

The effect of epoxidized natural rubber on the structure and properties of
Stereocomplex polylactide

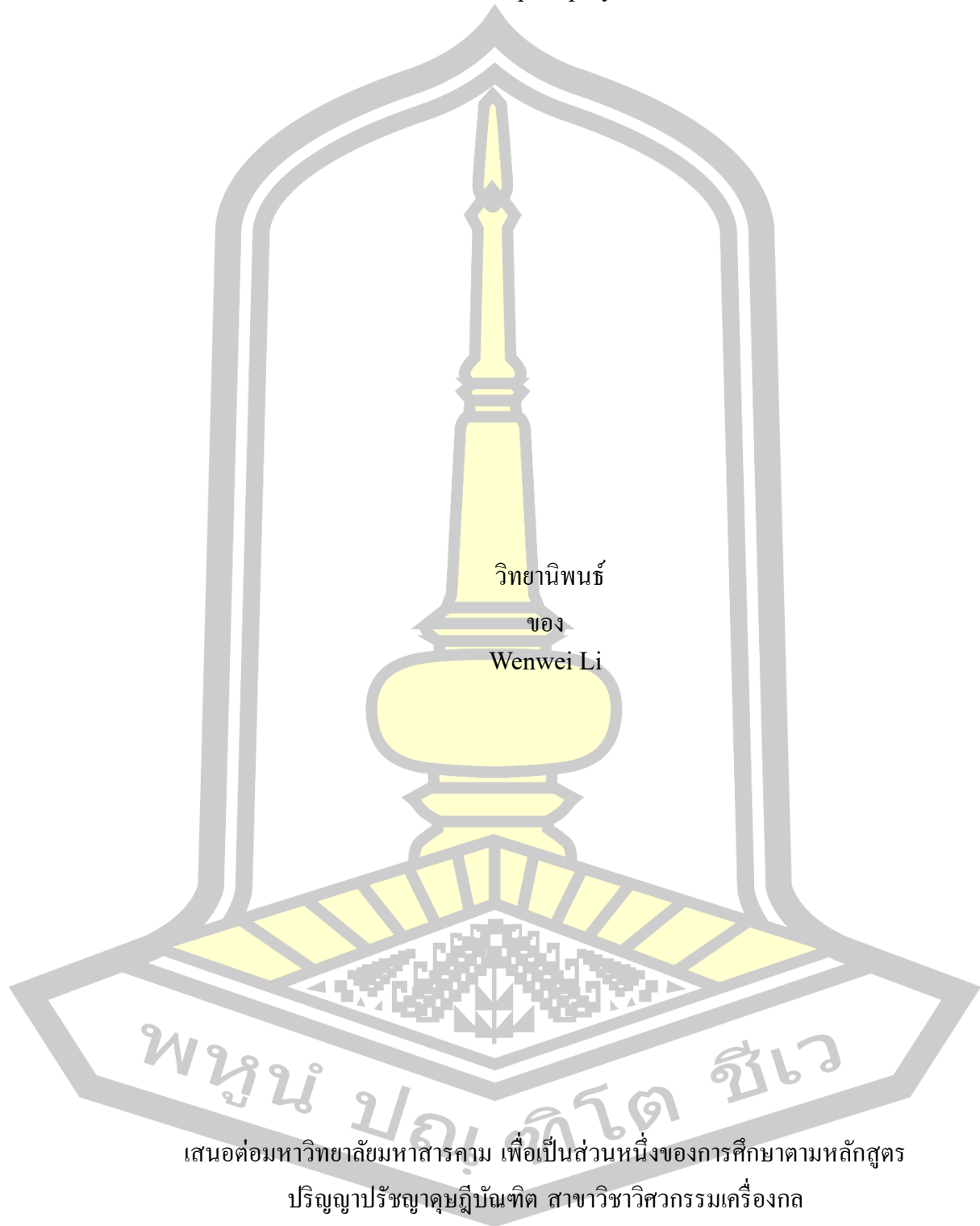
Wenwei Li

A Thesis Submitted in Partial Fulfillment of Requirements for
degree of Doctor of Philosophy in Mechanical Engineering

September 2025

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September 2025

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Doctor of Philosophy Mechanical Engineering at Mahasarakham University

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DEGREE	Doctor of Philosophy	MAJOR	Mechanical Engineering
UNIVERSITY	Maharakham University	YEAR	2025

ABSTRACT

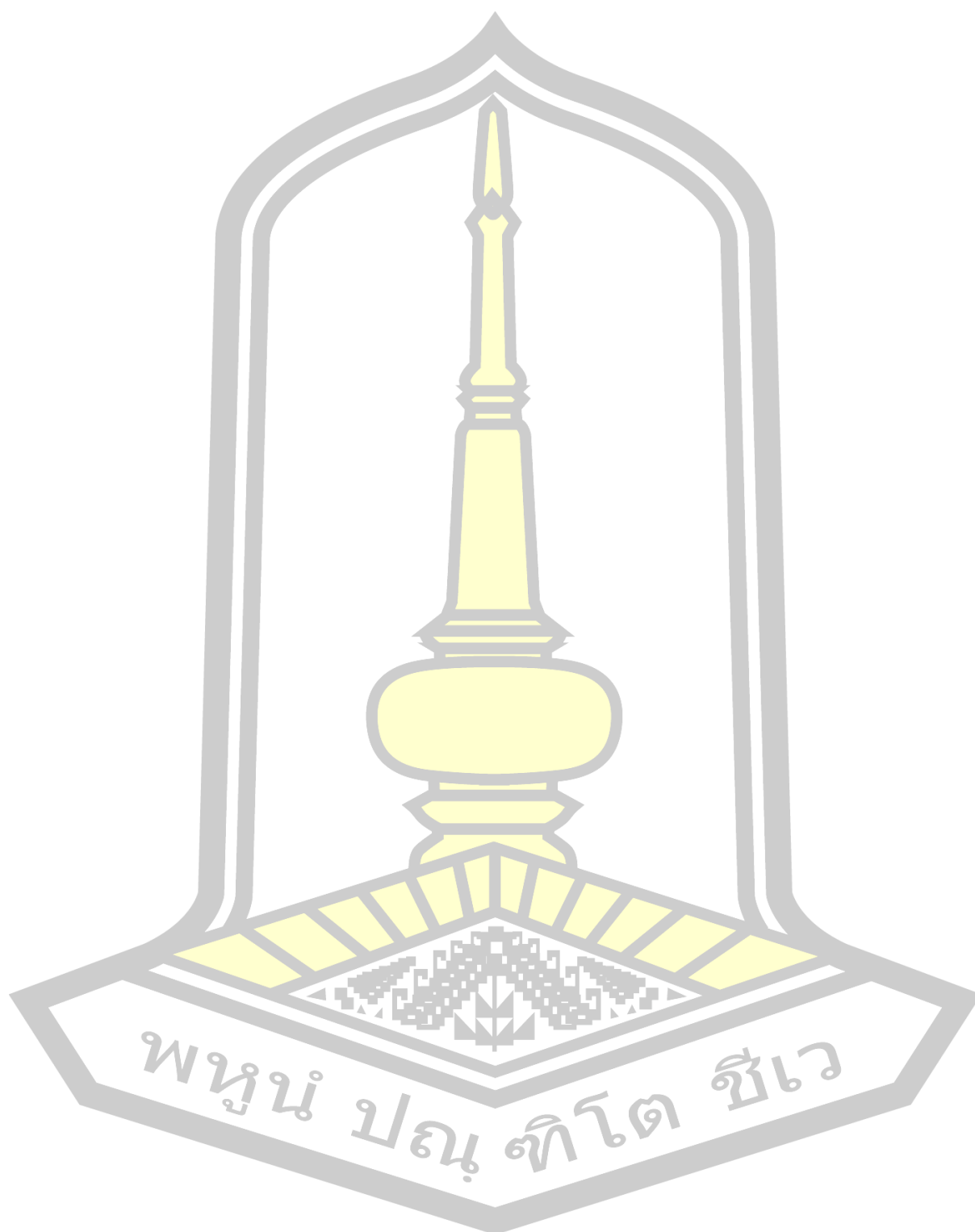
Polylactic acid (PLA), as a sustainable polymer known for its biodegradability and biocompatibility, suffers from a slow crystallization rate that limits its processing and application potential. Blending poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) leads to the formation of stereocomplex crystals (SC-PLA), which enhances heat resistance, crystallization rate, and mechanical strength. This study systematically investigates the effects of epoxidized natural rubber (ENR) and natural rubber (NR) on the crystallization behavior, thermal stability, and rheological properties of PLLA/PDLA blends, aiming to expand the functional versatility of PLA-based materials.

Experimental results demonstrate that ENR significantly promotes the formation of stereocomplex crystals. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses reveal that distinct SC crystallization occurs when the ENR content reaches 10 wt% or higher, while NR shows negligible impact. Polarized optical microscopy (POM) further confirms that ENR accelerates crystal growth and raises the onset crystallization temperature. Rheological tests indicate that the addition of 5 wt% ENR facilitates the formation of a stereocomplex crystal network, with higher ENR content increasing the blend's viscosity, elasticity, and viscoelasticity. Water contact angle measurements suggest that around 10 wt% ENR provides the optimal balance between polarity enhancement and interfacial compatibility.

Non-isothermal crystallization kinetics and activation energy analyses show that ENR reduces the energy barrier for SC formation, thereby promoting crystallization. However, thermogravimetric analysis (TGA) results show a decrease in thermal stability upon ENR incorporation—for instance, the T10% of the sample with 20 wt% ENR is about 21°C lower than that of the ENR-free blend. These findings establish ENR as an effective compatibilizer and crystallization accelerator for PLLA/PDLA blends, offering both theoretical insights and practical guidance for the development of high-performance PLA materials with improved processability and functionality.

Keyword : Poly(D-lactide), Poly(L-lactide), Epoxidized natural rubber, Thermal stability, Rheological properties, crystallization kinetics, non-isothermal

crystallization



ACKNOWLEDGEMENTS

As I come to the end of my doctoral journey at Mahasarakham University, Thailand, I would like to express my deepest gratitude to all those who have supported and accompanied me throughout this period of study and research in Mechanical Engineering.

First and foremost, I am sincerely thankful to my supervisor for the invaluable guidance, encouragement, and inspiration offered during my research on polylactic acid modification. From the formulation of research ideas to the refinement of experimental methods and the preparation of academic publications, my supervisor's insightful advice has been indispensable. Beyond academics, I am especially grateful for the kind support in daily life—for generously purchasing and lending me a motorcycle, which greatly facilitated my study and living in Thailand. This gesture of care and generosity will always be remembered.

At the same time, I would like to express my gratitude to Jun Shen, my colleague in the laboratory, as well as my senior and junior sisters who taught me experimental techniques in the early stages of my research. Their assistance and support have enabled me to grow continuously in my research and successfully publish three SCI papers. These achievements are not only the accumulation of academic research but also the crystallization of collective wisdom and collaboration.

Finally, I would like to extend my heartfelt thanks to my family. Your understanding, support, and encouragement have enabled me to persevere and complete my studies with unwavering determination.

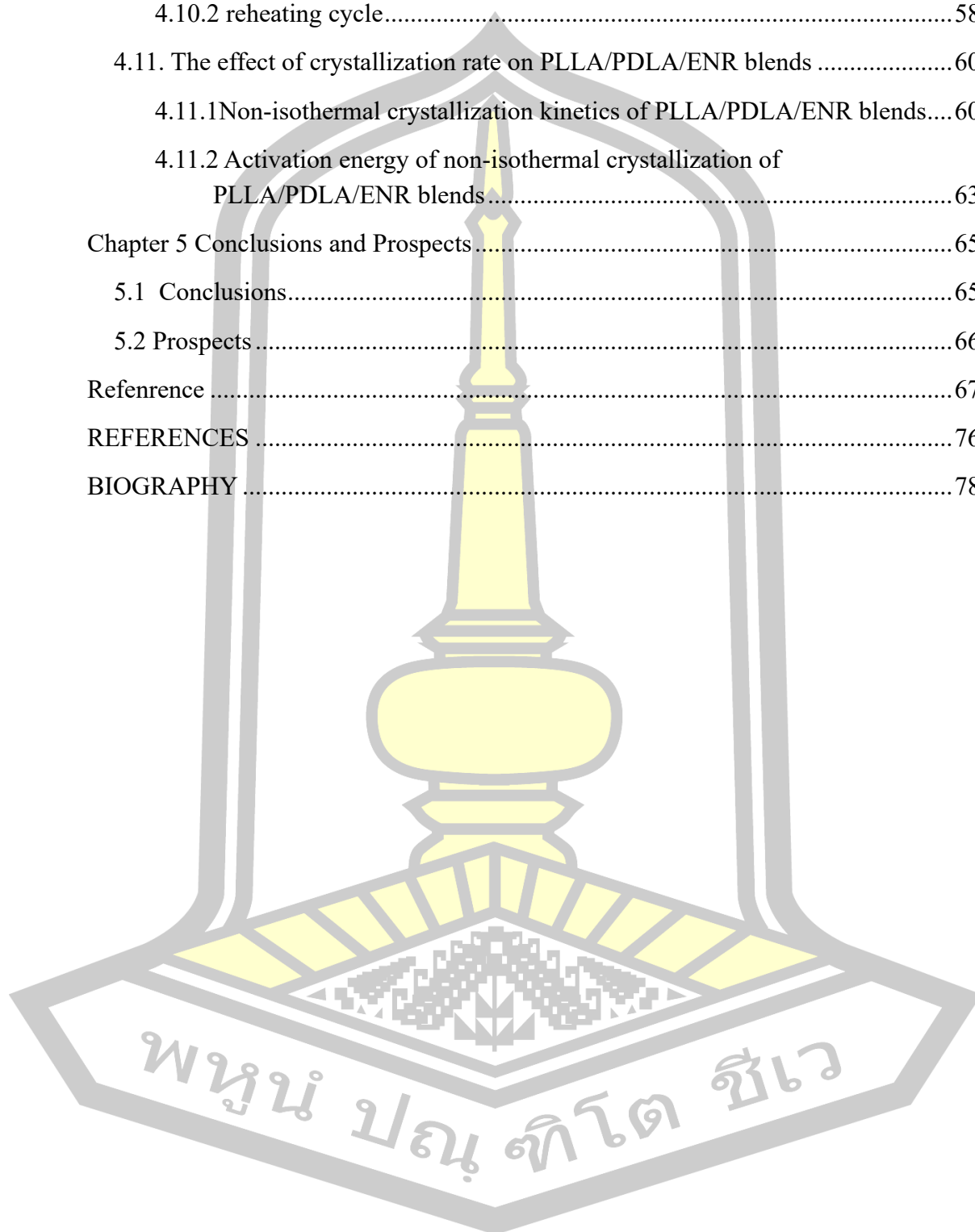
Wenwei Li

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Chapter 1 Introduction

1.1 Research background

After a long period of continuous innovation in industry and academia, plastics achieved large-scale production after the Second World War. Although plastics are simple polymers made up of small molecules repeatedly linked together, they are used in a wide range of applications due to their resistance to corrosion, transparency, light weight and strength. From food packaging to space exploration, plastics are used in almost all industrial sectors[1]. Household names in the plastics industry include polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC).

Despite the fact that plastic products bring great convenience to our lives, 90% of plastic products are used only once and then discarded, thus causing serious environmental pollution. Since the plastic revolution, 8.3 billion tons of plastic waste have been generated worldwide[2]. About 79 % of this is landfilled, resulting in up to 2.4 million tons of plastic waste passing through rivers and into the oceans each year[3]. One of the biggest advantages of plastic is its durability, and its robustness also means that plastic can exist in our environment for hundreds of years. Even when degraded, it never really goes away, but exists in the form of small pieces that are invisible to the naked eye (microplastics), which impede the growth of marine life and spread up the food chain. Therefore, in addition to solving the existing plastic waste problem, we need a new plastic future[4].

Reduce, reuse and recycle has been recognized as a universal solution to the growing problem of plastic waste. The dream is to create a circular plastics economy, where products are 100% recyclable, used for as long as possible, and with as little waste as possible[5]. So far, this dream has not been realized, but with more and more new initiatives, combined with support from governments and manufacturers, things are changing step by step. Currently, despite advances in recycling at the molecular level, progress is still slow[6, 7], and recycling is costly due to the dependence on human behavior and the poor thermal and mechanical properties of the materials

obtained from recycling. Furthermore, recycling will not curb our dependence on plastics, and if we want to maintain our current lifestyles, changes in the manufacture of plastics go hand-in-hand with effective recycling as the best option.

Recent successes in reducing plastic bag (PE) and beverage bottle (PET) waste in Europe have shown that lifestyles can be adapted, but plastic is so deeply ingrained in modern society that a plastic-free future seems impossible. A complete change in human behavior is difficult to achieve, as only 9% of plastic waste is recyclable. Therefore, in addition to the three solutions to the plastic waste problem of reducing use, reusing and recycling, a fundamental change is needed to make a significant impact on the plastic waste that seeps into the environment. In the future, finding new biodegradable polymers to replace traditional plastics with new plastics could be the answer.

In order to solve the environmental and energy problems, the development of biodegradable bio-based composites is one of the measures that have been taken by countries around the world. Microorganisms can break down biodegradable polymers into small molecules such as CO_2 , CH_4 and H_2O under certain conditions. Abiotic chemical reactions such as photodegradation, oxidation and hydrolysis also contribute to the degradation process[8]. There are many examples of biodegradable polymers, some produced from plants, animals or microorganisms, and some purely synthetic (man-made). Common biodegradable polymers are polylactic acid (PLA), polyhydroxyalkanoates (PHA), polycaprolactone (PCL), polyethylene cross . Polybutylene succinate (PBS) and Polybutylene terephthalate (PBT) etc[9]. Among them PLA is considered as the best alternative to existing plastics.

1.2 Polylactic acid (PLA)

Unlike other biodegradable polymers synthesized from petrochemicals or even conventional plastics, PLA is made from sustainable resources, such as corn, potato, rice or wheat starch, and the products decompose to produce CO_2 and H_2O when discarded, and then become raw materials for lactic acid under plant photosynthesis, making it a completely natural recycled polymer material[10, 11]. The life cycle of

PLA is schematically shown in Figure 1.1[12].

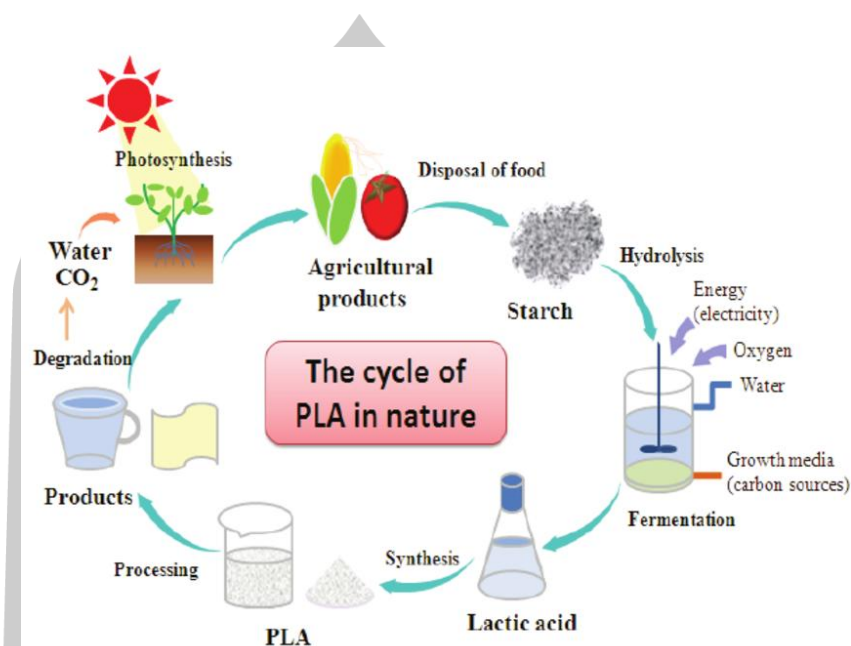


Figure 1 The cycle of PLA in nature

The development of PLA began in 1893 with the publication of a formula for lactic acid production by Bischoff and Walden. 1932 saw the development of low molecular weight polylactic acid by Carothers et al. 1954 saw the introduction of PLA in medical sutures, implants and drug delivery systems by Nemours and Ethicon. 1992 saw the laboratory production of polylactic acid fibers in the laboratory by Shimadzu in Japan using a melt-spinning method. In 1992, the Japanese company Shimadzu produced PLA fibers in the laboratory using the melt-spinning method. France's Fiber web company in 1997 began to trademark Deposa production of PLA fibers. 2002, the United States Cargill Dow LLC (Cargill Dow LLC) "NatureWorks" (NatureWorks) as a trademark, began to starch as raw material for the production of PLA, the annual output of 140,000 tons. In 2003, Dow LLC launched Ingeo TM, a PLA fiber spun from NatureWorks TM polymer. In 2005, Dow sold its shares to Cargill, which renamed its PLA business NatureWorks LLC .

The monomers of PLA are lactic acid. Lactic acid is derived from the microbial fermentation of sugar or starch from agricultural crops (e.g. corn, wheat or

rice). The lactic acid molecule has a chiral carbon atom, so it has two optical isomers, L-lactic acid and D-lactic acid. The monomer structure of lactic acid is shown in Figure 1.2 [13].

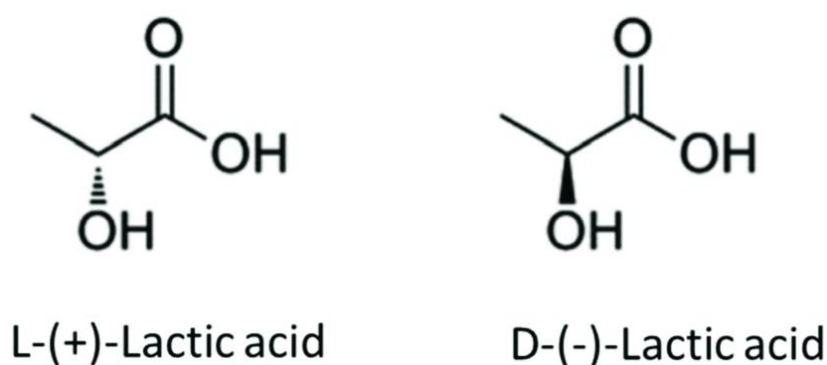


Figure 2 The monomers of PLA

1.3 Applications of polylactic acid

Initially, the main use of PLA was limited to medical applications such as implantable devices, tissue scaffolds, sutures, etc., because of the high cost of the polymers, their low availability, and limited molecular weight. In the last few years, new technologies have made the economical production of high molecular weight PLA a decisive factor for its wider application, and PLA has made great progress as an alternative to petroleum-based polymers (PET, PS, PE, etc.) in the packaging, textile, agricultural and industrial sectors [14].

1.3.1 Biomedical field

(1) Drug delivery vehicle

PLA and its composites can be used as a carrier for slow-release drugs. It can be decomposed into small molecules in living organisms, after which it is excreted through metabolic functions such as sweating, urination and defecation of the human body. Usually, these polymeric materials are used as controlled release carriers for drugs with short half-life, which reduces the number of drug administration, improves

drug efficacy, reduces patient's pain, effectively increases the way of drug administration, and also reduces the toxic side effects of drugs to a certain extent[15].

(2) Organization of engineering materials

Tissue engineering materials to restore the function of damaged tissues or organs play an indispensable role in surgical medicine. In general tissue engineering, scaffolds are used to temporarily replace damaged tissues in the human body, as a bridge to connect cells to regenerating tissues, and to reduce the impact on the normal vital activities of the body by giving a certain mechanical strength[16].

(3) Wound aids

As the first barrier of the human body, the skin can, to a certain extent, defend itself against external damage. If the skin is injured or broken, it needs a kind of artificial dressing that not only enhances the activity of human cells but also has the function of tissue regeneration to protect the injured or broken parts, avoid bacterial infection and promote wound healing. In other words, skin repair auxiliaries are required to have both bioactivity and functional similarity to human skin, and PLA is a natural choice for human skin repair materials[17].

(4) Medical sutures ss

Surgical sutures are vital materials in surgery. Without sutures, ligating blood vessels, stitching wounds, and connecting tissues would not be possible, and surgery could not be completed successfully. Traditional surgical sutures need to be removed after the wound has recovered, leaving scars on the skin where the injury occurred, and in severe cases, may require a second surgical procedure, causing the patient to suffer unnecessarily. With the advancement of science and technology, there are biocompatible sutures such as PLA, which can be automatically degraded and the degradation products can be absorbed by the human body after the wound recovers, so there is no need for a second surgery to remove the sutures. This not only reduces the risk of wound infection, reduces the pain of the patient, and makes the wound heal beautifully, but also reduces the workload of medical staff and improves medical efficiency[18].

1.3.2 Packaging area

Plastic bags, food containers, beverage containers and other plastic products are a major pillar of the packaging field. Traditional plastics in the life of the use will

cause a lot of "white trash", but PLA can be automatically degraded after use, will not pollute the environment. The United States Nature Works production of PLA has been used in a series of packaging applications, such as high-value films, rigid thermoformed containers and coated paper. BASF's 45% PLA polymer has been used in the manufacture of handbags, decomposable can liners, food packaging. The mechanical properties of commercially available PLA films and packaging materials are superior to those of polystyrene (PS) and comparable to PET[19].

1.3.3 Agriculture

Agricultural films play a great role in promoting crop growth and increasing crop yields, but traditional agricultural films are basically derived from petroleum-based polymers, and it is very difficult to dispose of the waste after use. After the crop growth period and maturity of the wind and sun after the intensity of the decline, split into small fragments left in the soil is difficult to remove, not only to hinder the development of crop roots and the absorption of water, but also with the wind in the air, causing serious environmental pollution. PLA is biodegradable, it can be degraded by microorganisms in nature, and also be decomposed by enzymes in plants and animals, and the final products are non-polluting CO and H₂O, which will not increase the burden on the environment, and thus it is regarded as the most promising biodegradable polymer. Therefore, after the use of PLA agricultural mulch film, the film can be directly degraded in landfills, avoiding the pollution caused by petroleum-based plastics. Some regions in Europe and China have begun to produce agricultural land film using corn as a raw material[20].

1.3.4 Automotive and electronics industry

In order to alleviate the pressure of the growing global shortage of petroleum energy and to prevent the further aggravation of the greenhouse effect, many companies have shifted from petroleum-based raw materials to PLA-based raw materials. In the electronics field, PLA-based plastics are used to make computer parts, cell phone cases, TV housings, and DVD player cases. These products emit about 15% less carbon dioxide over their entire life cycle, both in use and after disposal, than the petroleum-based plastics currently used. Moreover, PLA-based composites prepared by adjusting processing parameters, optimizing the molding process, and adding modifiers can achieve strength comparable to that of general-

purpose plastics[21]. Meanwhile, PLA has also been used as an engineering material in the automotive manufacturing industry. In 2003, Japan's Toyota Motor started to apply PLA to automotive parts by using PLA fibers in automotive foot mats and tire covers[22]. Toray and Mitsubishi have also successively applied PLA to the interior decorative items of automobiles. Domestic Chery Automobile also cooperated with the Chinese Academy of Sciences in 2009 to carry out research related to the application of PLA in automobiles[23].

1.3.5 Textile industry

The physical properties of PLA fibers are similar to those of the traditional fiber polyester, which is also prepared by conventional spinning processes. Like all polyester fibers, PLA fibers can be made into a wide range of fiber products such as filaments, monofilaments, and nonwovens, and can be blended with a variety of natural fibers by both wet and dry spinning methods. Because PLA fiber products have high gloss and good shape retention and other characteristics, so it is very suitable for clothing, currently on the market T-shirts, coats, windbreakers, dresses and so on have the figure of PLA fiber. Due to its appearance of drape, fluffy feel, hydrophobicity, non-irritating skin and other characteristics, especially for women's underwear and sportswear production. Nowadays, cotton fiber and PLA are also woven into blended yarns in foreign countries, and then this blended yarn is used to make household products such as toothbrushes, towels and shoe brushes[24].

1.4 Significance of the study

(1) Polylactic acid (PLA) has been recognized as a leader among various petroleum-based polymers over the past decades due to its renewability, degradability, biocompatibility, good mechanical properties, high transparency and low energy dependence. PLA has been considered the best among various petroleum-based polymers in the last few decades. However, PLA has some drawbacks such as poor crystallization properties and poor heat resistance which limits its application in certain fields. Mechanical, mechanical and physicochemical properties of polymers are closely related to the crystallization properties, so it is important to study the crystallization behavior of PLA to achieve its wide range of applications.

(2) Most of the existing studies on the modification of PLA use petroleum-based fillers, resulting in PLA composites that cannot be 100% degraded after disposal. So far, there is still a lack of research on the modification of PLA using completely renewable and degradable substances.

(3) ENR is a completely biodegradable thermoplastic polyester synthesized from renewable resources (NR), which has a high degree of crystallinity and can be used as a crystallization promoter for PLA.

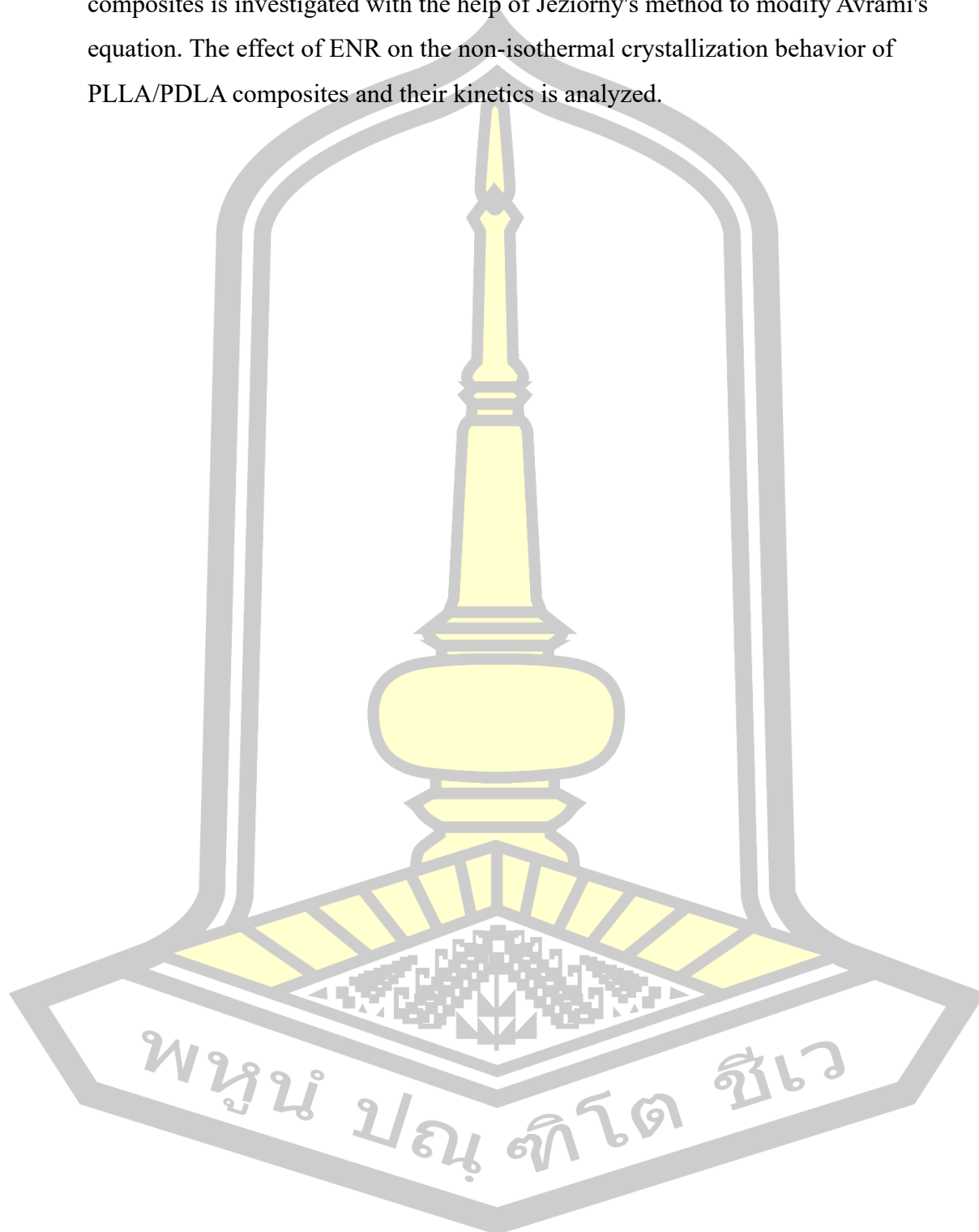
(4) The market sale of pure PLA glass transition temperature is generally about 55 °C, melting point in 150 ~ 170 °C, and to broaden the scope of application of PLA, must to a certain extent to improve its heat resistance. SC-PLA's melting point of 230 °C, compared with the pure PLA structure is more stable, the mechanical properties of better than the PLA, heat and hydrolysis resistance is more excellent. However, it is difficult to obtain stable SC-PLA, and it is found that the addition of ENR can solve this problem, so that the mixture has better heat resistance and processing stability at the same time.

1.5 Main studies

(1) PLLA and PDLA were mixed at a mass ratio of 50:50, and then, ENR in different ratios was added to the PLLA/PDLA blends, and PLLA/PDLA/ENR blends were obtained by co-mixing in a twin-screw extruder, and PLLA/PDLA/ENR composites with different formulations were obtained by melt extrusion injection molding.

(2) Differential scanning calorimeter (DSC) was used to characterize the glass transition, crystallization behavior and melting behavior of the composites; Ray diffractometer (XRD) was used to test the crystalline structure of the composites; Observation of the structural morphology of the samples using scanning electron microscopy (SEM); Thermogravimetric synchronous analyzer (TGA) was used to characterize the heat loss property of the specimens. We analyzed the effects of the addition of ENR, its amount and particle size on the crystallization behavior, crystalline structure, crystalline morphology and thermal stability of PLLA/PDLA.

(3) The kinetics of non-isothermal cold crystallization of PLLA/PDLA/ENR composites is investigated with the help of Jeziorny's method to modify Avrami's equation. The effect of ENR on the non-isothermal crystallization behavior of PLLA/PDLA composites and their kinetics is analyzed.



Chapter 2 Literature Reviews

2.1 Research on the modification of polylactic acid

PLA has many advantages, but there are also some shortcomings: such as poor toughness, lack of elasticity and flexibility, hard and brittle texture, slow crystallization rate, poor hydrophilicity and degradation rate need to be controlled, etc.[25]. These shortcomings limit its application in some fields. Therefore, the modification of PLA to improve its performance and reduce the production cost has become the main research direction of domestic and foreign researchers in recent years. So far, the modification methods of PLA are mainly categorized into two main groups: i.e., physical modification and chemical modification.

2.1.1 Physical modification

Physical modification is the co-mingling modification of base material and filler. Blending modification will not change the original properties of the material, but only targeted to optimize some of its performance deficiencies, and reduce production costs. Therefore, blending modification is currently the most widely used method of material modification. According to the different additive blends, PLA blending modification can be divided into nucleating agent blending modification, plasticizer blending modification, inorganic filler blending modification and other biodegradable materials blending modification, etc[21].

(1) Plasticizing blending

Plasticizing modification is to add a small amount of difficult to volatilize, low molecular weight, high boiling point small molecule chemicals into the polymer, in order to improve the mechanical strength and aging resistance of PLA in the process of use, and to expand its applicability in various fields. Madhavan et al.[26] modified the polymer PLA by using poly(ethylene glycol) (PEG) as a plasticizer, and after irradiating it for 2 min under the UV lamp, adding the polyethylene glycol blending. It was found that the elasticity and transparency of the blended PLA became better, and the elongation at break could reach 412.

(2) Nucleating agent blended with PLA

In order to accelerate the nucleation rate and improve the mechanical properties of PLA, a nucleating agent can be added to it and melt blended with it[27]. Fortunati et al.[28] used cellulose nanoparticles as nucleating agents to melt blend with PLA. It was found that the crystallinity of the composites with the addition of cellulose nanocrystals was improved as compared to pure PLA, while the Young's modulus and antimicrobial properties were increased.

(3) Inorganic filler blended with PLA

In recent years, many methods have been developed to prepare PLA-based bio-nanocomposites[29]. Zhang et al.[30] blended hydroxyapatite as a filler with PLA to prepare apatite/polylactic acid composites. It was found that the energy storage modulus of the samples with the addition of hydroxyapatite was more than three times higher than that of pure PLA. Meanwhile, the hydrophilicity of the samples was also greatly improved, expanding their applications.

2.1.2 Chemical modification

(1) Copolymerization modification

Copolymerization modification is the polymerization of lactic acid monomer or propylene crosspolymer prepolymer and the monomer molecules of the added modifier to obtain linear block, random, or even reticulated or stellate copolymers of ultrahigh molecular weight. Chen et al.[31] copolymerized PLA with a small amount of trimethylcyclohexane, and the modified composites showed an increase in elongation at break, impact resistance, and tensile stress compared with pure PLA, with the elongation at break increased by 20 multi-fold increase in elongation at break and 1.6-fold increase in impact resistance.

(2) Surface modification

Surface modification, as the name suggests, is a method of improving the physical and chemical properties of polymers by changing the properties of the film surface, such as increasing its surface polarity, increasing the cohesive energy density, etc. Surface modification methods can be divided into two types: non-permanent (non-covalent attachment of functional groups) and permanent (covalent attachment). Non-permanent surface modification methods include: coating, wrapping, migration of additives, and plasma treatment. Coating is the deposition or adsorption of the

modifier on the polymer surface. Typically, PLA is encapsulated with bionic apatite[32]. The encapsulation method neither adsorbs molecules of PLA nor requires reactive side chain groups. Zhu et al.[33] used three materials, alginate, chitosan and gelatin, to encapsulate the subsurface region of PLA in a process. As soon as PLA was exposed to these three materials, a polymer gel was rapidly generated on its surface so that biomolecules were able to diffuse into the solubilized PLA. Permanent surface modification methods are known to include: chemical binding using wet chemistry and photografting. Photografting can be further divided into vapor-phase grafting and liquid-phase grafting.

(3) Graft modification

Commonly used grafting modification methods are: chain transfer grafting, chemical grafting (solution method, suspension method, melt method, solid-phase method), radiation method and initiation method. Solution method is the earliest application of a grafting method, the method of low reaction temperature, side reactions and high purity of the product; melt method refers to the polymer under certain conditions into the extruder, mixer or open refiner, so that it is grafted with the grafting monomer and modifier in the molten state grafting reaction. Melt grafting method is one of the most widely used grafting modification methods due to its short reaction time, high grafting efficiency, simple equipment and other advantages. Because of its short reaction time, high grafting efficiency, no solvent, simple reaction equipment and continuous production, it is the most widely used grafting modification method[34].

(4) Cross-linking modification

Cross-linking modification is, as the name suggests, a method that allows polymers and bioactive molecules to form new chemical bonds under the catalytic action of cross-linking agents and thus generate macromolecular reticulated polymers. This method can improve the mechanical and thermal properties of polymers to a large extent, and present better processing properties, laying the foundation for the wide use of the materials. Quan et al.[35] used PLA/starch composites as matrix materials, and modified them with different kinds of isocyanates as cross-linking agents, and it was found that long-chained isocyanates could improve the tensile strength of PLA/starch composites. Akesson et al.[36] firstly melt copolymerized PLA

with two cross-linking agents, pentaerythritol and methylene succinic acid, to obtain a ternary composite, and then used methacrylic anhydride to functionalize the terminal hydroxyl group, and the final PLA was in the form of a four-armed star shape with a double bond at the end.

2.2 Poly(lactic acid) stereocomplexes

2.2.1 Origin of stereocomplexes

Stereocomplexes can be formed when the forces between a substance and a polymer of a different conformation or of a different degree of regularity are stronger than those between it and the same substance. The phenomenon of stereocomplexation was first discovered in nucleic acids and proteins by Corey, R. B. and Pauling, L. by hydrogen bonding between base pairs thereby giving proteins a double helical structure[37, 38]. The use of stereocomplexation technology has been one of the directions in the development of heat-resistant polylactic acid. Lactic acid has two enantiomers - levorotatory (L) and dextrorotatory (D), and it has been shown that poly(lactic acid) stereocomplexes (SC-PLA) formed from poly(levorotatory lactic acid) (PLLA) and poly(dextrorotatory lactic acid) (PDLA) have a melting point about 50° C higher than that of the respective homopolymers, which effectively enhances the heat-resistance of PLA[39]. PLLA and PDLA are usually α -crystalline, and their molecular chains are stacked by 103 helices to form a pseudo-orthorhombic crystalline system, whereas the crystalline structure of SC-PLA is transformed into β -crystalline, and in this β -stacking of 3-helices, the molecular chains of the left-handed and right-handed helices are arranged in a spaced arrangement to form a complementary structure, which results in a more tightly packed chain, and this tightly packed stacking results in more intense van der Waals forces among molecules, which leads to more intense van der Waals forces among molecules, and more intense Van der Waals forces among molecules. This close packing results in stronger intermolecular van der Waals forces, which increases the melting point of SC-PLA[40]. The strong interactions between the SC-PLA chains are attributed to the strong interactions between CH...O=C hydrogen bonding interactions[41]. PLLA is a melt-processable crystalline polymer whose mechanical properties of fibers and films

are generally comparable to those of polypropylene. However, PLA has poor injection moldability and thermal stability compared to general-purpose petroleum-based polymers, so the application of PLA has remained very limited to date.

2.2.2 Synthesis and preparation of stereocomplexes

Among many stereocomplexes explored and researched, PLA stereocomplexes have excellent properties, better physical and chemical properties than PLA, and thus attracted a lot of attention once discovered, and the study of their properties is becoming more and more extensive. The preparation methods of PLA stereocomplexes are mainly divided into solution crystallization and melt crystallization.

Solution crystallization is the solution blending of poly(dextro-lactic acid) PDLA and poly(lev-lactic acid) PLLA after dissolving them separately, when the concentration of the blends in the solution reaches a critical value, the blends gradually form an irreversible gel, and with the increase of the molecular weight of PLA, the critical concentration of the gel gradually decreases, and the rate of gel formation is accelerated with the ratio of the PDLA/PLLA blends getting closer and closer to 1/1, with the increase of the polymer concentration in the solution, the time of gel formation is shortened, and the DSC results show that this gel is the stereocomplex microgel formed by the interaction of PDLA and PLLA molecules. The gel formation time was shortened with the increase of polymer concentration in the solution, and the DSC results indicated that the gel was a stereocomplexed microcrystal formed by the interaction of poly(dextro-lactic acid) PDLA and poly(lev-lactic acid) PLLA molecular chains[42]. The gel was prepared by solution blending of poly(lactic acid) with poly(lactic acid). The stereocomplexes of poly(lactic acid) can be prepared by solution blending by mixing the PLLA and PDLA polymers and blending them at room temperature with mechanical stirring in different ratios. The intermolecular hydrogen bonding force of the stereocomplex is stronger, and the critical concentration for gel formation is much smaller than that of PLA molecular chains, and most of the good solvents for PDLA and PLLA, such as dichloromethane and trichloromethane, are used. After blending of the PDLA and PLLA solutions, the blended solution will be volatilized naturally at ambient temperature, and the polymer concentration will be increased slowly in the evaporation process, and will reach the

critical concentration for the formation of the stereocomplex first. During the evaporation process, the concentration of polymer increases slowly and reaches the critical concentration for the formation of stereocomplexes first, and then reaches the critical concentration for the formation of PLLA when it is crystallized alone, so the stereocomplexes will be formed preferentially. If the solvent evaporates slowly, the stereocomplex will be formed fully. If the solvent evaporation rate is too fast, the critical concentration will be reached before the stereocomplex is fully crystallized, which will lead to the formation of more PLA crystallized separately[43]. When the high molecular weight PDLA is mixed with PLLA solution, the solvent is evaporated to form a film, and then the same solvent is added to the membrane, which is plated again and again, so that the molecular chains which do not form stereocomplexes can be fully solubilized, and the stereocomplexes will not be solubilized, thus, the stereocomplexes will be formed preferentially. Chain will not be dissolved, so that more content of stereocomposite crystals can be obtained, the use of suitable solvents, repeated coating, not only can increase the content of stereocomplexes, at the same time to make the melting point of the complexes increased, but also effectively inhibit the formation of polylactic acid crystals alone[44].

Melt crystallization, in which the PDLA/PLLA blends were first melted and then isothermally crystallized, was found to be also significantly faster in the crystallization rate of the stereocomplexes and shorter in the crystallization induction period in the blends of small molecular weight PDLA/PLLA than in the crystallization of polylactic acid alone[45, 46]. As the D/L ratio approaches 1, the crystallization temperature of the stereocomplexes increases and the spherical crystal growth rate is faster. This may be related to the fact that hydrogen bonds can be formed between PLA of different conformations. PDLA/PLLA blends were used for melt spinning, and when stretched at lower temperatures, the melt-extruded fibers were obtained as PLA alone crystals, and when stretched at higher temperatures, fibers containing PLA alone crystals and stereocomplex crystals could be obtained[47]. In the area of PLA and stereocomplexes, the Institute of Chemical Engineering, Changchun, has done a lot of research work, such as combining different contents of PLA with the stereocomplexes. For example, after adding different contents of PDLA into PLLA to form blends, and then treating them with different temperatures, it was found that

whether the samples were in the partially melted or completely melted state, the formation of PLA stereocomplexes was prioritized[48, 49].

2.2.3 Properties of polylactic acid stereocomplexes

PLLA stereocomplexes can raise the melting point of PLLA by about 50 °C, which greatly improves the heat resistance of PLLA. The heat resistance of the stereocomplexes is not only reflected in the onset of decomposition temperature, but also in the high number of stereocomplexed microcrystals in the PLLA/PDLA blends even after processing and melting. In terms of thermal stability, the high molecular weight PLA prepared by ring-opening polymerization has reached the requirement that it can be processed many times. Although the melting point of PLA stereocomplexes has been increased by nearly 50 °C, its onset thermal decomposition temperature is basically indistinguishable from that of PLA. Therefore, in the melt processing, even if the high content of PLA stereocomplexes, or all stereocomplexes, still reflects the lack of heat resistance, which has become a bottleneck in the development and application of PLA stereocomplexes. However, a large number of scientists have investigated how to improve the heat resistance, and some progress has been made, e.g., Tsuji found that the stereocomplex crystals decrease the chain segment mobility and improve the thermal stability by isothermal degradation[50]. In addition, the use of fillers can also improve the thermal stability of materials, for example, clays can effectively restrict the movement of polymer chains by forming exfoliated or intercalated structures, or chemical bonding structures formed by using in situ polymerization methods of additives with the polymer molecular chains, both of which can improve the thermal resistance of polymers.

The melting point of the stereocomplexes formed in PDLA/PLLA blends is closely related to the optical purity of PDLA and PLLA, and no stereocomplexes crystallize when the optical purity of both PDLA and PLLA is below 76 %. With the increase of optical purity, the continuous length of repeating units with the same conformation in the molecular chain of PDLA and PLLA will increase, and the thickness of the wafer of the complex will also increase, so the melting point rises. High optical purity (100 %) of the blends, PLA stereocomplexes of the equilibrium melting point of 279 °C[46]. On the PLA stereocomplexes of 100 % crystallization of the melting braising value, there are not many reports, usually considered to be 142

J/g[51]. PLA crystallization is slower, limiting the scope of its use in the application of the general will be in the PLA products, the addition of crystallizing agent, nucleating agent, and the use of PLA products. Generally, crystallization nucleating agent is added into PLA products to accelerate the crystallization process, improve the crystallinity and increase the use temperature. The formation of stereocomplexes in PLA, the rate of individual crystallization of PLA also changes significantly. The optimal nucleation process is considered to be self-nucleation, since the crystalline and chemical structures are identical and the nuclei formed are uniformly distributed.

However, obtaining PLA with high SC content is not so simple. As with racemic blends of PDLA and PLLA, the homo- and stereo- crystallizations of the enantiomers happen simultaneously and compete with each other [52, 53]. Homocrystal (HC) formation, resulted in phase separation, reducing the PLA mechanical properties and heat distortion temperature [54, 55]. At the same time, the initial cooling state of PLLA/PDLA blends affected how they crystallized [48]. Chen et al. [56] found that pentaerythritol (PENTA) promoted SC crystallization, while inhibiting HC crystallization for high molecular weight PLLA/PDLA blends, as shown in Figure 2.1. When only 3 wt% PENTA was added, SC was produced exclusively. The production of SC crystals in PLLA/PDLA/poly(methyl methacrylate) (PMMA) blends was studied by Samuel et al. [57]: they created PLLA/PDLA/PMMA blends of high molecular weight polymers by melting them together in a two-screw extruder. The PLLA/PDLA/PMMA mixture was miscible and when the PMMA mass fraction grew, SC crystallinity increased. Bao et al. [58] also discovered that PEG increased PLLA/PDLA blend crystallinity during solidification from melts: the crystal structure depended on molecular weight and PEG content. Lower molecular weight or higher PEG content made SC grains crystallize faster.

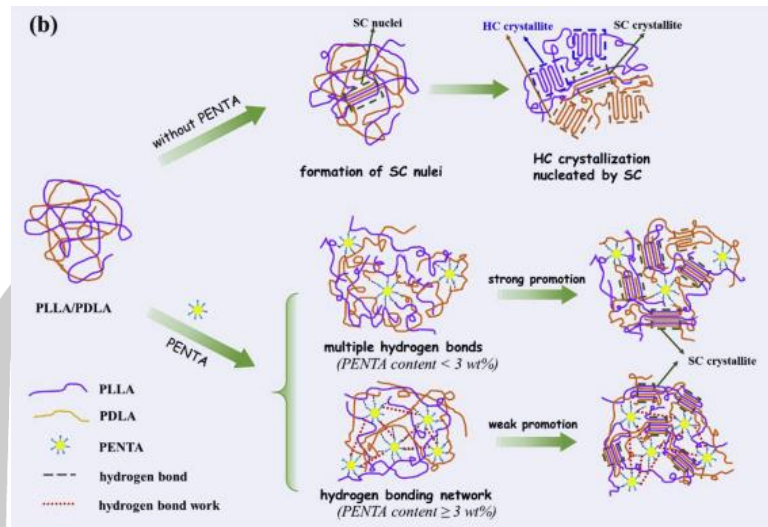


Figure 3 The structural evolution of the PLLA/PDLA blend and PLLA/PDLA/PENTA blend

The degradation of PLA-type materials is mainly in two ways: hydrolysis and enzymatic degradation. The degradation process is closely related to the concentration and temperature of the degradation solution, generally starting from the amorphous region first, and then to the crystalline region where the molecular chains are well arranged, and the degradation rate decreases slowly. The addition of polyglycolic acid (PGA) to PLLA allows the preparation of lactic acid-glycolic acid copolymers (PLGA) with a controlled degradation rate, which has a wide range of applications in drug slow-release systems and implantable bone materials. Although the degradation of PLLA/PDLA blends has not been studied much, it has important application value. Tsuji studied the stereocomplexes prepared in low molecular weight PLLA/PDLA blends, and the hydrolysis resistance of PLA stereocomplexes was higher than that of PLA due to the molecular chain arrangement would be more regular than that of the folded chain in PLA, and the hydrolysis resistance of PLA stereocomplexes was higher than that of PLA in comparison with that of solution blends. Compared with solution blending, the thickness of the lamellae of the stereocomplexes prepared by the melt blending method is larger, and during the hydrolysis process, PLA stereocomplexes can show better hydrolysis resistance - the molecular weight of the degraded residue is larger in the same time[59, 60].

2.3 Epoxidized natural rubber (ENR)

2.3.1 Natural rubber(NR)

Natural rubber is a type of natural gum derived from rubber trees, also known as rubber emulsion or rubber sap. The emulsion of the rubber tree contains rubber particles, which can be extracted during processing and formed into rubber products by adding sulfur and other treatments. Natural rubber has a wide range of uses in many industrial applications, including tire manufacturing, rubber piping, seals, and rubber shoes. Compared to synthetic rubber, natural rubber has excellent elasticity, abrasion resistance, and aging resistance, so it is still widely used in many areas[61, 62].

2.3.2 Preparation of epoxidized natural rubber

Epoxidized natural rubber (ENR) is prepared by chemically oxidizing the double bonds in natural rubber (NR). On the basis of retaining the molecular structure and properties of NR, the modified epoxy functional groups increase the polarity and intermolecular interactions of ENR, which leads to the improvement of its properties such as airtightness, oil resistance, and resistance to wet sliding, and also endows ENR with low rolling resistance and good compatibility with other materials. The excellent characteristics of epoxidized natural rubber are also recognized in[63]. The excellent characteristics of epoxidized natural rubber have also expanded its applications, and the preparation of epoxidized natural rubber has attracted attention in order to meet the production needs of people.

In the 1920s, it was discovered that ENR could be prepared by oxidizing NR with peroxyacetic acid, and it was not until around 1970 that the price of synthetic rubber increased due to the impact of oil, which led to an increasing number of studies on modifying NR to obtain high oil resistance[64]. The earliest epoxidation modifications were carried out in homogeneous solutions, using perbenzoic acid and peroxyacetic acid as modifying reagents, and then controlling different conditions during the reaction to achieve different epoxidation degrees.

With the development of society, the modification method in homogeneous solution is difficult to meet the requirements of industrialization, so the method of epoxidation in latex has been developed, which leads to a significant reduction in

production costs. Nowadays, ENRs are usually prepared by epoxidation of acidic NR latex with peroxyacetic acid or peroxyformic acid. There are two ways to prepare ENR by peroxyacetic acid-based epoxidation reagents.

The first method is prefabricated peroxyacid oxidation, whose modification mechanism is shown in Figure. 2.2[65]. In the modification of NR latex by peroxyacetic acid epoxidation, firstly, hydrogen peroxide and acetic acid were used to produce peroxyacetic acid, and then acetic acid was used to regulate the acidity and alkalinity in the reaction process, and finally, the epoxidization degree of the ENR was controlled by adjusting the ratio of the mass of the NR dry adhesive to the amount of the generated peroxyacetic acid.

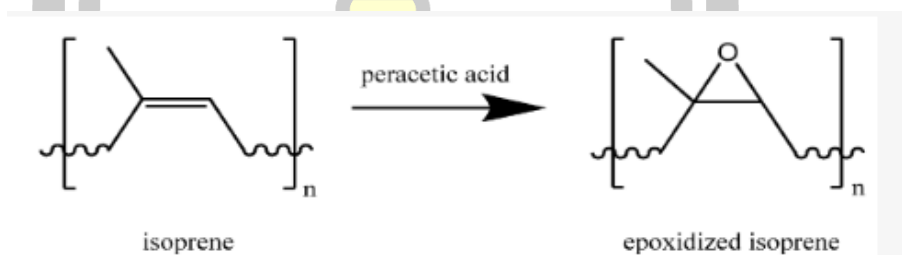


Figure 4 NR to ENR modification mechanism

Due to the poor stability of the storage process of peroxyacetic acid, it is easy to cause an explosion and needs to be calibrated and calculated before it can be utilized, which makes each batch of peroxyacetic acid less reproducible and inconvenient to produce, and the acetic acid generated in the production process also causes the epoxide group to open the ring and produce by-products. The difficulty of controlling the appropriate process conditions has hampered the industrial implementation of this method, so it has been used less frequently.

The second method is in situ epoxidation, in which peroxyformic acid is generated directly during the epoxy modification process and epoxidized in situ at the double bond of NR[66]. The oxygen activity of the newly generated peroxyformic acid is relatively strong, which can be directly reacted in the system, and the mass of dry glue NR and the concentration of hydrogen peroxide can be directly adjusted to prepare ENRs with various epoxy degrees, which is a widely used epoxidation

method because of the simplicity of the process, ease of operation, and the ability to satisfy the production requirements[67].

2.3.3 Structure and properties of epoxidized natural rubber

The oxidation of NR dry rubber by peroxyacetic acid to prepare ENR introduces epoxy groups into the molecular chain, but the structure of the NR molecular chain remains unchanged during the modification process, so most of the properties are retained, and the structural formula is shown in Figure 2.3[68]. With the substitution of the epoxy group for the double bond, the polarity of the rubber and the intermolecular forces increase after the modification. This gives ENR excellent airtightness, oil resistance, anti-slip and compatibility properties[69]. The introduction of epoxy groups improves the reactivity of ENR, and it is easy to have ring-opening reactions with hydroxyl, amino and carboxyl groups, so it is easier to improve the interfacial interactions with the fillers, thus promoting the uniform dispersion of the fillers and enhancing the compatibility of the two to improve the mechanical properties of the rubber, and thus promoting the application of ENR in various fields.

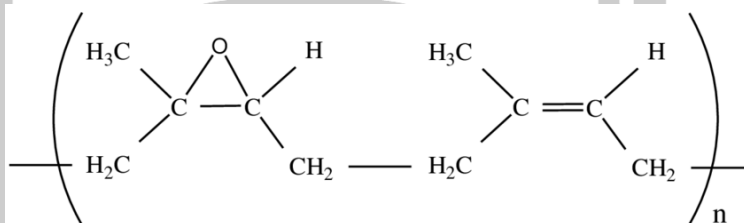
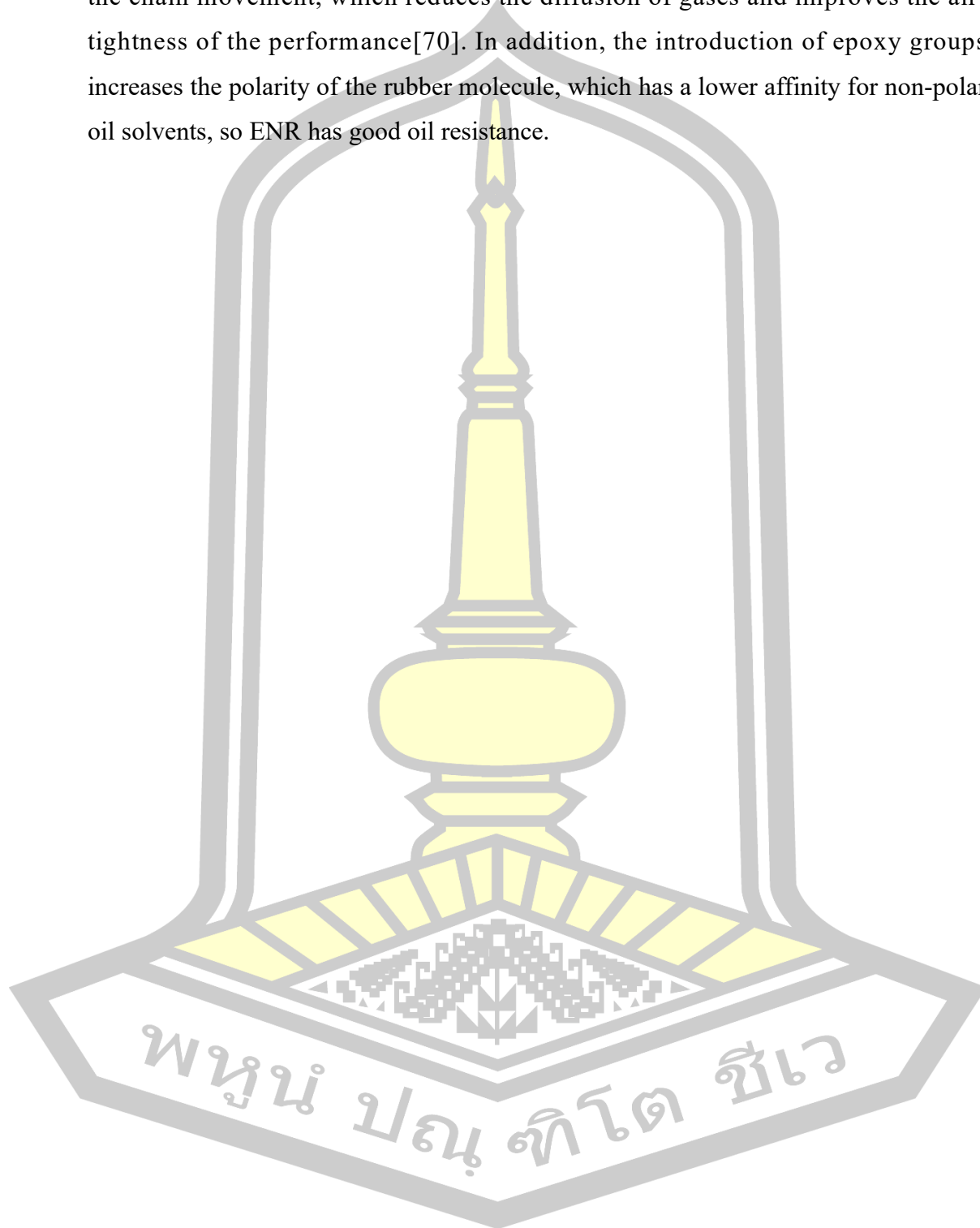


Figure 5 Molecular structure of ENR

Epoxidized natural rubber has high tensile strength because it retains the strain-induced crystallinity of natural rubber, but the introduction of epoxy groups restricts the movement of the molecular chains, resulting in low elasticity, which can be improved with increasing temperature. The properties of low epoxy epoxy natural rubber are basically the same as those of natural rubber, so it has a high vibration damping ability. The air permeability of ENR is related to the thermal movement of ENR molecular chains, the more intense the chain migration, the easier it is for gases to pass through, resulting in a high degree of air permeability. The introduction of

epoxy groups into ENR increases intermolecular forces, resulting in the restriction of the chain movement, which reduces the diffusion of gases and improves the airtightness of the performance[70]. In addition, the introduction of epoxy groups increases the polarity of the rubber molecule, which has a lower affinity for non-polar oil solvents, so ENR has good oil resistance.



Chapter 3 Research Methodology

3.1 Experimental materials

Total Corbion PLA (Thailand) Ltd. provided PLLA and PDLA. Gel permeation chromatography (GPC) was used to measure the number average molecular weight (Mn) and weight average molecular weight (Mw) of PDLA and PLLA. Tetrahydrofuran (THF) was used as eluent. Table 1 summarizes the materials used. Epoxidized natural rubber(ENR) was purchased from DYNATHAI Industries PCL, Thailand.

Table 1 Materials Characterization

	PLLA	PDLA
Code	L130	D120
Optical Purity	≥99% (L-isomer)	≥99% (D-isomer)
Weight-average molecular weight (Mw) (GPC)*1	1.8 X 10 ⁵	1.5 X 10 ⁵
Mw/Mn	1.93	1.69
*1 The GPC column was calibrated using the standard polystyrene with tetrahydrofuran (THF) as eluent at room temperature.		

3.2 Preparation of PLLA/PDLA with ENR blends

PLLA and PDLA were mixed in a 50:50 mass ratio, and then ENR in different ratios was added to the PLLA/PDLA blends, and the PLLA/PDLA/ENR blends were obtained by co-mixing in a twin-screw extruder at a screw speed of 60 r/min, a barrel temperature of 200 °C, and a duration of 10 minutes, until the blends became in the form of powder.

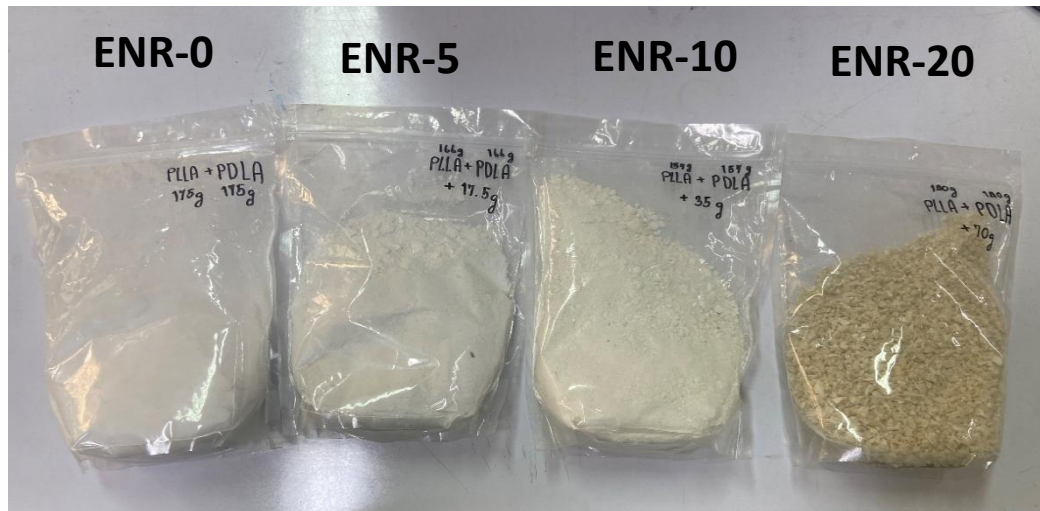


Figure 6 Sample of PLLA/PDLA and ENR blends

3.3 Experimental equipment

3.3.1 Thermal Performance Tests

Differential scanning calorimetry (DSC), a method of thermal analysis. The difference in power input to the specimen and reference material is measured as a function of temperature at a programmed temperature.

Thermal transition were analyzed using a differential scanning calorimeter (DSC; Pyris Diamond DSC4000, Massachusetts, USA). Samples (3-5 mg) were sealed in aluminum pans and tested under a nitrogen atmosphere. Each samples was heated from 0°C to 250°C at 10 °C/min, held isothermally for 3 minutes to erase thermal history, cooled to 0°C at 10 °C/min (first cooling cycle), and subsequently reheated to 250°C at 10 °C/min (second heating cycle). The parameters obtained included crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), cold crystallization temperature (T_{cc}), melting temperature (T_m), enthalpy of cold crystallization (ΔH_{cc}) and enthalpy of melting (ΔH_m).

The second heating curves were used to calculate the homocrystalline (HC) and stereocomplex crystalline (SC) content based on the following equations [71]:

$$X_{HC} = \frac{\Delta H_{m,HC} - \Delta H_{m,cc}}{\Delta H_{m,HC}^0 (1 - \alpha)} \quad (1)$$

$$X_{SC} = \frac{\Delta H_{m,SC} - \Delta H_{m,cc}}{\Delta H_{m,SC}^0 (1 - \alpha)} \quad (2)$$

where $\Delta H_{m,HC}$ and $\Delta H_{m,SC}$ are the melting enthalpy of homocrystals (HC) and stereocomposite crystallization (SC), respectively. $\Delta H_{m,cc}$ is the cold crystallization enthalpy; and α represents the weight fraction of NR or ENR in the blends. the reference melting enthalpies for 100% crystalline HC and SC $\Delta H_{m,HC}^0$, HC = 93 J/g and $\Delta H_{m,SC}^0$ = 142 J/g, respectively[72]. X_{HC} and X_{SC} denotes the homocrystallinity and stereocomplex crystallinity, respectively.

For isothermal crystallization, samples of 3-5 mg were sealed in aluminum pans. Each sample was initially heated from 0 °C to 250 °C at a rate of 10 °C/min, held at 250 °C for 3 min to remove any thermal history. The samples were then rapidly cooled to designated crystallization temperatures (T_c = 90 °C - 150 °C) at a rate of 50 °C/min. After being held at the crystallization temperature for an appropriate duration, the samples were again heated to 250 °C at a rate of 10 °C/min.

For non-isothermal crystallization, a reweighted sample (3–5 mg) was heated to 250 °C and held isothermally for 3 minutes in order to remove any prior thermal history in non-isothermal crystallization. After that, the samples were cooled to 0 °C at Various cooling rates (2, 5, 10, and 20 °C/min) and held for 3 min, followed by reheating to 250 °C at the rate of 10 °C/min.

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Figure 7 Differential scanning calorimetry (DSC)

3.3.2 Phase analysis

X-ray diffraction (XRD) is a research method to obtain information on the composition of a material, the structure or morphology of the atoms or molecules inside the material by performing X-ray diffraction on the material and analyzing its diffraction pattern.

The crystal structures of the blended samples were characterized using an X-ray diffraction (XRD) on an Analytical Bruker/D8 Advance instrument, operating at a wavelength of 0.154 nm. The instrument was set at an operating current of 40 mA and accelerating voltage of 40 kV. Scanning was performed at a rate of 2°/min, covering a 2θ from 5° to 30°. The characteristic peak areas were compared to the total crystal peak area to determine the stereocomplex crystallites content (XXRD.sc). The stereocomplex crystallites content (XXRD.sc) was calculated using Equation 3:[73]

$$X_{XRD.sc} = \frac{I_{sc}}{I_{hc} + I_{sc} + I_{amor}} \quad (3)$$

where I_{sc} is the sum of the regions under the scattering intensity peaks corresponding to the reflections of stereocomplex crystallites, I_{amor} is the integrated intensity of the amorphous halo, and I_{hc} is the integrated scattering intensity of the reflections of homocrystals.



Figure 8 X-ray diffraction(XRD)

3.3.3 Molecular Structure Tests

Fourier Transform Infrared Spectroscopy (FTIR) is mainly based on the chemical bond absorption frequency of infrared light to obtain information about the chemical bond, through the infrared data, combined with the spectral library can be qualitative and quantitative analysis.

FTIR spectra were used to confirm the synthesis of ENR. The spectra of ENR were determined using a Thermo scientific iS50 FT-IR spectrometer (America), operating in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .



Figure 9 Fourier Transform Infrared Spectroscopy (FTIR)

3.3.4 Morphological tests

Scanning electron microscope (SEM) is a low magnification scanning electron microscope with a maximum magnification of about 10 nanometers. Samples are prepared so that thin sized samples are not required for viewing using this SEM machine. Visualization is achieved by measuring electrons reflected from the sample surface. The image obtained from the SEM machine is a 3D image.

The microstructures of the samples were examined using emission scanning electron microscopy (JEOL, JSM-IT800) with an accelerating voltage of 10 kV. The sample was affixed to a conductive substrate using double-sided tape, evenly distributed to prevent agglomeration, and coated with a layer of gold via sputtering to enhance conductivity.

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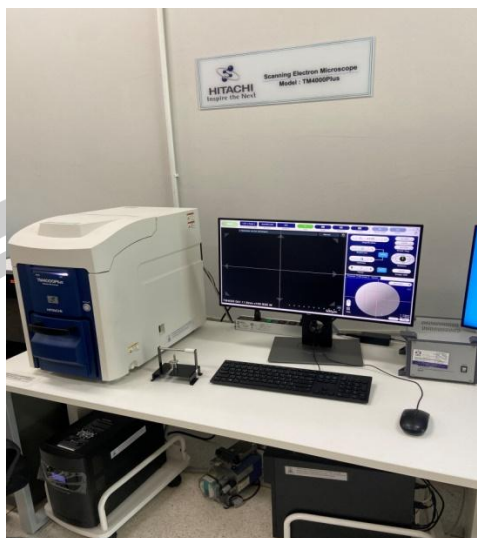


Figure 10 Scanning electron microscope (SEM)

3.3.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique used to analyze the thermal stability of polymers and the thermal properties of materials based on the use of a thermal equilibrium continuous measurement of weight change analytical data recorded as a thermometer showing the change in weight and temperature of the sample between 30-600 °C, and then the weight behavior of the decomposition is compared to the temperature used.

A PerkinElmer TGA 4000 was used to conduct thermogravimetric analysis (TGA). With a nitrogen flow rate of 19.8 ml/min, 10–15 mg samples were heated from 30 to 600 °C at a rate of 10 °C/min for each test. The weight decrease was noted and compared to the starting weight. The temperatures at which a 10% reduction in weight occurred were used to calculate the thermal degradation temperatures.



Figure 11 Thermogravimetric analysis (TGA)

3.3.6 Rheological Tests

Rheological tests is a window to observe the internal structure of polymer materials. The molecular weight and molecular weight distribution of polymer materials can be characterized through the response of molecular chains at different scales in polymer materials, such as plastics, rubbers, and resins, which can be used to carry out the quality inspection and quality control of raw materials, intermediate products, and final products in a fast, easy, and effective way.

The rheological properties of ENR-0, ENR-5, ENR-10 and ENR-20 blends were evaluated using a rotational rheometer (Anton Paar, MCR302e, Austria) at 180 °C. The dynamic frequency sweep test was performed over a range of 0.1–100 rad/s with a strain value set at 1%.





Figure 12 Rheometer

3.3.7 Polarizing microscope(POM)

Polarizing microscope is a type of microscope used to study so-called transparent and opaque anisotropic materials. Substances with birefringence can be clearly distinguished under polarizing microscope.

Crystal morphology was observed using a polarizing optical microscope (POM) (GX71, Olympus, Japan) equipped with a hot stage and a digital imaging system. Thin film ($\sim 100\text{ }\mu\text{m}$) were prepared by melting the samples on glass slides at $250\text{ }^{\circ}\text{C}$, holding for 3 min to erase thermal history and then cool to $30\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$. The evolution of crystal morphology was recorded continuously, and images were captured every minute from $150\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$.

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Figure 13 Polarizing microscope

3.3.8 Water contact angle

The water contact angle is an important parameter for measuring the wettability between liquid and solid surfaces. It represents the angle formed by a droplet on a solid surface and the tangent to that surface. By measuring the angle of water droplets, we can understand the hydrophilicity or hydrophobicity of solid surfaces.

Static water contact angle was measured at room temperature using a contact angle goniometer (SDC350KS, Kunshan Shengding, China). The samples were prepared by compressing powdered specimens into flat tablets. Prior to testing, the tablets were dried at 50°C under vacuum oven for 12 hours to remove surface moisture. A 5 μ L droplet of deionized water was carefully deposited onto the sample surface using a microsyringe, and the contact angle was recorded after 5 s. For each formulation, five measurements were taken at different positions, and the average value was reported.

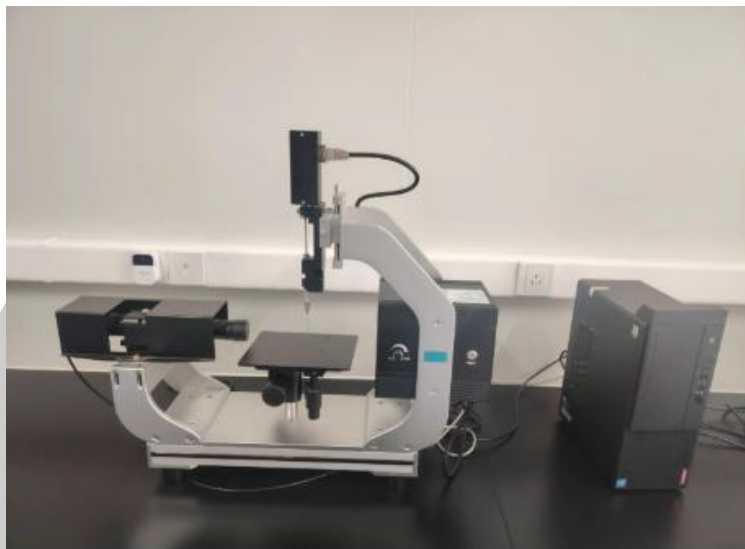


Figure 14 Contact angle measuring instrument



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Chapter 4 Results and Discussion

4.1 Effects of ENR on the crystallization of PLLA/PDLA blend

To investigate the effect of varying ENR content on the melt crystallization of PLLA/PDLA blends, isothermal crystallization experiments were conducted at 90 °C for 10 min. Figure 4.1 shows the DSC first heating curves for all samples as well as neat PLLA and PDLA. It can be seen that both the PLLA/PDLA mixture and the addition of ENR followed by the first heating process produce only SC crystals, and the melting temperature reaches about 220°C, while neat PLLA and PDLA have only HC crystals with a temperature of about 170°C.

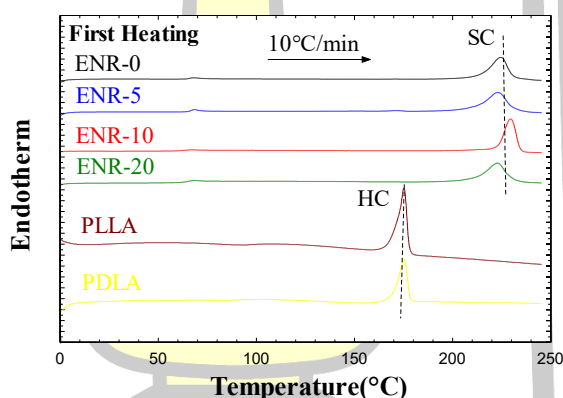


Figure 15 DSC first heating curves for all samples and for neat PLLA and PDLA

Figure 4.2 shows the melting thermograms after isothermal crystallization obtained from the DSC experiments, and the matching thermal characteristics of the samples displayed in Figure 4.2(a) are compiled in Table 2. After 10 min of isothermal crystallization, the ENR-0 sample displayed two distinct melting peaks at 171.4 °C and 222.6 °C during subsequent heating, which correspond to the successive melting of HC and SC crystals, respectively.[74] Notably, as the ENR content increased, the endothermic peak associated with HC crystals decreased, while the melting peak for SC crystals became more pronounced. As shown in Figure 4.2(b), SC crystallization predominated with the addition of ENR to the PLLA/PDLA blends.

In the ENR-10 and ENR-20 composites, only melting peaks at 214.3 °C and 205.1 °C were observed, indicating the exclusive formation of SC crystals. Furthermore, the melting temperature for both $T_{m,hc}$ and $T_{m,sc}$ decreased with increasing ENR content, which is attributed to ENR's plasticizing effect.[75] Because of the increased chain motility and decreased melting energy, the melting temperature was lowered.

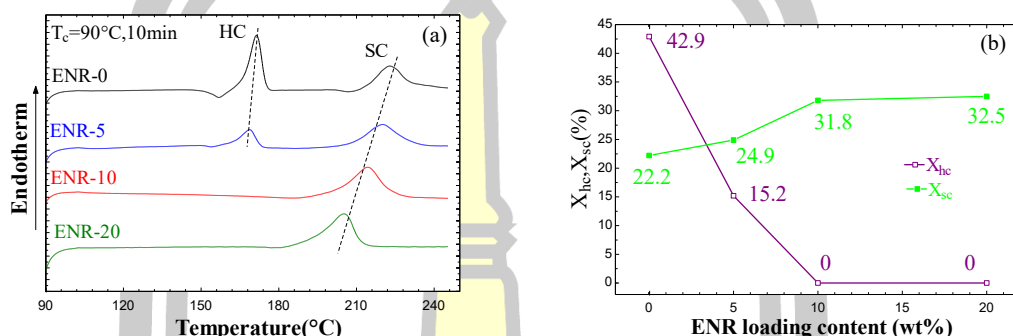


Figure 16 (a) DSC reheating curves of PLLA/PDLA/ENR after isothermal crystallization at 90 °C for 10 min and (b) the effect of ENR content on the crystallinities for X_{hc} and X_{sc}

Table 2 DSC data derived from reheating thermograms of PLLA/PDLA/ENR blends.

Sample	Homocrystal melting (HC)			Stereocomplex melting (SC)			
	$T_{m, hc}$ (°C)	$\Delta H_{m, hc}$ (J/g)	X_{hc} (%)	$T_{m, sc}$ (°C)	$\Delta H_{m, sc}$ (J/g)	X_{sc} (%)	XXRD.sc (%)
ENR-0	171.4	39.9	42.9	222.6	31.5	22.2	29.4
ENR-5	168.7	14.1	15.2	220	35.4	24.9	38.8
ENR-10	-	-	-	214.3	45.1	31.8	44.3
ENR-20	-	-	-	205.1	46.2	32.5	45.7

To determine the crystallinity of the PLLA/PDLA/ENR blends via XRD [XXRD.sc (%)], the samples were subjected to a thermal treatment similar to the DSC experiments. They were first heated to 250 °C for 3 min, then rapidly cooled to 90 °C and held at that temperature for 10 min, and finally analyzed by XRD at room

temperature. As shown in Figure 4.3, the primary peaks associated with HC appear at the 2θ of 16.6° and 18.9° , corresponding to the α -form PLA crystals in pseudo-orthogonal cells.[76, 77] The most prominent peaks related to SC crystallization were observed at the 2θ of 12.0° , 20.8° , and 24.0° , which correspond to SC in a triclinic unit cell.[78-80]

When the content of ENR in the blend exceeds 10 wt%, the HC peaks nearly disappear, indicating predominant formation of SC crystals. As expected, the intensity of the diffraction peak for SC crystals, as well as the calculated XXRD.sc values (as shown in Table 2), increased with the higher ENR content. The SC crystallinity increased from 29.4% for ENR-0 to 45.7% for ENR-20, aligning with the DSC results and reinforcing that ENR promoted SC crystallization in PLLA/PDLA blends.

Additionally, the SC crystallinity values obtained from XRD were higher than those from DSC. This difference may be due to the fact that XRD specifically detects the ordered crystalline region, whereas DSC captures the thermal transition of the entire sample, capturing both crystalline and amorphous phase.

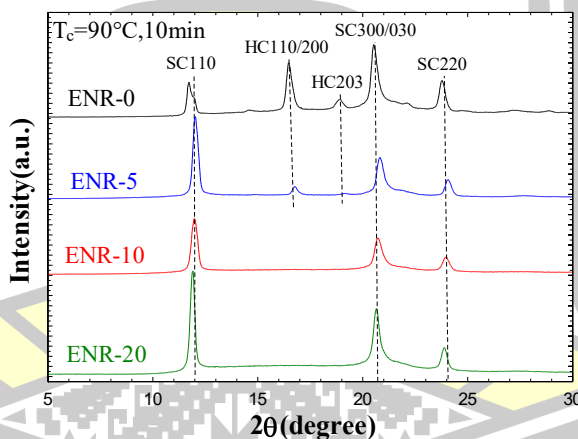


Figure 17 X-ray diffraction (XRD) patterns of PLLA/PDLA blends with different ENR contents after isothermal crystallization at 90°C

4.2 Effects of isothermal crystallization temperature on crystallization behavior

To thoroughly understand the effect of isothermal crystallization temperature on the crystallization rate of PLLA/PDLA/ENR blends, we investigated the isothermal crystallization behavior of a blend containing 5 wt% ENR. Because both HC and SC crystals existed in ENR-5, and isothermal crystallization temperatures ranging from 90°C to 150°C were also chosen, we wanted to observe the melting behavior of HC and SC crystals at temperatures lower than that of HC crystals (170°C) during the second DSC heating process, so as to clearly compare the effects of different isothermal crystallization temperatures on the two types of crystals. Figure 4.4(a) shows the isothermal crystallization curves of ENR-5 after 10 min of isothermal crystallization at temperatures of 90 °C, 110 °C, 130 °C, and 150 °C. At 90 °C, the blend exhibited slower crystallization, as indicated by broad crystallization peaks and longer crystallization times. As the crystallization temperature increased, crystallization occurred more rapidly, with the most pronounced crystallization observed at 130 °C, where the crystallization peak was sharpest and the crystallization half-time ($t_{1/2}$) was minimized at 2.2 min. However, at 150 °C, minimal to no crystallization occurred, likely because this temperature exceeded the optimal crystallization range for PLA, thereby suppressing the crystallization process.

Figure 4.4(b) presents the DSC reheating curves to 250 °C at a rate of 10 °C/min following isothermal crystallization. These results, along with the data in Table 3, show a significant reduction in HC crystallinity as the isothermal crystallization temperature increased, decreasing from 15.5% at 90 °C to 0.9% at 150 °C. In contrast, the crystallization temperature and enthalpy for SC crystals remained largely unchanged, with SC crystallinity consistently around 35%. This suggests that increasing the isothermal crystallization temperature inhibited HC crystallization in the blends, while exerting minimal influence on SC crystallization.

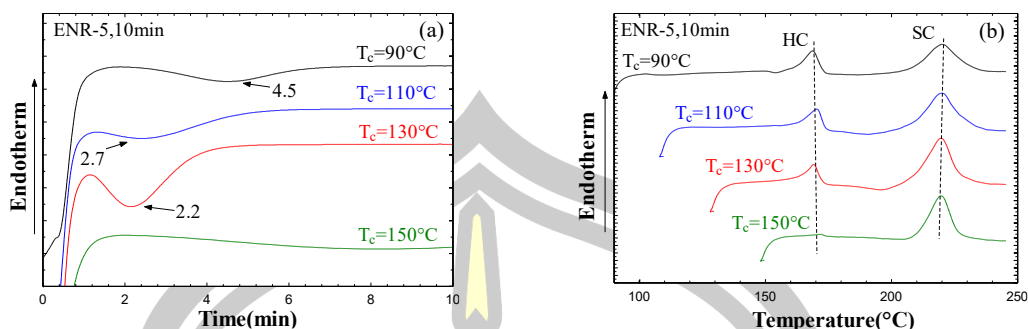


Figure 18 (a) Isothermal crystallization curves of ENR-5 at different temperatures, (b) DSC reheating curves of ENR-5 after crystallization.

Table 3 Isothermal crystallization and subsequent melting data of ENR-5 at various crystallization temperatures

T _c (°C)	Isothermal Crystallization t _{1/2} (min)	Subsequent melting					
		Homocrystal melting (HC)			Stereocomplex melting (SC)		
		T _{m,hc}	ΔH _{m,hc}	X _{hc}	T _{m,sc}	ΔH _{m,sc}	X _{sc}
		(°C)	(J/g)	(%)	(°C)	(J/g)	(%)
90	4.5	168.7	14.4	15.5	220	48.2	33.9
110	2.7	170.3	12.3	12.2	220	50.9	35.8
130	2.2	169.1	9.2	9.9	219.6	51.4	36.2
150	-	172	0.8	0.9	219.6	49.9	35.1

4.3 FTIR analysis

Figure 4.5 shows the FTIR spectra of ENR-0, ENR-5, ENR-10, and ENR-20 blends in the region of 3500–650 cm⁻¹. The peaks at 2962, 2916, and 2856 cm⁻¹ correspond to C-H extending from the -CH₂ group,[81] and the peaks within this region are mainly derived from ENR, as evidenced by the FTIR curves of neat ENR, which become more pronounced with increasing ENR content. The PLA peak at 1741 cm⁻¹ also shifted to a higher wavenumber in the blend with increasing ENR content, suggesting potential interactions between the ethylene oxide group of ENR and the

carboxyl end group of PLA.[82] The absorption at 1455, 1366, and 1306 cm^{-1} raised from the carbon atom in $-\text{CH}_2$. Bands at 1213, 1184, 1083, and 1038 cm^{-1} are attributed to C-O-C bending vibration,[83] while the bands at 870 and 755 cm^{-1} are due to the C-C stretching vibration.[84] No peak near 835 cm^{-1} , indicative of epoxy group vibrations, was observed, likely because the ENR in all the blends was insufficient to produce a detectable signal.

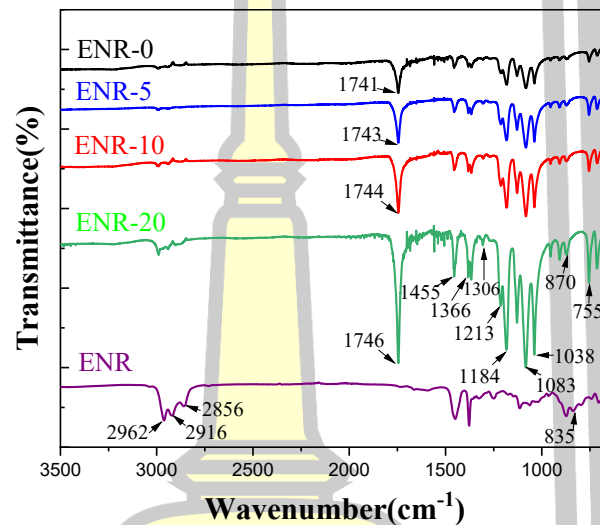


Figure 19 FTIR spectra for PLLA/PDLA composites with various ENR contents

4.4 Rheological properties

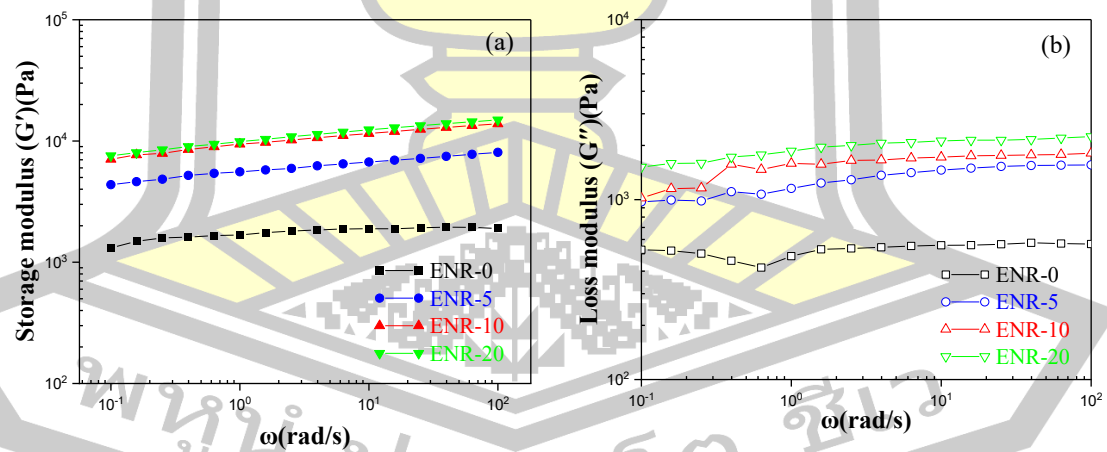
The rheological properties of polymers in the molten state are critical for determining their suitability for various processing conditions.[61] The incorporation of ENR into PLLA/PDLA composites has a significant impact on the materials' viscoelastic behavior. Rheological measurements of ENR-0, ENR-5, ENR-10, and ENR-20 composites were measured at 180 °C. Figure 4.6 demonstrates the dependence of storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$) of all samples.

As shown in Figure 4.6(a), PLLA/PDLA/ENR composite melt exhibited a much higher G' value compared to PLLA/PDLA(ENR-0) across the entire frequency range. This increase in G' was attributed to the reinforcing effect of ENR on the

PLLA/PDLA melt. Additionally, the G' of PLLA/PDLA/ENR composites increased progressively with higher ENR content, indicating that the formation of SC crystallization in the composites enhanced the melt's elasticity, resulting in a more solid-like behavior. This phenomenon was due to the large-scale relaxations of PLA chains being constrained by the SC crystals network formed in situ within the PLLA/PDLA/ENR composites.[85]

Similarly, the addition of ENR into PLLA/PDLA composites led to a steadily increase in G'' across the entire frequency range, further confirming the enhanced viscoelasticity of the materials.

The complex viscosity data presented in Figure 4.6(c) show that PLLA/PDLA(ENR-0) had the lowest $|\eta^*|$ value across all frequencies. The incorporation of ENR into PLLA/PDLA resulted in a marked increase in $|\eta^*|$, with the resulting composites displaying pronounced shear thinning behavior. This behavior is attributed to the formation of a network of SC crystallites within the melt. Previous studies by Liu et al. and Jing et al. have similarly demonstrated improved rheological properties in PLLA/PDLA blends due to the formation of SC crystals and their network structure.[86, 87]



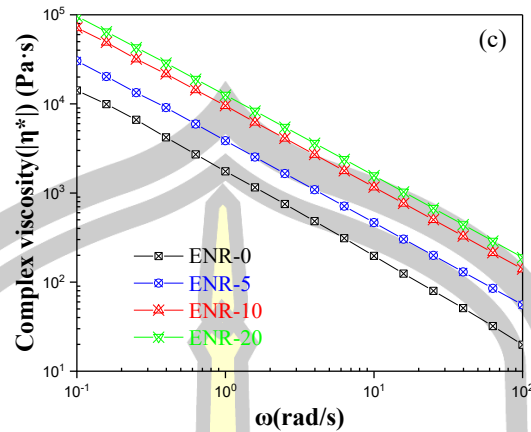


Figure 20 Rheological properties of PLLA/PDLA/ENR blends measured at 180°C.
 (a) Storage modulus (G') and (b) Loss modulus (G'') as functions of angular frequency.
 (c) Complex viscosity (η^*) indicating the flow behavior of the blends

Since the modulus is sensitive to percolated network structure, Figure 4.7 presents the G' and G'' value of the composites at 0.1 rad/s as a function of ENR content. The inflection points in these plots can indicate the percolation threshold for network formation.[88] In this study, the addition of 5 wt% ENR resulted in the formation of SC crystal network.

The finding suggests that SC crystals act as rheological modifiers, reinforcing the composite melts and enhancing their elastic properties. When the ENR content in PLLA/PDLA/ENR composites reached 5 wt%, the formation of the SC crystal network caused the shift in the viscoelastic behaviors from a liquid-like to a solid-like state.

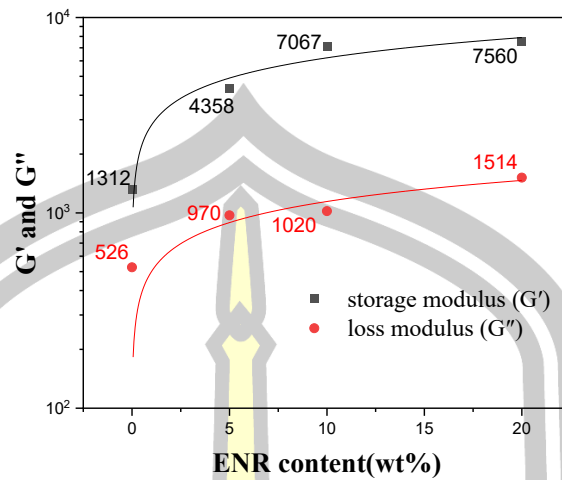


Figure 21 Plots of storage modulus (G') and loss modulus (G'') at 0.1 rad/s as a function of ENR content

Figure 4.8. illustrates the evolution of the crystallization type in the blends as the ENR content increases. A single PLLA or PDLA chain can form multiple hydrogen bonds with different ENR clusters, creating a complex network of hydrogen bonds that hinders the mobility of the enantiomeric chains to some extent. This occurs because the dispersed ENR clusters compact the PLLA/PDLA/ENR copolymer.[56] Interaction between the ethylene oxide group of ENR and the carboxyl terminal group of PLA, resulting in a decrease in HC crystallization and an increase in SC crystallization as the ENR content increases until complete SC crystallization is eventually formed.



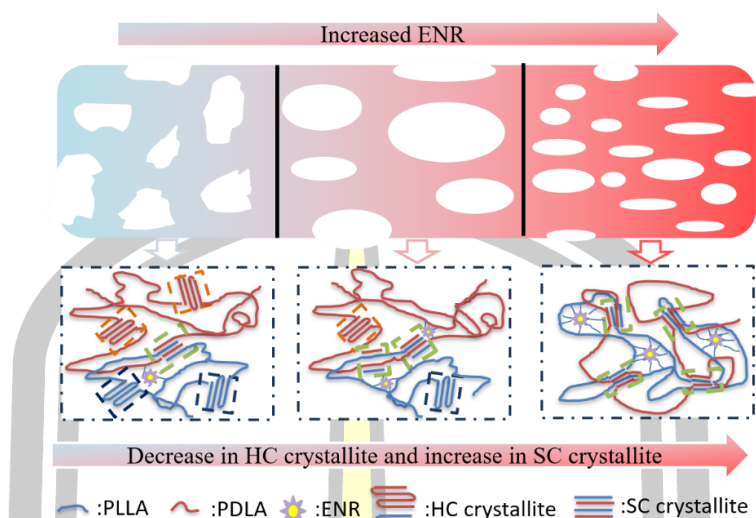


Figure 22 Scheme showing influence of ENR content on the development of crystalline structure

4.5 Scanning Electron Microscopy (SEM)

We examined the morphological characteristics of the PLLA/PDLA/ENR composites using scanning electron microscopy (SEM) at a magnification of 2000, as shown in Figure 4.9(a)-(d). It is difficult to distinguish the PLA and ENR phases from the figure, which indicates that there is a good interfacial compatibility between the two phases,[89] while the materials are highly entangled without any obvious defects or cracks and have random growth, and as the ENR content increases, they still show good dispersion in the PLA matrix, and this homogeneous distribution of the ENRs can significantly affect the mechanical and thermal properties of the materials.

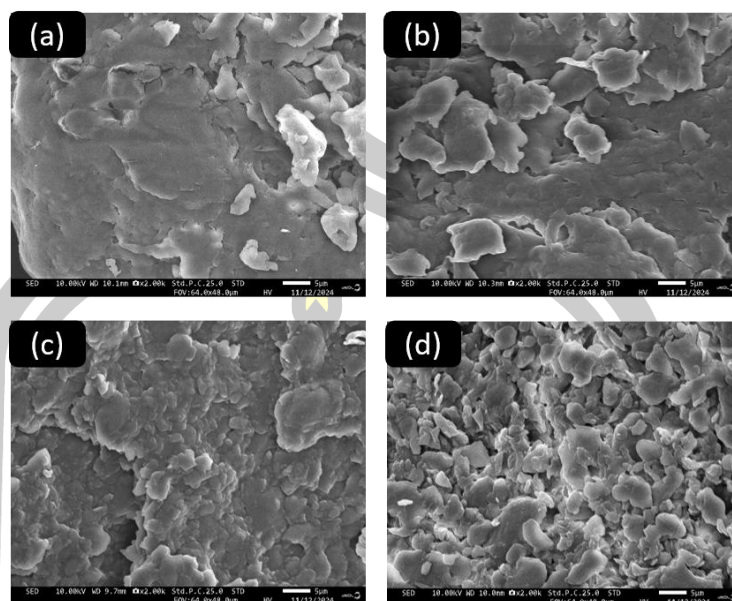


Figure 23 SEM images showing microstructures of (a) ENR-0, (b) ENR-5, (c) ENR-10, and (d) ENR-20

4.6 Thermogravimetric analysis (TGA)

The thermal stability of ENR-0, ENR-5, ENR-10, ENR-20, and neat ENR was assessed by measuring mass loss using TGA during heating from 30 °C to 600 °C. The results are shown in Figure 4.10 and detailed in Table 4, which includes T10% (the temperature at which 10% weight loss occurs), TMAX (the peak temperature on the DTG curve, representing the maximum rate of weight loss), and the residue (%) remaining at 600 °C. The results showed that pure ENR exhibited the lowest thermal stability, resulting in decreased T10% and TMAX values in all PLLA/PDLA blends as ENR content increased. Pongtanayut et al. and Liu et al. reported similar findings, observing reduced thermal stability in PLA/ENR blends with increasing ENR content.[90, 91]

The sample containing 20 wt% ENR had a T10% of 359.4 °C, approximately 21 °C lower than that of the PLLA/PDLA sample, indicating that adding ENR reduced the thermal stability of PLLA/PDLA blends.

Moreover, at 20 wt% ENR, a second stage of degradation appeared during thermal decomposition, suggesting reduced compatibility between ENR and PLA at

ENR content exceeding 20 wt%. This observation was further confirmed by DTG data, as the TMAX value for ENR-20 was approximately 12 °C lower than for ENR-0. Additionally, the residual mass increased significantly with the addition of ENR, producing more char, indicating that ENR contributes to ash formation during combustion.[92, 93]

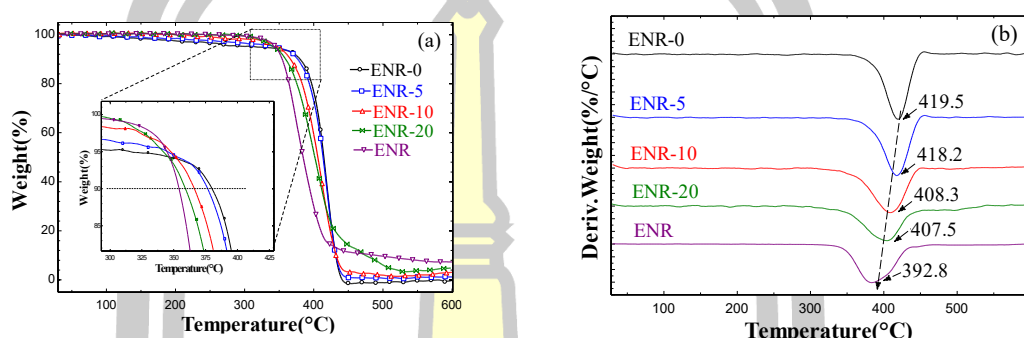


Figure 24 (a) TGA curves and (b) DTG curves for PLLA/PDLA composites with various ENR contents

Table 4 TGA analysis results: T_{10%}, T_{MAX}, and residual mass

Samples	T _{10%} (°C)	T _{MAX} (°C)	Residue (%) (600 °C)
ENR-0	380.3	419.5	0
ENR-5	377.1	418.2	1.22
ENR-10	366.6	408.3	3.32
ENR-20	359.4	407.5	4.96
ENR	354.2	392.8	7.36

4.7 Effect of NR and ENR on crystallization of PLLA/PDLA

4.7.1 Cooling cycle

Figure 4.11 shows the cooling process profiles of PLLA/PDLA/NR and PLLA/PDLA/ENR. It can be observed that with the addition of NR, PLLA/PDLA showed two crystallization peaks during the cooling process, which was attributed to the poor compatibility of NR with PLLA/PDLA, mainly due to the fact that NR is

nonpolar, while PLLA and PDLA are polar polymers, and this poor compatibility led to the presence of NR in the form of larger phase-separated particles in the PLLA/PDLA matrix. In contrast, only one crystallization peak appeared after the addition of ENR because of the increased polarity in ENR due to the introduction of epoxy groups, which led to the enhanced compatibility with PLLA/PDLA, as shown by the initial crystallization temperatures in Table 5, which were significantly higher in ENR-5 and ENR-10, but in all PLLA/PDLA/NR blends the initial crystallization temperature decreased.

In contrast, the incorporation of ENR resulted in a single crystallization peak, reflecting, enhanced compatibility with PLLA/PDLA due to the presence of epoxy groups, which increased ENR polarity. This improved miscibility promoted more homogeneous interaction and facilitated SC formation, as evidenced by the significantly higher Tonset values for ENR-5 and ENR-10 compared with neat PLLA/PDLA.

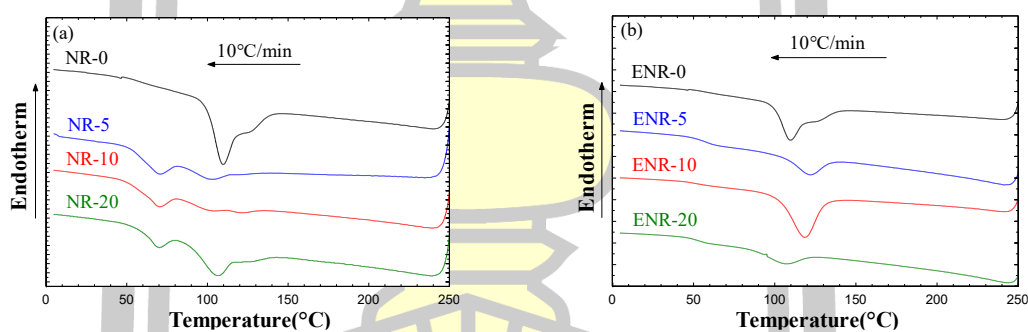


Figure 25 DSC cooling curves of (a) PLLA/PDLA/NR and (b) PLLA/PDLA/ENR at a cooling rate of 10°C/min

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Table 5 Differential scanning calorimetry (DSC) data derived from cooling thermogram of PLLA/PDLA/NR and PLLA/PDLA/ENR

Sample	T _c (°C)		ΔH _c (J g ⁻¹)		Tonset (°C)
ENR-0	109.7		-40		130.5
NR-5	69.7	102	-6.7	-7.7	125.6
NR-10	69.5	102.5	-7.1	-8.2	120.8
NR-20	69.3	106.2	-4.9	-24.5	118.3
ENR-5	121.5		-16.2		137.1
ENR-10	118.5		-41.8		135.7
ENR-20	106		-13.6		123.9

4.7.2 Reheating cycle

Figure 4.12 show the DSC reheating curves, while Table 6 presents the numerical calculation data for PLLA/PDLA/NR and PLLA/PDLA/ENR blends. We can see that there are two melting peaks in the PLLA/PDLA/NR blends around 170°C and 220°C, which belong to HC crystallization and SC crystallization, respectively, but the HC crystallization peak disappears when the ENR content exceeds 10 wt% in the PLLA/PDLA/ENR mixture. This was attributed to the addition of ENR leading to intermolecular interactions between PLLA and PDLA chains, which promoted the spatial complexation of the enantiomers. The epoxy groups in ENR reflected the hydrogen bonding with the hydroxyl terminals of PLLA and PDLA, which promoted SC crystallization and inhibited HC crystallization.

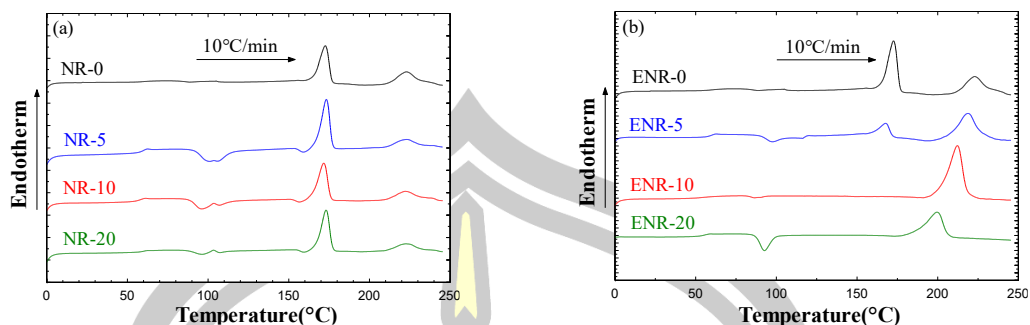


Figure 26 DSC reheating curves of (a) PLLA/PDLA/NR and (b) PLLA/PDLA/ENR at a rate of 10°C/min

Table 6 Differential scanning calorimetry (DSC) data derived from reheating thermogram of PLLA/PDLA/NR and PLLA/PDLA/ENR

sample	T _g (°C)	Cold crystallization		Homocrystal melting (HC)			Stereocomplex melting (SC)		
		T _{cc} (°C)	ΔH _{cc} (J/g)	T _{m,hc} (°C)	ΔH _{m,hc} (J/g)	XHC (%)	T _{m,sc} (°C)	ΔH _{m,sc} (J/g)	XSC (%)
ENR-0	61.0	88.2	-1.6	172.6	36.6	37.63	223	27.6	18.31
NR-5	49.5	84.7	-8.9	173.1	44.3	40.7	223.2	25.6	12.38
NR-10	41.9	76.1	-8.1	172.5	40.2	38.35	222.5	28.9	16.28
NR-20	40.0	71.4	-8.2	173.3	35.5	36.69	223.7	27.5	16.99
ENR-5	59.1	97.4	-5.4	167.9	13.2	8.83	218.8	46	30.1
ENR-10	55.3	86.5	-1.5	-	-	0	212.3	55.5	42.25
ENR-20	54.9	92.6	-14.2	-	-	0	199.7	39.6	22.36

Glass transition temperatures (T_g) of the blended are compared in Figure 4.13(a). Both NR and ENR decreases the T_g of stPLA, consistent with their plasticizing effect, which increased chain mobility and reduce rigidity [94]. Notably, NR induced a stronger reduction in T_g than ENR, due to its limited solubility in PLA and disruption of chain packing, which increased local segmental motion [95].

The influence of NR and ENR on crystallinity is shown in Figure 4.13(b). NR incorporation did not significantly alter crystallization behavior, whereas ENR

significantly enhanced SC crystallization. The highest SC crystallinity ($X_{SC} = 42.25\%$) was obtained for ENR-10, more than double that of neat stPLA, while HC crystallinity completely vanished. These results demonstrate that ENR acted as an effective heterogeneous nucleating agent, selectively promoting SC crystallization in PLLA/PDLA blends.

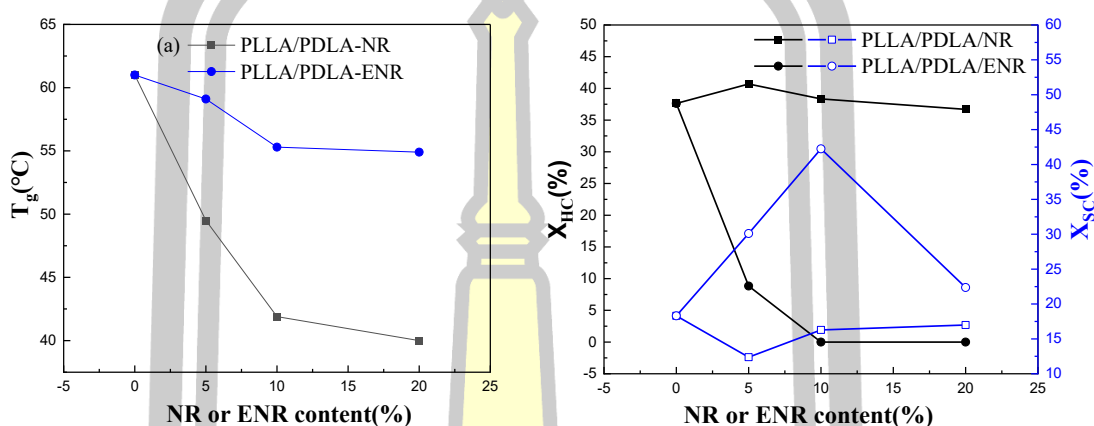


Figure 27 (a) T_g values, and (b) HC crystallinity (X_{HC}) and SC crystallinity (X_{SC}) of stPLA blends with varying NR and ENR contents

4.8 POM

The changes in crystal morphology of pure PLLA/PDLA (ENR-0), NR-10 and ENR-10 blends were studied by POM. POM micrographs of all the samples are shown in Figure 4.14, from which it can be seen that the ENR-10 blend showed sporadic crystallization at 140 °C and was the first sample to start crystallization, while ENR-0 and NR-10 did not show crystallization until 120 °C, suggesting that ENR was able to promote the crystallization of PLLA/PDLA blends, whereas NR had no promoting effect. As can be seen from Figure 4.14, compared to the crystallization of pure PLLA/PDLA (ENR-0), the size of the grains in the blends of NR-10 and ENR-10 became significantly larger, and complete spherical crystals could be observed, which is attributed to the fact that NR and ENR, as a kind of toughening agent, can reduce the brittleness of PLA and make its chain segments more pliable to increase the mobility of the molecular chains, and with the enhanced mobility of the

chain segments, the PLA molecules are more easily aligned around the nucleus, thus promoting grain growth.

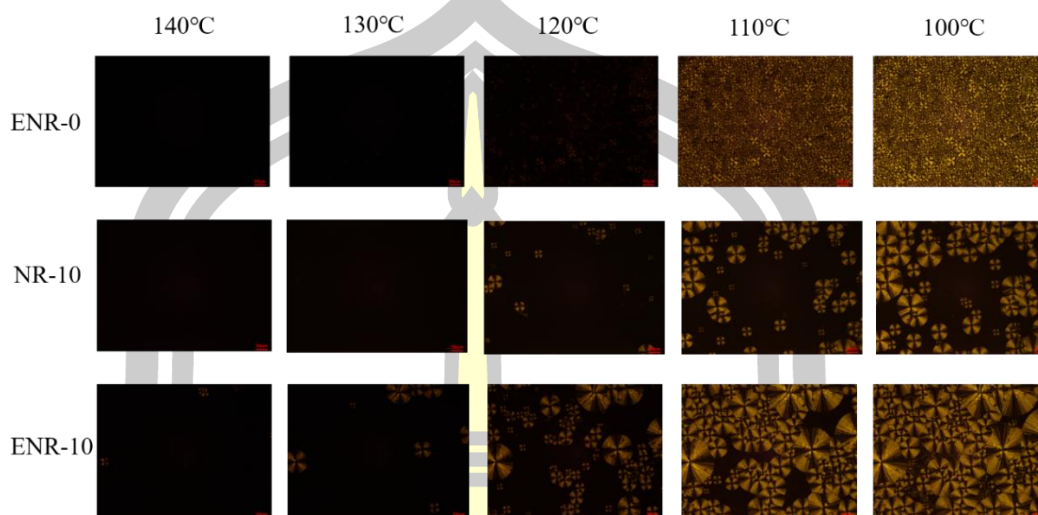


Figure 28 POM photographs of ENR-0, NR-10, and ENR-10 during cooling process (10 °C/min)

4.9 Contact Angle

The effect of ENR on the surface wettability of the stPLA blends is presented in Figure 4.15. At low ENR contents (5–10 wt%), the introduction of polar epoxy groups markedly increased surface polarity, leading to a significant decrease in water contact angle and hence improved hydrophilicity. This effect can be attributed to the uniform dispersion of ENR within the matrix and the surface localization of its epoxy functionalities. However, at higher ENR loading (20 wt%), a slight increase in contact angle was observed. This reversal is likely caused by phase separation and the preferential surface enrichment of the nonpolar rubber backbone, which diminished the effective exposure of epoxy groups. These findings indicate that a moderate ENR content of ~10 wt% provides the best balance between polarity enhancement and blend compatibility, yielding optimal surface hydrophilicity.

The molecular mechanism underlying this improvement is illustrated in Figure 4.16. The epoxy group of ENR can form hydrogen bonds with the terminal hydroxyl groups of PLLA and PDLA chains, thereby strengthening intermolecular interactions and promoting stereocomplexation. Enhanced chain contact and

compatibility not only improve bulk crystallization behavior (as confirmed by DSC and POM) but also contribute to the improved surface hydrophilicity observed at moderate ENR contents.

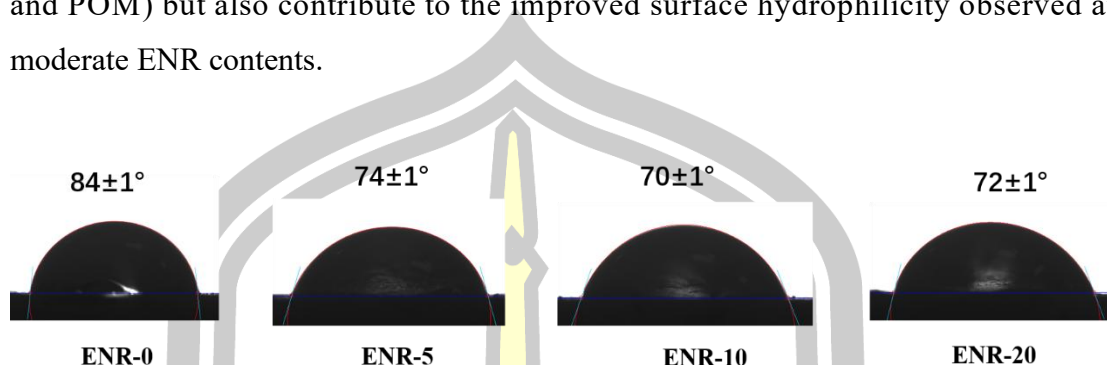


Figure 29 Water contact angle of PLLA/PDLA blends with different ENR contents

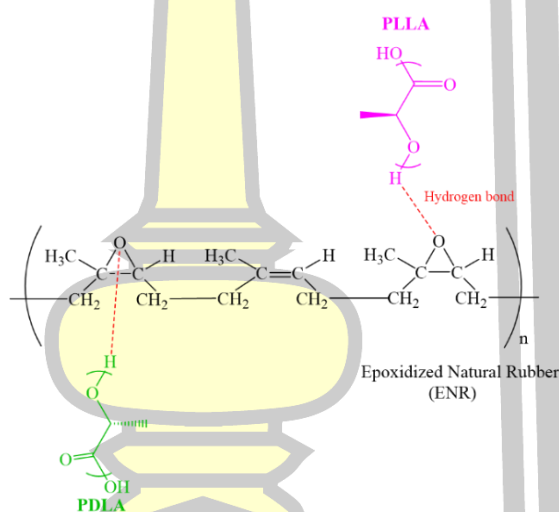


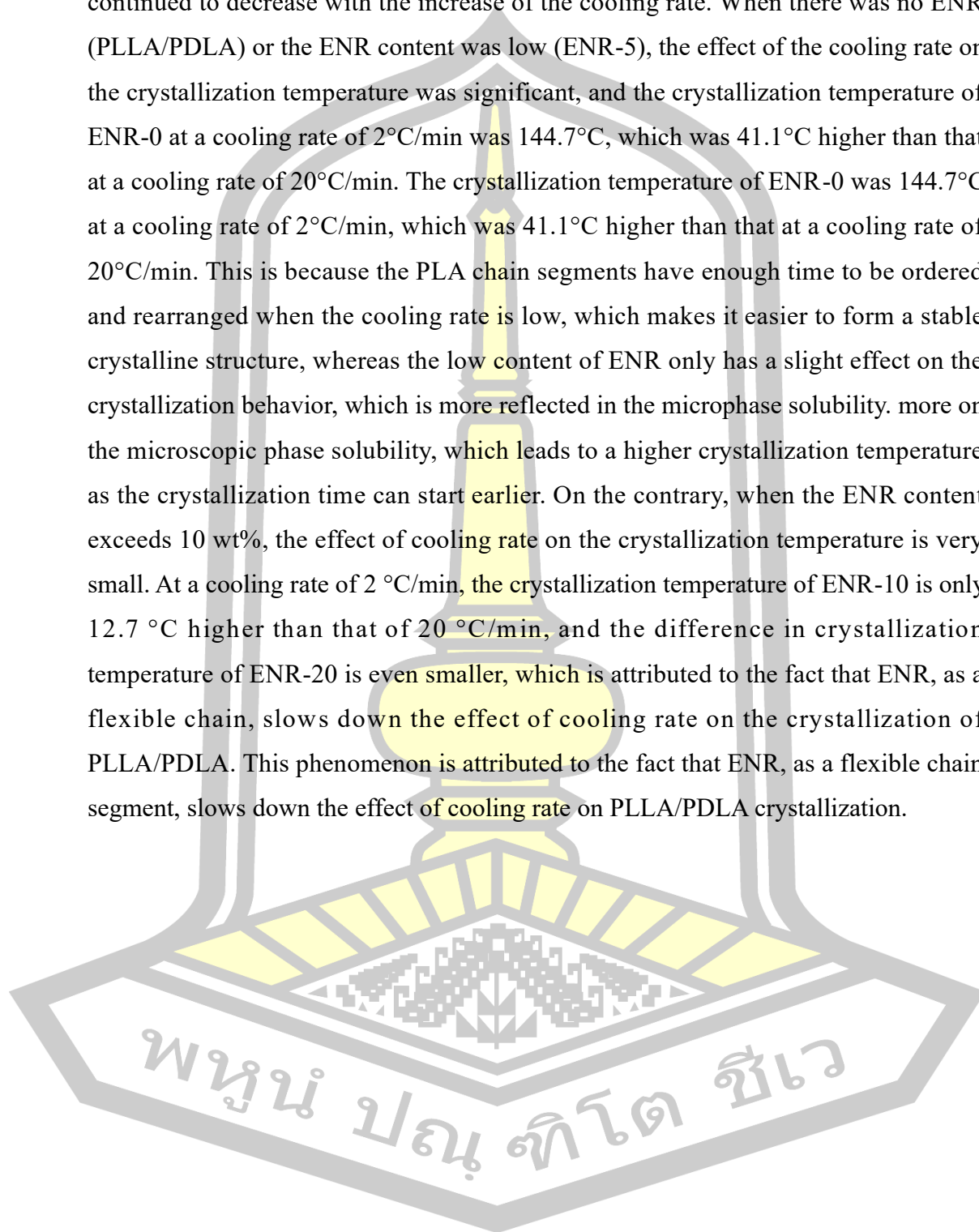
Figure 30 Schematic representation of interactions between PLLA, PDLA, and ENR chains

4.10. Non-isothermal crystallization and melting behavior of PLLA/PDLA/ENR blends

4.10.1 Cooling cycle

Figure 4.17 depicts the DSC thermograms of the PLLA/PDLA/ENR blend for the cooling processes (2, 5, 10 and 20°C/min), and Table 7 summarizes the parameters derived from the DSC curves.

As shown in Figure 4.17, the crystallization temperatures of all the samples continued to decrease with the increase of the cooling rate. When there was no ENR (PLLA/PDLA) or the ENR content was low (ENR-5), the effect of the cooling rate on the crystallization temperature was significant, and the crystallization temperature of ENR-0 at a cooling rate of 2°C/min was 144.7°C, which was 41.1°C higher than that at a cooling rate of 20°C/min. The crystallization temperature of ENR-0 was 144.7°C at a cooling rate of 2°C/min, which was 41.1°C higher than that at a cooling rate of 20°C/min. This is because the PLA chain segments have enough time to be ordered and rearranged when the cooling rate is low, which makes it easier to form a stable crystalline structure, whereas the low content of ENR only has a slight effect on the crystallization behavior, which is more reflected in the microphase solubility. On the contrary, when the ENR content exceeds 10 wt%, the effect of cooling rate on the crystallization temperature is very small. At a cooling rate of 2 °C/min, the crystallization temperature of ENR-10 is only 12.7 °C higher than that of 20 °C/min, and the difference in crystallization temperature of ENR-20 is even smaller, which is attributed to the fact that ENR, as a flexible chain, slows down the effect of cooling rate on the crystallization of PLLA/PDLA. This phenomenon is attributed to the fact that ENR, as a flexible chain segment, slows down the effect of cooling rate on PLLA/PDLA crystallization.



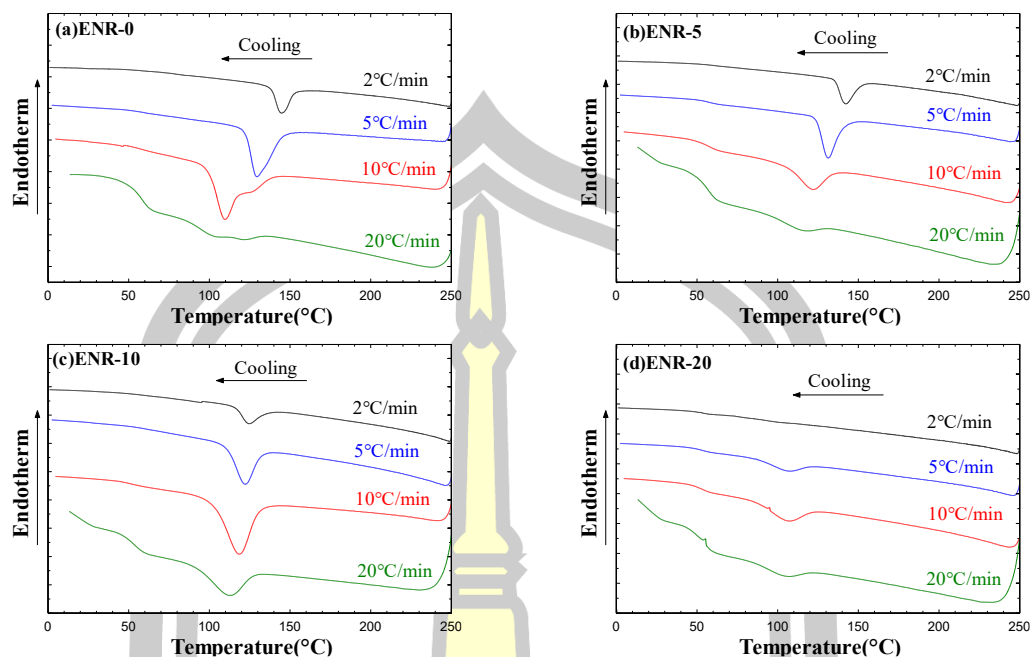


Figure 31 DSC cooling curves of ENR-0, ENR-5, ENR-10 and ENR-20 at various cooling rates (marked on the curves)

Table 7 Cold Crystallization Peak Temperature, Crystallization Half Time of ENR-0, ENR-5, ENR-10 and ENR-20, at various cooling rates

Sample	Cooling Rate (°C/min)	T _c (°C)	ΔH _c (J/g)	t _{1/2} (min)	1/t _{1/2} (min ⁻¹)
ENR-0	2	144.7	-48.1	4.3	0.23
	5	129.4	-53.3	3.2	0.31
	10	109.7	-43.5	2.6	0.38
	20	103.6	-6.9	1.6	0.63
ENR-5	2	142.3	-52.9	5.5	0.18
	5	131.4	-37.6	2.6	0.38
	10	121.5	-17.6	1.8	0.56
	20	115	-4.5	0.9	1.11
ENR-10	2	124.4	-41.9	6.7	0.15
	5	121.9	-43.5	2.6	0.38
	10	118.5	-41	1.7	0.59
	20	111.7	-13.2	0.8	1.25

Table 8 Cold Crystallization Peak Temperature, Crystallization Half Time of ENR-0, ENR-5, ENR-10 and ENR-20, at various cooling rates continue

Sample	Cooling Rate (°C/min)	T _c (°C)	ΔH _c (J/g)	t _{1/2} (min)	1/t _{1/2} (min ⁻¹)
ENR-20	2	-	-	-	-
	5	106.1	-14.2	3.9	0.26
	10	106	-12.9	1.8	0.56
	20	104.7	-4.4	0.9	1.11

The relative crystallinity (X_T) as a function of crystallization temperature (T) can be expressed for non-isothermal crystallization as follows:

$$X_T = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT} \quad (4)$$

where T_0 and T denote the beginning and end crystallization temperatures, and dH_c denotes the exothermic enthalpy of crystallization across an infinitesimal temperature range dT . The relationship between relative crystallinity X_T and temperature T is depicted in Figure 4.18(a-d). It can be clearly seen that with the increase of ENR content the crystallization temperature interval of the mixture is getting smaller and smaller, and when it reaches 20% ENR content, the crystallization temperature of the mixture is basically unaffected by the cooling rate.

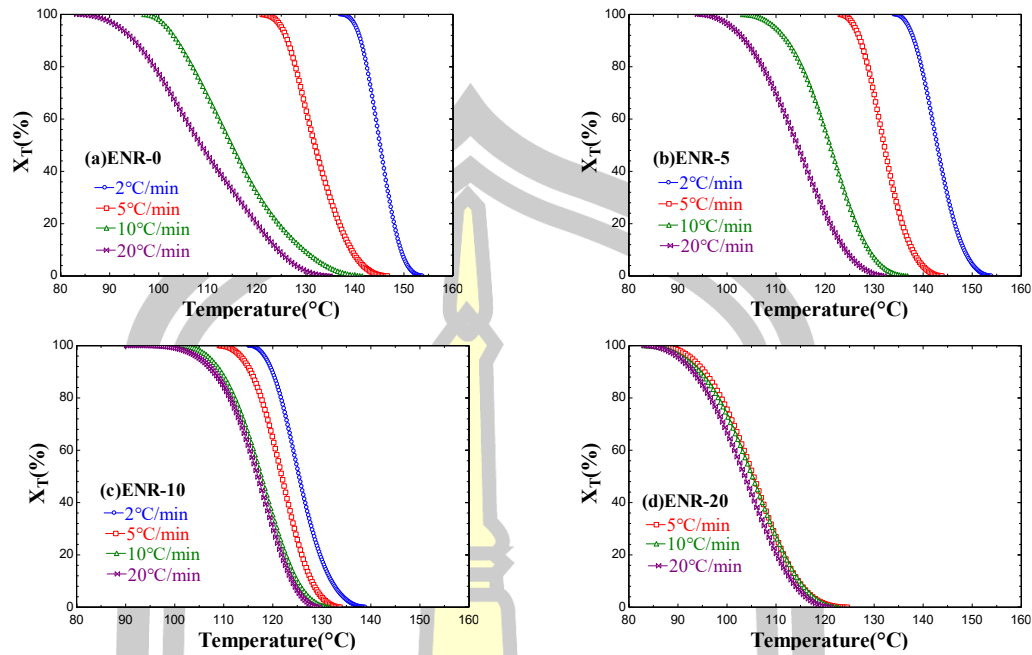


Figure 32 Plots of relative crystallinity (X_T) versus crystallization Temperature (T) for (a)ENR-0, (b)ENR-5, (c)ENR-10 and (d) ENR-20 at various cooling rates

Figure 4.18(a-d) shows the relative crystallinity versus crystallization temperature curves for ENR-0, ENR-5, ENR-10 and ENR-20 at different heating rates. It can be seen from the figure that the curves move to a lower temperature range as the heating rate increases. Figure 4.19 shows the relative crystallinity versus crystallization temperature for various mixtures at a heating rate of 5°C/min. It can be easily observed that the curve shifts to a lower temperature range with increasing ENR content for a given cooling rate, this is because as the ENR content increases, more PLLA molecular chains bind to the PDLA molecular chains to form cubic composite crystals, and this binding leads to a decrease in the temperature required for the cold crystallization process, this finding is important for the development of new PLA materials with specific thermal properties and crystallization behavior.

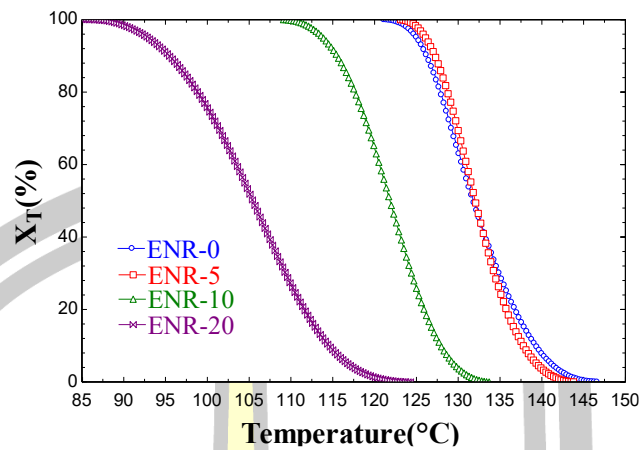


Figure 33 Plots of relative crystallinity (X_T) versus crystallization Temperature (T) for various blends at a cooling rate of 5 °C/min.

The following relationship[96] can be used to convert X_T data to X_t :

$$X_t = \frac{T_0 - T}{\Phi} \quad (5)$$

Where T is the temperature at crystallization time t and Φ represents the cooling rate. After converting the temperature to time, the curves in Figure 4.20(a-d) are obtained. The crystallization curves narrowed with increasing cooling rate for all samples, indicating a shorter time to crystallization completion.

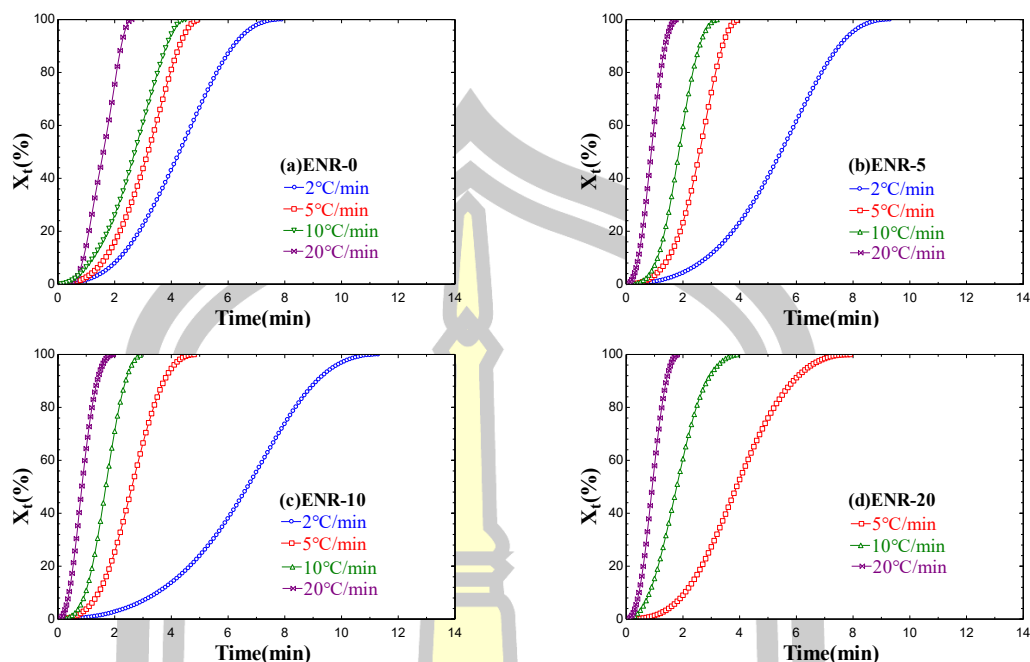


Figure 34 Plots of relative crystallinity (X_t) versus crystallization time (t) for (a)ENR-0, (b)ENR-5, (c)ENR-10 and (d) ENR-20 at various cooling rates

The crystallization half-life ($t_{1/2}$) is the time required to reach 50% of the final crystallinity of the sample. The supporting information in Table 7 summarizes the $t_{1/2}$ values for all samples at different heating rates. The variation of $1/t_{1/2}$ with ϕ for different contents of ENR and PLLA/PDLA blends is also listed in Table 7, from which the effect of Φ and ENR content on the variation of the overall crystallization rate can be clearly seen. It should be noted that the $1/t_{1/2}$ value increases with the increase in cooling rate.

It is important to quantitatively analyze the effect of ENR on the crystallization rate of PLLA/PDLA blends. The crystallization rate parameter (CRP) provides a better assessment of the polymer crystallization rate[97]. The CRP was determined using a linear relationship between $1/t_{1/2}$ and the cooling rate, with a higher slope representing a faster crystallization rate. Figure 4.21 shows a plot of $1/t_{1/2}$ versus cooling rate for all the samples. The CRP values of ENR-0, ENR-5, ENR-10, and ENR-20 were 0.022, 0.051, 0.059, and 0.060, respectively. The highest CRP value was obtained for ENR-20 in the blends, which indicated that ENR was effective in enhancing the crystallization rate of PLLA/PDLA blends.

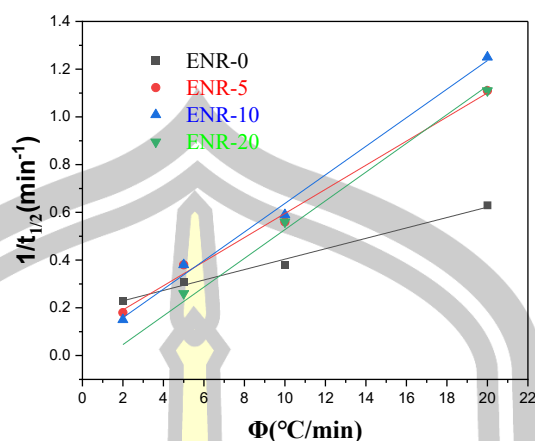


Figure 35 Effect of the ENR loading on the crystallization rate of PLLA/PDLA:
crystallization rate parameter

4.10.2 reheating cycle

Figure 4.22 and Table 8 show the DSC second heating curves and the accompanying parameters for cooling at rates of 2, 5, 10 and 20 °C/min. It can be seen that no cold crystallization peaks were observed at lower crystallization rates when the ENR content was lower than 10 wt%, which suggests that the initial crystallization was more adequate at lower cooling rates, leading to the disappearance of cold crystallization during the second heating process.

Two melting peaks can be observed in the neat PLLA/PDLA (ENR-0) curve, representing homogeneous crystallization (HC) and stereocrystallization (SC), and only one melting peak and two stereocrystallization peaks can be observed when the ENR content is more than 10 wt%, meanwhile, with the increasing ENR, it leads to the decreasing melting point of the copolymer, and the ENR-0 at 2 °C/min The $T_{m,sc}$ value of ENR-0 at 2 °C/min is 220.7 °C, and the $T_{m,sc}$ value of ENR-20 at 2 °C/min is 181.8 °C, which is a whole decrease of almost 39 °C. However, this melting point will still be higher than the melting point of ordinary PLLA or PDLA crystals. This phenomenon is attributed to the fact that the dispersion of ENR introduces some amorphous regions into the system, weakening the ordering of some crystals and leading to a lower melting point.

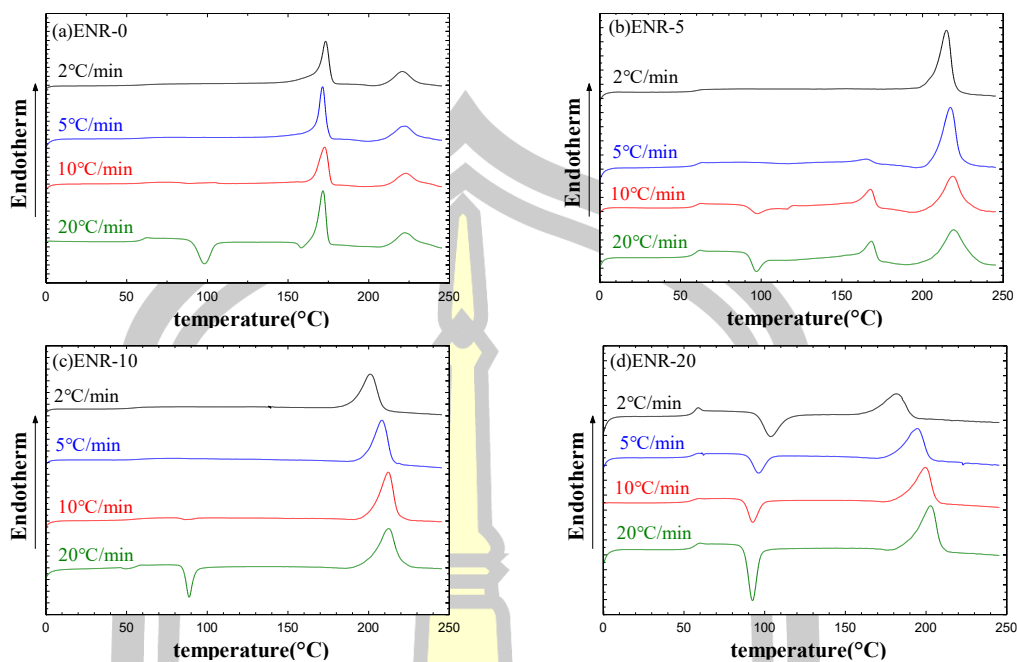


Figure 36 DSC reheating curves at a rate of 10°C/min of ENR-0, ENR-5 , ENR-10 and ENR-20 at various cooling rates (marked on the curves)

Table 9 Reheating parameters at 10°C/ min of ENR-0, ENR-5, ENR-10 and ENR-20 at various cooling rates

Sample	reheating							
	Cooling		Cold crystallization		Homocrystal melting		Stereocomplex melting	
	Rate	Tg	TCC	ΔHCC	Tm,HC	ΔHm,HC	Tm,SC	ΔHm,SC
	(°C/min)	(°C)	(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)
ENR-0	2	-	-	-	173.3	48.6	220.7	27.1
	5	-	-	-	171.4	49.1	222.7	31
	10	-	88.2	-1.5	172.6	39.8	223	27.6
	20	59	98.1	-28.6	171.6	38.2	222.4	30.2
ENR-5	2	59.7	-	-	-	-	215	50.9
	5	59.8	-	-	165.4	3.9	217.3	58
	10	59.1	97.2	-4.8	167.9	11	218.8	46.4
	20	58.5	96.9	-8.8	168.4	14.9	219.3	52

Table 10 Reheating parameters at 10°C/ min of ENR-0, ENR-5, ENR-10 and ENR-20 at various cooling rates continue

Sample	reheating							
	Cooling		Cold crystallization		Homocrystal melting		Stereocomplex melting	
	Rate	Tg	TCC	ΔHCC	Tm,HC	ΔHm,HC	Tm,SC	ΔHm,SC
	(°C/min)	(°C)	(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)
ENR-10	2	53.9	-	-	-	-	201	46.6
	5	56.3	-	-	-	-	208.1	49.7
	10	55.7	86.5	-1.5	-	-	212.3	55
	20	56.5	88.7	-16.2	-	-	212.5	56.7
ENR-20	2	55.2	103.7	-23.6	-	-	181.8	31.1
	5	54.5	96.2	-13	-	-	194.7	36.4
	10	54.5	92.6	-13.4	-	-	199.7	38.6
	20	56	92.4	-28.6	-	-	203	50.1

4.11. The effect of crystallization rate on PLLA/PDLA/ENR blends

4.11.1 Non-isothermal crystallization kinetics of PLLA/PDLA/ENR blends

The non-isothermal crystallization kinetics of polymers can usually be analyzed by the Avrami equation[98]. which in this case takes the form:

$$\lg [-\ln (1 - X(t))] = n \lg t + \lg K \quad (6)$$

Where n is the apparent Avrami index during non-isothermal crystallization and K is the non-isothermal crystallization rate constant. Taking into account the non-isothermal crystallization properties, in order to obtain the normalized cooling rate, the crystallization rate constant needs to be corrected from K to K_c as follows:.

$$\lg K_c = \frac{\lg K}{\phi} \quad (7)$$

where K_c is the corrected crystallization rate constant and $t_{1/2}$ is the crystallization half-time, is expressed as follows:

$$t_{1/2} = \left(\frac{\ln 2}{k_c} \right)^{\frac{1}{n}} \quad (8)$$

Figure 4.23 and Table 9. show plots of $\log[-\ln(1-X_t)]$ versus $\log t$ for PLLA/PDLA and PLLA/PDLA/ENR at different cooling rates, as well as linear fits to the Avrami exponents, n , K_c , and $t_{1/2}$. The value of n reflects the nucleation and growth mechanisms of the polymers, and for polymer crystallization, depending on the nucleation and growth mechanisms, the value of n is usually between 2 and 4. The n values for pure PLLA/PDLA at different temperatures are 2.62 and 3.37, respectively, which suggests that three-dimensional growth heterogeneous nucleation is the main crystallization mechanism. For the composites, the n values range from 2.47 to 3.14, which means that the crystallization mechanism of PLLA/PDLA remains almost constant despite the addition of ENR. Compared with pure PLLA/PDLA, the $t_{1/2}$ values of the mixtures with the addition of ENR decreased when the cooling rate was higher than 5 °C/min, and continued to decrease with the increase of the cooling rate, suggesting that ENR can improve the crystallization rate of PLLA/PDLA to a certain extent. ENR has a certain polarity (derived from epoxy groups) and can interact with the molecular chains of PLLA/PDLA, providing additional nucleation sites and accelerating the crystallization rate of PLLA/PDLA.

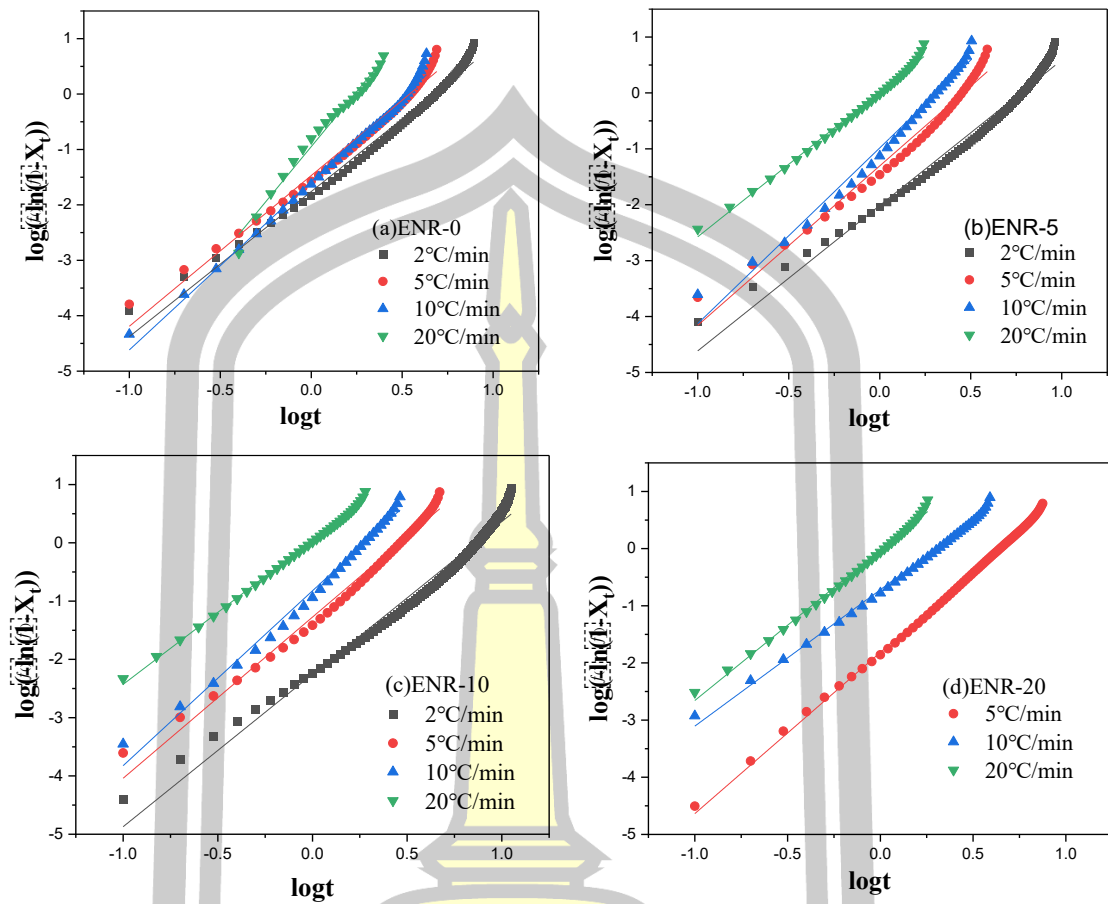


Figure 37 Plots of $\log[-\ln(1-X_t)]$ versus $\log t$ for (a) PLLA/PDLA, (b) PLLA/PDLA/3ENR, (c) PLLA/PDLA/5ENR, (d) PLLA/PDLA/10ENR at various cooling rates

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Table 11 Non-isothermal crystallization kinetics based on Jeziorny model

samples	Φ (°C/min)	n	KC (*102)	t1/2 (min)	R2
ENR-0	2	2.62	13.18	1.88	0.98601
	5	2.72	50.8	1.12	0.98285
	10	3.07	69.66	1	0.98832
	20	3.37	89.64	0.94	0.98452
ENR-5	2	2.6	9.89	2.11	0.97832
	5	2.85	54.7	1.09	0.97429
	10	3.14	79.8	0.96	0.98368
	20	2.59	100	0.87	0.99382
ENR-10	2	2.62	7.5	2.34	0.97928
	5	2.77	55.72	1.08	0.9862
	10	3	82.79	0.94	0.98862
	20	2.47	100	0.86	0.99656
ENR-20	-	-	-	-	-
	5	2.82	43.25	1.18	0.99822
	10	2.49	84.72	0.92	0.99522
	20	2.63	99.77	0.87	0.99489

4.11.2 Activation energy of non-isothermal crystallization of PLLA/PDLA/ENR blends

The non-isothermal crystallization activation energy (ΔE) of a polymer can be calculated using the Kissinger equation [20]:

$$\ln (\Phi / T_c^2) = \frac{-\Delta E_k}{R} (1/T_c) \quad (9)$$

Where: Φ for the heating rate, °C / min; R for the ideal gas constant, J / (mol•K); T_c for the peak crystallization temperature, °C.

The activation energy ΔE_k for the crystallization process, defined by Kissinger, is the activation energy required for the polymer chain segments to migrate

from the melt to the crystal surface, and its magnitude reflects the ease of crystal growth. Figure 4.24 shows the $\ln(\Phi/T_c^2)$ versus $1/T_c$ curves for PLLA/PDLA blends with different contents of ENR. From the slope of the straight line, ΔE_k can be calculated and the results are shown in Table 10. It can be seen that the ΔE values of PLLA/PDLA/ENR mixtures are all smaller than those of pure PLLA/PDLA, indicating that the crystal growth of the mixtures is made easier with the addition of ENR and the ΔE values of the samples are decreasing with the increase of ENR content.

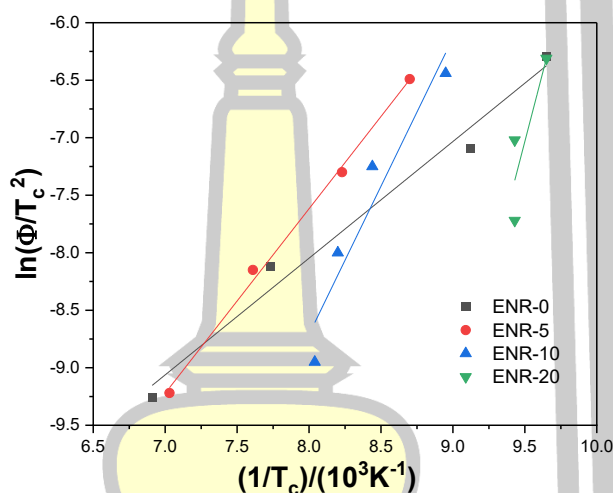


Figure 38 Plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ by the Kissinger equation

Table 12 Activation energy of PLLA/PDLA/ENR

Sample	ENR-0	ENR-5	ENR-10	ENR-20
ΔE_K (KJ•mol ⁻¹)	-299.7	-474.7	-765.5	-1430.1

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Chapter 5 Conclusions and Prospects

5.1 Conclusions

In this study, stereocomplex PLA (stPLA) blends containing natural rubber (NR) and epoxidized natural rubber (ENR) were successfully prepared via melt blending to investigate their crystallization behavior, rheological performance, thermal stability, and interfacial compatibility. The results demonstrated that ENR exhibited superior compatibility with PLA compared to NR, as confirmed by DSC, XRD, POM, FTIR, and SEM analysis. Specifically, ENR incorporation effectively promoted stereocomplex (SC) crystallization while suppressing homocrystal (HC) formation, with SC crystallization becoming dominant at ENR contents above 10 wt%. Isothermal crystallization tests revealed that higher crystallization temperatures inhibited HC formation without significantly affecting SC crystallization, further emphasizing the selective promotion effect of ENR.

Rheological analysis indicated that the addition of ENR markedly enhanced the viscoelastic properties of the blends by increasing the storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$). Water contact angle measurements further showed that ~10 wt% ENR achieved the optimal balance between polarity enhancement and interfacial compatibility. Non-isothermal crystallization kinetics and Kissinger analysis revealed that ENR incorporation significantly accelerated crystallization rates and lowered the activation energy, thereby reducing the barrier for SC crystal formation.

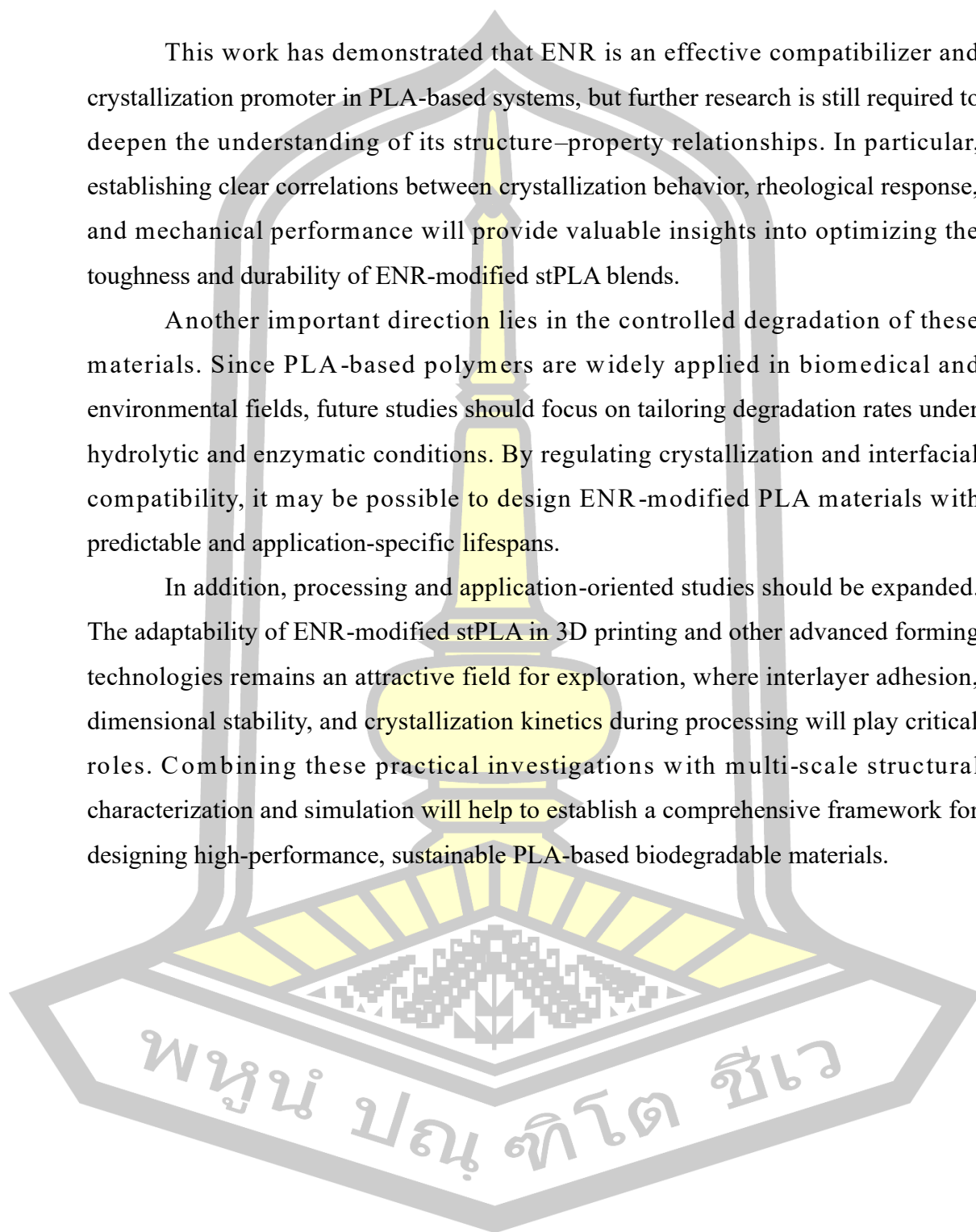
Although TGA analysis showed that ENR incorporation reduced the thermal stability of the blends, with decreasing decomposition temperatures as ENR content increased, the overall improvements in crystallization kinetics, interfacial compatibility, and rheological performance highlight the potential of ENR as an effective compatibilizer and crystallization promoter. Collectively, this work provides a feasible strategy for enhancing the processability, crystallization control, and performance of PLA-based biodegradable materials, thereby broadening their application potential in sustainable polymer engineering.

5.2 Prospects

This work has demonstrated that ENR is an effective compatibilizer and crystallization promoter in PLA-based systems, but further research is still required to deepen the understanding of its structure–property relationships. In particular, establishing clear correlations between crystallization behavior, rheological response, and mechanical performance will provide valuable insights into optimizing the toughness and durability of ENR-modified stPLA blends.

Another important direction lies in the controlled degradation of these materials. Since PLA-based polymers are widely applied in biomedical and environmental fields, future studies should focus on tailoring degradation rates under hydrolytic and enzymatic conditions. By regulating crystallization and interfacial compatibility, it may be possible to design ENR-modified PLA materials with predictable and application-specific lifespans.

In addition, processing and application-oriented studies should be expanded. The adaptability of ENR-modified stPLA in 3D printing and other advanced forming technologies remains an attractive field for exploration, where interlayer adhesion, dimensional stability, and crystallization kinetics during processing will play critical roles. Combining these practical investigations with multi-scale structural characterization and simulation will help to establish a comprehensive framework for designing high-performance, sustainable PLA-based biodegradable materials.



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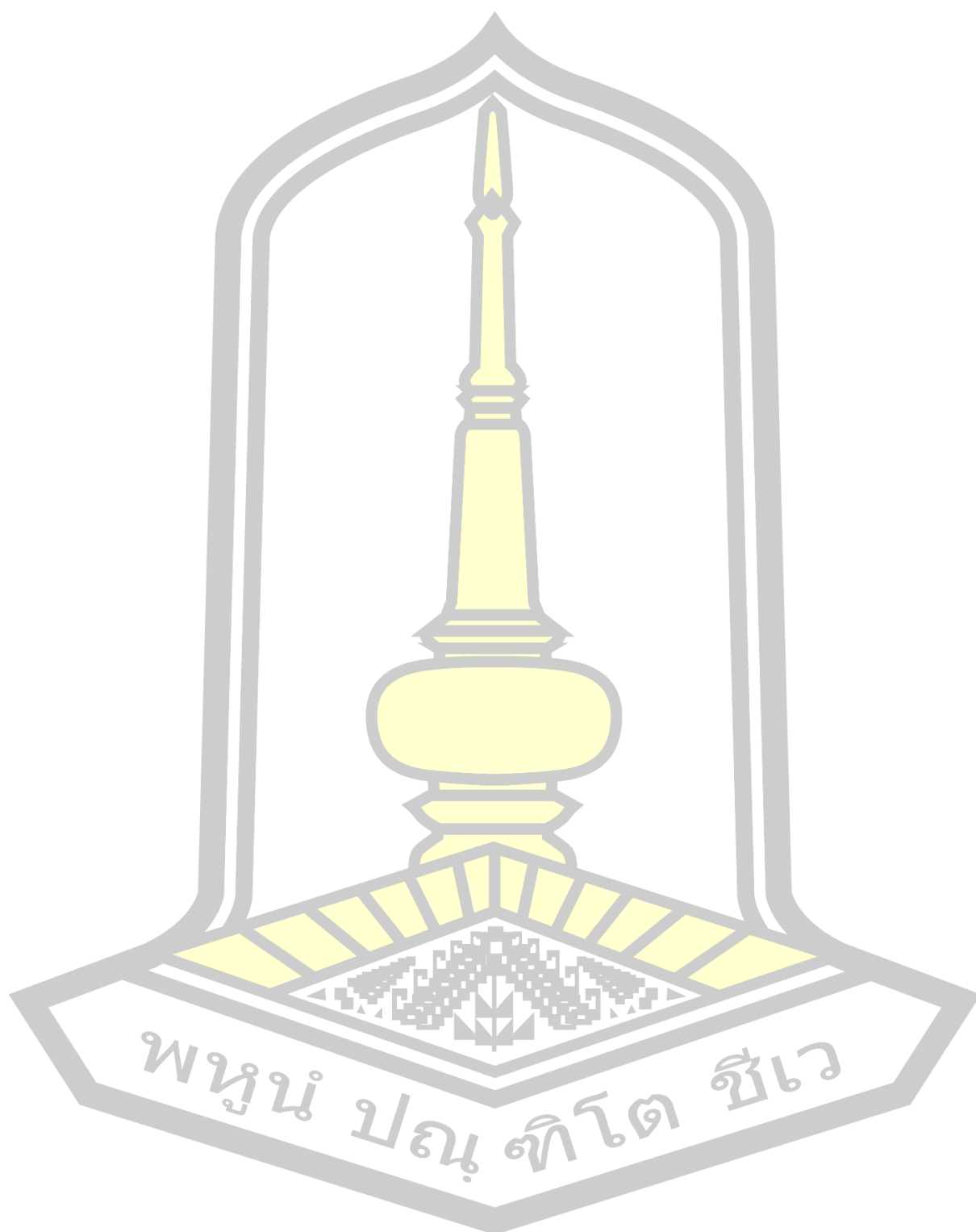
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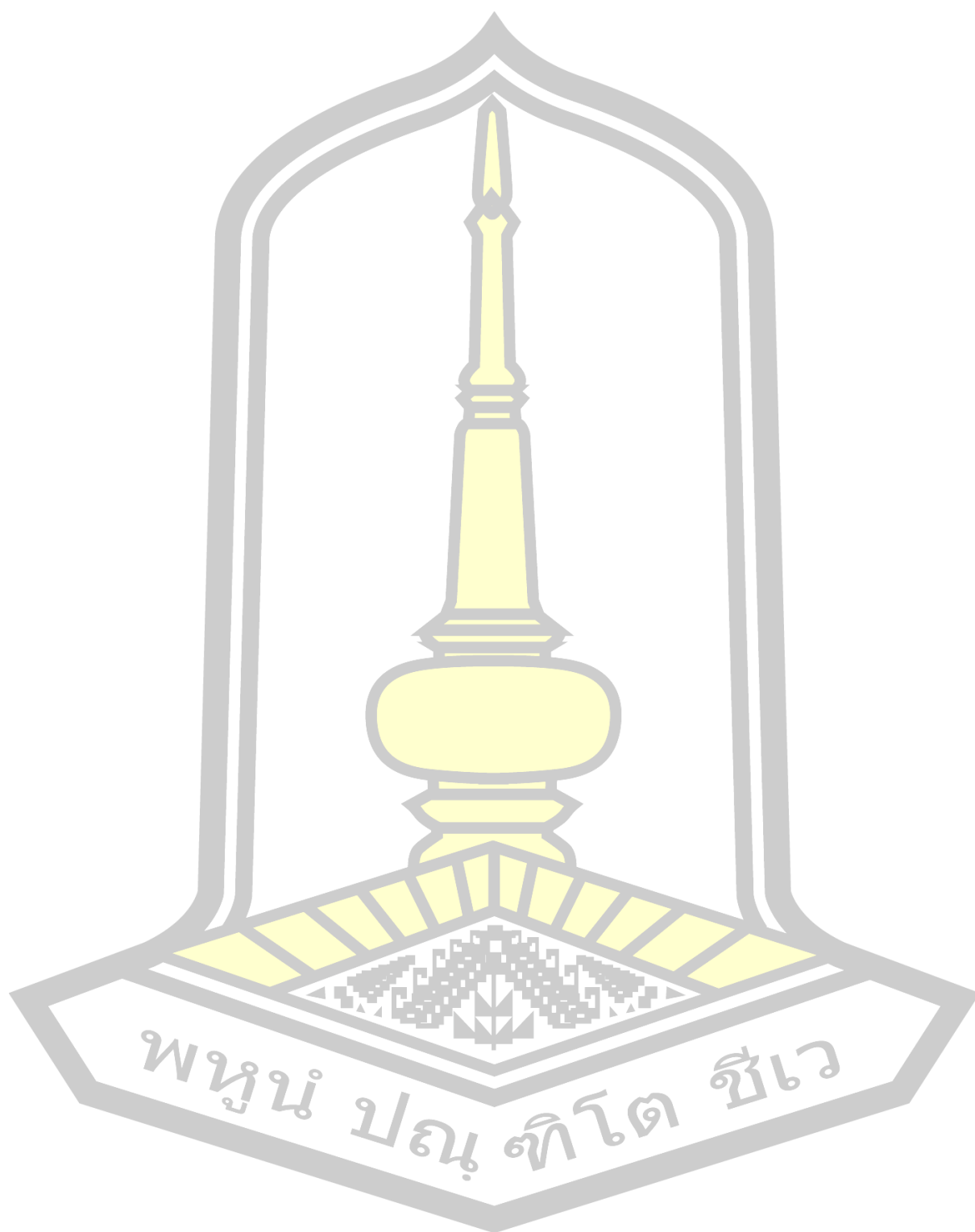
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