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INFLUENCE OF CONDUCTIVE ADDITIVE INCLUSIONS IN PLA-BASED
COMPOSITES

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
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COMPOSITES

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ABSTRACT

INFLUENCE OF CONDUCTIVE ADDITIVE INCLUSIONS IN PLA-BASED COMPOSITES

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The OS powder and Fe₃O₄ mica-based conductive pigment developed for this thesis were added to the PLA matrix in four different concentrations for loading ratios of 1%, 10%, 20%, and 30% to determine the optimal concentration. Using the tensile, hardness, and impact tests, dynamic mechanical analyses test, linear four-probe method, melt flow index measurements, and scanning electron microscopy methodology, respectively, the mechanical, thermo-mechanical, electrical conductivity, melt-flow, and morphological properties of composites were reported.

Tensile test results, tensile strength, and modulus characteristics of PLA decrease with additive integration, according to test results. However, PLA's elongation value decreased as OS and CP loadings increased. The composites' maximum tensile performance was attained as 20% of both CP and OS amounts were added. The unfilled PLA's Shore D value was increased by including OS and CP. At the same loading levels, carbon-based OS produced comparatively higher hardness values than CP, which comprised iron oxide and alumina silicate. In summary, composite samples exhibiting a 20% loading ratio of

both OS and CP showed significantly improved mechanical and thermo-mechanical performances compared to other composites. Composite films with 1% additives can be used in electrostatic packing. Additionally, fabricated composites can be used to produce 3D-printed components for applications where appropriate mechanical resistance and electrical conductivity specifications are required.

Keywords: Polylactic acid, Conductive pigment, Oltu stone, Polymer composites, Melt-blending

ÖZ

İLETKEN KATKI MADDELERİNİN PLA ESASLI KOMPOZİTLERE ETKİSİ

Aisha Rakea

Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya

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Bu çalışmada, PLA matrisine %1, %10, %20 ve %30 yükleme oranları ile Oltu taşı tozu (OS) ve mika bazlı Fe_3O_4 iletken pigment (CP) eklenerek optimum konsantrasyonlar araştırıldı. Elde edilen kompozitlere çekme, sertlik ve darbe testleri, dinamik mekanik analiz testi, doğrusal dört nokta iletkenlik ölçümü, erime akış indeksi ölçümleri ve taramalı elektron mikroskobu kullanılarak sırasıyla mekanik, termomekanik, elektriksel iletkenlik, erime akışı ve morfolojik ölçümler yapılarak elde edilen kompozitlerin özellikleri tanımlanmaya çalışıldı.

Kompozitlerin çekme testleri incelendiğinde, gerek PLA'nın çekme mukavemetinde ve modülüs değerlerinde gerek ise uzama miktarlarında OS ve CP artışı ile azaldıkları görüldü. Kompozitlerin maksimum çekme performansı OS ve CP miktarlarının %20 olduğu örneklerde elde edildi. Saf PLA'nın Shore D değerinin, OS ve CP eklemeleri ile arttığı gözlemlendi. Aynı yükleme seviyelerinde, karbon bazlı OS, demir oksit ve alümina silikat içeren CP'ye kıyasla nispeten daha yüksek sertlik değerlerine ulaştı. Özetle, hem OS hem de CP için %20'lik bir yükleme oranı sergileyen kompozit numuneler, diğer kompozitlerle karşılaştırıldığında kısmen daha iyi mekanik ve termomekanik özellikler gösterdikleri saptandı. Elektrostatik paketlemede %1 katkılı kompozit filmler kullanılabilir. Üretilen kompozitler, uygun mekanik ve elektriksel

iletkenlik özelliklerinin gerekli olduđu uygulamalar için 3D baskılı bileşenler oluşturmak için dizayn edilebilir.

Anahtar kelimeler: Polilaktik asit, İletken pigment, Oltu taşı, Polimer kompozitler, Eriyik harmanlama

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Figure A2. Resistivity curve of PLA/CP 30% composite samples45



LIST OF SYMBOLS/ABBREVIATIONS

CB	-	Carbon Black
CF	-	Carbon Fiber
CP	-	Conductive Pigment
DMA	-	Dynamic Mechanical Analysis
FDM	-	Fused Deposition Modeling
GNP	-	Graphene Nanosheets
MFI	-	Melt Flow Index
MWCNT	-	Multiwall Carbon Nanotube
OS	-	Oltu Stone
PAN	-	Polyacrylonitrile
PLA	-	Polylactic Acid
PP	-	Polypropylene
T _g	-	Glass Transition Temperature
TPU	-	Thermoplastic Polyurethane
SEM	-	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Introduction

The process of electrical conduction is greatly aided by conductive pigments, which are substances that contain carbon, such as graphene, graphite, carbon black, carbon nanotubes, and carbon-based materials found in nature. In addition to crucial characteristics like robust adhesion and resistance to corrosion. They are ideal for large-scale industrial applications because of these remarkable qualities.

Oltu stone, commonly found in the Erzurum area of Türkiye, offers good chemical and physical qualities and a high carbon content. Its physical attributes include high gloss, spectral transparency, and a conchoidal fracture pattern that fragments into curving, smooth surfaces that become continuously charged. Oltu stone is a semi-precious coaly stone and is generally named natural carbon black. Its chemical composition provides carbon and other components, which helps explain its excellent chemical stability and heat resistance [1-5].

A Polylactic acid-based biocomposite is one of the best alternatives to non-biodegradable and unsustainable composites. PLA is a biodegradable and sustainable polymer without adverse environmental or economic effects.

PLA-based composite materials can be processed using conventional techniques, including injection molding, compression molding, and, more recently, additive manufacturing to develop 3D filament materials [6, 7].

Furthermore, due to its unique properties, including its availability, biocompatibility, lightweight design, and biodegradability, PLA quickly displaces petroleum-based products. It's also a very beneficial biopolymer. It can be applied in many areas, including biomedical, food packaging, and commodity sectors [8-10].

Considering these research highlights, the influence of the additive concentration is the basis for research into conductive pigments-filled PLA composites or Oltu stone-reinforced PLA composites. Fabrication of PLA-based composites can be possible with the appropriate characteristics by using fundamental aspects of composites such as mechanical, thermomechanical, melt flow, and morphological qualities.

The melt mixing process is a standard method for producing PLA filaments with the necessary colors for 3D printing applications. This processing method is also the most favored option for achieving homogenous dispersion and practical optimization.

These factors led to the goal of this thesis project, which used the melt mixing method to examine the basic characteristics of PLA composites reinforced with CP and OS. Comparisons were made between the performances of CP and OS-loaded PLA-based composites and their concentration.

CHAPTER 2

BACKGROUND INFORMATION

2.1. Composite Materials

Composite materials are a mixture of two materials with distinct physical and chemical properties to enhance the properties of the primary material, such as strengthening mechanical, physical, or electrical conductivity [11]. It consists of a strong material (fibers) and a weaker material (matrix), which have different properties and are homogeneous microscopically [12]. Composite materials have examples encompass different kinds, such as:

1. Fiberglass consists of glass fibers inserted into a matrix characterized by strength and longevity.
2. Composites known as "flakes" consist of fibers that provide two-dimensional reinforcement to their base materials.
3. Composite materials that are layered or laminated are made up of several layers of one type or another. They can, therefore, be strengthened whenever such reinforcements are required.

2.1.1. Properties of Composites

Composite materials have various advantages, such as outstanding thermal properties and lightweight [13]. Additionally, lightweight reinforcement provides them with structural stability and fuel efficiency for vehicles made with composites [14]. These reinforcement structures are due to the style, type, application, and fabrication method they will be subjected to. The choice and application of these polymers depend on the mixing process that defines their quality. In summary, using composite materials is

crucial in different fields because of their remarkable characteristics and, thus, the flexibility they provide in various applications [12].

2.1.2. Applications of Composites

Composite materials are used in vast and varied fields, such as civil infrastructure, where fiberglass strengthens buildings and increases building aesthetics.

Composite materials are light and durable, so they are preferred in the aerospace industry. Composites make up most of the structure of the Boeing 787 "Dreamliner," one of the leading aircraft of its class [15].

Composite materials are utilized in electric applications for semiconductor manufacturing, shielding, and insulation for high dielectric strength and resistance to electromagnetic interference and moisture [16].

The use of composite materials in the automotive industry is essential. Composites have properties that make them suitable for manufacturing different automobile components, both internal and external. Also, the exceptional strength-to-weight ratio of composite materials' effect on reducing the overall weight of composite features is expected to contribute to lowering fuel consumption in vehicles, thus enhancing personal fuel savings by reducing the weight of vehicle components [14].

Due to their lightweight, biocompatibility, and other advantageous qualities are utilized in medical sciences composites for dental fillings, prosthetics, and even drug delivery systems [17].

In biomedical engineering, biocomposites are significant for various applications such as bone tissue engineering, drug delivery, and cancer treatment [17]. However, research continuously tries to avoid the challenges in machining to guarantee their efficacy in high-end medical tools.

2.2. Overview of Poly (lactic acid)-based Composites

Because of composite materials' excellent qualities, which increase their possible applications, researchers are becoming more interested in them. These materials are in greater demand every day. Composite materials are preferable to traditional bulk materials because they are exceptionally strong.

Conventional composites frequently employ synthetic polymers that come from products made from petroleum. Environmental issues prevent these polymers from being widely used since they are neither sustainable nor biodegradable and harm the environment when decomposing. In addition, the rapid depletion of petroleum resources due to their extensive use might lead to their complete exhaustion. A PLA-based biocomposite is one of the best alternatives to non-biodegradable and unsustainable composites. [18].

PLA is a sustainable polymer that is fully biodegradable and doesn't harm the environment or the economy. In biocomposites, natural fibers such as flax, coir, hemp, wheat straw, sisal, and so forth are used as reinforcing elements. At the same time, the matrix is composed of biopolymers derived from renewable resources like PLA and starch. Many sectors, including airplanes, cars, sports, medical, furnishings, and packaging for food, have found extensive use for composite materials [19].

It is crucial to examine how different fabrication techniques, such as compression molding, influence the mechanical characteristics of PLA-based composites.

2.2.1. PLA's Benefits and Drawbacks

Recently, researchers have focused their study on biocomposites because of concerns about the dwindling petroleum reserves and global sustainability. PLA is superseding petroleum-derived products according to unique properties such as being available, biocompatible, lightweight, and biodegradable, and it stands out as a favorable biopolymer. It has various applications, including biomedical industries, food packaging, and commodities. However, there are many challenges to using PLA, such as low impact strength, limited elasticity, and thermal resistance, among others, limiting its use in specific engineering sectors [20].

To address these problems, researchers found various strategies. Incorporation of natural additives with PLA has been proposed to reinforce its performance, as it forms hydrogen bonds between nano clay particles and PLA, showing a strong attraction. Although it may reduce the modulus of elasticity by the inclusion of plasticizers, PLA exhibits promise in improving PLA's brittleness. Moreover, to further enhance PLA's characteristics, natural fibers, cellulose, agricultural wastes, and natural minerals have been studied [21-30].

2.3. Processing Techniques of PLA-Based Composites

In general, conventional techniques for producing strands of reinforced polymer composites are used to produce green biocomposites. Three categories of production techniques are applied to biocomposite materials:

1. Closed molding processes: There are four techniques: spray layup, manual layup, filament winding, and autoclave procedures.
2. Open molding procedures involve three methods: resin transfer molding, injection molding, and compression molding.
3. Additive manufacturing processes.

2.3.1. Compression Molding

The process of creating composites based on PLA is called compression molding. For both thermoset and thermoplastic goods, this technique is most frequently used. This method provides PLA by adding improved or supplemental materials to the lower mold. The enhancing components are arranged like a fiber mat. High heat is applied to the mold to allow PLA to melt and mix evenly across the fiber mat. The mold is then subjected to high pressure, roughly 20 kPa, to get the final composite product shape. Products with great strength, rapid manufacturing rates, and exceptional dimensional precision are produced using this technique [31, 32].

2.3.2. Injection Molding and Extrusion Injection Molding

The hot (beyond the melting point) thermoplastic polymer mixture and fibers are pressed to fill the mold cavity using the injection molding technique. The part is taken out of the mold once the material has solidified. A practical and affordable method for producing complicated components on a large scale for commercial use, including automobile parts and consumer items, is injection molding.

During the extrusion injection molding process, PLA pellets and filler materials are fed into the barrel via a hopper. PLA melts in the extruder injection molding device when it is heated by a surface heater that is fixed to the barrels. It's not pure. With the aid of a rotating screw, filler components are mixed with it. This uniform PLA and fillers mixture is then pushed to inject the mold of the desired shape through the converging nozzle, reducing the chance of air entrapment. A mold typically consists of two parts: moving and stationary parts. The product is extracted from the mold by dividing its mobile component from its fixed component following the ingredients' solidification [33].

2.4. Conductive Pigment in Focus: An Examination of its Diverse Applications and Fundamental Characteristics

The conductive pigment is a fundamental component facilitating electrical conductivity and a spectrum of functionalities such as the formulation of conductive coatings, static electricity prevention, thermal management, electromagnetic shielding, and electrical conduction tasks.

The conventional repertoire of carbon-based conductive pigments comprises well-established entities like graphene, graphite, carbon black, carbon nanotubes, and naturally sourced carbon materials. However, recent advancements have introduced carbon pigments derived from coal tar, exhibiting exemplary electrical conductivity alongside resilience to low-temperature carbonization. This unique attribute suits them for extensive industrial applications [34].

The defining attributes of these conductive pigments encompass elevated electrical conductivity, robust adhesion properties, anti-corrosion capabilities, and superior performance in electrical heating applications [35].

2.5. Oltu Stone

Oltu stone, also known as Oltu marble or black amber, is a distinctive sedimentary rock native to Türkiye, celebrated for its unique physical and chemical properties [1-3].

OS's appearance is marked by a deep jet-black color, occasionally with green or grey undertones, and a smooth texture that becomes glossy after polishing. It has a lower hardness rating and density compared to many stones, making it easier to carve and shape.

When polished, OS displays a high luster and may show slight translucency. Its fracture pattern is conchoidal, breaking into smooth, curved surfaces, and it can accumulate a static electric charge like amber [1-5].

Chemically, OS is carbon-based with traces of other elements, contributing to its thermal resistance and relative chemical stability, although it remains vulnerable to certain corrosive substances [36, 37].

Overall, Oltu stone's unique blend of physical and chemical traits makes it a compelling subject for research, particularly in geological and material sciences, highlighting its enduring significance and diverse applications.

2.6. Literature Review

Guo et al. performed the addition of carbon black (CB) to poly (lactic acid) (PLA) composites to increase the conductivity, which is especially significant when the CB content reaches 8%. The conductive PLA/CB composites transition from insulator to conductor when the carbon filler content exceeds the critical filler content. However, the conductivity does not change much beyond 12wt% [38].

Guo enhanced the electrical conductivity of PLA/wood pulp/TPU composite systems thanks to the fused deposition modeling (FDM) process. Incorporating nano graphite into the composites at a 25% loading ratio significantly reduces the volume resistivity, forming a conductive network. This addition also improved thermal conductivity by 25.71%. Adding reduced graphene (rGO) with graphite to the composite increased the electrical and thermal conductivity more effectively than other materials, such as tannic acid functionalized graphite or multi-walled carbon nanotubes [39].

Yan et al. utilized the electrospinning, pinning, and carburizing procedures to develop polyacrylonitrile/graphene nanofiber composite yarns with improved mechanical and electrical conductivity. Because graphene was simple to incorporate into low-mass sections, the necessary graphitic structures formed, resulting in a maximum conductivity of 66.44 S/cm at 1100 degrees Celsius. Furthermore, the composite yarns' mechanical characteristics revealed a modulus of 14.63 GPa and a maximum stress of 59.49 MPa. [40].

Park et al. stated that by enhancing the dispersion effect and interface characteristic with the polymer matrix, based on the surface treatment of acid, isocyanate, and PA6-grafted on multi-walled carbon nanotube (MWCNT), the electrical conductivity of the composite was enhanced [41].

Lee et al. investigated the electrical conductivities, electromagnetic characteristics, and electromagnetic shielding efficiency of polypropylene (PP)/ carbon fiber (CF) composites. They changed the processing conditions to produce composites with

various fiber length distributions (FLD). In the PP/CF composites, longer fibers displayed higher electrical conductivity. They observed a comparable outcome when the fiber content increased [42].

In their research, Taipalus et al. found that using longer fibers or increasing the volume content of fibers might significantly improve the electrical conductivity of CF-reinforced blends of PP and polyaniline [43].

Kalaitzidou et al. inspected the electrical conductivity of PP-based composites containing diverse carbon fillers created through dissolve blending and infusion molding forms. Through their experimentation, they recognized the permeation limit for PP/CF composites, which fell inside the run of 8–10 vol % [44].

Ram et al. examined the permeation limit of polyvinylidene fluoride (PVDF) filled with brief carbon strands extending from 1 to 5 mm in length. Their discoveries uncovered permeation limits inside the extent of 0.54–1.00 vol. They saw a diminish within the permeation limit and an increment in electrical conductivity when longer filaments were utilized [45].

Dong et al. studied the thermal conductivity and electrical resistivity of electrospun polyacrylonitrile (PAN) / multiwall carbon nanotube (MWCNT) composite carbon nanofibers. Their results showed significant improvements with increasing MWCNT content. To illustrate the enhanced qualities of these composite nanofibers and show the potential of MWCNTs as adequate reinforcements in polymer materials, they used SEM, Raman spectroscopy, and XRD analysis [46].

Beniak et al. fabricated a conductive PLA material, highlighting its conductive properties due to carbon black particles in the matrix. According to their findings, the conductivity of conductive PLA increased with higher carbon black content but reduced the durability of the final product [47].

Lebedev et al. conducted a study related to thermally and electrically conductive bio-composites prepared using a mixture of PLA and graphite filler. They postulated improved thermal stability, mechanical properties, and electrical conductivity by integrating graphite into the PLA matrix [48].

Al-Rubaiai et al. studied the properties of 3D printed conductive PLA materials with electrically controlled stiffness for robotic and biomedical devices, showing a 98.6% reduction in Young's modulus at 80°C. The conductive PLA blend yielded a glass transition temperature of 56.7°C, a melting point of 153.8°C, and a thermal conductivity of 0.366 W/(mK) [49].

Tirado-Garcia et al. produced conductive PLA composites involving carbon black particles, exploring their mechanical, electrical, and thermal properties. The microstructural arrangement of CB particles in the polymer matrix was analyzed, highlighting the impact on conductivity and printing orientation [50].

2.7. Aim of The Study

In this thesis, PLA-based composites with varied concentrations of CP and OS were produced. The influence of OS and CP inclusions on mechanical, morphological, electrical, melt-flow, and thermo-mechanical properties was reported. The study's main objective was to determine the optimal concentrations of CP and OS for PLA-based composites with the help of experiment data involving tensile and impact resistance, morphological and electrical conductivity, melt-flow, and dynamic mechanical analysis. The findings of composites filled with CP and OS were compared to estimate the optimum loading level for each PLA/OS and PLA/CP composite.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

In this study, PLA was used as a polymer matrix, and conductive pigment and oltu stone powder were used as additives.

3.1.1 PLA polymer

In this thesis study, PLA was used as a pellet form under the trade name Ingeo Biopolymer and was purchased from Natureworks, USA. According to the manufacturer, the density and relative viscosity of this fiber grade PLA is 1.23 g/cm^3 (ASTM D792) and 3.1 (CD Internal viscotek technique).

3.1.2 Conductive Pigment

CP (Iriotec 8835) was supplied in granular form from Merck AG, Germany with a 15-micron mesh. It contains inorganic minerals such as mica and Fe_3O_4 and has a density of $3.8 - 4.0 \text{ g/cm}^3$, as provided by the producer.

3.1.3 Oltu Stone

OS was obtained in powder form with a 60-micron mesh size by a local supplier in Erzurum, Türkiye. The composition of OS powder was obtained by EDX analysis, and it exhibits the presence of 99% carbon and 1% sulfur contamination as displayed in the EDX graph in Figure 3.1.

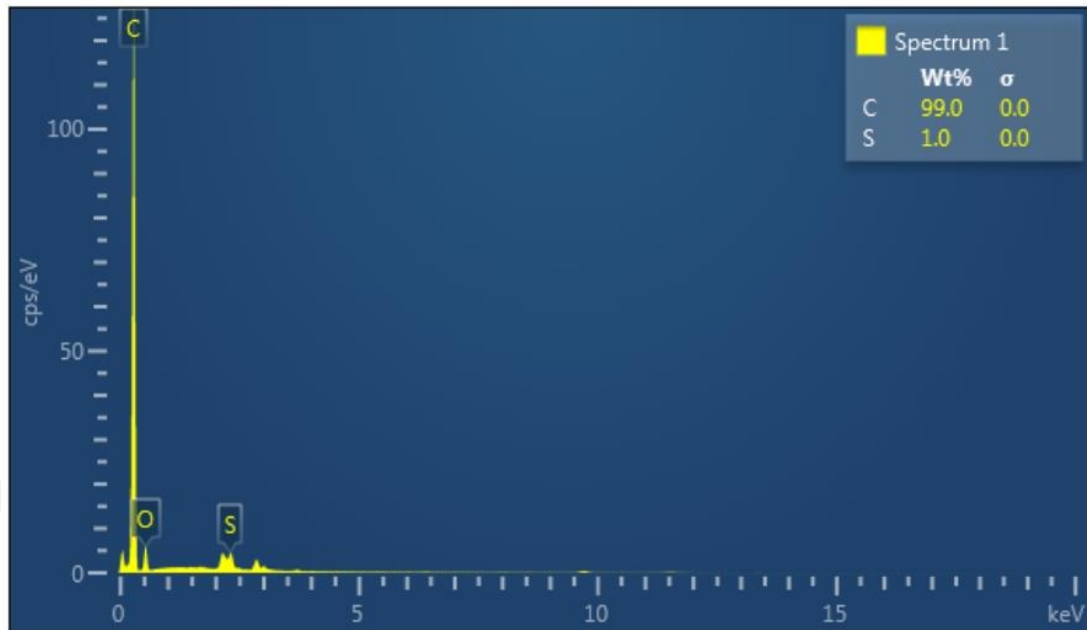


Figure 3.1. EDX graph of OS powder

3.2 Production Techniques

3.2.1 Melt Compounding

PLA polymer and additives were dried at 100°C for 2 hours to avoid moisture prior melt blending process. Composite samples were produced via laboratory-scale twin screw micro-compounder (MC15HT, Xplore Instruments, Holland), as displayed in Figure 3.2. Process parameters applied during the fabrication of composite samples are listed in Table 3.1.



Figure 3.2. Lab-scale Micro-compounder

Table 3.1. Compounding Parameters

Parameters	Specification	Unit
Mixing temperature	200	°C
Mixing time	5	min
Screw speed	100	rpm

3.2.2 Compression Molding

Composite samples obtained from the melt-blending process were shaped using a laboratory-scale hot-press instrument (Hidroliksan, Türkiye), as represented in Figure 3.3. Process parameters applied during compression molding are listed in Table 3.2.



Figure 3.3. Lab-scale Hot-press Instrument

Table 3.2. Compression Molding Parameters

Parameters	Values	Unit
Pressing temperature	200	°C
Compression Pressure	5	Bar
Holding time	2	min

Test specimens were shaped from film samples obtained from the compression molding process (Figure 3.4). The dimensions of dog-bone-shaped tensile test samples are displayed in Figure 3.5. The gauge length of test specimens is 100 microns.

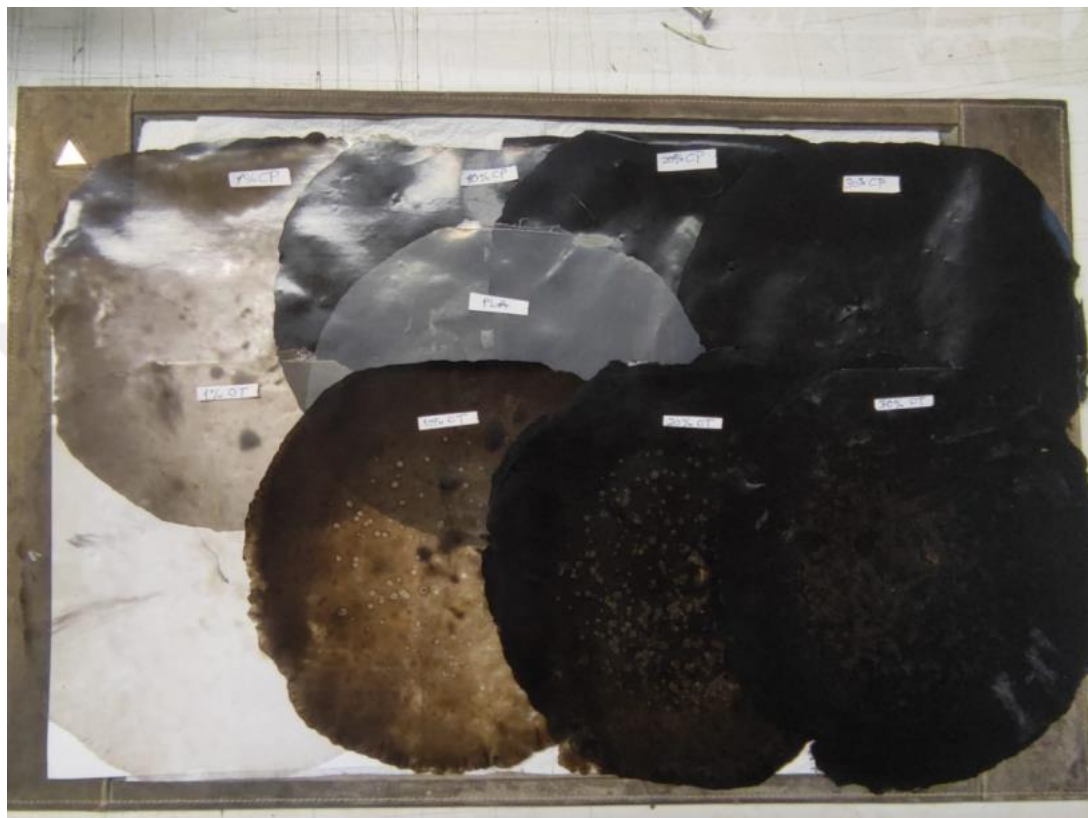


Figure 3.4. Produced Film Samples

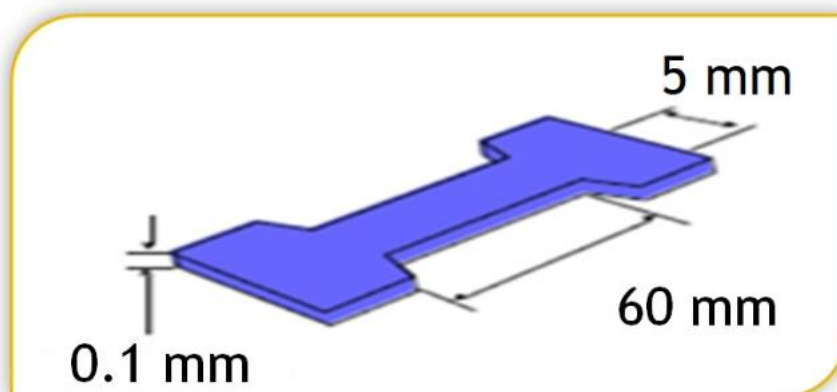


Figure 3.5. Dimensions of Tensile Test Sample

3.3 Characterization Methods

The characterization steps of test samples were carried out following related standards for each test method. All the experimental data were recorded as an average of a minimum of five specimens.

3.3.1 Tensile Test

Tensile test measurements of unfilled PLA and composites conducted by Lloyd Instruments LR 5K tensile testing machine in the accordance of ASTM D638 standard provide a test procedure for assessing the tensile properties of reinforced and unreinforced plastics, as displayed in Figure 3.6. A crosshead speed of 5 cm/min and 1 kN load cell were utilized during tensile testing.



Figure 3.6. Tensile Testing Instrument

3.3.2 Hardness Test

Hardness test measurements of unfilled PLA and composites were done using a Tronic digital shoremeter. The image of the Shore D durometer is shown in Figure 3.7.



Figure 3.7. Hardness Testing Device

3.3.3 Impact Test

An unnotched Izod impact test was performed via an impact tester (Coesfeld, Germany). Impact energy measurements were done according to ASTM D256 standard using a 1 J pendulum. Figure 3.8 displays the impact tester used in this study.



Figure 3.8. Impact Tester

3.3.4 Dynamic Mechanical Analysis (DMA)

DMA parameters of PLA and composites were recorded using a dynamic mechanical thermal analyzer (DMA 8000, Perkin Elmer, USA) in bending mode between the

temperature range of -3°C to 120°C with a heating rate of $5^{\circ}\text{C}/\text{min}$ and a constant frequency of 1 Hz.

3.3.5 Melt Flow Index Test (MFI)

MFI measurements of PLA and composites were carried out by a melt flow indexer (Coesfield Meltfixer LT, Germany), as represented in Figure 3.9. Measurements were recorded under a standard load of 2.16 kg at 200°C .



Figure 3.9. Melt Flow Indexer Instrument

3.3.6 Electrical Conductivity Measurements

Electrical conductivity values of composites were measured using the linear four-probe method via a controller device (Nanomagnetics Instruments, Türkiye) as shown in Figure 3.10. The current source of 10 microamperes and a test temperature of 30°C were applied during measurements. The parameters used in conductivity

measurements were a mobility range of $1-10^7$ cm² /Vs, the current range of ± 2 nA– ± 20 mA, a resistivity range of 10^{-4} – 10^9 Ω .cm and a magnetic field option of 1,0 T adjusted.



Figure 3.10. Electrical Conductivity Equipment

3.3.7 Scanning Electron Microscopy (SEM)

The morphological properties of composites were examined using an electron microscope (JSM-6400, Japan). The surfaces of fractured samples obtained from the impact test were coated with a thin layer of gold.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Tensile Properties of Composite

Tensile test parameters of OS and CP-loaded composites, including tensile strength, percent elongation at break, and tensile modulus, are listed in Table 4.1 and 4.2, respectively.

Table 4.1. Tensile test data of PLA and PLA/OS composites

Samples	Tensile Strength (MPa)	Tensile Strain (%)	Tensile Modulus (GPa)
PLA	46.7±0.6	4.1±0.3	1.7±0.2
PLA/OS 1%	34.4±0.5	3.7±0.4	1.5±0.3
PLA/OS 10%	38.1±0.3	2.9±0.3	1.9±0.3
PLA/OS 20%	42.2±0.4	2.6±0.5	2.4±0.2
PLA/OS 30%	30.5±0.4	2.3±0.3	1.6±0.2

Table 4.2. Tensile test data of PLA and PLA/CP composites

Samples	Tensile Strength (MPa)	Tensile Strain (%)	Tensile Modulus (GPa)
PLA	46.7±0.6	4.1±0.3	1.7±0.2
PLA/CP 1%	29.1±0.4	3.6±0.3	1.6±0.2
PLA/CP 10%	31.5±0.5	2.4±0.4	2.0±0.3
PLA/CP 20%	38.0±0.3	2.2±0.3	2.6±0.3
PLA/CP 30%	25.8±0.5	2.1±0.2	1.8±0.3

Tensile strength versus elongation curves OS and CP-containing composites are represented in Figure 4.1 and Figure 4.2, respectively.

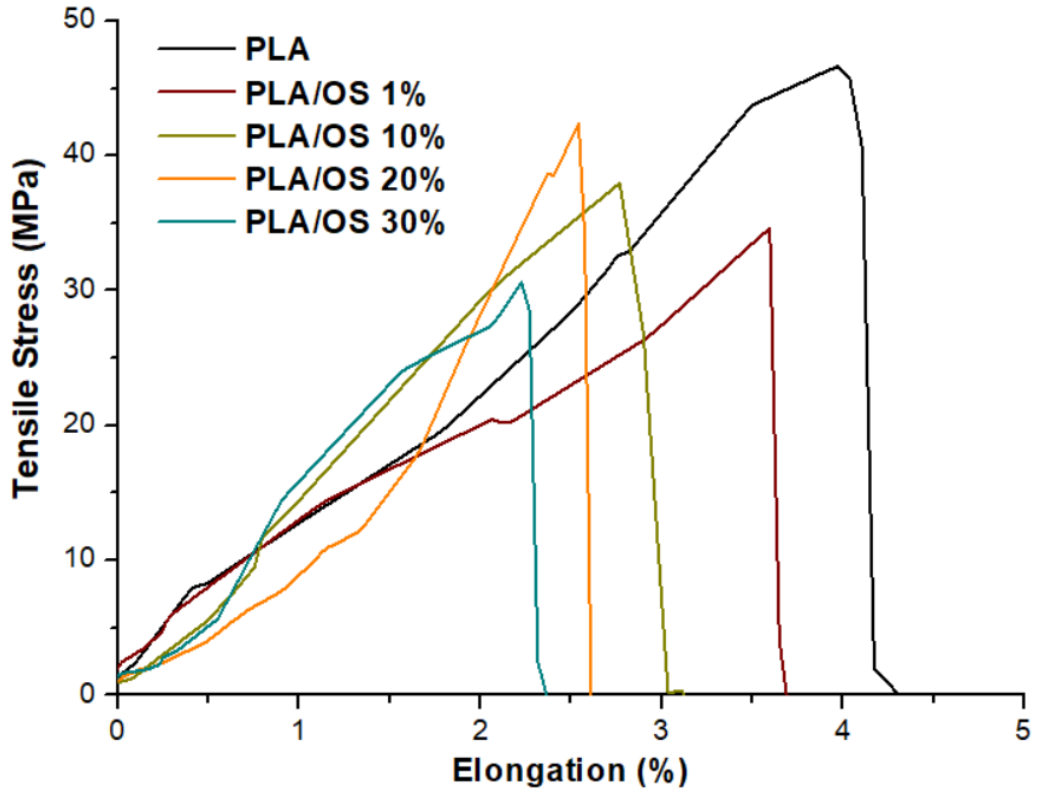


Figure 4.1. Tensile test curves of PLA and PLA/OS composites

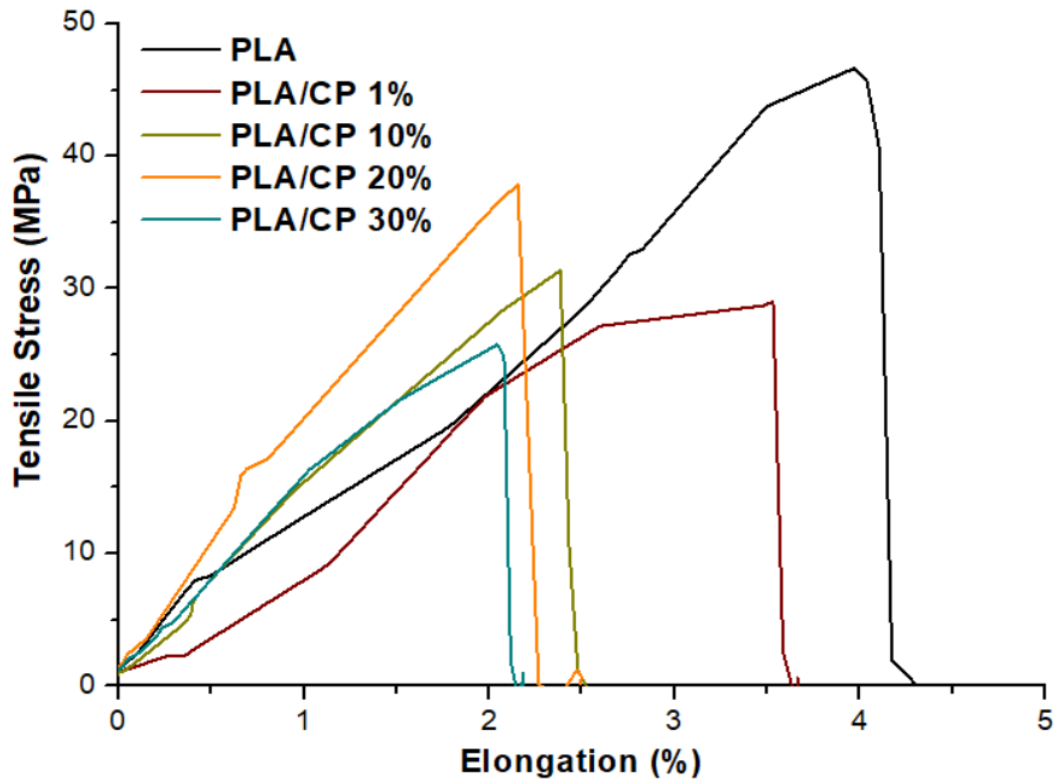


Figure 4.2. Tensile test curves of PLA and PLA/CP composites

The tensile test results and stress-strain curves of PLA and its OS and CP composites are given in Figure 4.1 and Figure 4.2, respectively. The tensile strength of pristine PLA exhibited a decreasing trend with OS and CP additions. Among the composites, the highest tensile strength was recorded for both 20% OS and 20% CP inclusions. Also, a continuous decrease in the tensile strain of PLA was found with OS and CP additions. While the inclusion of OS (20 wt%) caused a nearly 40% increase in the tensile modulus of unfilled PLA, the introduction of 20 wt% CP led to increase in tensile modulus by about 50%. On the other hand, the highest loading of additives (30%) caused a reduction in the stiffness of the PLA, which might be due to the further inclusion of particles caused by agglomeration formation since the interfacial interactions between particles and PLA were reduced.

4.2. Hardness Measurements of Composites

Shore D values of PLA/OS and PLA/CP composites are represented in Table 4.3 and Table 4.4, respectively.

Table 4.3. Hardness test data of PLA and PLA/OS composites

Hardness	PLA	PLA/OS 1%	PLA/OS 10%	PLA/OS 20%	PLA/OS 30%
Shore D	95.0±0.1	95.4±0.1	96.3±0.2	97.7±0.1	99.4±0.2

Table 4.4. Hardness test data of PLA and PLA/CP composites

Hardness	PLA	PLA/CP 1%	PLA/CP 10%	PLA/CP 20%	PLA/CP 30%
Shore D	95.0±0.1	95.2±0.1	95.9±0.1	96.8±0.1	98.0±0.2

Hardness is a typical indicator for polymers and their composites. D-type Shore hardness data of PLA-based composites filled with OS and CP are given in Tables 4.3 and 4.4. The shore hardness of neat PLA was recorded as 95.0. OS and CP additions increased the hardness of PLA progressively. While the 30% OS loading increased the hardness by 4.4 points, the 30% CP addition increment was 4.0.

4.3. Impact Resistance of Composites

The impact test is a high strain rate analysis determining the amount of energy absorbed by the sample during fracture. This absorbed energy is utilized to examine the ductile or brittle transition and gauge a material's toughness [51]. The impact energy results of the PLA and its composite samples are given in Figure 4.3. It can be obtained that OS and CP additions caused gradual reductions in the impact strength of PLA. The development of stress failures between the phase of the additives and the

PLA matrix can account for this phenomenon. The OS and CP inclusions reduced the PLA phase's capacity for deformation and caused a reduction in the total free energy of the composite system [52].

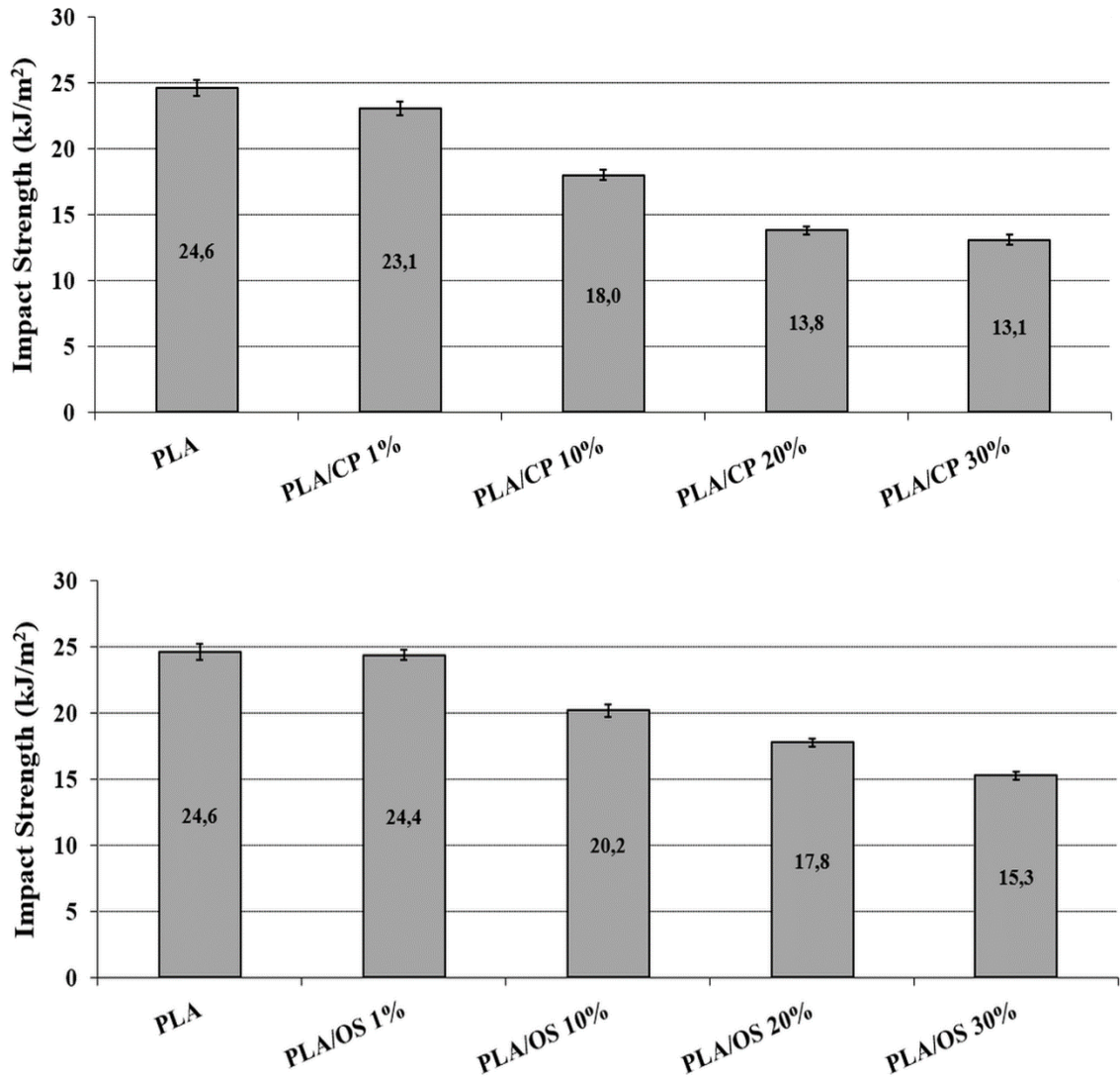


Figure 4.3. Impact energy values of PLA and composites

4.4. Thermo-mechanical Performance of Composites

Thermo-mechanical properties of pristine PLA, OS and CP-filled composites were characterized with the help of DMA. Their storage modulus curves are displayed in Figure 4.4 and Figure 4.5, respectively.

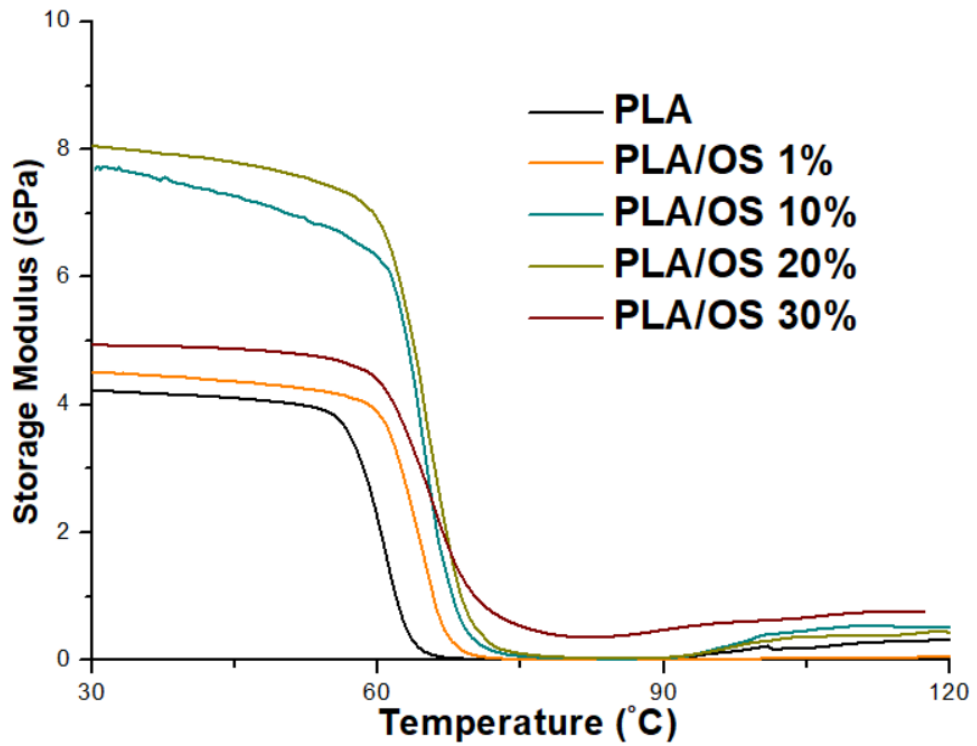


Figure 4.4. Storage modulus curves of PLA/OS composites

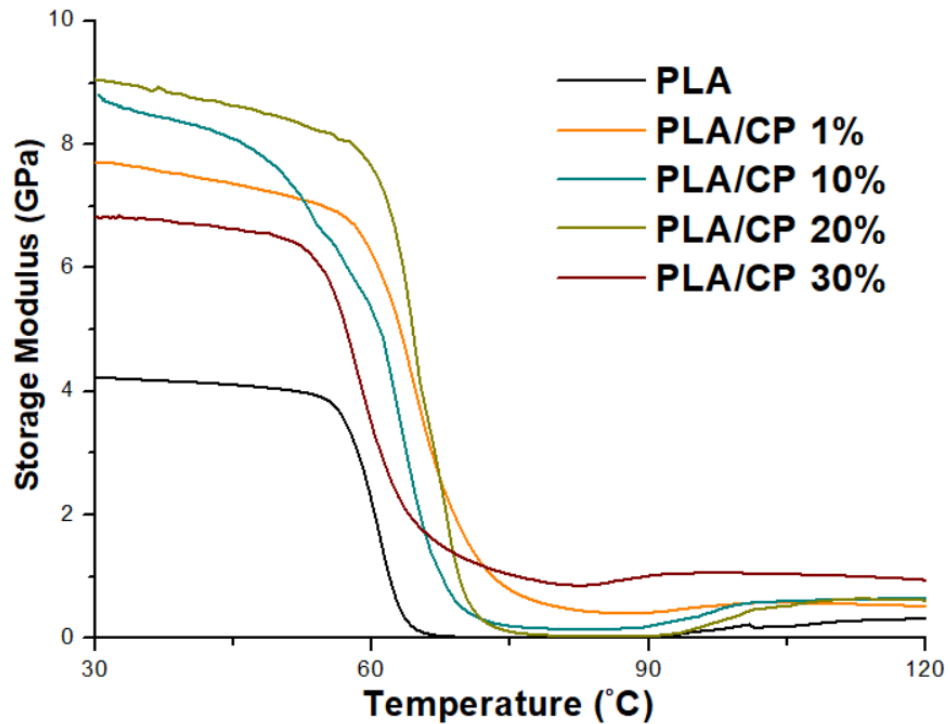


Figure 4.5. Storage modulus curves of PLA/CP composites

Figure 4.4 and Figure 4.5 reveal that the storage modulus of PLA and the composites decreases with the increase in temperature. The storage modulus of PLA experiences a sharp fall in the 60–80°C region, which is also the PLA's glass transition temperature (T_g). This decrease is due to the significant increase in mobility of the polymer chains around T_g of PLA. As can be seen in the curves, the composites' storage modulus was higher than that of PLA, revealing the reinforcing effect of the additives. However, incorporating OS into PLA resulted in a more extended plateau on the storage modulus than neat PLA, showing a higher softening temperature than with PLA itself. Nevertheless, a similar behavior was not observed for the CP-loaded composites. The highest values for the storage modulus were achieved for both PLA/OS 20% and PLA/CP 20% composites.

Table 4.5 The glass transition temperature (T_g) of the PLA and PLA / OS composite

Sample	The glass transition temperature (T_g)
PLA	66
PLA / OS 1%	71
PLA / OS 10%	75
PLA / OS 20%	71
PLA / OS 30%	69

Table 4.6 The glass transition temperature (T_g) of the PLA and PLA / CP composite

Sample	The glass transition temperature (T_g)
PLA	66
PLA / CP 1%	72
PLA / CP 10%	75
PLA / CP 20%	73
PLA / CP 30%	70

According to the indicated T_g values in Table 4.5 and Table 4.6 estimated from the peak points of Tan delta curves, all composite samples gave higher T_g than unfilled PLA. In the case of composites filled with OS, the highest T_g value was reached for adding ratio of 10% in which 9 °C improvement was obtained. PLA/OS 1% and PLA/OS 20% samples yield almost identical increments by 5 °C. Similarly, the T_g of PLA elevated from 66 to 75 °C with the addition of 10% CP. The increasing amounts of T_g for 1% and 20% loading levels of CP were nearly identical. The lowest enhancement among composites was found for the filling ratio of 30% in both cases of CP and OS-containing composites.

The ratio of loss modulus to storage modulus, which describes the material's damping reaction, yields the loss tangent ($\tan \delta$). The dependence of $\tan \delta$ vs. the temperature for neat PLA and the PLA/OS and PLA/CP composites is given in Figure 4.6 and Figure 4.7, respectively. The glass transition temperature of the PLA/OS and PLA/CP composites raised to a higher temperature due to the presence of the additives. The increase in T_g value might be related to the agglomeration of the additives, causing a decrease in chain mobility. Consequently, higher energy was essential to achieve chain mobility, which means higher T_g . [53] The highest T_g values were observed for the PLA/OS 10% and PLA/CP 10%. Figures 4.6 and 4.7 implied that the best damping property was achieved for neat PLA among composites, and it declined as the concentration of the additives increased. The lower damping properties of PLA/OS and PLA/CP composites can be attributed to the lack of interfacial interaction between the PLA and the additives.

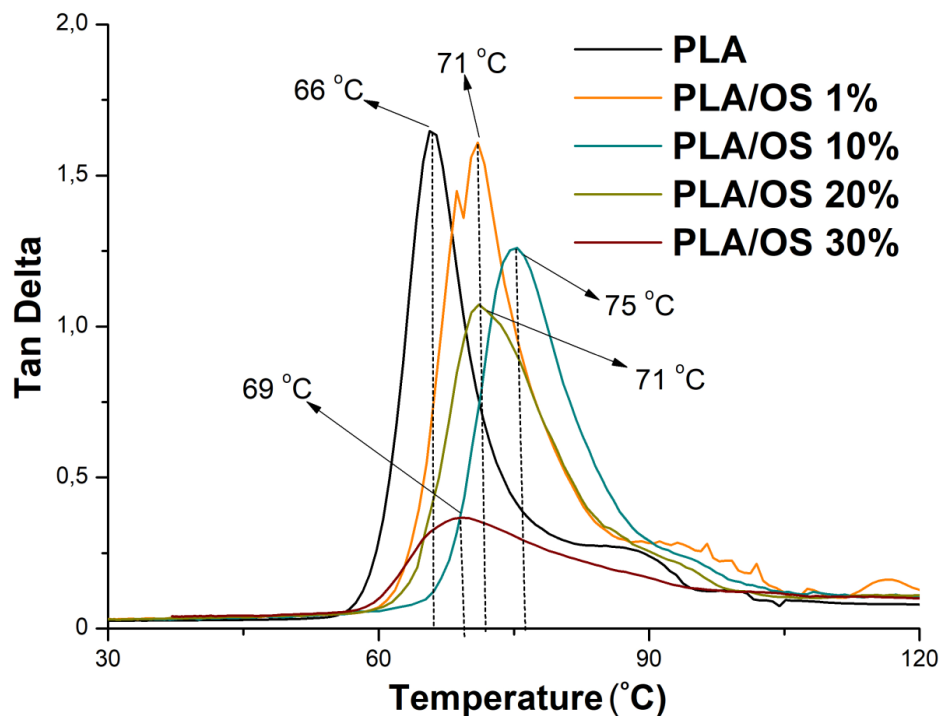


Figure 4.6. Tan Delta of PLA/OS composites

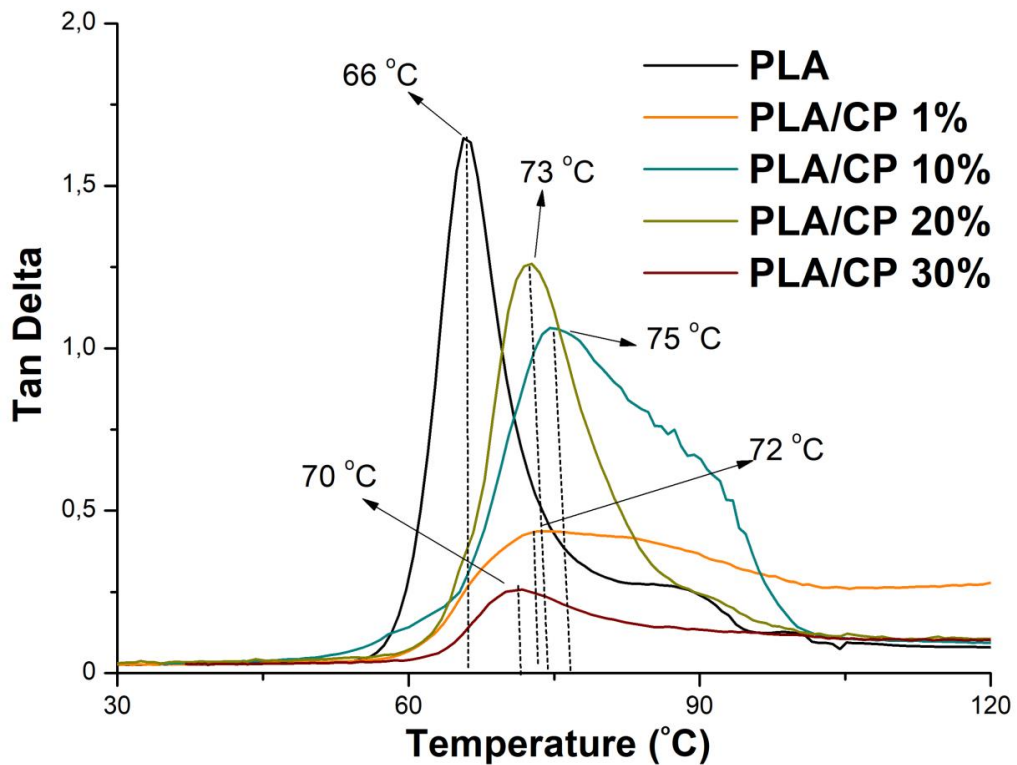


Figure 4.7. Tan Delta of PLA/CP composites

4.5. Melt-Flow Behavior of Composites

Melt-flow values of pure PLA and composites were determined by the MFI test. The MFI characterization gives information about changes in the viscosity of the molten PLA and the processability of PLA composites. As seen in Figure 4.8, OS and CP-reinforced composites display higher MFI values than pure PLA. The inclusion of particles with higher mass and density in the polymer matrix caused increasing trends in the MFI value of PLA. Composites involving OS exhibited slightly lower MFI values compared to CP-containing composite samples. This result may be explained by the difference in the agglomerate size for fillers. Accordingly, the addition of plate-like structure CP stems from mica particles in the polymer matrix. It contributes to the movement of macromolecules by dragging along the flow direction [54, 55].

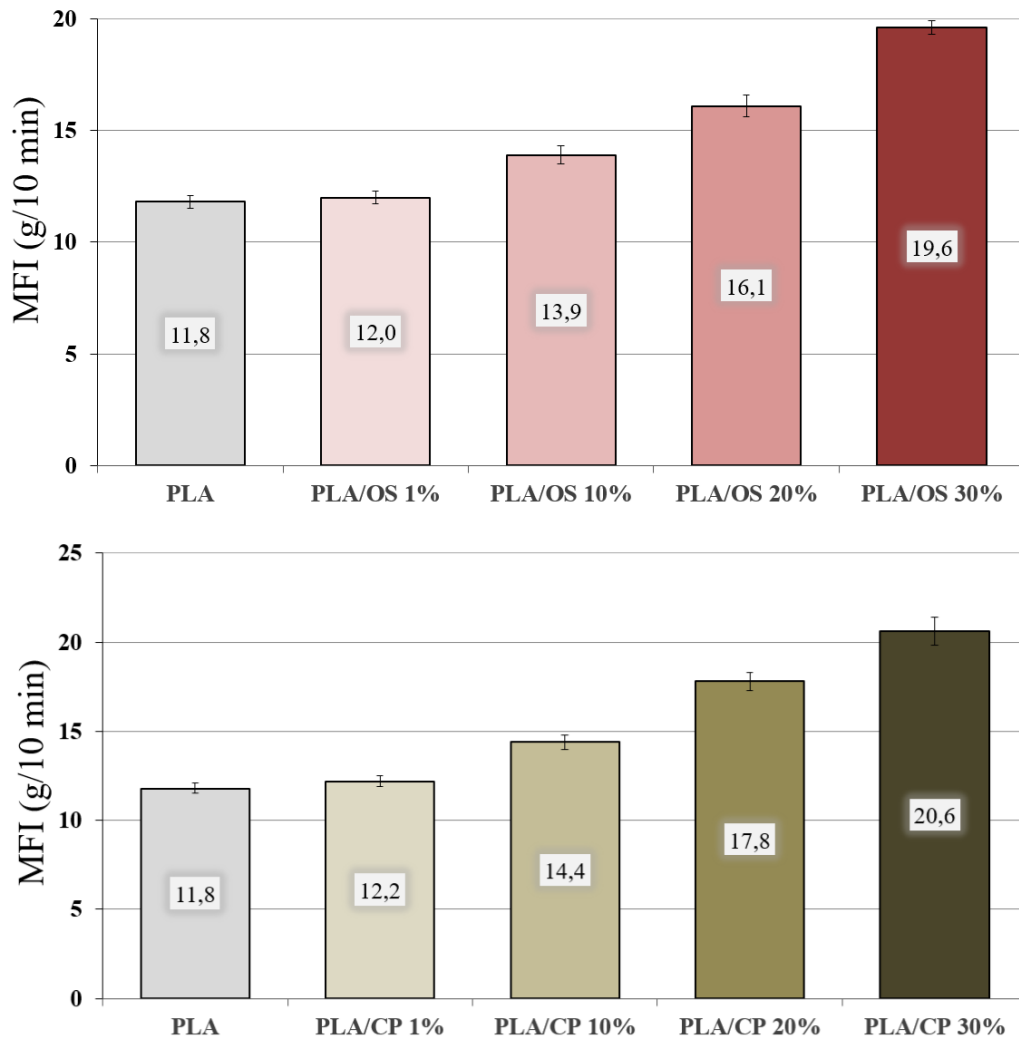


Figure 4.8. MFI data of PLA and composites

4.6. Electrical Conductivity Measurements of Composites

Electrical conductivity measurements of OS and CP-loaded composites are displayed in Figure 4.9 and Figure 4.10, respectively. The resistance curves obtained from linear probe measurements of composites involving a 30% filling ratio of OS and CP are given in the Appendix section.

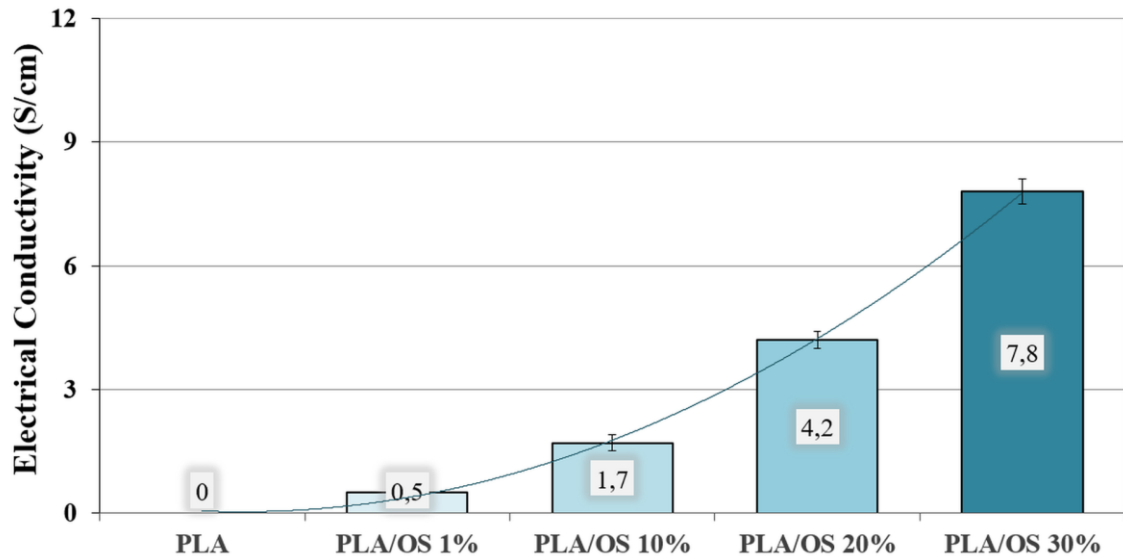


Figure 4.9. Conductivity data of PLA/OS composites

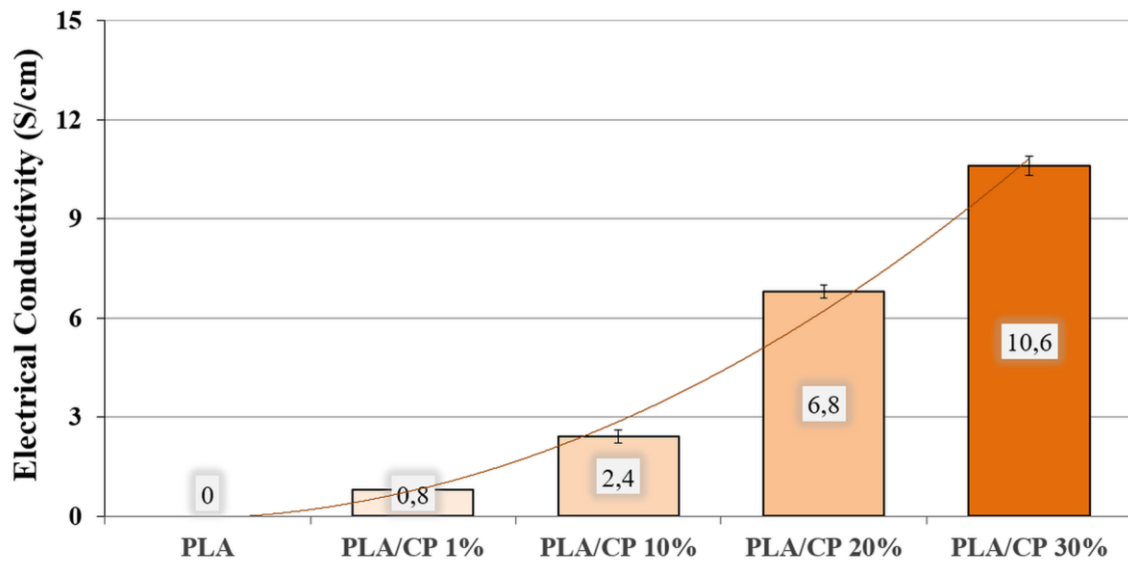


Figure 4.10. Conductivity data of PLA/CP composites

According to Figure 4.9, OS addition with a 1% loading amount caused no severe change in the conductivity of PLA. However, the electrical conductivity value sharply increased for PLA/OS 10%. Further inclusions of OS displayed an increasing trend in conductivity results. A similar trend was observed for CP-containing composites, as visualized in Figure 4.10. The incorporation of CP with 1% content led to a rise in the conductivity of PLA. This result implied that PLA/CP 1% composite film gained electro-static characteristics. Electrical conductivities were found to be improved for

highly-filled composites. CP-filled composites gave higher electrical conductivity values with respect to composite samples involving OS. The layered structure of mica-based CP may be responsible for this finding since the electrically conductive path can be achieved more efficiently owing to the high lift-to-drag ratio belonging to the structure of mica over the particulate structure of OS.

4.7. Morphological Properties of Composites

SEM micro-images of fractured surfaces obtained from impact tests of PLA/OS and PLA/CP composites are represented in Figure 4.11 and Figure 4.12, respectively.

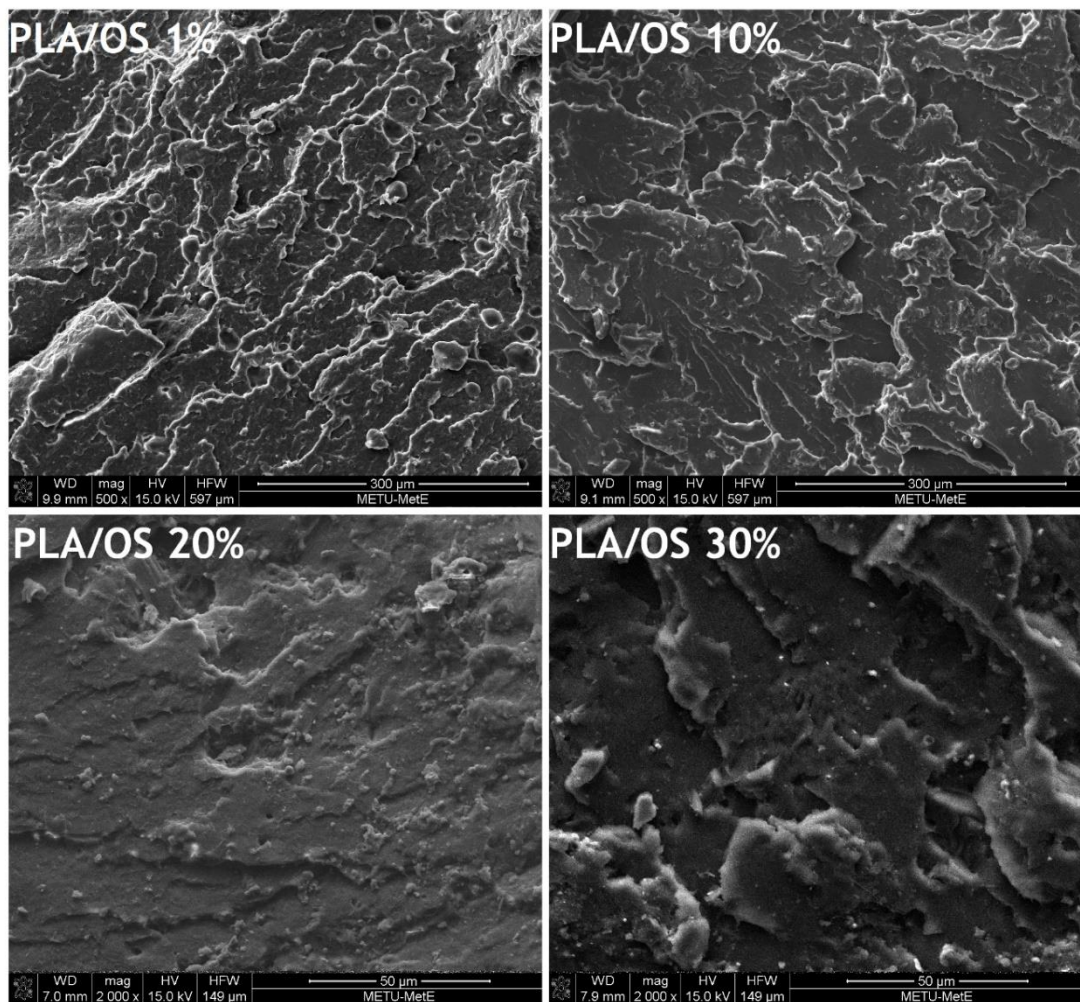


Figure 4.11. SEM micro images of PLA/OS composites

SEM micro-images of PLA/OS composites in Figure 4.11 visualized that OS particles dispersed uniformly into the PLA matrix for low-adding amounts of OS (1%, and 10%). On the other hand, agglomerated parts were formed after further additions of OS, which may stem from the lack of adhesion of the inert carbon-based surface of OS to the PLA phase.

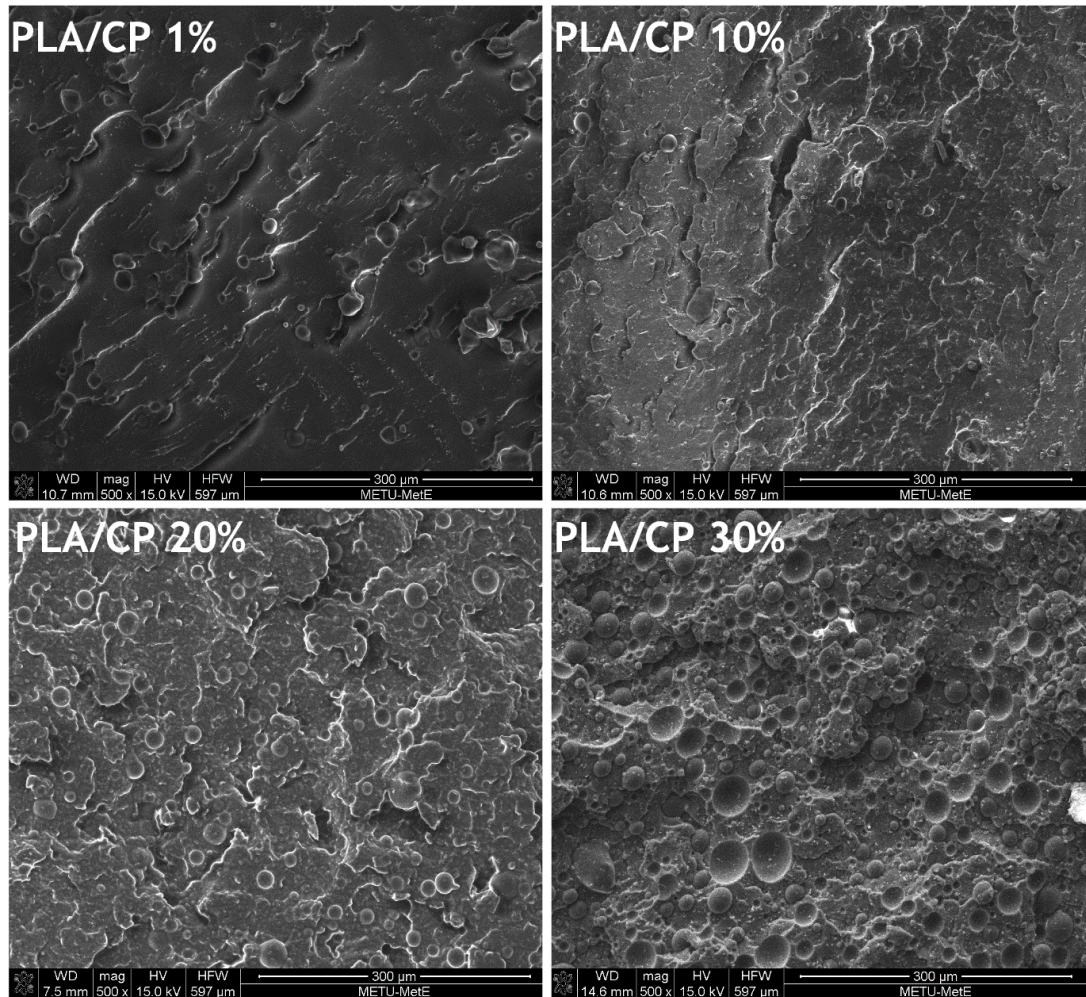


Figure 4.12. SEM micro images of PLA/CP composites

Similarly, CP particles exhibited homogeneous morphologies in the PLA phase for their 1% and 10% contents according to SEM images of PLA/CP composites in Figure 4.12. Further inclusions of CP caused disorientations of particles. Formation of mica particles more closely and even touching each other as seen in the micro-image of PLA/CP 30% yielded connection points in the structure related to reaching high conductivity values for this sample, as discussed in the previous section. The random

orientation of plate-like CP particles led to the achievement of a conductive path in the composite structure, in contrast to a drop-down in mechanical performance, which was attributed to the loss of dispersion homogeneity into the polymer phase.



CHAPTER 5

CONCLUSION

In this study, OS powder and Fe₃O₄/mica-based conductive pigment were used as additives for the PLA matrix. Fabrication techniques of composite materials, melt-compounding, and compression molding were chosen since they are cost-effective and practically applied in conventional production stages. The mechanical, thermo-mechanical, electrical conductivity, melt-flow, and morphological characteristics of composites were reported using tensile, hardness, and impact tests, DMA test, linear four-probe method, melt flow index measurements, and scanning electron microscopy technique, respectively.

According to tensile test results, the modulus parameters of PLA improved with the incorporation of additives. On the other hand, the elongation value of PLA declined with OS and CP loadings. The highest tensile performances of composites were achieved at the adding amount of 20% for both additives. Composites involving OS displayed higher tensile test results compared to CP-filled samples due to the carbon pollution of OS powder.

Shore D value of unfilled PLA enhanced with OS and CP inclusions. Carbon-based OS gave relatively higher hardness values than alumina-silicate and iron oxide-containing CP at their same loading levels.

The incorporation of both CP and OS caused dramatic reductions in the impact resistance of PLA, displaying a decreasing trend. OS-filled composites had a higher impact strength than composites involving CP.

DMA analysis revealed that the integration of additives enhanced the storage modulus and glass transition temperature parameters of unfilled PLA. The chain mobility of PLA declined after the additions of OS and CP. The highest thermo-mechanical

performances were observed for both PLA/OS 20% and PLA/CP 20% composites samples based on the DMA test data.

According to MFI test results, a low amount of OS and CP caused no remarkable changes in the MFI value of unfilled PLA. Accordingly, the processing steps of composites can be performed with no apparent problems in the case of additive manufacturing applications of PLA-based composite filaments involving CP and OS. MFI parameters improved for highly filled composite samples.

Electrical conductivity values of composites were found to be enhanced as the concentration of additives increased. CP-loaded composites gave relatively higher conductivity performance compared to OS. The integration of CP in the PLA matrix with a 1% adding amount donates a low quantity of electrical properties, which means that the use of PLA/CP 1% composite film can be considered in anti-static packaging applications.

Based on the SEM investigations, composites involving low contents of additives exhibited homogeneous dispersion. Conversely, inclusions of CP and OS with 20% and 30% loading levels caused the decline in dispersion homogeneity besides the increase in connection points of additive particles. The random orientation of layered CP particles resulted in a conductive transmission in the composite structure, as opposed to a reduction in mechanical performance caused by loss of distribution consistency within the polymer phase.

Overall, composite samples with a 20% loading ratio of both OS and CP displayed remarkably higher mechanical and thermo-mechanical properties among composites. Composite films involving 1% additives can be considered for electrostatic packaging purposes. Produced composites can be used in the development of 3D-printed parts in application fields that need suitable mechanical properties in addition to electrically conductive characteristics.

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APPENDIX A

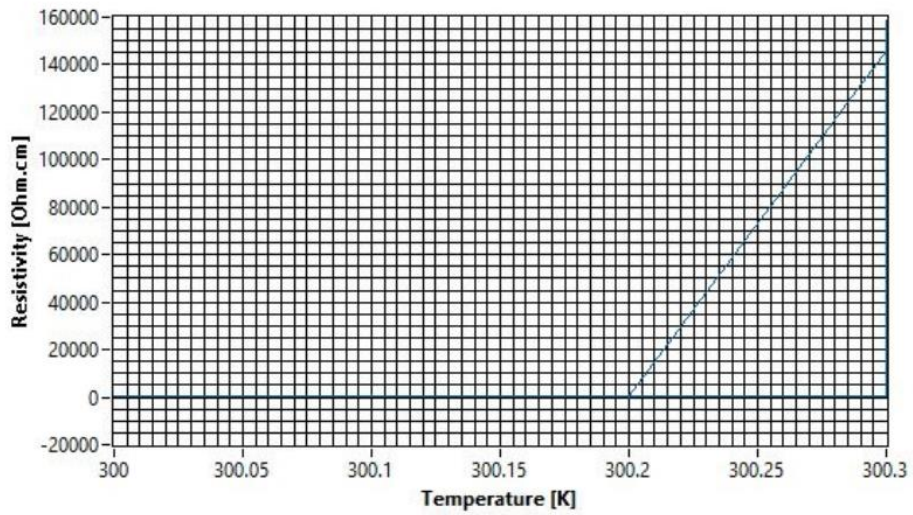


Figure A1. Resistivity curve of PLA/OS 30% composite samples

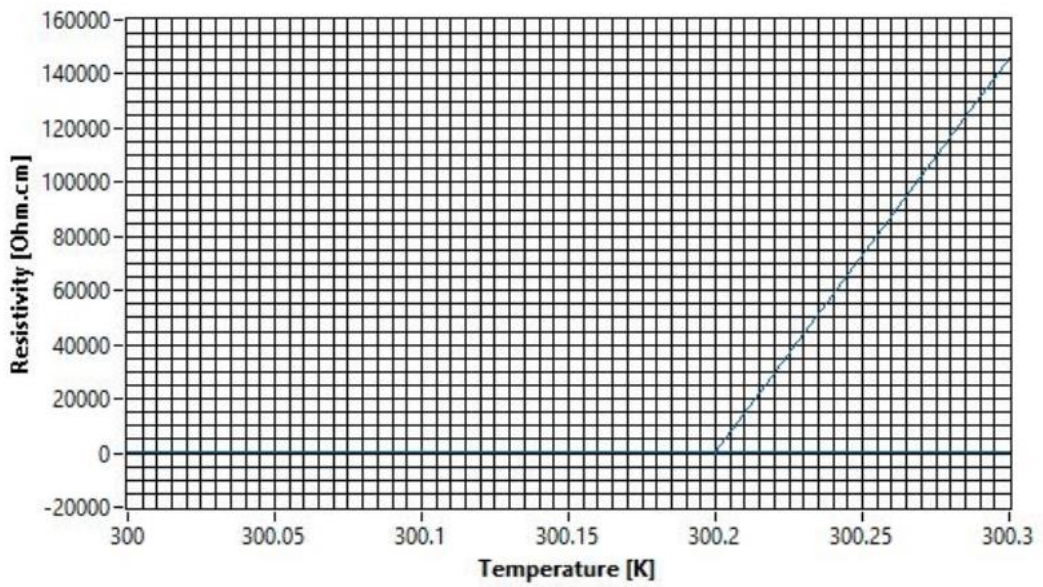


Figure A2. Resistivity curve of PLA/CP 30% composite samples

XXXXXS
GCPS