

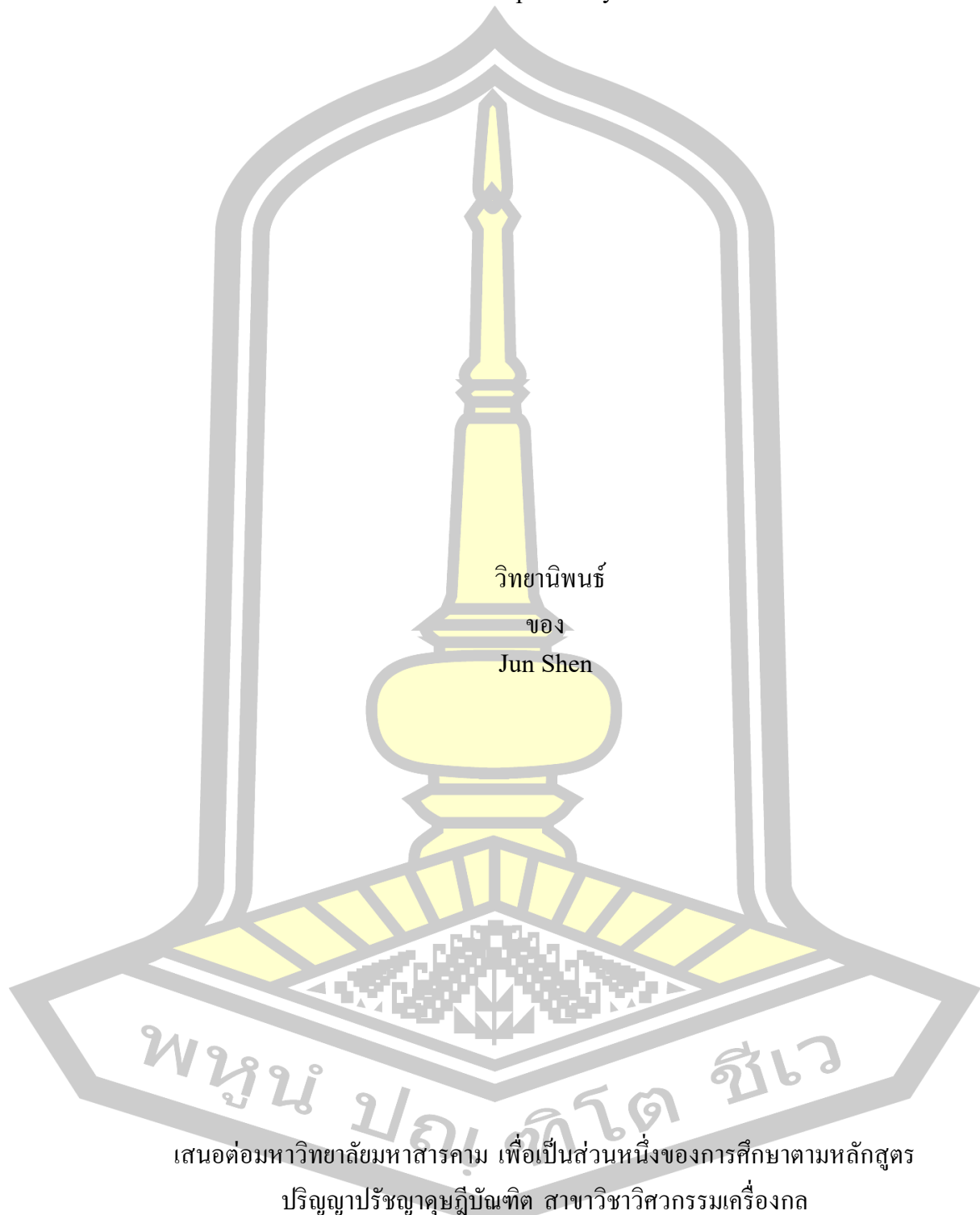
The effect of Poly(butylene succinate) on the structure and properties of
Stereocomplex Polylactide

Jun Shen

A Thesis Submitted in Partial Fulfillment of Requirements for
degree of Doctor of Philosophy in Mechanical Engineering
September 2025

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The effect of Poly(butylene succinate) on the structure and properties of
Stereocomplex Polylactide



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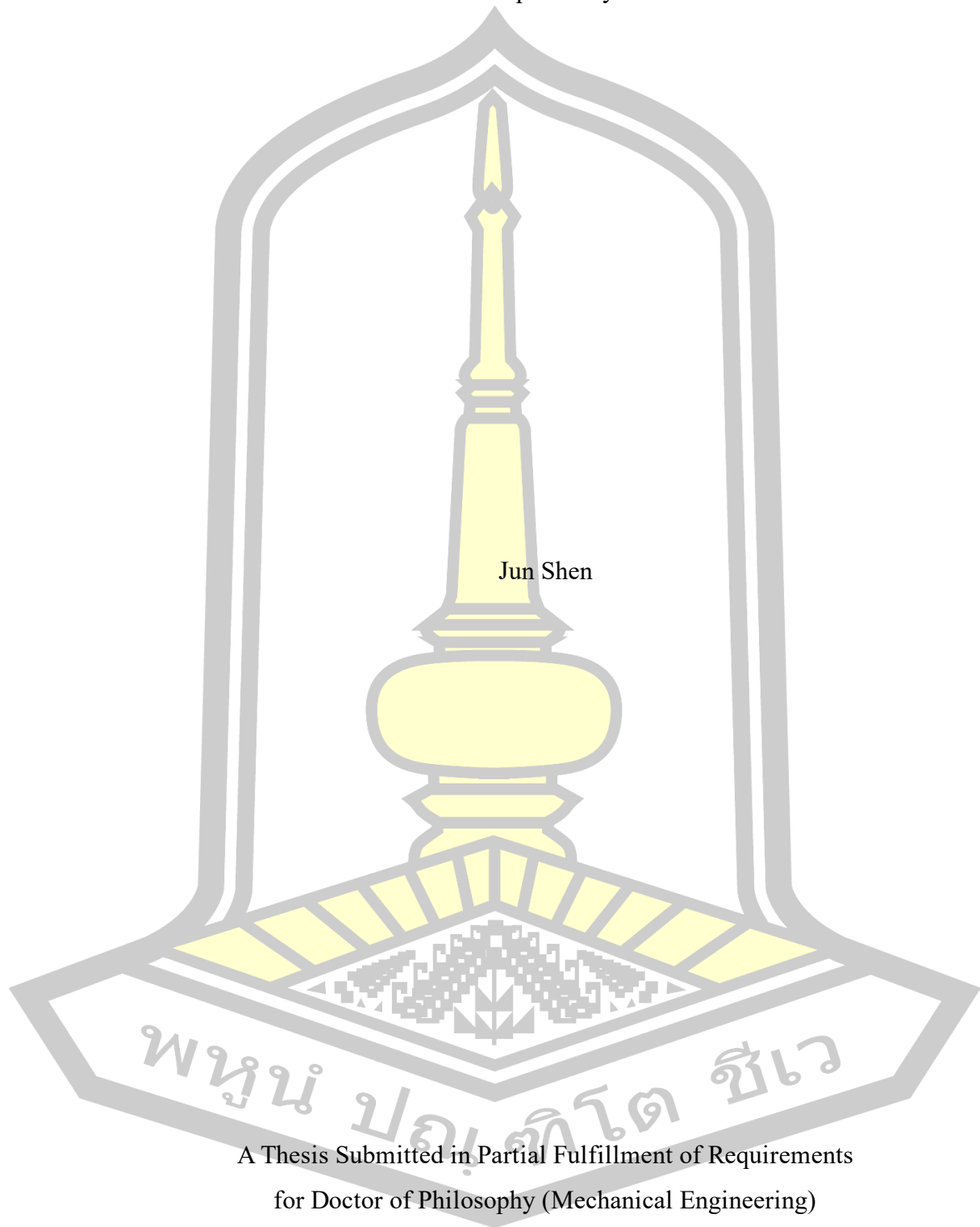
Jun Shen

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September 2025

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DEGREE Doctor of Philosophy **MAJOR** Mechanical Engineering

UNIVERSITY Mahasarakham **YEAR** 2025
University

ABSTRACT

Poly(lactic acid (PLA) is a recognized environmentally friendly and biodegradable green material, but its brittleness limits its wider application. This article investigates the effects of adding polybutylene succinate (PBS) as a toughening agent and epoxidized soybean oil (ESO) as a reactive compatibilizer on the properties of stereocomplex poly(lactic acid (PLLA/PDLA) composites. The results of mechanical performance testing, differential scanning calorimetry analysis, Fourier transform infrared spectroscopy testing, scanning electron microscopy, X-ray diffraction analysis, etc. show that scPLA has partial compatibility with PBS, and PBS can promote the formation of SC crystals. Non isothermal crystallization analysis further indicates that a lower cooling rate is conducive to the formation of SC crystals. This effect is particularly significant at a concentration of 30% PBS, where the trend is most pronounced, simultaneously, the elongation at break is higher.

ESO, as a compatibilizer, can promote the compatibility of PLLA/PDLA with PBS. FTIR testing shows that the formation of the blend is due to the ring opening reaction of ESO epoxy functional groups. DSC testing has shown that ESO can promote the crystallization of PLA stereocomplex (SC) crystals, forming 100% stereocomplex (SC) crystals at a content of 15%, improving the thermal processing performance of the material. The tensile test results indicate that ESO can be used as a plasticizer to enhance the elongation at break of PLLA/PDLA/PBS, but excessive ESO can lead to a decrease in elongation at break.

Keyword : PLLA/PDLA/PBS/ESO, Crystallization kinetics, Tensile test

ACKNOWLEDGEMENTS

From starting school at the age of 5 to completing a PhD at the age of 37, looking back on the journey back, there has been uncertainty along the way. As a Chinese, I felt surprised when I came to Thailand to study as a doctor, which is a bit incredible in my 35 years of step-by-step life.

But when I came to Mahasarakham University in Thailand at all costs, everything here made me feel very comfortable and at ease. First of all, I would like to thank my mentor Professor YOTTHA. I am fortunate to be a student of Professor YOTTHA, who is about the same age as me but has extensive knowledge and abilities. Professor YOTTHA personally guided us in getting started with polymer materials, taught us how to conduct experiments and write papers, and also showed great concern for us in our daily lives, even though the teacher is a family member. I hope that in the future, we can continue to communicate in scientific research, work, and life. Thank you very much.

Thank you to my classmates Li Wenwei and senior sisters. Without your help, I would not have been able to complete my doctoral studies. It was you who provided me with support.

Thank you to the colleagues at Hunan Vocational and Technical College of Mechanical and Electrical Engineering, especially those who studied together at Mahasarakham University. Your life in Thailand is so rich and exciting.

Thank you to my family for their support all the way. Without your hard work behind the scenes, I would not have been able to study abroad. You have worked hard.

The completion of my studies is just the beginning of my research journey. In the future, I will continue to use the knowledge I have learned from Professor YOTTHA to conduct scientific research and achieve better results.

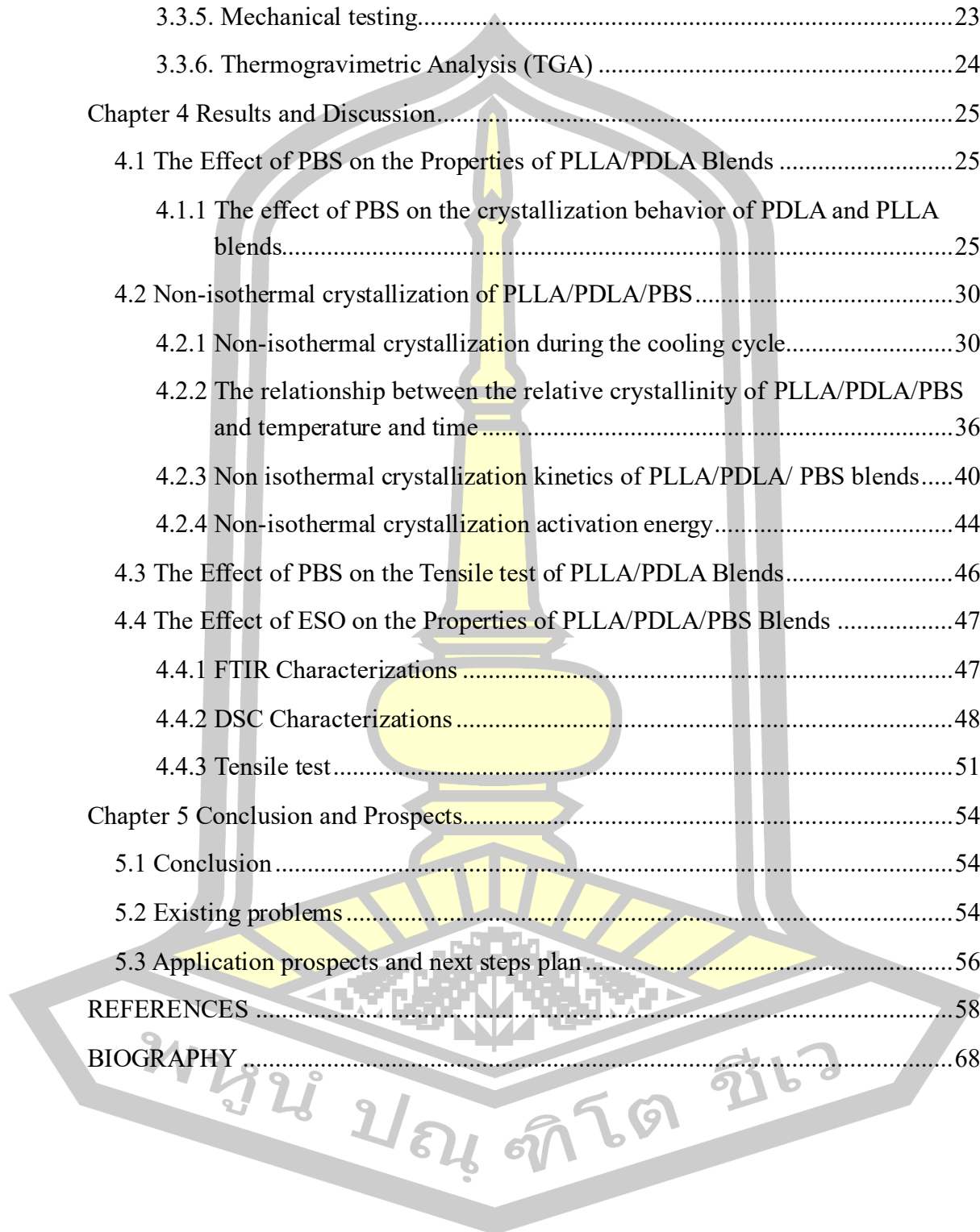
Thank you again to everyone who has helped me, thank you.

Jun Shen

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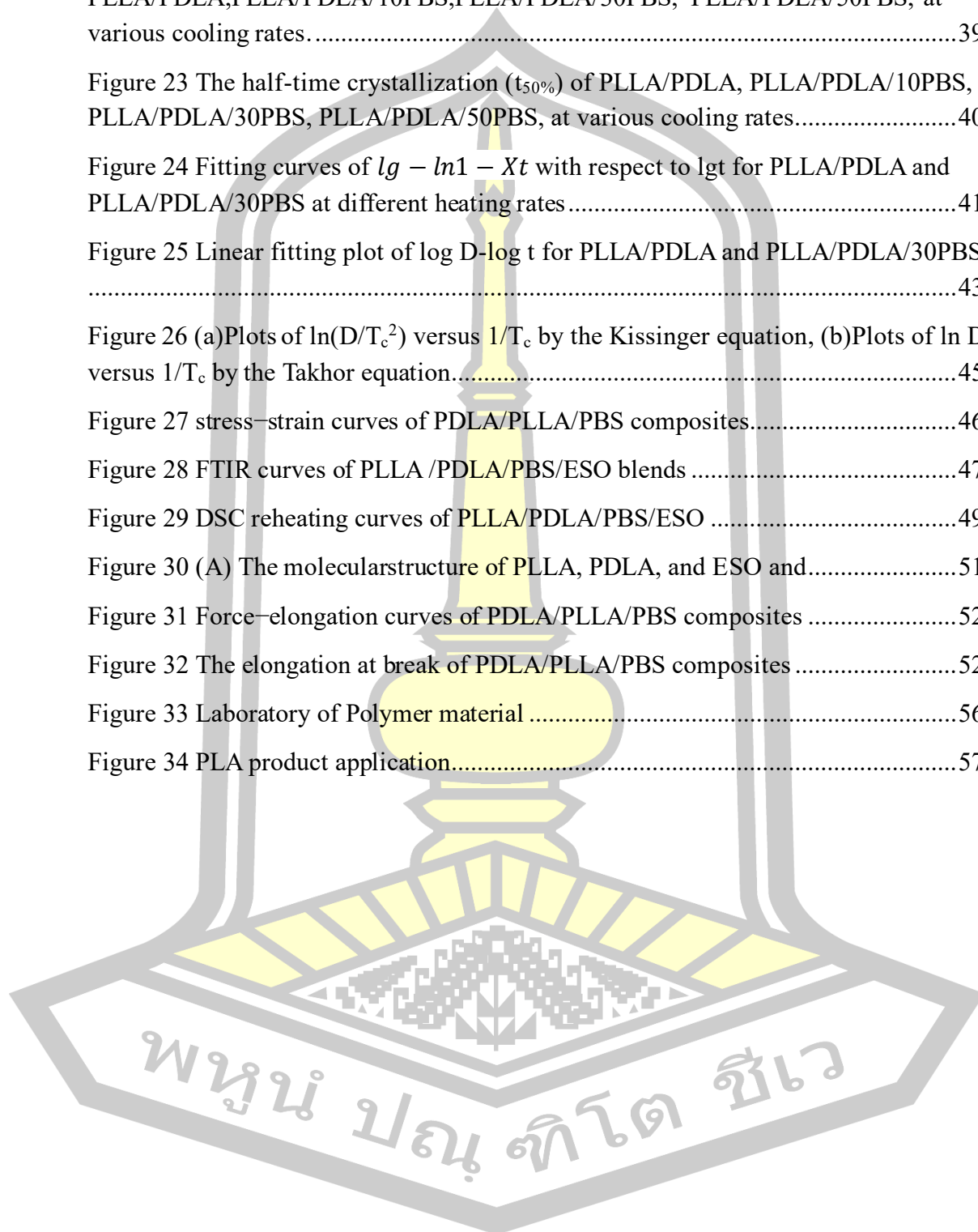
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Chapter 1 Introduction

1.1 Research background

Traditional petroleum-based plastics pose an increasing threat to the environment[1]; thus, using biodegradable polymers instead of petroleum-based non-biodegradable ones has become a current research focus[2, 3]. Polylactide (PLA), a biodegradable polymer with chemical formula $(C_3H_4O_2)_n$. The main raw materials are corn and cassava, etc. It can be completely degraded into carbon dioxide and water in nature and can also degrade in the human body. Polylactide (PLA) is considered one of the most promising alternatives to traditional plastics due to its excellent mechanical properties, biodegradability, and biocompatibility[4]. However, high molecular weight PLA has strong brittleness, low softening point, and rapid degradation/hydrolysis at high temperatures[5], which limits its industrial processing and application[6].

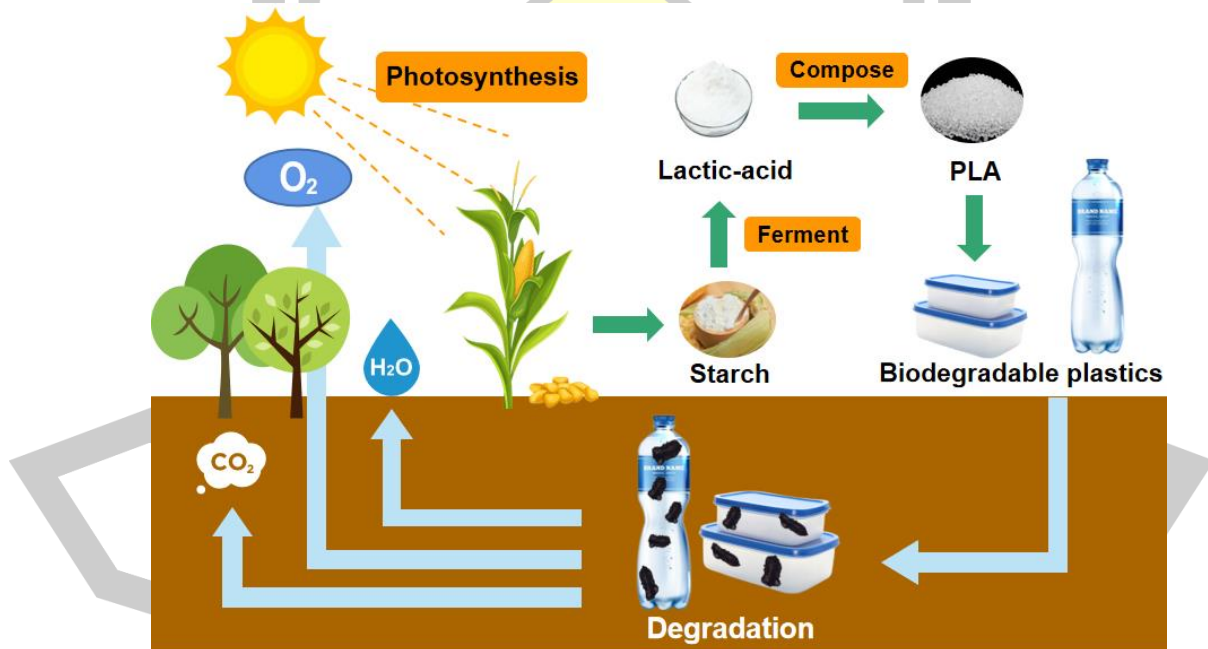


Figure 1 PLA life cycle

Many methods have been attempted to enhanced the brittleness and thermal stability of PLA materials and broaden their range of application, and among them, blending modification is one of the most economical and straightforward methods[7,

8]. Han et al. showed a significant improvement in the toughness of PLA/PBAT blends compared to pure PLA[9]. At the same time, the addition of epoxy soybean oil (ESO) as a solubilizer significantly increased the tensile strength, elongation at break, and notch impact strength of PLA/PBAT blends. Matta et al. prepared PLA/PCL blends using melt blending method. The results showed that the fracture ductility and impact toughness of PLA/PCL mixture were improved[10], and the addition of PCL increased the crystallization rate of PLA, but had little effect on the crystallinity.

PLA has two enantiomers, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), that combine to form polylactide stereocomplex (SC-PLA) through intermolecular hydrogen bonds and stereoselective interactions[11, 12]. SC-PLA has superior thermal properties compared to homopolymer crystals (HC-PLA), with a melting point (T_m) value of approximately 230 °C, which is about 50 °C higher than that of homogeneous crystals (HC-PLA)[13, 14]. Due to the higher melting point and excellent thermal properties of SC-PLA compared to enantiomers, the crystallization behavior of PLLA/PDLA blends has attracted attention. Moreover, the strong interaction between SC-PLA results in good improvements in various properties, such as mechanical properties, thermal stability, durability, mechanical properties, and hydrolysis[15, 16]. As a result, it has good application value in the field[17, 18]. The preparation process, structure, properties, and degradation performance of SC-PLA were well document by Tsuji[19] and Fukushima[20] et al. in the early stages. Seereocomplex crystals (SC) between enantiomers can form more quickly when PLLA-PEG-PLLA and PDLA-PEG-PDLA triblock copolymers with varying PEG flexible segment lengths are produced and melt blended, improving the mechanical and thermal mechanical properties of the final products[21]. SCPLA fibers with a molecular weight more than 300 kDa were quickly created by Pan et al[22]. via a thermally induced process. These fibers have good resistance to hydrolysis and high-temperature degradation. The amorphous region molecular chains of SCPLA were crosslinked by Bai et al. using crosslinking agents added to the high molecular weight enantiomers of melt blending, which improved the product's capacity to recrystallize[23].

PBS belongs to the aliphatic polyester group and is also a green, renewable, and environmentally friendly plastic. Not only does it have heat resistance and a high

glass transition temperature, but it also has high strength and toughness. Therefore, blending PLA and PBS can obtain materials with better comprehensive performance. Lertwongpipat N et al. improved the toughness of PLA by adding PBS[24]. Compared with pure PBS, the bending strength and modulus of the blend were significantly reduced. In PLA/PBS blend samples, the higher the PBS content, the easier it is to soften and bend. When the mass ratio of PLA to PBS is 80/20 and 60/40, the bending modulus of the blended sample decreases from 3.5 GPa to 3.2 GPa and 2.1 GPa, while the bending strength also decreases from 105.3 MPa to 90.9 MPa and 69.1 MPa.

In summary, scPLA is one of the most ideal ecological polymers, but material mixing is needed to achieve toughening and modification. PBS and ESO is this ideal material. At present, there is limited research on PLLA/PDLA/PBS/ESO blend materials. Therefore, it is necessary to conduct a comprehensive study on the structure, mechanics, and thermal properties of PLLA/PDLA/PBS mixture in order to expand its application and development.

1.2 Objectives

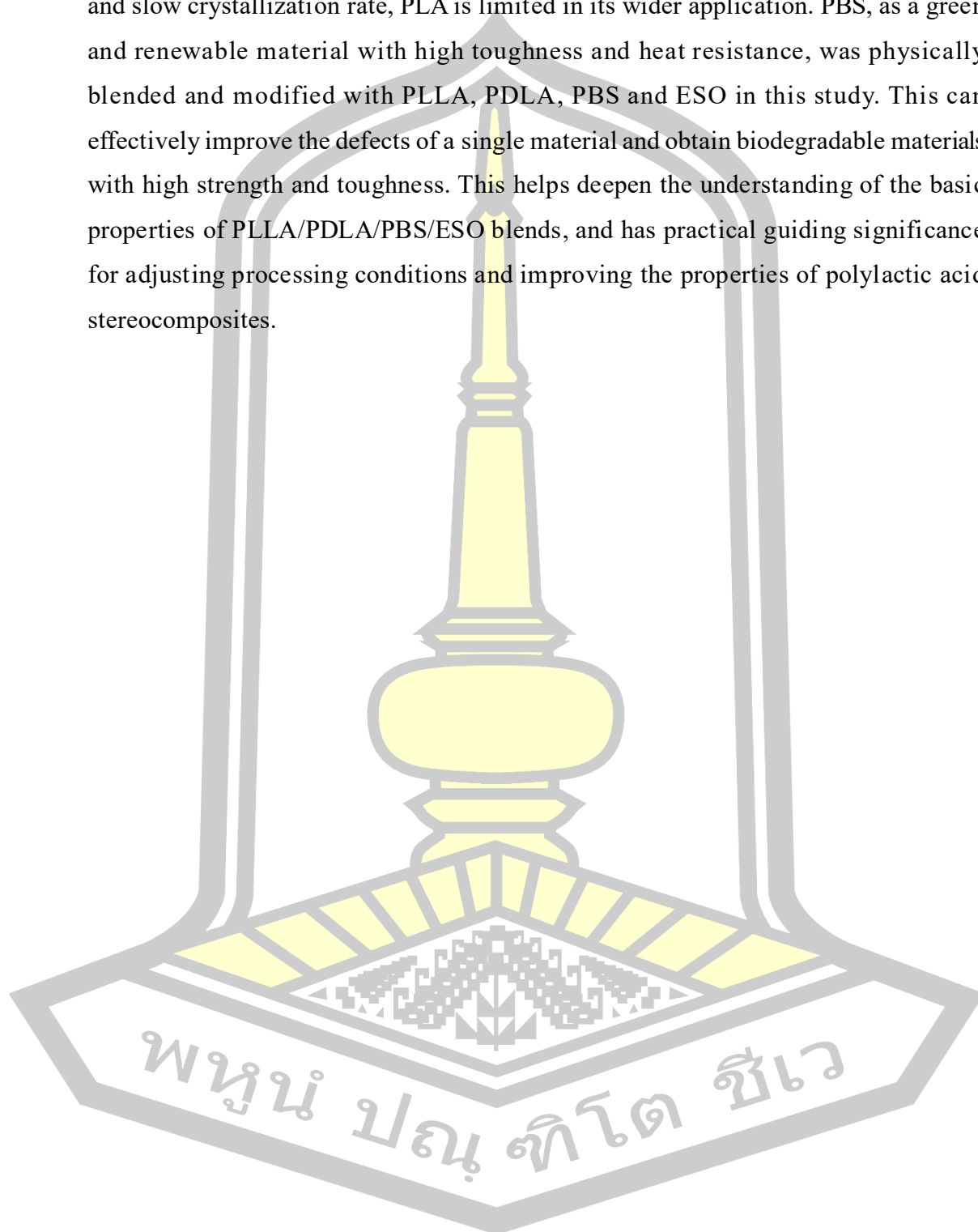
The key Objectives of this research are:

- 1) Prepared equal quantities of PLLA and PDLA blend to form a streocomplex, with effect of PBS 0-50 wt% addition.
- 2) Study on the mechanical properties, and thermal properties of PLLA/PDLA/PBS blend films.
- 3) Prepared PLLA/PDLA/PBS blend(35:35:30), with effect of ESO 0-20 wt% addition.
- 4) Study on the chemical structure, mechanical properties, and thermal properties of PLLA/PDLA/PBS/ESO blend films.

1.3 Benefits of the research

Advocating green and sustainable development, developing and utilizing renewable resources has become a research hotspot in the field of polymers. PLA has the strength of universal plastics and good biocompatibility, and is widely used in the

field of plastic products. However, due to its low elongation at break, poor toughness, and slow crystallization rate, PLA is limited in its wider application. PBS, as a green and renewable material with high toughness and heat resistance, was physically blended and modified with PLLA, PDLA, PBS and ESO in this study. This can effectively improve the defects of a single material and obtain biodegradable materials with high strength and toughness. This helps deepen the understanding of the basic properties of PLLA/PDLA/PBS/ESO blends, and has practical guiding significance for adjusting processing conditions and improving the properties of polylactic acid stereocomposites.



Chapter 2 Literature Reviews

2.1 Research status of PLA

2.1.1 The Structure and Performance of PLA

PLA is a linear, straight-chain polymer, also known as polylactide. In addition to having good biocompatibility and biodegradability, it also has many excellent properties, such as its high melting point (T_m is about 160-185°C), the glass transition temperature is higher (T_g is about 55-65°C)[25], but the values of T_m and T_g are slightly different for PLA of different molecular weights, and the crystallinity is roughly 0-37%. There are three main configurations of PLA, poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and polyracemic lactic acid (PDLLA).

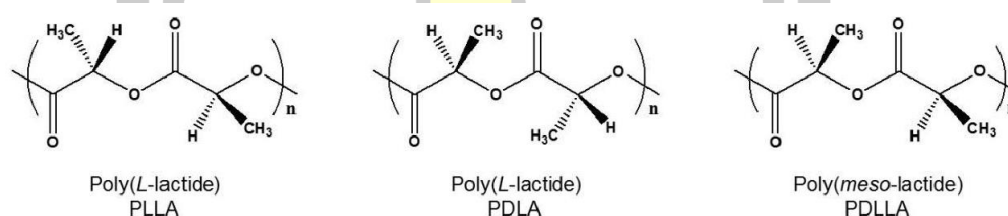


Figure 2 Chemical structure of PLLA\PDLA\PDLLA

PLA is a polymer material with both brittle and hard characteristics, and the mechanical properties of polyethylene terephthalate (PET) and polystyrene (PS) materials are similar. Table 1 shows a comparison of the mechanical properties of the relevant materials[26, 27]. From the table, we can see that the tensile strength, elastic modulus and flexural strength of PLA are better than those of PET and PS, but the elongation at break is much lower than that of PET, indicating that the application of PLA is limited due to the lower toughness of PLA.

Table 1 Comparison of PLLA,PET,PS

Performance	PLA	PET	PS
Tensile strength /MPa	58	55	44
Elastic modulus /GPa	3.7	2.7-4.0	3.0
Elongation /%	4-7	296	3
Impact Strength /J/m	27	60	21
Flexural Strength /MPa	98	87	75
Flexural modulus /MPa	3600	3600	2900
Vicat softening temperature/°C	58	80	99

2.1.2 The application of PLA

In recent years, due to its excellent biodegradability, PLA has been widely used[28], mainly including: (1) Injection products, most of which are disposable items, such as disposable lunch boxes, plastic bottles, milk bottles, and plastic toys; (2) Fiber products, PLA fiber is an environmentally friendly fiber. The fiber fabric made of PLA is very soft, with a silky luster and a good hand feel, making it very comfortable for people to wear; (3) Thin film products can be used for various food packaging bags[29], candy packaging bags, various card films, and various composite processing films. Yakdoui et al. prepared PLA/TiO₂, PLA/Al₂O₃, and PLA/TiO₂-Al₂O₃ nanocomposite films by melt mixing method[30]. The addition of metal oxides improved the heat resistance, barrier properties, mechanical properties, and antibacterial properties of the nanocomposite films. (4) The sustained-release drug carrier. Dissolves drugs in solution or disperses them in the matrix to produce drugs with sustained-release effects. The current research focus of sustained-release drugs is on how to control the release rate of drugs and the accuracy of targeted therapy[31]; In addition to the above fields, polylactic acid products are widely used in automotive parts, electronic commercial products, office supplies, adhesives, and coatings.

2.1.3 PLA modification

In order to improve the comprehensive performance of PLA, there are many modification methods, which can be roughly divided into chemical modification and physical modification. Compared to chemical modification, physical modification

methods are more direct, simple, and effective. Physical modification is mainly divided into several types: blending modification, composite modification, and plasticizing modification. Blending modification is one of the most economical and simple methods for modifying PLA. However, the mixing of incompatible two polymers greatly reduces the performance of the blended material. Therefore, adding an appropriate amount of chain extenders, compatibilizers, and crosslinking agents during the blending process to improve their compatibility has become a common method for obtaining high-performance blend materials.

1) PBAT

Due to its high fracture elongation, good toughness, and thermodynamic stability, PBAT is undoubtedly one of the best materials for toughening PLA. Jiang et al. prepared PLA/PBAT blend materials using melt blending method[32]. The results showed that the melt elasticity and melt viscosity of the blend increased with the increase of PBAT content; The addition of PBAT increased the crystallization rate of PLA, but had little effect on its crystallinity. With the increase of PBAT content, the toughness of PLA was significantly improved[33]. During the preparation of PLA/PBAT blend materials, Han et al. added epoxy soybean oil (ESO) as a solubilizer to improve the miscibility and mechanical properties of the blend[9]. The results showed that the tensile strength, elongation at break, and notch impact strength of PLA/PBAT blends solubilized by ESO were significantly improved. In addition to adding solubilizers, in order to improve the properties of PLA/PBAT blends, Ludwiczak et al. added two types of additives to the blends: chain extender (CE) and nano montmorillonite (MMT)[34]. The addition of chain extenders improves the interfacial adhesion of each component. Due to the layered structure of montmorillonite, the barrier properties of PLA/PBAT/MMT nanocomposites have been significantly improved.

2) PCL

PCL is a linear aliphatic semi crystalline polyester widely used in packaging, agriculture, medical devices, and other fields due to its biodegradability and biocompatibility[35]. Matta et al. prepared PLA/PCL blends using melt blending method. The results showed that the fracture ductility, impact toughness, and loss factor of PLA/PCL mixture were improved[10]. With the increase of PCL content, the

melt elasticity and melt viscosity of the blend increase; The addition of PCL increased the crystallization rate of PLA, but had little effect on its crystallinity. However, the processing window of PLA/PCL blend is narrow, which is not conducive to processing and molding. Jeon et al. used a melt blending method to select glycidyl methacrylate (GMA) as the reactant, and achieved crosslinking at the interface between PLA and PCL by increasing solubility through electron beam irradiation at room temperature[36]. Research has found that the interfacial adhesion of compatibilized blends is significantly improved; The impact strength, thermal stability, and rheological properties of the compatibilized PLA/PCL blend have been improved, and the biodegradability of the solubilized PLA/PCL blend is significantly better than that of pure PLA.

3) PHA

Montes et al. prepared PLA/PHB/TB blend membrane materials with different ratios using natural tributyl glyceride (TB) as a plasticizer and phase solvent by melt blending method[37]. Research has found that PLA and PHB are immiscible; As the TB content increases, the fracture elongation of the blended film increases; Adding PHB to the PLA matrix can improve the water resistance of the blend material, and the optimal performance combination is exhibited when the TB content is 10 wt%. Li et al. prepared PLA/P3HB4HB blend materials using melt blending method, and then subjected them to hot stretching at 90°C to a certain rate[38]. The results show that with the increase of P3HB4HB content, debonding and micropores occur at lower stretching ratios, and the presence of micropores reduces the density of the material. The porosity of the material also increases with the increase of stretching ratio and P3HB4HB content; The unstretched sample does not crystallize, and after stretching, the crystallinity of the sample rapidly increases to 40%, resulting in tensile induced crystallization; The high crystallinity induced by stretching significantly increases the modulus of the material.

4) PPC

PPC is a biodegradable polymer generated by co polymerization of CO₂ and epichlorohydrin, which has good mechanical properties and gas barrier properties. Inhmh et al. prepared PLA/PPC blend materials by melt blending method, and the results showed that with the increase of PPC content, the fracture elongation of the

blend increased[39]. When the PPC content was 30 wt%, the fracture elongation reached 173%, approximately 29 times that of pure PLA, indicating a significant improvement in toughness; PLA and PPC are partially miscible.

5) PLA intermixed with the inorganic filler

To improve the poor thermal stability of PLA, many researchers have added nucleating agents to PLA to enhance its thermal stability. The commonly used nucleating agents currently include SiO₂, talc powder, calcium carbonate, etc. Talc powder is widely used due to its significant nucleation effect and low price. Weaper et al. investigated the effect of talc powder on the mechanical properties and fracture toughness of PLA/PBS blends[40]. The results indicate that talc powder promotes PLA crystallization and hinders the growth of PBS crystallization. The tensile strength, Young's modulus, and impact strength of PLA/PBS/talc powder composite materials also increase with the addition of talc powder; Due to the addition of talc powder, the fracture toughness has been greatly improved.

In addition to the nucleating agents mentioned above, many metals and metal oxides are used to improve the mechanical properties and gas barrier properties of PLA materials. Nanoparticles such as Ag[41], ZnO[42], MgO[43], and TiO₂[44] can effectively regulate the water vapor permeability and oxygen permeability of PLA based composite materials. The above modification methods are all aimed at improving the overall performance of PLA by changing the monomer sequence, structure, and composition of its molecular chains, in order to meet the needs of products suitable for people's production and daily use. In the preparation of thin film materials, it is necessary to improve the toughness of polylactic acid through plasticizer modification or copolymerization synthesis modification.

Labrecque et al. used citrate as a plasticizer for PLA and used a single screw extruder to obtain modified PLA with plasticizer contents of 10%, 20%, and 30%, respectively[45]. Research has found that the glass transition temperature of PLA decreases and the elongation at break increases after the addition of citrate; When the plasticizer content is 20%, the plasticization efficiency is higher. After hydrolysis and enzyme degradation experiments, it was found that low molecular weight citrate increased the enzyme degradation rate of PLA, while the degradation rate of high

molecular weight citrate decreased compared to the degradation rate of unplasticized PLA, indicating that excessive citrate can inhibit the degradation rate of PLA.

Kyung man Choi et al. grafted low molecular weight acrylic acid polyethylene glycol onto PLA through a chemical reaction, and plasticized PLA[46]. The results of nuclear magnetic resonance spectroscopy (NMR), wide-angle X-ray diffraction (WAXD), and solvent extraction testing showed that low molecular weight acrylic acid polyethylene glycol was successfully grafted onto PLA; Through analysis of tensile properties, DSC, DMA, and hydrolytic degradability, it was found that the glass transition temperature (T_g) of PLA modified by grafting decreased by 20 °C, and the Young's modulus decreased from 1.2 GP to 0.4 GP; The elongation at break has increased by 380%.

2.2 Research status of PLA/PBS blend

2.2.1 The Structure and Performance of PBS

PBS is a biodegradable aliphatic polymer with high molecular weight and good thermal stability. Its raw materials mainly come from nature and it is a green, renewable, and environmentally friendly plastic[47]. Its mechanical properties are similar to those of general plastics such as PP. Due to its semi crystalline nature, PBS has both excellent elasticity and high strength. However, PBS is a polyester resin that is prone to hydrolysis reactions. Therefore, when conducting heat treatment, attention should be paid to the influence of moisture on the molecular weight of the material.

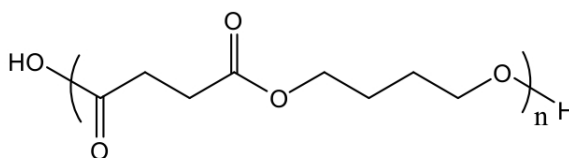


Figure 3 The molecular structure of PBS

The main synthesis methods of PBS include: (1) Direct esterification method, under low temperature conditions, 4-butanediol and succinic acid undergo dehydration reaction to obtain higher molecular weight PBS; (2) The ester exchange method, under high temperature, high pressure, and catalyst conditions, involves the

ester exchange reaction of binary acids and alcohols with a mass ratio of 1:1 to obtain PBS; (3) The cyclic carbonate method involves a chemical reaction between succinic acid and cyclic carbonate under catalyst conditions to obtain cyclic polyester; (4) Chain extension method, using a chain extender to condense the obtained polyester, further improving its relative molecular weight through chain extension reaction.

Due to its non-toxic, biodegradable, and good biocompatibility, PBS is mainly used in the fields of food packaging, agricultural films, disposable catering products, and biomedicine. Among them, the excellent film-forming properties of PBS make it important for applications in planting vessels, vegetation nets, and agricultural films; Secondly, adding inorganic particles to PBS for use in disposable daily necessities[48]; PBS has similar properties to PET, and has biocompatibility and biodegradability. It can also be used for spinning and medical product raw materials.

2.2.2 PLA / PBS mixed modification

In recent years, the researchers have mainly improved the performance of PLA by adding nucleating agents[49], blending with other polymers, and adding chain extenders. As an important aliphatic biodegradable material, PBS has high strength and toughness[50]. PBS modified PLA on the one hand, the material can not lose biodegradable properties[51]; on the other hand, the toughness effect of PBS on PLA is better than that of many other materials, and the mixing processing operation of PBS and PLA is simple. Therefore, in recent years, domestic and foreign scholars have conducted a lot of research on the blending and capacity modification of PLA and PBS[52, 53].

1) PLA/PBS simple blending

Under external forces, brittle polymers experience stress concentration and crack formation due to internal defects[54]. As energy cannot be dissipated in a timely manner, cracks develop into many destructive microcracks[55]. After the addition of PBS rubber particles to the brittle matrix PLA, the direction of crack propagation is changed, and stress is transferred from the brittle matrix to the rubber particles[56]. The microcracks that should have been formed in the brittle matrix then turn into a large number of smaller and less destructive microcracks, Rubber particles, on the other hand, consume energy by deforming or debonding from the matrix, or even

triggering shear yielding, ultimately achieving the goal of toughening. Jia et al. melt blended PLA with PBS, and the tensile strength of the blend increased by 10% to 40% compared to pure PLA, and the initial elastic modulus was also higher than pure PLA or PBS[32]. However, PLA and PBS have poor compatibility, weak interfacial bonding, and are prone to phase separation. In general, with the increase of PBS content in the blend, PBS particles aggregate, and the size of rubber particles in the matrix increases. The phenomenon of two-phase phase separation becomes more obvious, and when subjected to external forces, stress cannot be fully transmitted from the brittle PLA matrix to the rubber particles. The effectiveness of energy consumption decreases, and it cannot effectively prevent the growth of microcracks in the PLA matrix, resulting in a decrease in toughness improvement effect. Bhatia et al. found that when the PBS content exceeded 20%, the tensile modulus, tensile strength, and elongation at break of the blend decreased with the increase of PBS content.

In addition, PBS can affect the crystallization performance of PLA. PBS can reduce the cold crystallization temperature T_{cc} of PLA, increase the crystallization rate of PLA, and increase the crystallinity of PLA. There are two main reasons for these phenomena: one is the plasticizing effect of PBS on PLA, which improves the mobility of PLA chains and accelerates the alignment and orientation of PLA chains; another is the molten PBS droplets act as the crystalline nuclei of PLA. Some scholars have also shown that PBS can neither induce PLA crystallization nor increase the crystallinity of PLA.

2) Plasticization modification of PLA/PBS

In PLA/PBS blends, to improve the compatibility of the two phases and strengthen the interfacial bonding, plasticizers can be added for compatibilization. Due to the presence of a two-phase structure in PLA/PBS blends, their plasticization mechanism is much more complex than that of pure PLA. In PLA/PBS blends, plasticizers not only play a plasticizing role in PBS or PLA respectively, but also reduce the interfacial tension between PLA and PBS phases, promote the dispersion of rubber particles in brittle matrices, reduce the particle size of rubber particles in the matrix, and improve the compatibility between the two phases. Pivsa Art et al[57]. used 10% PEG to alter the phase morphology of PBS in the PLA matrix, reducing the size of PBS particles. Fortunati et al. used ATBC and isosorbide (ISE) to plasticize

PLA/PBS blends, reducing porous structural defects in the blends and enhancing interfacial adhesion. Gigante et al.[58] added ATBC to the PLA/PBS blend system, and the elongation at break increased to 572.7%. Somsunan et al. used polycarbonate (G40) to plasticize PLA/PBS blends, reducing the size of PBS particles in the PLA matrix and increasing the elongation at break of the blend to 72.3%, while reducing the glass transition temperature.

3) Using Non reactive Copolymers to Compatibilize PLA/PBS Blends

The ratio of length and quantity of PBS to PLA in the copolymer plays a regulatory role in the properties of the blend. Supthanyakul et al.[59] found that the addition of 3% PLLA40-PBS28-PLLA40 resulted in the optimal performance of the blend. Long block PBS-PLA can improve the compatibility of PBS/PLA blends more than short block PBS-PLA. At the same time, copolymers can not only enhance the compatibility of PLA and PBS, but also promote crystallization. Zhang et al.[60] found that PBS-PLA reduced the crystallization temperature and crystallinity of PBS/PLA blends. Supthanyakul et al. modified PLA/PBS blends with random poly (succinic acid co lactic acid) (rPBSL) and triblock copolymer PLLA-PBS-PLLA, respectively. They found that random poly (succinic acid co lactic acid) (rPBSL) or triblock copolymer PLLA PBS PLLA can serve as multifunctional additives, namely compatibilizers, plasticizers, and nucleators. The addition of rPBSL resulted in a decrease in T_g of PLA from 52 °C to 43 °C, a significant 4-fold increase in elongation at break, and a decrease in crystallization temperature from 103 °C to 85 °C[61]. rPBSL induced rapid nucleation, rapid growth, and uniform distribution of spherulites. The addition of triblock copolymer PLLA PBS PLLA has a similar effect, but compared to the former, the mechanical properties of the blend are not as good. T_g decreases from 50 °C to 20 °C, and the elongation at break increases by 2 times. This indicates that random copolymers have a better compatibilization effect on PLA/PBS blends.

4) Using reactive Copolymers to Compatibilize PLA/PBS Blends

The reaction mechanism usually includes two types: one is free radical reaction; One type is functional group reaction. Diisopropylbenzene peroxide (DCP)

is the initiator of PLA and PBS to generate free radicals, which react to form cross-linked or grafted copolymers during the mixing process. Its dosage is usually $\leq 0.5\%$ [62]. After Wang et al. added 0.05% to 0.2% DCP, the particle size of PBS in the blend decreased, and the notch impact strength of PLLA/PBS blend greatly increased. However, the modulus and strength monotonically decreased with the increase of DCP content, and the transparency of the blend improved. Ji et al. found that the mechanical properties of the blend were optimal when the DCP content was 0.2% and 0.3%, respectively[63]. Srimalanon et al. found that the addition of DCP significantly improved the fracture elongation and tensile toughness of the blend[64]. At the same time, the cross-linked or grafted copolymers generated during the reaction process play a nucleation role, shortening the total isothermal crystallization time of PLA/PBS blends and increasing the crystallization rate. However, with the increase of DCP content, the cross-linked or branched structures in the blends increase, hindering the movement of molecular chains. The cold crystallization ability of PLLA and the crystallinity of PBS gradually decrease.

MDI, LTI, and LDI couple PLA and PBS through the end group reaction of isocyanate groups with PLA and PBS, improving the compatibility of the two phases and ultimately enhancing the mechanical properties of the blend[65]. After adding LTI, Harada et al. increased the impact strength of the blend from 18 kJ/m² to 50- 70 kJ/m², and laser scanning confocal microscopy (LSCM) detected an increase in the number of PBS particles and a decrease in their size.

In addition, some other polymers with active functional groups are used to enhance the compatibility of PLA/PBS blends. Chen et al.[48] used organic clay (TFC) with epoxy functional groups to enhance the compatibility of PLA/PBS blends, and the results showed that 2% TFC reduced the dispersed phase size from 1.8 to 0.59 μm , enhancing the interfacial interaction between the two phases.

2.3 Research status of scPLA

In 1987, Ikada[66] discovered a complex of L-poly(lactid) (PLLA) and D-poly(lactid) (PDLA) - stereocomplex PLA (scPLA). From then on, people gradually understood scPLA and conducted in-depth research. ScPLA has superior thermal

performance compared to homopolymer crystals (PLLA or PDLA), with a melting point (T_m) value of approximately 230°C, which is about 50°C higher than that of homogeneous crystals (HC PLA). The strong interaction between scPLA results in significant improvements in various properties compared to pure PLLA or PDLA, such as mechanical properties, thermal stability, durability, mechanical properties, and hydrolysis properties. Therefore, it has great application value in various fields[67, 68].

1) The crystallization behavior of structured composite crystals

Structured composite crystals not only affect the morphology of polylactic acid spherulites, but also have a profound impact on the crystallization kinetics of polylactic acid[69]. Many scholars have found that orthorhombic composite crystals can serve as nucleating agents, significantly improving the crystallization kinetics of polylactic acid. When equal mass fraction PLLA is blended with PDLA, polylactic acid spherulites can be rapidly formed, the induction period of spherulites is shortened, and the growth rate of spherulites is significantly increased. Zhang et al. found that the rapid formation and significant increase in growth rate of spherulites are related to the hydrogen bonding of methyl oxygen and hydroxyl oxygen[70].

2) The application of scPLA

Biodegradable membrane; Biodegradable films with a structured composite structure based on polylactic acid can be prepared by solution coating method[71]. If the volatilization rate of molecular weight ingenuity agents is too high, it will hinder the formation of stereocomposite structures, resulting in low crystallinity of the obtained film and a large amount of homo crystals[72]. Although polylactic acid films containing stereocomposite structures can also be obtained by melt casting, the content of PLLA and PDLA must still be controlled.

Biodegradable fibers: Murdoch et al. prepared polylactic acid fibers containing orthostatic composite structures through melt spinning, and Tsuji mixed equal mass PLLA and PDLA in chloroform to prepare two types of polylactic acid fibers containing orthostatic composite structures, dry and wet[73].

Biodegradable microspheres: Loomis et al. prepared injectable microspheres with a stereocomposite structure containing cyclopropylmethy -lenediamine using an oil-water solvent evaporation method. The release rate varied depending on the

medium. The lag times for the release of cyclohexanone from microspheres in water, acid, and buffer solutions are 200230 and 240 hours, respectively. The drug release rates were 46 and 48355, respectively. De Jong et al. prepared the hydrogel with stereocomposite structure, and found that it can release the residual protein in six days[74]. Slager et al. also found that DDS particles with stereological complexes can be prepared from peptides containing L-configured, L-configured leuporelin, and PDLA[75].

Biodegradable hydrogel: The stereocomposite polylactide hydrogel can be placed in an aqueous medium by block or graft copolymers containing hydrophilic groups, L-lactyl unit sequences or D-lactyl unit sequences. The A-B diblock and A-B-A triblock copolymers of the enantiomeric polylactic acid (A) and polyethylene glycol (B) can be prepared into a hydrogel containing stereocomposite[76, 77]. On the other hand, Watanabe et al. prepared polylactic acid membranes with porous structures using PMBLA and PMBDLA, and discovered the morphology of cell adhesion and porous scaffolds[78].

Nucleating agent: Many scholars have found that adding a small amount of PDLA to PLLA can form orthorhombic composite crystals, which can act as heterogeneous nucleation points[79]. This nucleating agent can increase the number of polylactic acid spherulites per unit volume and the total crystallization rate of polylactic acid, but cannot change the growth rate of spherulites[80].

3) The performance of scPLA

Tsuji et al. improved the mechanical properties of PLA, such as tensile strength, Young's modulus, and elongation at break, by increasing SC crystallization[81]. Sarasua et al.[82] investigated in detail the effects of processing conditions and the blending composition of high molecular weight PLLA/PDLA on the crystallization type, crystallinity, and tensile properties of the product. They obtained scPLA products with various crystallinity and crystal forms by non isothermal curing of melt blended PLLA and PDLA on compression molded plates. Through tensile tests, the Young's modulus values of the products were found to be 3.5-4.2 GPa, strength values to be 62-71 MPa, and elongation at break to be 1-5%. The tensile performance is related to the composition and crystallinity of the blend, specifically manifested as: the Young's modulus of products with different

crystallinity is almost constant, while the ductility decreases with increasing crystallinity, and the fracture strength does not further improve after crystallinity exceeds 10%. Under the same curing conditions, the Young's modulus of SCPLA increases by about 25% compared to pure PLLA, but the ductility correspondingly decreases. On the other hand, by adding PDLA block copolymers containing flexible segments and blending them with PLLA, the molecular weight of the soft segments and the composition of the blend can be optimized, resulting in a semi crystalline structured composite with significantly improved modulus and strength. Sarasua et al.[83] 1:1 blended PLLA and PDLA with different molecular weights, and then subjected them to specific heat treatment to prepare almost completely structured films with high crystallinity, and compared their mechanical properties with non blended films. The results showed that the strength and toughness of the 1:1 blend were significantly higher than those of the non blend film, and were independent of molecular weight.

Tsuji et al.[84] measured the water vapor permeability parameter P of SCPLA films with crystallinity between 14-23%, which is lower than that of pure PLLA and PDLA films with crystallinity between 0-30%. When the crystallinity is 0-30%, the P values of pure PLLA, PDLA, and SC membranes rapidly decrease with the increase of crystallinity; The P value slowly decreases with the increase of crystallinity within the range of 30-100%. Interestingly, the mixed membrane of PLLA and PDLA can also delay water vapor permeation in a completely amorphous state. They explained this permeation phenomenon using the Nielsen model, assuming that the value of Nielsen model α in PLLA, PDLA, and mixed membranes ranges from 1 to 2.5. Combined with the study of SC crystal structure by Sarasua et al., it can be concluded that the correlation between P value and crystallinity is: when the crystallinity exceeds 30%, the amorphous region in the film is mainly composed of rigid amorphous regions, and the permeability is low at this time; When the crystallinity is between 0-30%, the amorphous region in the membrane is mainly mobile and amorphous, with high permeability[85].

Chapter 3 Research Methodology

3.1 Experimental materials

Total Corbion PLA (Thailand) Ltd. provided PLLA and PDLA. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the PLLA and PDLA were determined using gel permeation chromatography (GPC). Tetrahydrofuran (THF) was used as eluent. Table 2 summarizes the materials characterization. Polybutylene succinate (PBS), 1020MD, with a melt flow rate of 25 g/10 min, purchased from Showa Electric Co., Ltd. in Japan. RCI Lab scan Limited, Thailand, provided chloroform (CHCl_3).

Table 2 Materials Characterization

	PLLA	PDLA
Code	L130	D070
Optical Purity	$\geq 99\%$ (L-isomer)	$\geq 99\%$ (D-isomer)
Weight-average molecular weight (M_w) (GPC)*1	1.68×10^5	0.87×10^5
M_w/M_n	2.02	1.73

*1 The GPC column was calibrated using the standard polystyrene with tetrahydrofuran (THF) as eluent at room temperature.

3.2 Material preparation

To prepare the sample, PLLA and PDLA were dried in a vacuum oven at 80°C for 24 h. PLLA/PDLA(50:50) combined with varying amounts of PBS as shown in Table 3 were dissolved at a concentration of dissolve the material in 1 chloroform at a ratio of 1:10. The materials were then under vigorous stirring. The solutions were then cast onto petri-dishes, followed by solvent evaporation at room temperature for approximately 3 days and the obtained sample was further vacuum dried to constant weight. Final films thickness was approximately 0.5 mm.

Table 3 Composition of PLLA/PDLA (50/50) with added PBS.

Sample	PLLA(wt%)	PDLA(wt%)	PBS(wt%)
PLLA/PDLA	50	50	0
PLLA/PDLA/10PBS	45	45	10
PLLA/PDLA/20PBS	40	40	20
PLLA/PDLA/30PBS	35	35	30
PLLA/PDLA/40PBS	30	30	40
PLLA/PDLA/50PBS	25	25	50

Table 4 Composition of PLLA/PDLA (50/50)/PBS with added ESO.

Sample	PLLA (wt)	PDLA (wt%)	PBS (wt%)	ESO (wt%)
PLLA/PDLA	50	50	0	0
PLLA/PDLA/30PBS	35	35	30	0
PLLA/PDLA/30PBS/5ESO	35	35	30	5
PLLA/PDLA/30PBS/10ESO	35	35	30	10
PLLA/PDLA/30PBS/15ESO	35	35	30	15
PLLA/PDLA/30PBS/20ESO	35	35	30	20



Figure 4 Material dissolution and mixing

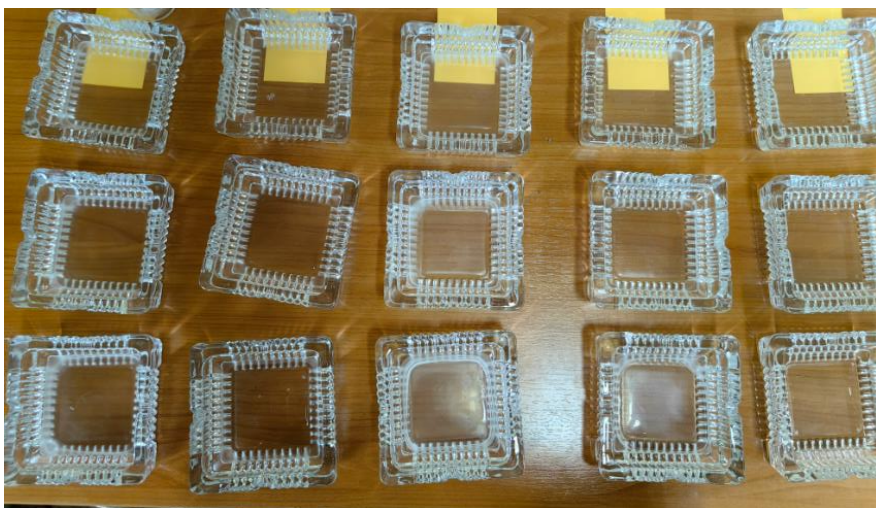


Figure 5 Sample drying

3.3 Testing and Characterization

3.3.1. Fourier transform infrared spectroscopy (FTIR)

Details of the components of the chemical structures of the blends were obtained with a Perkin Elmer Frontier FTIR spectrometer, scanned from 400 to 4000 cm^{-1} , in the attenuated total reflection mode.



Figure 6 Perkin Elmer Frontier FTIR spectrometer

3.3.2. X-ray diffraction analysis (XRD)

Sample crystallinities were determined from X-ray diffraction with an Analytical Bruker/D8 Advance BrukerBioSpin (Cu K α line source, filtered with a thin Ni filter, scanned at 2°/min, 2 θ from 5-40°). Film samples were mounted on the XRD platform and the computer-controlled goniometer was run in wide-angle mode.



Figure 7 D8 Advance BrukerBioSpin

3.3.3. Differential scanning calorimetry (DSC)

This experiment used a DSC (Pyris Diamond DSC4000, MA, USA) to conduct thermal analysis of the sample. In the experiment, high-purity N₂ was used as the protective gas, and 4-5mg sample was placed in an aluminum crucible.



Figure 8 Pyris Diamond DSC4000

1. For the experiment, we selected two testing procedures and measuring techniques, as follows: The effect of PBS on the crystallization behavior of PLLA/PDLA blend was studied by heating the samples from 0 °C to 250 °C at a heating rate of 10 °C/min and keeping them at a temperature for 3 minutes to eliminate any thermal history. Then, the samples were cooled down at a rate of 10 °C/min to 0 °C. After that, the samples were heated from 0 °C to 250 °C again at a heating rate of 10 °C/min to 250 °C (reheating cycle). The DSC scanning curve, melting temperatures and their enthalpies and crystallization temperatures and their enthalpies were recorded.
2. The samples were tested for non isothermal crystallization behavior at different cooling rates. To remove the thermal history, samples were heated from room temperature to 250 °C at a heating rate of 10 °C/min, and hold it for 3 minutes. They were then tested for non-isothermal crystallization by reduce the temperature from 250C to 0 °C at different cooling rates 2 °C/min, 5 °C/min, 10 °C/min and 20 °C/min. After that, the samples were heated from 0 °C to 250 °C again at a heating rate of 10 °C/min to 250 °C (reheating cycle). The DSC scanning curve, melting temperatures and their enthalpies and crystallization temperatures and their enthalpies were recorded.

The cold crystallization temperature and enthalpy ($T_{cc}, \Delta H_{cc}$), homo temperature and enthalpy ($T_{m,hc}, \Delta H_{m,hc}$) and stereocomplex melting temperature and enthalpy ($T_{m,sc}, \Delta H_{m,sc}$) were all measured. Eq.1-3 was

used to compute the degree of crystallinity of stereocomplex ($X_{c,sc}$), homocrystals ($X_{c,hc}$) and the total degree of crystallinity (X_c), respectively .

$$X_{c,sc}(\%) = 100\Delta H_{m,sc}/142 \quad (1)$$

$$X_{c,hc}(\%) = 100\Delta H_{m,hc}/93.2 \quad (2)$$

$$X_c(\%) = X_{c,sc} + X_{c,hc} \quad (3)$$

3.3.4. Scanning electron microscopy (SEM)

0.3 mm thick films were cryogenically fractured crosssection surface to expose the internal structure, sputtered with a ~ 20 nm layer of gold and SEM images were captured by SEM (TM4000Plus Tabletop Microscope, HITACHI) under 1000× magnification.



Figure 9 TM4000Plus Tabletop Microscope, HITACHI

3.3.5. Mechanical testing

15 mm×50 mm samples were cut from the films. The modulus of elasticity, tensile strength, and elongation at break were measured at 25 ± 2 °C on a tensile tester (MCT-1150, tensile machine. AiAnde. Japan) at a crosshead speed of 2 mm/min. Means and standard deviations for five replicates of each sample were reported.



Figure 10 MCT-1150 tensile machine. AiAnde. Japan

3.3.6. Thermogravimetric Analysis (TGA)

Thermal properties were measured by TGA (PerkinElmer, TGA4000, MA, USA) from 30 to 600 °C at 10 °C/min under a constant N₂ flow. Each test used 10-15 mg of the films. Mass loss was recorded and normalized against the initial mass. The temperature at 5 % weight loss (T5%) was reported as the decomposition temperature.



Figure 11 PerkinElmer, TGA4000

Chapter 4 Results and Discussion

4.1 The Effect of PBS on the Properties of PLLA/PDLA Blends

4.1.1 The effect of PBS on the crystallization behavior of PDLA and PLLA blends

1) First Heating cycle

The DSC analysis of the PDLA/PLLA sample, shown in Figure 12(a), revealed a singular melting peak around 230°C, indicating the formation of stereocomplex crystals [86]. Neat PBS, on the other hand, displayed a melting peak within the 100–110°C range. When the PBS content was below 30%, the composites appeared to exhibit miscibility, as no distinct PBS peak was observed. Nevertheless, when the PBS content reached 30% or higher, a distinct melting peak of PBS at 100–110 °C emerged in the DSC curve [87]. This indicates that the miscibility of PDLA/PLLA and PBS depends on the amount of PBS. At lower PBS concentrations, the blend appears miscible; but as the PBS content increases, phase separation occurs, highlighting limited compatibility between the two polymer systems. Additionally, the melting point (T_m) of PDLA/PLLA/PBS composites decreased progressively from 230 °C to 222 °C as the PBS concentration increased. This decrease in T_m indicated that PBS affected the thermal characteristics of the PDLA/PLLA blend. Zhang et. al. [88] attributed this decrease to partial miscibility at the PLLA/PBS interface, where the presence of PBS may enhance interaction between PLLA and PDLA, influencing the crystalline structure and subsequently altering the melting behavior of the stereocomplex crystals.

In order to further investigate the compatibilization between PDLA/PLLA and PBS materials, the crystallization process of PDLA/PLLA/PBS was tested using X-ray diffraction (XRD) method. Figure 12(b) shows the XRD characterization results of PDLA/PLLA, pure PBS, and PDLA/PLLA/PBS composites. From the position of $2\theta=19.56^\circ$, it can be seen that when the PBS content is 30% or more, the PDLA/PLLA/PBS composite material exhibits a diffraction peak unique to PBS material, indicating that the composite material is incompatible with PBS at this

time. This also confirms the results of partial miscibility between PDLA/PLLA and PBS materials in DSC testing.

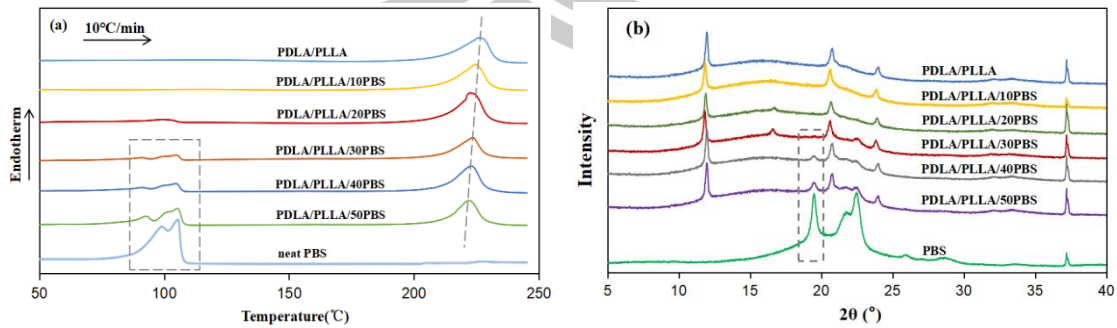


Figure 12 (a) First heating cycle and (b) X-ray diffraction characterization of PDLA/PLLA /PBS composites

2) Cooling cycle

Figure 13 shows DSC thermograms of PLLA/PDLA/PBS (0-50% contents) under a cooling rate of 10°C/min. The derived parameters, including the peak crystallization temperature and the enthalpy (T_c , ΔH_c), the difference between the initial crystallization and the peak crystallization ($T_{onset} - T_c$) are shown in Table 5.

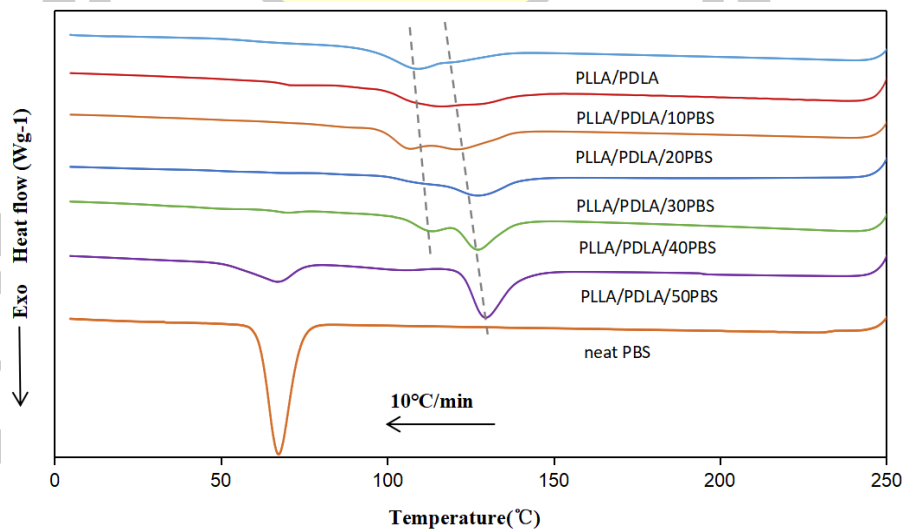


Figure 13 Cooling cycle at 10°C/min of PLLA/PDLA /PBS blends

Table 5 Differential scanning calorimetry (DSC) data derived from cooling thermogram of PLLA/PDLA/PBS.

Sample	Tc(°C)		ΔH_c (J/ g)	Tonset-Tc(°C)
	Tc1	Tc2		
PLLA/PDLA	100.24	109.02	-32.98	27.75
PLLA/PDLA/10PBS	100.40	109.05	-33.01	27.50
PLLA/PDLA/20PBS	100.62	109.27	-34.61	22.68
PLLA/PDLA/30PBS	106.09	127.21	-35.80	13.41
PLLA/PDLA/40PBS	107.71	127.01	-34.95	12.89
PLLA/PDLA/50PBS	-	129.58	-33.88	10.00

At approximately 70 °C, Figure 13 shows a peak in PDLA/PLLA/PBS composites, which Yoo et al. [89] identified as the crystallization peak of PBS. As the PBS content increased, this crystallization peak shifted to higher temperatures, suggesting that the composites with a higher PBS content exhibited a faster crystallization rate. This observation aligns with the findings of Park et. al. [90] and Yokohara et. al. [91], who also reported that PBS improved the crystallization rate of PLA.

Furthermore, Figure 11 shows that the cooling curve for PDLA/PLLA/PBS blends had two distinct crystallization peaks, suggesting the formation of two types of crystals: homopolymer crystal (TC1) and stereocomplex crystal (TC2).

As shown in Table 5 and Figure 14(a), the TC1 and TC2 of these two crystals increases with the increase of PBS content, until only one type of crystal is formed when the PBS content is 50%. Tonset-TC was used to estimate the total crystallization rate (Figure 14b). When the PBS content increase, the value of Tonset -Tc decreased from 27.75 to 10, this indicates that the overall crystallization rate of the blend is accelerating. And when the PBS content is greater than 30%, the Tonset -TC value remains almost unchanged, which is similar to the trend of TC.

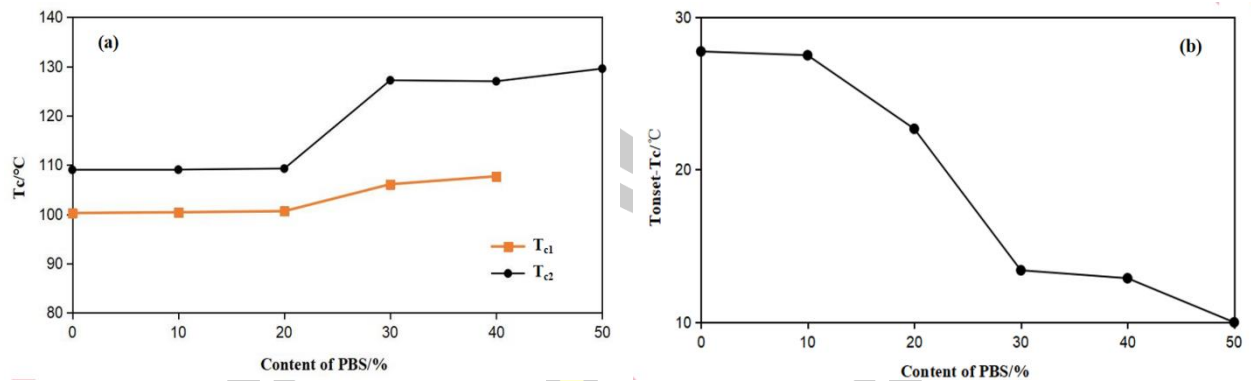


Figure 14 DSC derived parameters during cooling (a) crystallization temperature (T_c) and (b) the different between onset crystallization temperature and T_c ($T_{onset} - T_c$).

3) Reheating cycle

Figure 15 illustrates the DSC reheating curves of PDLA/PLLA/PBS composites and the variations in HC crystal and SC crystal, while corresponding quantitative data, including melting temperature and crystallization parameters, are summarized in Table 6.

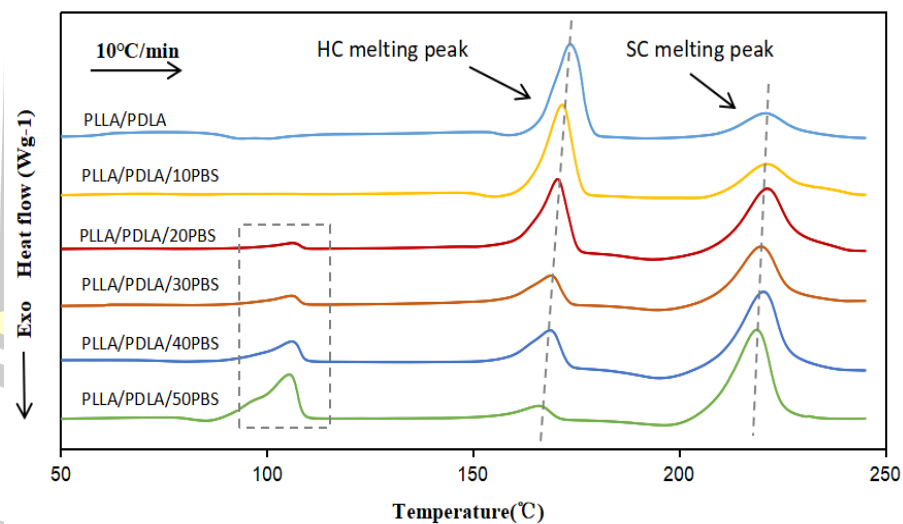


Figure 15 DSC reheating curves of PLLA/PDLA/PBS

Table 6 DSC results from the reheating process of PDLA/PLLA/PBS composites.

Sample	Homocrystal melting (HC)		Stereocomplex melting (SC)	
	T _{m,h}	ΔH _{m,h}	T _{m,sc}	ΔH _{m,sc} (J/g)
	(°C)	(J/g)	(°C)	
PDLA/PLLA	173.61	38.74	220.85	14.48
PDLA/PLLA/10PBS	171.60	35.58	221.15	18.28
PDLA/PLLA/20PBS	170.45	29.54	221.30	34.58
PDLA/PLLA/30PBS	168.98	17.68	219.62	43.00
PDLA/PLLA/40PBS	168.82	15.90	220.29	45.12
PDLA/PLLA/50PBS	165.99	6.00	218.76	47.51

Table 7 DSC results from the reheating process of PDLA/PLLA/PBS composites.

Sample	X _{hc} (%)	X _{sc} (%)	f _{sc} (%)
PDLA/PLLA	41.57	10.20	19.7
PDLA/PLLA/10PBS	38.18	12.87	25.21
PDLA/PLLA/20PBS	31.70	24.35	43.44
PDLA/PLLA/30PBS	18.97	30.28	61.48
PDLA/PLLA/40PBS	17.06	31.77	65.26
PDLA/PLLA/50PBS	6.44	33.46	83.86

During the subsequent heating cycle, two distinct melting peaks were observed: one for the homocrystal (HC) at around 170 °C, and another for the stereocomplex (SC) at around 220 °C. Without the presence of PBS, the PDLA/PLLA blend trended to crystallize as homocrystals. However, increasing PBS content resulted in a significant increase in the enthalpy of melting for stereocomplex crystals (ΔH_{m, sc}), while the enthalpy of melting for homocrystal (ΔH_{m, hc}) decreased. This trend, illustrated in Figure 16(a) indicates that PBS promoted SC crystallization, improving the thermal processing performance of the materials. This effect is likely

due to PBS's partial miscibility with the PDLA/PLLA blends, resulting in the formation of SC-structured composite crystals. Figure 16(b) illustrates the increase of SC crystallization as PBS content increases, with a noticeable slowdown in the growth rate once the PBS content exceeds 30%. Additionally, a distinct peak melting peak at 100-110 °C emerged when PBS concentration surpassed 20%, corresponding to the melting point of PBS, aligning with the findings from the first heating.

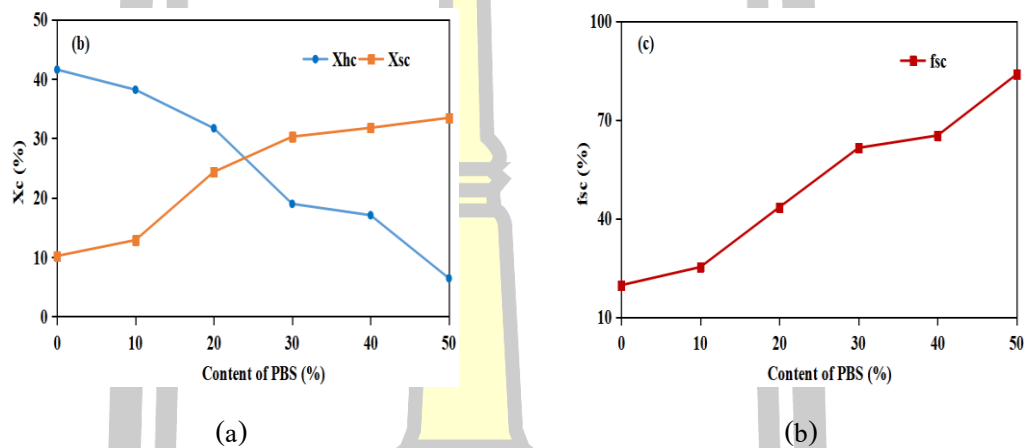


Figure 16 (a) Variations in X_{hc} and X_{sc} (b) Changes in f_{sc} of PDLA/PLLA/PBS composites.

4.2 Non-isothermal crystallization of PLLA/PDLA/PBS

4.2.1 Non-isothermal crystallization during the cooling cycle

1) Cooling cycle

Figure 17 shows the DSC thermograms of the cooling at a rate of 2, 5, 10, and 20 °C/min, while Table 7 summarizes the parameters determined from the DSC curves.

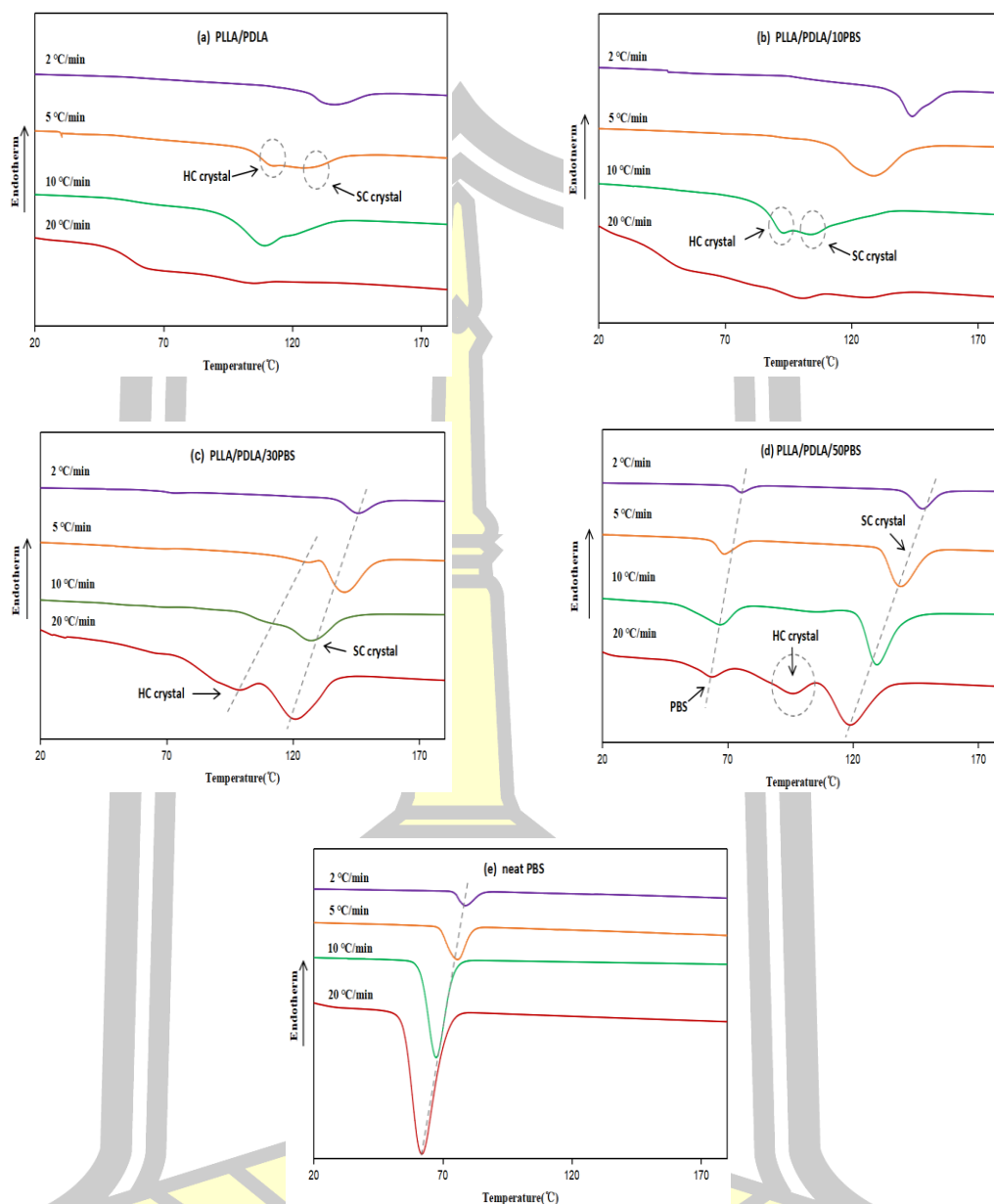


Figure 17 DSC cooling curves of PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS, PLLA/PDLA/50PBS and neatPBS at various cooling rates

Table 8 Cooling parameters of PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS and PLLA/PDLA/50PBS at various cooling rates

Sample	Cooling process			
	Rate D (°C/min)	TC (°C)	Δ HC (J/g)	Tonset-Tc (°C)
PLLA/PDLA	2	135.36	-50.1233	15.06
	5	112.36	-41.4109	27.14
	10	109.02	-32.0140	27.75
	20	104.33	-1.2224	8.25
PLLA/PDLA/10PBS	2	143.97	-55.8502	14.77
	5	128.61	-45.5153	14.38
	10	104.86	-32.9829	30.02
	20	100.04	9.8897	8.27
PPLLA/PDLA/30PBS	2	150.99	-56.8557	7.81
	5	140.29	-41.5224	12.02
	10	127.21	-35.8030	13.41
	20	120.72	-31.505	16.82
PLLA/PDLA/50PBS	2	147.84	-55.5147	8.44
	5	138.98	-50.0446	11.97
	10	129.58	-33.8810	10.58
	20	118.74	-28.2117	14.87

Figure 17 shows that as the cooling rates increased, the crystallization peaks shifted to lower temperatures. This shift occurs due to the phase transition process is temperature-dependence, with higher cooling rates inducing crystallization at lower temperatures, resulting in undercooling. A study by Yang et al.[92] on the non-isothermal crystallization behavior of PLA and D-mannitol blends observed a similar trend, where the crystallization temperature (T_c) decreased from 122 to 90 °C as the cooling rate increased from 2 to 40 °C/min. Moreover, higher cooling rates led to broader and smoother crystallization peaks, reflecting the inhibitory effect of faster cooling on crystallization.

In Figure 17, two distinct crystallization peaks —designated as HC and SC — appear simultaneously at a higher cooling rate, likely representing different crystalline phases or structures within the composite. Moreover, Figure 17 (d) and (e) highlight a distinct crystallization peak around 70°C, corresponding to the crystallization temperature of PBS within the composite.

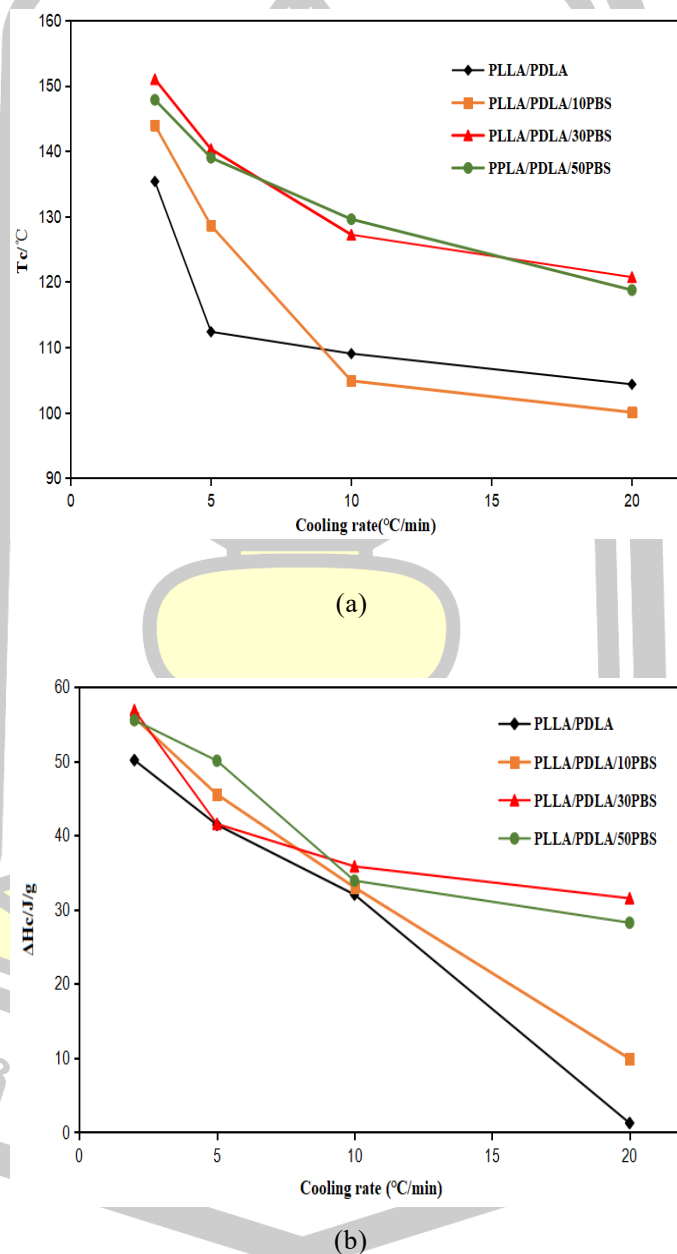


Figure 18 The effect of cooling rate on (a) T_c , (b) ΔH_c , of PLLA/PDLA/PBS

2) Reheating cycle after non-isothermal crystallization

Figure 19 and Table 8 show the DSC second heating curve and accompanying parameters of the cooling at a rate of 2, 5, 10 and 20°C/min . As shown in Figure 19, the cold crystallization peak only appears at a cooling rate of 20 °C/m in in PLLA and PLLA/10PBS, this indicates that the crystallization behavior is fully completed during cooling when the cooling rate is low.

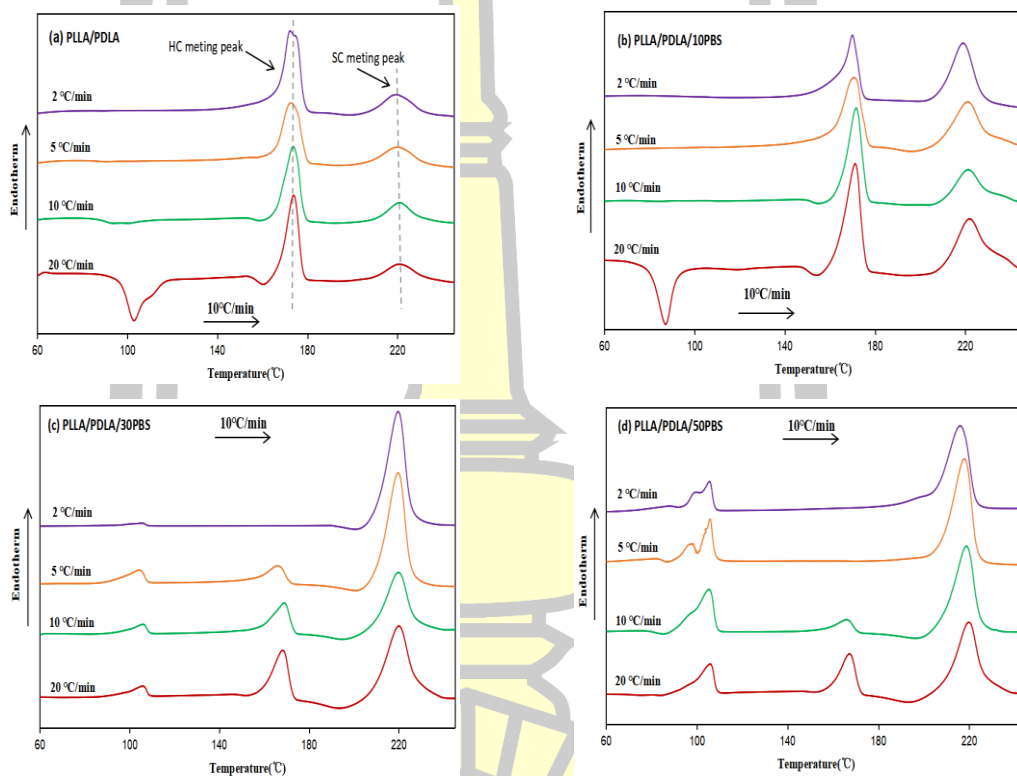


Figure 19 DSC reheating at 10°C/min curves of PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS and PLLA/PDLA/50PBS at various cooling rates

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Table 9 Reheating parameters at 10°C/ min of PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS and PLLA/PDLA/50PBS at various cooling rates

Sample	Cooling rate °C/min	reheating					
		Cold crystallization		Homocrystal melting		Stereocomplex melting	
		T _{cc} (°C)	ΔH _{cc} (J/g)	T _{m,HC} (°C)	ΔH _{m,HC} (J/g)	T _{m,SC} (°C)	ΔH _{m,SC} (J/g)
PLLA/PDLA	2	-	-	177.2	50.2	219.5	18.3
	5	-	-	172.6	41.1	220.0	19.1
	10	-	-	173.6	39.5	221.0	18.0
	20	102.9	-29.2	173.8	35.3	220.9	17.6
PLLA/PDLA /10PBS	2	-	-	170.0	29.5	219.0	33.2
	5	-	-	170.6	37.8	220.8	30.2
	10	-	-	171.6	35.5	221.2	25.9
	20	87.1	-20.1	171.2	36.7	221.8	37.6
PLLA/PDLA /30PBS	2	-	-	-	-	220.1	58.8
	5	-	-	166.3	9.2	219.8	50.7
	10	-	-	169.0	17.9	219.8	48.0
	20	-	-	168.3	19.1	220.0	46.4
PLLA/PDLA /50PBS	2	-	-	-	-	216.1	58.5
	5	-	-	-	-	217.7	54.0
	10	-	-	166.0	6.3	218.8	49.1
	20	-	-	167.3	16.2	219.8	43.1

The secondary heating curves consistently displayed two distinct melting peaks at approximately 170 °C and 220 °C, indicating the coexistence of HC (homocrystal) and SC (stereocomplex) crystallization. Notably, the melting peak associated with HC crystallization significantly diminished as the PBS content increased from 10% to 50%, suggesting that PBS influences the crystallization process, particularly by reducing HC crystallization. Moreover, under the same PBS concentration, slower cooling rates resulted in a reduction in the HC crystallization peak and an enhancement of the SC crystallization peak. This suggests that the cooling rate affects the crystallization kinetics, with slower cooling rates, promoting more pronounced SC crystallization, the reasons can be summarized into two points. Firstly, nucleation effect. At lower cooling rates, the nucleation effect of the mixture is more significant during the crystallization process, because the system has enough time to form more crystal nuclei. These crystal nuclei act as heterogeneous nucleating agents, reducing the energy barrier of crystallization and promoting the formation of crystals. The second is the formation rate. A lower cooling rate allows more time for

the molecules of the mixture to align and crystallize, thereby increasing the crystallization rate of the stereocomplex.

At a cooling rate of 2 °C/min, the secondary heating curves of PDLA/PLLA/30PBS and PDLA/PLLA/50PBS exhibited only a single SC crystallization peak suggesting that the stereocomplex crystals had fully formed under these conditions, which are favorable for stereocomplex formation. Additionally, Figure 19(c) and Figure 19(d) show peaks around 110 °C, corresponding to the melting point of PBS. These peaks remained consistent across different cooling rates, suggesting that the melting behavior of PBS was unaffected by the variations in cooling.

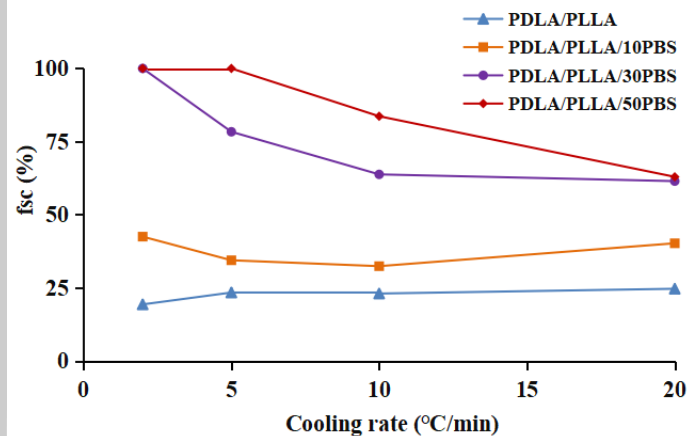


Figure 20 Variations in f_{sc} of PDLA/PLLA/PBS composites at different cooling rates.

Figure 20 illustrates the trend in the proportion of SC (stereocomplex) crystallization across various cooling rates. It is evident that different cooling rates had minimal impact on the f_{sc} when the PBS content was below 30%. When the PBS content exceeded 30%, a slower cooling rate led to an increase in f_{sc} . Additionally, at the same cooling rate, a higher PBS resulted in a greater proportion of f_{sc} , indicating that the addition of PBS facilitated the formation of stereocomplex crystal.

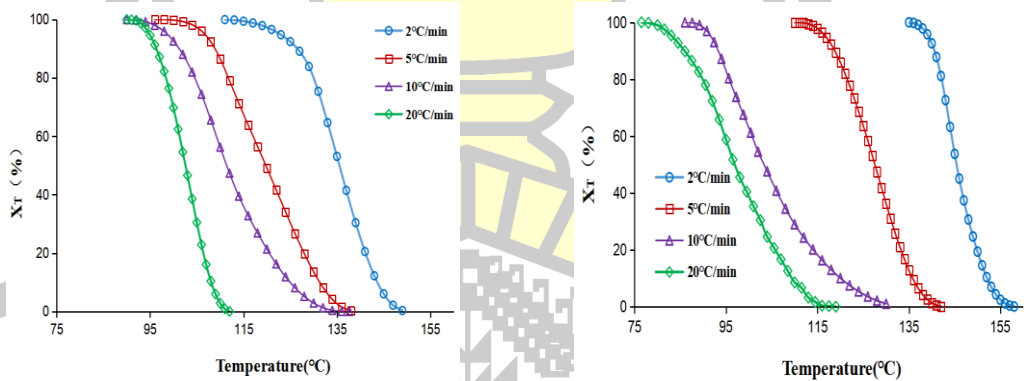
4.2.2 The relationship between the relative crystallinity of PLLA/PDLA/PBS and temperature and time

Relative crystallinity (XT) at any temperature (T) can be calculated by the following equation:

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

In equation (4), T_0 and T_∞ are the start and end temperatures of crystallization, respectively. dH_c is the exothermic enthalpy of crystallization over an infinitesimally

small temperature range dT [93]. Figure 21(a-d) shows the X_T - T curves for PLLA/PDLA/PBS blends. It is evident that the crystallinity at various cooling rates are all in the inverse S-shape. The nucleation process is relatively slow in the early stage of crystallization, and crystal growth is the main trend in the middle stage of crystallization. The crystallinity increases rapidly, and gradually stabilizes again in the later stage as the crystal grows. Meanwhile, from the curve in Figure 21, it can be seen that in the same sample, as the cooling rate decreases, complete crystallization is achieved earlier. This indicates that as the cooling rate increases, molecules do not have enough time to react and enter crystallization, resulting in undercooling phenomenon.



(a) PLLA/PDLA

(b) PLLA/PDLA/10PBS

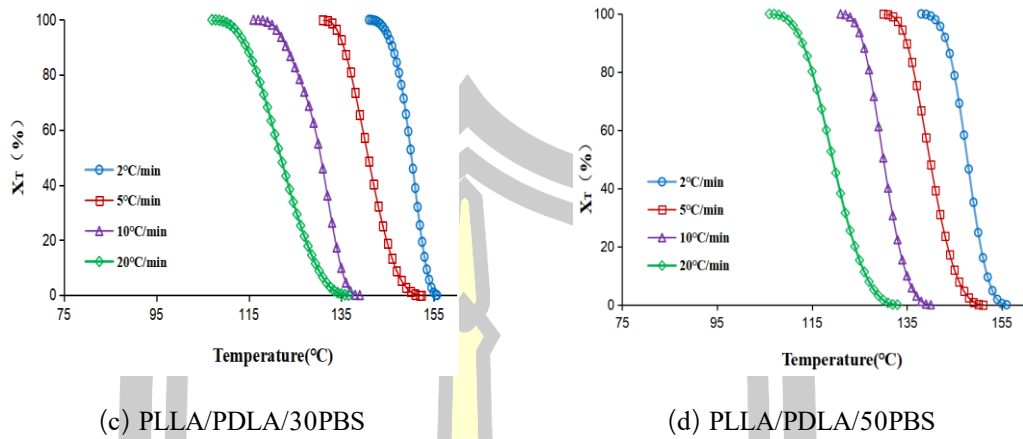


Figure 21 Plots of relative crystallinity (X_T) versus crystallization Temperature (T) for PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS, PLLA/PDLA/50PBS, at various cooling rates.

X_T data can be transformed to X_t using the relationship shown below[94] :

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

Where T is the temperature at crystallization time t and D represents the cooling rate. From Figures 22a and 22b, it can be seen that at a cooling rate of $2^\circ\text{C}/\text{min}$, PLLA/PDLA takes about 15 minutes to fully crystallize, while PLLA/PDLA/10PBS only takes 9 minutes to fully crystallize; At a cooling rate of $5^\circ\text{C}/\text{min}$, complete crystallization of PLLA/PDLA/10PBS takes only 6 minutes, indicating that the lower the cooling rate, the longer the crystallization time, and PLLA/PDLA/PBS composite materials are more prone to crystallization. The delayed effect of cooling rate on the crystallization of PLLA/PDLA/PBS blend can only be observed under low cooling rate ($2^\circ\text{C}/\text{min}$) conditions, and the X_t - t curve shows a clear S-shape. At a higher cooling rate, the melted PLA rapidly evolves into a glassy state, resulting in a straight X_t - t curve. In this case, the time for crystallization completion is shortened. The rise of the curve slows down significantly in the later stage of crystallization. The reason is that in the later stage, as the crystal grows larger, they contact with each other to form grain boundaries, which slows and delays the continuous growth of crystals, and eventually causes crystallization to stop. From the Figure 22, we can also see that when the PBS content is 30%, the crystallization time is the shortest.

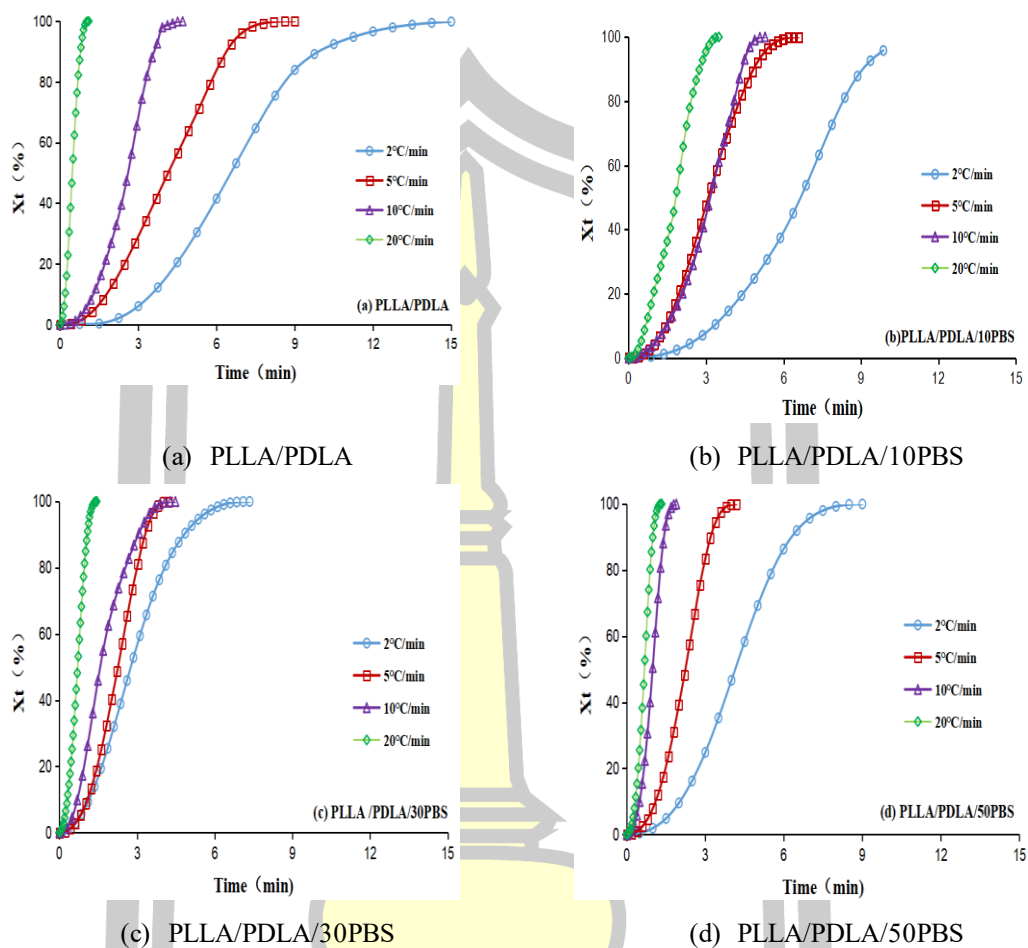


Figure 22 Plots of relative crystallinity (X_t) versus crystallization time (t) for PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS, PLLA/PDLA/50PBS, at various cooling rates.

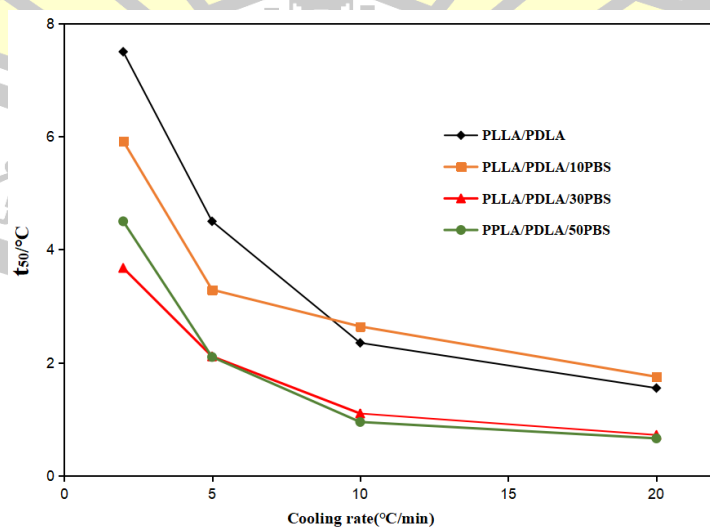


Figure 23 The half-time crystallization ($t_{50\%}$) of PLLA/PDLA, PLLA/PDLA/10PBS, PLLA/PDLA/30PBS, PLLA/PDLA/50PBS, at various cooling rates.

Figure 23 shows the relationship between $t_{50\%}$ and cooling rate. The $t_{50\%}$ of the same sample decreases with an increase in cooling rate, indicating that the crystallization rate of PLLA/PDLA/PBS increases at higher cooling rates. By comparing the $t_{50\%}$ values of different samples with the same cooling rate, it can be seen that when the PBS content is 10%, the $t_{50\%}$ values of PLLA/PDLA/PBS are not significantly different from those of PLLA/PDLA. However, further increasing the PBS content to 30% significantly reduces the $t_{50\%}$ value of PLLA/PDLA/PBS blends. However, as the PBS content continues to increase, the $t_{50\%}$ value no longer changes. This indicates that the effect is most pronounced when the PBS content reaches a certain value (30%), it can act as a "plasticizer or nucleating agent" in the PLLA/PDLA/PBS blend system, thereby weakening the hydrogen bonding between PLLA/PDLA molecules and facilitating the movement of molecular chains. And during crystallization, the molecular chains diffuse towards the crystal nucleus and form a regular structure, achieving the goal of promoting crystallization.

4.2.3 Non isothermal crystallization kinetics of PLLA/PDLA/ PBS blends

The processing of polymers is very complex and is influenced by factors such as their own molecular structure, chain segments, and processing temperature. The study of non isothermal crystallization kinetics can understand the crystallization behavior and crystal structure morphology of polymers under changing temperature fields.

1) Avrami method

The Avrami equation is an important theoretical model in the study of crystallization kinetics of polymer materials[95], as shown in equation (6).

$$1 - X_t = \exp(-Z_t * t^n) \quad (6)$$

In the formula: X_t is the relative crystallization fraction; Z_t is a non isothermal crystallization rate constant, which is related to the nucleation rate of polymers and the growth rate of crystals; t is time; n is the Avrami index.

The Avrami equation can be transformed to obtain the equation as shown in equation (7).

$$\lg[-\ln(1 - X_t)] = n \lg t + \lg Z_t \quad (7)$$

Plot $\lg t$ with $\lg[-\ln(1 - x)]$ to obtain Figure 24. According to the trend of curve changes under different cooling rates in the graph, it can be divided into two stages, the main crystallization stage and the secondary crystallization stage. The crystallization process in the secondary crystallization stage is more complex, so the curves deviate from the linear relationship. Linear fitting is performed on the main crystallization stage curve, and the slope of the obtained line is n , and Z_t can be calculated from the intercept of the line. The n and Z_t obtained at different cooling rates are listed in Table 9.

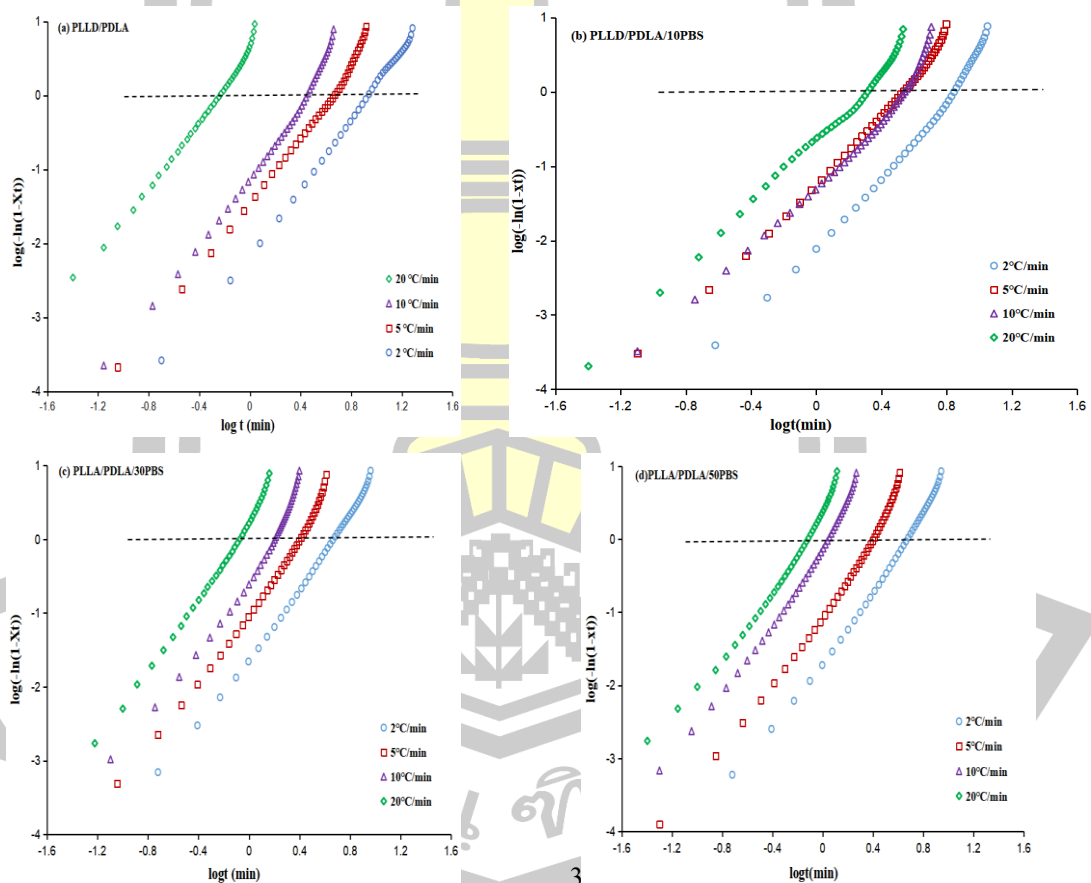


Figure 24 Fitting curves of $\lg[-\ln(1 - X_t)]$ with respect to $\lg t$ for PLLA/PDLA and PLLA/PDLA/30PBS at different heating rates

Table 10 Crystallization kinetics parameters of PLLA and PLLA/PDLA/30PBS

	D (°C/min)	Main crystallization stage		Secondary crystallization stage	
		n	Zt	n	Zt
PLLA/PDLA	2	2.22	-2.13	2.26	-2.09
	5	2.16	-1.44	3.70	-2.52
	10	2.23	-1.11	4.00	-1.8
	20	2.18	0.49	3.19	0.69
PLLA/PDLA/ 30PBS	2	2.31	-1.6	2.91	-2.0
	5	2.22	-0.61	4.1	-1.7
	10	2.31	-1.00	4.62	-0.99
	20	2.30	0.10	3.65	0.22

From Table 9, it can be seen that the average Avrami index during the main crystallization stage of PLLA/PDLA material is 2.20; The average Avrami index during the secondary crystallization stage is 3.29, therefore, in the early stage of crystallization, PLLA/PDLA first forms crystal nuclei; In the later stage of crystallization, the crystal nucleus gradually transforms into a spherical crystal, and the growth mode of the crystal at this stage is three-dimensional growth. In addition, it can be seen from Figure 24 that the slope of the curve suddenly increases in the last relatively short time, indicating that PLLA/PDLA spherulites cannot grow completely in a short period of time. Similarly, the Avrami index of PLLA/PDLA/30PBS composite material is different in two stages (the average Avrami index in the main crystallization stage is 2.29, while in the secondary crystallization stage it is 3.82). PLLA/PDLA and PLLA/PDLA/30PBS have similar Avrami index in the main crystallization stage, and their initial crystallization processes are relatively similar. However, in the secondary crystallization stage, the Avrami index of the two are significantly different, indicating that their crystal growth processes are completely different. This is because, in the early stage of crystallization, PBS acts as a heterogeneous nucleating agent, which can effectively promote the formation of needle shaped crystals in PLLA/PDLA; And the later crystallization process becomes more complex, in addition to the formation of spherical crystals, there are also collisions or secondary crystallization between crystals, resulting in significant differences from the crystallization behavior of ordinary crystals. Therefore, the Avrami equation cannot fully explain the non isothermal crystallization kinetics of PLLA/PDLA/PBS composite materials.

2) MO method

Due to the limitations of Avrami and Ozawa methods in describing the non isothermal crystallization process of polymers, the MO method [96] combines the two and derives the equation for crystallization time t and heating rate D , which is an effective method for studying the non isothermal crystallization process of polymers. The obtained straight lines often have a good linear relationship, and the physical meaning of the obtained non isothermal crystallization kinetics parameters is clear. The final expression is as follows (8).

$$\log D = \log F(T) - \alpha \log t \quad (8)$$

where the rate parameter $F(T) = [K(T)/k]^{1/m}$ and the physical meaning is the necessary value of cooling rate to reach a defined degree of crystallinity at unit crystallization time; $\alpha = n/m$, n is Avrami index, m is Ozawa index m . According to Eq.8, at a given degree of crystallinity, the plot of $\log D$ as a function of $\log t$ gives a straight line with $\log F(T)$ as the intercept and α as the slope (Fig.25). Table 10 shows the non isothermal crystallization kinetics parameters of composite materials calculated based on the slope and intercept of the straight line.

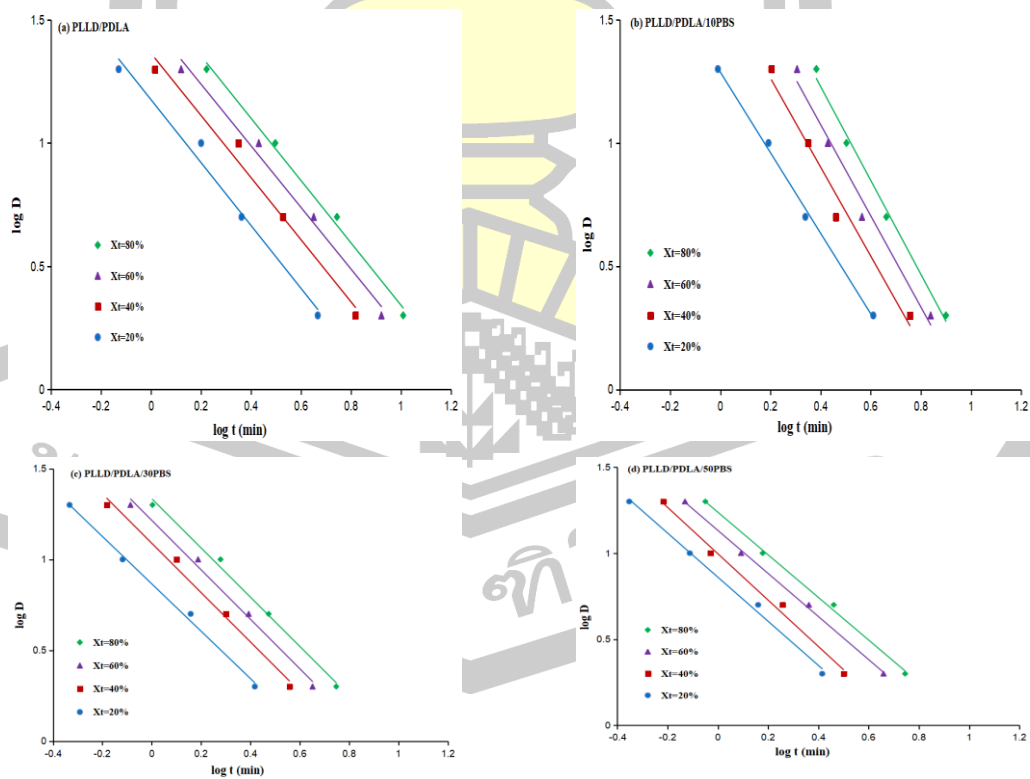


Figure 25 Linear fitting plot of $\log D$ - $\log t$ for PLLA/PDLA and PLLA/PDLA/30PBS

Table 11 Non isothermal crystallization kinetics parameters of PLLA/PDLA/PBS blend treated by Mo method

$X_t/\%$	PLLA/PDLA			PLLA/PDLA/30PBS		
	α	F(T)	R^2	α	F(T)	R^2
20%	-1.28	1.18	0.984	-1.30	0.87	0.996
40%	-1.26	1.36	0.989	-1.36	1.09	0.991
60%	-1.25	1.49	0.989	-1.36	1.22	0.993
80%	-1.26	1.61	0.994	-1.35	1.33	0.994

From Figure 25, it can be seen that the fitting curve processed by the Mo method has a good linear relationship, indicating that the MO method can well describe the non isothermal crystallization process of PLLA/PDLA/PBS composite materials.

From Table 10, it can be seen that the F(T) values of PLLA/PDLA and PLLA/PDLA/30PBS both increase with the increase of relative crystallinity. This indicates that a faster cooling rate is more conducive to the PLLA/PDLA/PBS composite material reaching a larger relative crystallinity per unit time, which is consistent with the conclusions in Figures 10 and 12. Furthermore, at the same relative crystallinity, the F(T) value of PLLA/PDLA is higher than that of PLLA/PDLA/30PBS, indicating that in order to achieve the same crystallinity, PLLA/PDLA requires a higher heating rate than PLLA/PDLA/PBS.

4.2.4 Non-isothermal crystallization activation energy

The activation energy (ΔE) [97] of non-isothermal crystallization can be calculated using formulas proposed by Kissinger and Takhor which consider the variation of peak temperature (T_c) with cooling rate [98], D is the cooling rate, R is the gas constant, value 8.314 J/(mol · K), and the formula are:

Kissinger model:

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

Takhor model:

$$\ln(D) = \frac{-\Delta E_T}{R} (1/T_c) \quad (10)$$

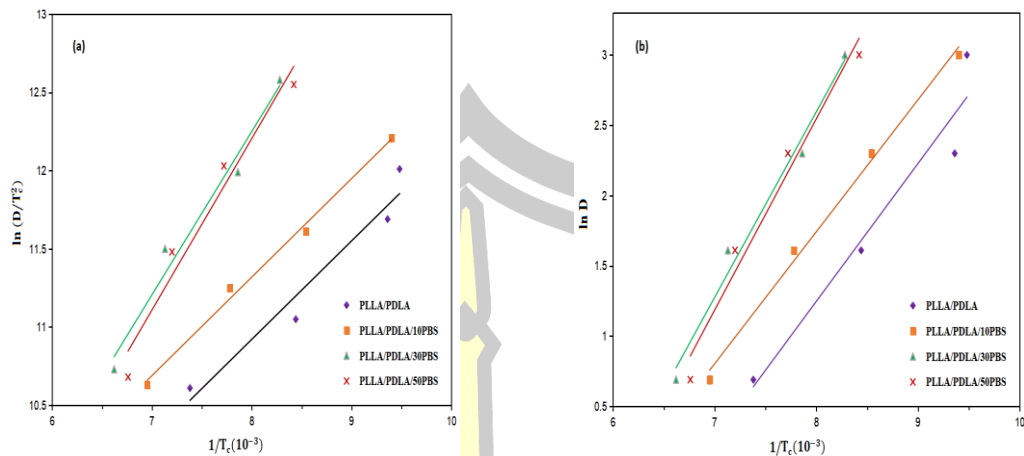


Figure 26 (a)Plots of $\ln(D/T_c^2)$ versus $1/T_c$ by the Kissinger equation, (b)Plots of $\ln D$ versus $1/T_c$ by the Takhor equation

Substitute D and T_c from Table 8 into the equation, plot $\ln(D/T_c^2)$ versus $1/T_c$ to obtain the data points in Figure 26(a), and plot $\ln D$ versus $1/T_p$ to obtain the data points in Figure 26(b). The non-isothermal crystallization activation energies can be calculated from the slope, that are ΔE_K and ΔE_T are listed in Table 11. The results indicate that the value and trends of ΔE_K and ΔE_T are basically the same, so both methods can be used to calculate the activation energy of non isothermal crystallization[99].

From Figure 26, and Table 11, it can be seen that the activation energy of non isothermal crystallization does not change significantly when 10% PBS is added to the PLLA/PDLA blends. When 30% PBS is added, the non isothermal crystallization activation energy significantly decreases, but when it continues to increase to 50%, the value of the non isothermal crystallization activation energy no longer increases accordingly. Based on the above results, we believe that when a small amount of PBS is added, the change in crystallization behavior is not significant until the content increases to 30%, which can significantly promote the crystallization of PLLA/PDLA/PBS blends. Further research can consider subdividing the PBS content range from 10% to 30%.

Table 12 Activation energy of PLLA/PDLA/PBS

Sample	ΔE_K (KJ•mol ⁻¹)	ΔE_T (KJ•mol ⁻¹)
PLLA/PDLA	-5.23	-8.15
PLLA/PDLA/10PBS	-5.24	-7.82
PLLA/PDLA/30PBS	-8.65	-10.97
PLLA/PDLA/50PBS	-9.15	-11.31

4.3 The Effect of PBS on the Tensile test of PLLA/PDLA Blends

The addition of PBS helps to improve the mechanical properties of PDLA/PLLA composites. The stress-strain curve is shown in Figure 27. We can see that pure PBS did not break after stretching, indicating its extremely high ductility. The PDLA/PLLA composites did not have a significant neck during the stretching process, with a fracture elongation of only 23.4%. With the addition of PBS, its elongation at break significantly increases. When the PBS content is 30%, the elongation at break reaches 62.4%, but as the PBS content continues to increase, there is a decreasing trend in elongation at break. This may be due to excessive PBS, which is incompatible with PDLA/PLLA materials and damages the interfacial bonding strength of the composites.

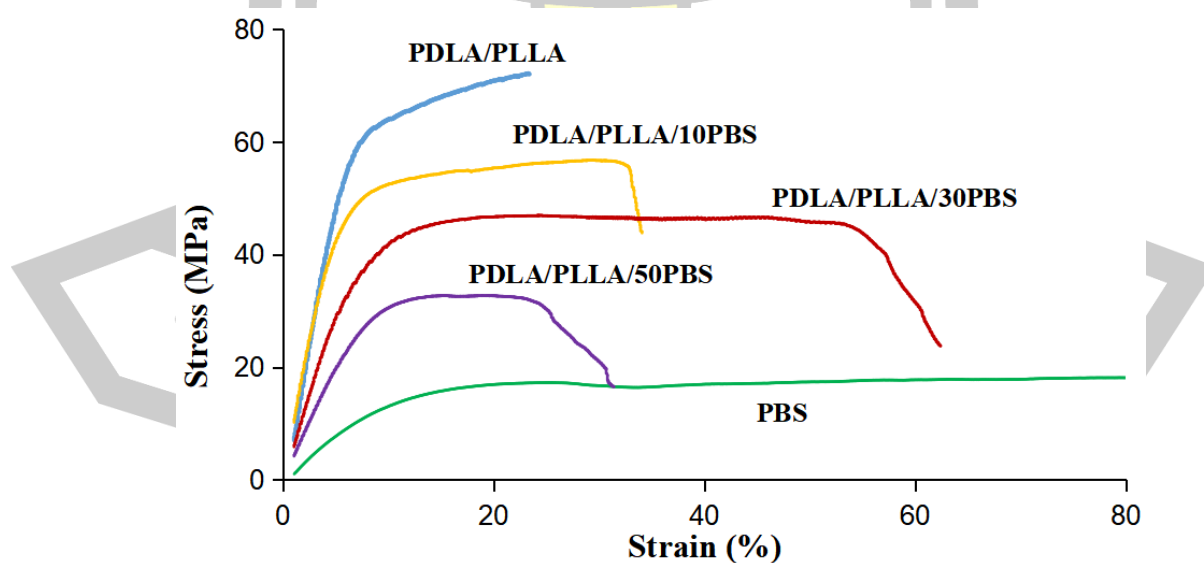


Figure 27 stress-strain curves of PDLA/PLLA/PBS composites

4.4 The Effect of ESO on the Properties of PLLA/PDLA/PBS Blends

4.4.1 FTIR Characterizations

FTIR spectroscopy is a powerful tool for determining the interactions and compatibility in polymer blends. In the spectra of compatible and incompatible polymer blends, the characteristic bands of each blend component may shift and combine, respectively[100]. The FTIR spectra of the PLLA/PDLA/PBS/ESO blends are shown in Figure 28. Table 12 lists the corresponding group attributions of the absorption peaks for the PLLA /PDLA/PBS/ESO blends.

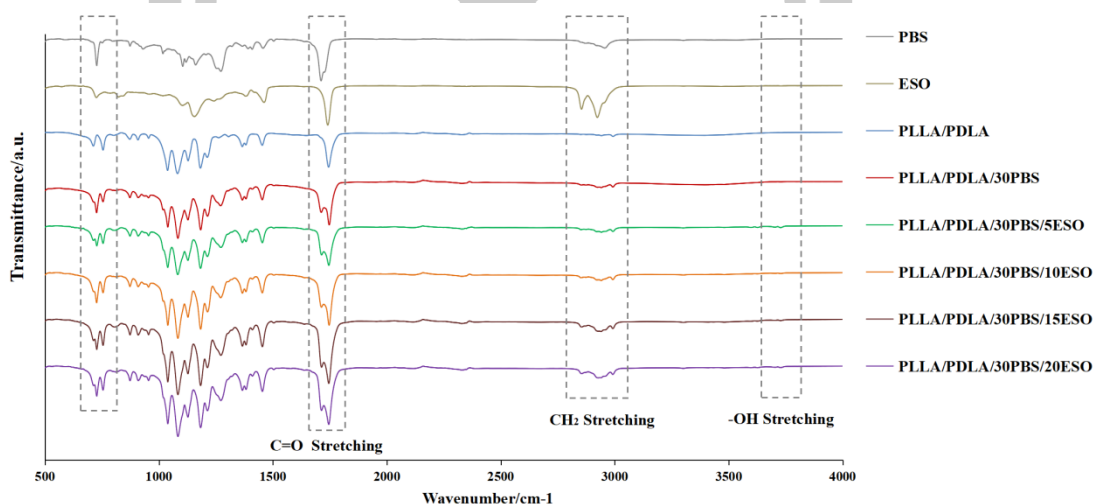


Figure 28 FTIR curves of PLLA /PDLA/PBS/ESO blends

Table 13 The group attributions of the absorption peaks for PLA, PBS and ESO blends

Attribution	Wavenumber (cm-1)				
	ESO	PBS	PLLA/PDLA	PLLA/PDLA/ 30PBS	PLLA/PDLA/ 30PBS/10ESO
-OH stretching	-	-	3708	3710	3711
-C-O-stretching	1104	1101	1076	1079	1080
C=O stretching	1736	1707	1740	1743	1743
-CH2 stretching	2917	-	-	-	2922
-CH3 stretching	-	2939	2972	2974	2974

The tensile vibration absorption peaks of the C=O functional groups in PLLA/PDLA and PBS, respectively, are at 1740 and 1707 cm^{-1} . The C–O– and C=O stretching bands of the PLLA/PDLA/PBS bio-blend shifted from 1076 and 1740 cm^{-1} (PLLA/PDLA) to 1079 and 1743 cm^{-1} , respectively, indicating a certain mutual effect between PBS and PLA and confirming the partial compatibility between PBS and PLLA/PDLA.

The results show that the $-\text{CH}_2$ asymmetric stretching peak (at 2915 cm^{-1}) of ESO appeared in the spectrum for the PLLA/PDLA/30PBS/10ESO (at 2922 cm^{-1}) blend. The $-\text{OH}$ vibration band shifted from 3708 cm^{-1} (for PLLA/PDLA) to 3711 cm^{-1} (for PLLA/PDLA/30PBS/10ESO) and the C–O–C vibration bands (of the epoxy group) disappeared at 724 and 867 cm^{-1} , possibly owing to the reaction or hydrogen-bond interaction of the PLLA/PDLA/PBS/ESO bio-blend[101]. This indicates that the formation of the blends was attributed to the ring-opening reaction of the epoxy functional group of ESO, and no epoxy functional groups exist.

4.4.2 DSC Characterizations

Figure 29 illustrates the DSC reheating curves of PDLA/PLLA/PBS/ESO composites and the variations in HC crystal and SC crystal, while corresponding quantitative data, including melting temperature and crystallization parameters, are summarized in Table 13.

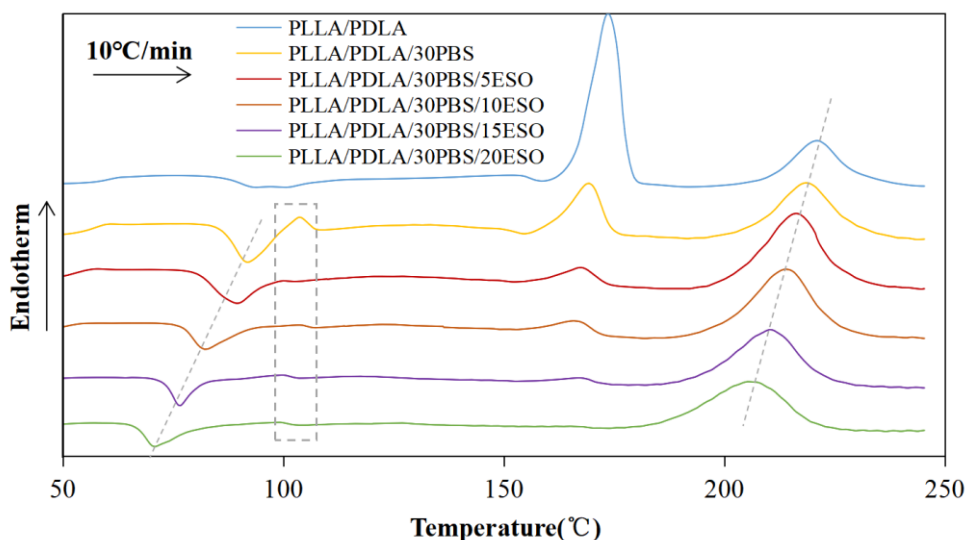


Figure 29 DSC reheating curves of PLLA/PDLA/PBS/ESO

Table 14 DSC results from the reheating process of PDLA/PLLA/PBS composites.

Sample	Tcc(°C)	Homocrystal melting (HC)		Stereocomplex melting (SC)	
		Tm,hc	ΔHm,hc	Tm,sc	ΔHm,sc
		(°C)	(J/g)	(°C)	(J/g)
PDLA/PLLA	93.70	174.62	38.74	220.85	14.48
PDLA/PLLA/30PBS	91.53	170.97	13.53	218.49	27.83
PDLA/PLLA/30PBS/5ESO	84.14	169.48	5.60	213.83	38.91
PDLA/PLLA/30PBS/10ESO	83.86	168.32	3.67	213.14	43.06
PDLA/PLLA/30PBS/15ESO	77.85	-	-	205.50	34.57
PDLA/PLLA/30PBS/20ESO	72.35	-	-	205.32	39.72

Table 15 DSC results from the reheating process of PDLA/PLLA/PBS composites.

Sample	Xhc	Xsc	fsc
	(%)	(%)	(%)
PDLA/PLLA	41.57	10.20	19.7
PDLA/PLLA/30PBS	14.51	19.60	57.46
PDLA/PLLA/30PBS/5ESO	6.01	27.40	82.01
PDLA/PLLA/30PBS/10ESO	3.94	30.32	88.50
PDLA/PLLA/30PBS/15ESO	0	100	100
PDLA/PLLA/30PBS/20ESO	0	100	100

Through DSC data, we can observe the effect of ESO on the compatibility of PLLA/PDLA/PBS blends. In the 100-110 °C region of the PLLA/PDLA/30PBS curve in Figure 29, we can see the presence of small peaks, indicating that there is still a small portion of incompatibility between PLLA/PDLA and PBS. However, when ESO is added, the peak disappears at this point, which proves that ESO can promote the compatibility between PLLA/PDLA and PBS materials. Meanwhile, with the increase of ESO content, the cold crystallization peak in the blend shifts to the left. The main reason is its plasticizing effect and nucleation inhibition effect. The addition of plasticizers significantly reduces the cold crystallization temperature and widens the peak deformation. The epoxy groups in ESO interact with the ester groups in PLA, further hindering the arrangement of PLA segments and causing the cold crystallization peak to shift towards lower temperatures.

During the reheating cycle, two distinct melting peaks can still be observed: one for the homocrystal (HC) at around 170 °C, and another for the stereocomplex (SC) at around 220 °C. With the addition of PBS, HC significantly decreased, but still existed, as emphasized earlier. However, as the content of ESO increases, HC continues to decrease and SC increases. When the ESO content reaches 15%, homocrystal (HC) basically disappear as shown in Figure 29. This trend indicates that ESO can promote SC crystallization, thereby improving the thermal processing performance of the material. This is consistent with the research of Wenwei Li[102], the addition of ESO led to intermolecular interactions between the PLLA and PDLA chains, promoting the spatial complexation of the enantiomers. The epoxy groups in ESO formed hydrogen bonds with the hydroxyl ends of PLLA and PDLA, promoting SC crystallization and inhibiting HC crystallization; further ESO acted as a plasticizer and increased the mobility of the PLA chains.

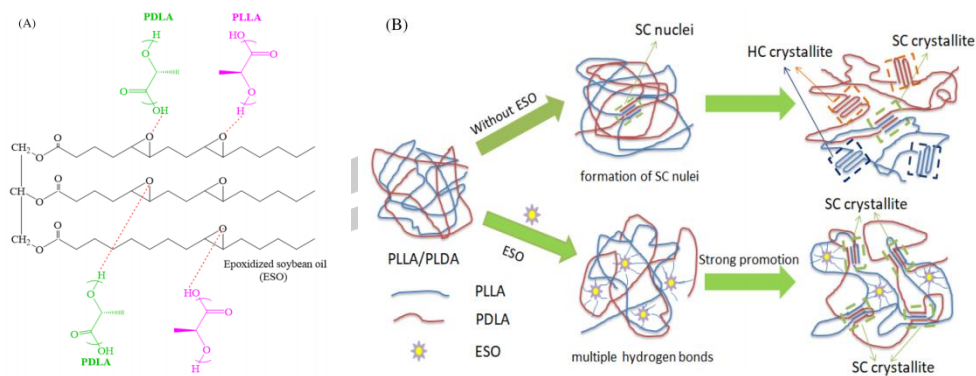


Figure 30 (A) The molecular structure of PLLA, PDLA, and ESO and (B) a schematic illustrating the crystallization of PLLA/PDLA blends in the absence and presence of ESO.

It was presumed that PLLA, PDLA and ESO molecules combined: PLA end groups hydrogen bonded to the ESO epoxy group, as Chen et al.[103] see Figure 30A. However, the enthalpy change on crystallization was not large enough to support chemical bond formation between the three components. Figure 30B. depicts a schematic representation of the structural evolution of PLLA/PDLA/ESO blends during nonisothermal crystallization, based on our measurements. The advantageous hydrogen bonding interactions between ESO's hydroxyls and PLLA or PDLA's carbonyls, was attributed to the improved ESO contribution to stereocomplex formation. The averaged distance between enantiomeric chains decreased, increasing the likelihood that the PLLA and PDLA chains may collide. The presence of ESO made the PLA chains more able to diffuse, in turn, caused more diffusion-controlled SC to form than HC during crystallization.

4.4.3 Tensile test

As discussed in Section 4.3, PBS serves as a synergistic additive to enhance the toughness of PLA blends. The study demonstrates that PBS significantly improves the elongation at break of PLA/PDLA composites. Furthermore, ESO—a small-molecule plasticizer—can intercalate between PLA molecular chains, increasing chain spacing and reducing intermolecular forces. This mechanism enhances segmental mobility and boosts material toughness. To evaluate the effects of varying ESO

concentrations on PDLA/PLLA/PBS blends, tensile tests were conducted on five different ESO ratios (0-20%). The test results of force and elongation distance are shown in Figure 31, the elongation at break shown in Figure 30.

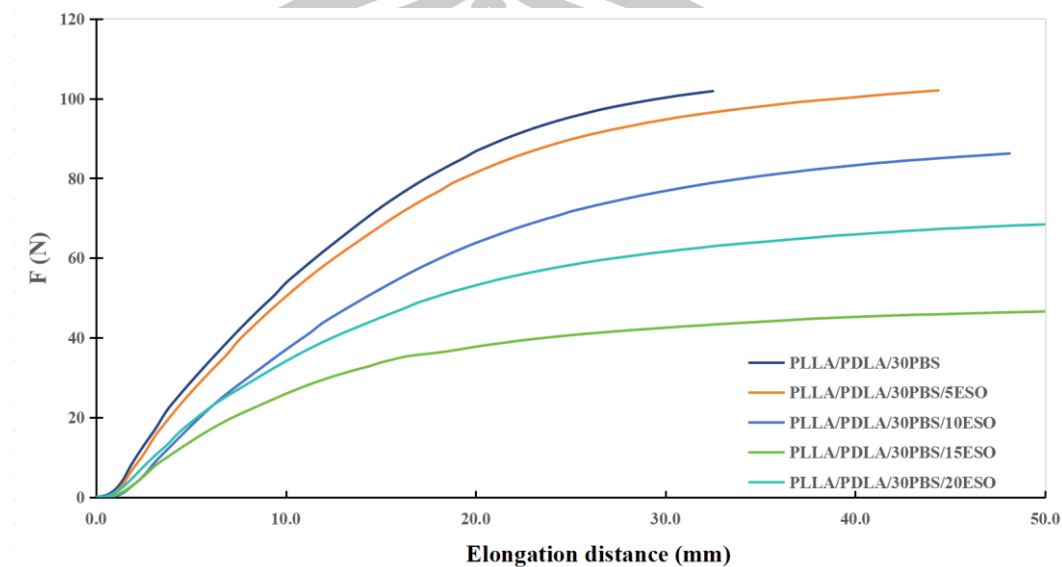


Figure 31 Force–elongation curves of PDLA/PLLA/PBS composites

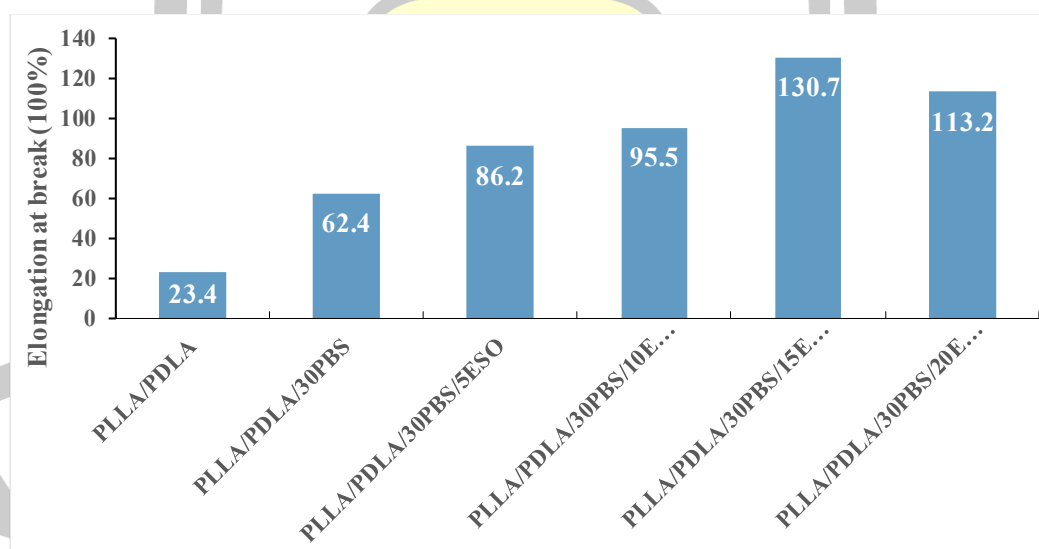
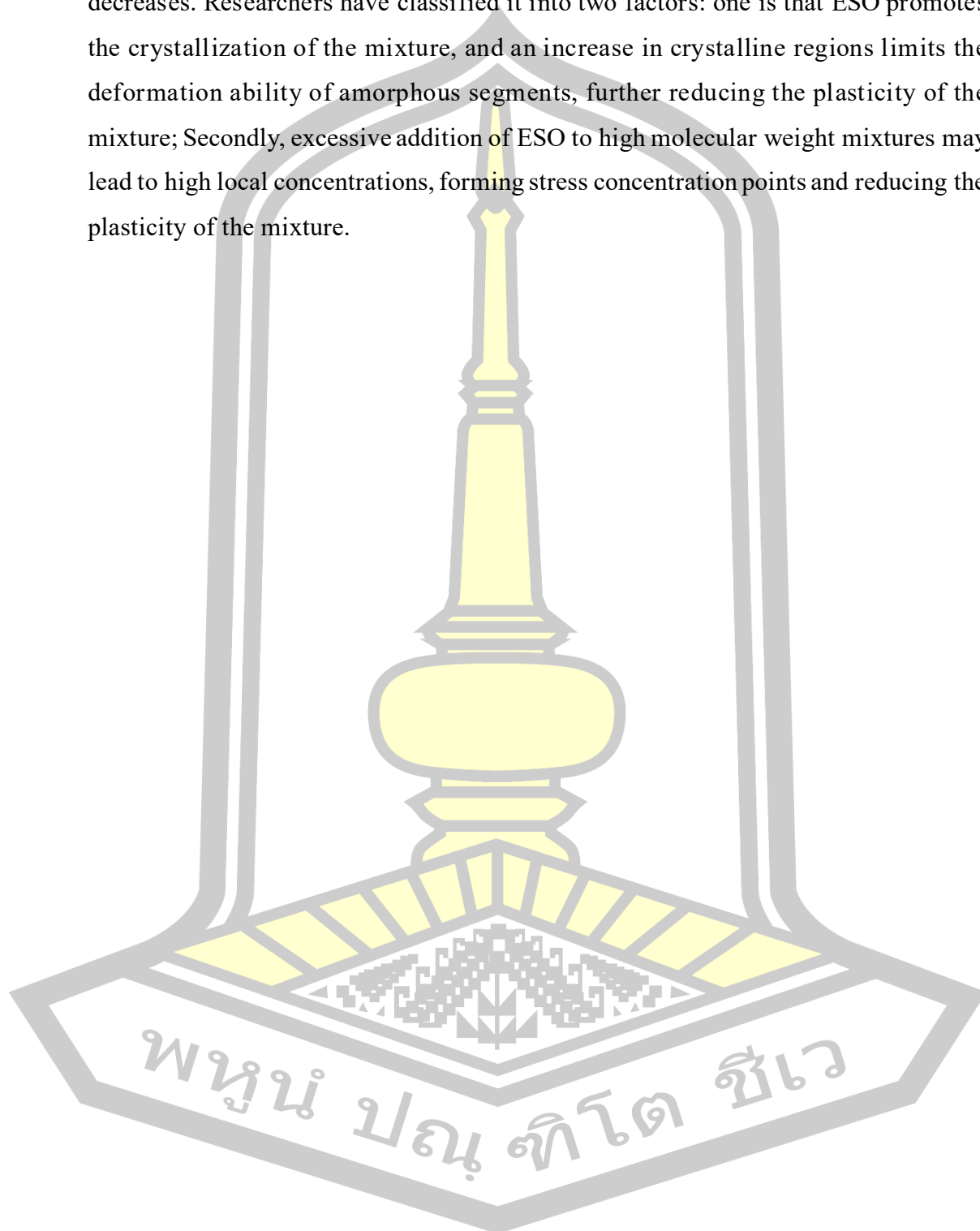


Figure 32 The elongation at break of PDLA/PLLA/PBS composites

From the Figure 32, it can be seen that the fracture elongation of PDLA/PLLA/30PBS blend is over 62.4%. After adding ESO, the fracture elongation rate gradually increases, and at a content of 15%, the fracture elongation exceeds

100% (50mm). But when the ESO content is at 20%, the elongation at break actually decreases. Researchers have classified it into two factors: one is that ESO promotes the crystallization of the mixture, and an increase in crystalline regions limits the deformation ability of amorphous segments, further reducing the plasticity of the mixture; Secondly, excessive addition of ESO to high molecular weight mixtures may lead to high local concentrations, forming stress concentration points and reducing the plasticity of the mixture.



Chapter 5 Conclusion and Prospects

5.1 Conclusion

The addition of poly(butylene succinate) (PBS) to PDLA/PLLA blends has a profound impact on their crystallization behavior, primarily due to the intermolecular interactions and nucleation effects introduced by PBS. The partial miscibility of PBS with both PLLA and PDLA promoted the formation of stereocomplex crystals, which enhanced the nucleation rate. PBS acted as a nucleation site, enabling the PLLA and PDLA chains to organize more efficiently during the crystallization process. Furthermore, the interactions among the polymers altered the crystallization kinetics by influencing the mobility of the polymer chains.

The non-isothermal crystallization analysis further revealed that lower cooling rates favored the formation of stereocomplex (SC) crystals. Additionally, at the same cooling rate, the inclusion of PBS increased the proportion of SC crystallization, with this effect being particularly pronounced at a 30% PBS concentration, where the trend was most noticeable.

ESO, as a compatibilizer, can promote the compatibility of PLLA/PDLA with PBS. FTIR testing shows that the formation of the blend is due to the ring opening reaction of ESO epoxy functional groups. DSC testing has shown that ESO can promote the crystallization of PLA stereocomplex (SC) crystals, forming 100% stereocomplex (SC) crystals at a content of 15%, improving the thermal processing performance of the material. The tensile test results indicate that ESO can be used as a plasticizer to enhance the elongation at break of PLLA/PDLA/PBS, but excessive ESO can lead to a decrease in elongation at break.

5.2 Existing problems

This paper has conducted limited research solely on the specific changes induced by compatibilizers and plasticizer in PLLA/PDLA/PBS-based composite materials. During the research process, unavoidable issues were encountered, such as incomplete data, minor inaccuracies in data precision, and the author's own limitations in professional knowledge and skills. There remains significant room for

improvement in the paper, and certain problems and shortcomings identified during the study warrant further exploration by subsequent researchers. These can be broadly summarized as follows:

1. In the course of this study, to facilitate the experimental process and comparison of test results, issues that might arise in actual industrial production of were not considered. All equipment was selected from the perspective of laboratory convenience for experimental research. Consequently, certain factors that could influence the experimental results may have been overlooked. When applying the research findings to practical scenarios, substantial additional data will be required to fill the gaps and further solidify the foundation to provide more precise experimental evidence. While the existence of these issues does not fundamentally compromise the general accuracy of the research and analysis in this paper, deeper investigations into PLA/PBS composite materials will enhance the practical significance of broadening their application fields and improve the understanding of PLA/PDLA/PBS/ESO -based composites.
2. Although research and development of biodegradable plastics have been progressing continuously, technological shortcomings persist. Some technologies, while environmentally friendly, still fall short in terms of production capacity compared to current production techniques. Therefore, certain assumptions in the experimental hypotheses involve the expectation that specific technologies, such as bio-fermentation, will advance further in application. These factors may limit the immediate applicability of the research in the current context, but the author believes they still hold value. On the other hand, due to limited expertise, this paper lacks comprehensive exploration of thermodynamic processes, crystallization mechanisms, and kinetics within the microscopic system. Thus, expanding research in these areas will be a key focus of future work.

5.3 Application prospects and next steps plan

1) Laboratory construction

At the school where I work, we built a Laboratory of Polymer Material based on the experimental conditions of Mahasharakham University, focusing on the research of PLA materials. Including the experimental instruments and equipment we use at Mahasharakham University, we have also purchased single screw extruders, spinning machines, coiling machines, etc.



Figure 33 Laboratory of Polymer material

2) Material Application Research

At present, PLA materials have been applied in China, and the PLA/PBS/ESO materials we have researched can be further applied in practical scenarios, including straws, packaging bags, spoons, etc.



(a) spoon



(b) straw

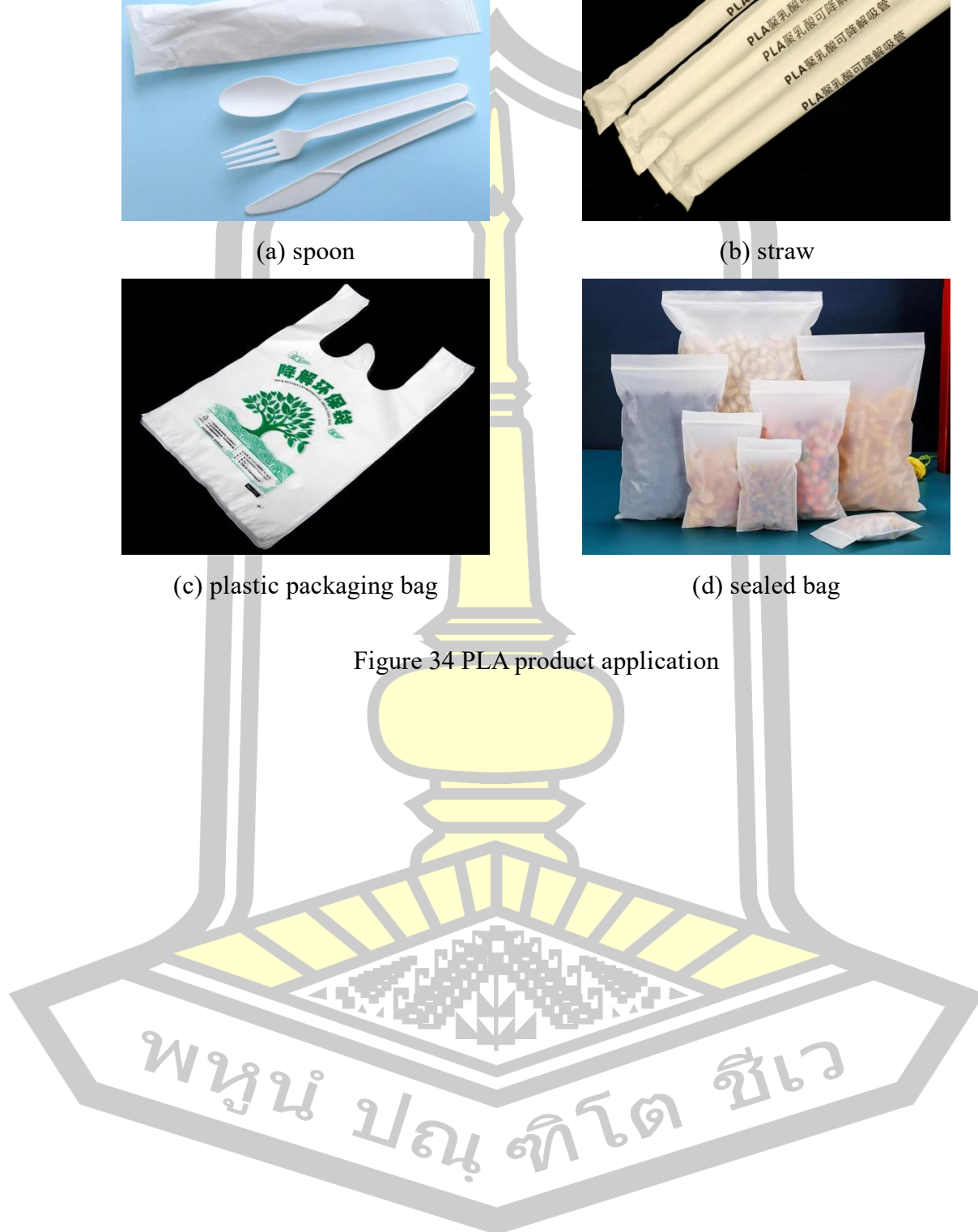


(c) plastic packaging bag



(d) sealed bag

Figure 34 PLA product application



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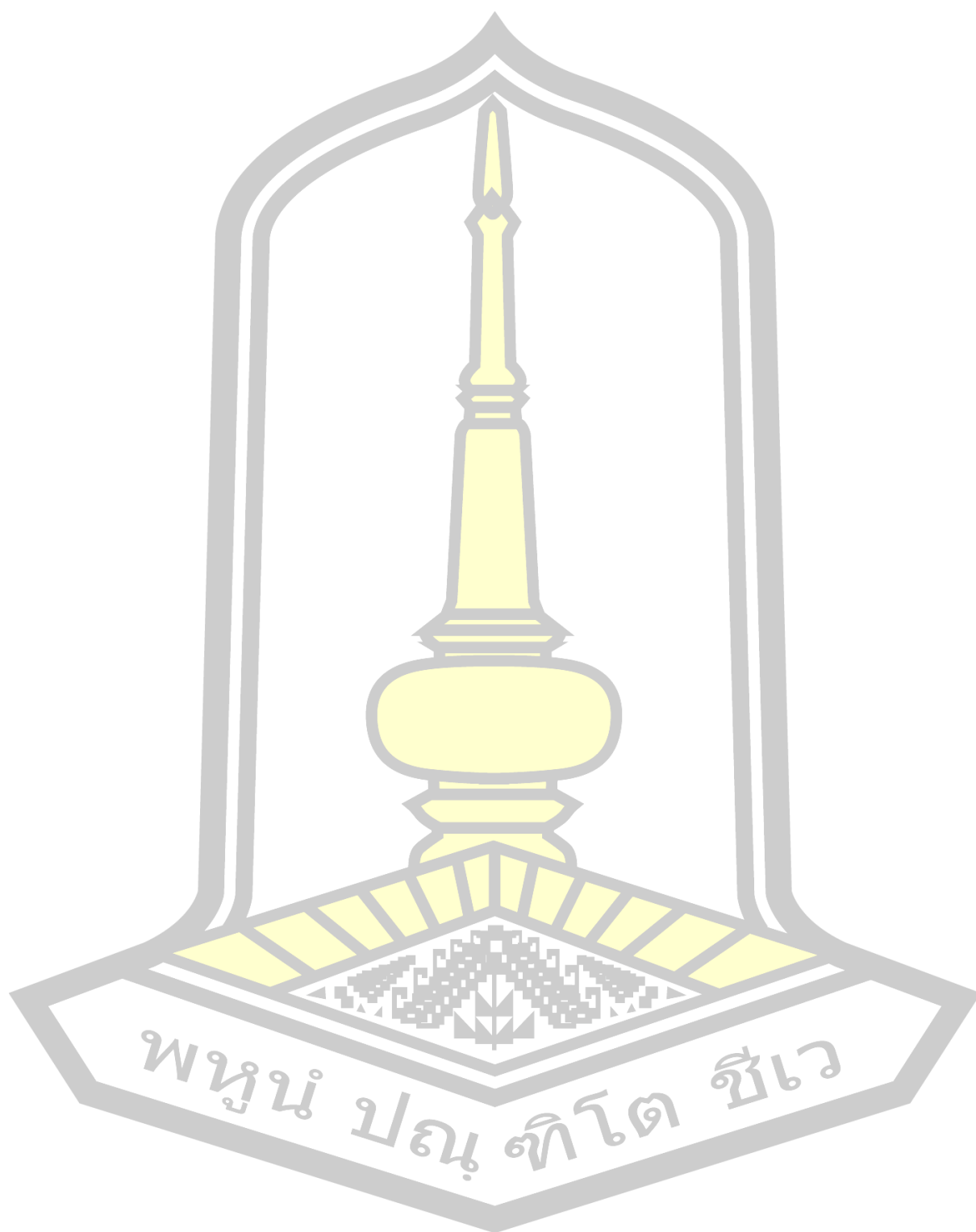
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Research output	Cai Gaiqian, Shen Jun, Jiang Zhihong, Ma Zhongli. Research on the Motion Parameters of Vertical Grinding Machine Based on Fractal Method [J]. Mechanical Science and Technology, 2014,33 (11): 1656-1660. DOI: 10.13433/j.cnki.1003-8728.2014.1110

