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By

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Elaboration and characterization of biobased blends poly lactic acid/poly (ε-caprolactone) (PLA/PCL)-Citrates

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INTRODUCTION

Many research groups have investigated the biodegradable polymer blends based on poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL), revealing that these blends were thermodynamically immiscible, which results in a multiphase structure with poor dispersion [1–10]. However, other studies revealed partial miscibility and some interfacial adhesion between the two phases [11–14]. Thus, the present study aimed to investigate the effect of citrate plasticizers and to reveal the performance of some compatibilizing agents on the miscibility of the biodegradable PLA/PCL polymer blends.

In this thesis, two different approaches were examined to enhance the miscibility of PLA/PCL blends by keeping the best attributes of these biodegradable blends. The first approach is dedicated to the plasticization of the binary blends with the addition of low molecular weight compounds such as citrate esters. The second one is dedicated to the microstructure and properties of these blends through the reactive blending. The compositions were selected from preliminary literature review. The melt blending process and the plasticization of the binary blends with Tributyl O-acetylcitrate-98% (ATBC) and Triethyl 2-acetylcitrate-99% (TEC) were carried out in an internal mixer (plastograph Brabender®). The reactive blending was performed using the aromatic isocyanate (PMDI), dicumyl peroxide (DCP), and maleic anhydride (MA). These three compatibilizing agents were found to be among the most efficient components to promote good polar interaction between PLA and PCL. The blend ratio was fixed to (80/20) and the blends were prepared under the same processing conditions.

The first part of this thesis reports on the study of blending and plasticizing effects on PLA/PCL crystallinity and miscibility. The rigid and plasticized blends at various ratios were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The results revealed a slight increase in the degree of crystallinity and a significant decrease in the glass transition temperature of PLA due to the addition of PCL. The citrate plasticizers were shown to lower the glass transition temperature and have much more enhanced the crystallization of PLA; however, a decrease in thermal stability of the blends has been promoted. Moreover, the rigid and plasticized blends were shown to be partially miscible.

The second part of this thesis is with the same aim of enhancing the miscibility between PLA and PCL as well as to investigate the effectiveness of the different

compatibilizing agents. The optimum blend ratio was determined as (80/20). PLA/PCL (80/20) blends were investigated by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourrier transform infrared (FTIR), X-ray diffraction (XRD), and by scanning electron microscopy (SEM). The results indicated that some chemical interaction occurred through the formation of carbamate bond between the –NCO groups of PMDI and the –OH group end-groups of PLA and PCL. The addition of DCP slowed down the performance of PMDI when both additives were used as a compatibilizing agent for the PLA/PCL blend. DSC results revealed significant variations in the crystallization and melting of PLA by the addition of PMDI. DCP slightly affected both melting and cold crystallization of PLA. The compatibilizing agents have promoted a slight decrease in the thermal stability of the blends. While the combination of PMDI and DCP has shown an antagonism effect on thermal stability. Enhanced thermal stability was observed with the addition of PMDI. XRD results revealed that the degree of crystallinity of the studied blends has decreased by the addition of the different compatibilizing agents. The effective interfacial reactions accomplished between the isocyanate functionalities of PMDI and carboxyl, hydroxyl end groups of the PLA/PCL blend was confirmed by SEM. The compatibilized blends exhibited smaller dispersed phase particle sizes and more occupied interface. However, the particle sizes of the compatibilized blends differ somewhat. More effective compatibilization was achieved by the addition of PMDI and (DCP + PMDI).

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DEDICATION

“This thesis work is dedicated to my late father who could not share the joy of my success, for his good example who has taught me to work hard for the things I aspire to achieve

To my dear mother for her ongoing love and unconditional support

To my precious brothers and sister, to my brother in law, my sisters in law and to my dearest niece

To my beloved grandparents

To all my family members for their constant support and encouragement during the challenges of graduate school and life

To my best friends”

–Nesrine

TABLE OF CONTENTS

Chapter I: Literature Review

Chapter II: State of Art

Chapter III: Materials and Methodology

Chapter IV: Blending and plasticizing effects on PLA/PCL crystallinity and miscibility

Chapter V: Microstructure and thermal properties of PLA/PCL blends through reactive blending

Chapter VI: General Conclusions and Recommendations

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

ATBC	Tributyl O-acetylcitrate-98%
DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared
MA	Maleic anhydride
PCL	Poly(ε-caprolactone)
PDMI	Aromatic isocyanate
PLA	Poly(lactic acide)
PLA-g-MA	Maleic anhydride grafted poly(lactic acid)
SEM	Scanning electron microscopy
TEC	Triethyl 2-acetylcitrate-99%
TGA	Thermogravimetric analysis
T_{onset}	Extrapolated start temperature of degradation
Tg	Glass transition temperature
Tm	Melting temperature
T_{1max}	Maximum degradation temperature in the first stage
T_{2max}	Maximum degradation temperature in the second stage
$T_{5\%}$	Temperature corresponding to 5 % of weight loss
$T_{50\%}$	Temperature corresponding to 50 % of weight loss
XRD	X-ray diffraction

Chapter I

LITERATURE REVIEW

Chapter I. Biodegradable polymers and blends

I.1. Introduction

Over the last decades, plastics have been taken a great proportion in the packaging market due to their great performance of flexibility, transparency, stability, and lightweight. In spite of their good properties, plastics also cause a series of environmental problems. Being derived from nonrenewable fossil fuel and gas resources, these plastics are persistent to chemical, physical, and biological degradation. Therefore, once discarded in nature after their service life, their wastes, are not biodegraded but accumulated in landfills owing to increasing difficulties of these wastes disposal [1, 2]. The overuse of all kinds of plastics has resulted in the pollution of air, land, ground water and oceans, which adversely affect humans and wildlife. According to the 2015 Fact Sheet reported by the United States Environmental Protection Agency, the recycling rate of plastic was only 9.1%, whereas more than 75% of plastic was landfilled [3]. At the same time, it is stated that 63% of the plastic waste came from the packaging applications. Thus, it is essential to find out an effective way to reduce the plastic packaging waste and to find alternative "environmentally-friendly" substitutes to the conventional plastics which satisfy the requirement of sustainability and degradability to low-toxic degradation products [4, 5]. With the raising awareness of sustainability, biodegradable plastics are taking place of conventional petroleum-based plastics globally, serving as an alternative solution to alleviate the over-loaded landfills by reducing plastic waste [6]. Being produced from renewable resources and also because of their desirable properties, recyclability, compostability and natural abundance, the use of biodegradable polymers is viewed as an ultimate solution for reducing the over dependency of plastic industry on fossil fuels. Furthermore, these also help in reducing environmental pollution since these are recycled by biological processes [7–9]. More and more researchers and industries have focused on the development of biodegradable plastics. A recent research announced that the global biodegradable plastics (such as poly(lactic acid) (PLA), polycaprolactone (PCL), starch blends, regenerated cellulose, polybutylene succinate (PBS), and poly(butyl acrylate) (PBA)) market was 19.54 billion USD in 2016, and it is estimated to reach 65.58 billion USD in 2022 [10].

I.2. Generalities about biodegradable polymers

According to the International Standardization Organization (ISO) and the American Society for Testing and Materials (ASTM), there are different definitions and criteria for compostable and biodegradable polymers and biodegradability. ASTM D6400, D6868 and D7081 specify that compostable polymers undergo degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues [5, 11]. It is also specified that biodegradable polymers are the materials that undergo biodegradation and change in chemical structure through the action of enzymes and active microorganisms such as bacteria, fungi, and actinomycetes. Biodegradation happens in the temperature range of 20 to 60°C and in a neutral or slightly acidic environment [12]. Full biodegradation corresponds to the full transformation of polymer into the low-molecular-weight molecules of water, carbon dioxide, and microbial biomass. Based on ASTM D6400, 90% degradation of the polymer in less than 180 days is required as a criterion for a polymer to be accepted as a biodegradable material [13]. The products of biodegradation are nontoxic and integrate into the living cycle of other organisms as a survival resource [14]. The biodegradation process or erosion of polymer chains into short fragments includes hydrolytic or enzymatic cleavage of selected bonds in the polymer chain and also physical bond break down [15]. Polymer characteristics such as crystallinity and molecular weight affect the biodegradation significantly [16].

In general, biodegradable polymers can be divided into two groups based on the difference of their origin: those derived from petroleum resources and those from renewable resources. Biodegradable polymers derived from petroleum resources are mainly synthetic plastics with hydrolyzable functions, such as urethane, amide, and ester. Compared with those derived from renewable resources, these polymers display better performance and lower cost but poorer biodegradability. The latter group, especially agro-polymers, which includes protein and polysaccharide, normally display poor mechanical properties and high cost, but better biodegradability compared with those derived from petroleum [17].

The life cycle of synthesized biodegradable polymers derived from renewable resources is shown in Figure I.1. Under the conditions of bacteria, water, and oxygen, polymer products will gradually biodegrade to biomass, carbon dioxide, and water, which will eventually become part of the agricultural feed stocks under the mechanism of photosynthesis, thus completing the cycle [17].

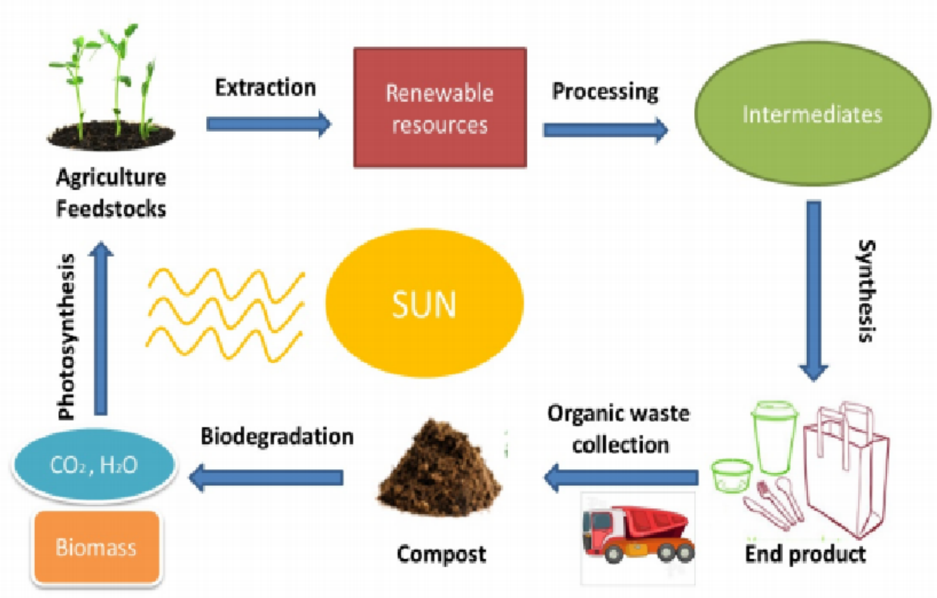

Figure I.1. Lifecycle of synthesized biodegradable polymers derived from renewable resources [17]

I.3. Biodegradation

As mentioned above biodegradation is a degrading process caused by biological activity, especially by enzymatic action, leading to a change in the chemical structure of the material. Depending on the degrading environment, the biodegradation could be divided into two categories: aerobic biodegradation and anaerobic biodegradation. Where $C_{Polymer}$ represents either a polymer or a fragment from any of the degradation processes defined earlier. The reacting processes are as follows:

Aerobic biodegradation:

$$C_{Polymer} + O_2 \Rightarrow CO_2 + H_2O + C_{Residue} + C_{Biomass} + \text{salts} \quad (1)$$

Anaerobic biodegradation:

$$C_{Polymer} \Rightarrow CO_2 + H_2O + CH_4 + C_{Residue} + C_{Biomass} + \text{salts} \quad (2)$$

Biodegradation is a long-lasting process (from a few months to years), and due to its biological nature, there are many factors that would affect the degradation rate. Some of them are environment-related factors, like microorganisms, temperature, moisture, and oxygen availability [18].

Microorganisms, as the major element in the biodegradation process, are the first important factor which is to ensure the breakdown of the molecular structure of plastics, and then the plastic could be fully assimilated by the environment. Regarding this, the other factors, like temperature, moisture, and oxygen, are crucial to support the bioactivity of microorganisms. In general, a higher temperature could accelerate the reacting process. However, temperatures above 60°C might kill some bacteria and reduce the moisture, and then affect the biodegradation rate. It is recommended that a temperature between 54 ~ 60°C is good for boosting the process of biodegradation [18].

Moisture is another essential factor for the biodegradation process since it is one of the basic living elements for the microorganisms. Proper percentage of moisture (50 ~ 60%) helps in the microbial development and metabolic activity and strengthen the further biodegradation of plastics. At the same time, excess water should be avoided in an aerobic biodegradation process because it may influence the air circulation and decrease oxygen availability [18].

For the aerobic biodegradation, the proper amount of oxygen is helpful for the respiratory action of microorganism. Thus, it is important to control the air flow rate. A low air flow rate can impede the microbial respiration and then affect their biological activity. Conversely, too much air would decrease the moisture and temperature of the degrading environment and then slow down the degrading rate [18].

I.4. Classification of biodegradable polymers

As shown in Figure I.2 biodegradable polymers can be classified into two main categories based on their origin (natural and synthetic) and into four categories, depending on their synthesis. Natural biodegradable polymers can be subclassified into the natural polymers and modified natural polymers. Synthetic biodegradable polymers can be synthesized from monomers obtained from petroleum products or monomers with natural origin [11, 19–21].

(a) polymers from biomass such as the agro-polymers from agro-resources which are also known as natural polymers, e.g., starch, cellulose, proteins like gelatin, casein, and silk, chitin, and chitosan, etc;

(b) polymers obtained by microbial production, e.g., the polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and bacterial cellulose etc;

(c) polymers chemically synthesized using monomers obtained from agro-resources, e.g., poly(lactic acid);

(d) polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources, like aliphatic polyesters (polybutylene succinate (PBS) and copolyesters poly(butylene succinate-co-adipate) (PBSA)), polycaprolactone (PCL), and aromatic polyesters (poly(vinyl alcohol) (PVA) and copolyester (poly(butylenes adipate-co-terephthalate) (PBAT)).

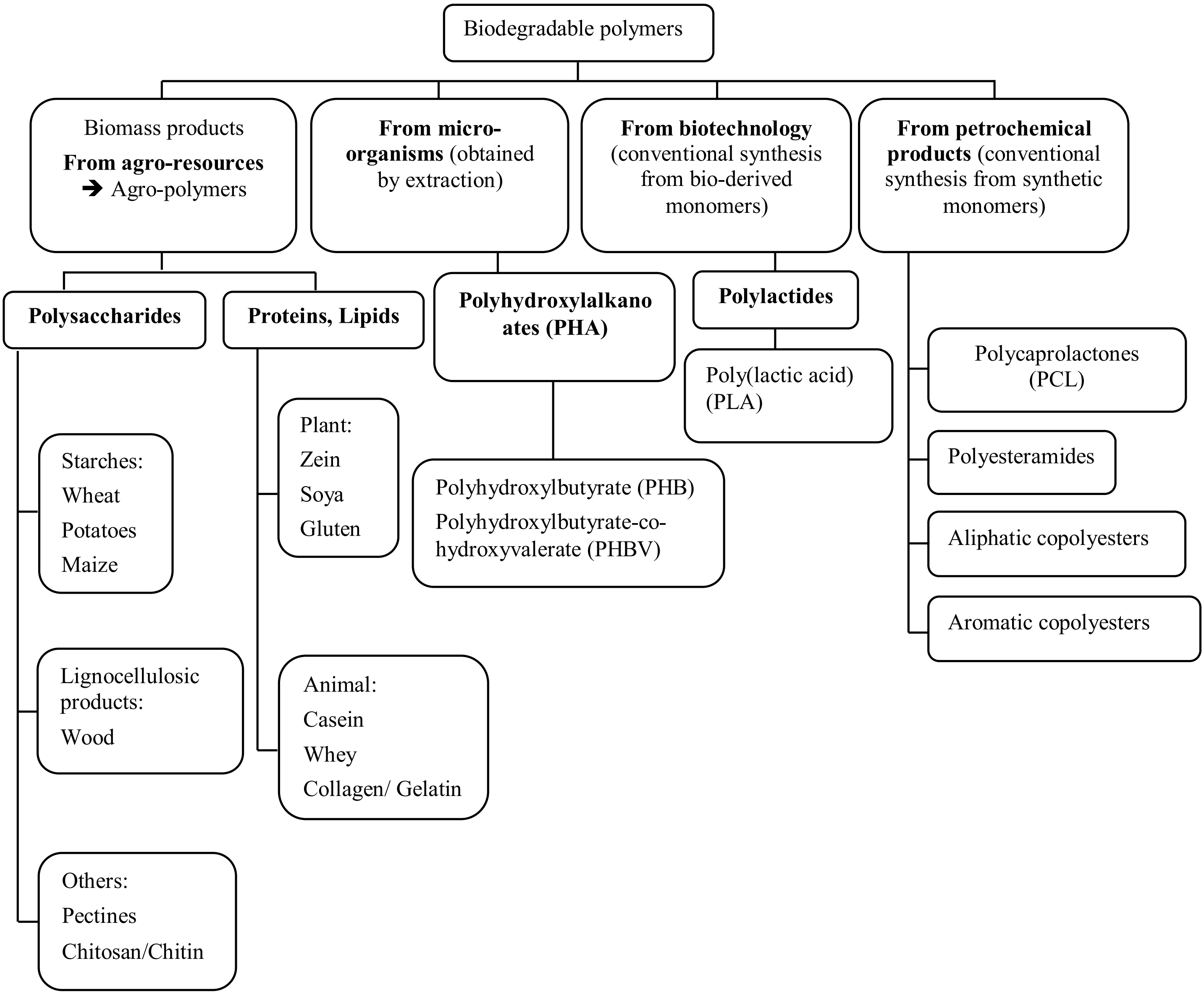

Figure I.2. Classification of the biodegradable polymers [20]

Currently, several different types of biodegradable polymers have been developed and entered the marketplace with a prediction of an increasing share in the next years. Among the most important biodegradable polymers that have attracted interest are PLA, PCL, PHA, PBAT, etc... [22].

I.5. Applications and market of biodegradable polymers

Biodegradable polymers present a wide range of promising properties in a number of applications. Because of their biodegradability, bioresorbability, and compatibility and also due to their initial high price, biopolymers such as PLA, poly(glycolic acid) (PGA), poly(lactic-co-glycolic acid) (PLGA) and PHA first found use exclusively in the biomedical and pharmaceutical domains. In these high added value fields, biodegradable polymers were involved as implants (vascular and orthopedic), bone fixation devices, various pins and screws, absorbable surgical sutures and drug delivery systems [5]. During the last decades of the last century, breakthrough and technical innovations in the synthesis of biopolymers led to their mass production which helped to decrease their price. This coupled with advanced knowledge of how biopolymers properties can be modified and tuned to meet market and end-use requirements have fueled interest in these materials to be used in other fields. Because of their good competitiveness, they are establishing themselves as alternatives to petrochemical polymers in a number of different markets such as biomedical, agriculture and packaging applications. In the packaging industry, biopolymers continue to attract more and more attention [5]. They are used as food and nonfood packagings, composting and carrier bags and food-service applications [5, 23]. In the agricultural application, biodegradable polymers are used as agricultural mulch film, planting containers and controlled release of agricultural chemicals, and in the textile sector, they are used as woven and nonwoven fabrics, and in some personal hygienic products such as disposable diapers [5].

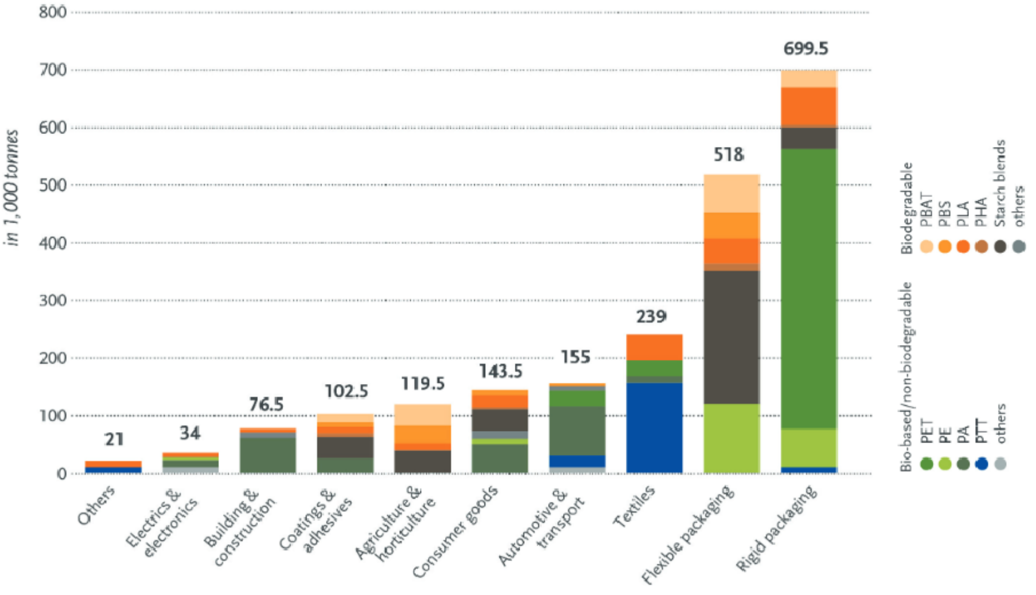

Figure I.3. Global production capacities of biopolastics in 2018 (by market segment) [24]

Bioplastics are used in an increasing number of markets, from packaging, catering products, consumer electronics, automotive, agriculture/horticulture and toys to textiles and a number of other segments. Packaging remains the largest field of application for bioplastics with almost 65% (1.2 million tonnes) of the total bioplastics market in 2018 [24].

The increase in the use of bioplastics in all market segments is driven by the increasing demand for sustainable products by consumers and brands alike due to a growing awareness of the impact on the environment and the need to reduce the dependency on fossil resources as well as the continuous advances and innovations of the bioplastics industry in new materials with improved properties and new functionalities. Currently, there is a bioplastic alternative for almost every conventional plastic material and corresponding application. Depending on the material, bioplastics have the same properties as conventional plastics and offer additional advantages, such as a reduced carbon footprint or additional waste management options, such as industrial composting [24].

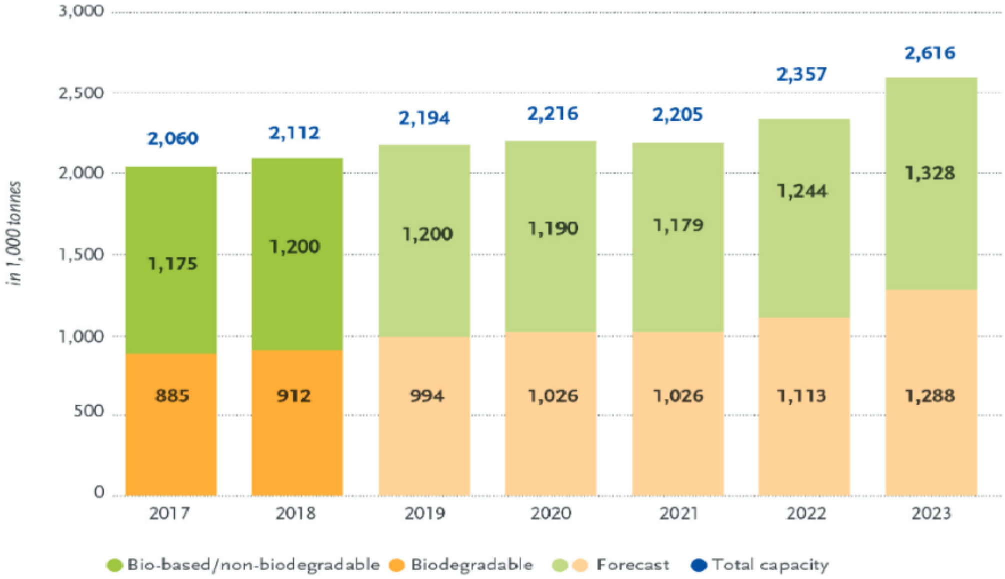

Figure I.4. Estimated global bioplastics production capacity (2017-2023) [24]

Currently, bioplastics represent roughly 1% of the 335 million tonnes of plastic produced annually. But as demand is rising, and with more sophisticated biopolymers, applications and products emerging, the market is continuously growing. According to the latest market data compiled by European Bioplastics in cooperation with the research institute nova-Institute (Hürth, Germany), global bioplastics production capacity is set to increase from around 2.19 million tonnes in 2019 to approximately 2.62 million tonnes in 2023 [24].

I.6. Poly(lactic acid): synthesis, structure, properties, and applications

I.6.1. Poly(lactic acid) (PLA)

Poly(lactic acid) or polylactide (PLA) is extracted from renewable resources such as starch, corn, sugars, potato, and other natural products. It is a hydrophobic polymer that can be degraded in the presence of enzymes and via a hydrolytic degradation process of the ester backbone [15]. PLA is one of the most extensively investigated biobased and biodegradable polymers due to its attractive mechanical strength, high melting temperature, sustainability, and relatively low cost. Therefore, biodegradability combined with the excellent properties of PLA, make it a promising material for short lifecycles applications such as packaging and electronics [25, 26].

I.6.2. Synthesis and stereoisomers of lactic acid

Lactic acid (2-hydroxypropanoic acid), $CH_3CH(OH)COOH$, was first isolated from sour milk by the Swedish chemist Carl Wilhelm Scheele in 1780 and first commercially available in 1881 [27, 28]. As shown in Figure I.5, the structure of lactic acid is characterized by a chiral carbon atom and exists in two optically active stereoisomers, namely L and D enantiomers. Racemic D,L-lactic acid consisting of the equimolar mixture of D- and L-lactic acid is produced via chemical synthesis.

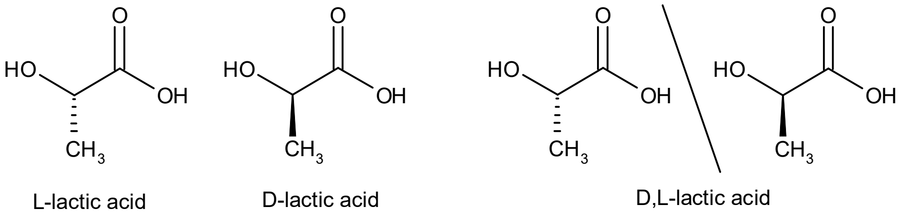

Figure I.5. Structure of L-, D- and DL-lactic acids [29]

L- and D-lactic acids are generally synthesized by fermentation using suitable micro-organisms. The commercial fermentative batch process, which takes from three to six days to complete is preferred because it allows producing optically pure L- (99.5%) and D-lactic acid (0.5%) and is environmentally benign bioprocess which uses low-cost renewable (biomass) feedstock as carbon source for the fermentation at low temperature and consumes low energy. Because of these advantages, approximately 90% of the total lactic acid produced worldwide is made by bacterial fermentation and the remaining portion is produced synthetically by the hydrolysis of lactonitrile by a strong acid. However, lactic acid from the microbial process is difficult to recover and its purification is a long multi-step process (ultra-filtration, nano-filtration, electrodialysis and ion exchange) which makes lactic acid more expensive.

Depending on the type of bacteria strain, two fermentation methods can be distinguished. The first is the hetero-fermentative process and the second known as the homo-fermentative method is the more extensively used in the industry which gives lower levels of by-products and greater raw material conversion (~90%). The raw materials (carbon source) for the fermentation can be refined sugar (glucose and sucrose) or any carbohydrates containing sugar from agricultural production and residues. For example, NatureWorks®, the worldwide leading producer of PLA, exclusively uses corn starch as raw material for lactic acid production via lactic fermentation [30].

I.6.3. Synthesis and stereoisomers of lactide

Lactide is obtained by distilling water from lactic acid, under mild conditions and vacuum without solvent, through a combined process of oligomerization and cyclization achieved by the catalytic depolymerization of the corresponding low-molecular-weight oligo (lactic acid) (OLLA) under reduced pressure, as shown in Figure I.6.

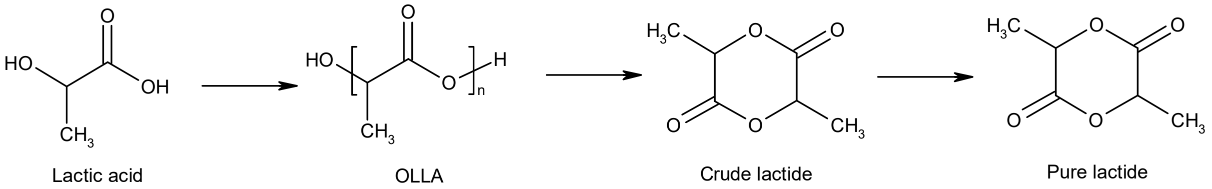

Figure I.6. Synthesis route to lactide from lactic acid via oligolactide [29]

Again, owing to the stereoisometric nature of the lactic acid, three stereo-forms of lactide are generated: D,D-lactide (D-LA), L,L-lactide (L-LA), and D,L-lactide (meso-LA) as shown in (Figure I.7). The physical properties including melting temperature, crystallization behaviors, and mechanical properties of PLA depend strongly on the stereochemical compositions [31, 32].

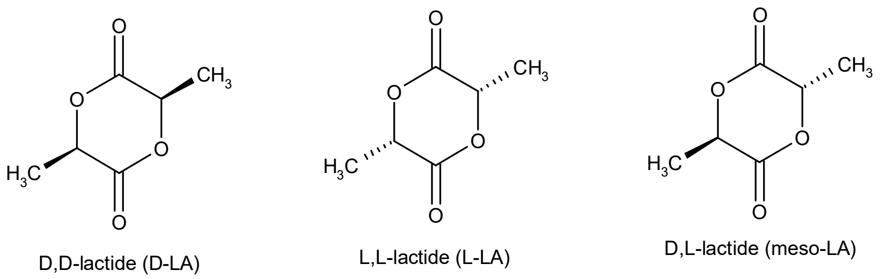

Figure I.7. Chemical structures of three stereoisomers of lactide [26]

I.6.4. Poly(lactic acid) production techniques

PLA was first synthesized by polycondensation, by Théophile-Jules Pelouze, in 1845 [33]. In 1932, Wallace Hume Carothers *et al.* developed a method to polymerize lactide into low-molecular-weight PLA. This method was later patented by Du Pont in 1954 [34]. Until late 1970, PLA was developed as biomedical material based on its bioresorbable and biocompatible nature. Its low-molecular-weight limited its application to therapeutic and pharmaceutical applications, protein encapsulation, and delivery systems [35–38]. Recently, the biomedical application of PLA has been extended to tissue engineering [39] including scaffold materials [40] as well as to biocompatible materials for sutures and prostheses [41] in which high- and low-molecular-weight PLA are used, respectively. In early 1990, Cargill Inc. succeeded in polymerizing high-molecular-weight poly(L-lactic acid) (PLLA) by ring-opening polymerization of L-lactide in industrial scale and commercialized the PLLA polymer in the mid of 1990s. Showing high mechanical properties in addition to a biodegradable nature, PLLA was thought to provide large opportunities to replace non-biodegradable oil-based polymers, such as poly(ethylene terephthalate) (PET) and polystyrene (PS), for short-term use such as food packaging and other consumer products [29, 42].

As shown in Figure I.8, the conversion of lactic acid monomer to high-molecular-weight PLA can be accomplished either by direct condensation polymerization or azeotropic dehydration and condensation. The ring-opening polymerization (ROP), as a third synthesis method, uses the lactide (lactic acid cyclic dimer) as the monomer, therefore it requires an intermediate step necessary for the preparation of the monomer. All of these three methods are discontinuous, and none of these is simple or easy to conduct; they all require rigorous control of conditions (temperature, pressure, and pH), the use of catalysts and long polymerization times, which implies high energy consumption [43].

Nowadays, direct azeotropic dehydration and condensation polycondensation and ROP are the most used production routes [44]. Lactide ROP is the most common way to produce high-molecular-weight PLA in the market due to its cost [45]. Depending on the stereo purity of the starting monomer, a family of polymers may be synthesized: pure poly-L-lactic acid (PLLA), pure poly-D-lactic acid (PDLA), and poly-D, L-lactic acid (PDLLA) [44]. Poly(lactic acid) and polylactide describe the same chemical product. Poly(lactic acid) defines polymers obtained from direct polycondensation reaction of the lactic acid monomer and polylactide those derived from the ROP of the intermediary lactide monomer, while the abbreviation (PLA) is used to describe both.

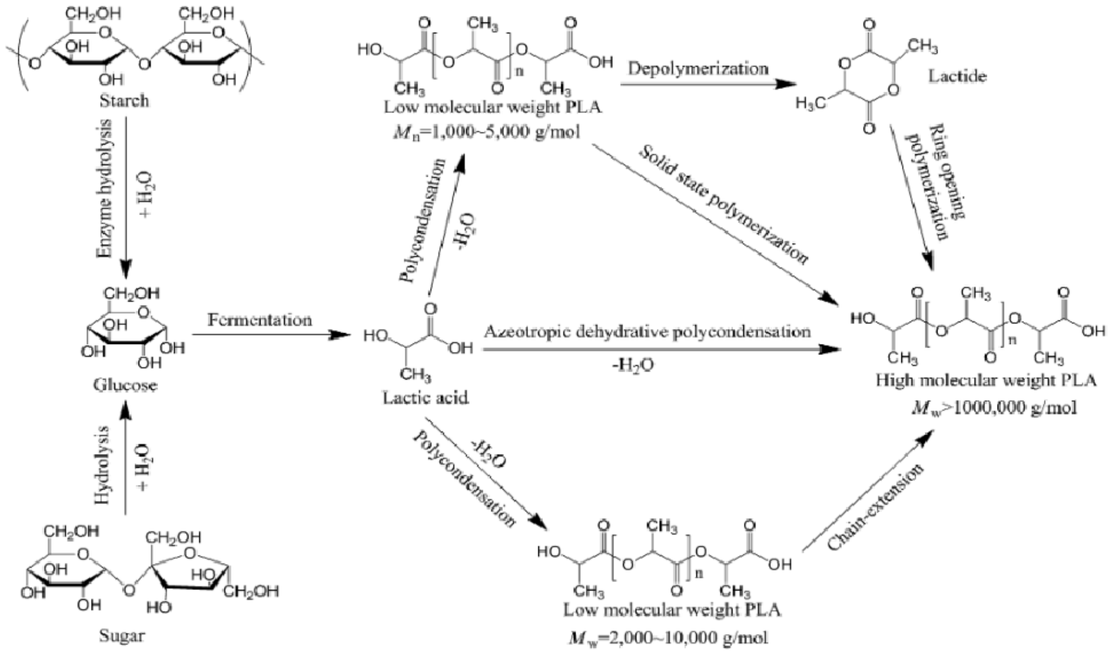

Figure I.8. Synthesis routes of poly(lactic acid) [43]

I.6.4.1. Direct condensation polymerization

Polycondensation of lactic acid to obtain PLA is possible by the reaction of the hydroxyl and carboxylic acid groups of lactic acid. By removing the water formed during this condensation reaction, the reaction proceeds toward the product side, PLA, as shown in Figure I.9. Due to the difficulty in removing byproducts completely from the highly viscous reaction mixture, the polymer produced through direct polycondensation is usually of low-molecular-weight (<50,000 $g.mol^{-1}$) and low quality. Even though it is the least expensive method involving solvents under high vacuum and high temperature, it is not common in the commercial manufacture of PLA because only low (to intermediate)-molecular-weight polymers (oligomers) can be obtained arising from the presence of impurities, viscosity build-up during polymerization and mainly from the difficulty to remove water from the condensation equilibrium reaction responsible for decrease in conversion and depolymerization [46, 47]. To increase the molecular weight, esterification-promoting adjuvants (bis(trichloromethyl) carbonate, dicyclohexylcarbodiimide, and carbonyl diimidazole) or chain extenders (epoxides such as butyl glycidyl ether, or isocyanates) are used, which obviously increase the steps and complexity of the production and also the cost of the final product [20, 44, 47]. In addition to these disadvantages, the final polymer may contain impurities and unreacted chain extenders which may be nonbiodegradable or nonbioresorbable additives [47].

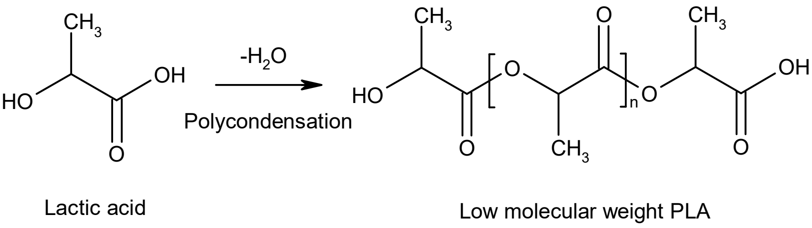

Figure I.9. Synthesis of low-molecular-weight PLA via direct polycondensation of lactic acid monomer [48]

I.6.4.2. Azeotropic dehydrative polycondensation

The azeotropic dehydrative polycondensation is a solvent-based technique developed and patented by Mitsui Toatsu Chemicals (Japan). In this process, schematically illustrated in Figure I.8, high-molecular-weight PLA is obtained by direct condensation of lactic acid without the use of chain extenders, coupling agents or esterification-promoting adjuvants and their associated drawbacks [20]. Because the polymerization takes place in solution, water of condensation is continuously and readily removed by azeotropic condensation of the lactic acid and the catalyst (Sn compounds: Sn, SnO or $SnCl_2$) in a refluxing, high boiling, aprotic solvent (diphenyl ether) under reduced pressure [20, 47, 49]. However, this technique gives considerable catalyst residues because of its high concentration needed to reach an adequate reaction rate. This can cause many drawbacks during processing, such as degradation and hydrolysis. For most biomedical and packaging applications, the catalyst toxicity is a highly sensitive issue. The catalyst can be deactivated by the addition of phosphoric acid or can be precipitated and filtered out by the addition of strong acids such as sulfuric acid. Thus, residual catalyst contents can be reduced to some ppm. In addition, the excess use of a solvent (fresh and dehydrated) during polymerization and non-solvent to collect the final polymer, makes this technique sound non-environmental, involving different steps, thus laborious and expensive [20, 49].

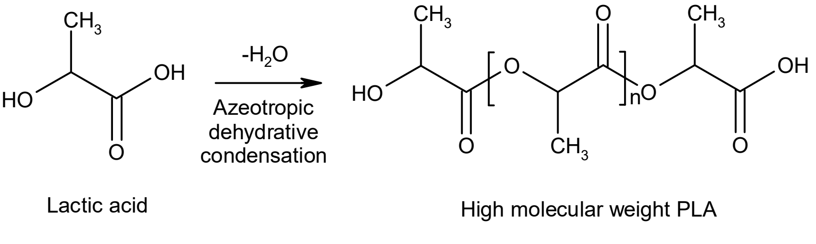

Figure I.10. Synthesis of high-molecular-weight PLA via azeotropic dehydrative polycondensation according to Mitsui process [50]

I.6.4.3. Ring-opening polymerization (ROP)

As previously stated, the first ring-opening polymerization of lactide produced low-molecular-weight PLA. After improvements in lactide purification, high-molecular-weight PLA was then obtained. At the early stage of PLA discovery, its high cost confined its application only to the biomedical field. This method produces pure high-molecular-weight PLA ($\overline{Mw}$>100 000 g.mol^{-1}) but necessitates first the preparation of the lactide and then its purification by vacuum distillation accomplished at high temperature without the use of a solvent which increases the overall cost of the polymerization [11, 51].

ROP, schematically shown in Figure I.11, can be carried out on a large scale by melt polymerization, which is the most used technique due to its simplicity and reproducibility, but bulk, solution, and suspension polymerization techniques are also possible. The polymerization mechanism can be cationic, anionic, or coordination-insertion type, depending on the catalyst and initiator concentration system. The polymerization is generally catalyzed by organo-metallic compounds such as the most used stannous octoate, as it provides high reaction rate, high rate of transformation, high-molecular-weight, and relatively mild reaction conditions [52]. Many nontoxic catalysts derived from magnesium, calcium, zinc, alkali metals, and aluminum, have been developed for the ROP of lactides to solve pollution problems caused by heavy metal catalysts [51, 53].

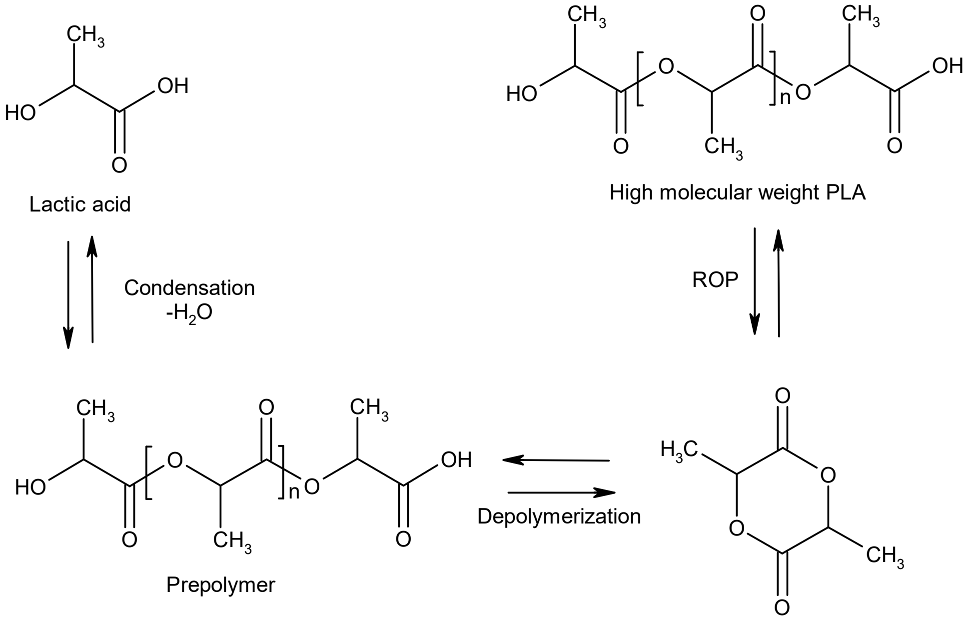

Figure I.11. Schematic of PLA production via ring-opening polymerization using lactide monomer [49, 54, 55]

A low-cost continuous process that allows the production of lactic acid based polymers had been developed by Cargill Dow LLC in the '90s. This environmentally friendly process involves synthesizing both lactide and PLA in the melt rather than in solution. Firstly, lactic acid is fermented from dextrose and condensed to produce the PLA prepolymer. Then the prepolymer is converted into lactide isomers through the use of a catalyst to increase the reaction rate. Finally, the lactide is purified through distillation and the high-molecular-weight PLA is produced through a ROP in the melt, completely eliminating the use of costly and environmentally unfriendly solvents as seen in Figure I.12. After the polymerization is complete, any remaining monomer is removed under vacuum and recycled to the beginning of the process [54–57].

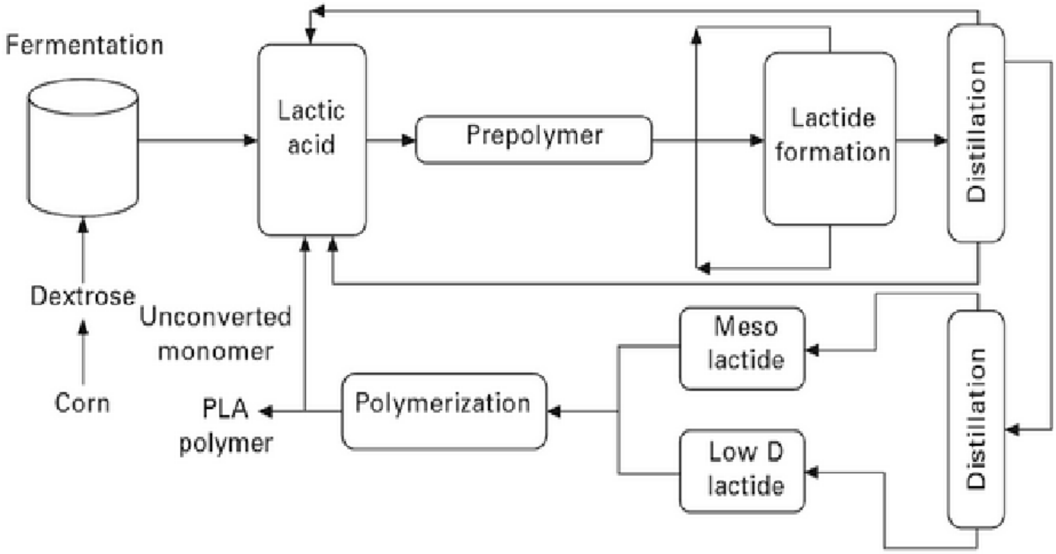

Figure I.12. The nonsolvent process to prepare poly(lactic acid) [54, 55]

I.6.5. Comparison and new trends of poly(lactic acid) synthesis and modification development

In summary, polycondensation is mostly used to produce PLA with low-molecular-weight using basic equipment and process, while ROP aims for the production of a wider range of molecular weight polymer by controlling the purity of lactide and its polymerization. Since each approach has its unique advantages and limitations, the selection of a specific method should be based on the application. For instance, drug release materials favor low-molecular-weight PLA as it could be degraded quickly while high-molecular-weight PLA is suitable for food packaging applications and textile products [46]. In light of current development, the advantages and disadvantages of different methods are summarized in Table.I.1.

Table.I.1. Advantages and disadvantages of different polymer synthesis methods [46]

Method	Advantages	Disadvantages
Azeotropic polycondensation	Low cost	Low yield
	Basic equipment	Low purity (usually with residual solvent and byproducts in polymer)
	Moderate temperature (<180°C)	Solvent waste and pollution
Solid state polycondensation	High purity (suppression of side reactions)	Low yield
	High-molecular-weight	Long duration
	Moderate conditions	Complicated operation
Ring-opening polymerization	High purity	Low overall yield
	Wide range of molecular weight	Long duration
	Availability in high-molecular-weight	Demanding condition
	Controlled polymer properties	Complicated operation

I.6.6. Properties of PLA

The properties of PLA, as those of other polymers, depend strongly on the stereochemical composition. By varying the chemical composition in terms of L- and D-enantiomers during synthesis, many important properties of PLA can be tailored to match the performance requirements for various applications. Furthermore, as for other polymers, the properties of PLA are significantly dependent on other factors such as molecular weight, annealing time, and processing temperature [5, 58, 59]. In this section, the PLA polymer crystallinity, optical, thermal, rheological, processing, solubility, barrier, physical, mechanical, and degradation properties are discussed.

I.6.6.1. Crystallinity

The crystallization kinetics of PLA has been extensively studied and found to be rather slow, as for PET [50]. The crystallization rate increases with a decrease in molecular weight and it is strongly dependent on the copolymer composition [60]. PLLA can crystallize in the presence of D-lactide [61]; however, as the structure becomes more disordered, the rate of crystallization decreases. Furthermore, the latter is essentially determined by the decrease in the melting point of the different copolymers. PDLA/PLLA stereo complexes are very efficient nucleating agents for PLLA, with increases in both crystallization rate and crystallinity, the latter of up to 60% [42, 58, 62].

PLA can be produced as totally amorphous or with up to 40% crystallinity, depending on the stereochemistry and thermal history [20]. The crystallinity, as a determinant factor in PLA performance, can be modified by adjusting the stereochemical composition of the polymer to produce semi-crystalline or amorphous PLA [50, 59]. The crystallization ability of polylactides decreases with chain stereo-irregularity, accordingly PLA derived from greater than 93% L-lactic acid are semicrystalline and, from between 50 and 93% L-lactic acid is strictly amorphous [20, 58, 60]. Macromolecular imperfections are responsible for the decrease in both the rate and the extent of PLLA crystallization. In practice, most PLAs are made up of L-and D,L-lactide copolymers, since the reaction media often contain some meso-lactide impurities. Depending on preparation conditions, PLLA crystallizes in three different forms (α, β, and γ) with the more stable one being the α-form [62].

I.6.6.2. Optical properties

Optical properties are very important in protecting and preserving products that are sensitive to visible and UV light until they reach the consumer. Compared to other traditional packaging materials, LDPE shows the highest transmission of UV light followed by PLA as shown in Figure I.13. Therefore, additives to block UV light transmission are needed in the case of PLA. Effective UV stabilizers are able to absorb UV light and thus prevent damage to light-sensitive packaged foods, resulting in retention of taste, extension of shelf life and improvement of product quality [59, 60].

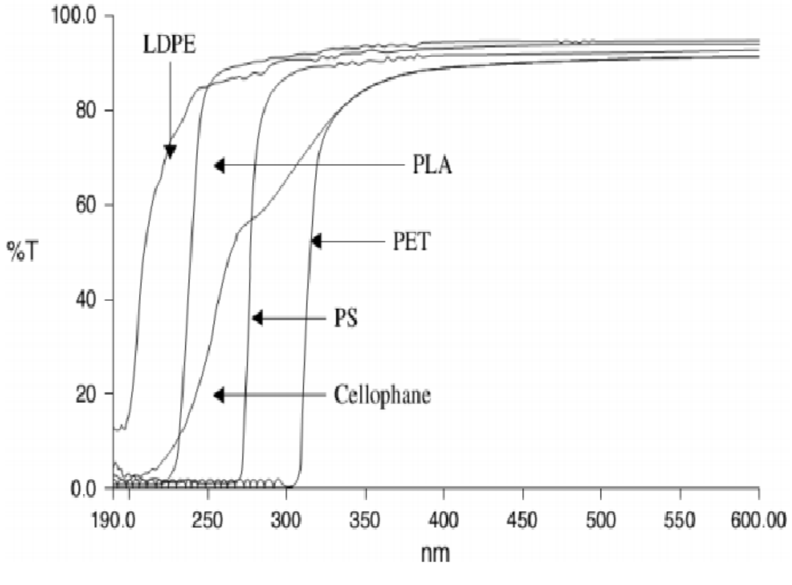

Figure I.13. Percent transmission versus wavelength for PLA, PS, LDPE, PET, and cellophane films [59, 60]

I.6.6.3. Thermal properties

As for any semicrystalline polymer, PLA exhibits both glass transition temperature (Tg) and melting temperature (T_m) but with relatively high Tg and low Tm as compared to other thermoplastics (Figure I.14). The Tg and Tm of PLA are dependent on both the Mw and the optical purity of the polymer (Table I.2). The typical value of Tg reported in the literature ranges from 50°C to 80°C which also depends on thermal history, quenching, and annealing. The reported Tm is in the range 130°C to 180°C, and 93J/g is the most referred PLA melt enthalpy for 100% crystallinity used to estimate the degree of crystallinity by differential scanning calorimetry (DSC) [42, 56, 63]. The presence of a double melting point in PLLA is generally found and attributed to slow rates of crystallization and recrystallization [50].

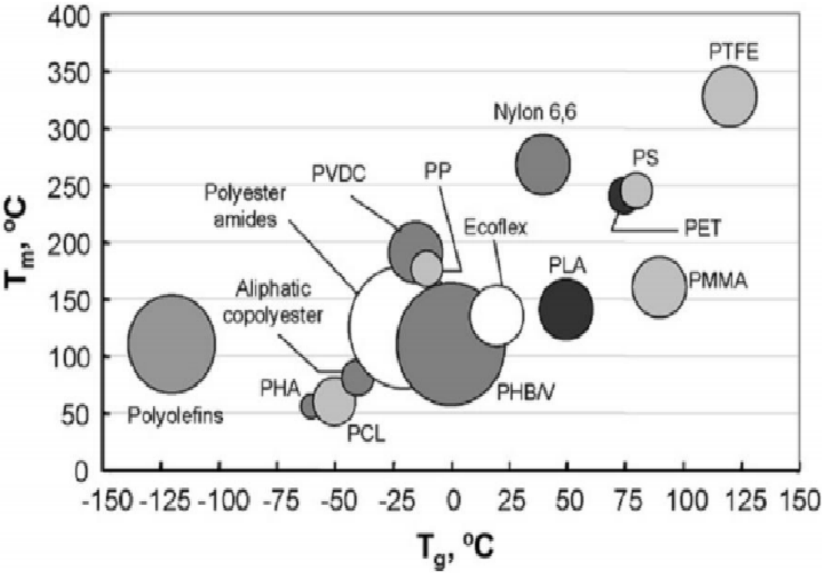

Figure I.14. Comparison of glass transition and melting temperatures of PLA with other thermoplastics [42]

Table I.2. Primary transition temperatures of selected PLA copolymers [42]

Copolymer ratio	Glass transition temperature (°C)	Melting temperature (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (L/D,L)-PLA	59	164
90/10 (L/D,L)-PLA	56	150
85/15 (L/D,L)-PLA	56	140
80/20 (L/D,L)-PLA	56	125

PLA also suffers from low heat distortion temperature (HDT) and Vicat softening point mainly due to its low Tg. HDT values of PLA are influenced neither by the molecular weight nor by crystallinity. However, those of the Vicat softening point, are influenced by crystallinity. HDT values of amorphous and crystalline PLA are in the ranges 55-57°C and

60-66°C, respectively, while those of Vicat penetration are in the intervals 59-60°C and 157-165°C for amorphous and crystalline PLA respectively [59]. In terms of thermal stability, PLA is considered a less stable polymer, exhibiting rapid loss of molecular weight during processing in the molten state. The ester linkage of PLA tends to degrade during thermal processing under hydrolytic conditions. The decomposition temperature of PLA lies between 230°C and 260°C attributed to various reactions of different mechanisms including (a) hydrolysis by trace amounts of water, (b) zipper-like depolymerization, (c) oxidative, random main chain scission, (d) intermolecular transesterification to monomer and oligomeric esters, and (e) intramolecular transesterification resulting in formation of monomer and oligomer lactides of low-molecular-weight [11, 30, 32, 36]. Thermal degradation of PLA is reported to be affected by the process temperature, residence time, presence of impurities of residual catalysts, moisture, crystallinity, % isomer, residual lactic acid, $\overline{Mw}$ and $\overline{Mw}$ distribution [11]. The decomposition of PLA leads to the formation of CO, CO_2, acetaldehyde and to volatile lactide which can result in fuming and/or fouling the processing equipment [64].

I.6.6.4. Rheological properties and processing

The actual commercial PLA resins can be processed, like all other thermoplastics, into various products using conventional technologies of processing including extrusion, injection molding, blow molding, thermoforming, fiber spinning and film forming [2, 51]. The properties of the polymer will, therefore, depend on the specific conditions during the processing steps. The main parameters during the melt processing are temperature, residence time, moisture content, and atmosphere. But the major problem in the manufacturing of PLA-based products is the limited thermal stability during the melt processing. To overcome such a drawback or to give PLA new properties, a large number of multiphase materials have been developed, mainly by mixing PLA with other products [65].

For processing and for the corresponding applications, the knowledge of PLA melt rheology is of particular interest. The shear viscosity of PLA polymers affects thermal processing, such as injection molding, extrusion, film blowing, sheet forming, fiber spinning and thermoforming. Polylactide melt behavior is similar to polystyrene [47]. PLA is characterized by low melt strength and poor shear-sensitivity of its melt viscosity, which can be overcome by introducing branching into its backbone either during compounding by adding peroxides or during polymerization by introducing monomers or multifunctional initiators [49]. Branched PLA displays high viscosity at low shear rates, making it more suitable for operations such as extrusion coating, extrusion blow molding, and foaming (Figure I.15) [49, 59].

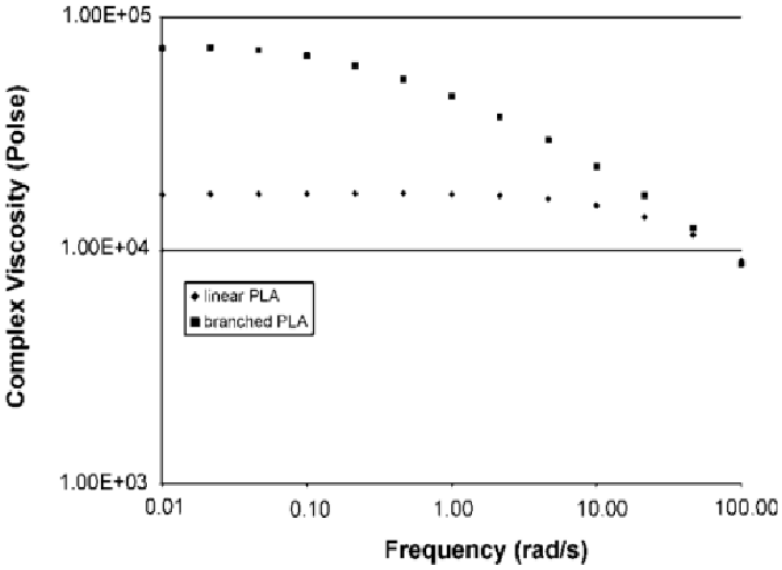

Figure I.15. Rheological properties of linear and branched NatureWorks PLA [49]

I.6.6.5. Solubility in solvents

Polylactides are soluble in dioxane, acetonitrile, methylene chloride, 1,1,2-trichloroethane, and dichloroacetic acid, but chloroform is the good solvent for PLA and for most of the corresponding copolymers. Ethylbenzene, toluene, acetone, and tetrahydrofuran only partly dissolve polylactides when cold, though they are readily soluble in these solvents when heated to boiling temperatures. Amorphous PLA is soluble in organic solvents, while crystalline PLA is soluble in chlorinated solvents and benzene at elevated temperatures and not soluble in acetone, ethyl acetate or tetrahydrofuran. Poly(rac-lactide) and Poly(meso-lactide) are soluble in many other organic solvents like acetone, pyridine, ethyl lactate, tetrahydrofuran, xylene, ethyl acetate, dimethylformamide, methyl ethyl ketone. All polylactides are insoluble in water, some alcohols and alkanes [20, 50, 58, 59].

I.6.6.6. Barrier properties

Because PLA finds a lot of applications in food packaging and medical applications, its barrier properties (mainly to carbon dioxide, oxygen, and water vapor) have been largely investigated [60]. PLA has good barrier properties to flavors and aromas with permeation properties to all gases similar to those of PS [11, 49, 66]. The CO_2 permeability coefficients for PLA polymers are lower than those reported for crystalline PS at 25°C and 0% relative humidity (RH) and higher than those for PET. Since diffusion takes place through the amorphous regions of a polymer, an increase in the extent of crystallization will inevitably result in a decrease in permeability. PET and PLA are both hydrophobic and the corresponding films absorb very low amounts of water, showing similar barrier properties, as indicated by the values of their water vapor permeability coefficient determined from 10°C to 37.8°C in the range of 40-90% RH [62]. In addition, PLA has good crease-retention and crimp, excellent grease and oil resistance, easy low-temperature heat sealability making it appropriate for numerous packaging applications and a good candidate to replace traditional polymers used in this area [49, 59].

I.6.6.7. Physical and mechanical properties

Physical and mechanical properties of PLA are dependent on a range of parameters, such as crystallinity, polymer structure, molecular weight and material formulation (plasticization, blending, reinforcing, etc.) [5, 20, 50, 67]. The density of PLA is 1.25 g.cm^{-3} and 1.29 g.cm^{-3} for amorphous and crystalline PLA which is lower than that of PET (1.34 g.cm^{-3}), but higher than that of other conventional polymers with densities in the range of 0.8-1.1 g.cm^{-3} [5, 43, 58, 59]. PLA is a clear, colorless and glossy polymer showing good appearance and transparency with a high gloss (105-200%) compared to PET (60-110%) and PP (75-90%) [58]. Because of its high Tg (above room temperature), PLA behaves as a glassy polymer just like PS. When subjected to tensile testing, PLA exhibits poor plastic behavior and fails in a brittle fashion with little strain softening (Figure I.6) [68]. Concerning its resistance to impact, PLA is notch sensitive and its impact strength is greatly affected by crystallinity. For low crystallinity (3-9%), the notched Izod impact strength of PLLA is in the range 2.0-3.0 kJ.m^{-2} while at higher crystallinity (45-70%) it is in the interval 3.0-7.0 kJ.m^{-2}. PDLA exhibits lower impact resistance in the range 1.5-2 kJ.m^{-2}. The unnotched impact strength for PLLA of low and high crystallinity in the range 13-20 kJ.m^{-2} and 18-35 kJ.m^{-2}, respectively, indicating higher differences than those observed for the notched counterparts [59].

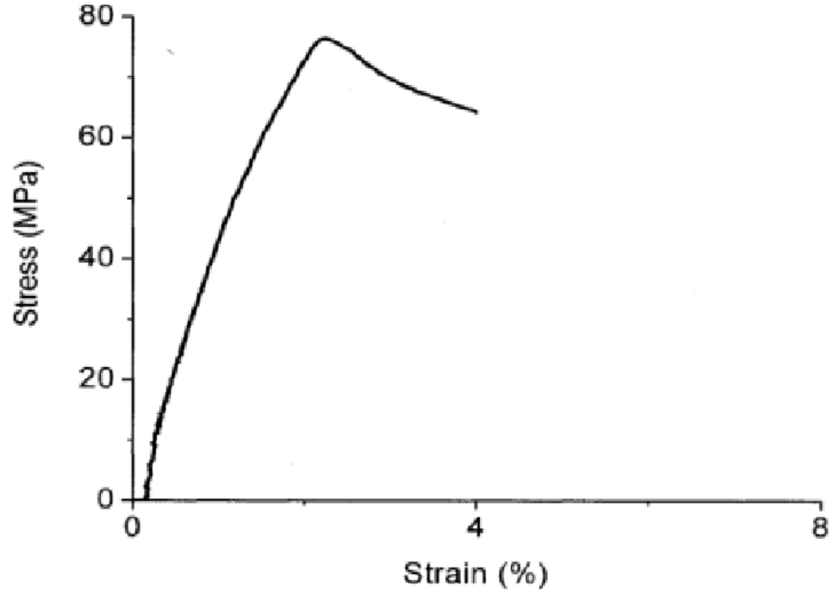

Figure I.16. A Typical stress-strain curve of PLA [68]

The mechanical properties of polylactides can vary to a large extent, ranging from soft and elastic materials to stiff and high strength materials [67]. Overall, PLA has good mechanical properties which are comparable to other commodity thermoplastics like PS and PET. As shown in Table I.3, PLA has high modulus (3-4 GPa) and tensile strength (45-60 MPa) but suffers from low Tg, low elongation (ductility) (4-10%) and impact strength, which are even lower than those of its homologous glassy polystyrene [50, 59].

Table I.3. Comparison of typical PLA properties with several petroleum-based commodity thermoplastic resins [43]

	PLA	**PET**	**PS**	**HIPS**	**PP**
Tg (°C)[a]	55	75	105	-	-10
Tensile strength at break (MPa)[a]	53	54	45	23	31
Tensile modulus (GPa)[a]	3.4	2.8	2.9	2.1	0.9
Elongation at break (%)[a]	6	130	7	45	120
Notched Izod IS ($J.m^{-1}$)[a]	13	59[66]	27	123	27[69] (i-PP)
Gardner impact (J)[a]	0.06	0.32	0.51	11.30	0.79
Cost ($/lb)[b]	1-1.5	0.70-0.72	0.99-0.72	1.01-1.03	1.15-1.17

PET: poly (ethylene terephtalate); PS: polystyrene; HIPS: high-impact polystyrene;

PP: polypropylene; i-PP: isotactic polypropylene homopolymer; IS: impact strength.

[a] Data mainly cited from ref. [70].

[b] Cost cited from “Plastics News”, March 31, 2011 except PLA resin.

I.6.6.8. Degradation

The primary mechanism of PLA degradation is the hydrolysis of the ester bond, followed by a bacterial attack on the fragmented residues. This process can be associated with thermal or biotic degradation and can be affected by various parameters such as the PLA structure, its molecular weight and distribution, its morphology (crystallinity), the shape of its samples and its thermal and mechanical history including processing, as well as, of course, the hydrolysis conditions [71]. In the environment, PLA degrades within several months of exposure to moisture, whereas in compost under high temperature and high humidity conditions, it may degrade within several weeks [43, 54]. The environmental degradation of PLA is a two-step process. First, the high-molecular-weight molecules are reduced to lower-molecular-weight species by, random chain scission of the ester bonds. In the second stage, the molecular weight reductions proceed until lactic acid and low-molecular-weight oligomers are formed which are then metabolized by microorganisms to yield carbon dioxide and water [43]. The degradation has been found to be an auto-catalyzed process due to the increasing amount of compounds containing carboxylic end-groups [43, 54].

I.6.7. PLA applications

In spite of its excellent properties, the commercial use of PLA has been historically confined in the biomedical applications owing to its high production cost [49]. Breakthrough and new innovations accomplished in the production of lactide monomer and the change of polymerization technique from batch to continuous process, helped to decrease the PLA price [51, 66]. In addition, the joint venture between Cagill LLC and Dow Chemical Company in 1997 allowed the large scale production of PLA under the trade name NatureWorks LLC which permitted PLA to change status from an engineering resin to a commodity plastic [52]. The cost performance balance helped PLA to compete well with general purpose petrochemical-based plastics [51, 66] and to forge roles in a wide range of end-use applications namely, packaging and the textile sectors and even in the automotive, building sector, cosmetics, and electronics which require more durable PLA products [1, 59]. Table I.4 summarizes some of the application sectors for PLA together with some examples.

Table I.4. Main applications for PLA [72]

Sector	Examples
Packaging	Food packaging, films, rigid thermoformed food and beverage containers, carrier bags and labels, coated papers and boards, battery packaging, windows for envelopes.
Agriculture	Sheet or molded forms for time-release fertilizers, plant clips.
Transportation	Parts of automobile interiors (head liners, upholstery, spare tyre covers).
Electric appliances and electronics	SC, computer keys, cases for Walkmans, wrappers for CD.
Houseware	Carpets
Other (fibers and fabrics)	Textiles and non-wovens

I.6.7.1. Medical, biomedical and pharmaceutical applications

Due to the bioresorbability and the biocompatible properties in the human body as well as the ability to degrade both in vivo and in vitro, PLA and its copolymers have been extensively employed to manufacture tissue engineering scaffolds, delivery system materials, or covering membranes, different bioabsorbable medical implants, as well as in dermatology, pharmaceutical, and cosmetics [73]. The main reported examples on medical or biomedical products are bone fracture internal fixation devices in surgery like screws, resorbable prostheses, and resorbable surgical sutures which do not need to be removed with a second operative procedure, degradable implants and tissue engineering porous scaffolds as reconstructive matrices for damaged tissues and organs [20, 52]. Recently, these biomedical applications have been extended to pharmaceutical and medical fields as microspheres and microcapsules which have been widely applied in drug delivery systems for the prolonged administration of a wide variety of medical agents [8, 11].

I.6.7.2. Packaging applications

PLA complies with most requirements for packaging applications and provides excellent physical and mechanical properties at a low price. When plasticized, PLA mimics and challenges conventional polymers used in this field such as PP, PET, LDPE, PVC and PS, and is considered as their main alternative and as one solution to alleviate solid waste disposal problems from this application stream which is, up to now, considered as the main source of environmental concerns due to the use of these non biodegradable polymers [54, 58]. Low toxicity, clarity, high gloss and transparency, reasonable barrier properties, good heat sealability and ease of printability and conversion into different forms as well as degradation in a biological environment such as soil or compost, have made PLA an ideal and viable material for packaging [42, 74]. Commercially available PLA packaging can provide better mechanical properties than PS and have properties more or less comparable to those of PET [20]. In high clarity packaging roles, PLA is a good alternative to PET and some cellulosic which is being used as candy wrap, optically enhanced films, and shrink labels as well as the sealant layer in form-fill coextrusion [52].

During the last decade, the use of PLA as a packaging material has increased, mainly in the area of fresh and short shelf-life products, such as fruit and vegetables and those whose quality is not damaged by PLA oxygen permeability [11, 20]. Due to his high cost, the initial use of PLA as a packaging material has been in high-value films, rigid thermoforms, food and beverage containers, and coated papers. [20]. PLA Films, produced by blown double bubble technology, are transparent and have acceptance by customers for food contact. Cast films have very low haze, excellent gloss, and moderate gas (O_2, CO_2, and H_2O) transmission rates desirable for consumer food packaging [54]. Other popular package applications include compostable and loose-fill bags, drinking cups, rigid thermoforms, food and beverage containers, lamination films (paper coatings), blister packages and single-use-bottles because of their resistance to fats and oils, as well as their ability to “block” flavors and aromas [20, 66].

I.6.7.3. Fiber and textiles

Fiber is one of the largest potential application areas for PLA. PLA is readily melt-spinnable and can be designed for many fiber applications. Fibers can be produced both by solvent and by melt-spinning processes and are drawn under different conditions to orient the macromolecules [45]. Some of the current fiber uses include hollow fiber-fill for pillows and comforters, bulk continuous filament for carpet, filament yarns, and spun yarns for apparel, spunbond, and other nonwovens and bicomponent fibers for binders and self-crimping fibers and nappies [20, 54]. PLA fiber can be combined with natural or regenerated fibers including cotton, wool, silk, viscose, and others along with synthetic fibers made from PET, nylon, and other petroleum-based synthetics. PLA can be included as a minor component (5-15%) or as the major fiber, depending on the balance of properties and appearance desired. Some of the beneficial characteristics of PLA fiber products include its natural soft feel, ease of processing, good resistance to UV, reduced flammability, and unique stain and soil resistance and facile dyeability [54]. Compared with natural fibers, PLA fibers demonstrate excellent resiliency, outstanding crimp retention and improved wicking [75].

I.7. Poly(ε-caprolactone) (PCL)

Polycaprolactone is a biodegradable aliphatic polyester produced through the ring-opening polymerization of the cyclic monomer ε-caprolactone (Figure I.17) using stannous octoate as catalyst and low-molecular-weight alcohols to control the molecular weight of the polymer [76]. It has a low melting point of around 60°C and a glass transition temperature of -60°C which make it a rubbery material and exhibits high permeability to low molecular species at body temperature. It is a linear and partially crystalline polymer with a crystallinity of around 40-50% [77].

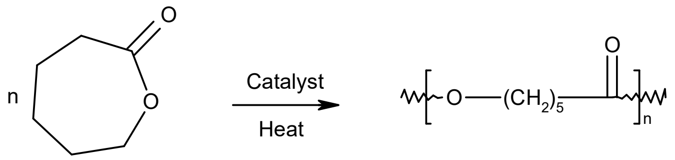

Figure I.17. Ring-opening polymerization of ε-caprolactone to polycaprolactone (PCL) [77]

I.7.1. Polymerization of poly(ε-caprolactone)

There are two main polymerization methods for polyesters including poly(ε-caprolactone), namely: polycondensation polymerization and ring-opening polymerization. The polycondensation polymerization has been reported as early as the 1930's by the esterification process of diols and dicarboxylic acids. Producing polymers with molecular weights even up to 30,000 g.mol^{-1} with this technique requires a high temperature and a long reaction time. This level of molecular weight results in moderate mechanical properties. Also control over the polydispersity and obtaining a nearly monodisperse polymer with this method, is hardly achievable. In addition, byproducts of polycondensation such as water should be constantly removed during the reaction [78]. ROP is an alternative efficient method to produce biodegradable polyesters in shorter reaction times and at a lower polymerization temperature with the ability to have control over the molecular weight and molecular weight distribution. This method mainly involves ROP of the cyclic ester monomer, lactone. The structure of the lactone monomer is shown in Figure I.18. Based on the catalytic system, ROP can be classified into the following groups: Cationic, anionic, monomer activated and coordination-insertion ROP.

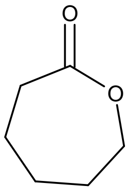

Figure I.18. The molecular structure of ε-caprolactone

Cationic and anionic ROP proceeds by the formation of cationic and anionic species. Scandium triflouromethanesulfonate, $Sc(OTf)_3$ has been used as a catalyst for cationic living ROP [78] as shown in Figure I.19. ROP of monomer activated method proceeds by the activation of the monomer molecules by a catalyst. Coordination-insertion ROP is known as the most common technique for this type of polymerization, which occurs by the coordination of the monomer to the catalyst and insertion of the metal-oxygen bond of the catalyst.

The presence of catalyst and initiator in a polymerization system can be associated with the intermolecular and intramolecular transesterification as side reactions. These reactions may lessen the molecular weight and broaden the molecular weight distribution. The occurrence of these side reactions is normally at the later stages of polymerization [79].

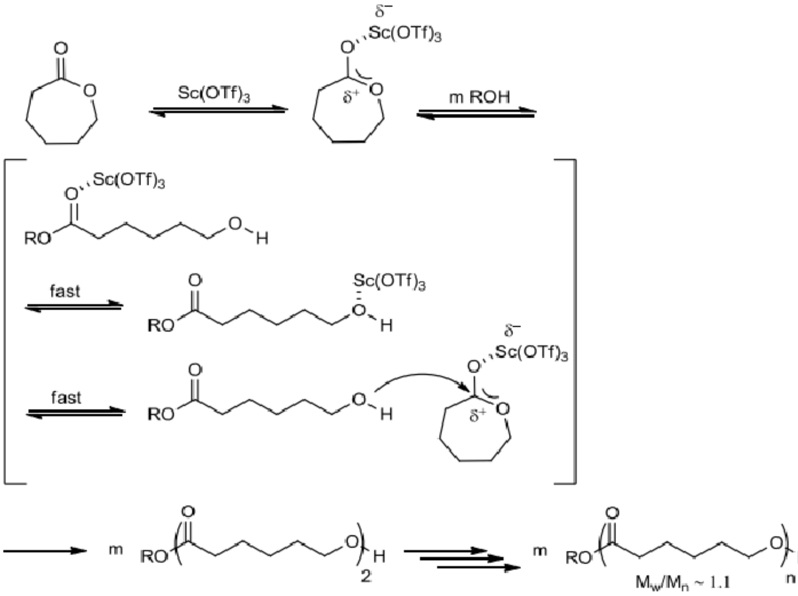

Figure I.19. Possible mechanism of cationic living ring-opening polymerization of ε-caprolactone by $Sc(OTf)_3$ as a catalyst [78]

Figure I.20 depicts the schematic of intermolecular and intramolecular transesterification reactions.

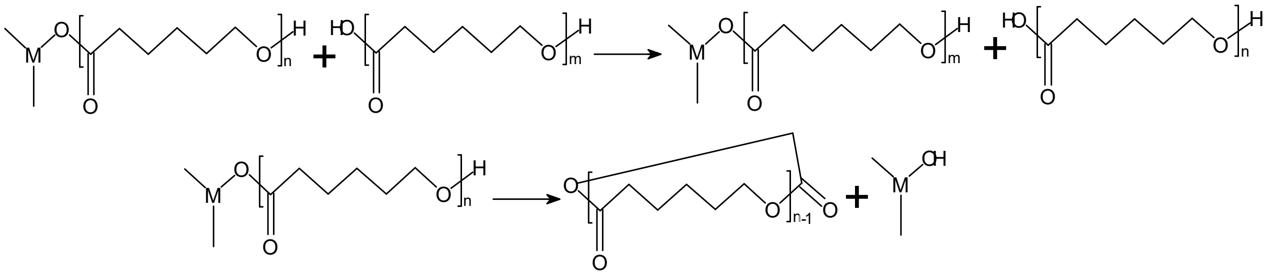

Figure I.20. Intermolecular and intramolecular transesterification reactions in the PCL polymerization process [79]

Various types of catalytic systems are used for ROP, namely metal based, organic and enzymatic catalysts. Metal-based catalysts include alkali-based compounds, which are anionic compounds used in anionic ROP method. Transesterification side reaction results in the loss of molecular weight control in this type of catalyst [79]. Satisfactory results have been obtained by using metal alkoxides such as Lanthanide boron hydride complexes as a catalyst in the polymerization of ε-caprolactone [80]. Alkaline earth-based catalysts, poor metal-based catalysts such as aluminum based and tin-based, transition metal-based such as zirconium-based and rare-earth metal-based catalysts such as scandium, lanthanum, and yttrium are other catalyst systems for ROP. Rare-earth catalysts have attracted significant attention as highly efficient catalysts that enable good control over the polymerization reaction. Rare-earth tris(amidate) complexes of yttrium have been used as initiators for the ROP of ε-caprolactone [81]. These complexes have shown significant ability to produce high-molecular-weight polyesters.

I.7.2. Properties of PCL

Polycaprolactone is known as a flexible polymer, which is very relatively compatible with natural polymers like starch, hydroxyapatite (HA), chitosan and synthetic polymers namely polyethylene glycol (PEG), polyurethane (PU), poly*(*ethylene oxide) (PEO), poly(vinyl alcohol*)* (PVA), poly(lactic acid) and poly(lactic-co-glycolic acid) (PLGA) [82–89]. PCL is miscible with a number of polymers such as poly(vinyl chloride) (PVC) [90]. The most common use of PCL is in the manufacture of polyurethanes and it can be used as a solid plasticizer for PVC as well. It finds also some biomedical applications based on its biocompatible character, mostly in controlled release of drugs, and some packaging applications thanks to its compostable character [91].

PCL is soluble in many solvents such as chloroform, dichloromethane, carbon tetrachloride, benzene, toluene, cyclohexanone, and 2-nitropropane at room temperature. In addition, It has a low solubility in acetone, 2-butanone, ethyl acetate, dimethylformamide and acetonitrile and is insoluble in alcohol, petroleum ether and diethyl ether [79, 90]. The versatility of PCL is due to the fact that it allows modification of its physical, chemical and mechanical properties by copolymerization or blending with many other polymers [92]. Currently, PCL is sold under two major trademarks of Capa® and Tone® produced by Perstorp and Union Carbide, respectively. Some of its typical thermophysical and mechanical properties are reported in Table I.5 [79].

Table I.5. Thermophysical mechanical properties of PCL [79]

Property	**Value**
Density, ρ ($g.cm^{-3}$)	1.071-1.200
Glass transition temperature, Tg (°C)	(-65)-(-60)
Melting temperature, T_m (°C)	56-65
Decomposition temperature, T_d (°C)	350
Tensile strength, σ (MPa)	4-785
Young modulus, E (GPa)	0.21-0.44
Elongation at breake, ε_b (%)	20-1000

I.7.3. Degradation of PCL

The degradation time for PCL varies between several months to several years (up to 4 years), and depends on the molecular weight, degree of crystallinity and the conditions of the exposed environment. Full degradation of PCL may happen in the presence of microorganisms [93]. Degrading agents attack the amorphous phase first, which leads to increasing crystallinity, while the molecular weight remains unchanged. Following that, ester cleavage results in loss of molecular weight [9, 16]. PCL degrades in hydrolytic as well as the enzymatic process by the random ester cleavage of carbonyl groups and then enzymatic surface erosion [94].

I.8. Modification approaches

In order to adjust the properties of polymers to the intended application, a wide variety of approaches is used for their modification, like plasticization, the incorporation of fillers and reinforcements, and blending.

I.8.1. Plasticization

Plasticization is often used for the modification of polymers to improve their processability and/or other properties demanded by a specific application. Plasticizers exchange the intermolecular bonds among polymer chains to bonds between the macromolecules and the small molecular weight compound, thus promoting conformational changes resulting in increased deformability. Both the glass transition and the processing temperature of the material decrease, thus enabling the melt processing of heat-sensitive polymers, at lower temperatures [95]. Because PLA is limited by its mechanical properties, plasticization is one approach to overcome the stiffness and low impact resistance [43].

I.8.2. Physical blending

Blending can be carried out by mixing of polymeric materials in the melt state without chemical reactions. A very wide range of properties can be achieved by this approach to meet the requirements of the targeted application in a relatively short time and for low cost compared to the development of new monomers and polymerization techniques [96].

I.8.3. Chemical approaches

Plasticization and physical blending offer convenient approaches to the modification of biopolymers, but similarly to commodity polymers very few biopolymer pairs are miscible or even compatible with each other. As a consequence, chemical routes, such as the chemical modification of the components or reactive compatibilization, are often used to achieve property combinations required in specific applications. Grafting, the preparation of block copolymers, or reaction with two or multifunctional compounds, are convenient ways to modify biopolymers and improve their compatibility with others. This approach is often used in compatibilization [96].

I.9. Polymer blends and miscibility

A polymer blend is a macroscopically homogeneous mixture of two or more different polymers, which can be binary, ternary, or quaternary depending on the number of constituents in the blend [97]. By emerging advanced technologies, the required properties of polymer materials have been more specific and targeted. The blending of polymers has been the most appropriate road to take to achieve optimal properties due to the high cost and difficulty of synthesizing new polymers. Polymer blends can be divided into different types considering the miscibility, immiscibility, partial miscibility, and compatibility of their components [98].

a) Miscibility is considered to be the scale of mixing of polymeric constituents of a blend yielding a material which exhibits the properties expected from a single phase material. It is sometimes erroneously assigned on the basis that a blend exhibits a single Tg or optical clarity. The miscible polymer blend can be defined as a blend of two or more polymers homogeneous down to the molecular level and fulfilling the thermodynamic conditions for a miscible multicomponent system.

b) A blend is considered immiscible or heterogeneous if it is separated into phases composed by individual constituents. Phase separation is also established from thermodynamic relationships. An immiscible polymer blend can be defined as the blend that does not comply with the thermodynamic conditions of phase stability.

c) A blend is considered partially miscible if there exists phase separation but each polymer rich phase contains a sufficient amount of the other polymer to alter the properties of that phase.

d) A compatible polymer blend is an immiscible polymer blend that exhibits macroscopically uniform physical properties throughout its whole volume. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the component polymers. Generally, the mechanical properties are employed as a reference for the degree of compatibility. The degree of compatibility is generally related to the level of adhesion between the phases and the ability to transmit stress across the interface. A compatible polymer blend corresponds to a commercially attractive polymer mixture that is visibly homogeneous, and that has improved physical properties compared with the constituent polymers.

However, the International Union of Pure and Applied Chemistry (IUPAC)'s definition of polymer miscibility is based on thermodynamic theory, which is not a useful method of detection. Thus, researchers have often shown optical clarity and single Tg as methods of detection of miscibility under the conditions of the experiment. However, optical clarity and a single Tg may be observed because they are just kinetically frozen in a state of apparent miscibility, which is not permanently miscible. So it is perfectly legitimate to observe clarity and Tg in order to make an experimentally based comment about the sample at that time but not to assume that the thermodynamic conditions for miscibility have been precisely met. Many researchers define miscible as those polymer blends or homogeneous polymer blends that show a single Tg from a single phase structure, while, immiscible blends or heterogeneous polymer blends separately show Tg of each polymer components. Compatible polymer blends exhibit macroscopically uniform properties due to strong interactions between the polymer components [73].

I.10. Factors affecting the miscibility and the immiscibility of polymer blends

I.10.1. Polarity

Polymers that are similar in structure or more generally similar in polarity, are less likely to repel each other and more likely to form miscible blends [100].

I.10.2. Specific group interaction

Polymers that are drawn to each other by hydrogen bonding, acid-base, charge transfer, ion-dipole, and donor-acceptor adducts or transition metal complexes, are less common, but when such attractions occur they are very likely to produce miscibility [101, 102].

I.10.3. Molecular weight

Lower-molecular-weight permits greater randomization on mixing and therefore greater gain of entropy, which favors miscibility. More surprisingly, polymers of similar molecular weights are more miscible, while polymers of very different molecular weights may be immiscible, even if they both have the same composition [103].

I.10.4. Crystallinity

When a polymer crystallizes, it forms a two-phase system. Thus, in a polymer blend when a polymer crystallizes, this adds another phase to the system. If both polymers in a blend crystallize, they will usually form two separate crystalline phases; it is quite rare for the two polymers to cocrystallize in a single crystalline phase [104].

I.10.5. Blend Ratio

Even though two polymers appear immiscible at a fairly equal ratio, it is quite possible that a small amount of one polymer may be soluble in a large amount of the other polymer [104].

I.11. General strategies for compatibilization of immiscible polymer blends

Compatibilization is a process of modification of the interfacial properties in an immiscible polymer blend that results in the formation of the interphases and stabilization of the morphology [97]. As it follows from thermodynamics, the blends of immiscible polymers obtained by simple mixing show a strong separation tendency, leading to a coarse structure and low interfacial adhesion. The final material then shows poor mechanical properties. On the other hand, the immiscibility or limited miscibility of polymers, enables the formation of wide range structures, some of which, if stabilized, can impart excellent end-use properties to the final material [105]. Two general methods used for compatibilization of immiscible polymers are reactive and non-reactive compatibilization.

I.11.1. Non-reactive compatibilization

The non-reactive compatibilization is accomplished by reducing the size of the dispersed phase. Premade amphiphilic compounds, like block or graft copolymers with segments that are miscible with their respective polymer components, show a tendency to be localized at the interface between immiscible blend phases. The copolymers anchor their segments in the corresponding polymer, reducing interfacial tension and stabilizing dispersion against coalescence. Random copolymers, sometimes also used as compatibilizers, reduce interfacial tension, but their ability to stabilize the phase structure is limited. Finer morphology and higher adhesion of the blend lead to improved mechanical properties. The morphology of the resulting two-phase (multiphase) material, and consequently its properties, depend on a number of factors, such as copolymer architecture (type, number, and molecular parameters of segments), blend composition and blending conditions [105, 106].

I.11.2. Reactive compatibilization

The reactive compatibilization is the process that allows generating in situ graft or block copolymers acting as compatibilizers during melt blending. These copolymers are formed by reactions at the interfaces between suitably functionalized polymers, and they link the immiscible phases by covalent or ionic bonds. In this process, the copolymers are formed directly at the interfaces, where they act like preformed copolymers. They reduce the size of the dispersed phase and improve adhesion. For this reason, the problem of the transport of the compatibilizer to interface is not relevant and structure control is easier than in the case of adding preformed copolymers. In order to achieve efficient compatibilization of polymer blends, the reactions between the functional groups should be selective and fast, and the mixing conditions should minimize the limitation of mass transfer in the course of the reaction [105, 106].

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Chapter II

STATE OF ART

Chapter II. Polymer blends based on PLA/PCL

II.1. Introduction

Nowadays, the increased interest in the use of polymers made of renewable raw materials is due to the huge environmental concerns mainly caused by accumulated plastic waste from petrochemical-based polymers. Biodegradable materials have been introduced to reduce plastic waste in landfills and alleviate the burden of the environment. Among the biodegradable plastics, poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL) are suitable materials regarding the replacement of petroleum-based plastics. These materials are expected to overcome the sustainability issues and environmental challenges due to their extraordinary versatility and compostability, which allows for easier waste management. The modification of PLA using the polymer blending technique to achieve suitable properties for different applications, has been receiving significant attention over the past few years. Hence, this section summarizes the recent advances in toughening PLA by blending it with PCL. In addition, various strategies, including reactive blending, copolymerization, and plasticization of PLA/PCL polymer blends are also discussed.

Poly(lactic acid) (PLA) has attracted considerable attention due to its good processability, tensile strength and high modulus [1, 2]. PLA is a semi-crystalline thermoplastic derived from the fermentation of 100% renewable and biodegradable resources (corn starch or other crop sources), and it is produced by ring opening polymerization (ROP) of lactide and lactic acid monomers [3, 4]. The properties of PLA are comparable to, or even better than, those of petroleum-based polymers, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polycarbonate (PC), and polyethylene terephthalate (PET). For example, compared with PS, PLA shows high strength and toughness, as well as low permeability performance against the transfer of several gases such as water vapor and methane [5]. PLA has higher tensile strength and flexural modulus compared with PE and PP [6]. In addition, PLA is quite permeable to water, and ester linkages hydrolyze quickly along the backbone of the polymer compared with the slow inherent rate hydrolysis of PET [7].

Due to great biocompatibility and good physical properties, PLA has raised a high interest in the commercial industry. Production of PLA resin pellets reduces 25 to 55% fossil energy use compared to petroleum-based polymers [8]. Despite its availability and good properties, PLA still has a number of drawbacks that limit its application in some fields. For example, low resistance to humidity and heat, and brittleness which results in a serious physical aging problem [3, 4]. In addition, even though the toughness of PLA is greater than that of PS, it is still lower than those of PET and PC; this might limit the applicability of PLA as a structural material. In this regard, several procedures, including polymer blending, copolymerization, plasticization, and reactive blending have been utilized to overcome the limitations of PLA materials. Among these procedures, polymer blending has received much attention as an easy and cost-effective method of fabricating materials for a wide range of applications [5].

Poly(ε-caprolactone) (PCL), a semi-crystalline thermoplastic polyester with good biodegradability and biocompatibility, is perhaps the most popular polymer used to blend with PLA to increase impact strength and solve the brittleness problem. PCL is a ductile polymer which has a high elongation value of 700%, and it also has a relatively low melting temperature of 60°C [5]. Based on these properties, several studies [9, 10] have been conducted on the research of PLA/PCL blend. And it was proved that the blend of PLA/PCL has complemented the shortcomings of each material. However, PLA/PCL blends still suffer from poor mechanical properties because of the phase separation and poor adhesion between the immiscible components of PLA and PCL [11]. Thus, many researchers have tried to improve the miscibility or the compatibility of PLA/PCL in different ways.

With respect to this area, the blends of PCL with PLA have been widely developed and investigated in the context of formulating practical applications in recent years [9, 11–24] Such as: Yang *et al.* [14] reported that the crystallization rate of PLA could be enhanced by blending with PCL due to the partial miscibility between these two polymers. Rodríguez *et al.* [15] revealed a separated crystallization of both components in the PLA/PCL blends and found that the spherulite radius of PCL was larger for the blends than for the neat PCL. Sakai *et al.* [18] investigated the effect of chain mobility on nucleation behavior in the PLA/PCL blends with various compositions and found that the presence of PCL activates PLA chain mobility. Harmansyah *et al.* [22] investigated the crystallization morphologies of PLA/PCL blends by “two-step crystallization” and found that PLA formed distorted banded spherulites in PLA/PCL blends. Zhang *et al.* [23] researched the nucleation and growth of spherulites for the below PLA layer in PCL/PLA double-layer film, and found that the spherulitic growth rate of the coarse spherulites, is higher than that of the well-defined spherulites.

In another study, the effect of two processing methods, injection molding, and hot pressing, on phase structure and mechanical properties of melt processed PLA/PCL blends, was investigated by Urquijo *et al.* [25]. The results showed that the injection molded specimens, compared with hot pressed specimens, presented much smaller PCL particles regardless of the blending method used. All blends were immiscible. The crystallinity of PLA increased slightly in the presence of poly(ε-caprolactone) (PCL), and the PCL exhibited fractionated crystallization in the presence of PLA. Some interfacial adhesion was observed in all cases. The stiffness of PLA/PCL blends decreased as the PCL content was increased and was independent of processing. Injection molded specimens showed ductile behavior and broke at elongation values close to 140%, while the elongation at break of the hot pressed specimens was clearly lower, most likely due to the larger size of the PCL particles. Although the impact strength of the blends remained low, it improved by approximately 200% with 30% PCL and by 350% with 40% PCL.

Ostafinska *et al.* [26] studied PLA/PCL blends prepared by melt-mixing and compression molding combined with fast cooling process. The blends produced by this specific process showed an optimal morphology and proper improvement of toughness. In addition to the processing method, they also mentioned that the promising composition of the blend was PLA80/PCL20 by weight which yields a well-balanced of stiffness and toughness. Rao *et al.* [27] prepared blends of biodegradable PLA and PCL, using Hakee Rheomix and characterized for rheological and mechanical properties. They found that with 10 wt.% of PCL, the elongation of the blend was tremendously increased up to 19% and the elongation continuously increased with increase in PCL content till 20 wt.% of PCL and thereafter it got reduced. Tensile strength of the PLA/PCL blends decreased with increasing PCL content. Tensile strength decreased by 35% for neat PLA with that of 20% PCL blend. Flexural strength decreased gradually with the addition of PCL. An increase in PCL content resulted in a gradual increase in toughness up to 20 wt.% of PCL and, thereafter, it decreased. Among the various blend proportions, 80/20% PLA/PCL blend exhibited the highest elongation and impact strength. Rheological results revealed that the melt elasticity and viscosity of the blends increased with increase in the concentration of PCL.

II.2. Addition of chain extenders

Usually, chain extenders are low-molecular-weight multifunctional compounds. The chain extension reaction normally occurs between the reactive functional groups of the chain extender and the polymer chain ends. Since normal melt processing time is sufficient to accomplish the chain extension reaction, this method is more desirable for industrial scale reactive compatibilization of polymer blends [28]. Among the chain extenders, there are many diisocyanates and triisocyanates [29] used to compatibilize the biodegradable polymer blends that are highly reactive with hydroxyl and amine groups. These melt blending polymers would create block or graft copolymers at the interface of the polymer mixture to improve the interaction between the blend components. Isocyanates were found to be one of the most efficient third components to improve the mechanical properties of the reactive blending of PLA/PCL blends. However, the blend compatibilized with isocyanates may not be suitable for direct food contact applications, although it could be safe when used in small amount and if a complete reaction with blended components exists [30].

Harada *et al.* [29] used lysine triisocyanate (LTI); lysine diisocyanate (LDI); 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (Duranate TPA-100); 1,3,5-tris(6-isocyanatohexyl)biuret (Duranate 24A-100) and an industrial epoxide-trimethylolpropane triglycidyl ether (Epiclon 725) as reactive compatibilizers of PLA/PCL blends. The impact strength results indicate that compatibility of PLA/PCL blend (in ratio 80/20) decreases in the sequence LTI > LDI > Duranate TPA-100 > Duranate 24A-100 > Epiclon 725. Furthermore, PLA/PCL blend compatiblized with LTI surpassed the impact strength of general-purpose poly (acrylonitrile-butadiene styrene) copolymer. This indicates that, in studied conditions, the isocyanates improved the impact strength of PLA/PCL blends, while the epoxides did not. The morphological studies indicated that isocyanate groups of LTI have reacted with terminal hydroxyl or carboxyl groups of both PLA and PCL, and the compatibility of PLA/PCL blends improved. Similar observations were described by Takayama and coworkers [32, 33], which proved that the addition of LTI decreases the immiscibility between PLA and PCL. This consequently resulted in an enhanced toughness of the PLA/PCL blends.

Carmona *et al.* [33] used methylene diphenyl diisocyanate (MDI) for modifying the interfacial adhesion between ternary PLA/PCL/TPS blends. The tensile strength and ductility of the blends were improved efficiently by incorporating 2 wt.% MDI. Other than MDI, Davoodi *et al.* [34] used triclosan/nHA as the compatibilizer to improve the miscibility of PLA/PCL/TPS blends, and the improved ternary blend suits for food packaging application. They also specified that with the increasing content of PCL, the interfacial affinity was also improved.

Ma *et al.* [30] prepared super-toughened PLA/PCL blends with MDI compatibilizer and glycerol by in situ reactive blending. This study proposed that the MDI reacted with glycerol to form crosslinked polyurethane (CPU) and that the -NCO groups of the MDI would react with polymers to increase the interfacial compatibility. The CPU formation and the improved compatibility of the PLA/20 wt.% PCL blend led to a dramatic increase in impact strength (55 $kJ.m^{-2}$) and elongation at break (139%) compared to neat PLA. The

PLA/PCL/MDI blend without glycerol resulted in lesser CPU formation because of the unavailability of the trifunctional reactive site. Therefore, the PLA/PCL/MDI blends without glycerol did not experience improved toughness.

Shen *et al.* [35] prepared a series of novel PLA/PCL biodegradable blends by the solution casting method. Low content of ethyl cellosolve-blocked polyisocyanate crosslinker (EC-bp) (0.5–2 wt.%) was used to improve the mechanical properties and interfacial adhesion of PLA/PCL blends. Better tensile properties and interfacial morphology were achieved. The addition of EC-bp has promoted a decrease in the degree of crystallinity (Xc) of PLA, while the addition of PCL enhanced the Xc of PLA. The storage modulus of the blends with EC-bp was enhanced compared to the ones without the isocyanate crosslinker due to the improved interfacial adhesion. The crosslinked products showed better thermal stability than the non-crosslinked ones.

II.3. Addition of peroxide

Peroxides are one of the compatibilizers used to improve properties of biodegradable polymer blends. When melt blending polymers with peroxide, the polymers can endure complex reactions that result in copolymer formation, crosslinking, and branching by hydrogen abstraction reactions. The formed copolymer might have a surface energy value between that of the blended polymers. Consequently, the copolymer could localize at the interface of the blended polymers [36] and prevent the coalescence of the molten polymer to form the inclusion phase with smaller size distribution. The blend compatibilized in the presence of peroxide can be used for indirect food contact application because peroxides are approved by the US Food and Drug Administration (FDA) as antioxidants/stabilizers in the polymer [37].

In a series of studies, dicumyl peroxide (DCP), 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane, and benzoyl peroxide have been used as initiators to compatibilize biodegradable polymer blends. Taking into account the relatively high bio content and the tensile properties of the polymers in interest, PLA/PCL (70/30 wt.%) blends were selected as optimum blends to study based on its performances with DCP initiator [38]. The morphology and mechanical properties were adjusted with the amount of DCP present. The most effective compatibility between the PLA and PCL was achieved with an optimum DCP concentration of 0.2 phr. Semba *et al.* [39] determined the effect of DCP crosslinking on the structure and mechanical properties of PLA/PCL blends. It was found that the diameter of the PCL particles decreased with a higher content of DCP during in situ compatibilization, which results in mechanical properties improvement for the PLA/PCL blend. The results indicated that mechanical properties of PLA/PCL blend in ratio 70/30 modified with 0.3 phr of DCP, are comparable to those of popular engineering polymers such as poly(acrylonitrile-butadiene-styrene) copolymer and high-impact polystyrene. On the other hand, they pointed out that, in the case of PLA/PCL blends, in situ fiber formation as reinforcing technique is strongly dependent for DCP content. It was observed that a higher concentration of DCP made the dispersed phase split, which caused the ductility of the PCL phase could not be imparted to the PLA matrix.

II.4. Maleic anhydride-functionalized compatibilizer

The maleic anhydride (MA) grafted biodegradable polymers are successfully prepared by free radical reactions for compatibilizing use. During melt blending, the grafted MA groups can react with hydroxyl groups of the blended components and form chemical bonds. It has been found that the MA grafted biodegradable polymers are effective compatibilizers to improve the compatibility between PLA/PCL [40], PLA/PBAT [41]105, PBAT/soy protein concentrate (SPC) [42], PBAT/starch [43, 44], and PCL/starch [45] blends.

Gardella *et al.* [40] proposed the maleic anhydride grafted poly(lactic acid) (PLA-g-MA) as effective compatibilizer of PLA/PCL blends. It was found that the presence of PLA-g-MA effectively decreased the size of PCL particles in the blend. The interfacial adhesion between PLA and PCL phases improved with the increasing of PLA-g-MA amount, which has a beneficial impact on the mechanical properties (increasing the elongation at break without deterioration of Young’s modulus) of PLA/PCL blends. The researchers denoted that full compatibilization could be accomplished by replacing the PLA with PLA-g-MA completely.

II.5. Addition of other reactive chemicals

Reactive chemicals such as phthalic anhydride (PA), 2,20-(1,3-phenylene)bis(2-oxazoline), glucidyl methacrylate (GMA), dioctyl maleate (DOM), and potassium sorbate are rarely used to compatibilize the biodegradable polymer blends.

Shin and Han [46] prepared PLA/PCL blends compatibilized with glycidyl methacrylate (GMA). It was noticed that the addition of GMA is suitable to decrease the size of PCL phase into PLA/PCL blends, while its impact on interfacial adhesion between phases was not sufficient to transfer the shear stress across the interface. Therefore, to improve the interfacial adhesion in PLA/PCL blends were subsequently treated by electron-beam irradiation. Morphological study and rheological properties indicated that GMA acts as a monomeric plasticizer and a reactive agent at the interface between PLA and PCL phases.

In another study, Shin and Han [47] studied the effect of the compatibility of PLA/PCL (80/20) blends compatibilized by reactive extrusion using Joncryl, GMA, and DCP and high-energy radiation, on the viscoelastic properties measured within the linear viscoelastic regime. Storage and loss moduli, complex viscosities, stress relaxation moduli, tanδ values, and morphology of blends were compared. Storage and loss moduli, complex viscosity, transient stress relaxation modulus, and tan δ of blends were analyzed and blend morphologies were examined. All compatibilized PLA/PCL blends had smaller dispersed particle sizes than the non-compatibilized blend, and well compatibilized blends had finer morphologies than poorly compatibilized blends. Viscoelastic properties differentiated well compatibilized and poorly compatibilized blends. Well compatibilized blends had higher storage and loss moduli and complex viscosities than those calculated by the log-additive mixing rule due to strong interfacial adhesion, whereas poorly compatibilized blends showed negative deviations due to weak interfacial adhesion. Moreover, well compatibilized blends had much slower stress relaxation than poorly compatibilized blends and didn't show tan δ plateau region caused by slippage at the interface between continuous and dispersed phases.

Wang *et al.* [48] reactively blended PLA and PCL using three catalysts/coupling agents in a Haake twin screw mixing chamber. Triphenyl phosphate (TPP) showed the best results as a coupling agent. It is apparent that for the reactive blends with PLA/PCL composition of 80/20, the tensile strength at break, elongation, and elastic modulus increased with molecular weight of PCL. Elongation at break increased initially for a PCL content of 20%, then decreased until it reaches 50%, and again increased to a maximum for 100% PCL. The addition of 2 phr TPP to PLA/PCL (80/20) during melt blending, resulted in higher elongation and tensile modulus but lower tensile strength at break. Degradation studies showed that the enzymatic degradation of reactively compatibilized blends was much higher than that of pure PLA and PCL, while the degradation rate of physical blends was in between that of pure PLA and PCL.

II.6. Addition of copolymers

The compatibility of the immiscible PLLA/PCL and poly-DL-lactic acid (PDLLA)/PCL blends was improved with block copolymer of PCL and poly(ethylene glycol) (PEG) [49]. The compatiblization of PLA/PCL blend with PCL-b-PEG copolymer showed improvement in mechanical performances. Choi *et al.* [50] utilized block copolymer of PLA–PCL as a compatibilizing agent to compatibilize the immiscible PLA/PCL blends. The improved compatibility led to a reduced inclusion phase size in the matrix. Tsuji *et al.* [51] have also compatibilized the immiscible PLA/PCL (80/20) blend with PLA–PCL diblock copolymer. In their study, the PLA/PCL blend with 10 wt.% block copolymer incorporation showed the elongation at break of 300%. On the other hand, the PLA/PCL blend without copolymer had only 175% elongation at break. In another study [52], the addition of 5% L-lac- tide/caprolactone copolymer (LACL) in 80/20 blend of PLA/PCL resulted in significantly improved elongation at break. The elongation at break of PLA/PCL blend was improved from 284% to 580% without severe loss in tensile modulus and strength. When 20% of LACL copolymer was incorporated into PLA/PCL blend, the blend showed maximum elongation at break of 652%. However, the addition of LACL resulted in a considerable loss in tensile strength and tensile modulus.

There are few studies [53–55] that used triblock copolymer of PLA–PCL–PLA as a compatibilizer in the PLA/PCL blend system. It was found that the PCL domain size was reduced significantly in the presence of triblock copolymer. For instance, the PCL domain size was reduced from 10-15 μm to 3–4 μm after the incorporation of 4 wt.% PLA–PCL–PLA triblock copolymer in PLA/PCL (70/30 wt.%) blend. The reduced PCL domain size led to an increase in the elongation at break from 2 to 53% [54]. Triblock copolymer, namely PE oxide–propylene oxide–PE oxide, was used to compatibilize PLA/PCL blend [56] because the PE oxide can be miscible with both blend components. As a result, this triblock copolymer can emulsify at the interface of this immiscible blend to improve the compatibility.

Dell'Erba et al. [9] synthesized a triblock PLLA-PCL-PLLA copolymer to use as a third component for PLLA/PCL reactive blending. The PLLA-PCL-PLLA copolymer acts at the phase boundary as an interfacial agent and produces a more homogeneous distribution of particle size and a lowering of the fraction of large domains. However, PLLA/PCL blends characterized by a fine dispersion of PCL domains can be obtained up to a 30 wt.% of PCL. The PLLA crystallization rate, both from the melt and the glassy state, was observed to be enhanced by the presence of PCL domains because of the increase in nucleation rate.

Wang *et al.* [57] synthesized poly (D,L-lactide-co-ε-caprolactone) (PLCA) and poly (D,L-lactide-coglycolide) (PLGA) and blended PLCA/PLGA by solution blending. The authors observed that the blend was immiscible but compatible. Other copolymers of PLA with PCL have been synthesized as a means of extending the applications of PLA [58]. In one example, PLLA/PCL blends were blended for biodegradable filtration membranes. The membranes were formed via the thermally induced phase separation process and were used to separate yeast cells from their suspension [59].

II.7. Composites/ nanocomposites

Many researchers published works on the compatibilization of immiscible PLA/PCL mixtures using a new strategy in the development of composites and nanocomposites for improving the interfacial adhesion between the polymer and the filler/nanofiller. PLA/PCL (42/58) blend nanocomposites were prepared with 1.5 titanium dioxide (TiO_2) nanoparticles. It was concluded that TiO_2 nanoparticles were located at the interface of the two phases due to kinetic effects and nanoparticles geometry [60]. PLA/PCL was also used by combining organomontmorillonites (OMt; Cloisite 15A and Cloisite 30B) with epoxy-functionalized graphene (Gr). They concluded that the compatibility of PLA/PCL is improved in the presence of organoclays and OMt/Gr mixtures [61]. Recently, Milovanovic *et al.* [62] have employed, for the first time, to impregnate PLA/PCL films with natural antibacterial agents such as thymol and thyme extract for bacterial growth control in food packaging.

Some studies on PLA/PCL blends-based nanocomposites, have also been reported using different types of micro- and nano-particles [63–67], such as carbon nanotubes [68], clays [69], sepiolite [70], montmorillonite [71], micro-talc [72], carbohydrate nanocrystals [73, 74] among others [75, 76], to improve the compatibility between PLA and PCL matrices.

In particular, in the last years, cellulose nanocrystals (CNC) have been widely used as reinforcement for PLA [77–79] as well as for PCL [80] due to its biodegradability, renewability and high stiffness. However, the homogeneous dispersion of CNC into PLA and PCL matrices is not easy to achieve due to their very different hydrolytic/hydrophobic response. Thus, CNC functionalization is required to improve the dispersion of the nanofillers in the polymeric matrix as well as the final properties of the nanocomposites [81, 82]. The strategy of grafting polymer chains at the surface of the CNC through a “grafting from” approach has been showed to be an effective way to obtain nanocomposites based on CNC and PLA and/or PCL matrices with enhanced final properties [81, 83]. Moreover, Goffin *et al.* [73] reported that the compatibilization of PCL/PLA blends can be strongly affected by the addition of polyester-grafted cellulose nanocrystals.

Sessini *et al.* [84] studied the effect of the addition of different modified and non-modified cellulose nanocrystals (CNC) nanofillers, on the shape memory properties of PLA/PCL blends in 70:30 proportion. They revealed that the compatibilization of the PLA/PCL blend was affected by the addition of the different CNC-based nanofillers. The affinity between the functionalized CNC and the blend components determine their localization. Better interfacial adhesion was obtained by the incorporation of CNC-g-PLLA into the blend matrix. This fact was confirmed by the improvement of the mechanical properties mostly for M70PLA/CNC-g-PLLA, which showed an increase in elastic modulus, tensile strength, and the elongation at break. The thermally activated shape memory response of the nanocomposites was not affected by the addition of CNC-based nanofillers, presenting excellent values for both strain recovery ratio and strain fixity ratio, higher than 80% and 98%, respectively.

Bouakaz *et al.* [61] studied the effect of combining organomontmorillonites (Cloisite®15A and Cloisite®30B) with epoxy functionalized graphene on the morphology and different properties of a poly(lactic acid) (PLA)/ poly(ε-caprolactone) (PCL) blend. The use of nanofiller mixtures caused significant enhancements in terms of storage and loss modulus of a PLA/PCL matrix, indicating a high degree of co-reinforcement in comparison to that observed when the nanofillers were filled separately. The results from transmission electron microscopy and the non-dependency of the storage modulus in the low frequencies showed that both graphene sheets and clay mineral layers resulted in a fine dispersion and better exfoliation in the PLA/PCL blend matrix. The compatibility of the biodegradable PLA/PCL blend was improved in the presence of organoclays and organoclay/graphene mixtures. PLA/PCL nanofilled blends exhibited higher barrier properties than the pure blend and interesting values were obtained by adding hybrids of organomontmorillonite and graphene, which were linked to their degree of intercalation and also to the existence of synergy between these nanofillers. Melt blending of PLA/PCL and all different nanofillers induced significant improvements in thermal stability.

Hoidy *et al.* [69] compatibilized PLA/PCL blends with organoclay (OMMT) and found that the presence of OMMT as a filler not only enhanced the dispersion and interfacial adhesion of polymer matrix but also improved mechanical properties and thermal stability of PLA/PCL blends.

II.8. Plasticization

Plasticizers are frequently used, not only to improve the transformation but also to increase the polymer chain mobility and to enhance the crystallization rate of polymers by reducing the energy required for its crystallization for the chain folding process [85]. Citrate esters are investigated as plasticizers for PLA. At least 20% of plasticizer needs to be introduced to lower its glass transition temperature (Tg), to increase ductility and to improve processability [19, 86–89].

Li *et al.* [90] studied the effect of ATBC on the performance of PLA/PCL composite packaging film. The mixture was melt extruded to prepare ATBC/PLA/PCL blend film first by pelleting and then film blowing. They found that ATBC had an effective influence on improving the compatibility of PLA and PCL and significantly enhanced the elongation at break of the composite film, from 6% to 250%. As the content of ATBC increased, the oxygen permeability of composite films increased first and then decreased, and it influenced the glass transition temperature and melt temperature of composite films. When the mass of ATBC accounts for 8% of the total mass of resin, the blend film has the optimal performance.

Al-Mulla *et al.* [91] studied the effects of epoxidized palm oil as plasticizer on the PLA/PCL blend prepared via the solution casting process. The addition of epoxidized palm oil reduced the tensile strength and modulus but increased elongation at break for the PLA/PCL blend. The highest elongation at break was observed for the blend with 10 wt % epoxidized palm oil content.

II.9. Other strategies

Some sporadic techniques have been reported in compatibilization of some specific immiscible PLA blends. Addition of a third polymer that is miscible with both PLA and the other component could improve the compatibility of PLA based blends. But due to the lack of such polymers, this technique can only be used in very special blend pairs. Poly(ethylene oxide) (PEO) is miscible with PLA and PCL and the presence of PEO in PLA/PCL blend could result in a single phase completely miscible blend under suitable conditions, as reported by Buddhiranon *et al.* [92].

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Chapter III

MATERIALS AND METHODOLOGY

Chapter III. Materials and Methodology

III. Introduction

In the present chapter, all materials used in our study and the summary of compositions of the prepared formulations are presented. In addition, the blend preparation procedures, the melt mixing processes, and the characterization techniques are explained in details.

III.1. Materials

Poly(lactic acid) 2002D (PLA) was purchased from NatureWorks LLC (Minnetonka, Minnesota, USA). Its specific gravity is 1.24 and its Melt Flow Index (MFI) is between 5-7 g/10 min at (210°C/2.16 kg). Its melting and glass transition temperature, provided by the supplier is 156°C, and 60°C, respectively.

The poly(ε-caprolactone) (PCL) used is (CAPA 6250, $\overline{Mw}$=25,000 g.mol^{-1}). It was a commercial product purchased from Perstorp PolyolsInc (Toledo, Ohio, USA). Its melting and glass transition temperature as reported by the supplier is 58-60°C, and -58°C, respectively.

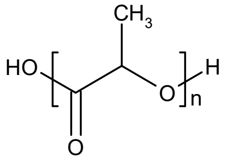
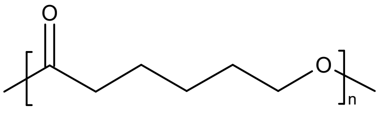
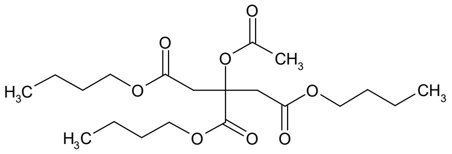
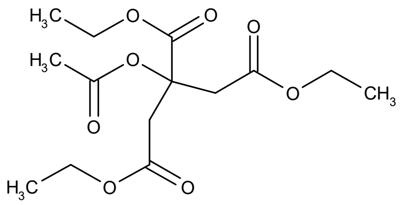
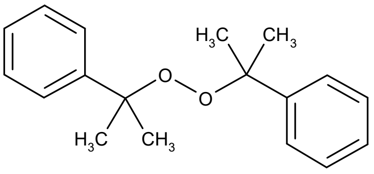
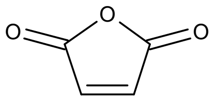
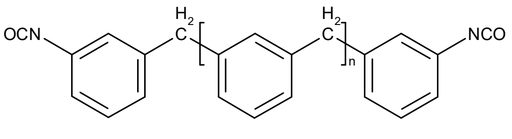
Tributyl O-acetylcitrate-98% (ATBC) and Triethyl 2-acetylcitrate-99% (TEC) were both used as received from Sigma Aldrich (France). The plasticizers were colorless viscous solution with a molecular weight of 402.48 and 318.32 g.mol^{-1}, respectively.

The isocyanate used in this study as a compatibilizing agent for PLA/PCL blends was an aromatic isocyanate based on 4,4'-diisocyanate diphenylmethane (MDI) Wannate PM-200 (PMDI) from Wanhua Chemical Group Co, LTD (China). It is a dark brown liquid with the content of 30.2-32.0 (wt.%) of -NCO and a functionality of about 2.6-2.7. Its viscosity is 150-250 mPa.s at 25°C.

99% pure dicumyl peroxide (Luperox DCP) (DCP) with a molecular weight of 270 g.mol^{-1} was purchased from Sigma Aldrich (France) and used as a free radical initiator.

The reactive modification of PLA was performed using 98% pure maleic anhydride (MA) with a molecular weight of 98.06 g.mol^{-1} purchased from VWR Chemicals (United States). All materials were used as received. The physical properties of PLA, PCL, ATBC, TEC, and the compatibilizing agents are summarized in Table III.1.

Table III.1. Summary of physical properties of PLA, PCL, ATBC, TEC, and the compatibilizing agents

	Molecular weight (g.mol^{-1})	Molecular structure
PLA	160,000–220,000	
PCL	25,000	
ATBC	402.48	
TEC	318.32	
DCP	270.37	
MA	98.06	
PMDI	340	

III.2. Blends preparation procedure

PLA/PCL blends were prepared with the aim of investigating and enhancing the miscibility and the properties of the blends. The first part of the study consists of the blending of PLA with PCL and plasticizing the system with the addition of citrate esters. The compositions were selected from preliminary literature review. According to the obtained results, the optimum blend ratio of PLA/PCL blends was determined as (80/20). The second part of the study is dedicated to the improvement of microstructure and properties of PLA/PCL (80/20) blends through reactive compatibilization. All PLA and PCL pellets were dried in an oven at 40°C overnight, to remove any excess moisture. ATBC and TEC, DCP, PMDI, and MA were used as received. The compositions of PLA/PCL rigid and plasticized blends with citrate esters and PLA/PCL (80/20) blends through reactive compatibilization are summarized in Table III.2 and Table III.3, respectively.

Table III.2. Summary of compositions of PLA/PCL rigid and plasticized blends with citrate esters

Sample	PLA (wt.%)	PCL (wt.%)	ATBC (wt.%)	TEC (wt.%)
PLA	100	0	-	-
PCL	0	100	-	-
PLAPCL10	90	10	-	-
PLAPCL20	80	20	-	-
PLAPCL30	70	30	-	-
PLAPCL10-20ATBC	70	10	20	-
PLAPCL20-20ATBC	60	20	20	-
PLAPCL30-20ATBC	50	30	20	-
PLAPCL10-30ATBC	60	10	30	-
PLAPCL20-30ATBC	50	20	30	-
PLAPCL30-30ATBC	40	30	30	-
PLAPCL10-20TEC	70	10	-	20
PLAPCL10-30TEC	60	10	-	30

Table III.3. Summary of compositions of PLA/PCL (80/20) blends through reactive compatibilization

Sample	PLA (wt.%)	PCL (wt.%)	PMDI (wt.%)	DCP (wt.%)	MA (wt.%)
PLAPCL20	80	20	-	-	-
PLAPCL20 2	80	20	2	-	-
PLAPCL20 D	80	20	-	0.3	-
PLAPCL20 D 2	80	20	2	0.3	-
PLA-g-MA PCL20	80	20	-	0.3	3

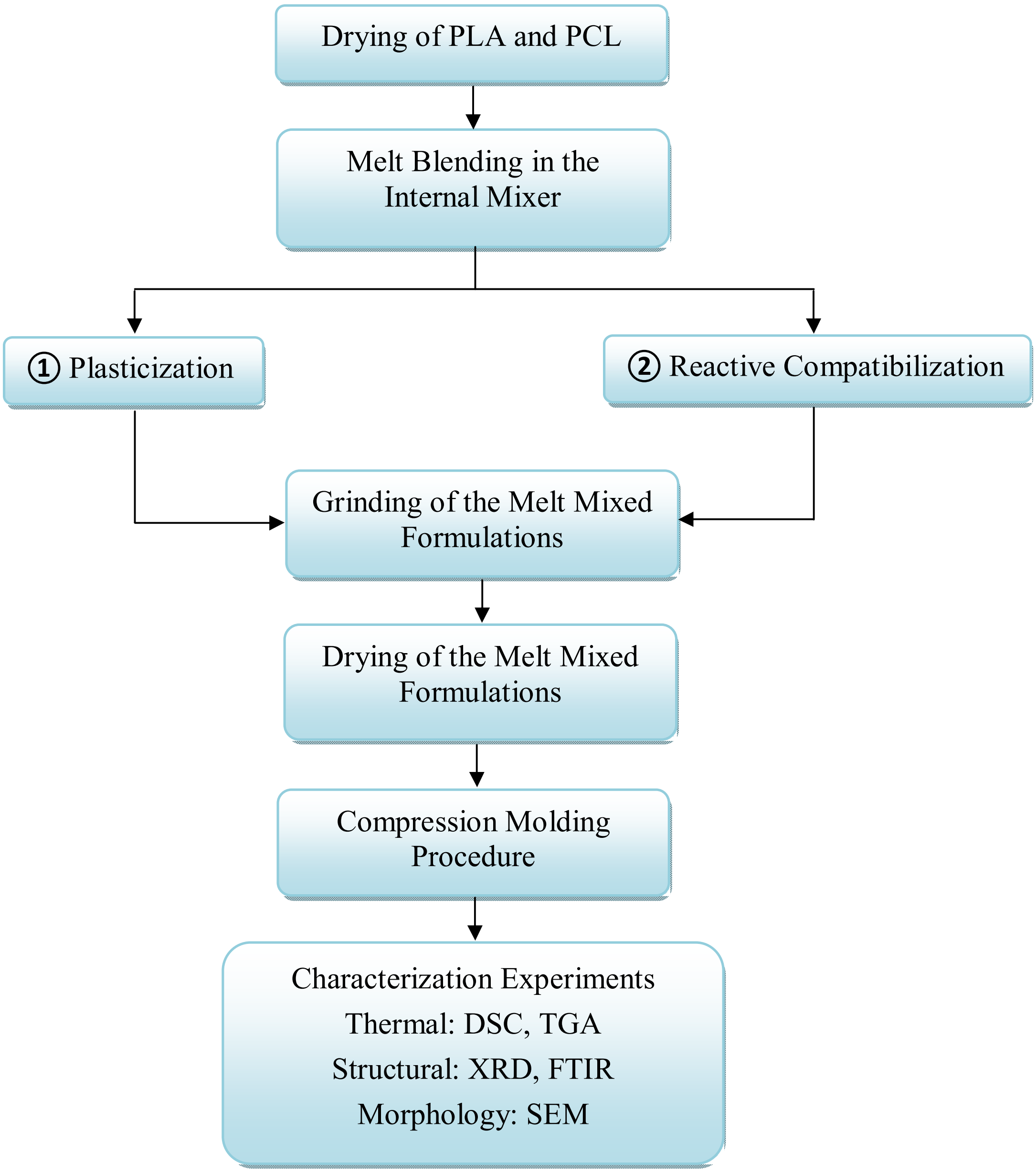


Figure III.1. Flowchart of the experimental work

III.3. Melt blending process

III.3.1. Blends with and without the addition of citrate esters

The melt mixing process of PLA/PCL blends was carried out using a 50 ml internal mixer (plastograph Brabender® LP2100 (Duisburg, Germany)) at a temperature of 180°C during 8 min cycle with 40 rpm screw speed.

III.3.2. Compatibilization of the blends through reactive blending

The PLA/PCL (80/20) blends were prepared using the same internal mixer at a temperature of 180°C during 10 min cycle with a 40 rpm screw speed. Different amounts of PMDI, DCP, and (DCP + PMDI) were added after 3 min of blending by increasing the screw speed to 60 rpm. With regard to the addition of MA, the chosen strategy consisted in grafting a fraction of PCL (20 wt.%) onto the PLA-g-MA (80 wt.%) backbone by reactive blending through a free radical process under the same processing conditions.

III.4. Compression molding process

The PLA/PCL melt mixed samples of different compositions (Table III.2) were cut into small pieces and then compression molded into 2 mm thick sheets and thin films at the temperature of 180°C for 5 min using CARVER™ hydraulic press (Hampton, New Hampshire, USA) at a pressure of 75Pa.

III.5. Characterization techniques

To investigate the effect of the addition of citrate esters and compatibilizing agents on the improvement of microstructure and PLA/PCL properties, the prepared formulations were analyzed using a variety of different techniques to determine specific properties. Each one of the following techniques is described in more detail in the following sections;

- Differential scanning calorimetry (DSC) for observing the thermal properties;
- Thermogravimetric analysis (TGA) for observing the thermal stability;
- X-ray diffraction (XRD) for calculating the extent of crystallinity;
- Scanning electron microscopy (SEM) for observing morphologies;
- Fourier transform infrared (FTIR) spectroscopy for observing the functional groups and the C-H environment along the back-bone.

III.5.1. Differential Scanning Calorimetry (DSC)

The main thermal transitions were investigated using a differential scanning calorimeter DSC/Q10 TA Instruments (New Castle, Delaware, USA), under a nitrogen flow of 50 ml.min^{-1}. To eliminate material's thermal record, samples were first heated to 180°C at a heating rate of 10°C min^{-1} and keeping this temperature for 3 min. The samples were then cooled down to -70°C at a cooling rate of 10°C min^{-1} and keeping this temperature for 3 min. Finally, they were reheated to 180°C at a heating rate of 10°C.min^{-1} and keeping this temperature again for 3 min and then jumping down to 25°C. All thermal properties were obtained from the second heating scan curves. The degree of crystallinity of PCL ($X_{c,\ PCL}$) in the blends was calculated from equation (1) with consideration of the amount of PCL in the blend [1]. For PCL, a 100% crystalline melting enthalpy ($\Delta H_{0,\ PCL}$) of 156.8 J.g^{-1} was assumed [2]. The degree of crystallinity of PLA ($X_{c,\ PLA}$) was calculated from equation (2), and for PLA, the 100% crystalline melting enthalpy ($\Delta H_{0,\ PLA}$) was taken to be 93 J.g^{-1} [3].

$$\mathrm{X_{c,PCL}}\ (\%) = \left[\frac{\Delta H_{m,PCL}}{\Delta \mathrm{H_{0,PCL}} \times W_{PCL}}\right] \times 100 \tag{1}$$

$$\mathrm{X_{c,PLA}}\ (\%) = \left[\frac{\Delta H_{m,PLA} - \Delta H_{cc,PLA}}{\Delta \mathrm{H_{0,PLA}} \times W_{PLA}}\right] \times 100 \tag{2}$$

Where W_{PCL} and W_{PLA} are the weight fractions of PCL and PLA in the blends, respectively; $\Delta H_{m,\ PCL}$ and $\Delta H_{m,\ PLA}$ are the melting enthalpies of PCL and PLA in the blends, respectively; and $\Delta H_{cc,\ PLA}$ is the cold crystallization enthalpy of PLA in the blends.

III.5.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of PLA/PCL blends was studied using a TGA Q500 analyzer TA Instruments (New Castle, Delaware, USA). The samples were heated from 10°C to 550 °C at a heating rate of 10 °C.min^{-1} under nitrogen atmosphere at the flow rate of 10 ml.min^{-1}. The onset temperature (onset) was determined from the thermogravimetric curves as being the temperature at which the weight loss begins. The temperatures corresponding to the weight loss of 5 % and 50 % were also determined from the thermogravimetric curves.

III.5.3. X-ray Diffraction (XRD)

The X-ray diffraction (XRD) of PLA/PCL blends was carried out using a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA). Scans were recorded in reflection using α radiation with a wavelength (λ) of 0.1542 nm at room temperature. The angle of incidence was varied from 8°C to 50°C in steps of $3°.\mathrm{min}^{-1}$. The accelerating voltage was 40 kV, and the tube current was 150 mA. A computer-aided curve fitting technique was used to separate crystalline and amorphous phases of diffractograms. The crystallinity was calculated by separating intensities using Gaussian and Lorentzian functions due to amorphous and crystalline phase on the diffraction phase. The degree of crystallinity X_c(%) was measured as the ratio of crystalline area to the total area as shown in equation (3):

$$\mathrm{X_c}\,(\%) = \left[\frac{A_c}{A_a + A_c}\right] \times 100 \tag{3}$$

Where A_c and A_a are the areas of crystalline and amorphous phases, respectively.

III.5.4. Scanning electron microscopy (SEM)

A Hitachi SU8010 scanning electron microscope (Tokyo, Japan) was used to study surface morphology. Prior to SEM, the studied samples were prepared by cryo-fracture, wherein the polymer strands extruded from a die face in injection molding process were immersed and kept in liquid nitrogen for 5 min and subsequently fractured. The freeze-fractured samples were then placed in a small vacuum chamber in order to characterize the microstructural morphology and the effect of the addition of the compatibilizing agents.

III.5.5. Fourier Transform Infrared (FTIR)

Infrared spectroscopy was used to identify the interactions of rigid, plasticized, and compatibilized PLA/PCL blends. For this, the formulations obtained by melt mixing were compacted into thin films by compression molding and then analyzed. All measurements were performed using a Perkin Elmer FTIR spectrum 1000 spectrophotometer (Waltham, Massachusetts, USA) in the range of 500 cm^{-1} to 4000 cm^{-1}.

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Chapter IV

Blending and plasticizing effects on PLA/PCL crystallinity and miscibility

Chapter IV. Blending and plasticizing effects on PLA/PCL crystallinity and miscibility

IV.1. Introduction

Over the past decades, biodegradable aliphatic polyesters have attracted increasing interest because of their potential applications in the biomedical field, and environmentally friendly materials. Among them, poly(ε-caprolactone) (PCL) is a biocompatible, biodegradable, permeable and flexible polymer with a relatively low melting point (about 60°C) and glass transition temperature (about -60°C), while its strength and degradation rates are relatively low for various applications, although its elongation at break is very high [1–3]. On the other hand, poly(lactic acid) (PLA) is another biodegradable polyester which is produced from renewable resources, highly transparent and rigid material with a relatively low crystallization rate. Products with high molar mass are usually produced from lactides and the lactic acid monomers via ring-opening polymerization route [4, 5]. However, under practical processing conditions, it is well known to show slow nucleation and crystallization rates and would nearly be 100% amorphous, which limits wider applications in sectors, such as automotive and packaging fields. Moreover, several other drawbacks limit its widespread use such as brittleness, hydrolysis under high humidity conditions, hydrophobicity, poor moisture and gas barrier, low heat resistance and high cost [6–11]. As a result, the combination of these polymers, via blending [5, 12, 13], and plasticization with low-molecular-weight compounds [11, 14, 15], are expected to remedy the aforementioned drawbacks of these two polymers and to improve properties in comparison with each individual component [16–18]. Polymer blending method has been extensively explored to improve the inherent physical and mechanical properties of the biodegradable materials and that has been preferred in the industry because of its simple preparation procedure, practicability and lower cost [19, 20]. As we know, the compatibility of the components strongly influences the mechanical and physical properties of polymer blends [21–24]. However, some studies have reported that the high-molecular-weight PCL and PLA in the blends, are usually immiscible, which make them suffer from poor mechanical properties due to the macrophase separation of the two components [25–27]. As for the systems of immiscible or partially miscible blends, it has been well documented that the mechanical properties of immiscible blends are strongly dependent on their crystallization behavior and morphologies [25]. Therefore, information concerning the crystallization and morphology of

PCL/PLA blends is crucial in efforts to control the mechanical function of materials from the application point of view.

In this chapter, the results concerning the blending and plasticizing of PLA with PCL and the addition of citrate ester plasticizers (ATBC and TEC) by melt mixing in an internal mixer (plastograph Brabender®) are presented. Thermal properties and the structure of the materials were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

IV.2. Differential Scanning Calorimetry (DSC)

DSC thermograms of neat PLA, neat PCL and rigid and plasticized PLA/PCL blends with ATBC and TEC at various concentrations, are shown in Figure IV.1. Parameters such as Tg, T_m, cold crystallization temperature (T_{cc}), melting enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}), and crystallinity (X_c) as estimated from this thermograms, are presented in Table IV.1.

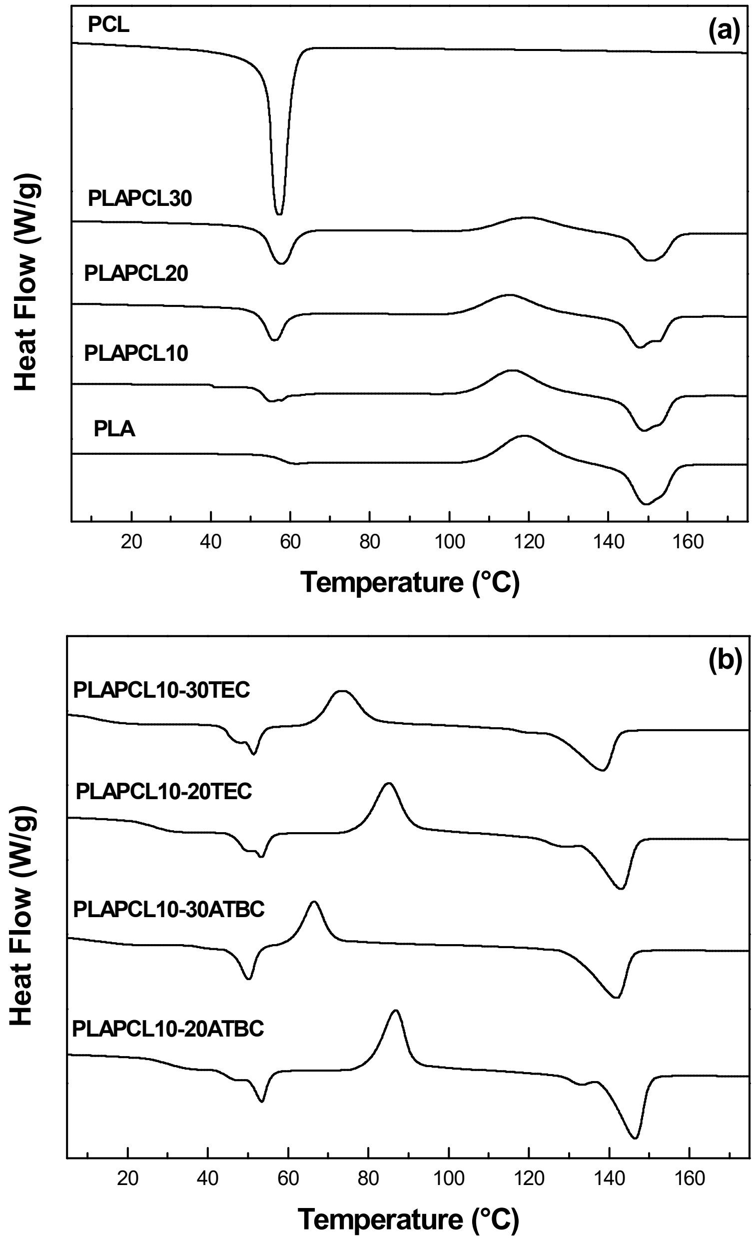


Figure IV.1. DSC thermograms of **(a)** rigid PLA/PCL blends and **(b)** plasticized PLA/PCL blends at various concentrations

The results confirmed that the as-received PLA is semi-crystalline, due to the clear glass transition and melting peaks around 58°C, and 149°C, respectively as shown in Figure IV.1(a). It is well known that PLA has a very low crystallization rate and that it primarily crystallizes during heating [28]. This is confirmed from Table IV.1 and Figure IV.1(a). In addition to the glass transition and melting peaks, a clear cold crystallization peak around 119°C and a very low crystallization rate of about 1.56% calculated from equation (2) (Chapter III) were reported. It is observed that the ΔH_{cc} was almost equal to the melting enthalpy, confirming that PLA does not form any crystals during the controlled cooling in the DSC analysis [29].

With regard to PCL, which is also semi-crystalline, a well-defined melting peak around 57°C and high crystallization rate of about 45.31% calculated from equation (1) (Chapter III) were reported, whereas no crystallization peak was noticed. Its glass transition peak is well-known to be around -60°C, but it wasn't detected in the scans. The melting enthalpy of neat PCL is much higher than that of neat PLA, indicating much higher crystallinity compared to PLA.

Table IV.1. Thermal properties and crystallinity of neat PLA, neat PCL, and rigid and plasticized PLA/PCL blends with ATBC and TEC at various concentrations

	PCL		PLA						
Sample ID	ΔH_m ($J.g^{-1}$)	T_m (°C)	Tg (°C)	ΔH_{cc} ($J.g^{-1}$)	T_{cc} (°C)	ΔH_m ($J.g^{-1}$)	T_m (°C)	X_{cPLA} (%)	X_{cPCL} (%)
PLA	-	-	58	28.64	119	30.10	149	1.56	-
PCL	71.05	57	-	-	-	-	-	-	45.31
PLAPCL10	5.93	55	41	24.02	116	27.66	149	4.34	37.81
PLAPCL20	12.47	56	46	20.94	116	24.85	148	5.25	39.76
PLAPCL30	17.78	58	45	16.14	120	20.57	150	6.80	37.79
PLAPCL10-20ATBC	7.48	53	30	18.97	87	25.43	146	9.92	47.70
PLAPCL20-20ATBC	13.22	55	31	15.96	88	22.40	147	11.54	42.15
PLAPCL30-20ATBC	17.08	54	36	12.93	91	18.44	147	11.84	36.30
PLAPCL10-30ATBC	7.66	53	12	12.34	66	23.48	142	19.96	48.85
PLAPCL20-30ATBC	14.54	52	21	13.45	77	21.32	144	16.92	46.36
PLAPCL30-30ATBC	20.80	53	28	13.16	85	19.42	146	16.82	44.21
PLAPCL10-20TEC	6.59	53	27	17.84	85	24.00	143	9.46	42.02
PLAPCL10-30TEC	7.21	51	13	15.44	73	20.39	138	8.87	45.98

These findings agree with the results obtained by others [30, 31]. In fact, polymers with low molecular weight have a high content of crystallinity [32]. After blending with PCL, the T_m of PLA somehow hasn't changed significantly with the addition of PCL, showing values around 149°C range. The same applies to the melting peak of PCL, it hasn't changed with varying PCL content, and it remains at 57°C as for neat PCL. Double peaks have been observed in the melting of the blends, which are located between 140°C and 160°C depending on PCL content. These findings reveal the existence of two different types of PLA crystals with different perfections within the system. The first endothermic peak shows PLA crystals with less perfection probably due to the presence of a limited amount of miscible PCL chains within the formed structure, which is in agreement with previous studies [15, 33].

However, with varying PCL content, some changes has occurred on the rest of the thermal properties of both PLA and PCL phases. The T_{cc} of PLA has barely shifted to a lower temperature, the ΔH_{cc} and ΔH_m of PLA have decreased, and the $\Delta H_{cc,PCL}$ has increased significantly, thus indicating that the crystallization of PLA may be affected by the addition of PCL [34]. As shown in Table IV.1, the $X_{c,PLA}$ has slightly increased by increasing the PCL content, suggesting that the presence of PCL favors the crystallization of PLA, acting as a nucleating agent [35, 36]. It should be noted that almost all the thermal transitions of PLA and PCL in rigid PLA/PCL blends appear at the same typical temperatures as those of the corresponding individual polymers, and the variation of Tg, T_{cc}, T_m and $X_{c,PLA}$ values is usually assigned to the interactions between components, which reveals a very weak interaction between these two polymers [37, 38].

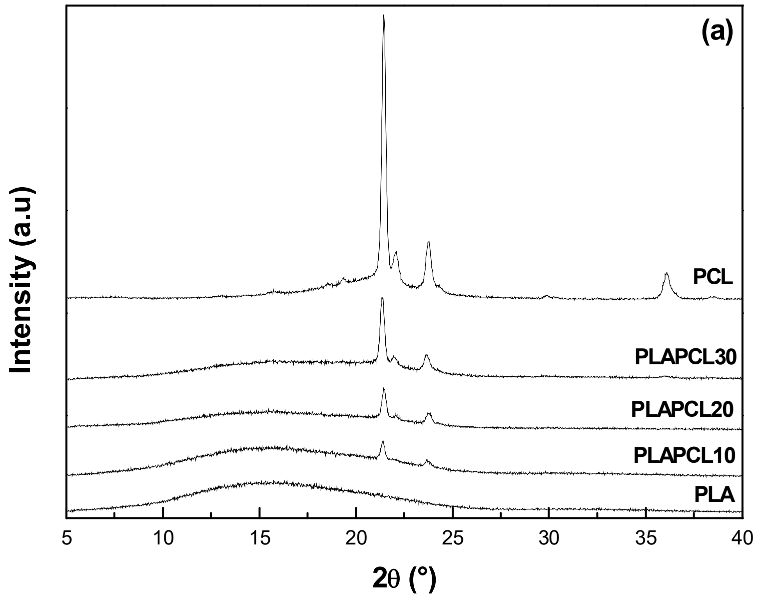
Several citrate esters are commercial plasticizers for PLA, including ATBC, and TEC [39]. The Tg, the melting peak or T_{cc} may shift due to the plasticizer's effect on the material [40]. The effectiveness of the plasticizer on PLA is expected by the reduction of the glass transition of the amorphous phase and by the depression of the melting point of the crystalline region [41].

As shown in Figure IV.1(b) and Table IV.1, the Tg of neat PLA has decreased by increasing the plasticizer content and has increased by increasing the PCL content for plasticized PLA/PCL blends. The largest reduction of Tg when compared with neat PLA was from 58°C to 12°C and 13°C for PLAPCL10 by adding up to 30 wt.% ATBC and TEC, respectively. The most probable explanation may be the low molecular weight of the plasticizer that allows it to occupy intermolecular spaces between polymer chains, reducing the energy for molecular motion and the formation of hydrogen bonding between the polymer chains, which in turn increases free volume and polymer chain mobility. These findings are in accordance with previous results [41–43].

As shown in Table IV.1, the T_{cc} of PLA has decreased from 119°C for neat PLA to 66°C and 73°C for PLAPCL10 by adding up to 30 wt.% of ATBC and TEC, respectively. The addition of the citrate plasticizers has also decreased the T_m of PLA. From Figure IV.2(a, b), the $X_{c,PLA}$ in plasticized blends has increased considerably depending on plasticizer content. For PLAPCL10 plasticized with 30 wt.% ATBC, the greatest crystallinity has been observed for a value of 19.96%, while only 9.46% and 8.87% for 20 wt.% and 30 wt.% TEC, respectively. This important increase in crystallinity of PLA by the addition of both ATBC and TEC suggests that the plasticizer increased the polymer chain mobility by reducing the energy required for crystallization. Similar results have been evidenced previously [6].

IV.3. X-ray Diffraction (XRD)

XRD is used to determine the nature of polymer by measuring the extent of crystallinity with respect to amorphous content. XRD patterns of PLA, PCL and rigid and plasticized PLA/PCL blends with ATBC and TEC are shown in Figure IV.2(a, b). The crystallinity obtained by this technique is calculated using equation (3) (Chapter III). Table IV.2 show the degree of crystallinity (Xc) of rigid and plasticized PLA/PCL blends.



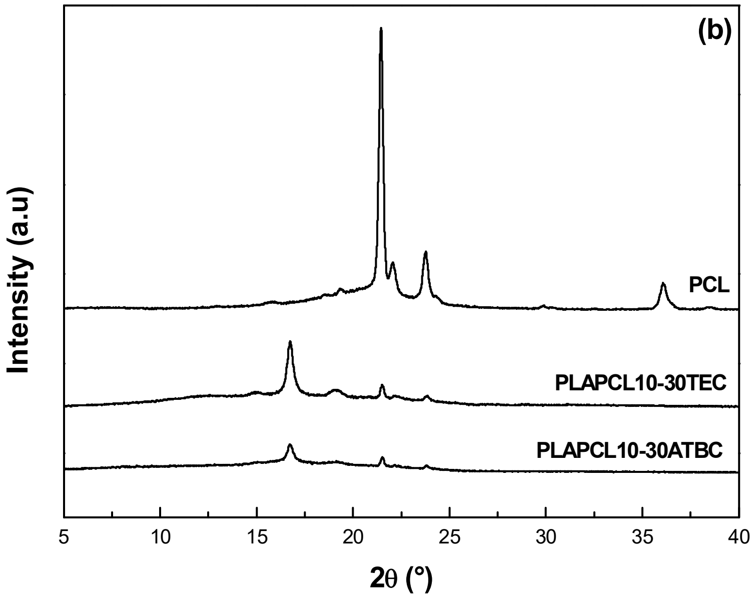


Figure IV.2. XRD spectra of **(a)** rigid PLA/PCL and **(b)** plasticized PLA/PCL blends at 30 (wt.%)

Table IV.2. Crystallinity of rigid and plasticized PLA/PCL blends

Sample ID	X_c (%)
PLA	0
PCL	52.26
PLAPCL10	37.28
PLAPCL20	43.35
PLAPCL30	37.36
PLAPCL10-20ATBC	45.84
PLAPCL20-20ATBC	45.87
PLAPCL30-20ATBC	52.36
PLAPCL10-30ATBC	43.25
PLAPCL20-30ATBC	23.30
PLAPCL30-30ATBC	22.18
PLAPCL10-20TEC	8.43
PLAPCL10-30TEC	30.39

The XRD spectrum of PLA in Figure IV.2(a) has shown a broad double peak between 5° and 40° corresponding to amorphous regions confirming that the PLA is completely amorphous after initial melting and cooling. This peak positions are in accordance with those reported articles [29, 43]. Although a slight X_c of about 1.56% was observed in the diffraction scanning calorimetry thermogram, no cristal structure was detected by XRD. The $X_{c,PCL}$ obtained from DSC and XRD is found to be 45.31% and 52.26%, respectively. The obtained results are in accordance with what has been stated where the crystallinity range for PCL is known to be between 42% and 60%.

The PCL diffractogram has shown several peaks between 15° and 40°, with two high-intensity and other low-intensity peaks between 20° and 25° and between 35° and 40°, respectively. Moreover, the peaks were sharp and distinct, which indicated that the sample was a crystalline material. Similar findings are in accordance with reported works [44–46]. In addition, the spectrum of the other blends has shown the same crystalline peaks overlapping the amorphous curve of PLA. The peak intensities vary with the variation of PCL content. The DSC observation of increasing crystallinity with increasing PCL content in the blends could, therefore, be confirmed by the XRD results. PLAPCL10-30ATBC and PLAPCL10-30TEC patterns shown in Figure IV.2(b) have shifted towards lower angles between 15° and 20°, which probably indicates the variation in the distance between parallel planes of atoms. According to Bragg’s law, if the spacing of the crystallographic planes changes, the Bragg angle should decrease towards lower 2θ values [47].

IV.4. Thermogravimetric Analysis (TGA)

TGA is the second most commonly used technique studying thermal degradation and stability of polymer materials. The thermogravimetric and derivative thermogravimetric experiments under nitrogen atmosphere were carried out to study the thermal degradation behavior of PLA, PCL and their blends, and to determine the impact of ATBC on the thermal stability of PLA. Curves of all the samples are shown in Figure IV.3 and their thermal properties are summarized in Table IV.3.

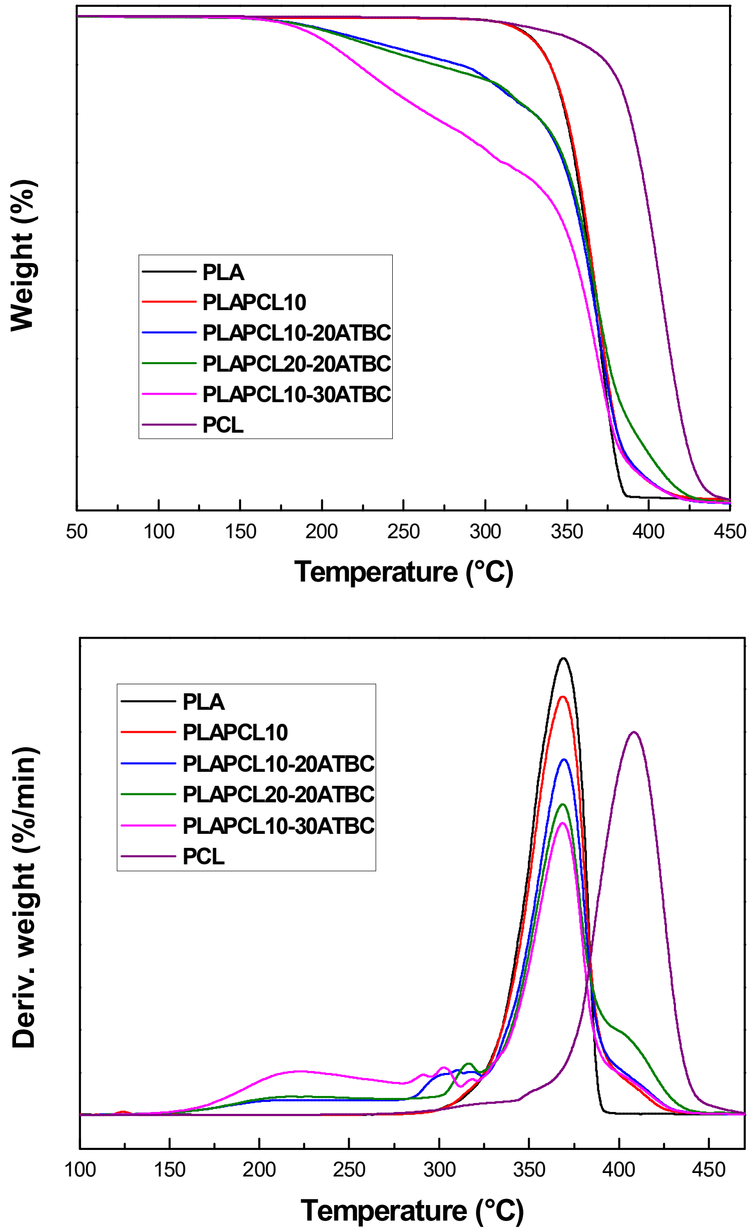


Figure IV.3. TG/DTG thermograms of rigid and plasticized PLA/PCL blends at various concentrations

Table IV.3. Thermal properties of PLA/PCL blends at various concentrations

Sample	T_{onset} (°C)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	$Residu_{475°C}$ (%)
PLA	345	330	364	369	1.22
PCL	382	355	405	407	0.59
PLAPCL10	345	329	365	368	1.06
PLAPCL20	344	328	365	366	1.07
PLAPCL30	343	329	368	366	0.82
PLAPCL10-20ATBC	175	227	362	369	0.35
PLAPCL20-20ATBC	178	220	364	368	0.44
PLAPCL10-30ATBC	183	201	356	368	0.42

Thermogravimetric curves obtained in nitrogen atmosphere have displayed a single-stage decomposition for PLA, PCL and a double stage for their rigid blend (PLAPCL10). It can be noted that the PLA degradation had occurred at lower temperatures, at around 345°C, while the PCL degradation had taken place at around 382°C. PCL is known to have extraordinary thermal stability at high temperature compared to other polyesters due to its high degree of crystallinity (45-60%) and its high hydrophobicity [28, 48]. The addition of citrates has affected the thermal stability of PLA. The weight loss of the plasticized blends has occurred in a two-stage decomposition. A significant shift in the onset temperature has been observed compared to the rigid PLA/PCL blend. Derivative thermogravimetric curves have displayed a clear range temperature between 291°C and 316°C corresponding to the evaporation of citrate plasticizer components, where as mentioned by the supplier, the boiling point of ATBC is known to be 173°C. The temperature corresponding to the degradation of 5 % and 50% of the sample ($T_{5\%}$ and $T_{50\%}$, respectively) for the rigid blends, is almost equal to the pristine PLA, while, for the plasticized blends $T_{5\%}$ and $T_{50\%}$ is lower than for the pristine PLA, indicating that the PCL and the plasticizer addition have promoted a decrease in the thermal stability of PLA.

IV.5. Conclusions

With the increase of PCL content, DSC revealed a depression in both Tg and ΔH_{cc} of PLA. The X_c of PLA in rigid PLA/PCL blends slightly increased compared with neat PLA, suggesting the presence of PCL may favor the crystallization of PLA and acting as nucleating agent. The plasticizing effect was highlighted through the significant decrease in Tg, T_m and ΔH_{cc} of PLA. Depending on the plasticizer and on its content, the $X_{c,PLA}$ in plasticized blends increased considerably compared to neat PLA, confirming that the plasticizer increased the polymer chain mobility by reducing the energy required for crystallization. The changes shown by DSC indicate the partial miscibility of both rigid and plasticized PLA/PCL blends. XRD confirmed that PLA is partially amorphous. Moreover, PCL sample was also confirmed to be a highly crystalline material. TGA showed that the addition of ATBC has promoted a decrease in thermal stability of PLA/PCL blends.

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Chapter V

Microstructure and thermal properties of PLA/PCL blends through the reactive blending

Chapter V. Microstructure and thermal properties of PLA/PCL blends through reatcive blending

V.1. Introduction

The blending of polymers provides a powerful route for obtaining materials with improved property/cost performances. Since most blended polymers are immiscible, compatibilization is then required to obtain maximum synergy [1]. The achievement of compatibilization, whether by addition of a third component or by inducing in situ chemical reactions between blend components, has played an important role in the development of polymer blends. In any case, compatibilization can in principle interact in complex ways to influence final blend properties. One effect of compatibilizers is to reduce the interfacial tension in the melt, causing an emulsifying effect and leading to extremely fine dispersion of one phase in another. Another major effect is to increase the adhesion at phase boundaries. A third effect is to stabilize the dispersed phase against growth during annealing [2, 3].

The poly(lactic acid) (PLA) used in our study is a semi-crystalline material with approximately 4% D-lactic acid monomer. As such, PLA has very slow nucleation and crystallization rates. Its degree of crystallinity and its glass transition temperature (Tg) obtained by differential scanning calorimetry (DSC) from our previous study are 1.56 % and 58°C, respectively [4]. The decrease of its glass transition temperature was achieved through the incorporation of poly (ε-caprolactone) (PCL) and citrate esters. The first part of the study consisted of the blending of PLA with PCL and plasticizing the system with citrate esters. The studied PLA/PCL blends were shown to be partially miscible and the optimum blend ratio was determined as 80/20. In order to improve the phase interface, a third component is usually used as compatibilizer. This part of the study is dedicated to the improvement of microstructure and thermal properties of PLA/PCL blends through reactive compatibilization by fixing the blend ratio and by preparing blends using the same processing conditions. Aromatic isocyanate (PMDI), dicumyl peroxide (DCP), and maleic anhydride (MA) were investigated as potential compatibilizing agents for the PLAPCL20 system, with the aim of enhancing the final properties of the blend. All specimens were analyzed by Fourier transform infrared spectrospcopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

V.2. Fourier Transform Infrared (FTIR)

Figure V.1 shows IR-spectra of PLA, PCL, and PMDI. It can be observed that all spectrum exhibited very similar patterns for the C=O stretch at about 1720–1750 cm^{-1}. The PLA and PCL spectrum showed CH_3 stretching at 3000–2940 cm^{-1}. The C=O cm^{-1} stretching at 1750 cm^{-1} and the O-C=O stretching at 1180–1080 cm^{-1} are characteristics of ester bonds for both polymers [5]. The spectrum of PMDI was characterized by N-H and N=C=O peaks around 3400 cm^{-1} and 2260 cm^{-1}, respectively. C=C stretching around 1600 cm^{-1}, and CH_2 and CH_3 stretching around 3044 cm^{-1} and 2922 cm^{-1}, respectively.

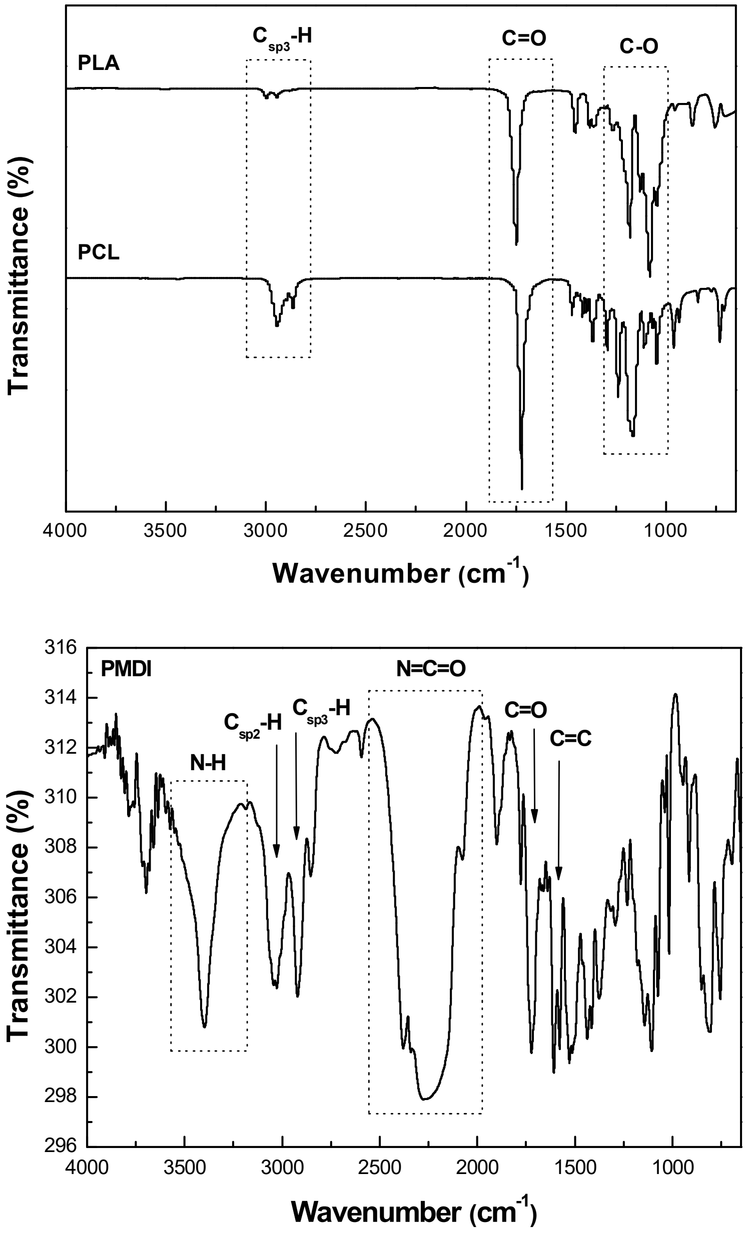

Figure V.1. FTIR spectra of PLA, PCL, and PMDI

Figure V.2 shows a comparison of FTIR spectra of PLAPCL20 blends with and without PMDI. PLAPCL20 exhibited similar peaks as the individual constituent components. The C_{sp3}-H and C=O stretching were clearly visible at 2994 cm^{-1} and 1750 cm^{-1}, respectively. Therefore, it can be concluded that the blend of PLA and PCL is formed only by physical interaction [6]. PLAPCL20 2 spectrum clearly showed an appearance of the characteristic N-H peak (3350 cm^{-1}) and the aromatic C=C bending peaks at 1600, 1533, and 1510 cm^{-1}. A total disappearance of the characteristic N=C=O peak (2260 cm^{-1}) after the addition of PMDI into the polymer blend was also observed. This proved that a chemical interaction occurred through the formation of a carbamate bond between the isocyanate from PMDI and the hydroxyl group end-group of PLA and PCL [7].

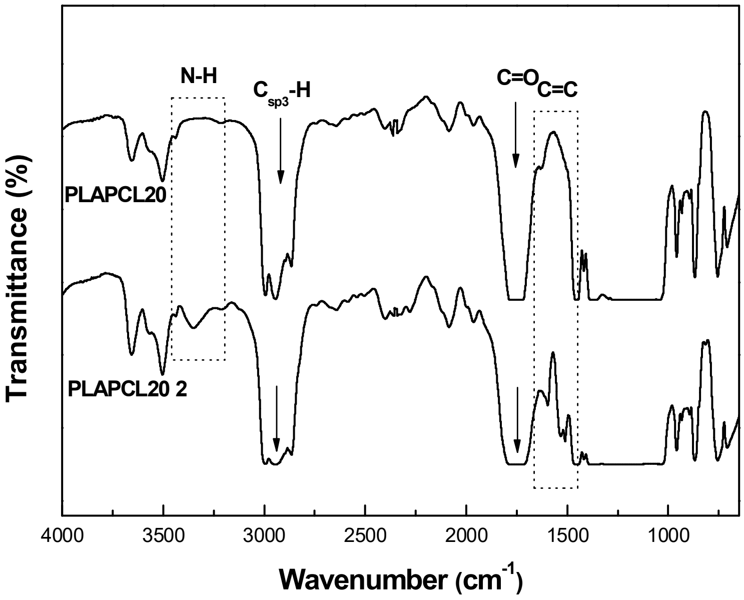

Figure V.2. Comparison of FTIR spectra of PLAPCL20 blends with and without PMDI

Based on Figure V.1 and Figure V.2, the apparent change of peak intensity and shape around 1720–1750 cm^{-1} and 1760 cm^{-1}, respectively, corresponding to the carbonyl peak, was also observed. This peak appeared to be doublets with higher normalized peak intensities. However, after the addition of PMDI, these peaks appeared as single broad peaks (Figure V.2). This transformation indicates identical bond motion in the carbonyl groups of the two different blends (PLAPCL20 and PLAPCL20 2). This is in agreement with previous works by Dong *et al.* [8], Pardini *et al.* [9] and Vilay *et al.* [7], which showed changes in peak shift and intensity as a result of the change of interaction due to the secondary forces. These results indicate that PMDI may react with both PLA and PCL, as illustrated by the predicted reaction (Figure V.3). The reaction might increase the interfacial adhesion between PLA and PCL and produce grafting and crosslinking parts in the blend. As a result of this mechanism, the morphological properties may also be improved [7].

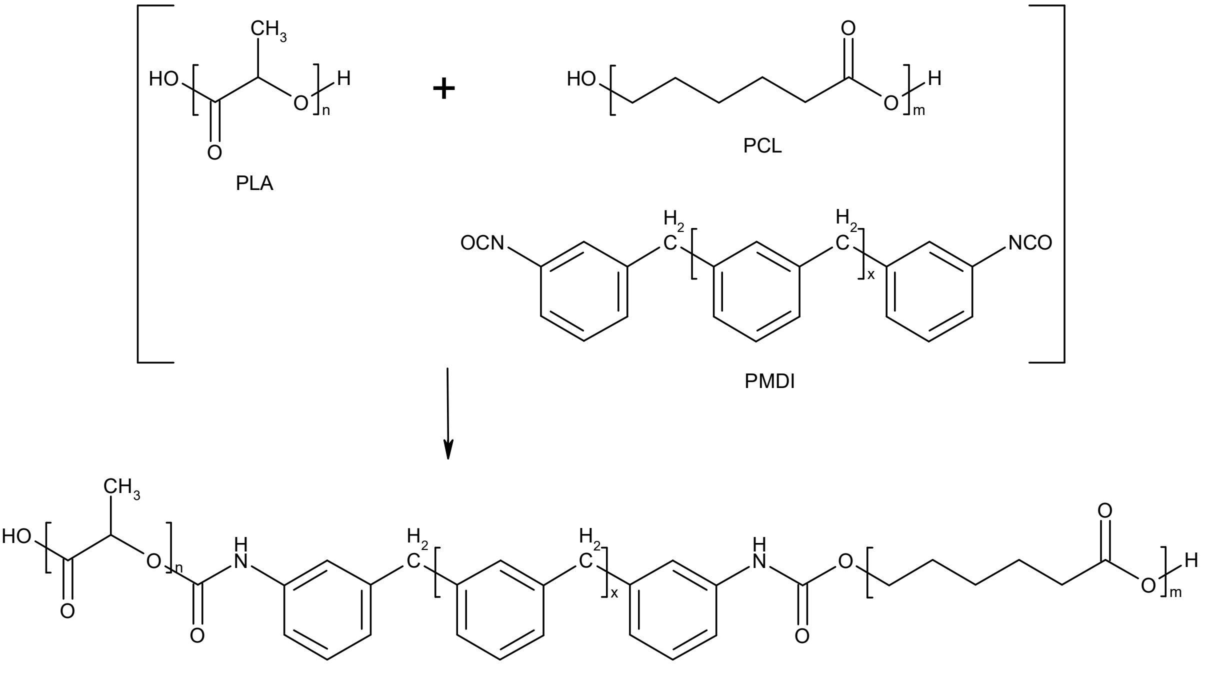

Figure.V.3. Expected reaction of PLA, PCL, and PMDI

Figure V.4 shows a comparison of FTIR spectra of PLAPCL20 blends with and without DCP, (DCP + PMDI), and MA. Based on Figure V.4, PLAPCL20 D doesn't show any characteristic peak. Peroxide was added to PLA/PCL binary blend to induce chemical crosslinking. The proposed reaction for PLA/PCL crosslink formation is shown in Figure V.5. It is well known that the peroxide decomposes to R^{∞} radicals, which abstract hydrogen from both PLA and PCL to yield free radicals. In PCL, the free radical is next to the carbonyl group, so β-scission of PCL radical occurred to yield a primary radical. The molecular structure of PCL containing many secondary hydrogen atoms facilitates easy abstraction of hydrogen atom by peroxide than PLA molecules. The tendency of hydrogen abstraction is reflected in the changes of the carbonyl group of PCL. The primary alkyl radicals resulting from PCL scission can easily access the tertiary radicals of PLA to form cocrosslinks [10].

For PLAPCL20 D 2, a weak characteristic N-H peak at 3350 cm^{-1}, was observed (Figure V.4) after the addition of 0.3 (wt.%) DCP and 2 (wt.%) PMDI into the polymer blend. This can be attributed to the interaction of a small portion of free radicals of PLA and PCL with PMDI. C=C stretching was clearly visible around 1600-1650 cm^{-1}.

Since the amount of maleic anhydride present in the PLAPCL20 blend is small (3 wt. %), the C=O stretching of maleic acid or anhydride peak is very weak and might be overlapping with the carbonyl band of PLA (Figure V.4). Possibly, the extent of grafting is too low [11]. The proposed reaction of PLA and MA, and the expected reaction of PLA-g-MA and PCL are shown in Figure V.6 and Figure V.7, respectively.

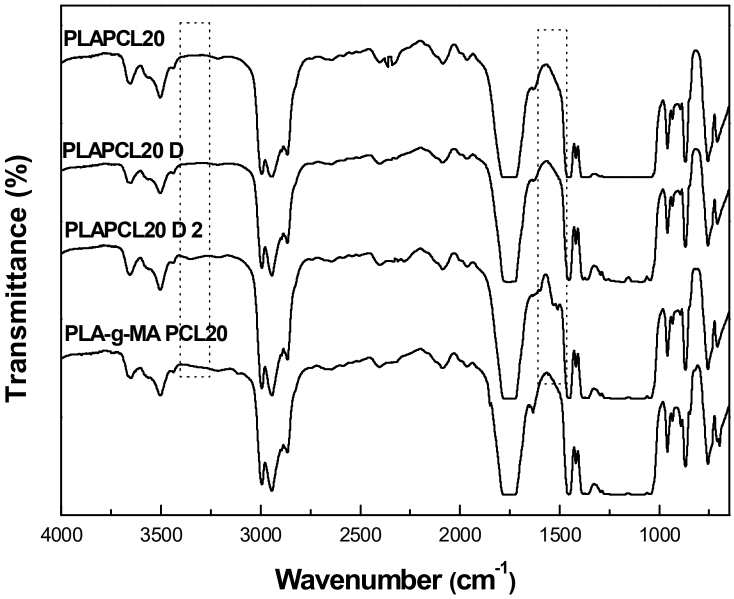

Figure V.4. Comparison of FTIR spectra of PLAPCL20 blends with and without the addition of the different compatibilizing agents

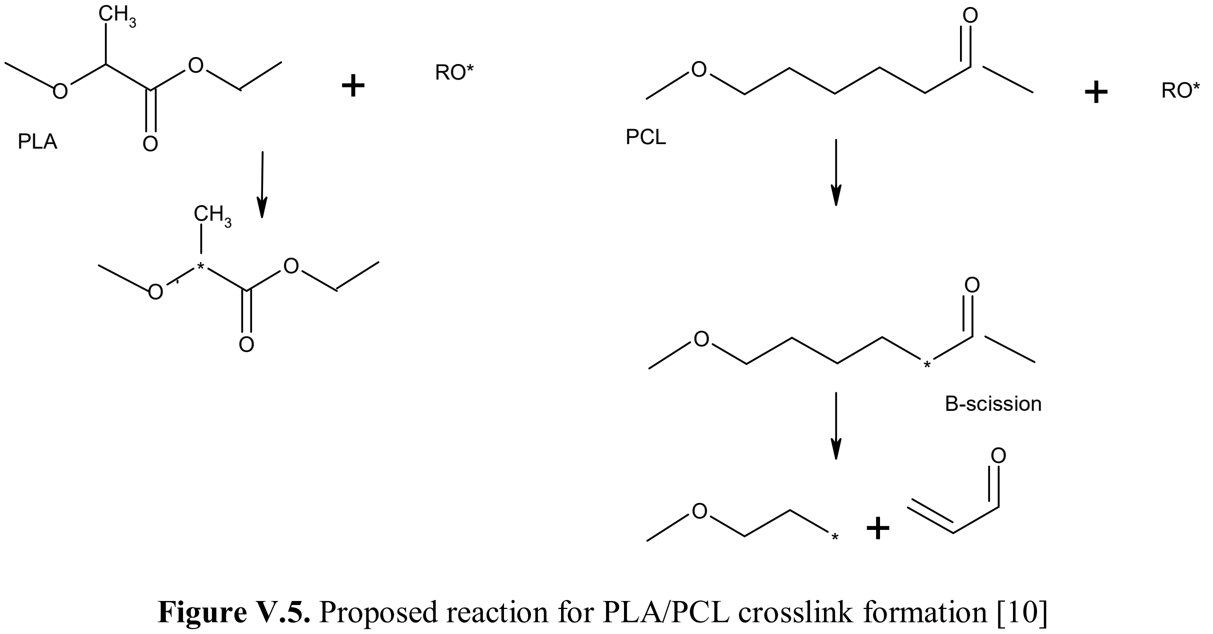

Figure V.5. Proposed reaction for PLA/PCL crosslink formation [10]

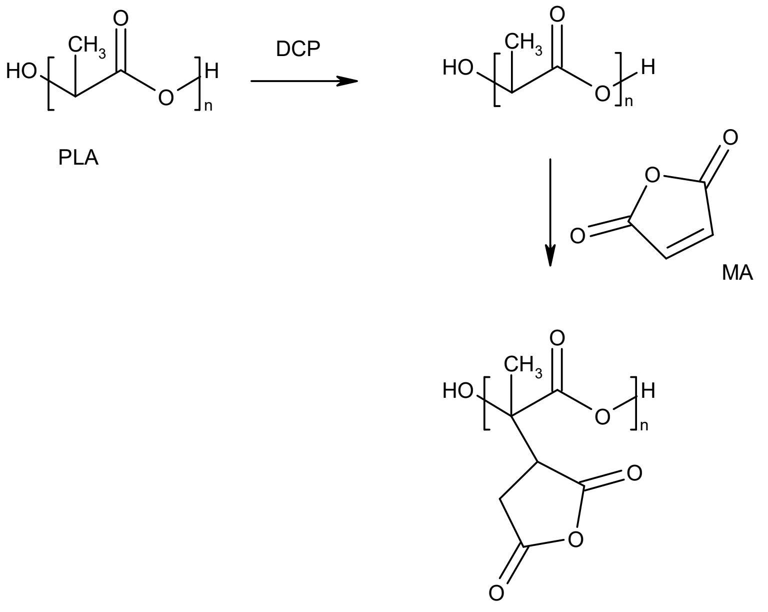

Figure V.6. Proposed reaction of PLA and MA

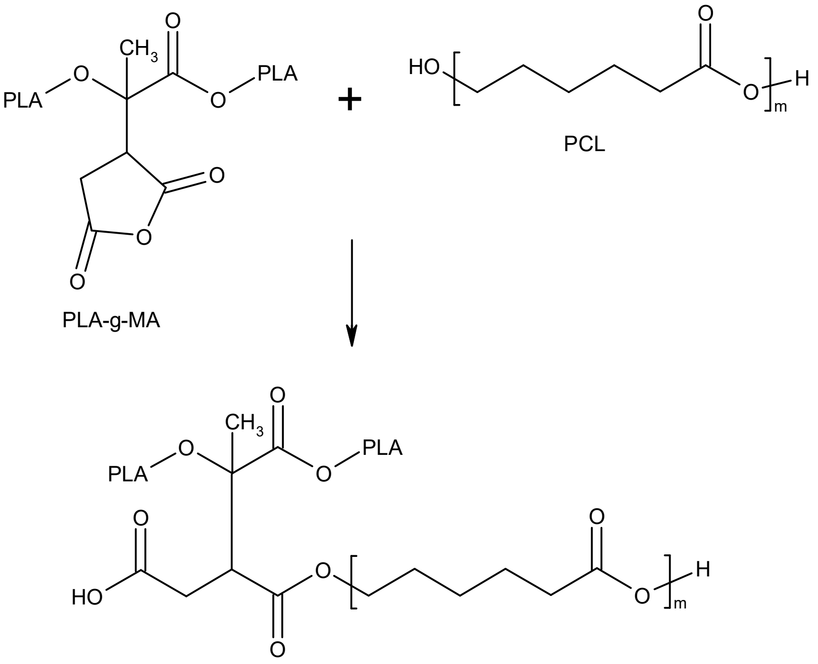

Figure V.7. Expected reaction of PLA-g-MA and PCL

V.3. Differential Scanning Calorimetry (DSC)

The thermal properties of the PLA/PCL (80/20 wt.%) were studied by means of differential scanning calorimetry (DSC). Figure V.8 reports the DSC thermograms of PLAPCL20 blends in the absence and presence of the different compatibilizing agents as recorded during the second heating scan. Thermal properties and crystallinity are summarized in Table V.1.

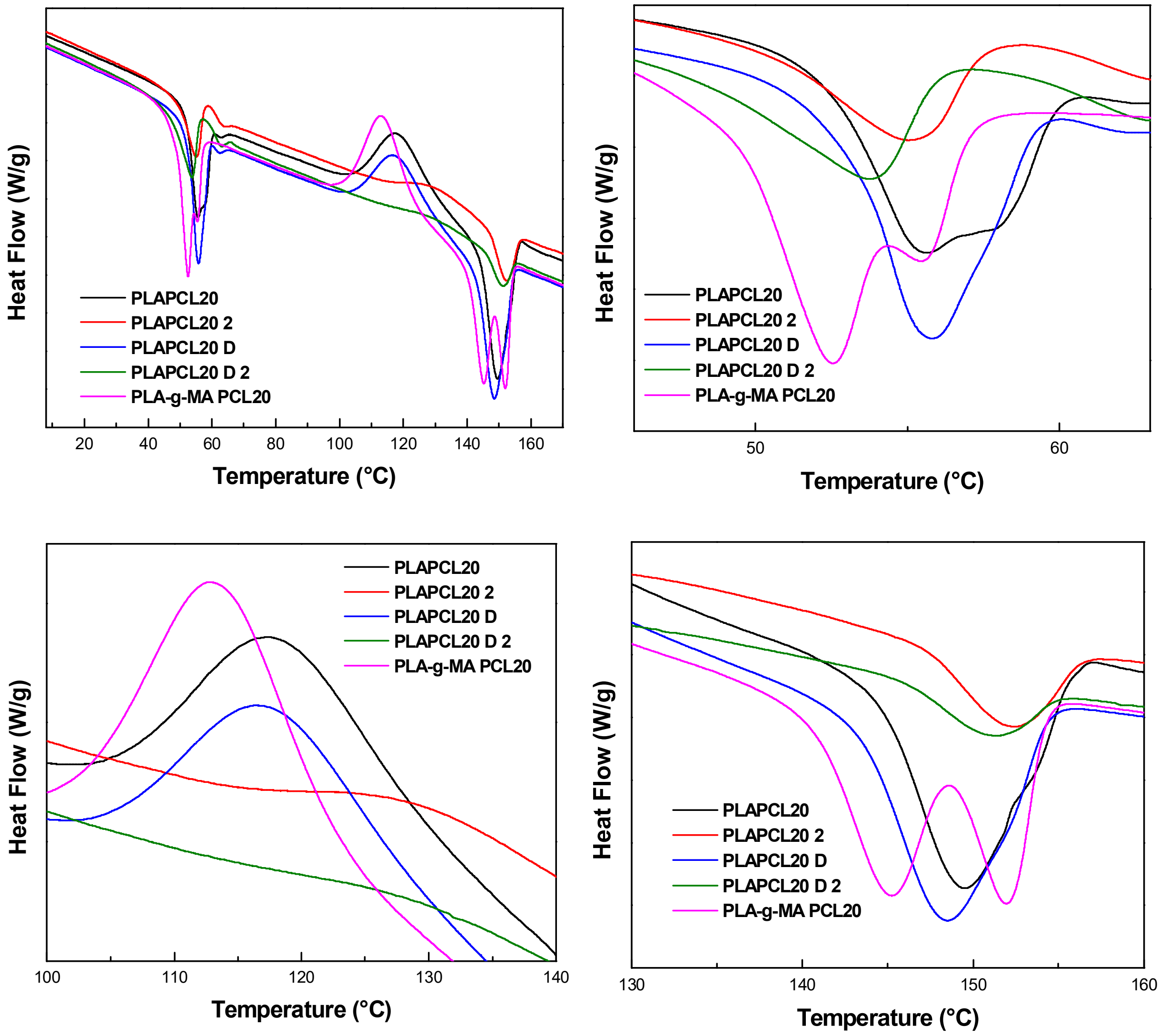

Figure V.8. DSC thermograms of PLAPCL20 blends with and without the addition of the different compatibilizing agents

Table V.1. Thermal properties and crystallinity of neat PLA, neat PCL and PLAPCL20 blends with and without the addition of the different compatibilizing agents

	PCL		PLA					
Sample	ΔH_m (J/g)	T_m (°C)	ΔH_{cc} (J/g)	T_{cc} (°C)	ΔH_m (J/g)	T_m (°C)	X_{cPLA} (%)	X_{cPCL} (%)
PLAPCL20	9.86	56	20.23	118	22.14	149	2.56	31.44
PLAPCL20 2	7.14	55	5.96	129	6.68	152	0.61	22.76
PLAPCL20 D	9.96	56	19.22	118	19.38	148	0.21	31.76
PLAPCL20 D 2	7.23	54	3.04	129	3.21	151	0.22	23.05
PLA-g-MA PCL20	13.52	53	22.18	113	22.74	145	0.75	43.11

From Figure V.8 and Table V.1, all the blends show the same thermal transitions: the glass transition (Tg) of the PLA matrix, the PCL melting peak (these two transitions being superimposed, the glass transition wasn't detected in the scans), the exothermic cold crystallization and the endothermic melting peak of PLA. With comparison to the PLAPCL20 blend, the addition of PMDI and (DCP + PMDI) does not seem to significantly affect the melting behavior of PCL, while significant variations in the crystallization and melting of PLA can be observed: the cold crystallization peak shifted toward higher temperatures, and the cold crystallization and melting enthalpy decreased significantly (Table V.1). This result may be explained by considering that PMDI affects the crystallization behavior by inhibiting the crystallization of PLA in the PLA/PCL blend [12]. The addition of DCP does not seem to affect the melting behavior of PCL, while slight changes have been observed for the melting and cold crystallization of PLA.

With the addition of PLA-g-MA, the melting enthalpy of PCL increased. The melting and the cold crystallization peak of PCL and PLA, respectively, split into two peaks and shifted toward lower temperatures (52.5°C, 55.5°C for PCL, and 145°C, 152°C for PLA). The presence of double/multiple melting peaks, is a commonly observed phenomenon for semicrystalline polyesters, caused by the existence of melting and recrystallization processes [13]. In the specific case of PLA, some authors have interpreted it as arising from a phase transition (from the less stable α' form to the more perfect α polymorph, melting at a higher temperature) [14, 15]. Whatever mechanism is taking place during the heating scan of the PLA matrix (recrystallization or phase transition), it is clear that such a behavior is influenced by the PLA-g-MA addition in the blend. As shown in Table V.1, the $X_{c,PLA}$ has significantly decreased due to PMDI, (DCP + PMDI), DCP and MA addition. $X_{c,PCL}$ has also decreased due to the addition of PMDI and (DCP + PMDI) while it has increased due to the addition of MA.

V.4. Thermogravimetric Analysis (TGA)

The thermal stability and thermal degradation of the PLA/PCL blends were evaluated by the TGA technique under nitrogen atmosphere. The TGA and DTG curves of the uncompatibilized and compatibilized blends with PMDI, DCP, and MA are shown in Figure V.9. The data determined are listed in Table V.2.

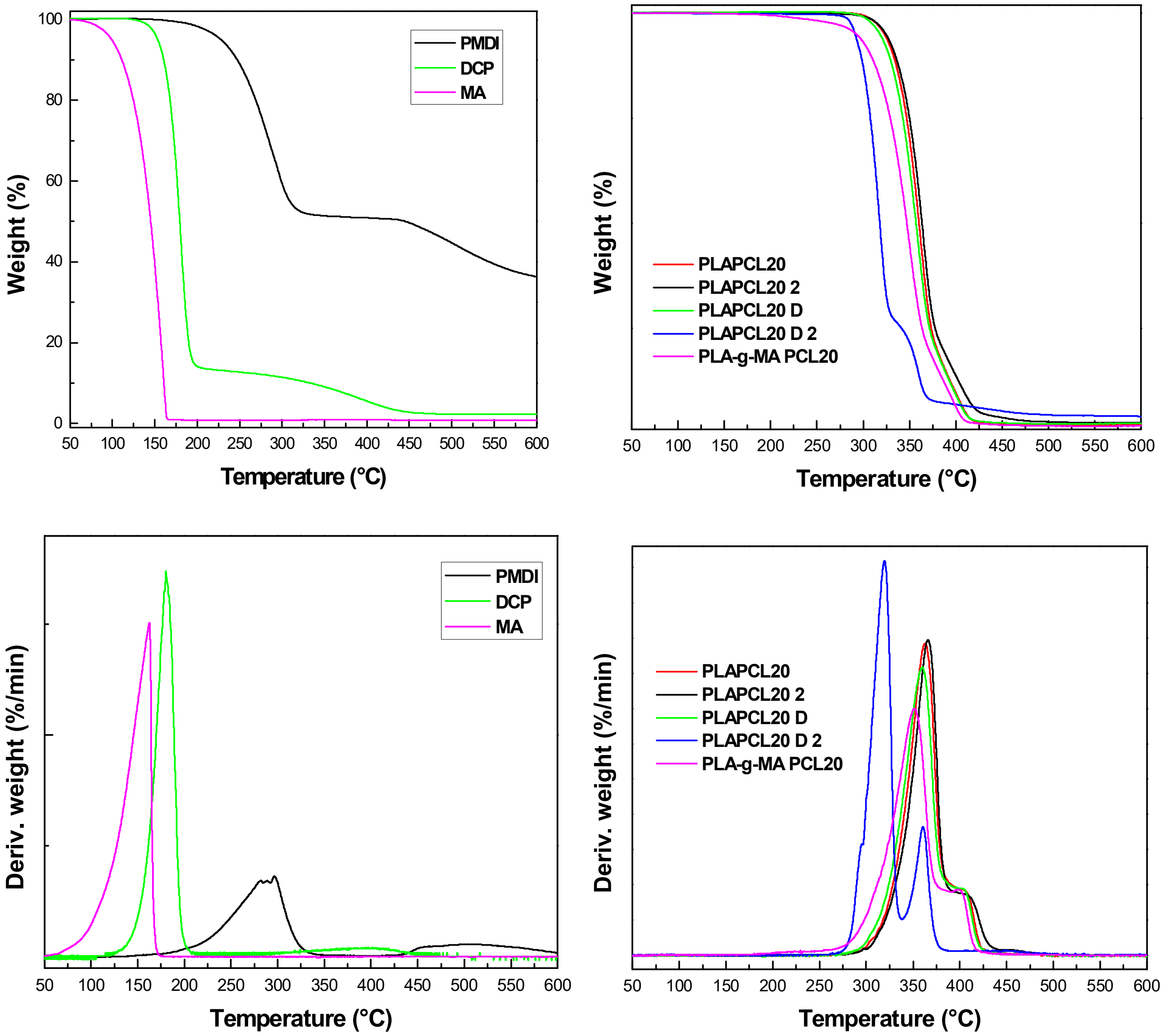

Figure V.9. TG/DTG thermograms of DCP, PMDI, MA, and PLAPCL20 with and without the addition of the different compatibilizing agents

Table V.2. Thermal properties of DCP, MA, PMDI, and PLAPCL20 blends with and without the addition of the different compatibilizing agents

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{1max} (°C)	T_{2max} (°C)	$Residu_{500°C}$ (%)
DCP	154	179	180	-	2.32
MA	99	145	163	-	0.78
PMDI	228	446	296	-	44.68
PLAPCL20	323	360	363	-	2.02
PLAPCL20 2	324	363	366	-	2.74
PLAPCL20 D	318	357	360	-	2.32
PLAPCL20 D 2	291	318	320	361	4.42
PLA-g-MA PCL20	293	347	352	399	1.80

2: PMDI, D: DCP, MA: maleic anhydride

Thermogravimetric curves of DCP, PMDI, and the studied blends have displayed two steps of decomposition. According to T_{1max} summarized in Table V.2, the addition of the different compatibilizing agents does not seem to significantly affect the thermal stability of PLAPCL20 blends. The temperature corresponding to the degradation of 5 % ($T_{5\%}$) of PMDI, DCP, and MA, is very low compared to that of the studied blends. However, $T_{5\%}$, $T_{50\%}$, and T_{1max} of the compatibilized blends, have decreased with the addition of DCP and MA compared to the reference blend PLAPCL20, indicating that the compatibilizing agents have promoted a slight decrease in the thermal stability of the blends. While the combination of PMDI and DCP has shown an antagonism effect on thermal stability. With regard to PLAPCL20 2, the enhanced thermal stability may be due to the increase of molecular weight of the blend during melt processing of PLA/PCL and PMDI because the chain extender reconnects the polymer chains that break down during processing [16, 17].

V.5. X-Ray Diffraction (XRD)

XRD patterns of the PLAPCL20 and compatibilized PLAPCL20 blends are shown in Figure V.10. The crystallinity obtained by this technique is calculated using equation (3) (Chapter III). Crystallinity of PLAPCL20 and PLAPCL20-compatibilizer blends are summarized in Table V.3.

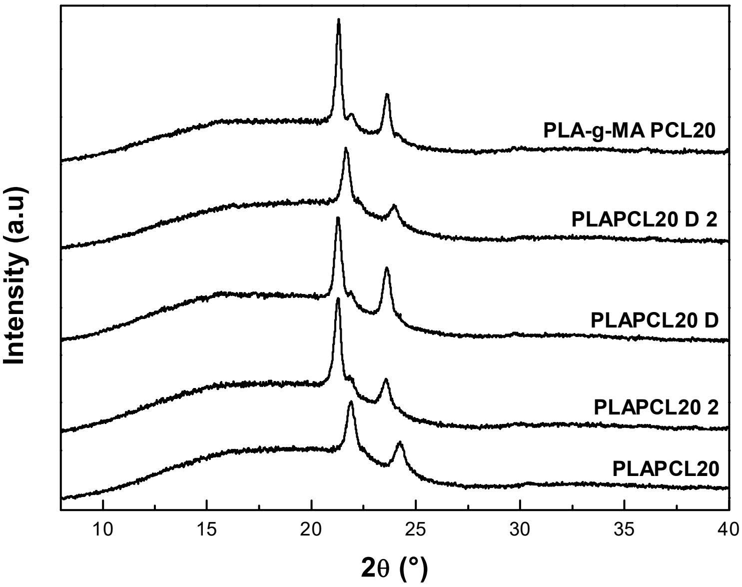

Figure V.10. XRD spectra of PLAPCL20 blends in the absence and presence of the different compatibilizing agents

Table V.3. Crystallinity of PLAPCL20 and compatibilized PLAPCL20 blends

Sample	X_c(%)
PLAPCL20	43.49
PLAPCL20 2	33.05
PLAPCL20 D	40.63
PLAPCL20 D 2	41.15
PLA-g-MA PCL20	43.10

As shown in Figure V.10, the XRD spectrum of PLAPCL20 has shown in addition to the broad peak between 10° and 20° several peaks between 20° and 25°; with two sharp and distinct high-intensity peaks and other low-intensity peaks. The broad peak corresponds to the amorphous regions while the sharp peaks correspond to the crystalline regions, indicating a semicrystalline structure. The peak intensities of PLAPCL20 blends with the addition of PMDI, DCP, and MA vary in comparison with the reference PLAPCL20 blend and PLAPCL20 D 2. The main sharp peak of PLAPCL20 2, PLAPCL20 D, and PLA-g-MA PCL20 have slightly shifted towards lower angles, which probably indicates the variation in the distance between parallel planes of atoms [18]. The degree of crystallinity of the studied blends has decreased by the addition of the different compatibilizing agents.

V.6. Scanning Electron Microscopy (SEM)

Many of the properties of polymer blend are affected by their morphology or the interfacial interactions of individual blend components. Therefore, controlling the morphology is a key factor for the tailoring of the final properties of the composite materials [19, 20]. Figure V.11 shows the SEM images of the cryo-fractured surfaces of PLAPCL20 blends in absence and presence of the compatibilizing agents at 10, 20, 50µm magnification.

The shapes, sizes, and spatial distributions of phases are the results of complex interplay between components viscosities, interfacial adhesion, blend composition, and processing conditions [21]. The first sample (PLAPCL20) shows a typical sea-island morphology [13, 22], where the discrete PCL spherical domains, with dimensions ranging between 0.38 and 8.58 µm, are dispersed all over the PLA matrix which is typical of an immiscible blend. The specimens did not exhibit such spherical structures for PLAPCL20 2 and PLAPCL20 D 2, indicating that the immiscibility between PLA and PCL was dramatically decreased with the addition of PMDI and (DCP + PMDI). This result suggests that by adding PMDI, the PCL domains decreased, as did the diameter of the droplets, indicating good interfacial adhesion between PLA and PCL phases.

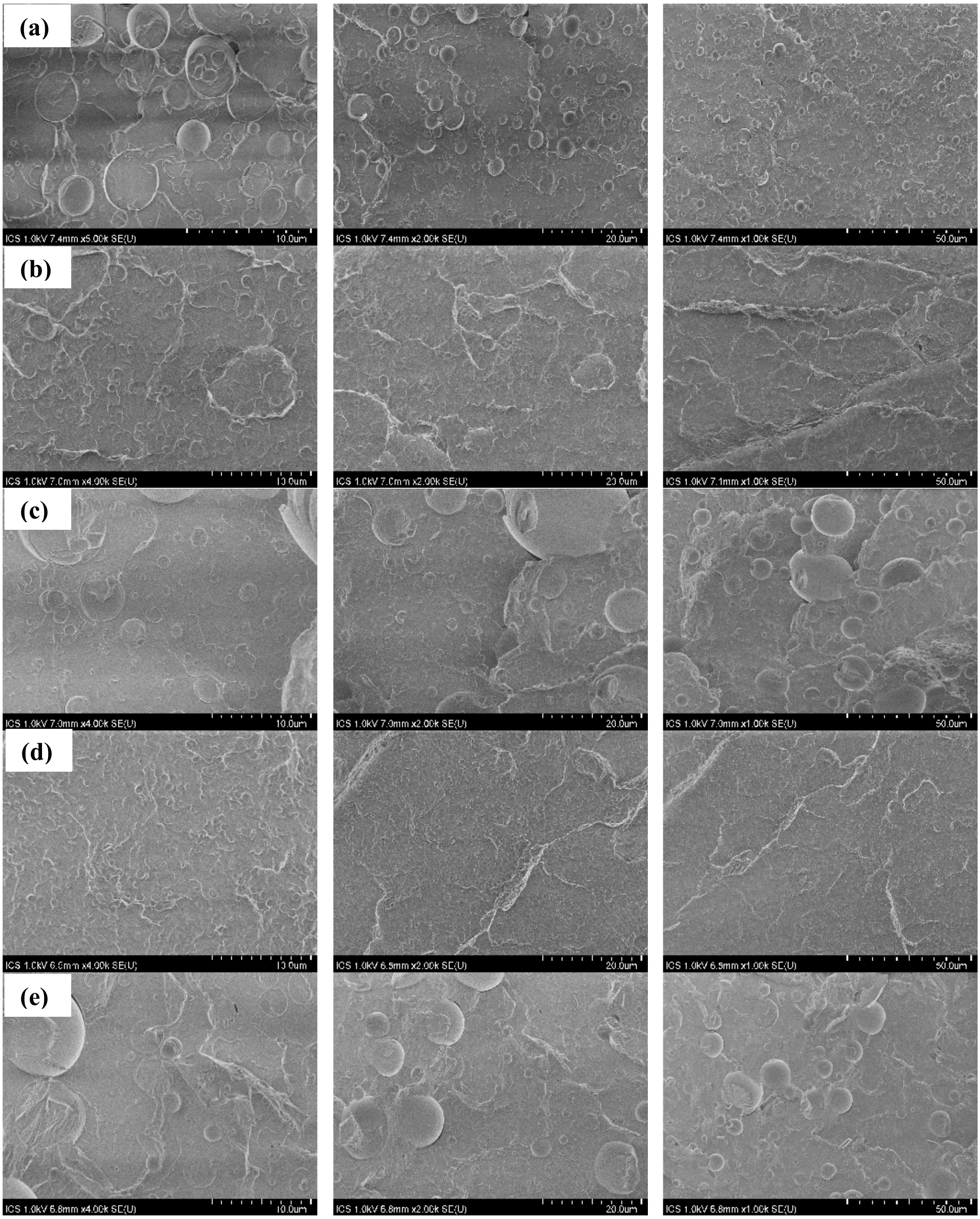

Figure V.11. SEM images of cryo-fractured of (a) PLAPCL20, (b) PLAPCL20 2, (c) PLAPCL20 D, (d) PLAPCL20 D 2, (e) PLA-g-MA PCL20 blends

These improvements were attributed to the effective interfacial reactions accomplished between the isocyanate functionalities of PMDI and carboxyl, hydroxyl end groups of the PLA/PCL blend as discussed earlier, based on the FTIR results. Finally, we can say that the microstructure of the PLAPCL20 blends was properly tuned and the size of PCL domains was reduced significantly due to the reactive compatibilization effect of PMDI. Similar results have been evidenced previously [7, 22–24].

In the case of PLAPCL20 D and PLA-g-MA PCL20, the SEM morphological characterization shows inhomogeneous microstructure, revealing a clear immiscible behavior. The compatibilized blends exhibited smaller dispersed phase particle sizes and more occupied interface. However, the particle sizes of the compatibilized blends differ somewhat [25]. The radii of dispersed phase particles of blends followed the sequence: PLAPCL20 > PLAPCL20D > PLA-g-MA PCL20 > PLAPCL20 2 ~ PLAPCL20 D 2. Generally, more effective compatibilization resulted in finer blend morphology, and thus, PLAPCL20 2 and PLAPCL20 D 2 would be better compatibilized than PLAPCL20 D and PLA-g-MA PCL20.

V.7. Conclusion

FTIR results indicated that some chemical interaction occurred through the formation of carbamate bond between the –NCO groups of PMDI and the –OH group end-groups of PLA and PCL. The addition of DCP slowed down the performance of PMDI when both additives were used as a compatibilizing agent for the PLA/PCL blend. DSC revealed significant variations in the crystallization and melting of PLA by the addition of PMDI. DCP slightly affected both melting and cold crystallization of PLA. The addition of PLA-g-MA in the blend induced the presence of double/multiple melting peaks, caused by the existence of melting and recrystallization processes. The compatibilizing agents have promoted a slight decrease in the thermal stability of the blends. While the combination of PMDI and DCP has shown an antagonism effect on thermal stability. Enhanced thermal stability was observed with the addition of PMDI probably due to the increase of molecular weight of the blend during melt processing of PLA/PCL and PMDI. XRD revealed that the degree of crystallinity of the studied blends has decreased by the addition of the different compatibilizing agents. The main sharp peak of PLAPCL20 2, PLAPCL20 D, and PLA-g-MA PCL20 have slightly shifted towards lower angles probably indicating the variation in the distance between parallel planes of atoms. The effective interfacial reactions accomplished between the isocyanate functionalities of PMDI and carboxyl, hydroxyl end groups of the PLA/PCL blend was confirmed by SEM. The compatibilized blends exhibited smaller dispersed phase particle sizes and more occupied interface. However, the particle sizes of the compatibilized blends differ somewhat. The radii of dispersed phase particles of blends followed the sequence: PLAPCL20 > PLAPCL20D > PLA-g-MA PCL20 > PLAPCL20 2 ~ PLAPCL20 D 2. More effective compatibilization resulted in finer blend morphology, and thus, PLAPCL20 2 and PLAPCL20 D 2 would be better compatibilized than PLAPCL20 D and PLA-g-MA PCL20.

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Chapter VI

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Chapter VI. General conclusions and recommendations

VI.1. General conclusions

The main conclusions of the study on blending and plasticizing effects on the crystallinity and miscibility of PLA/PCL blends are outlined as follows:

- PCL acted as a nucleating agent for PLA by promoting a slight increase in the degree of crystallinity and a significant decrease in the glass transition temperature of PLA;
- ATBC and TEC have lowered the glass transition temperature and have enhanced much more the crystallization of PLA than the addition of PCL;
- The addition of PCL and the citrate ester plasticizers have promoted a decrease in the thermal stability of PLA;
- Based on the depression of Tg and the enhancement of the crystallinity of PLA, PLA/PCL blends were shown to be partially miscible.

The effects of PMDI, DCP, (DCP + PMDI), and MA additives on microstructure and thermal properties of PLA/PCL (80/20) blends were also investigated, and the following main results were obtained:

- The effectiveness of PMDI was demonstrated by the interesting obtained results compared to the other compatibilizing agents;
- Some chemical interaction occurred through the formation of carbamate bond between the –NCO groups of PMDI and the –OH group end-groups of PLA and PCL;
- The addition of DCP slowed down the performance of PMDI when both additives were used as a compatibilizing agent for the PLA/PCL blend;
- The addition of PLA-g-MA influenced the melting of PCL and the cold crystallization of PLA. The presence of double/multiple melting peaks was caused by the existence of melting and recrystallization processes related to the addition of PLA-MA in the blend.
- DCP was added to PLA/PCL binary blend to induce chemical crosslinking; however, it does not show any characteristic peak;
- The compatibilizing agents have promoted a slight decrease in the thermal stability of the blends. While the combination of PMDI and DCP has shown an antagonism effect on thermal stability;

- Enhanced thermal stability was observed with the addition of PMDI probably due to the increase of molecular weight of the blend during melt processing of PLA/PCL and PMDI;
- The compatibilized blends have exhibited smaller dispersed phase particle sizes and more occupied interface. However, the particle sizes of the compatibilized blends differ somewhat;
- More effective compatibilization has resulted in finer blend morphology, and thus, PLAPCL20 2 and PLAPCL20 D 2 were considered as better compatibilized than PLAPCL20 D and PLA-g-MA PCL20.

VI.2. Recommendations

Several research aspects need deep investigations for future research works. In this regard, the following additional investigations could, therefore, be recommended:

- Since the study aimed to prepare a material for packaging applications, it is recommended to study other properties of the PLA/PCL plasticized blends such as water vapor and gas permeability, and to evaluate the effect of the rate of ATBC and TEC on the barrier properties of the material;
- Further investigations on the morphology of the rigid and plasticized PLA/PCL bends are needed to confirm the partial miscibility between PLA and PCL;
- Further studies are needed to understand the chemical role and to confirm the effect of DCP and MA on PLA/PCL properties;
- Exploring the mechanical, tensile, and rheological properties of the plasticized and compatibilized blends is also recommended;
- In addition to the differential scanning calorimetry (DSC), hot stage microscopy (HSM) is recommended to further study the crystallization kinetics of the plasticized and compatibilized blends and mainly to gain a better understanding of the relationship between crystallization temperature, melting temperature and overall degree of crystallinity, as well as crystallization and growth rates;
- Finally, it is recommended exploring the effect of PMDI, DCP, and MA on the biodegradability of PLA/PCL blends.

Article

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Blending and plasticising effects on the behaviour of poly(lactic acid)/poly(ε-caprolactone)

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Abstract

Polymer blending is one of the most convenient methods to be used to overcome the limitations of some single properties of polymers and to achieve the combinations required for specific applications. Another feasible common practice is the incorporation of additives of low molecular weight such as plasticisers to impart flexibility, improve toughness and lower the glass transition temperature (T_g). This study focused on the effects of blending and plasticising on the crystallisation behaviour of poly(lactic acid) (PLA)/poly(ε-caprolactone) (PCL). PCL with longer degradation time compared with other polymers was blended with PLA to overcome the limitation of its brittleness and poor thermal stability. Acetyl tributyl citrate (ATBC) and acetyl triethyl citrate (TEC) were used as plasticiser in PLA/PCL blends. The rigid and plasticised blends at various ratios were analysed by differential scanning calorimetry, thermogravimetric analysis and X-ray diffraction. The results revealed a slight increase in the degree of crystallinity and a significant increase in the T_g of PLA due to the addition of PCL. The addition of ATBC has promoted a decrease in thermal stability of the blends. The slight increase in the degree of crystallinity suggested that PCL acted as a nucleating agent. The citrate plasticisers were shown to lower the T_g and have much more enhanced the crystallisation of PLA. Moreover, the rigid and plasticised blends were shown to be partially miscible.

Keywords
Mixing, citrate plasticisers, packaging, plasticisation, polyesters, biodegradable polymers

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Introduction

In recent years, there has been an increased interest in the use of polymers made of renewable raw materials. The advantage over traditional materials is due to the huge environmental problems mainly created by petrochemical-based polymers.[1–3] Biodegradable materials are expected to overcome the sustainability issues and environmental challenges in the near future. This is due to their low cost, extraordinary versatility and compostability, which allows for easier waste management.[3,4] These properties have targeted applications in various fields specifically such as packaging, agricultural, textile, pharmaceutical, electronic or medical domains.[5]

Poly(lactic acid) (PLA) is a highly transparent and rigid material with a relatively low crystallisation rate and is produced from renewable resources such as corn, sugar beets and so on. Products with high molar mass are usually produced from lactides and the lactic acid monomers via ring-opening polymerisation route. It is one of the most promising alternatives to conventional plastics due to its biodegradability, sustainability, high melting temperature (T_m) and mechanical strength compared to those of many petroleum-based plastics.[6,7] However, under practical processing conditions, it is well known to show slow nucleation and crystallisation rates and would be nearly 100% amorphous, which limits wider applications in sectors, such as automotive and packaging fields. Moreover, several other drawbacks limit its widespread use such as brittleness, hydrolysis under high humidity conditions, hydrophobicity, poor moisture and gas barrier, low heat resistance and high cost.[8,9–13]

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Among the several approaches that are believed to be effective in enhancing the crystallisation process of semi-crystalline polymers are blending with polymers with high crystallinity, nucleating agents such as inorganic compounds, low-molecular-weight organic compounds and polymeric nucleating agents. Plasticisation with low-molecular-weight compounds has been widely explored to keep the best attributes of these biopolymers.[4,13,14] The nucleating agent will lower the surface free energy barrier towards nucleation and thus initiates crystallisation at higher temperature upon cooling.[8] According to recent studies, the biodegradable poly(ε-caprolactone) (PCL) is reported to be an effective polymeric nucleating agent for PLA.[15,16] Many research groups have reported on biodegradable PLA/PCL blends, revealing that these blends were thermodynamically immiscible, which results in a multiphase structure with poor dispersion and some interfacial adhesion when the majority phase is PCL but not when it is PLA .[17–19] In contrast, some studies revealed partial miscibility, first of all, since the lack of specific interactions between PCL and PLA leads to partial miscibility of their blends, and the PLA -rich phase seems to partly dissolve the PCL.[16,20] Similarly, the solubility parameters of both materials are close to each other, that is, 9.2 and 10.1 cal cm^{-3}, respectively.[14]

Considerable efforts have been made to enhance the miscibility of PLA and PCL blends using generally known techniques. Prepared diblock PLA-PCL[21] and triblock PLA-PCL-PLA[22] were used as compatibiliser between PLA and PCL. The results showed that the elongation at break of the PLA/PCL blends with the diblock and triblock increased to 71.4% and 53%, respectively. In addition, some molecule compatibilisers have been used in PLA/PCL blends, such as glycidyl methacrylate,[23] dicumyl peroxide[24] and lysine triisocyanate.[25] These compatibilisers reduced the size of the dispersed phase and improved the toughness of the PLA matrix. However, these small molecule compatibilisers are unsuitable environmentally friendly material. Hence, maleic anhydride-grafted PLA was used in different blend systems, such as those based on polyethylene glycol.[26]

Many researchers published works on the compatibilisation of immiscible PLA/PCL mixtures using new strategy in the development of composites and nanocomposites for improving the interfacial adhesion between the polymer and the filler/nanofiller. PLA/PCL (42/58) blend nanocomposites were prepared with 1.5 titanium dioxide (TiO_2) nanoparticles. It was concluded that TiO_2 nanoparticles were located at the interface of the two phases due to kinetic effects and nanoparticles geometry.[27] PLA/PCL was also used by combining organomontmorillonites (OMt; Cloisite 15A and Cloisite 30B) with epoxy-functionalized graphene (Gr). They concluded that the compatibility of PLA/PCL is improved in the presence of organoclays and OMt/Gr mixtures.[28] Recently, Stoja et al.[29] have employed for the first time to impregnate PLA/PCL films with natural antibacterial agents such as thymol and thyme extract for bacterial growth control in food packaging.

Plasticisers are frequently used, not only to improve the transformation but mainly to increase the polymer chain mobility and to enhance the crystallisation rate of polymers by reducing the energy required for its crystallisation for the chain folding process.[8] Citrate esters are investigated as plasticisers for PLA. At least 20% of plasticiser needs to be introduced to lower its glass transition temperature (T_g), increase ductility and improve processability.[13,18–20,30] Recently, much attention has been turned to the study of PLA crystallisation behaviour because crystal structure and arrangement of crystallites have been reported to have a profound effect on the physical and mechanical properties of biodegradable polymers.[8]

Only few researchers have studied the influence of the addition of plasticisers on the miscibility and crystallisation of PLA/PCL blends. The effect of PCL contents and triethyl 2-acetyl citrate (TEC) and tributyl O-acetyl citrate (ATBC) as plasticiser at various compositions on PLA/PCL blends were investigated. In this study, a series of rigid and plasticised PLA (2002D) and PCL (CAPA6250) were prepared by melt mixing at various concentrations. A slight increase in the degree of crystallinity suggested that PCL acted as a nucleating agent. TEC and ATBC are biodegradable plasticisers that have been blended with PLA/PCL. By adding up to 30%, these citrate plasticisers were shown to lower the T_g. Moreover, the rigid and plasticised blends were shown to be partially miscible. Therefore, the effects of blending and plasticising on the crystallisation behaviour of PLA/PCL were investigated.

Experiment

Materials

The selected commercial PLA grade was PLA 2002D purchased from NatureWorks LLC (Minnetonka, MN, USA). It is a semi-crystalline extrusion material with approximately 4% D-lactic acid monomer. As such, PLA has very slow nucleation and crystallisation rates and the specimen would be nearly 100% amorphous after being rapidly cooled during injection moulding, and it is characterised by the presence of only one hydroxyl terminal group. Its average molecular weight (M_w), T_g and T_ms are about 160,000–220,000 g mol^{-1}, 60°C and 156°C, respectively. Its specific gravity is 1.24, and its melt flow index is between 5 g 10 min^{-1} and 7 g 10 min^{-1} at 210°C/2.16 kg. The PCL (CAPA 6250, $M_w = 25{,}000$ g mol^{-1}) used in this study was a commercial product from Perstorp Polyols Inc. (Toledo, OH, USA). Its melting point and T_g reported by the supplier are 58–60°C and −58°C, respectively. Its viscosity is about 1.5 million mPa·s at (100°C). Because PLA is a highly hygroscopic thermoplastic and absorbs moisture from the atmosphere, all specimens were dried in an oven at 60°C overnight to remove any excess moisture. Both ATBC and TEC were used in colourless liquid form as received from

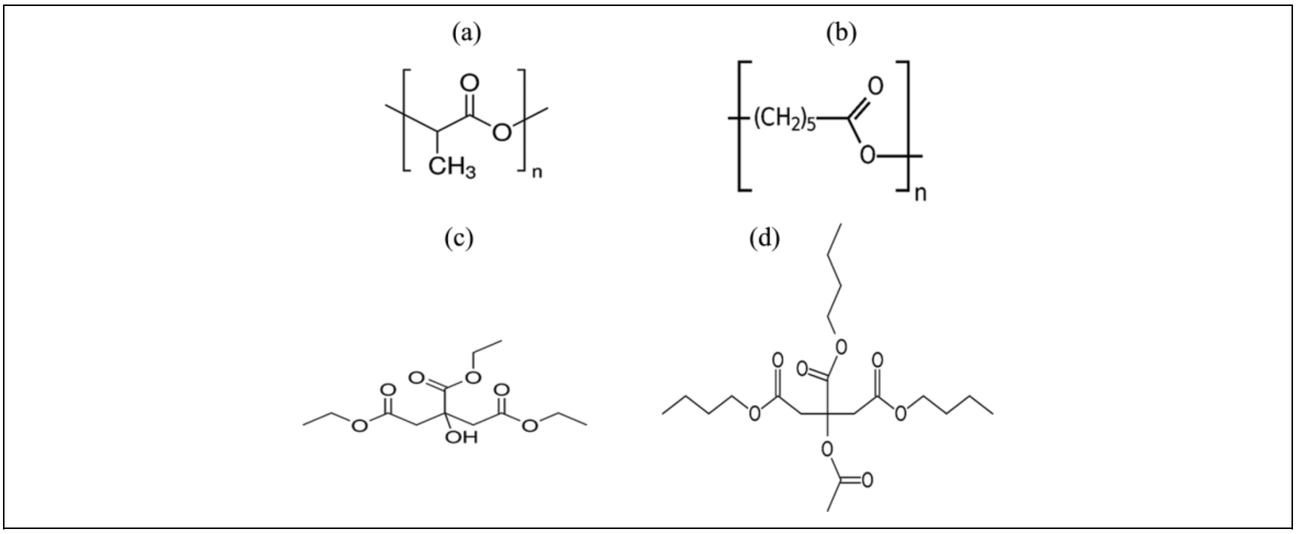

Figure 1. Chemical structure of (a) PLA, (b) PCL, (c) TEC and (d) ATBC.
PLA: poly(lactic acid); PCL: poly(ε-caprolactone); TEC: acetyl triethyl citrate; ATBC: acetyl tributyl citrate.

Table 1. Summary of compositions of rigid and plasticised PLA/PCL blends with ATBC and TEC.

Sample	PLA (wt%)	PCL (wt%)	ATBC (wt%)	TEC (wt%)
PLA	100	0	–	–
PCL	0	100	–	–
PLAPCL10	90	10	–	–
PLAPCL20	80	20	–	–
PLAPCL30	70	30	–	–
PLAPCL10-20ATBC	70	10	20	–
PLAPCL20-20ATBC	60	20	20	–
PLAPCL30-20ATBC	50	30	20	–
PLAPCL10-30ATBC	60	10	30	–
PLAPCL20-30ATBC	50	20	30	–
PLAPCL30-30ATBC	40	30	30	–
PLAPCL10-20TEC	70	10	–	20
PLAPCL10-30TEC	60	10	–	30

PLA: poly(lactic acid); PCL: poly(ε-caprolactone); TEC: acetyl triethyl citrate; ATBC: acetyl tributyl citrate.

Sigma-Aldrich (France), with a molecular weight of 402.48 g mol^{-1} and 318.32 g mol^{-1}, respectively. Chemical structure of (a) PLA, (b) PCL, (c) TEC and (d) ATBC are represented in Figure 1.

Preparation method

To prepare rigid and plasticised blends, PLA pellets were dried in an oven at 60°C overnight. PCL, ATBC and TEC were used as received. Appropriate quantities were measured and poured in a container and then were manually mixed by shaking. The melt mixing process of PLA/PCL blends was carried out using a plastograph Brabender LP2100 (Duisburg, Germany) at a temperature of 180°C during 8-min cycle with 40 r min^{-1} screw speed. The obtained samples were cut into small pieces and then compression moulded into 2-mm-thick sheets and thin films at the same temperature (180°C) for 5 min using a hydraulic press at a pressure of 75 Pa. Subsequently, the composition of rigid and plasticised PLA/PCL blends with TEC and ATBC are summarised in Table 1.

Characterisation methods

Differential scanning calorimetry

The main thermal transitions were investigated using a differential scanning calorimeter (DSC/Q10; TA Instruments (New Castle, Delaware, USA)), under a nitrogen flow of 50 ml min^{-1}. To eliminate the material's thermal record, samples were first heated to 180°C at a heating rate of 10°C min^{-1} by keeping this temperature for 3 min. The samples were then cooled down to −70°C at a cooling rate of 10°C min^{-1} by keeping this temperature for 3 min. Finally, they were reheated to 180°C at a heating rate of 10°C min^{-1} by keeping this temperature again for 3 min and then jumping down to 25°C. All thermal properties were obtained from the second heating scan curves. The degree of crystallinity of PCL ($X_{\mathrm{c,\,PCL}}$) in the blends was calculated from equation (1) with consideration of the amount of PCL in the blend.[18] For PCL, a 100% crystalline melting enthalpy ($\Delta H_{0,\,\mathrm{PCL}}$) of 156.8 J g^{-1} was assumed.[31] The degree of crystallinity of PLA ($X_{\mathrm{c,\,PLA}}$) was calculated from equation (2), and for PLA, the 100% crystalline melting enthalpy ($\Delta H_{0,\,\mathrm{PLA}}$) was taken to be 93 J g^{-1}.[32]

$$X_{\mathrm{C,\,PCL}}\,(\%) = \frac{\Delta H_{\mathrm{m,\,PCL}}}{\Delta H_{0,\,\mathrm{PCL}}\,W_{\mathrm{PLA}}} \times 100 \tag{1}$$

$$X_{\mathrm{C,\,PLA}}\,(\%) = \frac{\Delta H_{\mathrm{m,\,PLA}} - \Delta H_{\mathrm{CC,\,PLA}}}{\Delta H_{0,\,\mathrm{PLA}}\,W_{\mathrm{PLA}}} \times 100 \tag{2}$$

where W_{PCL} and W_{PLA} are the weight fractions of PCL and PLA in the blends, respectively; $\Delta H_{\mathrm{m,\,PCL}}$ and $\Delta H_{\mathrm{m,\,PLA}}$ are the melting enthalpies of PCL and PLA in the blends, respectively and $\Delta H_{\mathrm{cc,\,PLA}}$ is the cold crystallisation enthalpy (ΔH_{cc}) of PLA in the blends.

X-Ray diffraction

The X-ray diffraction (XRD) of PLA/PCL and PLA/PCL/plasticiser films studied was carried out using a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA). Scans were recorded in reflection using α radiation with a wave length (λ) of 0.1542 nm at room temperature. The angle of incidence was varied from 8°C to 50°C in steps of 3° min^{-1}. The accelerating voltage was 40 kV, and the tube current was 150 mA. A computer-aided curve fitting technique was used to separate crystalline and amorphous phases of diffracted graphs. The crystallinity was calculated by separating intensities using Gaussian and Lorentzian functions due to amorphous and crystalline phase on diffraction phase. The degree of crystallinity (X_{c}; %) was measured as the ratio of crystalline area to the total area as shown in equation (3):

$$X_{\mathrm{C}}\,(\%) = \frac{A_{\mathrm{c}}}{A_{\mathrm{a}}} \times 100 \tag{3}$$

where A_{c} and A_{a} are the areas of crystalline and amorphous phases, respectively.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the PLA/PCL/plasticiser samples was studied using a TGA Q500 analyser (TA Instruments) (New Castle, Delaware, USA). The samples were heated from 10°C to 550°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere at the flow rate of 10 ml min^{-1}. The onset temperature (onset) was determined from the thermogravimetric curve as being the temperature at which the weight loss begins.

Results and discussion

Differential scanning calorimetry

DSC thermograms of neat PLA, neat PCL and rigid and plasticised PLA/PCL blends with TEC and ATBC at various concentrations are shown in Figure 2. Parameters such as T_{g}, T_{m}, cold crystallisation temperature (T_{cc}), ΔH_{m}, ΔH_{cc} and X_{c} are presented in Table 2.

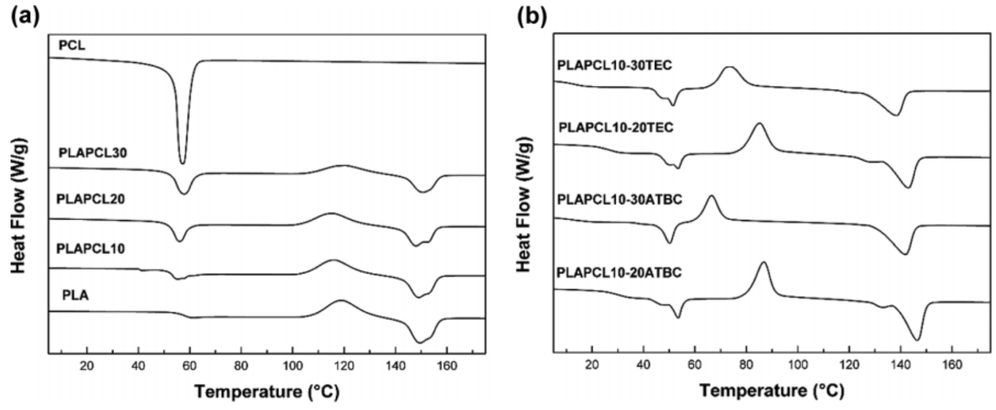

Figure 2. DSC thermograms of (a) rigid PLA/PCL blends and (b) plasticised PLA/PCL blends at various concentrations.
DSC: differential scanning calorimetry; PLA: poly(lactic acid); PCL: poly(ε-caprolactone).

Table 2. Thermal properties and crystallinity of neat PLA, neat PCL and rigid and plasticised PLA/PCL blends with ATBC and TEC at various concentrations.

Sample	T_g (°C) (PLA)	ΔH_m (J g^{-1}) (PCL)	T_m (°C) (PCL)	ΔH_{cc} (J g^{-1}) (PLA)	T_{cc} (°C) (PLA)	ΔH_m (J g^{-1}) (PLA)	T_m (°C) (PLA)	$X_{c,\ PLA}$ (%)	$X_{c,\ PCL}$ (%)
PLA	58	–	–	28.64	119	30.10	149	1.56	–
PCL	–	71.05	57	–	–	–	–	–	45.31
PLAPCL10	41	5.93	55	24.02	116	27.66	149	4.34	37.81
PLAPCL20	46	12.47	56	20.94	116	24.85	148	5.25	39.76
PLAPCL30	45	17.78	58	16.14	120	20.57	150	6.80	37.79
PLAPCL10-20ATBC	30	7.48	53	18.97	87	25.43	146	9.92	47.70
PLAPCL20-20ATBC	31	13.22	55	15.96	88	22.40	147	11.54	42.15
PLAPCL30-20ATBC	36	17.08	54	12.93	91	18.44	147	11.84	36.30
PLAPCL10-30ATBC	12	7.66	53	12.34	66	23.48	142	19.96	48.85
PLAPCL20-30ATBC	21	14.54	52	13.45	77	21.32	144	16.92	46.36
PLAPCL30-30ATBC	28	20.80	53	13.16	85	19.42	146	16.82	44.21
PLAPCL10-20TEC	27	6.59	53	17.84	85	24.00	143	9.46	42.02
PLAPCL10-30TEC	13	7.21	51	15.44	73	20.39	138	8.87	45.98

PLA: poly(lactic acid); PCL: poly(ε-caprolactone); TEC: acetyl triethyl citrate; ATBC: acetyl tributyl citrate; T_g: glass transition temperature; ΔH_m: melting enthalpy; T_m: melting temperature; ΔH_{cc}: cold crystallisation enthalpy; T_{cc}: cold crystallisation temperature; X_c: degree of crystallinity.

X-Ray diffraction

XRD is also used to determine the nature of polymer by measuring the extent of crystallinity with respect to the amorphous content. The XRD patterns of PLA, PCL and rigid and plasticised PLA/PCL blends with TEC and ATBC are shown in Figure 3.

The crystallinity obtained by this technique is calculated using equation (3). The values of X_c of rigid and plasticised PLA/PCL blends are shown in Table 3 and Figure 3.

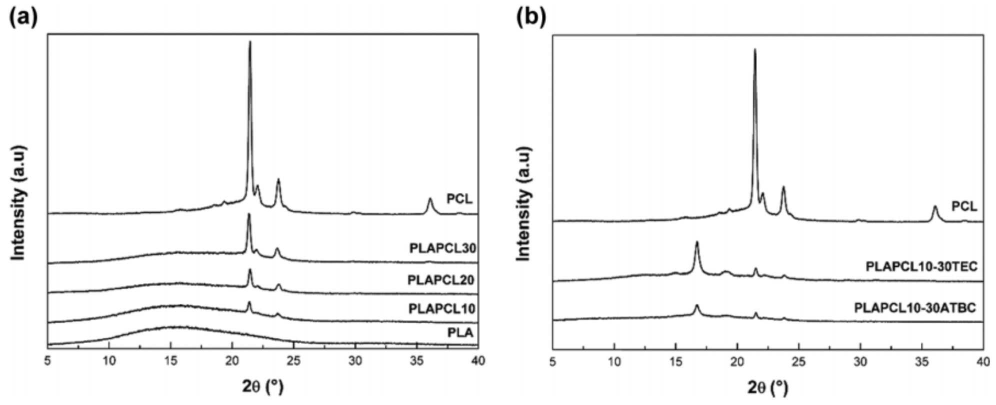

Figure 3. XRD spectra of (a) rigid PLA/PCL and (b) plasticised PLA/PCL blends at 30 wt%.
XRD: X-ray diffraction; PLA: poly(lactic acid); PCL: poly(ε-caprolactone).

Table 3. Crystallinity of rigid and plasticised PLA/PCL blends.

Sample	Crystalline phase (%)	Amorphous phase (%)	X_c (%)
PLA	0	63.27	0
PCL	6.86	6.27	52.26
PLAPCL10	18.85	31.71	37.28
PLAPCL20	13.83	18.07	43.35
PLAPCL30	16.43	27.55	37.36
PLAPCL10-20ATBC	15.14	17.88	45.84
PLAPCL20-20ATBC	24.97	29.46	45.87
PLAPCL30-20ATBC	22.84	20.78	52.36
PLAPCL10-30ATBC	24.67	32.37	43.25
PLAPCL20-30ATBC	13.61	44.79	23.30
PLAPCL30-30ATBC	12.75	44.73	22.18
PLAPCL10-20TEC	5.37	58.35	8.43
PLAPCL10-30TEC	18.54	42.46	30.39

PLA: poly(lactic acid); PCL: poly(ε-caprolactone); TEC: acetyl triethyl citrate; ATBC: acetyl tributyl citrate; X_c: degree of crystallinity.

Thermogravimetric analysis

TGA is the second most commonly used technique studying thermal degradation and stability of polymer materials. The thermogravimetric and derivative thermogravimetric experiments under nitrogen atmosphere were carried out to study the thermal degradation behaviour of PLA, PCL and their blends and to determine the impact of ATBC on the thermal stability of PLA. Curves of all samples are shown in Figure 4, and their thermal properties are summarised in Table 4.

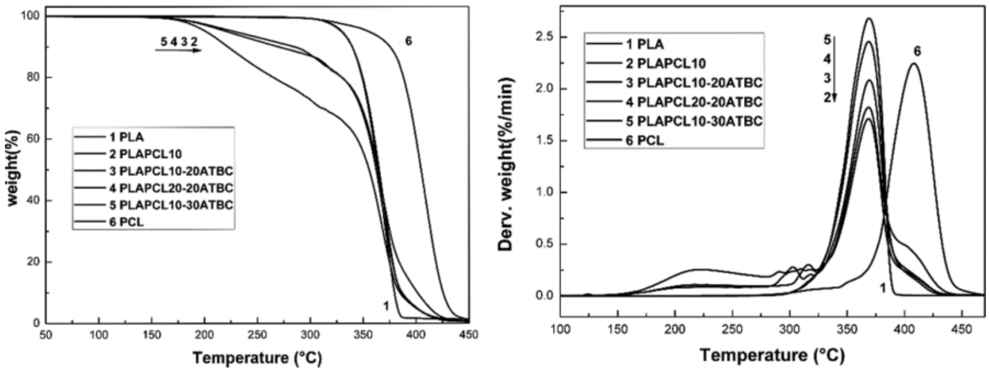

Figure 4. TG/DTG thermograms of rigid and plasticised PLA/PCL blends at various concentrations.
PLA: poly(lactic acid); PCL: poly(ε-caprolactone).

Table 4. Thermal properties of PLA/PCL blends at various concentrations determined by TG/DTG.

Sample	T_{onset} (°C)	T_{max} (°C)	$Residu_{475°C}$ (%)
PLA	345	369	1.22
PCL	382	407	0.59
PLAPCL10	345	368	1.06
PLAPCL20	344	366	1.07
PLAPCL30	343	366	0.82
PLAPCL10-20ATBC	175	369	0.35
PLAPCL20-20ATBC	178	368	0.44
PLAPCL10-30ATBC	183	368	0.42

PLA: poly(lactic acid); PCL: poly(ε-caprolactone); TG: thermogravimetric; DTG: derivative thermogravimetric; TEC: acetyl triethyl citrate; ATBC: acetyl tributyl citrate.

Differential scanning calorimetry

The results confirmed that the as-received PLA is semi-crystalline, due to the clear glass transition and melting peaks around 58°C and 149°C, respectively, as shown in Figure 2(a). It is well known that PLA has a very low crystallisation rate and that it primarily crystallises during heating.[33] This is confirmed from Table 2 and Figure 2(a). In addition to the glass transition and melting peaks, a clear cold crystallisation peak around 119°C and a very low crystallisation rate of about 1.56% calculated from equation (2) were reported. It is observed that the ΔH_{cc} was almost equal to the melting enthalpy, confirming that PLA does not form any crystal during the controlled cooling in the DSC analysis.[34]

With regard to PCL, which is also semi-crystalline, a well-defined melting peak around 57°C and high crystallisation rate of about 45.31% calculated from equation (1) were reported, whereas no crystallisation peak was noticed. Its glass transition peak is well known to be around −60°C, but it wasn't detected in the scans. The melting enthalpy of neat PCL is much higher than that of neat PLA, indicating much higher crystallinity compared to PLA.

These findings agree with the results obtained previously.[35,36] In fact, polymers with low molecular weight have a high content of crystallinity.[37] After blending with PCL, the T_m of PLA somehow hasn't changed significantly with the addition of PCL, showing values around 149°C range. The same applies to the melting peak of PCL, it hasn't changed with varying PCL content, and it remains at 57°C as for neat PCL. Double peaks have been observed in the melting of the blends, which are located between 140°C and 160°C depending on the PCL content. These findings reveal the existence of two different types of PLA crystals with different perfections within the system. The first endothermic peak shows PLA crystals with less perfection probably due to the presence of a limited amount of miscible PCL chains within the formed structure, which is in agreement with previous studies.[14,38]

However, with varying PCL content, some changes have occurred on the rest of the thermal properties of both PLA and PCL phases. The T_{cc} of PLA has barely shifted to a lower temperature, the $\Delta H_{cc,\,PLA}$ and $\Delta H_{m,\,PLA}$ of PLA have decreased and the $\Delta H_{cc,\,PCL}$ has increased significantly, thus indicating that the crystallisation of PLA may be affected by the addition of PCL.[39] As shown in Table 2, the $X_{c,\,PLA}$ has slightly increased by increasing the PCL content, suggesting that the presence of PCL favours the crystallisation of PLA, acting as a nucleating agent.[40,41] It should be noted that almost all the thermal transitions of PLA and PCL in rigid PLA/PCL blends appear at the same typical temperatures as those of the corresponding individual polymers, and the variation of T_g, T_{cc}, T_m and $X_{c,\,PLA}$ values is usually assigned to the interactions between components, which reveals a very weak interaction between these two polymers.[32,42]

Several citrate esters are commercial plasticisers for PLA, including ATBC and TEC.[43] The T_g, the melting peak or T_{cc} may shift due to the plasticiser's effect on the material.[44] The effectiveness of the plasticiser on PLA is expected by the reduction of the glass transition of the amorphous phase and by the depression of the melting point of the crystalline region.[45]

As shown in Figure 2(b) and Table 2, the T_g of neat PLA has decreased by increasing the plasticiser content and has increased by increasing the PCL content for plasticised PLA/PCL blends. The largest reduction of T_g when compared with neat PLA was from 58°C to 12°C and 13°C for PLA/PCL 10 (PLAPCL10) by adding up to 30 wt% ATBC and TEC, respectively. The most probable explanation may be the low molecular weight of the plasticiser allows it to occupy intermolecular spaces between the polymer chains, reducing the energy for molecular motion and the formation of hydrogen bonding between the polymer chains, which in turn increases free volume and polymer chain mobility. These findings are in accordance with previous results.[45–47]

As shown in Table 2, the T_{cc} of PLA has decreased from 119°C for neat PLA to 66°C and 73°C for PLA/PCL 10 (PLAPCL10) by adding up to 30 wt% of ATBC and TEC, respectively. The addition of citrate plasticisers has also decreased the T_m of PLA. From Figure 3(a) and (b), the $X_{c,\,PLA}$ in plasticised PLA/PCL blends has increased considerably depending on the plasticiser content. For PLA/PCL 10 (PLAPCL10) plasticised with 30 wt% ATBC, greatest crystallinity has been observed for a value of 19.96%, while only 9.46% and 8.87% for 20 wt% and 30 wt% TEC, respectively. This important increase in crystallinity of PLA by the addition of both ATBC and TEC suggests that the plasticiser increased the polymer chain mobility by reducing the energy required for crystallisation. Similar results have been evidenced previously.[8]

X-Ray diffraction

The XRD spectrum of PLA in Figure 3(a) has shown a broad double peak between 5° and 40° corresponding to amorphous regions confirming that the PLA is completely amorphous after initial melting and cooling. This peak positions are in accordance with those reported articles.[34,47] Although a slight X_c of about 1.56% was observed in the diffraction scanning calorimetry thermogram, no crystal structure was detected in the XRD. The $X_{c,\,PCL}$ obtained from DSC and XRD is found to be 45.31% and 52.26%, respectively. The obtained results are in accordance with what has been stated where the crystallinity range for PCL is known to be between 42% and 60%.

The PCL spectrum has shown several peaks between 15° and 40°, with two high-intensity and other low-intensity peaks between 20° and 25° and between 35° and 40°, respectively. Moreover, the peaks were sharp and distinct, which indicated that the sample was a crystalline material. Similar findings are in accordance with those reported works.[48–50] In addition, the spectrum of the other blends has shown the same crystalline peaks overlapping the amorphous curve of PLA. The peak intensities vary with the variation of PCL content. The DSC observation of increasing crystallinity with increasing PCL content in the blends could, therefore, be confirmed by the XRD results. Poly(lactic acid)/poly(ε-caprolactone)10-30 tributyl O-acetyl citrate (PLAPCL10-30ATBC) and poly(lactic acid)/poly(ε-caprolactone)10-30 triethyl 2-acetyl citrate (PLAPCL10-30TEC) patterns shown in Figure 3(b) have shifted towards lower angles between 15° and 20°, which probably indicates the variation in the distance between parallel planes of atoms. According to Bragg's law, if the spacing of the crystallographic planes changes, the Bragg angle should decrease towards lower 2θ values.[51]

Thermogravimetric analysis

Thermogravimetric curves obtained under nitrogen atmosphere have displayed a single-stage decomposition for PLA, PCL and their rigid blend (PLAPCL10). It can be noted that the PLA degradation had occurred at lower temperatures, at around 345°C, while the PCL degradation had taken place at around 382°C. PCL is known to have extraordinary thermal stability at high temperature compared to other polyesters due to its high X_c (45–60%) and its high hydrophobicity.[33,52] The addition of citrates has affected the thermal stability of PLA. The weight loss of the plasticised blends has occurred in two-stage decomposition. A significant shift in the onset temperature has been observed compared to the rigid PLA/PCL blend. Derivative thermogravimetric curves have displayed a clear temperature range between 291°C and 316°C corresponding to the evaporation of citrate plasticiser components, where as mentioned by the supplier, the boiling point of ATBC alone is known to be 173°C.

Conclusions

With the increase of PCL content, DSC revealed a depression in both T_g and ΔH_{cc} of PLA. The $X_{c,\,PLA}$ in rigid PLA/PCL blends slightly increased compared with neat PLA, suggesting the presence of PCL may favour the crystallisation of PLA and acting as a nucleating agent. The plasticising effect was highlighted through the significant decrease in T_g, T_m and ΔH_{cc} of PLA. Depending on the plasticiser and on its content, the $X_{c,\,PLA}$ in plasticised PLA/PCL blends increased considerably compared to neat PLA, suggesting that the plasticiser increased the polymer chain mobility by reducing the energy required for crystallisation. The changes shown by DSC indicate the partial miscibility of both rigid and plasticised PLA/PCL blends. XRD confirmed that PLA is partially amorphous. Moreover, PCL sample was also confirmed to be a highly crystalline material. TGA showed that the addition of ATBC has promoted a decrease in thermal stability of PLA/PCL blends. The rigid and plasticised PLA/PCL films show less transparency than that of the pure films.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Abstract

Polymers produced from low cost renewable resources and with lower energy consumption that are biodegradable and non-toxic to the environment have gained wide interest. This thesis work focuses on the modification of PLA using the polymer blending technique, the plasticization, and the reactive compatibilization to achieve suitable properties for packaging application. For this aim, two different approaches were examined to enhance the miscibility of PLA/PCL blends by keeping the best attributes of these biodegradable blends. The first approach was dedicated to the plasticization of the binary blends with the addition of low molecular weight compounds such as citrate esters. The second one was dedicated to the improvement of microstructure and properties of these blends through the reactive compatibilization. Thermal, structural, and morphological tests were conducted to analyze the performance of the citrate plasticizers and the compatibilizing agents on the miscibility and on the properties of the studied blends.

Keywords: poly (lactic acid), blend, plasticization, citrate esters, reactive compatibilization, miscibility, compatibility.

Résumé

Les polymères produits à partir de ressources renouvelables à faible coût et à faible consommation d’énergie, biodégradables et non toxiques pour l’environnement, ont suscité un large intérêt. Ce travail de thèse porte sur la modification du PLA en utilisant la technique de mélange de polymères, la plastification et la compatibilisation réactive pour obtenir des propriétés appropriées pour une application d'emballage. À cette fin, deux approches différentes ont été examinées pour améliorer la miscibilité des mélanges PLA/PCL en conservant les meilleurs attributs de ces mélanges biodégradables. La première approche était dédiée à la plastification des mélanges binaires avec l’ajout de composés de faible poids moléculaire tels que les esters de citrate. La seconde était dédiée à l'amélioration de la microstructure et des propriétés de ces mélanges grâce à la compatibilisation réactive. Des tests thermiques, structuraux et morphologiques ont été réalisés pour analyser les performances des plastifiants au citrate et des agents compatibilisants sur la miscibilité et les propriétés des mélanges étudiés.

Mots-clés: acide polylactique, mélange, plastification, esters de citrates, compatibilisation réactive, miscibilité, compatibilité.

ملخص

قد اكتسبت البوليمرات المنتجة من الموارد المتجددة منخفضة التكلفة والاستهلاك الطاقوي التي هي قابلة للتحلل الحيوي وغير سامة للبيئة اهتماما واسع النطاق. يركز هذا البحث على تعديل بوليمير حمض اللاكتيك باستخدام تقنية خلط البوليمر، التَلْدِين، والانسجام التفاعلي لتحقيق خصائص مناسبة لتطبيق تغليف المواد. تحقيقا لهذه الغاية، تم فحص طريقتين مختلفين لتحسين امتزاج الخلائط PLA/PCL من خلال الحفاظ على أفضل سمات هذه الخلطات القابلة للتحلل الحيوي. الطريقة الأولى خصصت لتَلْدِين الخلطات الثنائية بإضافة مركبات ذات وزن جزيئي منخفض مثل استرات السيترات. أما الثانية فكرست لتحسين البنية المجهرية وخصائص هذه الخلطات من خلال التوافق التفاعلي. أجريت الاختبارات الحرارية والهيكلية والمورفولوجية لتحليل أداء الملدنات السترات وعوامل التوافق على الامتزاج وعلى خصائص الخلائط المدروسة.

كلمات مفتاحية: بوليمر حمض اللاكتيك، مزيج، تَلْدِين، استرات السيترات، الانسجام التفاعلي، الإمتزاجية، الانسجام.