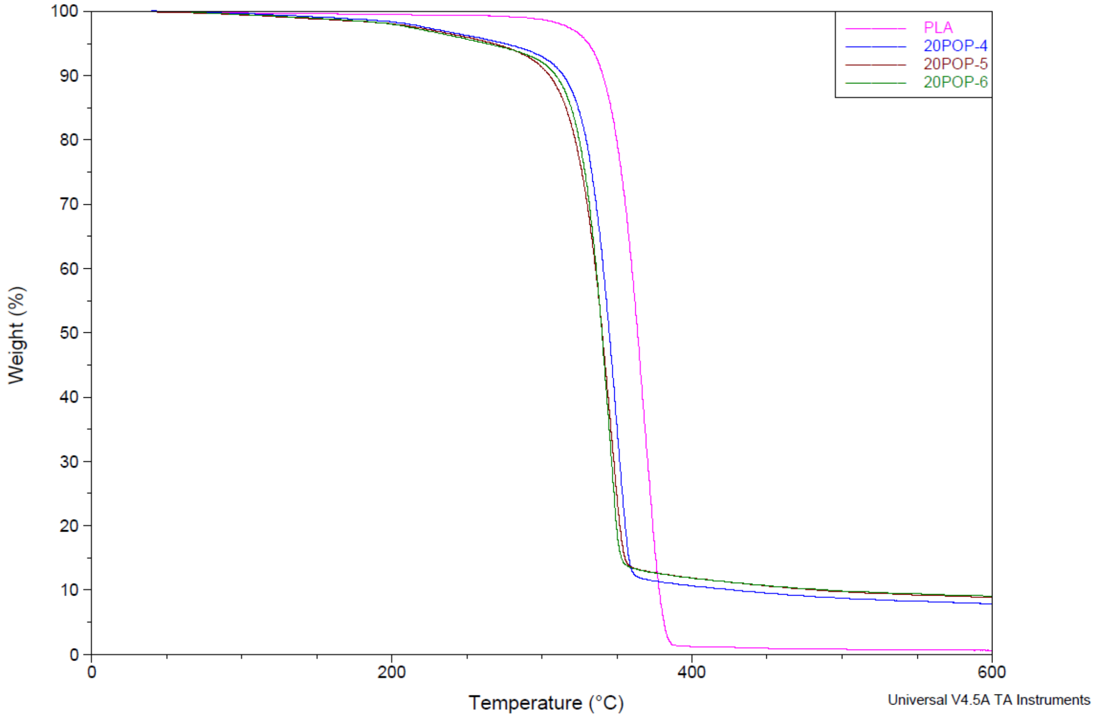


Figure 4.6. TGA curves for PLA and 20% POP powder filled PLA composites

Table 4.1 TGA data for PLA and POP powder filled PLA composites.

Composite Name	**Temperature at 5% Mass Loss (°C)**	**Temperature at 10% Mass Loss (°C)**
PLA	330	340
05POP-4	327	337
05POP-5	320	330
05POP-6	318	330
10POP-4	310	325
10POP-5	306	319
10POP-6	268	300
15POP-4	293	316
15POP-5	279	303
15POP-6	266	294
20POP-4	274	314
20POP-5	267	305
20POP-6	262	309

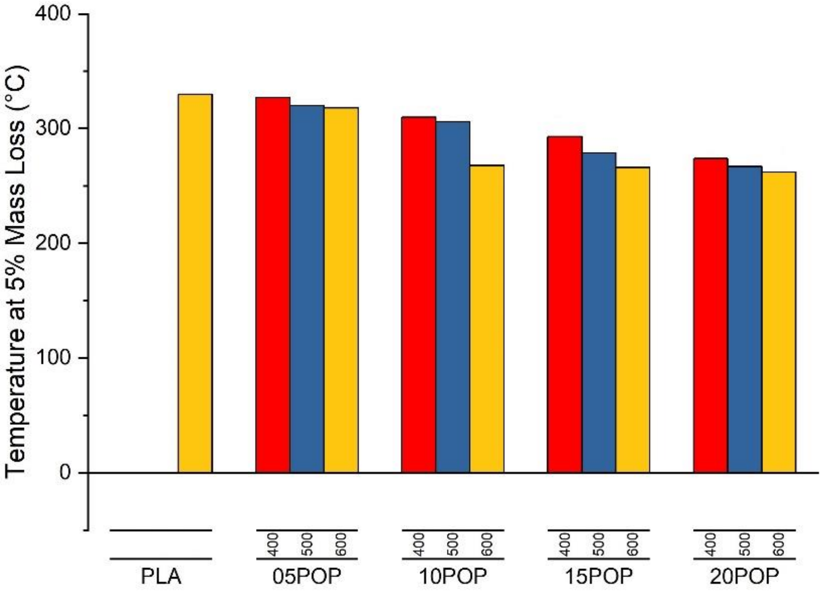


Figure 4.7. Temperatures at 5% mass loss of PLA and its composites for comparison

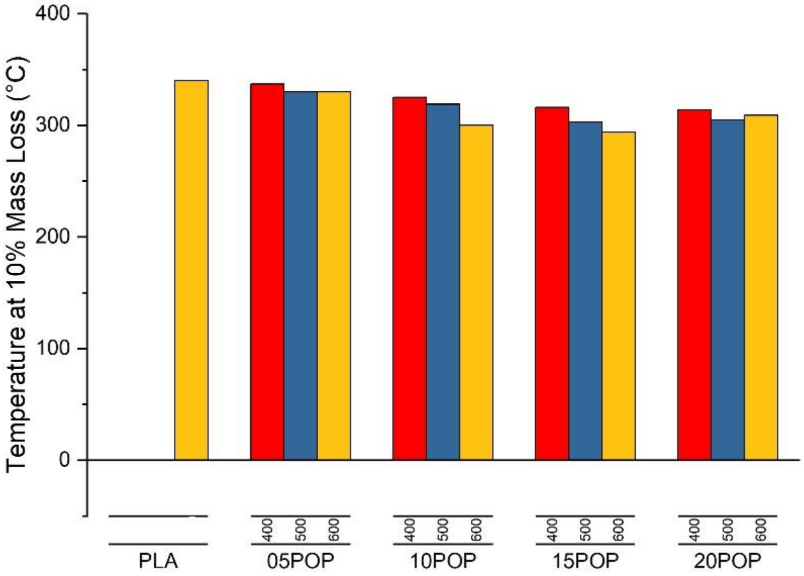


Figure 4.8. Temperatures at 10%mass loss of PLA and its composites for comparison

The degradation temperatures at 5% and 10% mass loses are decreased as the POP powder content increased which means the composites filled with POP powder demonstrated reduced thermal stability. This is owing to the fact that POP powder has a lower heat absorption capability than PLA due to its organic structure. As the weight fraction of POP powder in the composites increased, POP powder in the composites absorbed lower heat, necessitating a lower temperature to reach the threshold energy for the degradation process to begin (Altay et al., 2018).

The results are matching with the literature that composites of PLA filled with natural additives showed same temparature decreases at 10% mass loss occured with comparing neat PLA. In literature, 20%wt kenaf and 20%wt rice husk loaded PLA composites produced by extrusion-injection molding method has 10% mass losses at 321°C and 305°C respectively (Yussuf et al., 2010).

And it is noted that there are effect of used screw rotational speed on mass losses. The degradation temperatures at 5% and 10% mass loses are decreased as the screw rotational speed is increased. Especially temparetures at 5% mass loses with 600rpm is getting lowering.

4.3 DSC Results

Figure 4.6 shows the DSC curves of POP power filled PLA composites and neat PLA. Table 4.2 summarizes the glass transition temperature (T_g), melting temperature (T_m), crystallisation temperature (T_c), melting entalphy (ΔH_m) and the crystallisation enthalpy (ΔH_c) obtained from Figure 4.6.

The composites' degree of crystallinity (X_c) is calculated using the following equation:

$$Xc = \left[\frac{\Delta Hm - \Delta Hc}{\Delta Hm^{\circ}} x \frac{1}{P_{PLA}}\right] x100 \tag{4.1}$$

PPLA is the weight fraction of PLA in the composite, and $\Delta H_m°$ is the melting entalphy of 100 % crystalline PLA (93 J/g) (Aragón-Gutierrez et al., 2020).

It is clearly seen that during melting DSC thermogram of PLA and 5% POP filled composites show two endotherm peaks. Many semicrystalline polymers, including PLA have multiple melting behavior. A melt-recrystallization model has been used by many researches to explain double melting behavior. The meltings are occurred melting of some of original crystals and melting of crystals formed by melt-recrystallization process during a heating respectively. Hence peaks are occurred at a lower temperature, while the later at a higher temperature. Recrystallization that is based in model is occurred during exothermic peak that appears between the double melting peaks. In summary, melting is accomplished by melting the original crystals, recrystallization, and then melting the recrystallized crystals (Yasuniwa et al.,2003).

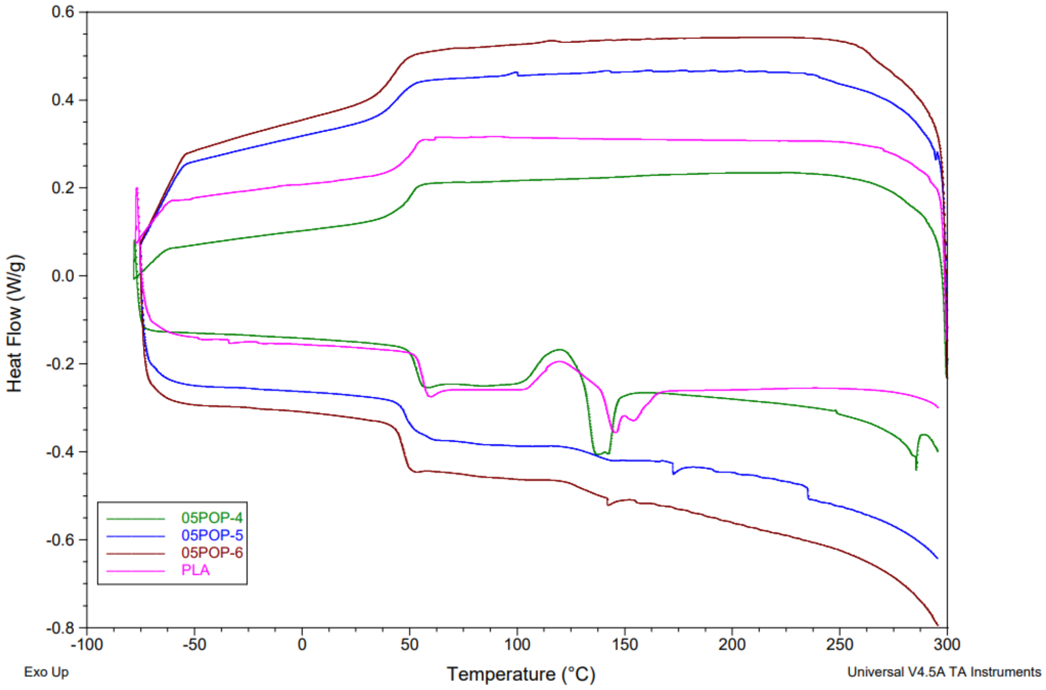


Figure 4.9. DSC curves for PLA and 5% POP powder filled PLA composites

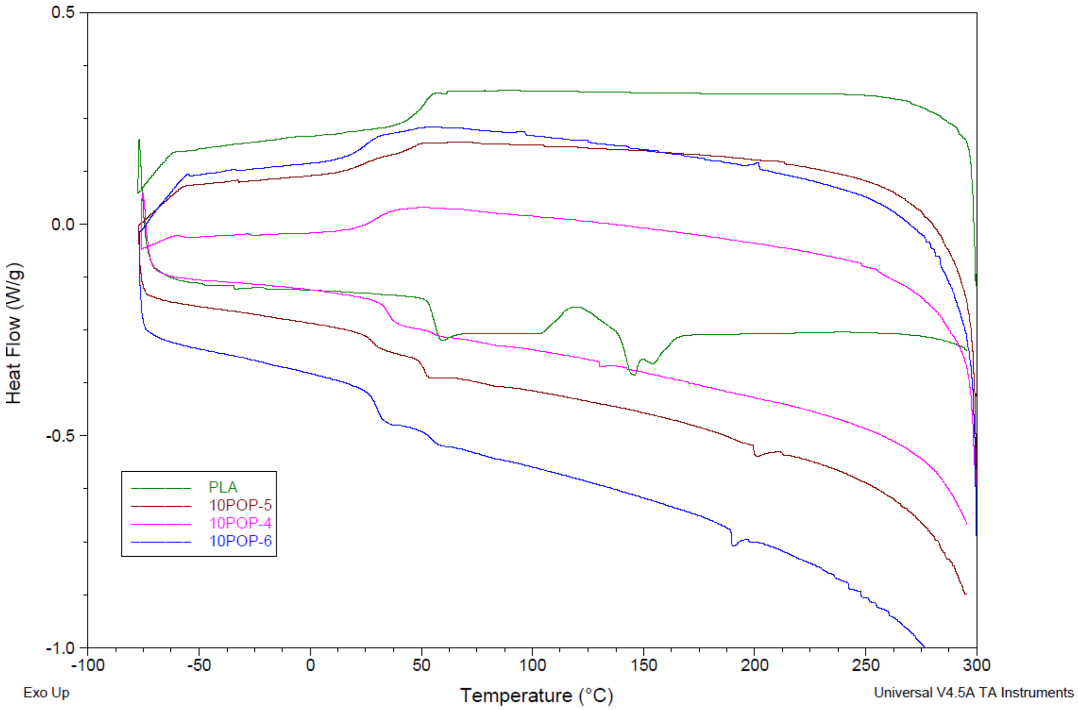


Figure 4.10. DSC curves for PLA and 10% POP powder filled PLA composites

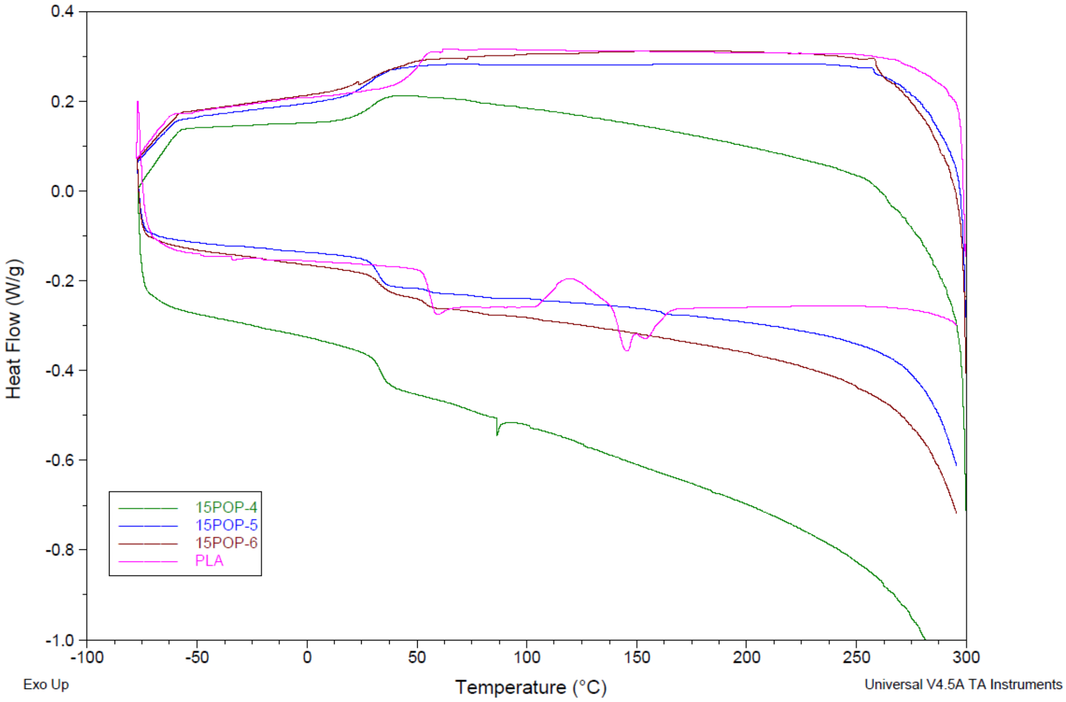


Figure 4.11. DSC curves for PLA and 15% POP powder filled PLA composites

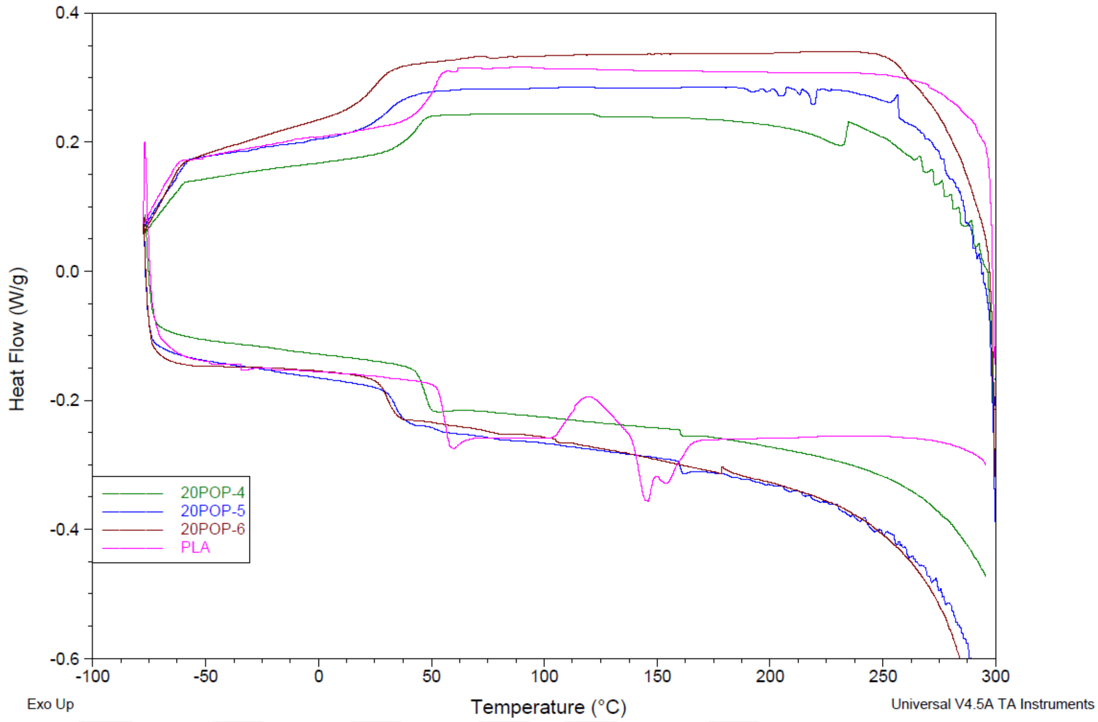


Figure 4.12. DSC curves for PLA and 20% POP powder filled PLA composites

Table 4.2. DSC data results for PLA and POP powder filled PLA composites.

	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	X_c (%)
PLA	55	109	6.4	146	154	14.2		8.28
05POP -4	54	103	10.3	136	142	15.7		6.07
10POP-4	35	-	-	130	-	0.31	-	-
15POP-4	33	-	-	86	-	0.49	-	-
20POP-4	48	-	-	160	-	0.08	-	-
05POP-5	48	-	-	172	235	0.42	0.39	-
10POP-5	51	-	-	200	-	0.49	-	-
15POP-5	32	-	-	163	-	0.11	-	-
20POP-5	34	-	-	161	-	0.21	-	-
05POP-6	47	123	0.7	142	157	1.09	0.12	0.57
10POP-6	30	-	-	190	-	1.05	-	-
15POP-6	33	-	-	-	-	-	-	-
20POP-6	30	-	-	178	-	0.33	-	-

* (-) means no peak is observed

According to Table 4.2 T_g values of the composites recorded during the first heating cycle decreased as the POP powder concentration in composite increased. Reason of this could be POP powder as an organic waste’s moisture absorption activity, which resulted in the creation of hydrogen bonds with polymeric chains. These bonds increase free volume leads to increase the mobility of the PLA polymer chains, and resulted by decreased T_g.

On the other hand, POP powder had an significant effect on crystallinity and crystallization temperature.. The degree of crystallinity decreased to 27 % when 5% POP powder was added to the blends. Additionally there are no crystallization and T_{m2} peaks at higher POP powder concentrations. Multiple melting phenomena is explained above, according to that model recrystallization is necessary for second melting. But no recrystallization is occurred due to blocked of crystallization by higher concentrations of POP powder Crystallization of neat PLA and 5 % POP powder loaded PLA at 600 rpm begin at 109 °C and 123°C, respectively. That is the other proof of POP powder has a reverse effect on crystallization of PLA. Because of the increased contact sites between the PLA matrix and the organic POP powder phase, crystallization is delayed. These can be related to the fact that the reinforcement causes difficulties during polymeric chain migration. As a result, chain folding of polymeric molecular segments may be prevented at the polymeric crystal's developing face resulting material develops a totally amorphous microstructure.

4.4 TMA Results

In the presence of fillers, thermomechanical analysis can be utilized to examine the movement of polymer chains. It's a method for measuring filled materials that's extremely sensitive (Atagur et al.,2020). CTE is one of the factors that can be used to describe the thermal characteristics of polymer composites.

The CTE was calculated in the longitudinal direction, which is the direction in which the melt flows during injection molding. As shown in Figure 4.13, the CTE was measured for POP powder weight fractions of 5–20%. CTE value of PLA is measured as 77.27 (μm/m °C). For all filler loadings, increase in CTE along the longitudinal direction was seen at a measured temperature. The 10 wt% POP powder loaded composites have strickly higher CTE values at 500 and 600 rpm than other concentrations (Figure 4.4).

Table 4.3. CTE data for PLA and POP powder filled PLA composites

Composite Name	**Coefficient of Thermal Expension (μm/m°C)**
PLA	77.27
05POP-4	77.02
05POP-5	87.6
05POP-6	77.72
10POP-4	82.01
10POP-5	109.5
10POP-6	145.1
15POP-4	74.6
15POP-5	88.03
15POP-6	88.22
20POP-4	85.98
20POP-5	87.72
20POP-6	91.49

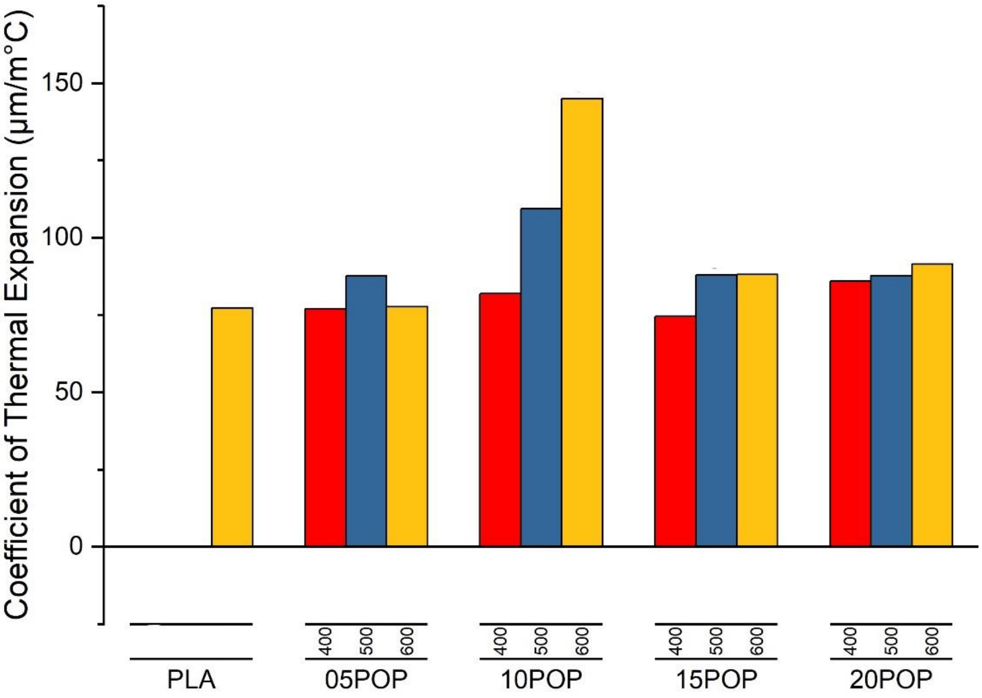


Figure 4.13. CTE values of PLA and its composites

4.5. HDT-Vicat Results

HDT is well-known for determining the performance of plastic materials at elevated temperatures, and it is frequently employed in the material selection process as the maximum continuous usage temperatures in industry. Table 4.4 shows the HDT and Vicat softening temperature values of PLA and its blends. PLA's HDT value was increased when 5-10% of POP powder were loaded into it. But in 15-20% POP powder filled composites HDT values started to reduce. Composites at lower concentrations demonstrated relatively higher HDT values which could be due to the better fiber-polymer interactions. Furthermore, in this investigation, 15POP-6 had the lowest HDT value. There is no significant difference between used screw rotational speeds on HDT values.

A substance's softening temperature at which the amorphous polymer begins to soften. It has to do with the polymer's structure as well as its molecular weight and size. Reported that the Vicat softening point of composites increased as the POP powder content increased. Composites at lower concentrations (5-10%) demonstrated relatively higher Vicat softening values which could be due to the better fiber-polymer interactions.

Table 4.4. HDT and vicat softening temperature values of samples.

Composite Name	Heat Distortion Temperature (°C)	Vicat Softening Temperature (°C)
PLA	45.65	51.20
05POP-4	60.50	60.55
05POP-5	54.50	63.50
05POP-6	57.60	62.45
10POP-4	48.40	60.20
10POP-5	48.40	55.30
10POP-6	46.10	54.55
15POP-4	46.00	55.95
15POP-5	38.30	53.85
15POP-6	36.40	53.35
20POP-4	37.80	52.80
20POP-5	38.20	51.05
20POP-6	40.40	51.50

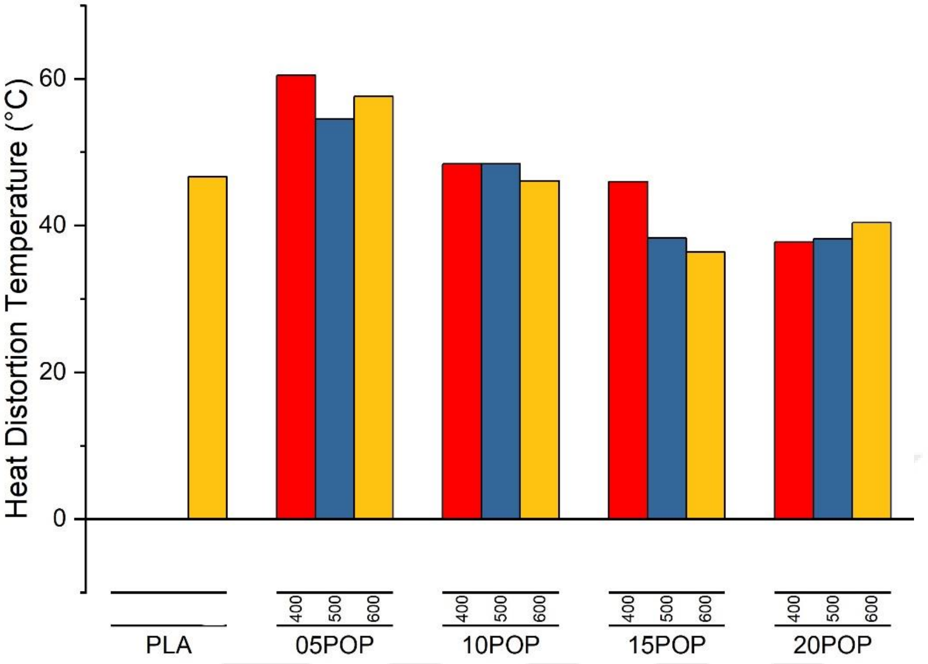


Figure 4.14. HDT values of smples for comparison

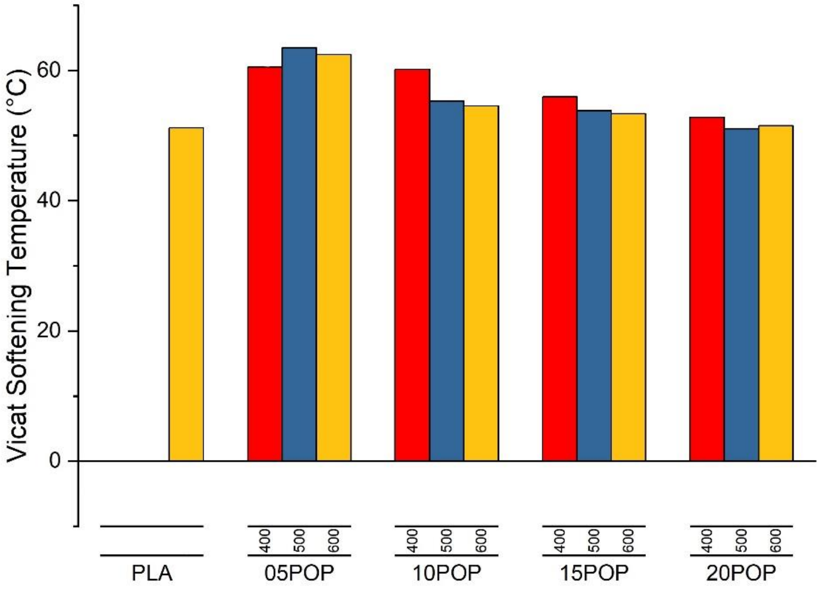


Figure 4.15. Vicat Softening temperatures of composites for comparison

4. 6 Mechanical Test Results

Table 4.5 demonstrates the mechanical characteristics of PLA and its composites having various weight fractions of POP powder. The tensile and flexural strength of PLA and its composites are shown in Figure 4.7. The PLA's tensile and flexural strengths were measured at 67 and 81.58 MPa, respectively. The addition of POP powder reduced the tensile strengths of PLA, in contrast increased flexural strengths for 5%filled composites as shown in Figure 4.7. It seem that mechanical strengths of composites decreased as the POP powder content increased. The results are coherent with HDT results.

Tensile and flexural strength decreased to 71 and 34 MPa, respectively, when the POP powder weight percentage was 15%. There are significant reduces in strength values. It is thought that the main reason for this situation is the matrix/reinforcement interface incompatibility. In order to solve this problem, it is recommended to apply two different methods. Firstly, by making surface modifications into the reinforcement material, it can be ensured that the POP powder particles are distributed homogeneously into the matrix material by opening the layers. Secondly, during the production of composite material, matrix material and reinforcement material can be added to the device as well as a compatibilizing agent to increase the matrix/interface compatibility.

Table 4.5 Mechanical properties of PLA and its composites.

	Tensile Strength	Tensile Modulus	Percent Elongnation at Break	Flexural Strength	Flexural Modulus
	MPa	MPa	%	MPa	MPa
PLA	67	2770	9	82	2894
05POP-4	55	2490	3	101	2490
05POP-5	54	2352	3	98	2352
05POP-6	52	2118	2	90	2118
10POP-4	45	2376	2	86	2376
10POP-5	46	2368	3	87	2368
10POP-6	42	2394	4	77	2394
15POP-4	40	2286	2	71	2286
15POP-5	43	2330	6	80	2330
15POP-6	34	2205	8	71	2205
20POP-4	37	2246	11	74	2246
20POP-5	35	2229	6	74	2229
20POP-6	34	2230	10	76	2230

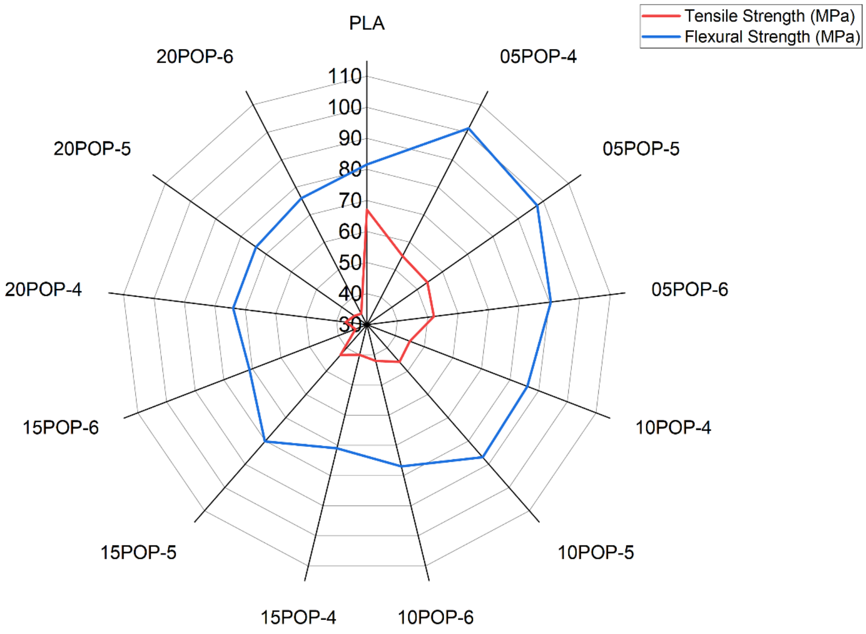


Figure 4.16. Tensile and flexural strength values of PLA and its composites.

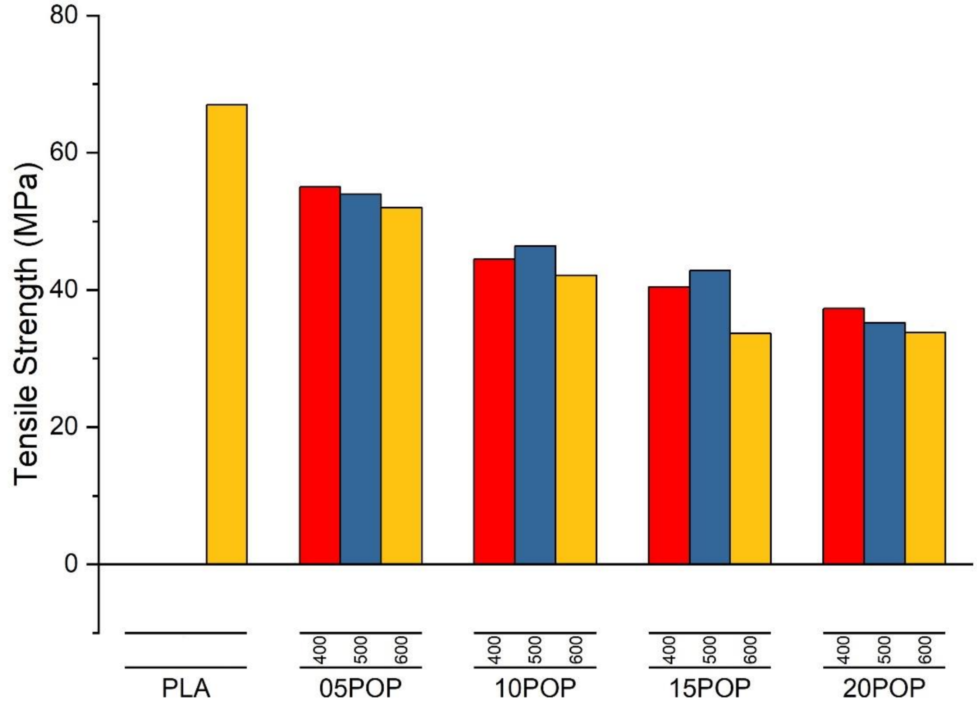


Figure 4.17. Tensile strength values of composites

Effect of screw rotational speeds on tensile strengths can be observed at Figure 4.17. According to results it is seen that composites have same POP powder concentration has greater tensile strength values at lower screw rotational speeds. The main reason of this can be breaking of POP powder fibrils in higher screw rotational speeds that affect negatively the strength.

4.7 Impact Test Results

Figure 4.18 illustrates the composites' notched and unnotched izod impact strengths at various filler amounts. The PLA's impact strengths are 4.5 kJ/m^2 and 20 kJ/m^2, respectively, when notched and unnotched. Almost all composites' impact strengths, both notched and unnotched, are clearly inferior to PLA's.

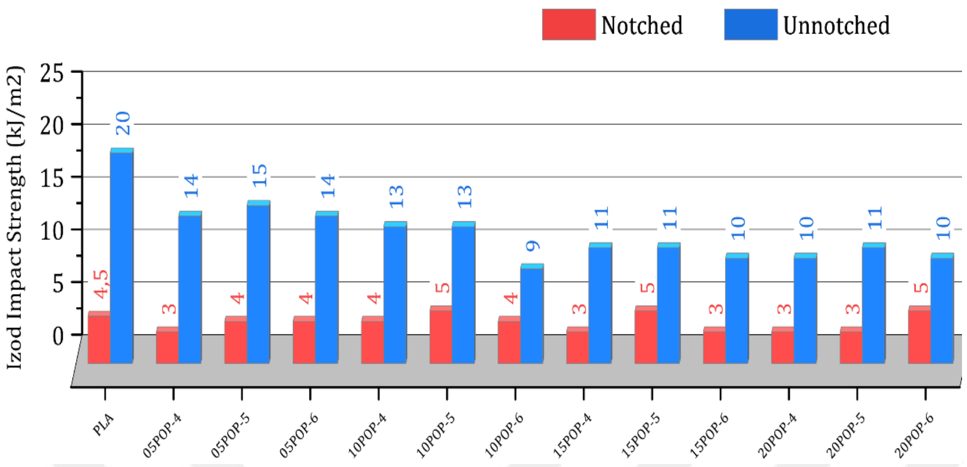


Figure 4.18. Notched and unnotched izod impact strength values of PLA and its composites

With the increased loading amount of the POP powder, the composites' impact strength was reduced comparatively and can be observed that Figure 4.19. Poor interfacial bonding between the filler and the PLA matrix is to blame for the composites' considerable loss in impact strength.

Microspaces between the filler and the polymer matrix are resulted by poor interfacial bonding, and when impact occurs, these microcracks propagate rapidly, reducing the impact strength of the composites (Altay et al., 2018).

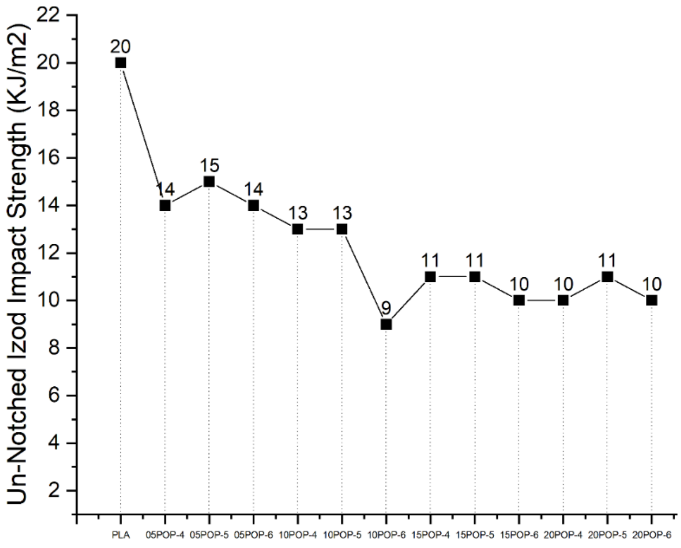


Figure 4.19. Unnotched izod impact strength values of PLA and its composites

4.8 Antimicrobial Activity Test Results

Inhibition percentage of PLA and its composites against Staphylococcus aureus (S.aureus) and Escherichia coli (E.coli) are summarized at Table 4.6. Neat PLA has no any antimicrobial activity against S. aureus and E. coli. Antimicrobial performance of composites are enhanced correlated to POP powder concentration is increased. Even at 5% POP powder addition increased the antimicrobial activity approximately 55.5 % for both bacteria. 20% POP powder filled composites have above %99 inhibition resulting by killing all bacteria.

According to JIS Z 280124, the effectiveness value (R) must be equal to or greater than 2 in order for the substance to be accepted as antibacterial (Pittol et al., 2017). The below 15% POP powder concentrations, composites did not achieve a R value of 2.0 in the measurement against the S. aureus and E. coli population in the current study. On the other hand, composites filled with 15% and 20% POP powder presented better antibacterial effectiveness (R = 3.01 and greater) as seen as Table 4.6.

That must be noted there is no significant difference between used screw rotational speeds on antimicrobial activities, it is all relevant to POP powder concentrations.

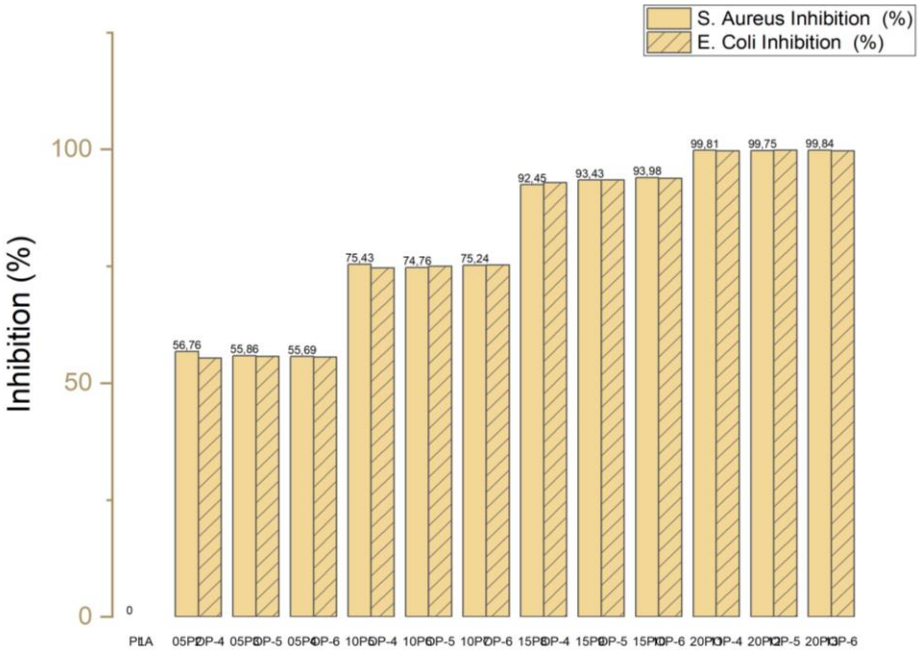


Figure 4.20. Antimicrobial activities of PLA and its composites against S.Aureus and E.Coli

Table 4.6. Inhibition percentages and R values of PLA and its composites against S.Aureus and E.Coli

	Staphylococcus aureus	**Escherichia coli**	**R Values**
PLA	0	0	-
05POP-4	56.76	55.34	1.12
05POP-5	55.86	55.68	1.15
05POP-6	55.69	55.59	1.21
10POP-4	75.43	74.65	1.24
10POP-5	74.76	75.02	1.27
10POP-6	75.24	75.32	1.29
15POP-4	92.45	92.91	3.01
15POP-5	93.43	93.45	3.12
15POP-6	93.98	93.83	3.26
20POP-4	99.81	99.65	4.75
20POP-5	99.75	99.81	4.92
20POP-6	99.84	99.67	5.02

The results of this research are promising even comparising with non-natural loaded PLA composites in litarature. For example, in one study antimicrobial activity of PLA is as a matrix loaded with chitosan filler containing silver nanoparticles (AgCS-PLA) are investigated. Regarding results it is seen that composites filled with 7% w/w AgCS has inhibition percentages % 99.98 and %99.99 against E. coli and S. aureus, respectively (Nootsuwan et al., 2018).

To compare in the aspect of natural fillers there are some researches; composites of PLA/PBAT with concentration (%3.125) of some essential oils (clove, cinnamon and eucalyptus) is produced by SCM. And their antimicrobial activities were observed above 90% inhibition against both S. aureus and E. coli (Sharma et al., 2020). Different techniques are also tried to extent the antibacterial activity time of PLA composite films. Based on the inclusion approach, cinnamaldehyde was added to -cyclodextrin for that purpose and films are prepared again by SCM. The antibacterial activity of the film against E. coli was 37.4% when the cinnamaldehyde inclusions concentration was 5% (Khalid et al., 2018). In our research we achived around 55% inhibition at same 5% concentration.

To enhance antimicrobial activity of POP powder filled PLA composites produced by extrusion some improvements can be applied as; surface modification or encapsulation of POP powders, using freezing dry method for POP powder instead of heating drying to save volatile essential oils and other antimicrobial agents in POP powder that can be deteriorated due to high temperature or these promising composites can be filled with few amounts of other antimicrobial agents besides POP powder that will not harm the compostability performance of composites.

4.9 SEM Results

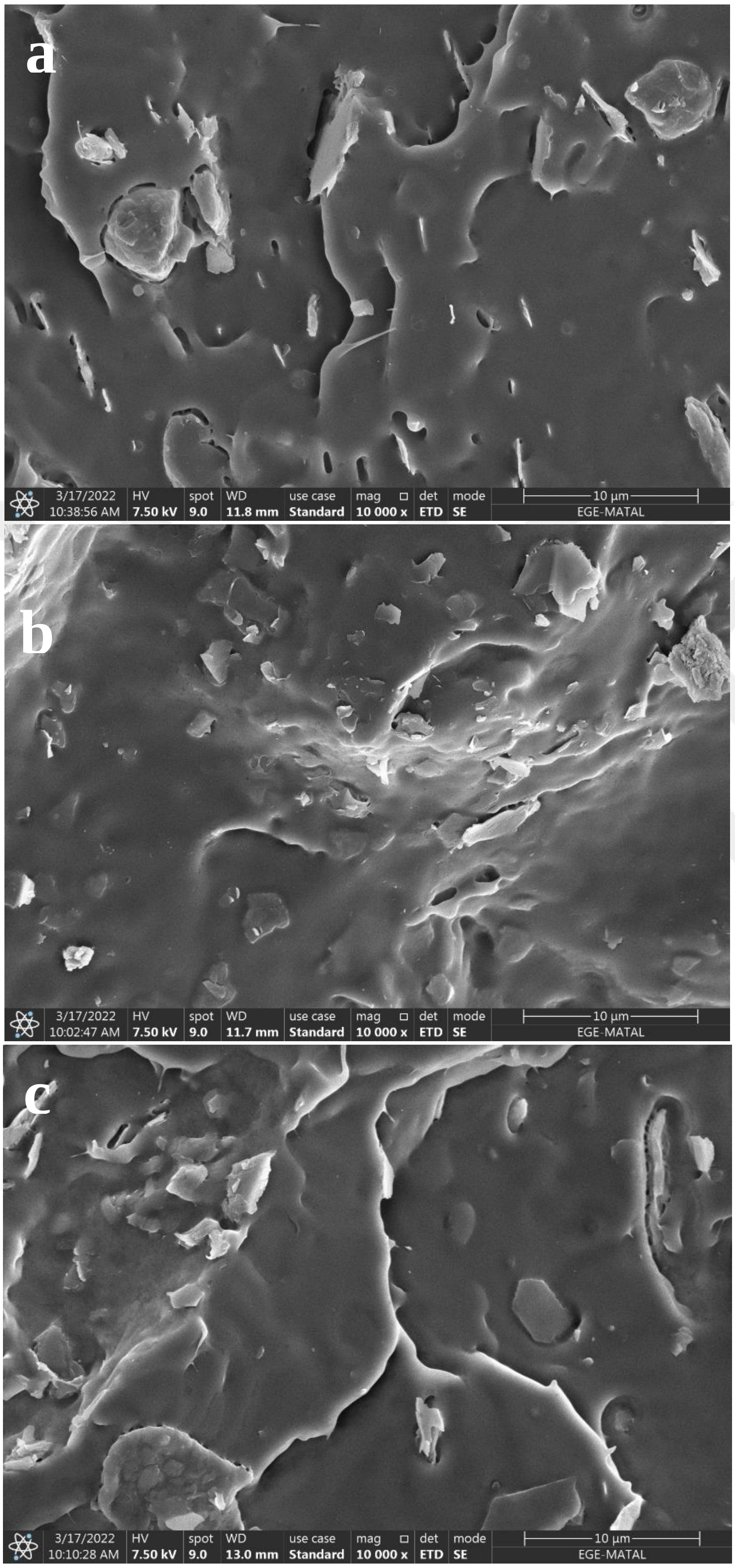


Figure 4.21. SEM images; a) 05POP-4, b) 05POP-5, c) 05POP-6

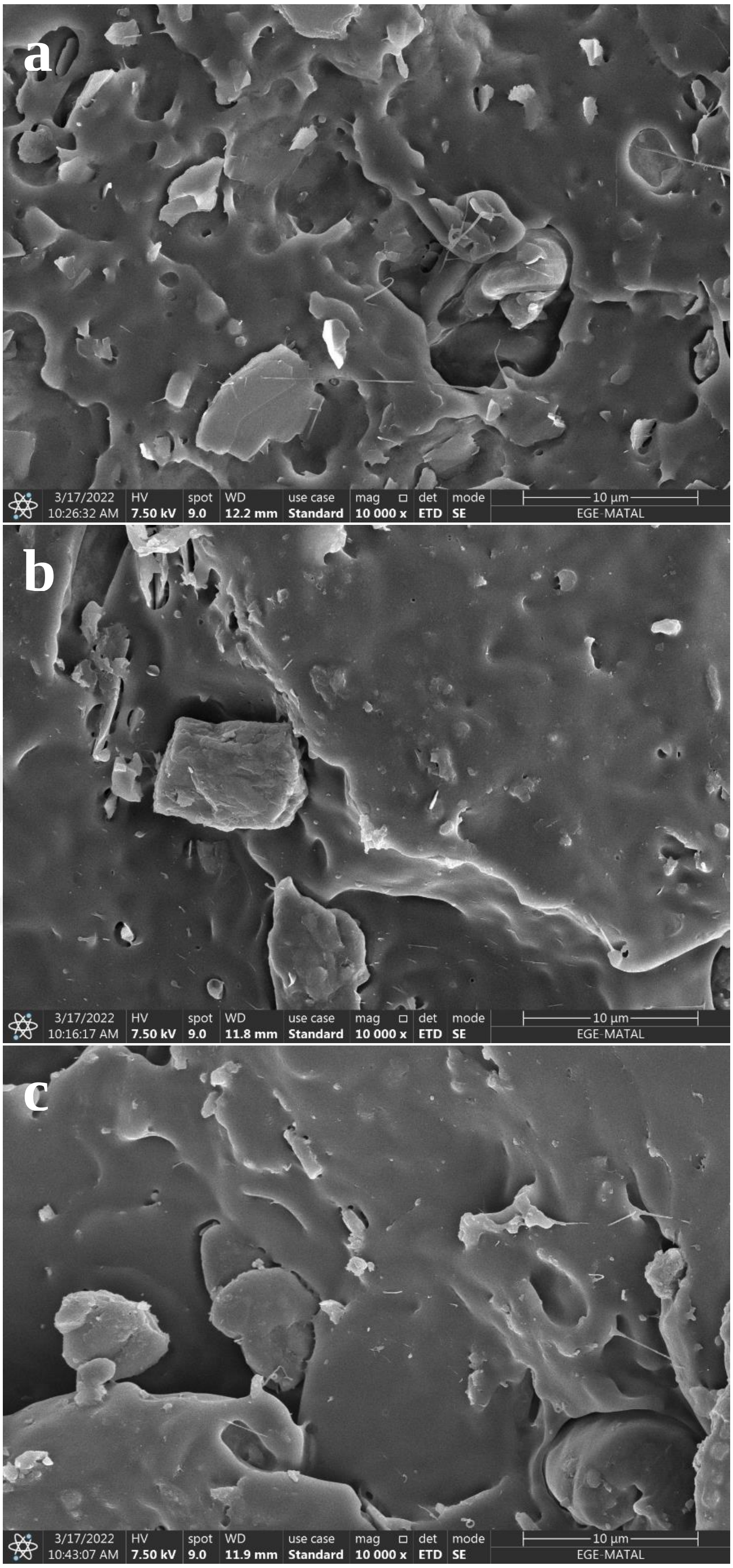


Figure 4.22. SEM images; a) 10POP-4, b) 10POP-5, c) 10POP-6

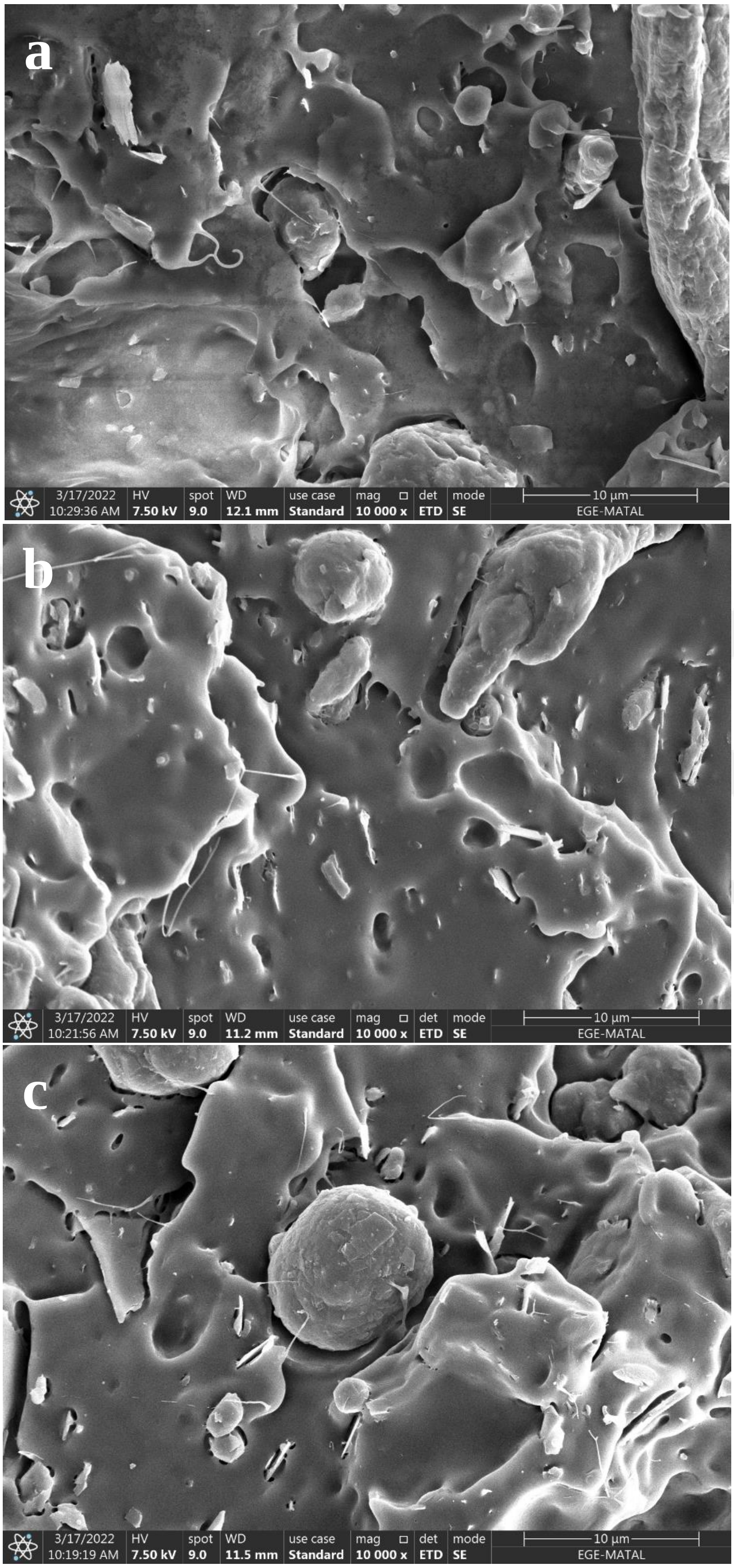


Figure 4.23. SEM images; a) 15POP-4, b) 15POP-5, c) 15POP-6

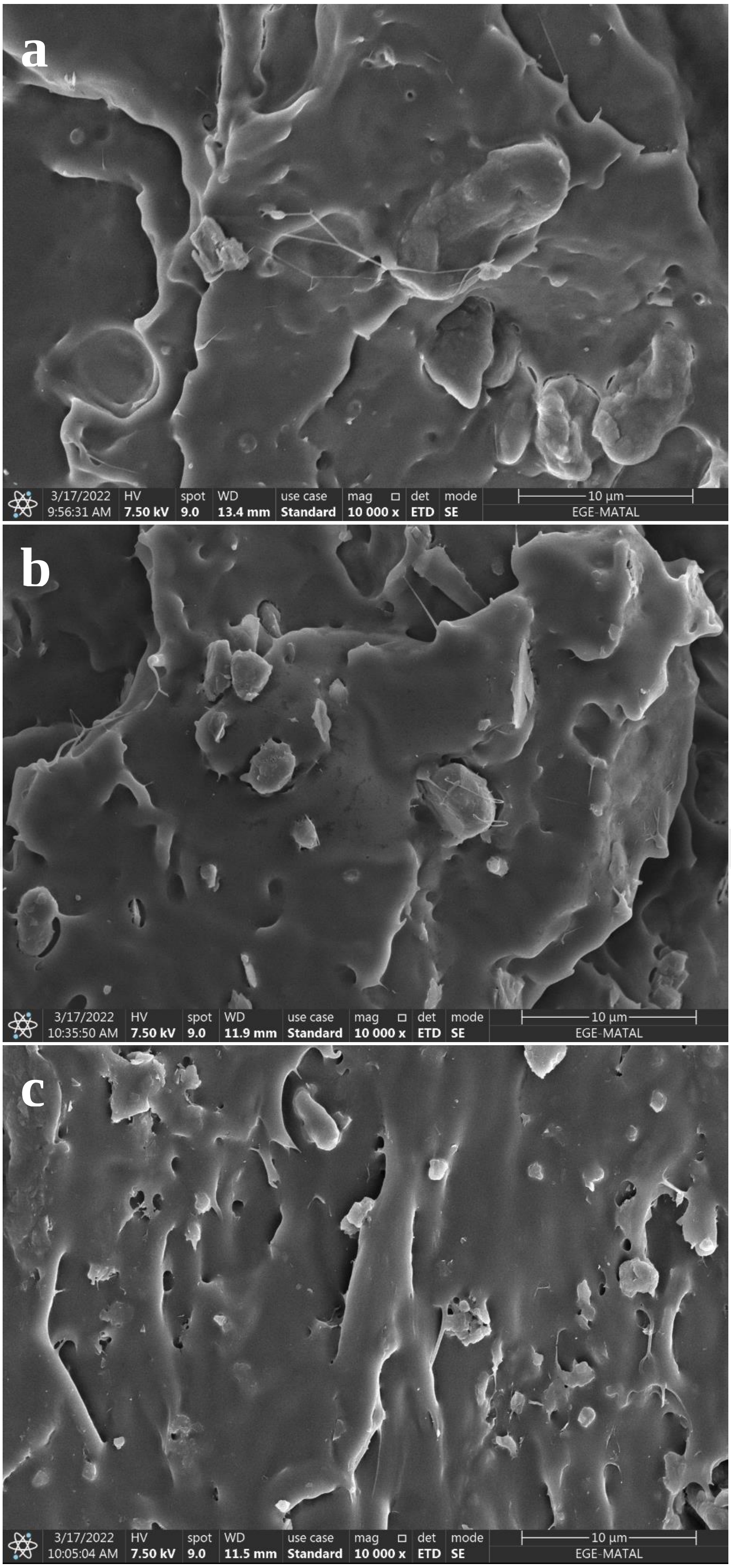


Figure 4.24. SEM images; a) 20POP-4, b) 20POP-5, c) 20POP-6

SEM pictures of composites are shown in Figure 4.21, Figure 4.22, Figure 4.23 and Figure 4.24. Air holes can be seen in the composites surfaces, and gaps are more intensive in Figure 4.23 and Figure 4.24 which POP powder concentrations are greater. The presence of air gaps in the structure can be explained by the fact that the POP powders absorbed moisture from the air after drying process. These holes suggest weak interfacial adhesion, which is verified by composite tensile testing and impact testing data. It can also be seen that the size of POP powder particles are not uniform.

As the amount of POP powder in the polymer increases, some areas of agglomeration in the polymer was observed and that resulted in locations where the POP powder distribution is not uniform, affecting the mechanical properties of the composites.

5. CONCLUSION

The influence of an organic waste filler, pomegranate peel (POP) powder, on the mechanical, thermal properties and antimicrobial activities of PLA composites were examined in this work. Extrusion technique was used for creating POP powder filled composites. POP powder is being used for the first time as both an antibacterial and a reinforcing agent manufactured by extrusion instead of SCM.

Alternatives for commercial petroleum based polymers are being researched that are made from renewable resources that compose in nature without leaving harmful or hazardous leftovers such as toxics. As a consequence of decades of researchs, a variety of biodegradable polymers with varied properties have been found. PLA has the biggest share of global biodegradable polymer manufacturing capacity due to its wide range of applications, cheap access to raw materials, and excellent manufacturing know-how. Also POP powder is an biobased/natural filler in contrast commerticial antimicrobial additives.

With the increased loading amount of the POP powder, mechanical and impact strengths of composites decreased. The composites' significant loss in impact strength is due to poor interfacial bonding between the filler and the PLA matrix. Poor interfacial bonding causes microspaces between the filler and the polymer matrix, and when impact occurs, these microcracks propagate quickly, lowering the impact strength of the composites. When the POP powder weight percentage reached 15%, tensile strength reduced by %49. The addition of POP powder resulted in decrease the tensile strengths, in contrast increased flexural strengths for 5% filled composites. The results are coherent with HDT results.

SEM examination revealed the shape of the interface as well. It can be noticed that POP powder is not uniform in size. Furthermore, the composites formed have air spaces, and adequate POP powder dispersion is not achieved, especially in higher concentration of POP powder contents lead to agglomeration. These results are matching with mechanical and impact test results. In test results decreases in mechanical and impact strengths with the increased loading amount of the POP powder are also observed. The incompatibility of the matrix/reinforcement interface is regarded to be the main cause of this problem. To solve this problem firstly modifying the surface of the reinforcement material can be done to ensure that the POP powder particles are distributed uniformly throughout the matrix material by opening the layers. Secondly, matrix and reinforcing materials, as well as a compatibilizing agent, can be introduced into composite material to improve matrix/interface compatibility.

In DSC thermogram there are not any crystallization peak above 5% POP powder loading means that POP powder has an anti-crystallization impact on PLA. Crystallization is delayed due to the increased contact sites between the PLA matrix and the organic POP powder phase. These could be connected to the fact that the reinforcement makes polymeric chain migration difficult. As a result, chain folding of polymeric molecular segments may be inhibited at the growing face of the polymeric crystal, resulting in a completely amorphous microstructure.

The antibacterial activity against A. aureus E. coli is enhanced by 55.5% roughly when POP powder was added at a concentration of 5%. Composites with 20wt.% POP powder have a 99 % inhibition rate against both bacteria. The composites filled with 15wt.% and 20wt.% POP powder presented better antibacterial effectiveness is great as to accept the material as being antibacterial.

To sum up, POP powder offers advantages over the inorganic additives such as being biobased, organic food waste utilization and safe zone for usage areas directly contact food or human body. These composites can be used for surgical sutures, covering surfaces of some medical devices, handles of shopping basket like major super markets already do, some disposable covers to use in shoe cupboards and disposable facial mask that use almost everyone due to COVID-19. Enhancing mechanical strengths and achievement antimicrobial performance at lower concentrations of POP can be the scope of further studies.

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TEŞEKKÜR

Yüksek bilgi birikimi ve mesleki deneyiminin yanısıra, yüksek lisans eğitimim esnasında vermiş olduğu destek ve teşvikler sayesinde motive olmamda ve istikrarlı bir şekilde çalışmamda çok büyük emeği olan tez danışmanım, değerli hocam Doç. Dr. Lütfiye ALTAY'a sonsuz teşekkür ediyorum. Benden desteklerini esirgemeyen, zorluklarda yolumu açan sevgili hocam Doç.Dr. Mehmet SARIKANAT'a, çalışmalar esnasında belirttiği değerli önerileri ve teknik bilgi desteğinden dolayı çok teşekkür ediyorum.

Araştırmalarımda ve yüksek lisans hayatımda yardımlarını esirgemeyen Merve SAĞLAM'a,

Sundukları imkân ve çalışma ortamı için IMS POLYMERS ailesine,

Kariyerimde ve eğitim hayatımda her zaman destekçim olan, maddi ve manevi desteği hiçbir zaman eksik etmeyen ve bana her daim benden çok inanan aileme teşekkürü bir borç bilirim.

Yoluma ışık tutan, beni her düştüğümde kaldırıp yüreklendiren mentörüm, başarı kaynağım eşime özellikle minnettarım. Bu tezi sonsuz destekleri ve teşviklerinden ötürü eşim, Öztaç KORKMAZ'a ithaf ediyorum.

24 / 01 / 2021

Melike TUNÇALP

ÖZGEÇMİŞ

ÖĞRENİM DURUMU

- Ege Üniversitesi Makine Mühendisliği Yüksek Lisans *2018 – 2022*
- Ege Üniversitesi, Kimya Mühendisliği (İngilizce) *2011- 2017*
- Ege Üniversitesi, Makine Mühendisliği (Çift Anadal programı) *2013- 2017*
- Atakent Anadolu Lisesi *2007-2011*

İŞ TECRÜBESİ

- Vestel Elektronik Sanayi ve Ticaret A.Ş. / Kıdemli Mekanik Tasarım Uzmanı

  Mart 2020 –

  İş Tanımı;

  1) TV-Panel, TV-arka kapak , TV yardımcı komponent (Örn; speaker box, bracket holder, bracket wifi vb.) mekanik tasarımı
  2) Design for Manufacturing (DFM)
  3) TV ürün grubu sürdürülebilirlik sorumlusu
     a. Alternatif plastik malzeme arayışları
     b. Yalınlaştırışmış tasarımlar
     c. Daha az malzemenin kullanıldığı tasarımlar

- Bak Ambalaj San. Tic. A.Ş. / Ar-Ge Merkezi Mühendisi
  Ekim 2017 – Mart 2020

  İş Tanımı;

  1) Fikri Mülkiyet ve Sinai Haklar (FSMH) sorumlusu
  2) TÜBİTAK ve Ar-Ge Merkezi projeleri yürütücüsü
  3) 3189142 nolu "Esnek Gıda Ambalajları İçin Türkiyede İlk Kez Geliştirilecek Düşük Migrasyon Değerlerine Sahip Poliüretan Bazlı Retort Flekso Mürekkep ve Retort Esnek Gıda Ambalajı Tasarımı" adlı Tübitak Projesi Yürütücüsü, 2018-2020
  4) 3180281 nolu "Yüksek Hızlı Düşey Paketlemeye Uyumlu Esnek Ambalaj ve Isıyı İstenen Hızda ve Optimum Bir Şekilde İletilebilen Yapıştırma Çenesi Tasarımı ve Üretimi" adlı Tübitak Projesi Yürütücüsü, 2018 - 2020
  5) Geliştirilen yeni ürünlerle ilgili teknik makaleler ve posterlerle bilimsel kongrelere katılım

     * II. International Joint Science Congress of Material and Polymers kongre katılımı, 2018, Dures- Arnavutluk

     * EnviroChem Uluslararası Çevre Kimyası Kongresi poster Katılımı, 2018, Antalya
  6) Minitab ile Deney Tasarımı (DOE)

- TÜPRAŞ A.Ş, İzmir
  Ağustos 2016- Eylül 2016

  Yaz Stajı
- Viking Kağıtçılık A.Ş, İzmir
  Haziran 2014- Temmuz 2014

  Yaz Stajı

YABANCI DİL & BILGISAYAR PROGRAMLARI

- İspanyolca (Seviye A+) Kursu, Universidad de Alicante, İspanya
- İngilizce (Upper Intermediate)
- Almanca (A1), Goethe-Institut, İzmir
- Catia V5; Makine Mühendisleri Odası, İzmir
- Creo
- Autocad
- Microsoft Office
- SAP
- Minitab
- TA Universal Anaylsis

YAYINLAR

- Sever, K., Atagür, M., Tunçalp, M., Altay, L., Seki,Y., and Sarıkanat, M., 2018, The Effect of Pumice Powder on Mechanical and Thermal Properties of Polypropylene, Journal of Thermoplasttic Composite Materials, 1-15

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