Thesis for the Degree of Master of Engineering

A Study on the Degradation Behavior and Mechanical Properties of Bio-based Polymers

by

Sangho Kim

Department of Polymer Engineering

The Graduate School

Pukyong National University

February 2024

A Study on the Degradation Behavior and Mechanical Properties of Bio-based Polymers
(바이오 기반 고분자의 분해 거동과 기계적 물성 연구)

Advisor: Prof. Won-Ki Lee

by

Sangho Kim

A thesis submitted in partial fulfillment of the requirements
for the degree of

Master Engineering

in Department of Polymer Engineering, The Graduate School,
Pukyong National University

February 2024

A Study on the Degradation Behavior and Mechanical Properties of Bio-based Polymers

A dissertation
by
Sangho Kim

Approved by:

(Chairman) **Prof. Yun-Seok Jeon**

(Member) **Prof. Gavande Vishal Madhukar**

(Member) **Prof. Won-Ki Lee**

February 16, 2024

CONTENTS

List of Schemes

List of Tables

List of Figures

바이오 기반 고분자의 분해거동과 기계적 물성 조절

김상호

부경대학교 대학원 고분자공학과

요약

Polycarbonate(PC)는 투명성, 내열성 및 기계적 특성이 우수해서 광범위하게 사용되는 엔지니어링 플라스틱이다. 하지만 PC의 원료인 비스페놀 A(BPA)는 내분비계 장애 물질로 분류되는데 합성 후, PC 내에 미량 존재하여 인체나 환경에 오염이 영향을 미친다. 따라서 BPA 대체하기 위하여 바이오매스 소재인 전분을 이용해서 만든 아이소바이드를 기반으로 한 바이오 PC 개발에 대한 연구가 진행되고 있다. 이러한 바이오 기반 고분자는 소재에 따라 분해 등의 특성을 보이기도 하는데 NaOH를 이용한 알칼리 용액, Proteinase K 효소 용액, 그리고 토양조건에서 인장 시편을 침지 시킨 후, 노출시간에 따른 기계적 물성을 분석하였다. 석유화학 기반 PC와 바이오 기반 PC(Mitsubishi)와 삼양사 개발 바이오 PC는 알칼리, 효소 조건에서는 분해 거동을 보이지 않았으나 토양조건에서 바이오 SY-PC의 경우 약간의 분해 거동을 나타내었다.

Poly(butylene succinate) PBS는 기계적 강도, 연성, 인성, 내충격성의 좋은 절충점으로 인해 가장 흥미로운 생분해성 고분자 중 하나이며, PBS의 특성을 변화시키기 위해 개질시킨 poly (butylene succinate-co-butylene adipate-co-ethylene succinate-co-ethylene adipate) (PBEAS)를 개발시켰다. 한편 PLA는 상업적으로 사용되는 친환경 고분자 중 하나이지만 취성과 상대적으로 가수분해 속도가 느리기 때문에 적용하기에 제한적이다. 고분자의 특성에 대한 시너지 효과를 위해 PLA/PBS와 PLA/PBEAS 블렌드를 제조하여, 핫프레스로 제작한 인장 시편으로 NaOH를 이용한 알칼리 용액, Proteinase K와 Lipase 효소 용액을 분해 조건에서 노출 시간에 따른 물성을 시간의 함수로 조사하였다. PLA는 알칼리와 Proteinase K 효소에서 분해성을 보였고 PBS와 PBEAS는 Lipase 효소에서 분해성을 나타냈다.

생분해성 고분자는 상업화된 제품으로 설계하기 위해서는 초기 분해 특성에 관한 연구가 선행되어야 한다. 본 연구에서는 니더와 핫프레스를 통해 제작한 후 인장 시편에서의 분해성 연구를 하였다. 화학적·물리적 개질을 통한 바이오 고분자는 다양한 조건에서의 분해성 및 물성 조절 연구를 통해 제품의 적용 분야를 넓힐 수 있으며, 이는 새로운 생분해성 고분자의 상업적 설계를 위한 기초자료가 될 수 있다.

Chapter 1. Introduction

1.1. Research Significance

It is interesting to note that the most common feedstock for producing plastic comes from fossil fuels like petroleum and natural gas. These materials have been used for several decades to create high-quality plastic that can be used in a wide range of applications [1]. However, the long-term use of petroleum polymers has led to a major disadvantage. These materials are not biodegradable and can accumulate in the environment. It has caused significant environmental problems, and as a result, there's been a growing need to develop eco-friendly materials. Recent government policies focused on energy conservation, carbon dioxide reduction, and sustainable practices are driving research towards the use of renewable and sustainable biopolymers [2].

As we strive to become more environmentally conscious, the use of bio-based and biodegradable plastics is becoming increasingly popular. These types of plastics have been found to have improved environmental performance over traditional synthetic polymers, making them a more sustainable option. Some of the most commonly used biodegradable polymers include polylactide (PLA), poly(butylene succinate) (PBS), poly(3-hydroxybutyrate) (PHB), and poly(butylene adipate-co-terephthalate) (PBAT) [3-7]. These biodegradable polymers are capable of being broken down under acidic or base conditions or by selective enzymatic breakdown. By utilizing these biodegradable options, we can help reduce our reliance on petroleum-based polymers and work towards a more sustainable future [8,9]. Among all the biodegradable polymers, PLA and PBS are considered more important for several reasons, primarily due to their significant contribution to environmental sustainability and their diverse range of applications. Its biodegradability, biocompatibility, reduced carbon footprint, and versatility lie in its positive impact on environmental sustainability, and it has the potential to replace conventional petroleum-based plastics in various applications.

Assessment of degradation properties is crucial for biodegradable polymers to ensure that they meet environmental goals, perform effectively in specific applications, and comply with regulations. Understanding how these materials break down over time is fundamental to their responsible use and commercial viability. There are several reasons which are very crucial for assessing the degradation properties of biodegradable polymers.

Environmental Impact: Biodegradable polymers are designed to break down into harmless byproducts under natural environmental conditions. Understanding their degradation properties is essential to assess their environmental impact. This ensures that they do not persist in ecosystems, contribute to litter, or harm wildlife.

Sustainability: Biodegradable polymers are often considered more sustainable alternatives to traditional plastics. Assessing their degradation properties helps confirm that they meet sustainability goals, as they can reduce the reliance on non-renewable resources.

Product Lifecycle: Understanding how a biodegradable polymer degrades over time is vital for predicting the lifespan of products made from these materials. This information is crucial for product design, especially in applications where degradation is desirable, such as single-use packaging.

Biomedical and Pharmaceutical Applications: Biodegradable polymers are used in various biomedical applications, such as drug delivery systems and surgical implants. Controlling and understanding the degradation rates of these materials is critical for ensuring safe and effective use.

Waste Management: Biodegradable polymers are often used in disposable products, such as food packaging and agricultural films. Knowing how they degrade in industrial composting facilities or natural environments helps in waste management and disposal decisions.

Performance and Durability: In some cases, biodegradable polymers need to maintain their structural integrity for a certain period before degrading. Understanding their degradation properties allows for the design of materials that meet specific durability requirements.

Regulatory Compliance: Many regions have regulations and standards for biodegradable materials. Testing and verifying degradation properties are often required to meet regulatory compliance and labeling requirements.

Predicting Material Behavior: Knowledge of degradation properties allows manufacturers and researchers to predict how biodegradable polymers will behave in various environments and applications. This information informs material selection and product design.

In this dissertation, we worked on biodegradable and bio-based polymers including PLA, PBS, PBEAS, and bio-based PC. We PLA offers brittleness, limited heat resistance, and slow biodegradability. To overcome these shortcomings, ongoing research and development efforts continuously address some of these issues through various physical and chemical methods such as copolymerization, blending, and surface treatment [10-15]. Among them, the blending method was used with highly flexible PBS materials to overcome the shortcomings of PLA and was investigated by many researchers, and the results showed an improvement in processing properties as well as mechanical properties [10-13]. Polybutylene succinate (PBS) is a biodegradable synthetic polymer that belongs to the family of aliphatic polyesters. PBS represents one of the promising biodegradable materials that can contribute to the development of more sustainable and environmentally friendly products in various industries. Its properties and versatility make it a polymer of interest in the ongoing efforts to reduce the environmental impact of plastics. PBS is gaining attention in various fields, including packaging, textiles, and biomedical applications, due to its unique combination of properties.

Similar to PBS, another biodegradable polymer (modified version of PBS), poly(butylene succinate-co-butylene adipate-co-ethylene succinate-co-ethylene adipate) (PBEAS), was developed to improve the strength and flexibility of PBS. PBEAS is a unique biodegradable copolymer that combines the properties of various monomers. This copolymer is produced through the polymerization of monomers, including butylene succinate, butylene adipate, ethylene succinate, and ethylene adipate. The incorporation of these different monomers imparts distinctive characteristics to the resulting PBEAS material. PBEAS exhibits excellent biodegradability, making it an eco-friendly choice for various applications. The incorporation of both butylene and ethylene units into PBEAS enhances its flexibility, toughness, and elongation characteristics. It makes PBEAS suitable for applications requiring high resilience and impact resistance. Furthermore, the diverse monomers in PBEAS provide tunability of properties, allowing for tailoring its mechanical, thermal, and barrier properties to specific applications. This versatility makes PBEAS a promising material for various sectors, including packaging, agriculture, fishing industries, and biomedical applications. Apparently, researchers have been working to improve the mechanical strength and flexibility of PBEAS and trying to mimic the nylon-based fibers for fishing nets [10].

Polycarbonate (PC) stands as an engineering thermoplastic renowned for its exceptional combination of properties, including high heat resistance, optical clarity, and remarkable toughness [16]. However, bisphenol A (BPA), the raw material of PC, is classified as an endocrine disruptor. After synthesis, a small amount of PC is present in the PC, causing human or environmental exposure. Historically, most BPA-based PCs were produced using the phosgene process, which, despite its advantages such as easy synthesis and excellent properties, has significant drawbacks, including the use of highly toxic phosgene and chlorinated solvents. Phosgene is a noxious gas that poses severe health risks, including respiratory problems and lung damage, while chlorinated solvents are hazardous to both human health and the environment [17]. In this case, replacing bisphenol A (BPA)-based PC with bio-based PC offers environmental sustainability and biodegradability benefits, reducing reliance on petrochemical sources. Unlike conventional petrochemical plastics, plastics made of isosorbide are not toxic, degrade well, and have excellent transparency and hardness. Currently, it is a bio-based PC that can be widely applied to various fields, such as electronics exterior materials, automobile interior materials, and eco-friendly building materials [18]. In this study, we present the characterization and degradation behavior of synthesizing bio-based PC (biopolymer) as an alternative to BPA-based PC.

1.2. Objectives and scope of the work

The scope and objectives of the study on the degradation behavior and mechanical properties of bio-based polymers are essential for advancing the understanding and application of these materials in a more environmentally sustainable manner. The research can help inform the design of products, waste management strategies, and environmental policies related to biodegradable and bio-based polymers.

In this dissertation, chapter 3 presents the characterization of bio-based PC as an alternative to BPA-based PC. Thermal and mechanical properties were confirmed through DSC, TGA, and UTM. The degradation behavior of dog-bones produced through kneaders was studied in hydrolytic solutions, enzymatic solutions, and soil conditions. Chapter 4 includes a study focused on evaluating the mechanical and thermal characteristics of PLA/PBS and PLA/PBEAS blends. We have used PBS and PBEAS for blending with PLA to overcome its shortcomings. The manufactured PLA/PBS and PLA/PBEAS blends were manufactured through a Hot press to investigate mechanical and thermal properties through UTM and DSC. The degradation behavior was confirmed by the decreased mechanical and thermal properties of the alkaline and enzymatic degradation of the blends.

Chapter 2. Theoretical background

2.1. Biodegradable polymers

There are two types of bioplastics (Figure 1), bio-based polymers and biodegradable polymers. Bio-based polymers, often referred to as biopolymers, represent a class of materials derived from renewable resources. These polymers offer a sustainable alternative to traditional petroleum-based plastics and hold significant promise for reducing environmental impact and supporting a more circular economy. Bio-based polymers are gaining prominence in various industries due to their eco-friendly attributes and versatile applications. Bio-based polymers are sourced from renewable feedstocks, which can include plants, microorganisms, and agricultural byproducts. This reduces the reliance on finite fossil resources and supports sustainability. Biodegradable polymers can be classified based on their origin, chemical structure, and properties. Here is a classification of biodegradable polymers:

1. Coming from biomass products

Biodegradable polymers derived from agro-resources are environmentally friendly materials produced from crops or residues. These polymers offer a sustainable and renewable alternative to traditional petroleum-based plastics. Here are some examples of biodegradable polymers that originate from agro-resources, such as starch-based polymers, protein-based polymers, sugarcane bagasse-based polymers, etc. They play a crucial role in reducing the environmental impact associated with the production and disposal of plastic products.

2. Biodegradable polymers originated from microorganisms

Biodegradable polymers produced by microorganisms are known as Polyhydroxyalkanoates (PHAs). PHAs are a family of biodegradable polyesters synthesized by various microorganisms as intracellular carbon and energy storage compounds. They are considered environmentally friendly because they can be produced from renewable resources, such as plant sugars, and can biodegrade in natural environments. Here are some examples of biodegradable polymers coming from microorganisms, such as poly(3-hydroxybutyrate) (PHB), poly(3-hydroxyvalerate) (PHV), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), etc. PHAs produced by microorganisms offer several advantages, including biodegradability, renewability, and versatility. They can replace traditional petroleum-based plastics in various applications, reducing the environmental impact associated with plastic waste. Additionally, their production process can utilize carbon sources derived from organic waste materials, making them even more sustainable.

3. Biodegradable polymer originated from renewable resources

Biodegradable polymers produced from renewable resources are derived from plant-based materials and other natural sources. These polymers are considered environmentally friendly because they are sourced from sustainable and renewable feedstocks. Some examples of biodegradable polymers coming from natural renewable resources are PLA, cellulose-based polymers, PGA, PBS, polyethylene furanoate, etc. These biodegradable polymers offer sustainable alternatives to conventional petroleum-based plastics and help reduce the environmental impact of plastic waste. They are often used in single-use and short-term applications, as they can be composted or naturally biodegraded, contributing to a more sustainable and circular economy.

4. Biodegradable polymers originated from classical chemical synthesis

Biodegradable polymers that originate from classical chemical synthesis are typically created through the polymerization of monomers using conventional chemical processes. These polymers can be tailored for specific applications and exhibit biodegradability while offering versatility and a wide range of properties. Some examples of biodegradable polymers originating from classical chemical synthesis include polycaprolactone (PCL), polydioxanone (PDO), poly(trimethylene carbonate) (PTMC), polyesteramides, poly(ε-decalactone), etc. These biodegradable polymers produced through classical chemical synthesis provide a range of mechanical and thermal properties that can be tailored for specific applications. They are valued for their biodegradability and are used in the medical field, as well as in environmentally friendly packaging and other short-term use applications.

The objective of most biodegradable polymers is to degrade naturally through enzymatic and soil degradation and hydrolysis, resulting in environmentally friendly byproducts such as CO_2, water, biomass, and other natural substances (Figure 2). The extent of biodegradability of the polymer varies depending on the supply of the polymer as well as specific chemical structures and degradation conditions. The main chains of biodegradable polymers contain amide, ester, and ether functional groups and can be composed of natural or synthetic resins. Polymers that are biodegradable and sourced from nature can either occur naturally or be artificially created from renewable sources. Many natural biodegradable polymers are blended with non-renewable synthetic biodegradable polymers manufactured by petrochemical resources because marketable polymer products must meet the performance conditions of the desired function (Figure 3).

2.1.2. Biomass based polymers

It is important that biomass-based polymers do not necessarily have to be biodegradable, unlike biodegradable polymers. Most polymers are not biodegradable. Biomass polymers are mainly derived from renewable plant feedstocks and can be recycled naturally [19,20]. In contrast, bio-based materials may be essentially non-recyclable [4]. Recyclability is determined by the chemical structure of the polymers. In addition, a recyclable polymer may be obtained through renewable biological resources or petroleum resources. Furthermore, petroleum polymer materials, including biomass components, can also be considered bioplastics [21]. The main advantages of using biomass-based polymers over synthetic products are to limit fossil fuel use and reduce greenhouse gas emissions. In this regard, biomass-based polymers derived from renewable resources can decrease dependence on fossil fuels and their negative impact on the environment.

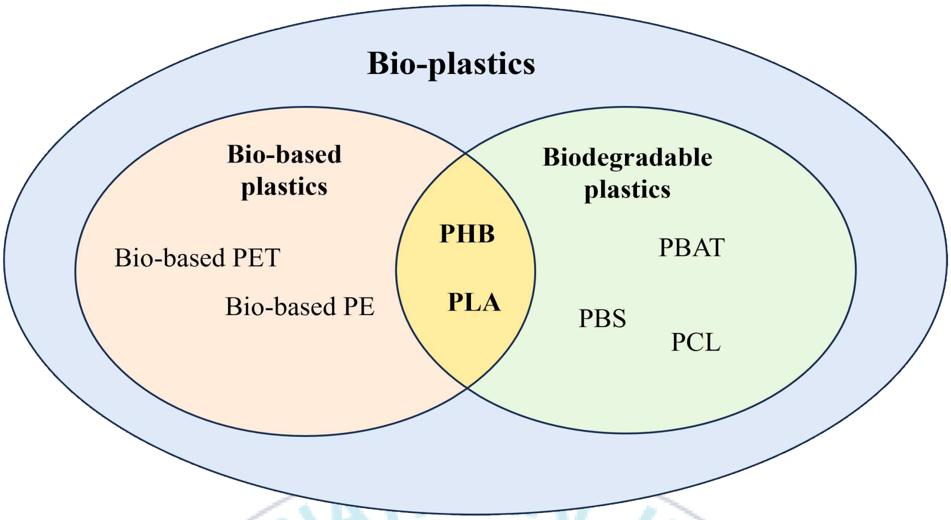


Figure 1. The relationship between bio-based plastics and biodegradable plastics.

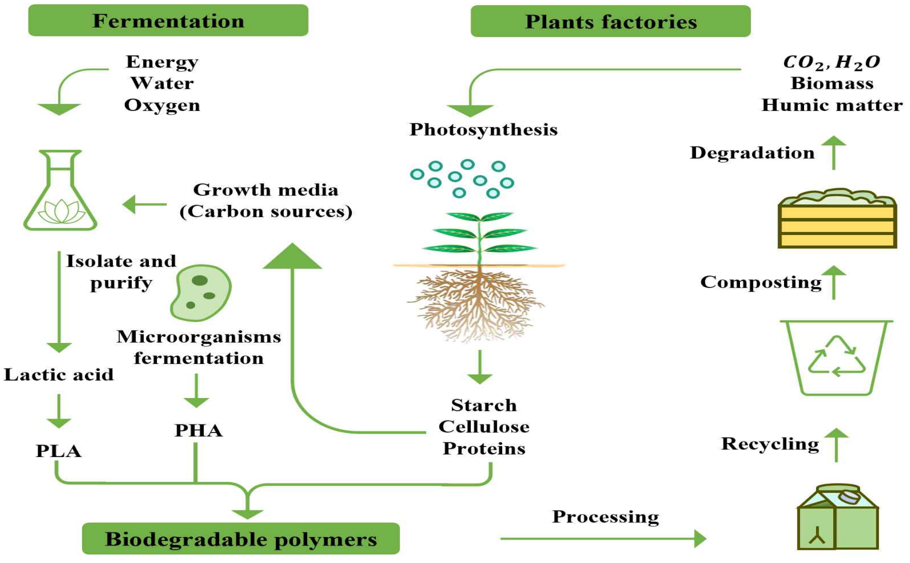


Figure 2. Cyclic biological process of biodegradable polymers [5].

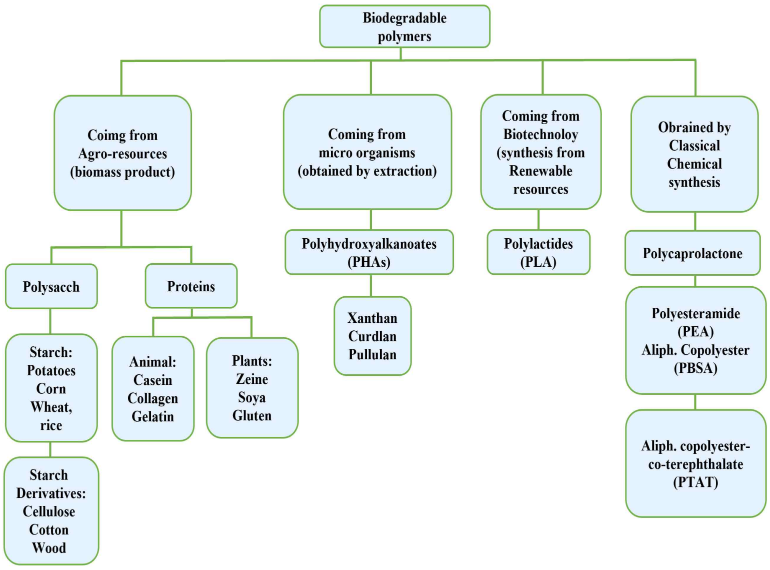


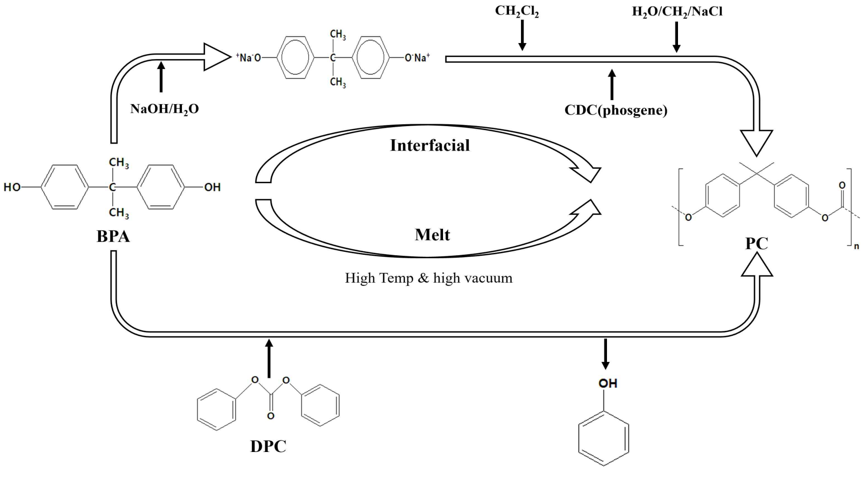
Figure 3. Classification of biodegradable polymers based on their resources [3–6].

2.2. Polycarbonate

PC is a representative high-functional thermoplastic polymer used as an industrial material because it is stronger and lighter than traditional plastics. PC is an engineering plastic known for its unique combination of properties, including high impact resistance, optical clarity, and heat resistance. PC is widely used in various industries such as electronic component housings, automobiles, and optical materials due to its high thermal stability, excellent mechanical strength, and light transmittance. Polycarbonate is composed of repeating carbonate groups (-O-CO-O-) in their polymer chain. The most common type is derived from the reaction between bisphenol A (BPA) and phosgene. This type of polycarbonate is known as bisphenol A polycarbonate (BPA-PC).

2.2.1. Synthesis of PC

Polymerization methods for PC include the interfacial polymerization process and the melt trans-esterification process (Scheme 1). The interfacial process is a process using solvents and most often follows a reaction path using phosgene. This is called the phosgene process. First, bisphenol A and sodium hydroxide are reacted to produce sodium salt of bisphenol A. Then, the sodium salt of bisphenol A is reacted with phosgene to produce PC. Here, the disodium salt of BPA reacts with phosgene dissolved in a chlorinated organic solvent of CH_2Cl_2. However, this process has a major disadvantage in that it uses phosgene. Therefore, a melting process is used, which is one of the PC synthesis methods that does not use phosgene. This process is a transesterification reaction of BPA with diphenyl carbonate (DPC) and produces phenol as a by-product [22,23].

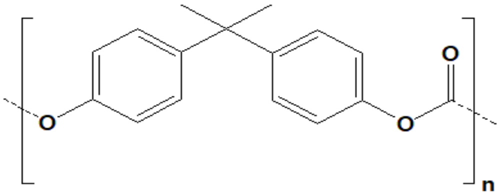


Scheme 1. Synthesis of PC [22].

2.2.2. Properties of PC

PC is an engineering plastic with high strength, impact resistance, and chemical resistance. It also provides excellent optical properties as an amorphous polymer. It is similar to PMMA or it is plastic with a light transmittance of over 90 % like glass. PC exhibits excellent mechanical properties over a broad temperature range due to the presence of polar groups. PC exhibits a high glass transition temperature of 140 – 150 °C, a high melting point of 270 – 300 °C, a high softening point of 150 – 190 °C, and a high tensile strength of 60 – 80 MPa. PC exhibits excellent impact strength even at low temperatures (Table 1).

Table 1. Properties of PC

PC	Properties
Structural formula	
Chemical formula	$(C_{16}H_{18}O_5)_n$
Density	1.20 g/cm^3
Glass transition temperature (T_g)	140~150 °C

2.2.3. Bio-based PC

Traditionally, BPA-based PC was produced using the phosgene method. This has the advantage of being easy to synthesize and having excellent performance, but it also has serious disadvantages, such as the use of highly toxic phosgene and chlorinated solvents. The representative monomer, BPA, is an environmental hormone that mimics the effects of estrogen, and its use is regulated because it can cause side effects such as decreased brain function, decreased sexual function, and breast cancer. In order to resolve this problem, many studies on products that alternate petroleum-based substances have currently received a lot of attention. Therefore, research and development are ongoing for bio-based PC on isosorbide made using starch, a biomass material that can replace BPA [24]. Bio-based PC is more environmentally friendly compared to BPA-based PC and has high transparency, excellent optical properties, and excellent scratch resistance. Moreover, the impact strength is similar to that of BPA-based PC. It can be used in a wide range of applications, including optical and energy-related parts, replacement for high-performance glass parts, electronic devices, automobile housing, and interior and exterior decoration.

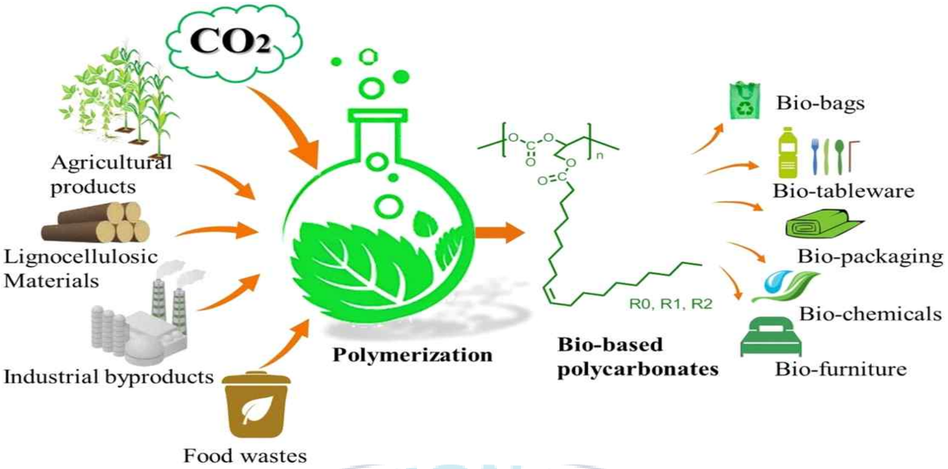


Figure 4. Bio-based polycarbonate is manufactured from a wide range of bio-based raw materials and CO_2 [25].

2.3. Polylactide

When compared to traditional petroleum-based polymers, PLA serves as a sustainable and eco-friendly alternative, as it contributes to a reduction in CO_2 emissions throughout the production process. PLA is derived from renewable biomass, such as cassava, corn, sugarcane, and other starches that are fermented (Figure 5). The future of the PLA is bright. Degradation of PLA is achieved through acidic or basic conditions or the use of certain enzymes, such as Proteinase K [26]. In addition, the production of PLA continues to increase year by year, making it widely used in packaging, biomedical industries, electronics, transportation, agriculture, and other fields (Figure 6).

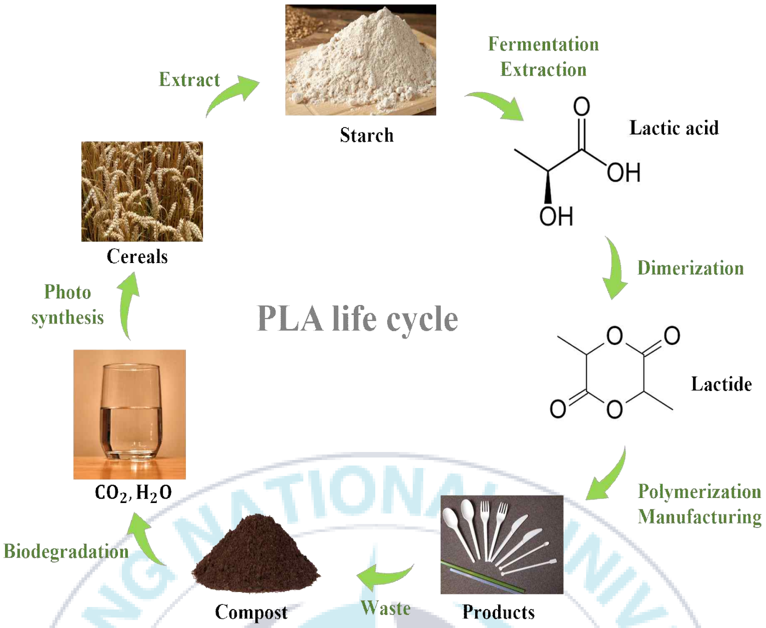


Figure 5. Schematic representation of PLA production [27].

Figure 6. Application of PLA [28].

2.3.1. Synthesis of PLA

PLA can be synthesized through various polymerization processes such as condensation polymerization and ring-opening polymerization, as well as direct methods such as azeotropic dehydration (Scheme 2). Manufacturing technologies usually use ring-opening polymerization and direct polymerization. Direct condensation polymerization includes melt polycondensation and solution polycondensation. Direct condensation polymerization requires fewer reaction steps and is more cost-effective compared to ring-opening polymerization. However, the main disadvantage is the lower molecular weight of the resulting polymer, which is caused by the balance between free acid, oligomers, and water during the reaction. So, PLA is an effective technology for obtaining high molecular weight polymers using lactide through ring-opening polymerization. Ring-opening polymerization demands the use of heavy metal-based catalysts, such as chlorides of tin and zinc and stannous octoate. In addition, ring-opening polymerization methods include bulk polymerization and solution polymerization (Figure 7). A simple method for obtaining high molecular weight polymers is bulk polymerization, but molecular weight control is challenging due to the absence of a solvent to automatically accelerate the reaction. However, in solution polymerization, the molecular weight can be controlled by adjusting reaction time, temperature, solvent amount, and catalyst concentration.

Scheme 2. Synthesis of PLA from L- and D- lactic acids [29].

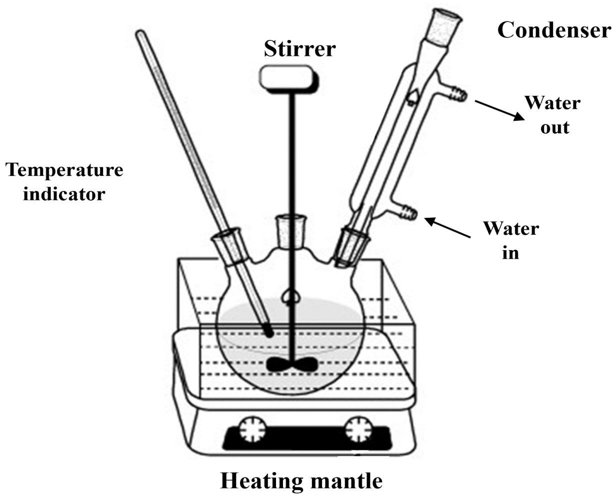
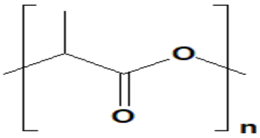


Figure 7. Synthetic tools for PLA polymerization.

2.3.2. Properties of PLA

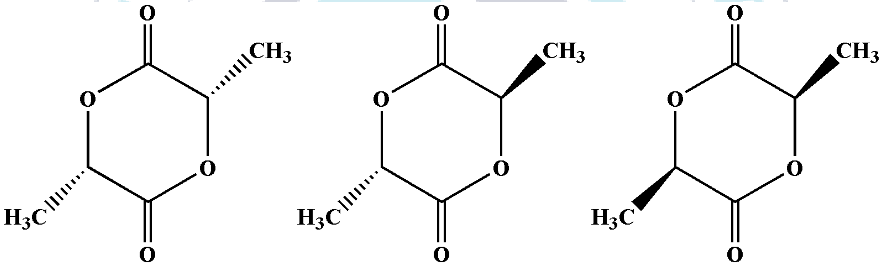
PLA is a biodegradable polymer widely used in many applications due to its excellent properties, similar to those of commercial plastics. Most PLA is a semi-crystalline polymer with a glass transition temperature of 55 ~ 65 °C and a melting temperature of 150 ~ 170 °C (Table 2). However, due to its brittleness, PLA has been limited to many applications. To overcome these shortcomings, materials can be designed by copolymerization, blending, stereocomplexation, and adding additives through physical and chemical modification [30].

Table 2. Properties of PLA

PLA	Properties
Structural formula	
Chemical formula	$(C_3H_4O_2)_n$
Density	1.210~1.430 g/cm^3
Melting temperature (T_m)	150~180 °C
Glass transition temperature (T_g)	50~65 °C
Crystallization temperature (T_c)	100~120 °C

2.3.3. Stereochemical PLA

Lactides include L-, D-, and meso-stereochemical forms due to the chiral properties of lactic acid (Figure 8). Modulation of polymer stereochemistry can produce PLA with significantly different properties. Therefore, PLA with various properties and crystalline structures can be synthesized through the copolymerization of stereochemical lactides. l-PLA and d-PLA are semi-crystalline polymers, but dl-PLA is an amorphous polymer. Furthermore, stereocomplexes can be formed by blending equimolar amounts of l-PLA and d-PLA [30]. It has high heat resistance, tensile strength, and increased resistance to degradation.



L-lactide **Meso-lactide** **D-lactide**

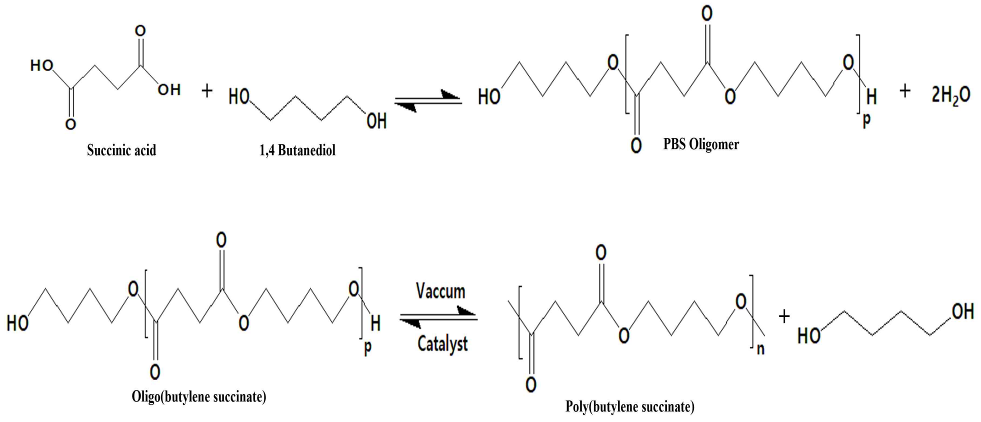
Figure 8. Stereoisomeric forms of lactides [31].

2.4. Poly(butylene succinate)

Poly(butylene succinate) (PBS) is a cost-effective alternative that is a semi-crystalline thermoplastic polyester. It is biodegradable, has excellent chemical and thermal resistance, and has melt processability. This PBS can be used in a variety of fields, such as textiles, including melt-blown, monofilament, multifilament, and flat. and is also used in the plastics industry as an injection-molded product and in the medical field. Additionally, PBS is highly utilized in food packaging, fishing nets, and fishing lines. Due to its many applications, PBS holds much promise as a polymer with vast potential.

2.4.1. Synthesis of PBS

PBS can be synthesized through two primary methods: the esterification process from succinate diesters and the direct esterification process from the diacid. The most commonly used method is the direct esterification of succinic acid with 1,4-butanediol to create PBS. This two-step process entails an initial esterification between the excess diol and the diacid, which results in the removal of water. Second, the oligomers that are produced from this process are then trans-esterified under a vacuum with a catalyst like titanium, zirconium, tin, or germanium derivatives.

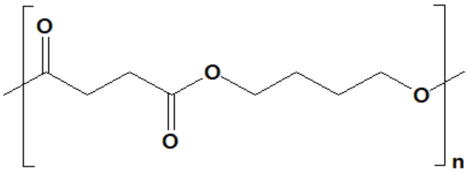


Scheme 3. Synthetic routes of PBS (Up: Step I, Down: Step II).

2.4.2. Properties of PBS

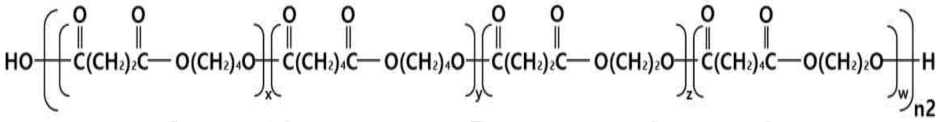
PBS is biodegradable and has properties similar to polypropylene. Among general biodegradable polymers, PBS has high heat resistance and high compatibility with fibers. By utilizing these properties, it is possible to achieve properties that cannot be achieved alone in a compound with other resins and materials. PBS is more flexible and has a lower melting point of 90 - 120 °C and a glass transition temperature of −45 - 10 °C (Table 3). In the case of mechanical properties, the tensile strength is lower than that of PLA, but the elongation rate is high, which can compensate for the brittleness of PLA. PLA/PBS blends provide excellent performance.

Table 3. Properties of PBS

PBS	Properties
Structural formula	
Chemical formula	$(C_8H_{12}O_4)_n$
Density	1.26 g/cm^3
Melting temperature (Tm)	90~120 °C
Glass transition temperature (Tg)	-45~10 °C
Crystallization temperature (Tc)	100~120 °C

2.4.3. Poly(butylene succinate-co-butylene adipate-co-ethylene succinate-co-ethylene adipate)

Previously used PBS fishing nets had to be more flexible, stronger, and mechanically sound for specific purposes. Accordingly, the National Institute of Fisheries Science (Korea) developed Poly(butylene succinate-co-butylene adipate-co-ethylene succinate-co-ethylene adipate) (PBEAS) by modifying PBS and adding adipic acid and ethylene glycol. PBEAS material has been developed as fishing gear and has similar mechanical strength to existing nylon-based fibers, showing equivalent fishing performance. It is an eco-friendly bioplastic with properties suitable for use as a fishing net material and price competitiveness.



$$HO\left[\left(\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}-O(CH_2)_4O\right)_x\left(\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-O(CH_2)_4O\right)_y\left(\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}-O(CH_2)_2O\right)_z\left(\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-O(CH_2)_2O\right)_w\right]_{n2}H$$

Figure 9. Structure of PBEAS.

2.5. Degradation of polymers

Polymer degradation occurs through various chemical, physical, and biological processes, such as hydrolysis, biological activity (e.g. enzymes, soil), thermal activation, oxidation, photolysis, etc., resulting in cleavage of the main and side chains. Degradation of polymers is affected not only by the environment but also by chemical and physical properties, including molecular weight, presence of terminal carboxyl and hydroxyl groups, degree of crystallinity, and water permeability. Environmental factors that have a significant impact on microorganisms and soil degradation include temperature, pH, humidity, and the presence of oxygen [32].

2.6. Control of the degradation rate of biodegradable polymers

In the case of degradable polymers, mechanical properties decrease rapidly once degradation begins [33]. Therefore, for biodegradable products manufactured for long-term use, it is necessary to conduct prior research on degradation behavior because the initial degradation rate is one of the important factors determining the lifespan of the product. Biodegradable products have different requirements; some products need to be degraded quickly and others need to be degraded slowly. So, manufacturers should be able to commercialize to meet customer needs. In addition, since biodegradable polymers are more expensive than general polymers, the study of degradability control is essential. Therefore, degradation control studies can reduce costs by reducing the amount of material required for production. These solutions are effective for commercialization because they can be sustainable and customized while reducing costs. There are several means of regulating degradation, including chemical and physical alterations such as copolymerization, blending, and surface treatment (Figure 10).

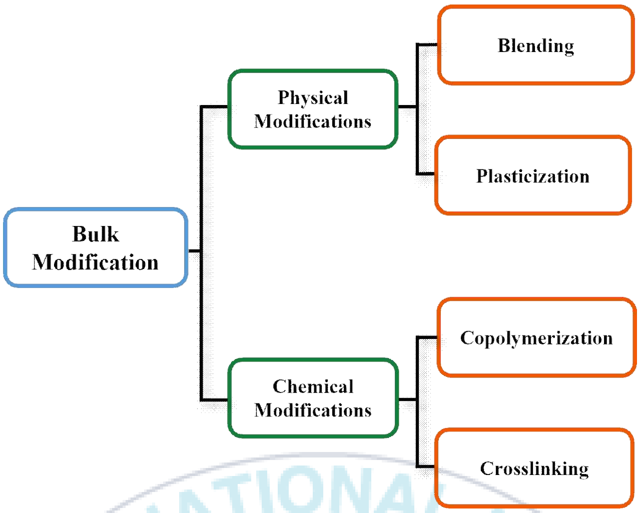


Figure 10. Classification of modification methods.

2.6.1. Copolymerization

Copolymers are created by combining two or more monomer units. The unique properties of a copolymer are determined by the arrangement of these units within its chain. Linear copolymers are categorized as alternating copolymers, random copolymers, or block copolymers, while branched copolymers are classified as graft copolymers or star copolymers. The composition and type of copolymer are determined by the reactivity ratio of monomer A (rA) and the reactivity ratio of monomer B (rB), which are calculated using the Mayo-Lewis equation. Many studies have conducted on degradation, specifically the incorporation of comonomers such as hydrophilic or hydrophobic comonomers and their effects.

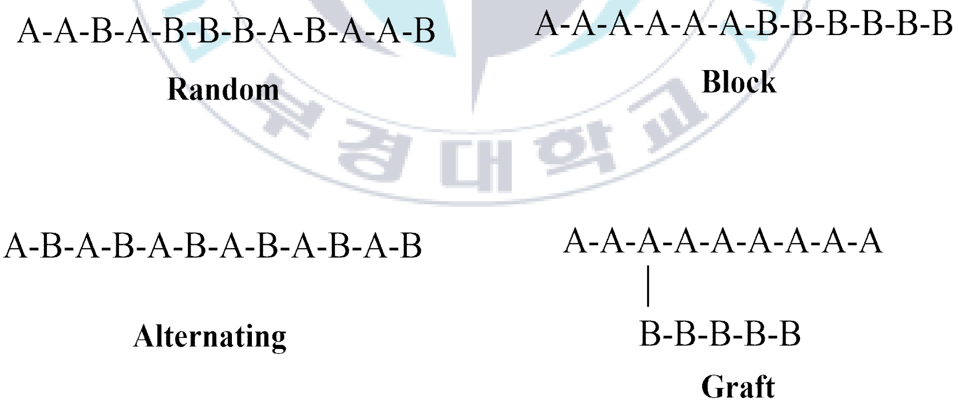


Figure 11. Type of copolymers [34].

2.6.2. Blend

Polymer blends are a physical modification made by mixing two or more polymers. Beyond the individual component properties, the morphology of the blends and the interactions between different polymers can be harnessed to influence the characteristics of the blend. Polymer blending has garnered growing attention within both the scientific and industrial sectors. Because of the use of commercialized polymers, a cost-effective strategy for achieving the desired properties in material production is to blend materials different from biodegradable polymers PLA. So, many studies have been conducted on PLA/PBS blends [10-13]. It is also about improving the shortcomings of conventional polymers and creating new materials. To obtain appropriate properties through physical blending, the blends must have some degree of compatibility. The method of determining the compatibility of polymer blends can be determined by the thermal behavior of the glass transition, melting temperature (DSC and DMA), and morphology (SEM, TEM, and AFM).

Chapter 3. Degradation behavior and mechanical properties of bio-based polycarbonates

3.1. Experimental

3.1.1. Materials

A commercial bisphenol A (BPA)-typed polycarbonate (LOTTE-PC) was supplied by LOTTE Chemicals (Korea). Among bio-based PCs, Durabio PC (D-PC) was purchased from Mitsubishi (Japan), and bio-PC synthesized by Samyang (SY-PC) was obtained from Samyang (Korea). Sodium hydroxide was purchased from Icatayama Chemicals (Japan). Tris(hydroxymethyl)amino-methane and Proteinase K were purchased from Sigma-Aldrich (USA). Hydrochloric acid (HCl) solution was purchased from Samchun (Korea). Soil for the degradation test was purchased from ABNEXO (Korea).

Table 4. The molecular weight of PCs

Sample	GPC		
	Mn	Mw	PDI
LOTTE-PC	28k	61k	2.2
D-PC	23k	47k	2.1
SY-PC	19k	39k	2.0

3.1.2. Preparation of sample films

Before the melting process, all materials were dried in a vacuum to remove moisture. LOTTE-PC was melted at 220 °C for 7 min in a kneader (PBV-0.1, Irie Shokai Co., Ltd., Japan) with a screw speed of 50 rpm. Second, D-PC and SY-PC were melted at 180 °C for 7 min in a kneader with a screw speed of 50 rpm. The obtained samples were fabricated at the same molding temperature under pressing for 5 min with a compression press (QM900S QMRSYS, Korea) of 15 MPa and then cooled at room temperature. The thickness of the films was maintained at about 300 - 350 ㎛.

3.1.3. Measurement

Thermal properties were performed by differential scanning calorimetry (DSC 1, Mettler Toledo Inc., Switzerland), and thermal stability, decomposition temperature, decomposition speed, and mass loss were performed by thermogravimetric analysis (TGA 7, PerkinElmer Inc., USA). DSC and TGA are performed at a heating rate of 10 °C/min under a nitrogen atmosphere. Mechanical properties were measured with a Tinius Olsen (H1KT, USA) equipped with a 100 Kgf load sensor applying a stretching rate of 10 mm/min. A minimum of ten dog-bone shaped replicas of each film were cut and used for the tensile testing, and the results were provided as the average value ± standard deviation.

3.2. Results and discussion

3.2.1. Thermal properties

The thermal properties, thermal stability, and thermal decomposition behavior of LOTTE-PC and bio-based PCs were studied by DSC and TGA and are showed in Figure 12 and Table 5. In the DSC curves showed in Figure 12 (A), LOTTE-PC typically exhibits a relatively high glass transition temperature (Tg) of approximately 141.3 °C. In contrast, both bio-based D-PC and SY-PC display lower Tg values, approximately 122 °C and 123.6 °C, respectively. TGA provides valuable insights into the thermal stability of polymers. When comparing BPA-based PC (LOTTE-PC) and bio-based PCs (D-PC and SY-PC), distinct differences in their TGA properties become apparent. BPA-based PC (LOTTE-PC), derived from petrochemical sources, typically exhibits excellent thermal stability with onset temperature $T_{d5\%}$ of around 440 °C. In contrast, bio-based PCs (D-PC and SY-PC), sourced from renewable materials, may display much lower thermal stability, with $T_{d5\%}$ of around 332 °C for D-PC, and 330 °C for SY-PC due to their different chemical structures. BPA-based PC contains an aromatic chemical structure, and bio-based PCs contain an alicyclic chemical structure [35]. The oxygen bond (-O-) in isosorbide can be broken easily compared with the double bond in the unsaturated aromatic structure [36]. Therefore, BPA-based PC has higher thermal stability than bio-based PCs because the chemical stiffness of BPA-based PC is higher than that of bio-based PCs.

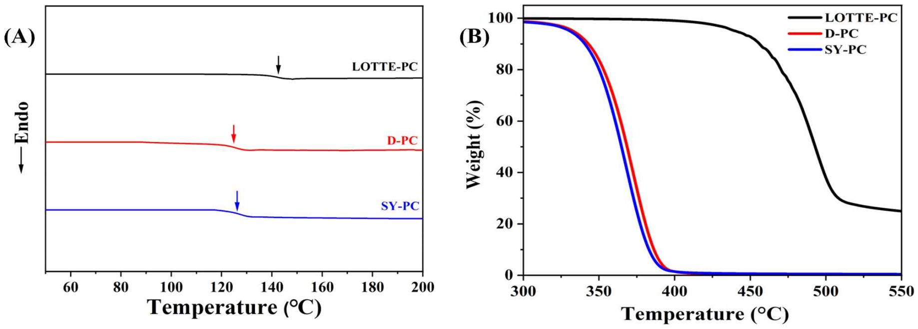


Figure 12. (A) DSC and (B) TGA curves of PCs. (The arrows indicate Tg)

Table 5. Glass transition temperature (Tg) and thermal decomposition temperature (T_d) of PCs

Sample	DSC	TGA			
	Tg (°C)	$T_{d5\%}$(°C)	$T_{d10\%}$(°C)	$T_{d20\%}$(°C)	$T_{d50\%}$(°C)
LOTTE-PC	141.3	440	456	470.2	492.8
D-PC	122	332	342	353	368
SY-PC	123.6	330	340	349	364.8

3.2.2. Mechanical properties of the bio-based PCs

Figure 13 illustrates stress-strain curves for LOTTE-PC, D-PC, and SY-PC, and the data are summarized in Table 6. D-PC and SY-PC show the higher tensile strength. LOTTE-PC has a slightly lower tensile strength of 61.7 MPa than bio-based PCs but shows an excellent elongation of 110.6 %. The mechanical properties of bio-based PCs are consistent with previous results [37,38]. In general, bio-based PCs exhibit brittleness due to the high stiffness of isosorbide [38]. For a better understanding of bio-based PCs, it is imperative to conduct methodical and thorough investigations into their mechanical properties.

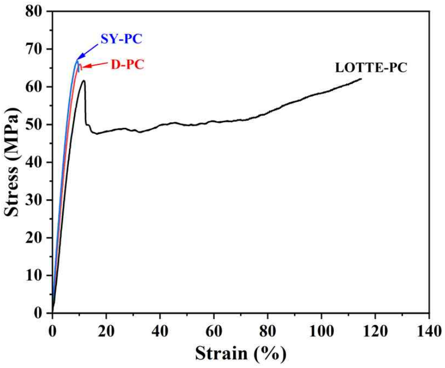


Figure 13. Example of stress-strain curves of PCs.

Table 6. Mechanical properties of PCs

Sample	Tensile strength (MPa)	Elongation at break (%)
LOTTE-PC	61.7 ± 5.3	110.6 ± 8.6
D-PC	64.2 ± 5.6	10.6 ± 2.1
SY-PC	65.5 ± 4.8	9.8 ± 1.6

3.2.3. Alkaline and enzymatic degradations

To study degradation experiments, ten dog-bone shaped replicas of each PC film with a thickness of 300 - 350 ㎛ were cut and used for degradation studies. Before the degradation experiment, each specimen was immersed in an alkaline solution and a Proteinase K solution for a certain time at room temperature. The alkaline solution at pH 11.5 was prepared by adding NaOH. It was replaced with a fresh solution every five days to maintain a consistent concentration. To prepare an enzymatic solution, 1 mg of Proteinase K is added to the Tris-HCl buffer solution. The buffer solution was prepared using a 50 mM Tris(hydroxymethyl)aminomethane aqueous solution, and the pH was adjusted to 8.6 by adding an HCl solution. The samples were periodically taken out, carefully washed in distilled water twice, dried at room temperature for 24 hours, and then dried in an oven at 40 °C for 12 hours. The weight loss % was calculated by the following equation:

$$\text{Total weight loss (\%)} = \frac{w - w^t}{w} \times 100 \qquad (1)$$

Where w is the weight before degradation and w^t corresponds to the weight after degradation for a certain time.

3.2.3. Effect of alkaline and enzymatic degradation on the mechanical properties

The weight loss of the PC films after exposure to alkaline and enzymatic conditions was monitored as a function of degradation time. Figures 14 and 15 show the change in the mechanical properties of PCs. After alkaline degradation for 3 months, the LOTTE-PC, D-PC, and SY-PC films did not show any weight loss. As shown in Figure 14, there are no significant changes in weight loss as well as the mechanical properties of LOTTE-PC, D-PC, and SY-PC films. For enzymatic degradation, Proteinase K which is active in PLA was selected. The PC films were exposed to the buffer solution with Proteinase K for 7 days, as shown in Figure 15. The enzymatic degradation was the same as the results of the alkaline hydrolysis. Because all PCs are primarily composed of carbonate groups, which are relatively stable in alkaline and Proteinase K environments, Also, these materials lack hydrolyzable bonds like esters and amides which exist in hydrolyzable polymers. These bondings are more susceptible to cleavage in the presence of water and alkaline and enzymatic conditions, leading to degradation [39]. Therefore, LOTTE-PC, D-PC, and SY-PC were stable for alkaline and Proteinase K.

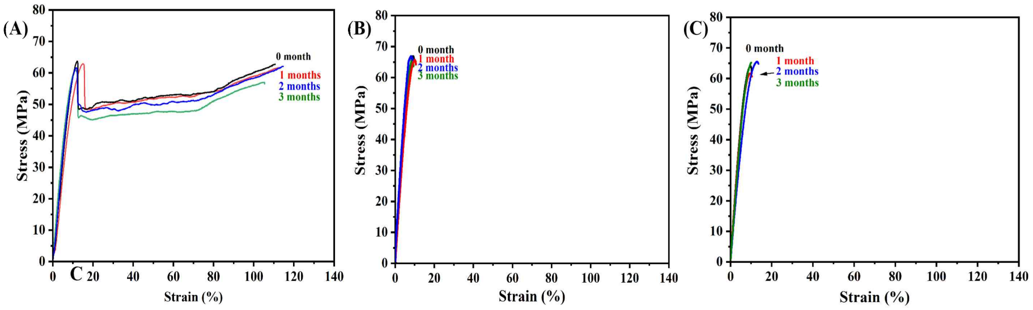


Figure 14. Stress-strain curves of (A) LOTTE-PC, (B) D-PC, and (C) SY-PC after alkaline exposure for 3 months.

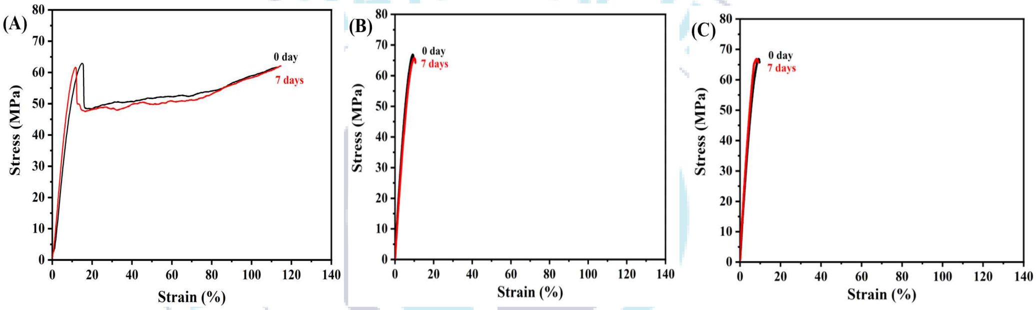


Figure 15. Stress-strain curves of (A) LOTTE-PC, (B) D-PC, and (C) SY-PC after Proteinase K enzymatic exposure for 7 days.

3.2.4. Soil burial test degradation

For the soil burial test, ten dog-bone shaped replicas of each SY-PC film sample with a thickness of 300 - 350 ㎛ were buried within soil-filled glass containers, creating a controlled environment to assess biodegradability. The soil was carefully chosen to be free from contaminants, and the test containers were sealed after filling the floor with water to stimulate natural soil activation. The soil burial test experiments were conducted at 58 ℃. After a desired time, each specimen was washed with distilled water twice, dried at room temperature for 2 days, and then dried in an oven at 40 ℃ for 2 days. The samples were taken periodically and analyzed for weight and mechanical properties.

3.2.4. Effect of soil burial test degradation on the mechanical properties

It was known that the mechanical properties of polymers rapidly decreased when degradation occurred. The previous studies showed that bio-based PCs were very stable to alkaline or Proteinase K. Here, we conducted a soil burial test on SY-PC. Because soil includes many fungi and bacteria, this test involved burying dog-bone shaped samples in commercial soil, maintaining a temperature of 58 °C and a constant moisture of 80 %. We retrieved them from the buried soil as a function of time, examined weight loss, and assessed the impact on their mechanical properties, as shown in Figure 16. After 160 days, the weight reduction of SY-PC was about 0.842 %, but the tensile strength decreased about 77.3 % from 63 MPa to 14.3 MPa, and the elongation decreased about 82.7 % from 8.7 % to 1.5 %. The results indicate that SY-PC was degraded in the soil.

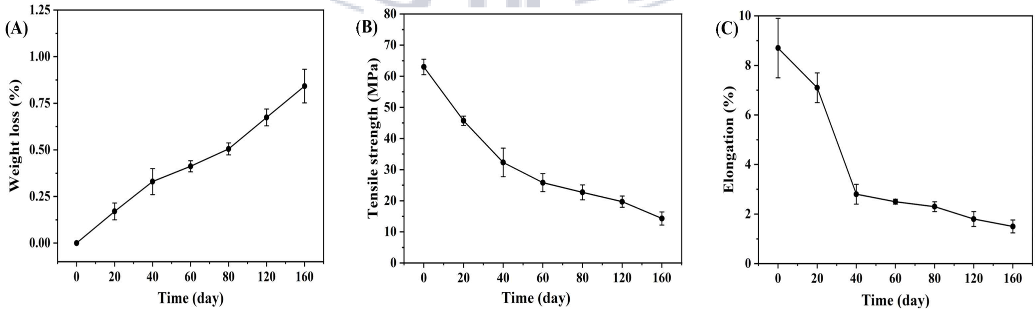


Figure 16. (A) % weight loss, (B) tensile strength, and (C) elongation of SY-PC as a function of degradation time in soil burial test.

3.3. Conclusions

In this study, bio-based PCs synthesized using isosorbide are an environmentally friendly material that suppresses BPA emissions. The mechanical properties of D-PC and SY-PC showed notably higher tensile strength but lower elongation than LOTTE-PC. Thermogravimetric analysis reveals that the decomposition temperature of LOTTE-PC is approximately 100 °C higher than that of both D-PC and SY-PC. Under NaOH (pH 11.5) and Proteinase K enzymatic conditions, LOTTE-PC, D-PC, and SY-PC exhibit resistance to alkaline and Proteinase K. D-PC exhibited remarkable resistance to degradation, with no weight loss or deterioration in mechanical properties observed in the soil. In contrast, after the soil burial test, SY-PC experienced significant degradation, as evidenced by weight loss, decreased tensile strength, and elongation.

Chapter 4. Mechanical and Thermal characteristics of Sustainable PLA/PBS and PLA/PBEAS blends

4.1. Experimental

4.1.1. Materials

PLA (L-lactide/D-lactide: 98.6/1.4) with an average molecular weight of 200,000 was purchased from Nature Works LLC (USA). PBS (Mn: 44,051) and PBEAS (Mn: 45,284) were obtained from Anchor Bioplastics (Korea). Sodium hydroxide was purchased from Icatayama Chemicals (Japan). Tris(hydroxymethyl)amino-methane, Proteinase K, and phosphate buffer were purchased from Sigma-Aldrich (USA). Lipase was purchased from EMD Millipore Corp. (USA). Hydrochloric acid (HCl) solution was purchased from Samchun (Korea).

4.1.2. Preparation of blend films

PLA, PBS, and PBEAS were dried in the vacuum oven at 40 °C to remove moisture before melt processing. First, various weight percentages (100/0, 80/20, 50/50, 20/80, and 0/100) of PLA/PBS and PLA/PBEAS blends were physically mixed. The blends were melted at 170 °C for 7 min in a kneader (PBV-0.1, Irie Shokai Co., Ltd., Japan) with a screw speed of 50 rpm. The films blend were prepared with a compression press (QM900S QMRSYS, Korea) at 170 °C molding temperature under 7 MPa for 3 min press time and then cooled to room temperature. The thickness of the films was maintained at 200 - 250 ㎛.

4.1.3. Measurement

Mechanical properties were measured with a Tinius Olsen (H1KT, USA) equipped with a 100 Kgf load sensor applying a stretching rate of 10 mm/min. A minimum of ten dog-bone shaped replicas of each blend film were cut and used for the tensile testing, and the results were provided as the average value ± standard deviation. The thermal properties before and after degradation of the blend films were measured by differential scanning calorimetry (DSC, 1, Mettler Toledo Inc., Switzerland) up to 200 °C at a heating rate of 10 °C/min and cooling down to 0 °C at a cooling rate of 200 °C/min under a nitrogen atmosphere. The crystallinity Xc was calculated by an equation the following:

$$Xc\ (\%) = [(\triangle Hm \ / \ \triangle Hm^{100} \ \mathrm{X} \ W)] \ \mathrm{X} \ 100 \tag{2}$$

Where ΔHm(J/g) is the melting enthalpy, W is the weight fraction of PLA and PBS, PBEAS in the blends, and $\triangle Hm^{100}$ is the melting enthalpy of the 100 % crystalline PLA ($\triangle Hm^{100}$ = 93.7 J/g), PBS ($\triangle Hm^{100}$ = 110.3 J/g), or PBEAS ($\triangle Hm^{100}$ = 110.5 J/g).

4.2. Results and discussion

4.2.1. Mechanical properties of blend films

We prepared PLA/PBS and PLA/PBEAS blends with various weight percentages by melt blending, and sample identification is listed in Table 7. The tensile stress-stain curves of the prepared samples are characterized. PLA shows a brittle nature with a tensile stress of 53.1 MPa and a tensile strain of 5.8 %. however, PBS and PBEAS show better toughness than PLA with a tensile stress of 26.5 and 28.5 MPa, and the tensile strain can be as high as 20.5 % and 23.6 %, respectively. However, the introduction of PBS and PBEAS will improve the mechanical properties of PLA to some degree. As shown in Figures 17 (A) and (B), when the composition of PBS and PBEAS increases to 80 %, the blends show good elongation properties with tensile strains of 13.4 % and 14.8 %, respectively. However, when the composition of PBS and PBEAS is increased to 20 %, the blend exhibits favorable tensile properties, boasting tensile stresses of 38.5 MPa and 40.3 MPa, respectively.

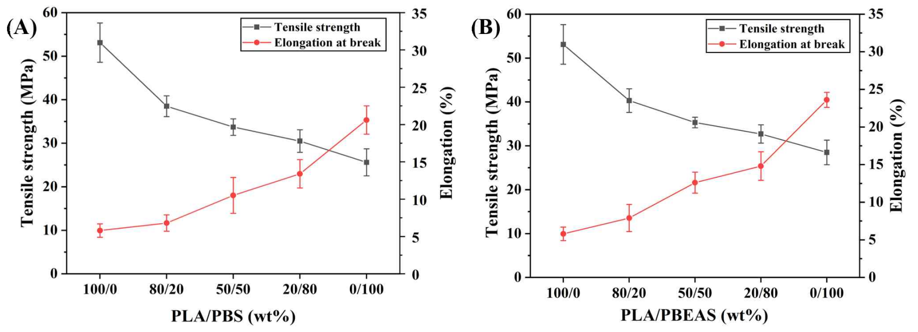


Figure 17. Tensile strength and elongation of the (A) PLA/PBS and (B) PLA/PBEAS blends before degradation.

Table 7. Mechanical properties of the PLA/PBS and PLA/PBEAS blends before degradation

Sample		Tensile strength (MPa)	Elongation at break (%)
PLA		53.1 ± 4.5	5.8 ± 0.9
PLA/PBS (by wt%)	80/20	38.5 ± 1.9	6.8 ± 0.7
	50/50	33.7 ± 2.8	10.8 ± 1.2
	20/80	30.5 ± 2.7	13.4 ± 2.1
PBS		26.5 ± 2.3	20.5 ± 1.9
PLA/PBEAS (by wt%)	80/20	40.3 ± 2.7	7.9 ± 1.8
	50/50	35.3 ± 1.2	12.6 ± 1.4
	20/80	32.7 ± 2.1	14.8 ± 1.9
PBEAS		28.5 ± 2.8	23.6 ± 2.0

4.2.2. Thermal properties of blend films

The thermal stability of PLA/PBS and PLA/PBEAS blends before degradation was measured. The compatibility of the blend and thermal properties, including glass transition temperature (Tg) and melting temperature (Tm), was analyzed by the DSC, and the detailed corresponding thermal properties are summarized in Table 8. The Tm values for PLA, PBS, and PBEAS were confirmed to be 155.3 °C, 114.6 °C, and 111.3 °C, respectively. The compatibility of polymer blends is closely related to the interaction between the amorphous regions of each component. The compatibility of PLA/PBS and PLA/PBEAS blends was confirmed by observing a decrease in the Tg of PLA. The Tg of PLA was measured at 59.3 °C, and approximate similar Tg values were observed in PLA/PBS and PLA/PBEAS blends with (80/20) and (50/50). In all PLA/PBS and PLA/PBEAS blends, two distinct Tm values were identified. Furthermore, the decrease in Tg was most pronounced when the PBS and PBEAS contents were up to 20 wt%. However, as the PBS and PBEAS content increased, this decrease in Tg became less pronounced, and in the case of PLA/PBS (20/80) and PLA/PBEAS (20/80) blends, the Tg could not be confirmed due to the small amount of PLA. Conversely, the relative fraction of crystalline regions kept increasing. Consequently, our findings suggest that the PLA/PBS and PLA/PBEAS blends exhibit partial miscibility, aligning with previous research [40-43].

Table 8. Thermal properties of PLA/PBS and PLA/PBEAS blends before degradation

Sample		Thermal properties	
		Tg (℃)	Tm (℃)
PLA		59.3	155.3
PLA/PBS (by wt%)	80/20	57.1	153.9/114.8
	50/50	56.3	154.2/114.7
	20/80	-	153.2/115
PBS		-	114.6
PLA/PBEAS (by wt%)	80/20	57.5	155.4/111.0
	50/50	56.6	154.7/111.7
	20/80	-	154.8/111.9
PBEAS		-	111.3

4.2.3. Alkaline and enzymatic degradations

To evaluate the weight loss and impact on mechanical and thermal properties of the blends, eight dog-bone shaped replicas of each blend sample with a thickness of 200-250 μm were cut and utilized for degradation studies. Prior to the degradation experiment, each specimen was immersed in an alkaline solution, Proteinase K, and Lipase enzymatic solution for a certain period at room temperature. The alkaline hydrolysis was performed at pH 11 by adding NaOH. It was replaced with a fresh solution every five days to maintain a constant concentration. To prepare an enzymatic degradation solution, 1 mg of Proteinase K is added to the Tris-HCl buffer solution. The buffer solution was prepared using a 50 mM Tris(hydroxymethyl)aminomethane aqueous solution, and the pH was adjusted to 8.6 by adding an HCl solution. In the Lipase enzymatic solution, 3 mg of Lipase is added to the phosphate buffer. The buffer using Lipase was made with phosphate buffer APHA, and the pH was adjusted to 7.2. The samples were periodically taken out, carefully washed with distilled water twice, dried at room temperature for 24 hours, and then dried in an oven at 40 °C for an additional 12 hours. The weight loss % was calculated by the following equation:

$$\text{Total weight loss (\%)} = \frac{w - w^t}{w} \times 100 \tag{3}$$

Where w is the weight before degradation and w^t corresponds to the weight after degradation for time.

4.2.3.1. Wight loss by alkaline degradation

Degradation is a crucial aspect of the application of biodegradable materials. The weight loss after degradation to alkaline conditions of PLA/PBS and PLA/PBEAS blends was monitored as a function of degradation time, and Figure 18 shows the weight loss percentages for these materials. After the hydrolytic degradation for 9 weeks, we observed an increase in weight loss for the PLA/PBS and PLA/PBEAS blends as the degradation time advanced in the hydrolysis environment. In contrast, pure PBS and PBEAS exhibited minimal weight loss during this process. It was known that the slow hydrolysis of PBS, PBEAS, and blends with 80 wt% PBS and PBEAS contents was due to their high crystallinity, which prevented the infiltration of water molecules into the ester bond matrix. The delay in hydrolysis observed in PBS, PBEAS, and blends containing 80 wt% PBS and PBEAS can be attributed to their high crystallinity, which hinders the penetration of water molecules into the ester bond matrix. This delay is thought to be a consequence of the interaction between the blend chains, which, in turn, slows down the hydrolysis of PLA/PBS and PLA/PBEAS blends with ester bonds that have a propensity for fast hydrolysis. On the other hand, the amorphous area in PLA and blend films showed the highest hydrolysis rates because amorphous regions with irregular chain structures show higher water diffusion than crystalline regions. Notably, alkali ions diffused into the amorphous PLA chains of PLA/PBS and PLA/PBEAS blends (80/20 by wt%), leading to an accelerated hydrolysis process and subsequently higher weight loss in the blend films. Furthermore, the presence of PBS and PBEAS increases the specific surface area of PLA and creates a gap between particles, facilitating the diffusion of alkali ions into the blend. This phenomenon contributes to the accelerated degradation observed in PLA/PBS and PLA/PBEAS blends [44,45]. As a result, the incorporation of PBS and PBEAS accelerates the hydrolysis of PLA within specific PLA/PBS and PLA/PBEAS blend ratios, enhancing overall biodegradability.

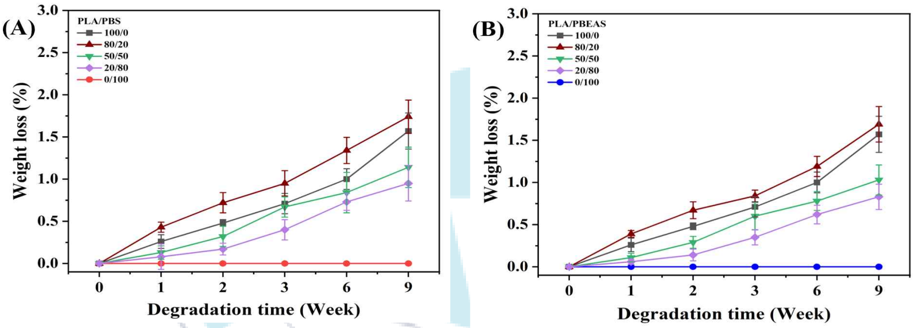


Figure 18. Changes in weight loss of (A) PLA/PBS and (B) PLA/PBEAS blends as a function of degradation times in the presence of an alkaline medium at pH 11.

4.2.3.2. Effect of alkaline degradation on the mechanical properties of blend films

The decrease in mechanical properties is one of the signs that determine the impact of the degradation behavior of biodegradable polymers. Figures 19 and 20 presented the changes in tensile strength and elongation at break % for PLA/PBS and PLA/PBEAS blends, respectively, as they underwent degradation in the alkaline solution (pH 11). Notably, substantial changes in mechanical properties were observed from week 2 to week 6, occurring before any measurable mass losses, as shown in Figure 18. This indicates that in alkaline conditions, mass loss can be detected in all blend samples as early as the first week. The decline in mechanical properties in PLA/PBS and PLA/PBEAS blends, preceding quantifiable mass loss, suggests polymer degradation within the bulk, attributed to chain scissions and reduced molecular weight [46,47] Furthermore, the decrease in tensile strength for PLA/PBS (80/20) and PLA/PBEAS (80/20) blends occurred more rapidly than in pure PLA, consistent with the weight loss data. After 9 weeks, the tensile strength of the PLA/PBS (80/20) and PLA/PBEAS (80/20) blends decreased to 73.2 % and 71.9 %, respectively. In contrast, the mechanical properties of pure PBS and PBEAS remained within an error margin without experiencing a decline. Interestingly, the introduction of PBS and PBEAS into the blend samples appeared to facilitate the degradation of PLA. The ester groups in PLA underwent hydrolysis, causing molecular chain breakage and consequently leading to reduced mechanical properties [46-48].

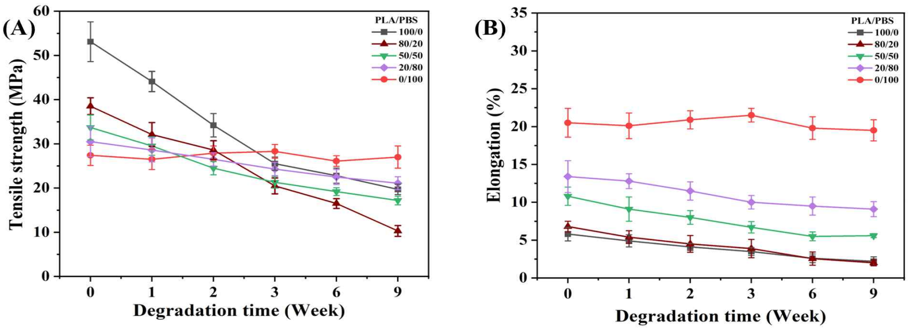


Figure 19. (A) Tensile strength and (B) elongation of PLA/PBS blends with various degradation times in the presence of an alkaline medium at pH 11.

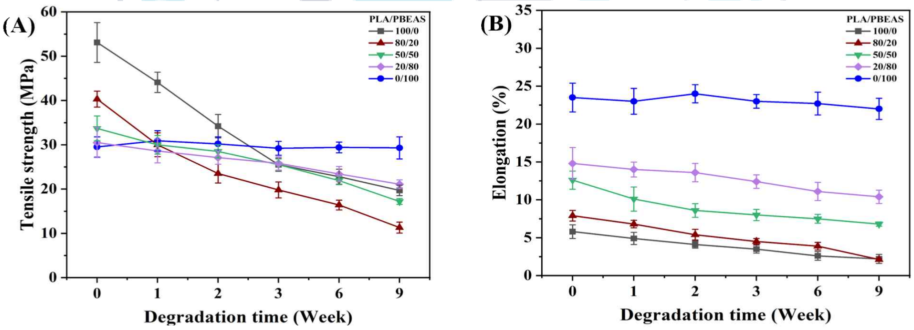


Figure 20. (A) Tensile strength and (B) elongation of PLA/PBEAS blends with various degradation times in the presence of an alkaline medium at pH 11.

4.2.3.3. Effect of alkaline degradation on the thermal properties of blend films

We conducted an additional investigation into the thermal properties of PLA/PBS and PLA/PBEAS blends using DSC following the alkaline degradation process, and the results are presented in Figure 21 and Table 9, both before and after degradation. After 9 weeks of hydrolysis, we observed slight reductions in Tg, Tm, and crystallinity for the PLA/PBS (80/20) and PLA/PBEAS (80/20) blends, indicative of a faster degradation rate compared to pure PLA. PLA also showed a decrease in Tg, Tm, and crystallinity; the Tg and Tm decreased by 0.5 °C to 58.8 °C and by 0.6 °C to 154.7 °C, respectively. In the case of the PLA/PBS (80/20) blends, the PBS component melted at a lower temperature than the PLA component. The Tg of the PLA region decreased by 0.8 °C to 56.3 °C, and the Tm of the PLA region decreased by 0.9 °C to 153.0 °C. Interestingly, the presence of PBS had a minimal impact on the Tm of the blend system. Similarly, in the case of PLA/PBEAS (80/20), the PBEAS component of the blends first melted at a lower temperature than the PLA component. The Tg of the PLA region decreased by 1.5 °C to 56 °C, and the Tm of the PLA region decreased by 1.9 °C to 153.5 °C. The crystallinity was calculated using Equation (2). The analysis of crystallinity in the PBS and PBEAS regions was difficult because it overlapped with the Tc area of the PLA. However, the decrease in crystallinity of the PLA region can be attributed to the small size of hydroxide ions, allowing them to simultaneously impact amorphous and crystalline regions at the same time. Additionally, the decreased crystallinity may result from damage to the crystalline structure and the simultaneous degradation of crystalline and non-crystalline regions of polyesters [49]. Another important reason may be that the decrease in melting enthalpy can occur due to the surface structural change of the crystalline regions during hydrolytic degradation [50].

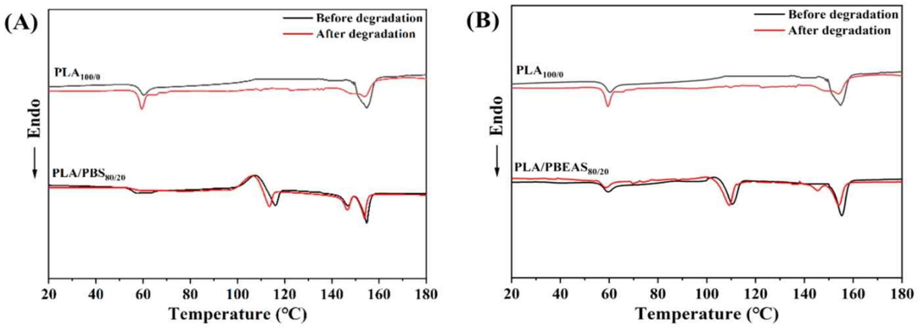


Figure 21. DSC curves of the (A) PLA and PLA/PBS (80/20) blends and (B) PLA and PLA/PBEAS (80/20) blends before and after degradation in the presence of an alkaline medium.

Table 9. Thermal properties of PLA, PLA/PBS (80/20) blends, and PLA/PBEAS (80/20) blends before and after degradation in the presence of an alkaline medium

Sample	Time (Week)	Thermal properties			
		Tg (℃)	Tm (℃)	△Hm (J/g)	Xc (%)
PLA	0	59.3	155.3	37.5	40
PLA	9	58.8	154.7	33.4	35.6
PLA/PBS (80/20)	0	57.1/-	153.9/114.8	27.3/-	36.4/-
PLA/PBS (80/20)	9	56.3/-	153/114.6	21.6/-	28.8/-
PLA/PBEAS (80/20)	0	57.5/-	155.4/111	26.8/-	35.7/-
PLA/PBEAS (80/20)	9	56/-	153.5/109.8	22/-	29.7/-

4.2.3.4. Weight loss by enzymatic degradation

Enzymatic degradation of biodegradable polymers involves the breakdown of polymer chains catalyzed by specific enzymes present in biological systems. These enzymes target the polymer's chemical bonds, initiating the degradation process. In this process, enzymes act as catalysts, accelerating the hydrolysis of ester, amide, or other susceptible bonds within the polymer structure. For instance, Lipase catalyzes the breakdown of ester linkages in polyesters, while proteases target peptide bonds in proteins or peptides.

Proteinase K and Lipase enzymatic were used to investigate the degradation behavior of PLA/PBS and PLA/PBEAS blends under enzymatic conditions, and the weight loss after degradation was monitored as a function of degradation time. Figures 22 and 23 show the weight loss ratio of PLA/PBS and PLA/PBEAS blends after Proteinase K and Lipase enzymatic degradation, respectively. After the Proteinase K enzymatic degradation for 24 hours, it was observed that the weight loss of PLA/PBS and PLA/PBEAS blends increased as the degradation time progressed. Conversely, PBS and PBEAS did not show any weight loss during degradation, confirming that the Proteinase K enzymatic mainly degrades only PLA in the blend. After the Lipase enzymatic degradation for 3 weeks, an increase in weight loss in PBS and PBEAS was observed as the degradation time progressed [51]. In contrast, it was confirmed that since PLA did not show any weight loss during degradation time, the Lipase enzymatic mainly degraded

PBS and PBEAS in the blends. Enzymatic degradation, like alkali degradation, the amorphous region showed a higher degradation rate than the crystalline region in blend films. Proteinase K enzymatic ions diffused into the amorphous PLA chains of the blends (80/20 wt%). Lipase enzymatic ions diffused into the amorphous PBS and PBEAS chains of the blends (20/80 wt%). This enzymatic degradation process is accelerated and results in higher weight loss in the blended films. Additionally, with a certain content of polymers, it increases the specific surface area of the blends and creates gaps between particles to promote the diffusion of enzyme particles into the blends. This phenomenon contributes to the accelerated degradation observed in PLA/PBS and PLA/PBEAS blends [44,45]. As a result, in the case of Proteinase K enzymatic degradation, the addition of PBS and PBEAS in the PLA/PBS and PLA/PBEAS blends accelerates the enzymatic degradation of PLA. Lipase enzymatic degradation accelerates the enzymatic degradation of PBS and PBEAS by adding PLA within the PLA/PBS and PLA/PBEAS blend ratios, enhancing overall biodegradability.

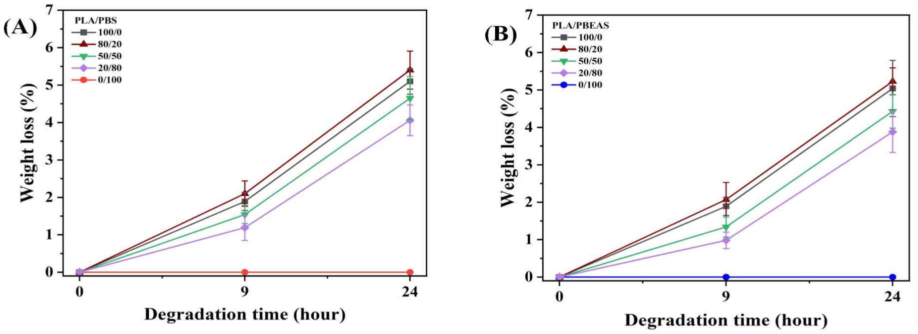


Figure 22. Changes in weight loss of (A) PLA/PBS and (B) PLA/PBEAS blends as a function of degradation times in the Tris-buffer solution containing 1 mg of Proteinase K.

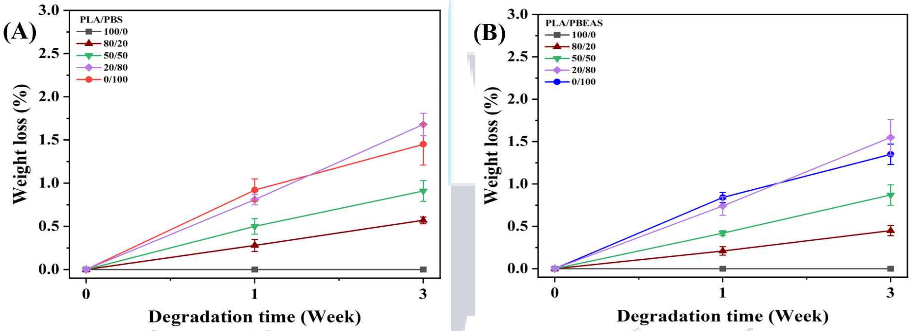


Figure 23. Changes in weight loss of (A) PLA/PBS and (B) PLA/PBEAS blends as a function of degradation times in the Phosphate buffer solution containing 3 mg of Lipase.

4.2.3.5. Effect of enzymatic degradation on the mechanical properties of blend films

For further investigation of the PLA/PBS and PLA/PBEAS blends after enzymatic degradation, we conducted tensile tests by UTM. Figures 24 and 25 depict the alterations in tensile strength and elongation at break % concerning the degradation in Proteinase K enzymatic conditions for PLA/PBS and PLA/PBEAS blends, respectively. Figures 26 and 27 illustrate the degradation in Lipase enzymatic conditions for the same. The decrease in mechanical properties can be attributed to chain scission and a decrease in molecular weight. In the case of Proteinase K enzymatic degradation, the PLA/PBS (80/20) and PLA/PBEAS (80/20) blends exhibited a faster decrease in tensile strength under the influence of Proteinase K enzymatic compared to pure PLA, which was consistent with the data on weight loss. [44,45]. After 24 hours, the tensile strength of PLA/PBS (80/20) and PLA/PBEAS (80/20) blends decreased to 83.8 % and 80.0 %, respectively. In contrast, pure PBS and PBEAS retained their mechanical properties without any significant decrease within the margin of error. However, when PBS and PBEAS were introduced into the blended samples, PLA degradation was accelerated, akin to the effects of alkali degradation. Proteinase K enzymatic shows a decrease in molecular weight and mechanical properties by degrading PLA through ester bond cutting. In the case of Lipase enzymatic degradation, the PLA/PBS (20/80) and PLA/PBEAS (20/80) blends exhibited a faster decrease in tensile strength under the influence of Lipase enzymatic compared to pure PBS and PBEAS, which was consistent with the data on weight loss. After 3 weeks, the tensile strength of the PLA/PBS (20/80) and PLA/PBEAS (20/80) blends decreased to 70.1 % and 68.9 %, respectively. On the other hand, pure PLA maintained its mechanical properties without any significant decrease within the margin of error. The introduction of PLA into the blended sample was found to accelerate the degradation of PBS and PBEAS. Lipase is degraded through the hydrolases enzymatic process that occurs in the ester bonding of PBS and PBEAS and thus shows a decrease in molecular weight and mechanical properties. Interestingly, the introduction of certain polymer content to the blend samples has been shown to facilitate degradation, with molecular chain scission through enzymatic degradation resulting in decreased mechanical properties [46-48].

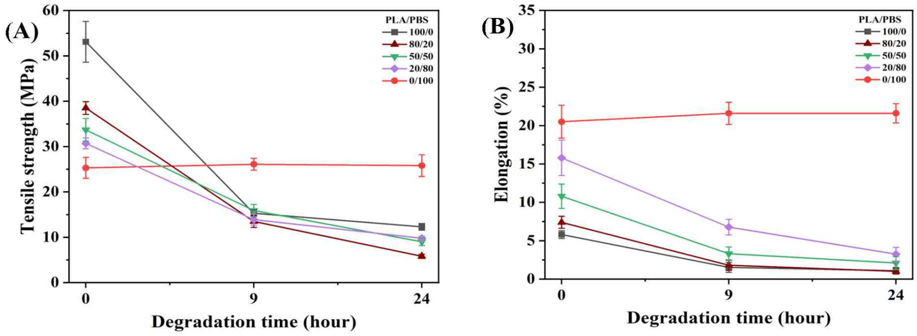


Figure 24. (A) Tensile strength and (B) elongation of PLA/PBS blends with various degradation times in the Tris-buffer solution containing 1 mg of Proteinase K.

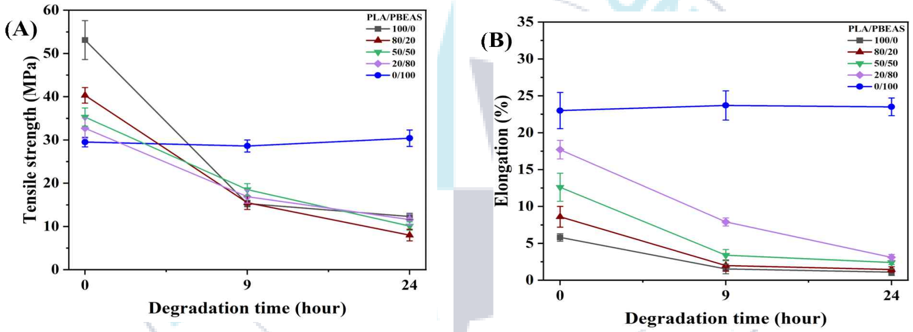


Figure 25. (A) Tensile strength and (B) elongation of PLA/PBEAS blends with various degradation times in the Tris-buffer solution containing 1 mg of Proteinase K.

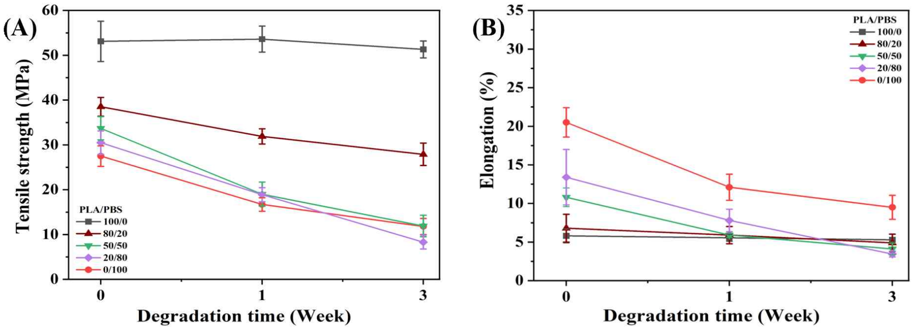


Figure 26. (A) Tensile strength and (B) elongation of PLA/PBS blends with various degradation times in the Phosphate buffer solution containing 3 mg of Lipase.

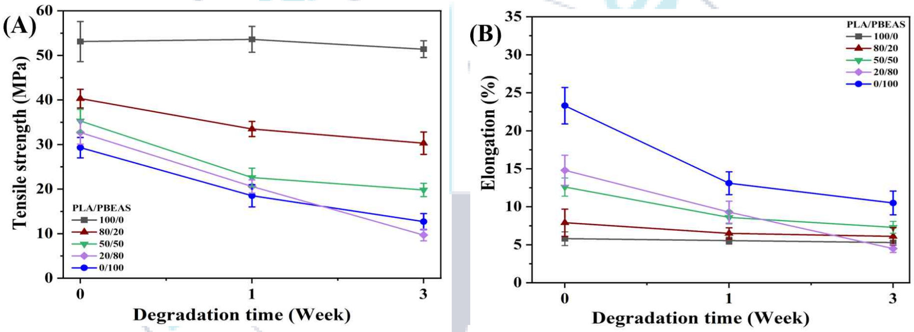


Figure 27. (A) Tensile strength and (B) elongation of PLA/PBEAS blends with various degradation times in the Phosphate buffer solution containing 3 mg of Lipase.

4.2.3.6. Effect of enzymatic degradation on the thermal properties of blend films

Besides the mechanical properties, the thermal properties of the blends after enzymatic degradation are investigated. The primary method of polymer degradation is the scission of either the main or side chains. As a result of this process, the thermal properties of polymers have significantly decreased. After enzymatic degradation, the blended polymers showed faster degradation behavior than the pure polymers. In Figure 28 and Table 10, the Tg and Tm of pure PLA in 24 hours of Proteinase K enzymatic degradation decreased from 1.7 °C to 57.6 °C and from 1.8 °C to 153.5 °C, respectively. In the case of the PLA/PBS (80/20) blends, the Tg of the PLA area decreased by 1.9 °C to 55.2 °C, and the Tm decreased by 2.1 °C to 151.8 °C. Similarly, for PLA/PBEAS (80/20), the Tg of the PLA region decreased by 1.8 °C to 55.7 °C, and the Tm decreased by 1.9 °C to 153.5 °C. In Figure 29 and Table 11, Tm of pure PBS decreased by 0.7 °C to 113.9 °C during 3 weeks of Lipase enzymatic degradation, and Tm of pure PBEAS decreased by 0.5 °C to 110.8 °C, respectively. For the PLA/PBS (20/80) blends, the Tm of the PBS region decreased by 1.2 °C to 113.8 °C. For the PLA/PBEAS (20/80) blends, the Tm in the PBEAS region decreased by 1.2 °C to 110.7 °C. The crystallinity was calculated using Equation (2), and crystallinity increased after enzymatic degradation. Because enzymes are large, they have poor accessibility to crystalline parts and preferentially degrade the amorphous parts of the polymer [52]. As a result of selective enzymatic attacks, crystallinity increased after degradation.

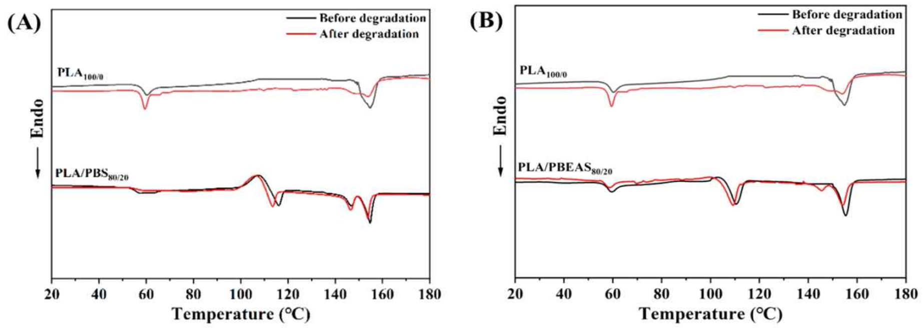


Figure 28. DSC curves of the (A) PLA and PLA/PBS (80/20) blends and (B) PLA and PLA/PBEAS (80/20) blends before and after degradation in the presence of Proteinase K.

Table 10. Thermal properties of PLA, PLA/PBS (80/20) blends, and PLA/PBEAS (80/20) blends before and after degradation in the presence of Proteinase K

Sample	Time (hour)	Thermal properties			
		Tg (℃)	Tm (℃)	△Hm (J/g)	Xc (%)
PLA	0	59.3	155.3	37.5	40
PLA	24	57.6	153.5	41	43.7
PLA/PBS (80/20)	0	57.1/-	153.9/114.8	27.3/-	36.4/-
PLA/PBS (80/20)	24	55.2/-	151.8/114.5	32.6/-	42.1/-
PLA/PBEAS (80/20)	0	57.5/-	155.4/111	26.8/-	35.7/-
PLA/PBEAS (80/20)	24	55.7/-	153.5/111.1	31.6/-	42.1/-

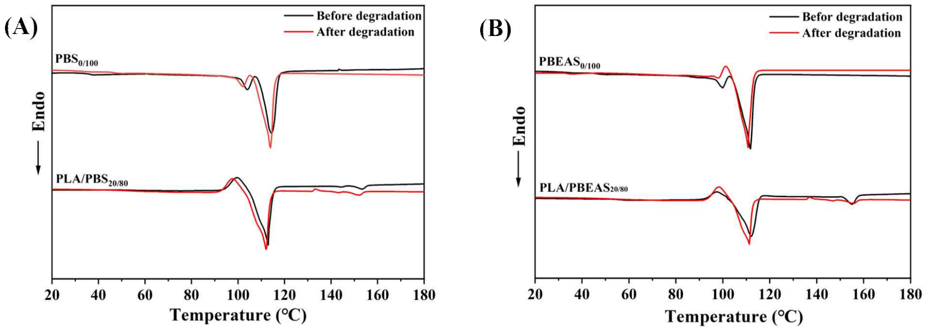


Figure 29. DSC curves of the (A) PBS and PLA/PBS (20/80) blends and (B) PBEAS and PLA/PBEAS (20/80) blends before and after degradation in the presence of Lipase.

Table 11. Thermal properties of PBS, PBEAS, PLA/PBS (20/80) blends, and PLA/PBEAS (20/80) blends before and after degradation in the presence of Lipase

Sample	Time (Week)	Thermal properties			
		Tg (℃)	Tm (℃)	△Hm (J/g)	Xc (%)
PBS	0	-	114.6	58.9	53.4
PBS	3	-	113.9	63.3	57.4
PBEAS	0	-	111.3	62.3	56.4
PBEAS	3	-	110.8	66.3	60.1
PLA/PBS (20/80)	0	-	153.2/115	2.69/-	14.3/-
PLA/PBS (20/80)	3	-	153.2/113.8	2.7/-	14.4/-
PLA/PBEAS (20/80)	0	-	154.8/111.9	2.4/-	12.8/-
PLA/PBEAS (20/80)	3	-	154.7/110.7	2.35/-	12.5/-

4.3. Conclusions

In this study, PLA/PBS and PLA/PBEAS blends were fabricated using the melt blending technique. To understand the degradation behavior of these blends, dog-bone specimens were immersed in the presence of NaOH solutions and enzymatic solutions for specific durations. DSC investigated thermal properties before and after the degradation of the blends. The alkaline degradation of samples leads to a decrease in their crystallinity, whereas the enzymatic degradations show increased crystallinity due to the different sizes of degradation mediums. In particular, the mechanical properties of the degraded samples decreased to approximately 70 % of virgin ones when their weight loss was about 1.5 wt%. From the results, the early degradation behavior of commercial products is closely tied to their lifespan and mechanical properties, and the blend method offers the potential to control an initial degradability behavior that is deeply related to mechanical properties during their commercial use.

References

[1] T. Hottle, M. Bilec, and A. Landis, *Polym. Degrad. Stab.*, **98(9)**, 1898 (2013).

[2] R. Babu, K. Connor, and R. Seeram, *Prog. Mater. Sci.*, **2**, 1 (2013).

[3] A. Z. Naser, I. Deiab, and B. M. Darras, *RSC Adv.*, **11**, 17151 (2021).

[4] T. Iwata, *Angew. Chem. Int. Ed.*, **54(11)**, 3210 (2015).

[5] Y. Zhong, P. Godwin, Y. Jin, and H. Xiao, *Adv. Ind. Eng. Polym. Res.*, **3(1)**, 27 (2020).

[6] Y. Tokiwa, B. P. Calabia, C. U. Ugwu, and S. Aiba, *Int. J. Mol. Sci.*, **10(9)**, 3722 (2009).

[7] V. Gavande, D. Im, Y. Jin, K. T Lim, and W. K. Lee, *Mol. Cryst. Liq. Cryst.*, **706(1)**, 55-61 (2020).

[8] R. A. Gross and B. Kalra, *Science*, **297(5582)**, 803 (2002).

[9] W. K. Lee and J. A. Gardella, *Langmuir*, **16(7)**, 3401 (2000).

[10] Y. Hyun, S. Park, H. Kwak, and H. Jin, *Polymer(Korea)*, **45(3)**, 398 (2021).

[11] X. Hu, T. Su, P. Li, and Z. Wang, *Polym. Bull.*, **75**, 533 (2017).

[12] J. Park and S. Im, *J. Appl. Polym. Sci.*, **86(3)**, 647 (2002).

[13] K. Shi, Z. Bai, T. Su, and Z. Wang, *Int. J. Biol. Macromol.*, **126**, 436 (2019).

[14] D. Im, S. Lee, V. Gavande, H. Lee, C. H. Lee, and W. K. Lee, *Mol. Cryst. Liq. Cryst.*, **706(1)**, 108-115 (2020).

[15] Y. Kwon, V. Gavande, S. Kim, D. Im, and W. K. Lee, *Mol. Cryst.*

Liq. Cryst., 764(1), 81-89 (2023).

[16] D. G. Legrand, and J. T. Bendler, Handbook of polycarbonate science and technology. CRC Press (1999).

[17] M. Zaborowska, J. Wyszkowska, A. Borowik, and J. Kucharski, *Int. J. Mol. Sci.*, 22(23), 12753 (2021).

[18] S. Park, J. Lee, H. Lee, J. Park, N. Lee, Y. Son, and S. Park, *Addit. Manuf.*, 31, 100974 (2020).

[19] M. J. L. Tschan, E. Brule, P. Haquette, and C. M. Thomas, *Polym Chem.*, 3(4), 836-851 (2012).

[20] T. Gurunathan, S. Mohanty, and S. Nayak, *Compos. Part A: Appl Sci. Manuf.*, 77, 1-25 (2015).

[21] Y. Tsang, V. Kumar, P. Samadar, Y. Yang, J. Lee, Y. Ok, H. Song, K. H. Kim, E. Kwon, and Y. Jeng, *Environ. Int.*, 127, 625-644 (2019).

[22] SAMYANG Advanced Polymeric Materials R & D Center.

[23] R. Yoganathan, R. Mammucari, and N. Foster, *Mater.*, 3(5), 3188-3203 (2010).

[24] S. Yum, H. Kim, and Y. Seo, *Polym.*, 179, 121685 (2019).

[25] S. Cui, J. Borgemenke, Z. Liu, and Y. LI, *J. CO2 Util.*, 34, 40-52 (2019).

[26] V. Gavande, G. Kim, B. Kim, Y. Jin, S. H. Jang, J. H. Chun, and W. K. Lee, *Mol. Cryst. Liq. Cryst.*, 742(1), 133-138 (2022).

[27] X. Li, Y. Lin, M. Liu, L. Meng, and C. Li, *J. Appl. Polym. Sci.*, 140(7), e53477 (2023).

[28] N. Zaaba, M. Jaafar, *Polym Eng Sci.*, 60(9), 2061-2075 (2020).

[29] J. Sun, J. Shen, S. Chen, M. A. Cooper, H. Fu, D. Wu, and Z. Yang, *Polym.*, **10(5)**, 505 (2018).

[30] D. Im, V. Gavande, H. Y. Lee, and W. K. Lee, *Materials*, **16(14)**, 5087 (2023).

[31] N. Sharmin, Nusrat, C. Rudd. *J. Mater. Sci.*, **52**, 8733-8760 (2017).

[32] K. M. Nampoothiri, N. R. Nair, and R. P. John, *Bioresour. Technol.*, **101(22)**, 8493 (2010).

[33] W. K. Lee, J. H. Ryon, and C. S. Ha, *Polym. Sci. Technol.*, **13(1)**, 65-74 (2002).

[34] S. Jadoun, D. S. Rathore, U. Riaz, and N. P. S. Chauhan, *Eur. Polym. J.,* **115**, 110561 (2021).

[35] J. Park, M. Koo, S. Cho, and M. Lyu, *Macromol. Res.*, **25**, 1135-1144 (2017).

[36] B. Lee and J. Ryu, *Trans. KSAE,* **11**, 64 (2003).

[37] C. Lee, H. Takagi, H. Okamoto, and M. Kato, *Polym. J.*, **47**, 639–643 (2015).

[38] L. Feng, W. Zhu, C. Li, G. Guan, D. Zhang, Y. Xiao, and L. Zheng, *Polym. Chem.*, **6(4)**, 633-642 (2015).

[39] G. Kim, V. Gavande, V. Shaikh, and W. K. Lee, *Molecules*, **28(12)**, 4810 (2023).

[40] D. Im, V. Gavande, H. Lee, T. Iwata, and W. K. Lee, *Polym. Degrad. Stab.*, **186**, 10957 (2021).

[41] Y. Deng and N. L. Thomas, *Eur. Polym. J.*, **71**, 534 (2015).

[42] R. Somsunan and N. Mainoiy, *J. Therm. Anal. Calorim.*, **139(3)**, 1941 (2020).

[43] T. Messin, S. Marais, N. Follain, A. Guinault, V. Gaucher, N. Delpouve, and C. Sollogoub, *J. Membr. Sci.*, **598**, 117777 (2020).

[44] Y. Wang, Y. Xiao, J. Duan, J. Yang, and C. Zhang, *Polym. Bull.*, **73**, 1067 (2016).

[45] S. Su, R. Kopitzky, S. Tolga, and S. Kabasci, *Polym.*, **11(7)**, 1193 (2019).

[46] J. Jung, M. Ree, and H. Kim, *Catal. Today*, **115(1)**, 283 (2006).

[47] Y. Phua, N. Lau, K. Sudesh, and W. Chow, *Polym. Degrad. Stab.*, **97(8)**, 1345 (2012).

[48] Z. Huang, L. Qian, Q. Yin, N. Yu, T. Liu, and D. Tian, *Polym. Test*, **66**, 319 (2018).

[49] Z. Bai, Y. Liu, T. Su, and Z. Wang, *Polym.*, **10**, 90 (2018).

[50] H. Tsuji, *Macromol. Biosci.*, **5(7)**, 569 (2005).

[51] D. Im, V. Gavande, E. Park, D. Kim, and W. K. Lee, *Mol. Cryst. Liq. Cryst.*, **758(1)**, 64-70 (2023).

[52] R. Wei, D. Breite, C. Song, D. Grasing, T. Ploss, P. Hille, R. Schwerdtfeger, J. Matysik, A. Schulze, and W. Zimmermann, *Adv. Sci.*, **6(14)**, 1900491 (2019).