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**GEBZE TECHNICAL UNIVERSITY**
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# ENHANCING THE COMMERCIAL APPLICATIONS OF POLYLACTIC ACID BY IMPROVING ITS CRYSTALLINITY AND MECHANICAL PROPERTIES WITH BORON MINERALS

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**A THESIS OF MASTER OF SCIENCE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING**

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**LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

# BOR MİNERALLERİ İLE POLİLAKTİK ASİTİN KRİSTALİNLİĞİNİ VE MEKANİK ÖZELLİKLERİNİ İYİLEŞTİREREK TİCARİ UYGULAMALARININ GELİŞTİRİLMESİ

**OĞULCAN KOCAGÜL**

**YÜKSEK LİSANS TEZİ**
**MALZEME BİLİMİ VE MÜHENDİSLİĞİ BÖLÜMÜ**

DANIŞMAN: DR. ÖĞR. ÜYESİ MERVE MOCAN

**TEMMUZ 2024**

## MASTER of SCIENCE JURY APPROVAL FORM

A thesis submitted by Oğulcan Kocagül defended on 19/07/2024 before the jury formed with the 16/07/2024 date and 2024/38 numbered decision of the GTU Graduate Administration Board, has been accepted as a MASTER of SCIENCE thesis in the Department of Material Science and Engineering.

### JURY

MEMBER

(THESIS ADVISOR) : ASSIST. PROF. MERVE MOCAN

MEMBER : ASSOC. PROF. EMEL KURAM

MEMBER : ASSIST. PROF. GÜLŞAH YAMAN UZUNOĞLU

### APPROVAL

Gebze Technical University Graduate Administration Board

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SIGNATURE/SEAL

# ABSTRACT

The increasing levels of plastic pollution in our environment have led to a growing interest in the development of sustainable alternatives. Polylactic acid (PLA) polymer stands out as an environmentally-friendly material due to its bio-based character, biodegradability and low carbon footprint. However, in some applications such as automotive and home appliances, the thermal and mechanical properties of the PLA may be insufficient. Therefore, those properties of the PLA should be enhanced by increasing the crystallinity of the polymer. Here boron-based minerals, colemanite and ulexite, as abundant materials in Türkiye, are offered as nucleating agents for PLA.

To observe the thermal and mechanical effects of the addition of 1, 2, 5 and 10% ulexite and colemanite minerals (and 3% bio-based plasticizer to the 2% ulexite formulation) to PLA; differential scanning calorimetry (DSC) (glass transition temperature, melting temperature, and crystallization%), thermogravimetric analysis (TGA), tensile and impact tests were carried out. Scanning electron microscopy (SEM) analysis was performed to investigate the microstructure of the compounds.

Analyses show that 2% of ulexite additive increased the Heat Deflection Temperature of PLA from 53 to 92 °C. The results showed that the addition of colemanite increased the Izod impact values of PLA from 22 to 30 kJ/m$^2$. According to the DSC results, % crystallinity increased by 57% from 13.88 to 21.84. There were also noticeable improvements on elongation at break values. Although the tensile stress values were lower than that of PLA, they were still acceptable for the target applications. Good distribution of boron based additives was observed on the SEM photos up to 2% loading. This research not only expands the application potential of PLA, an eco-friendly material but it also does it in a more environmentally friendly manner by eliminating the need for an additional annealing step necessary to improve the thermal and mechanical properties of PLA. Also, this research showed the possibilities of using ulexite and colemanite minerals, which are important resources in Türkiye, to enable the application of PLA for high heat applications.



**Keywords: Bio-based and biodegradable polymers, High heat PLA, Heat distortion temperature, Boron minerals, Colemanite, Ulexite, Automotive and home appliances.**

# ÖZET

Çevremizdeki artan plastik kirliliği seviyeleri, sürdürülebilir alternatiflerin geliştirilmesine olan ilginin artmasına yol açmıştır. Polilaktik asit (PLA) polimeri biyo-esaslı karakteri, biyolojik olarak parçalanabilirliği ve düşük karbon ayak izi nedeniyle çevre dostu bir malzeme olarak öne çıkıyor. Ancak otomotiv ve ev aletleri gibi bazı uygulamalarda PLA'nın termal ve mekanik özellikleri yetersiz kalabilmektedir. Bu nedenle PLA'nın bu özellikleri, polimerin kristalliği arttırılarak geliştirilmelidir. Burada Türkiye'de bol miktarda bulunan bor mineralleri, kolemanit ve üleksit PLA için çekirdekleştirici ajan olarak sunulmaktadır.

%1, 2, 5 ve 10 üleksit ve kolemanit mineralleri ile %2 üleksit katkılı PLA'ya %3 biyo-esaslı plastikleştirici ilavesinin termal ve mekanik etkilerini gözlemlemek amacıyla, Diferansiyel Taramalı Kalorimetri (DSC) (camsı geçiş sıcaklığı, erime) sıcaklık ve kristalleşme %'si ile Termogravimetrik Analiz (TGA), çekme ve darbe testleri yapıldı. Bileşiklerin mikroyapısını araştırmak için Taramalı Elektron Mikroskobu (SEM) analizi yapıldı.

Testler %2'lik üleksit katkısının PLA'nın ısıl çarpılma sıcaklığını 53 °C'den 92 °C'ye çıkardığını göstermektedir. DSC sonuçlarına göre kristalinite yüzdesi 13.88'den 21.84'e çıkarak %57'lik artış göstermiştir. Sonuçlar, kolemanit ilavesinin PLA'nın Izod darbe değerlerini 22'den 30 kJ/m$^2$'ye çıkardığını göstermiştir. Kopma değerlerindeki uzama konusunda da iyileştirmeler sağlanmıştır. Çekme gerilimi değerleri daha düşük olmasına rağmen hedef uygulamalar için hala kabul edilebilir düzeydeydi. SEM fotoğraflarında bor minerallerinin %2 eklemeye kadar iyi bir şekilde dağıldığı görüldü. Bu çalışma, çevre dostu bir malzeme olan PLA'nın uygulama potansiyelini genişletirken aynı zamanda PLA'nın mekanik ve termal özelliklerini iyileştirmek için gerekli olan tavlama adımını ortadan kaldırarak bunu daha çevre dostu bir şekilde gerçekleştirmektedir. Ayrıca bu araştırma, Türkiye'de önemli kaynaklar olan üleksit ve kolemanit minerallerinin yüksek sıcaklık istenen uygulamalarında PLA'nın kullanabilmesine olanak sağlamıştır.

**Anahtar Kelimeler: Biyo-esaslı ve biyobozunur polimerler, Yüksek sıcaklığa dayanıklı PLA, Isıl çarpılma sıcaklığı, Bor mineralleri, Kolemanit, Üleksit, Otomotiv ve elektrikli ev aletleri.**

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# LIST OF SYMBOLS AND ABBREVIATIONS

PLA: Polylactic Acid

TGA: Thermogravimetrical Analysis

DSC: Differantial Scanning Calorimeter

SEM: Scanning Electron Microscope

HDT: Heat Deflection Temperature

$T_m$: Melting Temperature

$T_g$: Glass Transition Temperature

$T_{crys}$: Crystallization Temperature

$X_c$: Crytallinity Percentage

$\Delta H_m$: Enthalpy of Melting

$\Delta H_{cc}$: Enthalpy of Cold Crytallization

$\Delta H_{mo}$: Enthalpy of 100% Crytallized PLA's Melting

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# 1. INTRODUCTION

This research aims at investigating the effect of boron minerals (ulexite (is going to mentioned as ULX on this thesis) and colemanite (is going to mentioned as CLM on this thesis.)) on the mechanical and thermal properties of PLA polymer which would make these substances more valuable for enlarging potential application areas. The use of nucleating agents to improve the properties of PLA is a known method in the literature. However, colemanite and ulexite have not been used as nucleating agents in PLA materials. One of the boron minerals colemanite has showed to increase heat resistance of polyproplene material in a study in literature **[Durgun et al, 2022]**. Results showed that additive of boron minerals have increased the %crystallinity of the polymer 57%. Through data analysis, it was found out that ulexite had a distinct effect on raising the HDT value which is considered critical in determining its application areas. It is expected that results from this work can extend the uses for PLA that support new materials supposed to meet changing needs across industries **[Auras et al, 2010].** Unlike other studies which used annealing in the literature, in this study, high temperature resistant PLA was developed without the need for annealing step thanks to boron minerals addition **[Simmons et al, 2019][Wootthikanokkhan et al, 2013].**

## 1.1. Theoretical Information

### 1.1.1. Plastic Pollution

An urgent and pressing issue in the environment today is plastic pollution. The global use of plastics in different industries, combined with inefficient systems of waste management, has led to the accumulation of plastic litter on landmasses and seas.

Biodiversity, human health, and economic stability are all at risk due to plastic pollution. Marine animals often confuse plastics debris for food materials leading to ingestion and entanglement resulting into injury or death. Also, it serves as a transfer mechanism for invasive species and dangerous pathogens as well as causes severe ecological damage. The abundance of microplastics (small pieces of plastics less than 5 mm) makes them a concern for human health effects. Microplastics have been discovered in various food items and drinking water sources which raise questions on their long-term effects on human health.

To approach the plastic pollution, policy interventions, technological innovations and public awareness campaigns must be made. Governments should make regulations that will help in reducing single-use plastics and improve recycling as well as waste management infrastructure. There is hope for technological advancement which can aid in dealing with this problem such; biodegradable plastics or recycling technologies among others another thing which needs to be done is investing more money into these areas both private and public sectors should work together towards achieving success of these projects. But all said and done it can only happen through creating knowledge among citizens on environmental hazards caused by usage of plastics thus empowering them with knowledge that leads to wise decision making hence reduction of waste produced there of **[Eriksen et al, 2014].**

By 2030, approximately half a billion tons of plastic waste will be produced every year worldwide, which highlights the need for immediate action on what is rapidly becoming an emergency situation. In other words, plastic pollution is a complex issue that needs to be dealt with at various levels – locally, nationally and globally. We can also abate the effects of plastics on our environment as well as make tomorrow safer for generations by putting in place effective strategies, investing in technology and creating awareness among people **[Eriksen et al, 2014].**

### 1.1.2. Bio-based and biodegradable polymers

Bio-based polymers are seen as potential substitutes for traditional plastics due to global environmental challenges posed by them. This type of polymer is created from biomass from plants, animals and microorganisms which makes it sustainable and ecofriendly. Another important benefit lies with their possibility of biodegradability: most bio-based polymers break down into non-toxic substances through natural processes thus reducing litter accumulation within ecosystems **[Chen & Patel, 2012].**

Moreover, use of biopolymers could help reduce carbon footprint associated with production of plastics because these products come from renewables sources hence less dependence on fossil fuels which aligns well with efforts towards attaining sustainability in different countries around world. European Union's circular economy plan called European Green Deal was launched on December 2019 to address climate change and environmental degradation. The aim here being transitioning EU economy

into one that is low-carbon, more circular so reducing green house gases emissions as well as protecting biodiversity. The initiative involves multiple actions such as increasing renewable energy capacity building efficiency promoting sustainable agriculture practices waste reduction investing research innovation among others.Climate neutrality goal should be realized by 2050 hence this strategy forms part.

However, there are still difficulties in commercialization level when producing bio-based polymer needed meet market demand due cost competition, technological limitation, infrastructure insufficiency have to first overcome these barriers so that we can start using them instead of our usual plastics. Research is on-going aimed at improving performance as well make them more cost effective. Additionally, development biopolymers are being supported by innovation in synthesis methods, processing techniques end-of-life options this has been pushing us towards sustainable future **[Chen & Patel, 2012].**

## 1.2. PLA

PLA is a bio-based polyester, which can be made either from sugarcane, corn-starch or cassava roots among other renewable resources. It has attracted much attention because of its eco-friendliness and ability to cut down on petrochemical plastics consumption **[Rasal et al, 2010].**

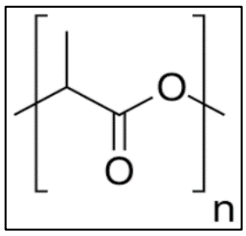


**Figure 1.1:** Chemical structure of PLA.

## 1.2.1. Properties of PLA

*Mechanical Properties:* The tensile strength of PLA is high, which means that it can be used for packaging or textiles depending on how much force needs to be withstood. However, this polymer has low resistance against impact heat hence making it brittle especially when exposed to temperatures above its melting point; this limits its application range in different fields where more demanding conditions prevail.

*Thermal Properties:* The glass transition temperature (Tg) of PLA is relatively low.

*Biodegradability:* Industrial composting conditions can cause PLA to break down into water and carbon dioxide. This property of the material makes it very suitable for use in items that are only used once because they have a short life such as packaging materials and disposable products.

*Properties of Chemicals:* PLA mainly consists of lactic acid monomers and is an aliphatic polyester. Its chemical formula is $(CH_4O_2)_n$, with a repeating unit -[O-CH($CH_3$)-CO]- (polylactic acid). There are three stereochemical forms for PLA which are poly-L-lactide (PLLA), poly-D-lactide (PDLA) and poly-DL-lactide (PDLLA) these have different physical properties as well as degradation rates.

*Biocompatibility:* PLA can be degraded by the human body thus making it useable in temporary implants and medical equipments such as sutures, stents or drug delivery systems **[Rasal et al, 2010].**

## 1.2.2. Crystallization of PLA

Mechanical strength, thermal resistance and biodegradability are among the final properties of PLA which are determined by its crystallization behavior. Higher stiffness in PLA is associated with higher degrees of crystallinity. Besides, tensile strength and heat resistance are also influenced by the amount of crystallinity but this only happens at the expense of flexibility. On one hand, annealing as well as other types of thermal treatment can be used to induce or speed up crystallization process while on another hand nucleating agents can be incorporated into the polymer matrix so that they provide sites for crystal formation. The stereochemistry of PLA especially PLLA versus PDLA affects its ability to crystallize. Homopolymers may have less mechanical and thermal stability when compared with stereocomplex crystals obtained after blending these stereoisomers. Therefore, it is necessary to know how best we can

control this phenomenon if we want PLA perform optimally in different areas **[Suryanegara et al, 2009].**

### 1.2.3. Advantages and Disadvantages of PLA

*Biodegradability:* PLA can break down under industrial composting conditions into water and carbon dioxide. This feature helps reduce environmental pollution over long periods thereby saving landfills.

*Renewable Resources:* PLA is produced from renewable agricultural products thus reducing reliance on finite fossil fuel resources while supporting local economies based on farming activities.

*Biocompatibility:* Due to being non-toxic as well as having biocompatible qualities; PLA finds application in various medical fields like producing sutures, implants and drug delivery systems.

*Lower Carbon Footprint:* The production process for making PLAs has lower greenhouse gas emissions throughout its life cycle when compared with petroleum-based plastics such as PC therefore contributing towards mitigating climate change efforts.

PLA has a much lower carbon footprint than PC. Carbon footprint per kg material for PLA amounts 0.5 kg whereas for PC it accounts 4.2 kg carbon for each kg of material. The production of PLA involves fermentation biomass which absorbs $CO_2$ from atmosphere leading to reduced levels of these gases being released into environment while on the other hand PC relies upon petrochemical processes resulting in higher $CO_2$ emissions and greater ecological impact **[Rasal et al, 2010].**

*Mechanical Properties:* PLA has good tensile strength (approximately 70 MPa), however it is brittle with low impact strength, which means that it may not be suitable for applications requiring high durability or toughness.

*Thermal Stability:* Because the heat distortion temperature of PLA is around 60°C PLA cannot withstand temperatures over this value hence limiting its use in some areas where exposure to heat above this range occurs frequently.

*Cost:* Normally PLAs are more expensive than traditional plastics because they have more expensive raw materials and require elaborate manufacturing techniques thereby making widespread adoption difficult due to financial constraints.

*Hydrolytic Degradation:* In presence moisture over time, PLA can break down through hydrolysis thus affecting its stability over long durations under certain conditions.

## 1.2.4. Synthesis of PLA

Lactic acid is polymerized to make PLA by synthetic method called ring-opening polymerization of lactide as well as direct condensation polymerization process using two different approaches. One of them involves fermentation of carbohydrates which results into lactic acid while the other one is a cyclic dimer produced from lactic acid known as lactide. For industrial purposes, it is preferable to employ the latter method since higher molecular weights can be achieved there this way during polymerization reaction leading to formation high molecular weight polylactide good for industry applications.(Figure 1.2.4.1)

In order to synthesize PLA through direct condensation polymerization technique, water has to be removed while lactic acid undergoes polymerization without any interference. This method seems easy but getting high molecular weights remains difficult due equilibrium limitations encountered in the reaction process **[Tsuji, 2005].**

Lactide acts as an intermediate compound in ring opening polymers where PLA formed after undergoing various stages involving polymerization. This technique gives better control over molecular weight as well as other properties of resulting polymers thus making it suitable for large scale production **[Tsuji, 2005].**

## 1.2.5. Applications of PLA

PLA is known for its versatility and eco-friendliness which makes it widely used in many sectors. Some areas where PLA can be applied include;

*Packaging:* This polymer finds great application in food packaging since it easily degrades into compost within a short time after use without any negative impact on the environment. Moreover, disposable cutlery made from this material can also be thrown away together with food hence reducing waste generation during events or at home while still maintaining cleanliness around us.

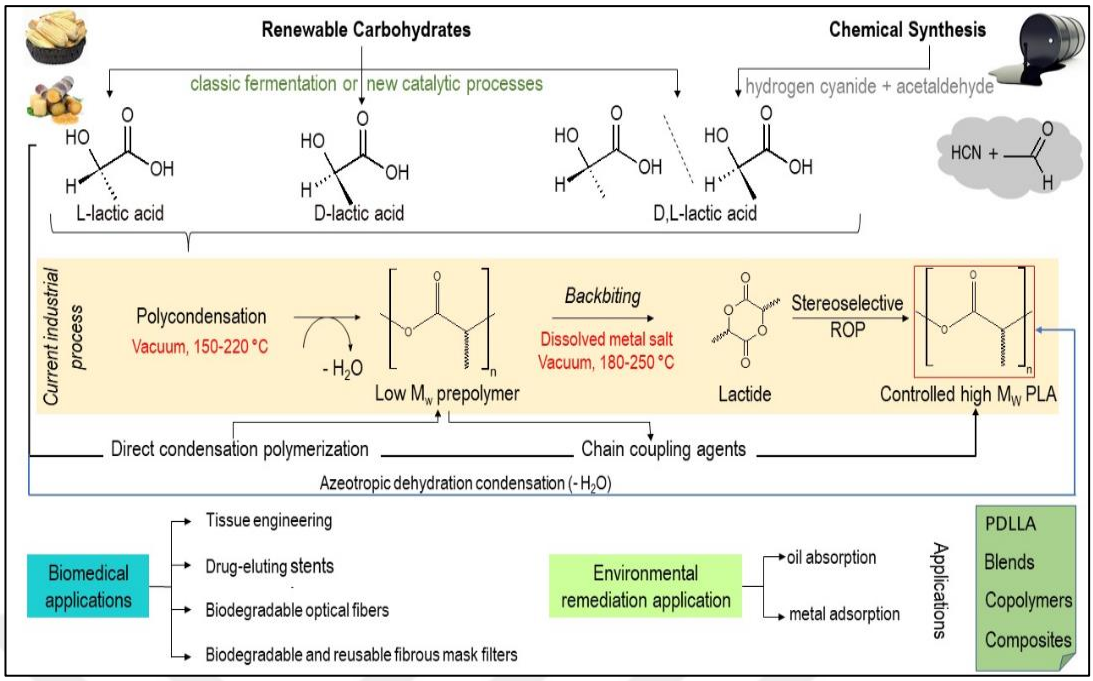


**Figure 1.2:** Synthesis of PLA **[de França et al, 2022].**

*Textiles:* PLA fibers are good substitutes to traditional synthetic fibers because they have similar characteristics but do not cause harm like those derived from fossil fuels. In addition, clothing made from such fibers has been found to provide comfort especially during hot seasons when people sweat more than usual thereby leading improved air circulation around body surface thus enhancing cooling effect of sweat evaporation process.

*Medical:* In the surgical field, biocompatible PLA is used for implants, drug delivery systems and tissue engineering scaffolds.

*Agriculture:* PLA is used in biodegradable mulch films which are being utilized to reduce plastic waste in agricultural practices **[Nagarajan et al, 2016].**

## 1.2.6. Enhancing Properties of PLA

Despite having many benefits; PLA cannot be widely used due to its mechanical and thermal properties. Different approaches are considered so that these drawbacks can be addressed as follows **[Su et al, 2019].**

*Blending* – Mixing with other polymers increases flexibility, toughness and impact resistance. Polybutylene adipate terephthalate blended PLA is example of this **[Al-Itry et al, 2014].**

*Fillers* – Using fillers such as talc can improve the mechanical and thermal properties of PLA which can act as reinforcing agents, nucleating agents thereby increasing mechanical properties, heat deflection temperature (HDT) and/or crystallinity **[Nofar et al, 2013].**

*Annealing* – Annealing is a process that strengthens the properties of a material by heating and cooling in a proper manner. When applied to PLA, annealing has the potential to enhance the crystallinity which improve mechanical characteristics like rigidity and/or strength. Moreover, PLA has a relatively low HDT (around 55 °C). This means that when subjected to heat and load for extended periods of time it becomes less heat resistant. However, through annealing its HDT can be increased thereby making it more durable under such conditions **[Simmons et al, 2019] [Wootthikanokkhan et al, 2013].**

Ultimately, this means that PLA holds great promise as a material in our efforts towards creating sustainable plastics. Researchers currently work around its limitations which will not only diversify its applications but also enhance performance in those already existing **[Carrasco et al, 2010].**

### 1.2.7. Nucleating Agents

Nucleating agents are substances added to plastics that promote or accelerate crystallization process. They do this by creating new sites for crystals to form during cooling from melt or solidification from solution in polymers like PLA (polylactide). Common examples include minerals e.g., talc. The higher rate of crystallization achieved with nucleating agents leads to increased degree of crystallinity hence better mechanical properties such as tensile strength while at same time improving thermal stability through raising HDT values. Additionally, it creates more uniform fine grained crystal structure which improves overall polymer performance across all areas. Employing nucleating agents thus becomes indispensable when trying tailor made properties of PLA that meet different needs within various industries **[Zhao et al, 2021].**

## 1.3. Ulexite

Ulexite has been called “TV rock” or “television stone” because it can display images like a mirror does on one side of its surface when light shines through another side. This mineral – sodium calcium borate hydroxide hydrate, also known as boronatrocalcite – usually occurs near other borate minerals such as colemanite and borax within evaporitic sedimentary basins.

The exceptional property is due to the fact that ulexite acts like an optical fiber: it guides light from one end to another by total internal reflection. In this case, however, instead of being made out of glass or plastic material like in modern telecommunications cables, the fiber here consists of thin tubes formed by layers upon layers of tiny crystals. Therefore, any image placed close enough to either surface will be transported along these tubes until it reaches opposite end where it can be viewed with naked eye.

Beside this interesting feature; ulexite also serves as a source for boron which is widely used in various industries. Boric acid derived from ulexite finds application in production of glassware, ceramics and enamels while boric oxide acts as raw material for making optical fibers and high performance batteries among others. Furthermore agriculture sector benefits greatly from using boron since it promotes healthy growth in plants thereby increasing crop yields both quantity and quality wise **[Sugozu et al, 2018].**

Research concerning this particular stone continues developing overtime due to its diverse applications across various fields of science and technology. New research has been centered around making boron extraction more efficient and creating new materials and methods that take advantage of the strange optical qualities of the element. Additionally, scientists are still investigating how ulexite forms in order to find and use it more effectively. This mineral can be used for many things such as industrial manufacturing or even future optical technologies, so we need to keep studying it while also mining sustainably. As we explore the potential of this multifaceted mineral, ulexite may play a crucial role in future technological and industrial developments **[Şener et al, 2000].**

### 1.3.1. Chemical Structure of Ulexite

The complicated borate system of ulexite comprises sodium ($Na^+$) and calcium ($Ca^{2+}$) ions. Its chemical formula, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$, represents borate groups, hydroxyl groups, and water molecules within its monoclinic crystalline lattice. It is constructed from linked $BO_3$ and $BO_4$ units which form a network that stabilize the structure. These hydroxyls groups and waters molecules are hydrogen bonded to each other across the matrix thus giving more stability to the mineral as well acting as nucleating agents for it too. Many B-atoms provide sites where polymers can interact or nucleate with PLA among others due to presence of various borons in this compound. This complex composition greatly contributes towards improving crystallization and performance of plastics like ulexite **[Guzel et al, 2016].**

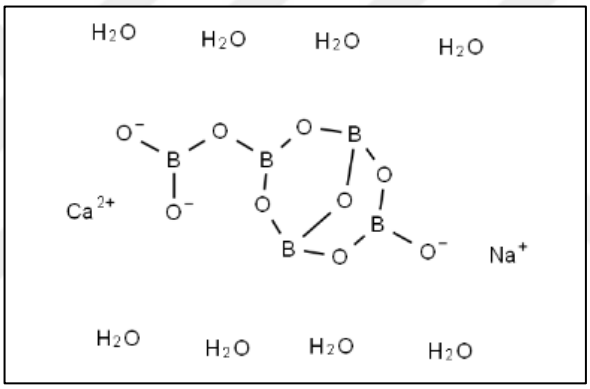


**Figure 1.3:** Chemical structure of ulexite.

### 1.3.2. Properties of Ulexite

In polymer composites, ulexite functions as a good nucleating agent which accelerates the rate and extent of polymer crystallinity. Its inclusion into polymers enhances thermal stability alongside other mechanical properties such as tensile strength and rigidity. Furthermore, the boron content in ulexite imparts flame-retardant nature to polymers thereby widening their potential applications. Also important about ulexite is that it is relatively affordable as well as being abundant in nature hence making it an economically viable additive for use on biodegradable plastics like PLA **[Guzel et al, 2016].**

## 1.4. Colemanite

Colemanite, a significant borate mineral, is important in many industries because it contains a lot of boron. It was named after an American geologist called William T. Coleman and usually forms in evaporite deposits alongside other borates such as ulexite and borax. Its chemical formula is $Ca_2B_6O_{11}\cdot 5H_2O$, meaning that colemanite is a hydrated calcium borate mineral **[Guzel et al, 2016].**

Primarily, colemanite serves as a source of boron necessary for many industrial processes. For example, compounds derived from this mineral are widely used in glassmaking and ceramics production since they increase thermal resistance and mechanical strength respectively. Durability and chemical resistance of glasses are improved by adding boric acid which also makes them suitable for different applications like fiber optics or cookware used in laboratories among others.

Research on colemanite is still ongoing which mainly focuses on improvement in both extraction methods and its utilization efficiency as far as different industries are concerned. In addition to this, material science innovations have also identified potential use of colemanites for development of new materials having enhanced properties.

As a result, colemanite remains a key mineral among borates used widely across various industrial sectors including agriculture. This owes to its rich content in boron that makes it invaluable during generation ceramics, fertilizers, glasses, detergents, flame retardants etcetera **[Guzel et al, 2016].**

### 1.4.1. Chemical Structure of Colemanite

The chemical structure of colemanite consists of a borate framework with calcium (Ca) ions and hydroxyl (OH) groups, as represented by its formula $Ca_2B_6O_{11}\cdot 5H_2O$. This structure features a network of borate units, including $BO_3$ and $BO_4$ groups, which are interconnected to form a stable monoclinic crystalline lattice. The presence of calcium ions within this framework helps to balance the charge and stabilize the overall structure. The hydroxyl groups and water molecules are integrated into the lattice through hydrogen bonding, contributing to colemanite's stability and effectiveness as a nucleating agent **[Bilici et al, 2021].**

This complex borate structure provides numerous nucleation sites that interact with polymer chains during the crystallization process, facilitating the formation of crystalline regions in polymers like PLA. Understanding the chemical structure of colemanite is essential for optimizing its use in enhancing the thermal and mechanical properties of polymer composites **[Guzel et al, 2016].**

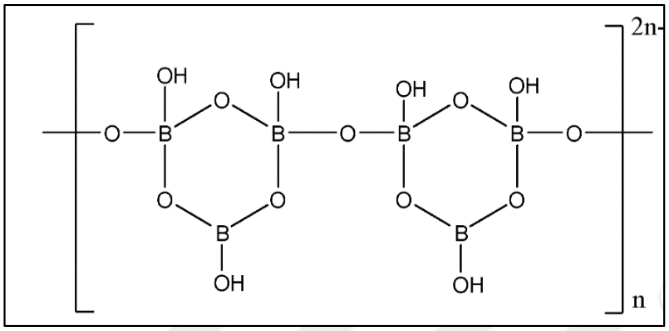


**Figure 1.4:** Chemical structure of colemanite.

## 1.4.2. Properties of Colemanite

Another important borate mineral that can be used to improve crystallization behavior and thermal properties is colemanite.

Colemanite can improve the heat resistance and strength of polymers due to its boron content. Colemanite, apart from being a nucleating agent, can also serve as a fire retardant hence can be used in many more applications. This mineral is recognized for its ability to disperse well in polymer matrices thereby ensuring evenness of distribution and reliability of performance improvement. Colemanite has relatively low price and wide distribution in nature which makes it applicable for industrial use when enhancing properties of both biodegradable or conventional plastics is considered practical **[Yildiz, 2004].**

# 2. EXPERIMENTAL

## 2.1. Materials

In this thesis, Luminy L175 PLA of Total Corbion with an melf flow index of 8 g/10 min measured at ISO 1133-A (210 °C/2.16kg) was used. Molecular weight of PLA is 175.000 g/mol. Loxiol G10 V, a bio-based plasticizer with a melting temperature lower than 0 °C, was used. Boron minerals ulexite and colemanite (size: 45 microns) were purchased from Eti Maden. The properties of all these materials are given in Table 3.1. The chemical structure of PLA is shown in Figure 1.2.1.

**Table 2.1: Properties of the polymer and additives.**

| Properties | Unit | PLA | Plasticizer | Ulexite | Colemanite |
|---|---|---|---|---|---|
| Chemical Composition | - | $(C_3H_4O_2)n$ | - | $NaCaB_5O_6(OH)_6 \cdot 5H2O$ | $Ca_2B_6O_{11} \cdot 5H_2O$ |
| Melting Temperature | °C | 175 | < 0 | - | - |
| Size | µm | - | - | 45 | 45 |
| MFI (210 °C/2.16 kg) | g/10 min | 8 | - | - | - |
| MFI (190 °C/5 kg) | g/10 min | 3 | - | - | - |

## 2.2.Experimental Design

Compounds which include PLA and 1, 2, 3, 5, 10% proportions of each mineral (ulexite: ULX, colemanite: CLM) mixed and extruded (PF: as plasticizer) the numbers next to code corresponds to the percentage of the mineral added. The compositions of the blends are shown in Table 2.2.

**Table 2.2:** The prepared compounds.

| Materials | ULX1 | ULX2 | ULX5 | ULX10 | CLM1 | CLM2 | CLM5 | CLM10 | ULX2PF |
|---|---|---|---|---|---|---|---|---|---|
| PLA (wt%) | 98.7 | 97.7 | 94.7 | 89.7 | 98.7 | 97.7 | 94.7 | 89.7 | 94.7 |
| ULX (wt%) | 1 | 2 | 5 | 10 | - | - | - | - | 2 |
| CLM (wt%) | - | - | - | - | 1 | 2 | 5 | 10 | |
| Lubricant (wt%) | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Plasticizer (wt%) | - | - | - | - | - | - | - | - | 3 |

The effect of the mineral type, ratio and plasticizer on the mechanical and thermal properties has been observed.

## 2.3. Processing and Sample Preparation

### 2.3.1. Extrusion

A Coperion branded ZSK26 twin screw extruder was utilized, featuring an intermeshing co-rotating screw with a diameter of 26 mm and L/D ratio of 40 (Figure 2.1). This extruder had 1 non-heating zone, serving as the first zone connected to the main feeder, and 10 heating zones. Three feeders were connected to the extruder, with the main feeder and the first side-feeder being utilized for sample preparation. The main feeder was responsible for feeding the polymer to the machine, connected to the first zone. There were also two side feeders on the barrel, with the first being located on the fourth heating zone, capable of feeding polymer to the mixture. Vacuum was applied at the tenth heating zone. The temperature profile was set from the feeder to the die, with a constant screw rotation speed of 500 rpm, ranging from 140-200-190-180-160-150-140-140-190 °C. The extrudates were cooled in a water bath and shaped into pellets through a granulating unit.

Ulexite and colemanite minerals of 45-micron size were mixed in the external mixer and fed from the main feeder to ensure homogeneous mixing in the PLA matrix. During the extrusion process, the speed was used as 500 rpm. Production capacity is determined as 6 kg/hour. The rovings coming out of the extrusion mold were cooled in 20 °C water.

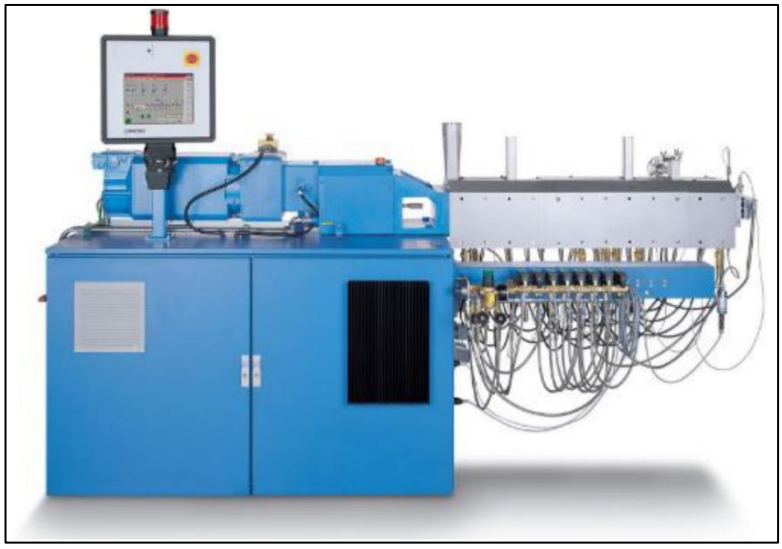

**Figure 2.1:** Twin-screw extruder.

### 2.3.2. Injection Molding

Before the injection molding process, the samples were subjected to a 4-hour drying period in an oven at 80 °C to decrease the moisture content. An Arburg 420C injection molding machine with a screw diameter of 25 mm and L/D ratio of 20 was utilized to create standard test samples for tensile, impact, and heat deflection temperature tests. The barrel temperature ranged from 180 °C to 165 °C from nozzle to hopper. The injection molding machine is displayed in Figure 2.2 After drying, the moisture content of the material is below 200 ppm, indicating that it is ready for injection molding.

Since the aim of this study was to increase the crystallinity of PLA the prepared compounds were molded at high mold temperatures around 100 °C. In experiments performed above and below this temperature, demolding problems of the test samples were observed. Above this temperature, demoulding problems were observed as the temperature was close to the melting temperature of the material. Below this temperature, demoulding problems were observed due to the amorphous structure of the material and its inability to crystallize.

Rest of the processing parameters were given below,

- The injection speed was determined as 25 mm/s.
- The maximum pressure formed during injection was seen in the range of 750-800 Bar.

- Since sink marks were seen on the part surface, the packing pressure was set as 1200-1100-1100 Bar.
- Packing time was determined as 5- 4- 4 s.
- The switchover point was determined as 5 mm.
- Plastification speed was determined as 14 rpm.
- Back pressure was set as 100 Bar.
- The cooling time was determined as 60 seconds to ensure crystallization and stiffen the part.


**Figure 2.2:** Injection molding machine.

## 2.4 Characterization

### 2.4.1. Mechanical Characterization

#### 2.4.1.1. Tensile Test

The tensile test is a means of gauging a material's ability to resist forces that cause it to pull apart, as well as determining the extent to which the sample elongates before breaking. The test involves placing samples onto the handles of a test device and pulling them until they break, within a specific grip range. For ISO 527, the typical test speed is either 5 or 50 mm/min to assess strength and elongation, and 1 mm/min to measure modulus. An extensometer is used to calculate elongation and tensile modulus. To measure tensile modulus and tensile strength at yield of dog bone-shaped (Figure 2.3) specimens at 23 °C, a Zwick Universal Tensile Testing Machine Z050 (Figure 2.4) was employed. $L_0$ is overall length, L is length of narrow grips,W is width of narrow area,$W_0$ is overall width, D is length of narrow area, T is thickness. Samples

were tested at a tensile speed of 5 mm/min, following ISO 527 standards. The thesis reports the average of three results.

### 2.4.1.2. Impact Test

The ability of a material to resist fracture when subjected to a shock load or stress at high speed is known as impact resistance. This quality is measured by the impact energy, which is directly proportional to the area under the stress-strain curve and indicates the toughness of the material.

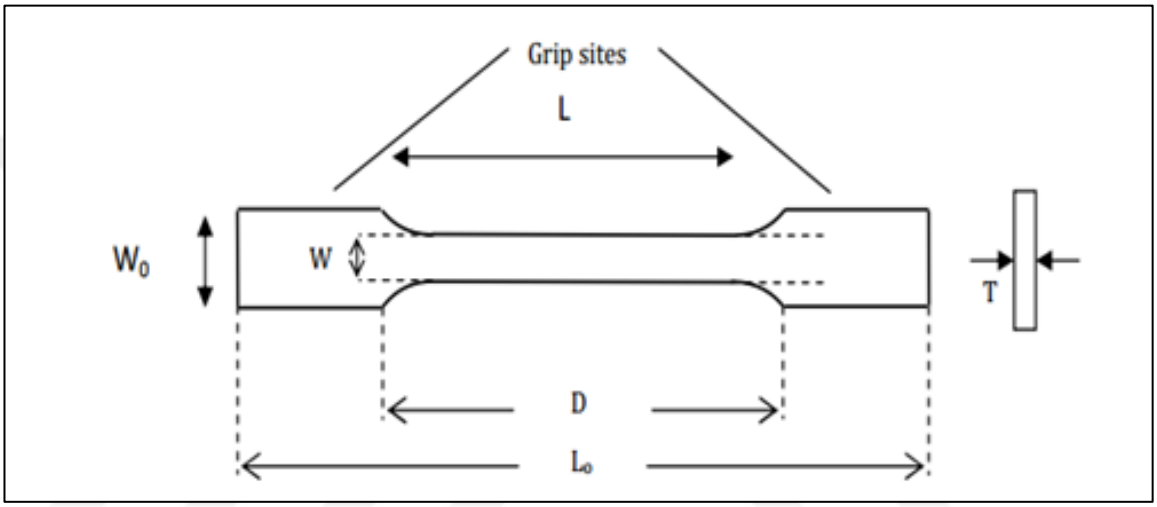


**Figure 2.3:** Schematic of tensile test specimen.

**Figure 2.4:** Tensile testing machine.

Tests for impact resistance include Izod and Charpy, with the former being a vertical placement of the test specimen and the latter being horizontal. The Ceast Resil Impactor 6957 Izod Impact Test Machine was used to measure the unnotched Izod

impact strength of standard samples with dimensions of 4 ± 0.2 mm in thickness, 10 ± 0.2 mm in width, and 80 ± 0.2 mm in length, in accordance with ISO 180 standard. The average value of five results is reported in this thesis.

**Figure 2.5:** Impact testing machine.

## 2.4.2.Thermal Characterization

### 2.4.2.1.Differantial Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique used to measure the changes in heat flow associated with changes in the physical and chemical properties of a sample. TA Instruments DSC Q2000 device were used in this study.

The sample is heated or cooled at a controlled rate while the heat flow is measured. DSC can be used to determine the glass transition temperature, melting point, crystallization temperature, and other thermal properties of a sample. It is a commonly used technique in material science, polymers, and pharmaceutical industries.

**Figure 2.6:** Differantial scanning calorimetry device.

$$X_c(\%) = \Delta H_{m-}\Delta H_{cc}/\Delta H_{mo} \times \mathbf{100} \qquad \text{(Eq.1)}$$

The crystallinity% of PLA samples, Xc, was calculated using Equation 1, where $\Delta H_{m*}$ is the melting enthalpy detected in DSC thermograms, and $\Delta H_{mo}$ is the melting enthalpy of 100% crystalline PLA as 93.6 J/g **[Hung et al, 2013].**

### 2.4.2.2 Thermogravimetrical Analysis

TA Q500 TGA device has used for the thermogravimetric analysis (TGA). TGA test is a method used to determine the thermal stability and composition of a material. The test involves subjecting a sample to a controlled temperature ramp which is 10 °C/min and monitoring the weight loss or gain of the sample as a function of temperature.

The TGA test can provide information on the thermal properties of a material, such as its decomposition temperature, and can be used to analyze the composition of the material by identifying the weight loss associated with specific chemical reactions.

**Figure 2.7:** Thermogravimetrical analysis device.

### 2.4.2.3 Heat Deflection Temperature (HDT)

The sample is prepared by positioning it between two supports with a visible gap in between. A specific force is applied at the center of the specimen. Then, it is placed in a container filled with silicone oil and the temperature of this chamber increases uniformly at a rate of 2 ± 0.20 C° per minute. The temperature which causes deformation equal to 0.254 mm under 0.45 MPa stress is known as heat distortion temperature (HDT). This test differentiates materials that lose stiffness over small range of temperatures from those capable of bearing loads at elevated temperatures.

Instron HV6M HDT Tester (Figure 2.8) was used to measure HDT values according to ISO 75 standard where three readings were taken for each sample and their average recorded in thesis report.

**Figure 2.8:** HDT and Vicat tester.

### 2.4.3. Morphological Characterization

#### 2.4.3.1. Scanning Electron Microscopy (SEM)

To examine the fractured surface morphology of the samples, Phenom XL Thermo Scientific scanning electron microscopy (SEM) was employed after subjecting them to fracture at -40 ºC in liquid nitrogen with the magnification ratio as 1000x.

**Figure 2.9:** Scanning electron microscopy.

# 3. RESULTS AND DISCUSSION

## 3.1. Mechanical Properties

**Table 3.1:** Tensile test results.

| Sample Codes | Stress at Break (MPa) | Strain at Break (%) |
|---|---|---|
| Pure PLA | **73.3 ±0.35** | 3.77 ±0.03 |
| ULX1 | 66.7 ±0.10 | 3.43 ±0.03 |
| ULX2 | 51.8 ±0.26 | 1.38 ±0.03 |
| ULX5 | 63.6 ±0.20 | 2.83 ±0.01 |
| ULX10 | 53.7 ±0.17 | 1.47 ±0.02 |
| CLM1 | 69.2 ±0.10 | **5.51 ±0.01** |
| CLM2 | 68.6 ±0.20 | **4.75 ±0.03** |
| CLM5 | 61.3 ±0.10 | **4.96 ±0.01** |
| CLM10 | 62.7 ±0.20 | 3.43 ±0.02 |
| ULX2PF | 41.6 ±0.20 | **4.79 ±0.01** |

According to the tensile test results given in Table 3.1, tensile strength of the compounds was lower than pure PLA. The tensile strength of the samples shows a decreasing trend as the mineral content increases. Tensile strength values of CLM were generally higher compared to ULX samples. The existence of plasticizer resulted in higher decrease in the tensile strength, as expected. Another advantage of CLM was observed in the elongation at break values. CLM2 has 26 %, CLM5 has 32 % increase in the elongation at break value. CLM1 has increased strain at break value of PLA up to 46%.

Nevertheless, colemanite-added compounds yielded better results in elongation than that of pure PLA. Additionally, 27% increase in the elongation at break value was observed in the compound containing plasticizer. When the results are examined in general, the tensile test results of blends containing colemanite were better than those containing ulexite. Elongation at break values are better in compounds containing colemanite than in compounds containing ulexite.

The fact that the test results have very low standard deviations in both the tensile test and elongation at break confirms the study and shows the consistency of the sample production process.

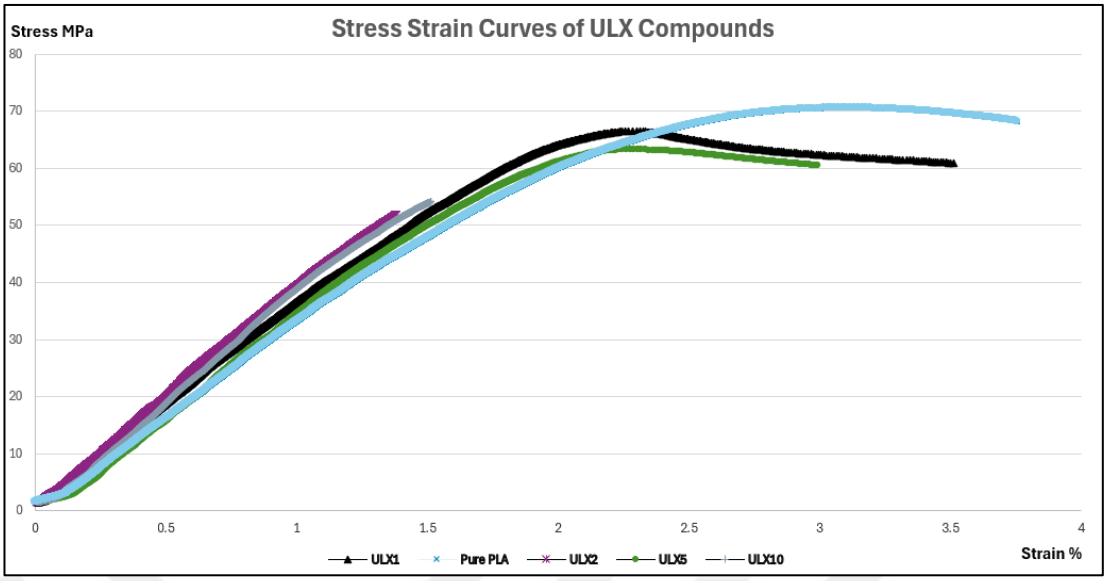


**Figure 3.1:** Stress Strain Curves of ULX Compounds.

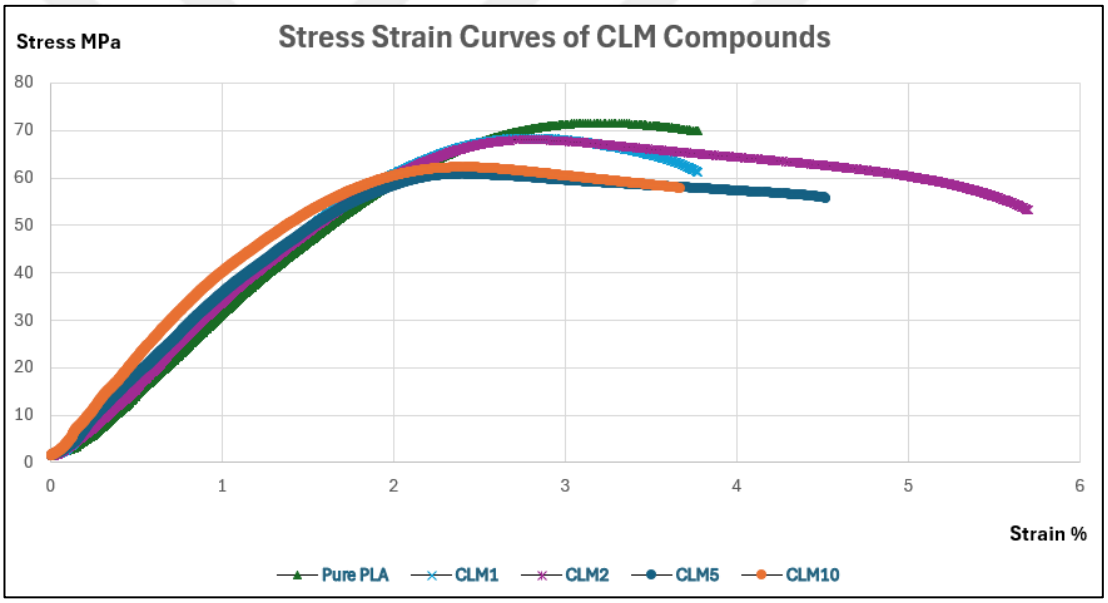


**Figure 3.2:** Stress Strain Curves of CLM Compounds.

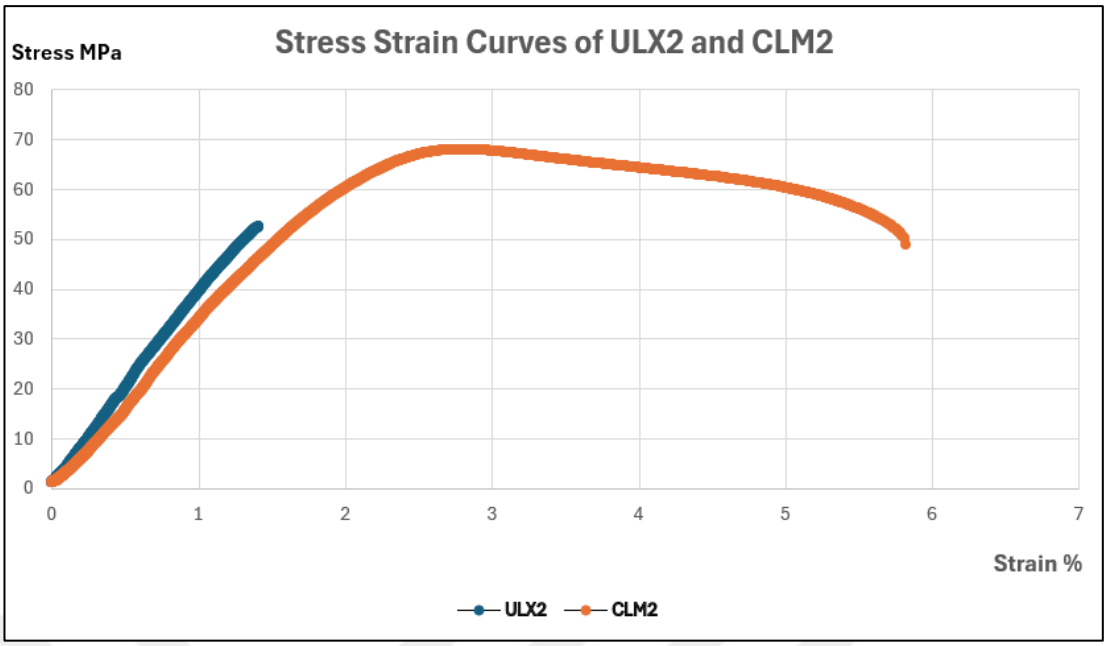


**Figure 3.3:** Stress Strain Curves of ULX2 and CLM2 Compounds.

In the study of Durgun et al., the addition of 7% colemanite to the polypropylene polymer changed the 19.5% decrease in tensile strength to 8.4% when the polymer was kept at 300 °C for 56 days **[Durgun et al, 2022].** The tensile strength of PLA was increased by producing a blend of PLA/Polybutylene succinate that has a clear cut cell structure and higher crystal content. Furthermore, elongation at break value increased %140, impact strength increased %370 in presence of an extra chain extender **[Bing et al, 2024].**

**Table 3.2:** Impact test results

| Sample | Izod Impact-Unnotched (+23°C) (kJ/m$^2$) |
|---|---|
| Pure PLA | 22.6 ±0.17 |
| ULX1 | **24.6 ±0.49** |
| ULX2 | **23.6 ±0.10** |
| ULX5 | 21.2 ±0.17 |
| ULX10 | **31.4 ±0.26** |
| CLM1 | **28.0 ±0.17** |
| CLM2 | **30.2 ±0.26** |
| CLM5 | **29.9 ±0.20** |
| CLM10 | 20.4 ±0.10 |
| ULX2PF | **29.6 ±0.20** |

According to Izod impact test results, an improvement in impact resistance was observed in a significant part of the compounds compared to pure PLA. The best result

was observed in the compound with 10% ulexite. In addition, an increase up to 29.6 $kJ/m^2$ in the impact resistance value was observed in the plasticizer-added compound, as expected. As a result, 10% ulexite increased impact resistance up to 39%. Colemanite additives increased impact strength of PLA up to 37%. Polymer additives also helps to increase impact strength of PLA polymer. In the literature, a study examines alternative ways of increasing the impact strength and elongation at break of PLA/Polybutylene succinate blends. Lysine triisocyanate was used as compatibilizer by Harada et al. as a reactive processing agent; they discovered that the impact strength for 90/10 wt% PLA/PBS blend rose from 18 $kJ/m^2$ to 60 $kJ/m^2$ **[Harada et al, 2007].**

By increasing the resistance of PLA polymer to impact, it gains durability. This implies that it can withstand severe conditions over a longer period. As PLA's ability to resist impacts were improved, then it will find more uses in industries as well as automotive.

Although the impact resistance of PLA is generally increased by compounds produced with different polymers, elastomers, in this study, achieving this development with boron minerals, an abundant resource in Türkiye, has been an original attempt in terms of creating a sustainable and low-cost solution.

## 3.2 Thermal Properties

### 3.2.1 DSC Results

DSC tests were evaluated on the first heating curve to examine the effect of the plastic injection process on crystallinity (Table 3.3). The crystallization peaks appeared after mineral addition to PLA. The highest crystallinity rate was obtained for 10% ulexite added compound (21.84%) followed by 5% and 2% ulexite added compound (21.47% and 20.98%), then plasticizer containing 2% ulexite added PLA had 20.84% crystallization. Afterwards, 10% colemanite containing PLA had 20.34% of crystallization. The lowest crystallization (13.88%) was observed for Pure PLA. It is observed that crystallization ratio increased from 13.88% to 21.84%. Addition of boron minerals increased the crystallinity of the PLA up to 57%. When we examine it on the basis of mineral type, it was observed that compounds containing ulexite have higher crystallinity ratios than compounds containing colemanite. This result is also supported by the fact that the elongation at break values of compounds containing colemanite were higher than those of compounds containing ulexite.

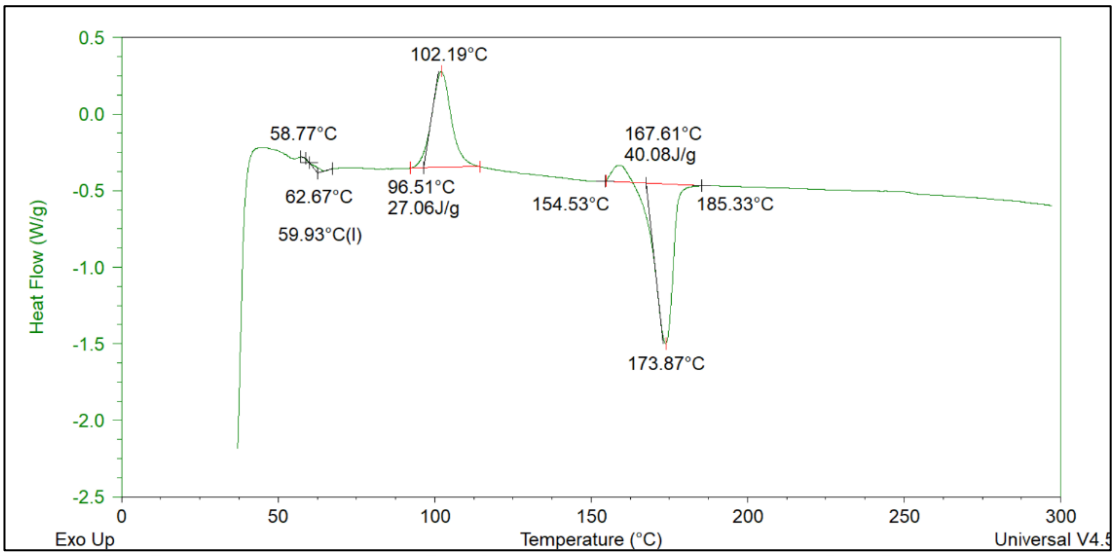


**Figure 3.4:** 1st heating curve of pure PLA.

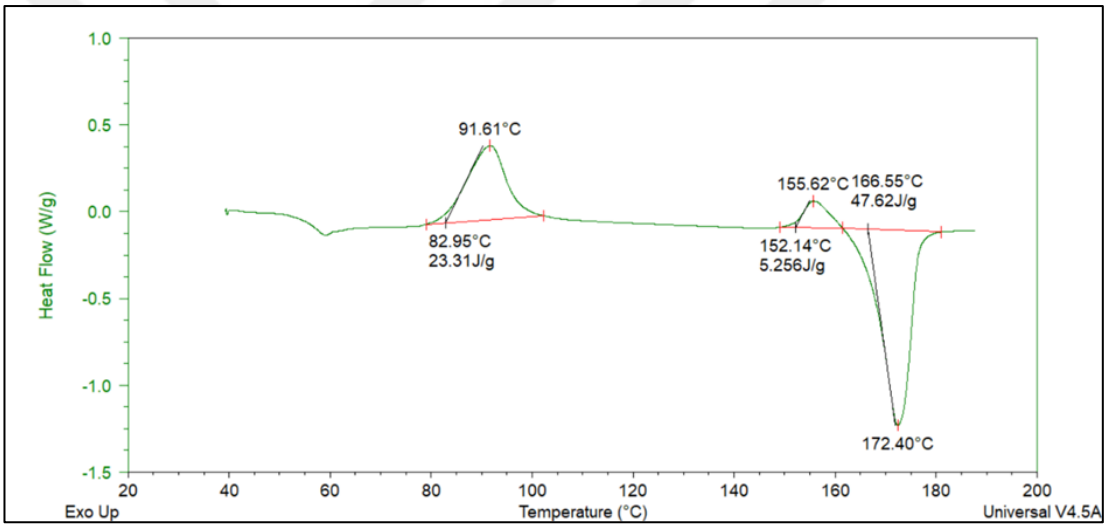


**Figure 3.5:** 1st heating curve of ULX2.

As an another way of increasing crytallinity of the PLA, Zhao has found significant improvement on the crystallinity rates after compounding and injecting PLA with other polymers like PBS **[Zhao et al, 2021].**

**Table 3.3:** DSC test results.

| Sample Codes | Tg (°C) | Tcrys (°C) | Tm (°C) | Crystallinity% |
|---|---|---|---|---|
| Pure PLA | 62.7 | 102.2 | 173.9 | 13.88 |
| ULX1 | 58.3 | 91.6 | 172.6 | **19.24** |
| ULX2 | 58.5 | 91.6 | 172.4 | **20.98** |
| ULX5 | 58.9 | 91.9 | 172.3 | **21.47** |
| ULX10 | 59.1 | 92.1 | 172.2 | **21.84** |
| CLM1 | 58.9 | 93.3 | 173.1 | **18.67** |
| CLM2 | 59.9 | 93.6 | 173.0 | **16.06** |
| CLM5 | 59.1 | 91.8 | 173.1 | **19.86** |
| CLM10 | 59.0 | 92.1 | 173.2 | **20.34** |
| ULX2PF | 56.3 | 88.7 | 171.8 | **20.84** |

When the crystallization temperatures are examined, except for ULX2PF compoud, other compounds has Tcrys between 91.6 °C and 93.6 °C. The ULX2PF compound containing plasticizer has a lower crystallization temperature because it contains additives that facilitate core movements. Tcrys results were between 91.6 °C and 92.1 °C in compounds with ulexite addition. In compounds with colemanite addition, the Tcrys value increased up to 93.6 °C. The highest value was seen in the compound with 2% Colemanite added. There was no significant change on Tg and Tm values of compounds. Tg and Tm results were adequate for aimed applications.

## 3.2.2. TGA Results

When testing thermal decomposition temperatures, temperatures at which 5% and 10% of the masses of the compounds were lost under temperature were taken into account. When the TGA test results are examined, the highest thermal degradation temperature belonged to pure PLA. Afterwards the best result was obtained from CLM1 compound (345.32 and 350.95 °C). After CLM1 compound, CLM2 is the second best compound which has 4 °C less than CLM1. Rest of the compounds lost 10 % of their mass between 320 – 330 °C. Here, it can be interpreted that pure PLA had a good thermal resistance, the addition of mineral increases shear stress during extrusion and injection, and the small amount of moisture contained in the mineral might expose PLA to hydrolytic degradation.

**Table 3.4:** Thermogravimetrical analysis results.

| Sample Codes | %5 mass loss temperature (°C) | %10 mass loss temperature (°C) |
|---|---|---|
| Pure PLA | **359.20** | **365.86** |
| ULX1 | 324.72 | 329.57 |
| ULX2 | 320.88 | 327.36 |
| ULX5 | 321.27 | 327.88 |
| ULX10 | 322.47 | 328.71 |
| CLM1 | 345.32 | 350.95 |
| CLM2 | 340.93 | 346.70 |
| CLM5 | 314.13 | 319.72 |
| CLM10 | 317.50 | 321.63 |
| ULX2PF | 318.93 | 326.70 |

On Velghe's study also supported this reasoning where they examined the effect of processing and the moisture content on the degradation of PLA polymer **[Velghe et al, 2023].** Nevertheless, these thermal degradation values are quite sufficient for automotive, which is one of the target applications, as the highest observed temperature for automotive interior was found as 76 °C **[Grundstein et al, 2009].**

## 3.2.3. HDT Results

**Table 3.5:** HDT test results.

| Sample Codes | HDT 0,45 MPa (°C) |
|---|---|
| Pure PLA | 53 |
| ULX1 | **60** |
| ULX2 | **92** |
| ULX5 | 57 |
| ULX10 | **61** |
| CLM1 | 57 |
| CLM2 | 57 |
| CLM5 | 58 |
| CLM10 | 57 |
| ULX2PF | **82** |

According to HDT test results, mainly two compounds standed out. ULX2 increased the HDT level by 74% to 92 °C. ULX2PF compound containing 3% plasticizer and 2% ulexite increased the HDT level by 55%, up to 82 °C. In other compounds, the results varied between 57 °C and 61 °C. This HDT increase brought by ulexite did not

continue as the ulexite ratio increased, but rather disappeared. This shows that ulexite works as a nucleating agent in the polymer matrix with an optimum amount of 2%. Following this improvement, plasticizer was added to the ULX2 compound and it was tested whether HDT would increase further. As a result, the HDT of the ULX2PF compound was higher than all compounds except ULX2 but was lower than the ULX2 compound. Adding plasticizer to PLA facilitated the movement of nucleating agents and polymer matrix, thus widening the crystallization temperature range and increasing the HDT value. This HDT increase achieved with the ULX2 compound has been an important gain that can expand the usage areas of PLA polymer. Compared to other studies in the literature, increasing HDT through the injection process was a promising development in this study. As seen in most studies, HDT increase could be observed with annealing **[Wootthikanokkhan et al, 2013][Simmons et al, 2019]**. This work offers an extra advantage of not needing an extra annealing step that saves energy resources.

The fact that the 2% ulexite added compound, which has the highest HDT temperature, does not have the highest crystallinity, shows that the HDT crystallinity relationship is not always directly proportional.

According to HDT results, the addition of ulexite can greatly expand the usage areas of PLA polymer. The thermal properties of PLA that have been improved by adding an ulexite mineral, make the material more capable at high temperatures. This means that at 53°C, PLA can deform at temperatures above 60 °C. However, when 2% ulexite mineral is added to PLA, its HDT value can increase up to by 30 °C, making it heat resistant and applicable in areas where higher temperatures are required.

Another aspect of increasing the HDT level of PLA is that it expands its scope of use in various sectors. For example, the automotive industry needs materials that can withstand high pressure and temperature conditions; therefore, with increasing HDT values, underhood parts or engine components can be produced from PLAs. Similarly, electronic devices require materials that can withstand high heat, and printed circuit boards, among others, can be also produced from these compounds **[Wunderlich, 2005].**

## 3.3.Morphological Properties

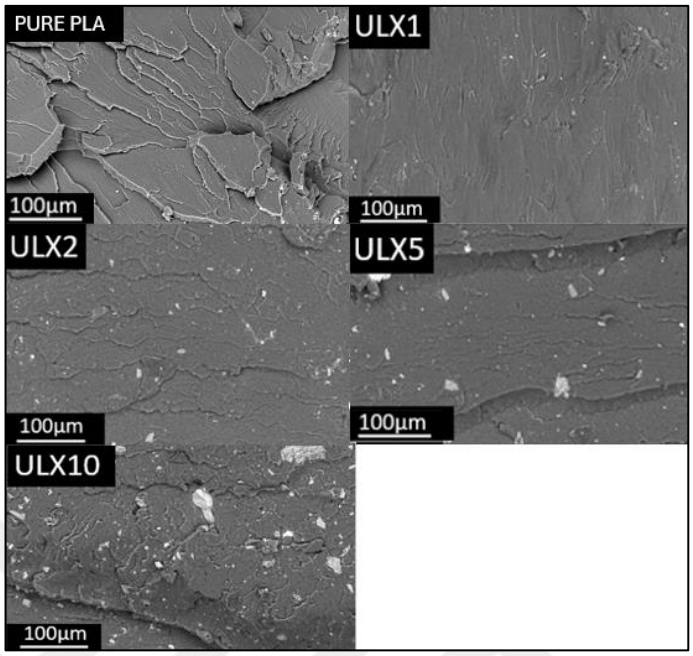


**Figure 3.6:** SEM images of ULX compounds.

When the SEM images of the compounds of ulexite were examined, a smooth surface was obtained. Minerals has an homogeneous distribution up to 2%. When the ratio of mineral increased to 5%, agglomeration of the minerals occured. The homogeneous distribution of minerals in the polymer matrix shows that the desired mixing has been achieved in the sample preparation processes of extrusion and injection until 2% of mineral loading.

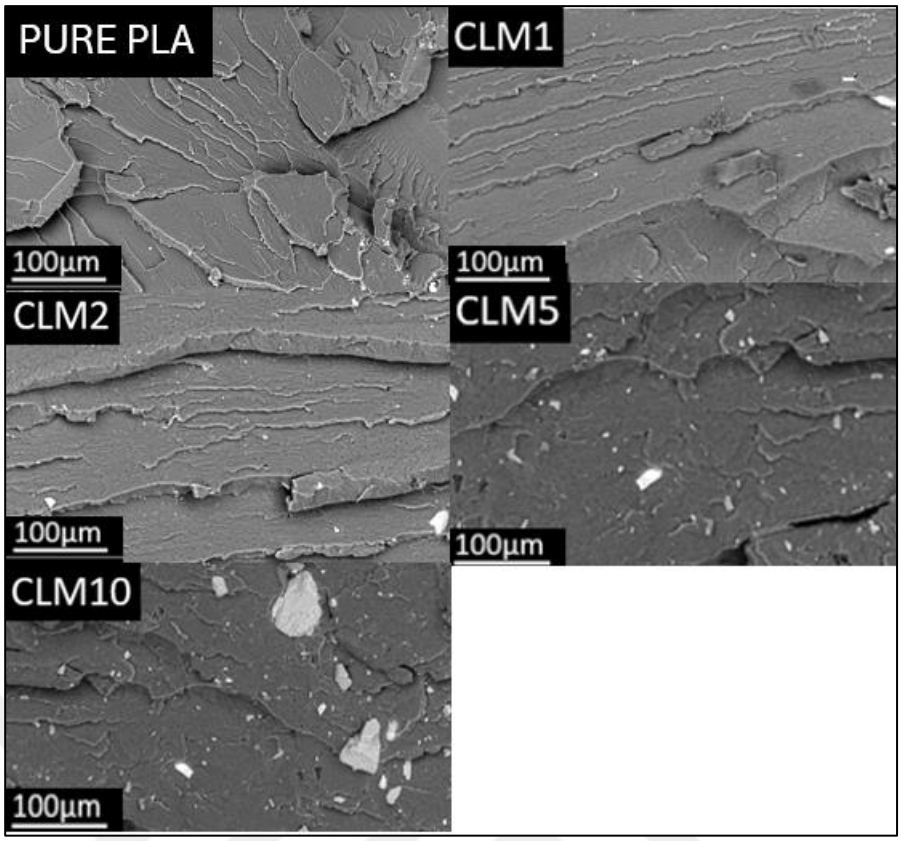


**Figure 3.7:** SEM images of CLM compounds.

When the SEM images of the compounds of colemanite were examined, much rougher surfaces were obtained. Similar to ulexite, minerals had an homogenius distribution until 2% of loading, and when the ratio of mineral increased to 5%, agglomerations were observed. The homogeneous dispersion of minerals in the polymer matrix as observed from morphological studies, indicates that the required compounding was performed successfully during the preparation stage through extrusion and injection until 2% of loading.

When the SEM images of the compounds with 2% ulexite and colemanite addition were examined (Figure 3.3.3), it was observed that the ulexite were more homogeneously mixed into the polymer matrix. This is necessary for the mineral to be used as a nucleation agent. A rougher surface structure of CLM2 can be clearly observed in these photos. It can be seen at (Figure 3.1.3) that ULX2 has more brittle characteristic then CLM2. As it seen on Gao's study, smooth surface mentions brittle characteristics of the PLA material. **(Gao et al., 2017)**

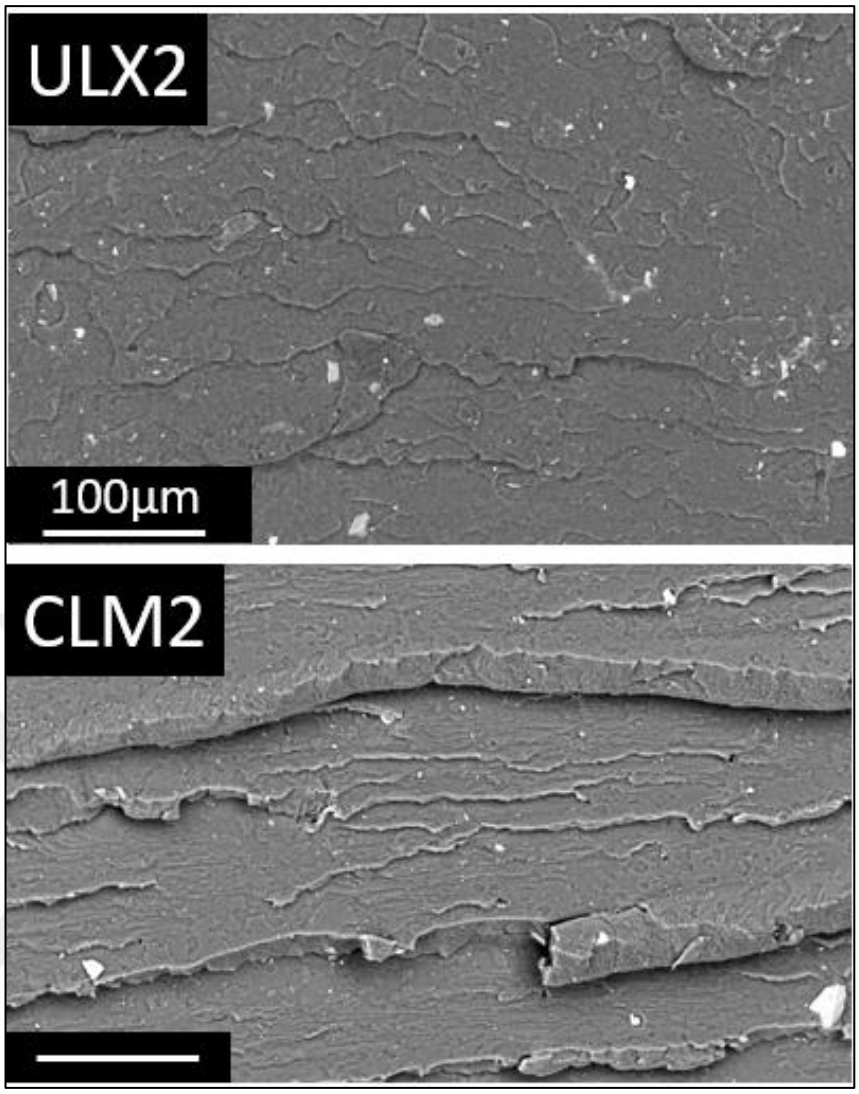


**Figure 3.8**: SEM Images of ULX2 and CLM2.

In the study of Murariu et al., where they compounded PLA with $CaSO_4$ particles, improved mechanical behavior was explained by good filler dispersion in the polyester matrix (up to 40% loading) and abundant interactions between $CaSO_4$ particles with ester groups of PLA chains as confirmed by the fitting of predictive math models to composite mechanics and scanning electron microscope images of fracture surfaces **[Murariu et al, 2007].**

# 4. CONCLUSIONS

In this study, boron minerals ulexite and colemanite were added to PLA polymer to improve the properties of PLA. HDT value increased significantly from 53 °C to 92 °C in PLA containing 2% ulexite (ULX2). In presence of 3% plasticizer into ULX2, HDT increased from 53 °C to 82 °C. The impact value of 10% ulexite-added PLA increased from 22.6 kJ/m$^2$ to 31.4 kJ/m$^2$. The impact value of colemanite-added PLA, was increased up to 30 kJ/m$^2$. When the crystallinity ratios are examined, with the addition of boron mineral, the crystallinity ratio increased by 57%, from 13.88% to 21.84%.

With all these improvements, the potential of expanding the usage areas of PLA polymer, which can be a solution against plastic pollution, has emerged. Thanks to its high temperature resistance, boron mineral added PLA can be used in applications such as automotive and home appliances. While producing sustainable products with lower carbon footprints, the proposed method is also sustainable as it eliminates the need for an additional annealing step, thereby conserving energy resources. Additionally, this research enhanced the potential of using ulexite and colemanite minerals, which are important resources in Türkiye.

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# BIOGRAPHY

**Name Surname:** Oğulcan Kocagül

**Experience:** Polymer Processing, Engineering Plastics, Biopolymers

**Bachelor Degree:** Kocaeli University – Mechanical Engineering

**High School:** Beşiktaş Sakıp Sabancı Anatolian High School

# PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

Kocagül Oğulcan, Mocan Merve, “Enhancing Mechanical and Thermal Properties of PLA by Incorporatıng Ulexite and Colemanite Minerals” Poster Presentation. 14. ULUSLARASI LİF ve POLİMER ARAŞTIRMALARI SEMPOZYUMU 24-25 Mayıs 2024, Bursa, Türkiye.