REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE

MINISTERE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE SCIENTIFIQUE

UNIVERSITÉ 20 AOÛT 1955 SKIKDA

FACULTE DE TECHNOLOGIE

DÉPARTEMENT DE GÉNIE DES PROCÉDÉS

Mémoire

En vue de l'obtention du diplôme de

Master

Filière : Génie des procédés

Spécialité : Génie des Polymères

The Study of Effects of Various Copolymers as Compatibilizers on Rheology, Morphology Development, and Mechanical Properties of Thermoplastic Elastomers based on Poly(Lactic Acid)/Natural Rubber (PLA/NR) Blends.

Soutenu le 18/06/2023

Réalisé par :
- EL HABIB Ahmed
- BOUZOUALEGH Salim
- AÏDOUK Houssem

Encadré par :
- Dr. BELHAOUES Abderrahmane

Année Universitaire 2022 - 2023

Dedication

DEDICATION

Firstly, I thank God for giving me the health and the determination to start and finish this Master Thesis.
I dedicate my graduation:
To my parents may God save them;
To my brothers: Mouadh, Khaled, and Iheb;
To my friends: Ahmed, Younes, Boumdien, Nedjmeddine, Salim, Hani, Yahia, Sirine, and Aya.
To my supervisor Dr. BELHAOUES Abderrahmane for being supported during the preparation of this Master Thesis;
To everyone who was always there for me.
Last but not least, I want to thank me
I want to thank me for believing in me,
I want to thank me for doing this hard work. I wanna thank me for having no days off. I wanna thank me for never quitting. I wanna thank me for always being a giver and trying to give more than I receive. I wanna thank me for trying to do more right than wrong. I wanna thank me for being me at all times.

Ahmed Elhabib

I would like to dedicate my master-thesis

To my family especially our parents whose unbelievable endurance, unconditional love, and untouchable devotion have been monumental

To all my brothers and sisters

To those who will be happy with this new goal in my study career

To all my best friends

To anyone who has ever taught us anything.

There are many friends and other family members who need to be listed for their part in this master-thesis.

Finally, this master- thesis is dedicated to all those who believe in the richness of learning, and, we would like also like to dedicate this modest review to all those who have devoted their lives to bringing the faded ambiguity to the complete shininess of Clarity.

Salim BOUZOUALEGH

I dedicate this master thesis

To my mother who supported and encouraged me during these years of study. May she find here the testimony of my deep gratitude.

To my very dear father

You have always been by my side to support and encourage me. May this work reflect my gratitude and affection.

To my supervisor, Dr : (belhaoues Abderrahmane) for all his valuable advice, for his active listening, his availability Indeed. Thanks to him, I was able to have a solid working base on which I could rely to carry out well my approach to research and analysis thank you very much doctor.

To my brothers, my grandparents and those who shared with me all the emotional moments during the realization of this work. They warmly supported and encouraged me throughout my journey.

To my family, my loved ones and to those who give me love and liveliness.

To all my friends who have always encouraged me, and to whom I wish more success to all those I love .

Thank you!

Houssem AÏDOUK

Acknowledgments

Acknowledgments

In the name of Allah, the Most Merciful and Benevolent.

Thank you, Allah, the All-Powerful, for giving us the strength, direction, and patience to finish this Master's thesis.

First and foremost, there are many individuals who have contributed significantly to our completion of this beautiful journey over the years. We would like to express our gratitude to all of those individuals for their significant influence and assistance, and we would like to thank them for it.

Furthermore, we would like to take this opportunity to thank our supervisor, Dr. Belhaoues Abderrahmane, for his helpful direction, insightful discussions, and support throughout this bibliographic research.

We would like to express our appreciation to Dr. Krid Ferial, Head of the Process Engineering Department at Skikda University's Faculty of Technology.

We would like likewise to put on record our appreciation to every one of our instructors at Skikda-College, where we have concentrated on a Polymer Engineering specialty.

These acknowledgments would only be complete if we took into consideration our family. We need to particularly offer our profound thanks to our dearest guardians for their unending help. They have supported us throughout our Master's studies and have been there for us at all times.

Last but not least, we would like to express our gratitude to each and every member of our family for supporting, inspiring, and encouraging our efforts.

To this end, we assume a sense of ownership with any missteps that might have happened in this work.

Table of Contents

Table of Contents

List of Figures

List of Tables

List of Abbreviations

Abbreviations	Description
AFM	Atomic force microscopy
BIIR	Brominated butyl rubber
BR	Butadiene rubber
CNT	Carbon nanotube
CA	Compatibilizing agent
Tc	Crystallization temperature
DCP	Dicumyl peroxide
DRS	Dielectric relaxation spectroscopy
DSC	Differential scanning calorimetry
DMA	Dynamic mechanical analysis
DMTA	Dynamic mechanical thermal analysis
EPR	Electron paramagnetic resonance
ΔHm	Enthalpy of mixing
ΔSm	Entropy of mixing
ENR	Epoxidized natural rubber
ENR-g-MA	Epoxidized natural rubber grafted with maleic anhydride
ESO	Epoxidized soybean oil
EPDM	Ethylene-propylene- diene monomer
EPR	Ethylene-propylene rubber
FRES	Forward recoil spectrometry
FT-IR	Fourier transform infrared spectrometer
ΔGm	Gibbs free energy of mixing
NR-g-GMA	Glycidyl methacrylate-grafted natural rubber
HDPE	High density polyethylene
HTLNR	Hydroxyl-terminated liquid natural rubber
IR	Infrared spectroscopy
IRRDB	International Rubber Research and Development Board
LNR	Liquid natural rubber
LCST	Lower critical solution temperature
Tm	Melting temperatures
NR	Natural rubber
NR-g-PAA	Natural rubber grafted with Poly(acrylic acid)
NR-g-PVAc	Natural rubber grafted with poly(vinyl acetate)
NBR	Nitrile-butadiene rubber
NMR	Nuclear magnetic resonance
Phr	Parts by weight per hundred parts of resin

PAA	Poly(acrylic acid)
PA	Polyamide
PBT	Poly(butylene terephthalate)
PCL	Polycaprolactone
PC	Polycarbonate
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PLA	Poly(lactic acid)
PLA-g-MA	Poly(lactic acid) grafted Maleic Anhydride
PLA-g-ENR	Poly(lactic acid) grafted with epoxidized natural rubber
NR-graft-PLA	Natural rubber grafted with poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PP-g-MAH	Polypropylene grafted maleic anhydride
PS	Polystyrene
PTT	Poly(trimethylene terephthalate)
PVC	Poly vinyl chloride
PAS	Positron annihilation spectroscopy
1H-NMR	Proton-nuclear magnetic resonance
ROP	Ring-opening polymerization
SALB	South American leaf blight
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SE	Sorbitan ester
TLNR	Telechelic liquid natural rubber
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPEs	Thermoplastic elastomers
TPVs	Thermoplastic vulcanizates
ToFSIMS	Time-of-flight secondary ion mass spectrometry
Tg	Transition temperature
UV	Ultraviolet
UCST	Upper critical solution temperature
ϕi	Volume fraction of component

General Introduction

General Introduction

Polymer blends are a combination of two or more polymers that are physically mixed together to create a new material with improved properties. However, the combination of different polymers can often result in immiscibility, which causes phase separation, leading to reduced mechanical, thermal, and other properties of the blend. To overcome this issue, the compatibilization of polymer blends is used to enhance the compatibility between the different polymers.

Compatibilization is the process of modifying the chemical structure of one or both polymers in the blend to improve the adhesion and interaction between them and prevent phase separation. It involves the addition of a third component, called a compatibilizer or a compatibilizing agent. The compatibilizer molecules can migrate to the interface between the two polymers and create a bridge, or a covalent bond, between the two polymer phases, thereby improving the interfacial adhesion and reducing the interfacial tension.

Compatibilization can be achieved through various methods, such as Physical blending (non-reactive compatibilization), Reactive blending (reactive compatibilization), Technological compatibilization (Dynamic vulcanization), in-situ polymerization, as well as grafting reaction. Reactive blending involves adding the functional groups to the polymer chains, which can react with the functional groups of the other polymer in the blend. In-situ polymerization consists of the polymerization of a monomer at the interface between the two polymers, creating a covalent bond between the two polymer phases. Grafting consists of the attachment of a polymer chain to the surface of one of the polymers, which can then interact with the other polymer in the blend.

Compatibilization of polymer blends has several advantages, such as improved mechanical properties, thermal stability, and processing characteristics. It also enables the creation of new materials with unique properties that cannot be achieved with individual polymers alone. Overall, compatibilization is an essential technique for improving the performance and versatility of polymer blends in various applications.

Poly(lactic acid) (PLA) and natural rubber (NR) are two polymers with distinct properties. PLA is a thermoplastic polymer derived from renewable resources, such as corn starch and sugar cane, while NR is a natural polymer obtained from latex of rubber trees. Blending PLA and NR can lead to materials with improved properties, such as increased

flexibility, toughness, and elongation at break. However, the immiscibility of these two polymers can lead to phase separation and reduced mechanical properties.

To overcome this issue, compatibilization of PLA/NR blends is used to improve the interfacial adhesion between the two polymers. The process involves the addition of a third component, which can improve the adhesion between PLA and NR and prevent phase separation. The choice of a suitable compatibilizer for PLA/NR blends is critical to achieve the desired properties.

Several studies have been carried out to investigate the effect of compatibilization on the properties of PLA/NR blends. Different types of compatibilizers, such as maleic anhydride grafted PLA (PLA-g-MA), NR-g-MA, and epoxidized natural rubber (ENR), have been used to improve the compatibility of PLA/NR blends. The use of these compatibilizers has resulted in improved mechanical properties, such as tensile strength, young's modulus, elongation at break, and impact strength.

This Master thesis is composed of two chapters. The first of which presents a theoretical background on the main polymers used in the study, thermodynamics of polymer blends, and the different strategies of compatibilization of polymer blends. The second chapter presents a state of the art of the research workers which carried out in the field of compatibilization of PLA/NR polymer blends. The overall results and conclusions of this research work is discussed in the last part.

Chapter I
Theoretical Background
Compatibilization of Poly(lactic acid)/Natural Rubber Thermoplastic Elastomer Blends

I.1. Introduction

In this chapter we present an overview of the polymers involved in this study. Emphasis is made on thermoplastic elastomers (TPEs) and those based on natural rubber (NR) and the different strategies used for compatibilization.

I.2. Poly(lactic acid)

I.2.1. Background of poly(lactic acid)

Consumer plastics produced by several multinational companies throughout the world are concentrated on petroleum-based polymers **[1]**. The use of naturally obtained polymers and biopolymers is restricted in engineering and commodity polymer composite sections. Petroleum-based polymers are nonbiodegradable, and most biodegradable polymers do not give high strength for external use **[2]**. Synthetic biodegradable polymers are comparatively new than other commodity plastics **[3]**. The commonly used synthetic biodegradable polymers are polylactic acid (PLA), this polymer belongs to the polylactone family. Besides its biodegradability, this synthetic polymer is also non-toxic and less expensive compared to naturally abundant polymers **[4]**.

PLA was assumed to be a potential biomaterial due to its nontoxicity and excellent compatibility with human cells **[5]**, besides has been used in several therapeutic and pharmaceutical industries such as drug carriers **[6]**.

I.2.2. Synthesis method of poly(lactic acid)

Lactic acid is the basic building block of PLA. lactide acid is industrially manufactured by fermentation of carbohydrates or chemical synthesis of resources such as coal, petroleum product, and natural gas. Lactic acid reactions are described in Equations **(1-4).**

$$CH_3CHO + HCN \rightarrow CH_3CHOHCN \quad (1)$$

$$CH_3CHOHCN + 2H_2O + \frac{1}{2} H_2SO_4 \rightarrow CH3CHOHCOOH + \frac{1}{2} (NH_4)2SO_4 \quad (2)$$

$$CH_3CHOHCOOH + CH_3OH \leftrightarrow CH_3CHOHCOOCH_3 + H_2O \quad (3)$$

$$CH_3CHOHCOOCH_3 + H_2O \leftrightarrow CH_3CHOHCOOCH_3 + CH_3OH \quad (4)$$

Naturally, lactic acid molecules can be obtained in plants, microorganisms, and animals. Based on the application requirements, lactic acid with different degrees of purities can be determined. Different stereoforms of lactide are shown in **Figure I.1**.

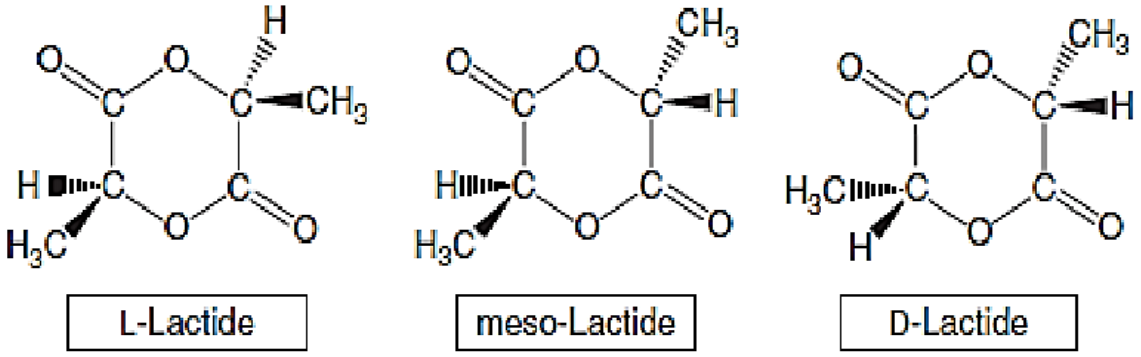

Figure I.1. Illustrates the chemical structures of L-, meso-, and D-lactides **[7]**.

In cyclic dimer processing of lactic acid two PLA molecules combine, and it rises to L-lactide or LL-lactide, D–lactide, or dd-lactide. Meso-lactide or LD-lactide also can be made by both molecules of L-lactic acid and D-lactic acid. Raclactide, a racemic lactide, is formed by the mixture of L- and D-lactides. By depolymerization of low molecular weight PLA under decreased pressure lactide can be obtained. Previous studies have emphasized that lactic acid isomer feedstock, temperature, the catalyst's nature as well as content are the effective parameters for the amount of lactide isomer formed during the process **[7-9]**. Indeed, the separation between each stereoisomer is essential to examine the final PLA structure during the process. This process can be determined due to the difference in boiling points between meso- and L- or D-lactide **[7]**.

Lactic acid (2-hydroxy propionic acid), the simplest hydroxy acid exists in two optically active configurations of L(+)-isomer and D(-)-isomer. The L(+)-isomer is specified to be made in humans and other mammals. Furthermore, the bacterial system is the source of both D(-)- and L(+)-enantiomers processes **[9]**. Lactobacilli amylophilus, L. bavaricus, L. casei, L. maltaromicus, and L. salivarius are known as the organisms that mainly yield L(+)-isomer. Besides, L. delbrueckii, L. jensenii, or L. acidophilus yield the D-isomer or mixtures of both **[9]**. Based on the particular strain of Lactobacillus, a wide range of carbohydrates can be utilized in fermentation. This process is mostly prepared in great quantities (around 200 kT per year) by the bacterial fermentation of carbohydrates. According to the type of bacteria used, the fermentation process can be categorized into different types (I) the heterofermentative method,

and (II) the homofermentative process. Therefore, it modifies the process of lactic acid with an inferior level of by-products, principally with the industrial application **[7,9]**. The previous study has suggested that during this process most of the simple sugars with agronomic sources can be employed. These sources can be (1) glucose, maltose, and dextrose from corn or potato starch; (2) sucrose from cane or beet sugar; and (3) lactose from cheese whey. Furthermore, protein, and complex nutrients such as B vitamins, amino acids, and nucleotides are other materials that organisms require during the process. These materials can be purveyed from corn steep liquor, yeast extract, cottonseed flour, or soy flour **[10]**. Finally, lactide units can be considered as a more complex macromolecule architecture known as copolymers.

I.2.2.1. Polymerization from lactic acid

Lactic acid is the main monomer for preparing PLA and its derivative copolymers. For preparing PLA from lactic acid, two different polymerization techniques are adopted. The first one is the polycondensation reaction which is the first discovered method to prepare PLA. The second one is the ROP which can produce comparatively higher molecular weight PLA than polycondensation reactions. Other than these methods, dehydration and enzymatic polymerization are also taking place but in a very limited fashion **[11]**. **Figure I.2** shows the basic adopted production techniques applied for the synthesis of PLA, besides **Figure I.3** shows Synthesis of PLA stereoforms via ring-opening polymerization.

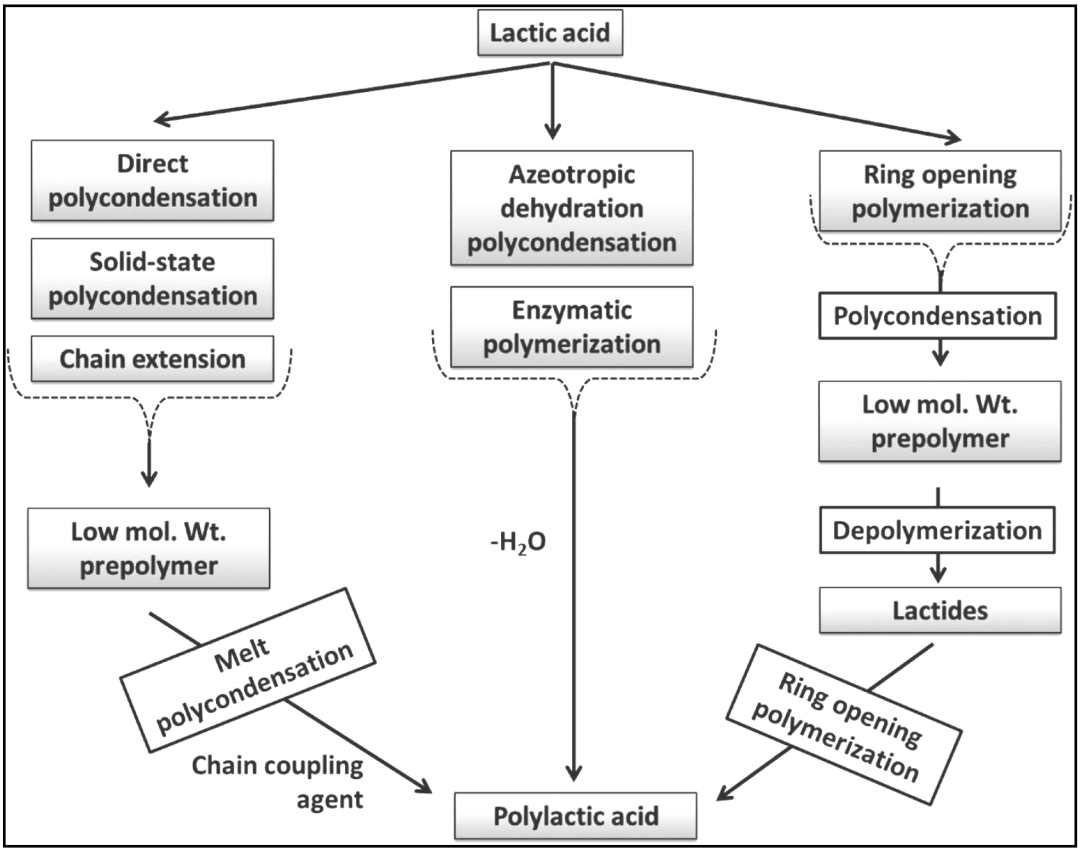

Figure I.2. Different synthetic approaches for the preparation of poly(lactic acid).

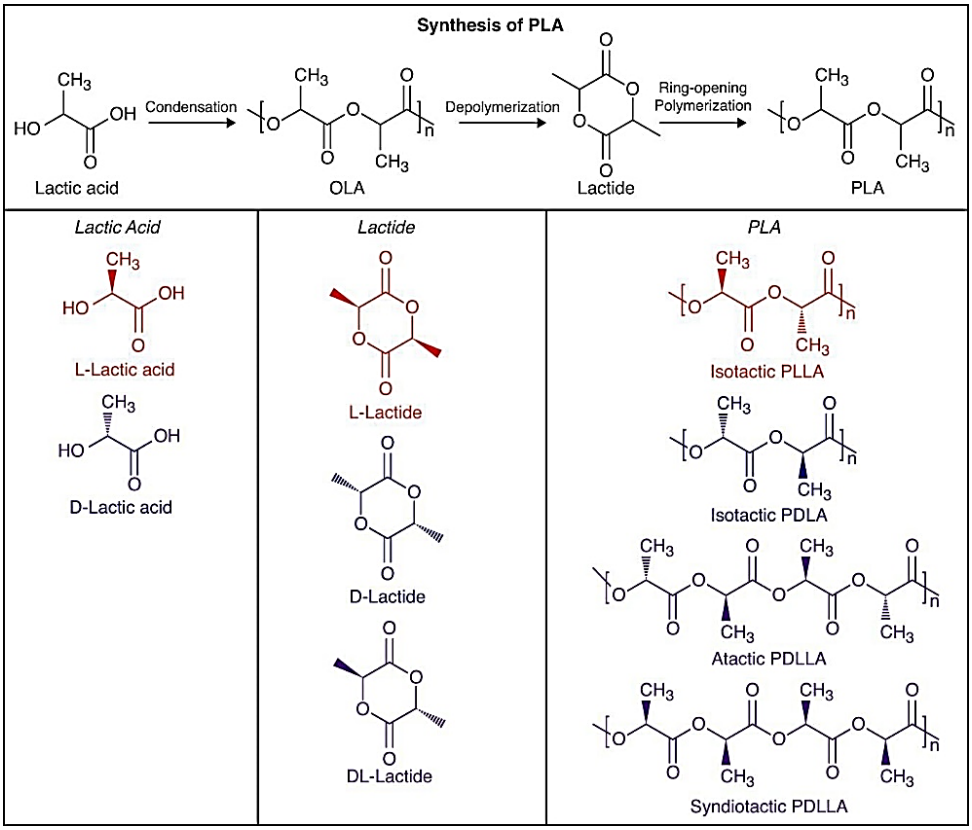

Figure I.3. Synthesis of PLA stereoforms via ring-opening polymerization **[12].**

I.2.2.1.1. Production of PLA by polycondensation

Condensation polymerization of lactic acid normally takes place in a solvent with a high vacuum and high temperature. This polycondensation can be performed in a bulk system by using a distillation column. This process is not solely dependent on the catalyst which means polycondensation could take place with or without a catalyst system provided or the reaction conditions should be rigorous. But in this process, high-molecular-weight polymer preparation is a little difficult. The intermediate oligomer of PLA is sometimes used in polyurethane synthesis, which is controlled by a different catalyst system. This aforementioned approach was used by Carothers, and later that was adopted by Mitsui Toatsu Chemicals Inc. for manufacturing of low molecular weight lactic acid, the catalyst system is very much significant in polymer synthesis. The most common catalyst systems used for this purpose are boric acid or sulfuric acid, which are well-known for their acceleration type of behavior in the esterification and transesterification process. But the high-temperature reaction always affects side reactions. Due to these side reactions, the resultant PLA causes a molecular weight of 3000 for racemic mixtures and 6500 for pristine L-lactide. The yield could be improved by using non-acidic transesterification catalysts like lead monoxide. Low-molecular-weight PLA is used for biodegradable adhesive applications like glues and lacquers. Due to the highly abundant hydroxyl and carboxylic groups at their terminal of the polymer change, these are very much suitable for cross-linking with inorganic and organic multivalent moieties.

Polycondensation also produces a moderate molecular weight of 10,000 by using precise control in the solvent ratio or by using azeotropic solvents. This type of polymer is used independently as a thermoplastic matrix and as a coupling agent for isocyanates oxides and peroxides for better mechanical properties. Though polycondensation has several merits, for industrialization, this process has limited applicability **[11]**.

I.2.2.1.2. Production of PLA by ring-opening polymerization (ROP)

Lactide is a cyclic dimer of lactic acid which is produced under water-less mild conditions. This monomer is verified under the vacuum distillation process without using any solvent. The molecular weight of the end product is highly dependent on the quality of the lactide dimer used in the polymerization process. Moreover, the purification of lactide dimer is also responsible for the preparation of a wide range of molecular weight distribution of the PLA.

PLA production has been started for the last ten years, which means it is a newcomer in the thermoplastic polymer industry compared to the other commodity thermoplastics. The currently used catalyst for this purpose is stannous octoate which is an industrially approved catalyst system. Besides, stannous octoate zinc salts are commonly used in France. ROP takes place in bulk, melt or solution processes where the precursor material is the lactide. In terms of the mechanic stick point of hue ROP of lactides also takes place in cationic anionic and coordination type modes. There are several synthetic parameters which are playing significant roles in the molecular weight obtained from ROP. The specific synthetic parameters are initiator systems, change control agent, catalyst concentration, co-initiator system, monomer to initiator ratio, reaction temperature and the duration of the polymerization process. These synthetic parameters affect the degree of polymerization and crystallinity of the end product. Low initiator concentration and high duration of polymerization provide a high-molecular weight polymer with high mechanical properties. The racemic mixture of the monomer imposes enantiomeric purity and distinguishable chain microstructure of the end product. In recent days, stannous octoate is the only used catalyst for preparing PLA from lactides. The high-temperature synthesis method is accepted by the US Food and Drug Administration because of low racemization and very low toxicity of the end product **[11]**.

I.2.3. Properties of poly(lactic acid)

Poly(lactic acid) (PLA) is a biodegradable and biocompatible polymer that has gained significant attention in recent years due to its renewable nature and potential use as an environmentally friendly alternative to traditional petroleum-based plastics. Here are some of the PLA properties :

- Biodegradability: PLA is biodegradable, meaning it can be broken down by microorganisms in the environment and converted into natural substances such as carbon dioxide and water.
- Mechanical properties: PLA has good mechanical properties, including high stiffness, strength, and toughness, which make it suitable for a range of applications.
- Thermal properties: PLA has a relatively low melting point of around 160-180°C, and it is not resistant to high temperatures. However, it can be modified with various additives to improve its thermal stability.
- Transparency: PLA is transparent, making it suitable for use in packaging applications where the contents need to be visible.

- Barrier properties: PLA has good gas barrier properties, which make it suitable for use in food packaging applications.
- Processability: PLA can be processed using a range of techniques, including injection molding, extrusion, and blow molding.
- Biocompatibility: PLA is biocompatible, meaning it does not cause an adverse reaction when in contact with living tissue. This property makes it suitable for use in medical applications such as sutures and drug delivery systems.
- Renewable source: PLA is derived from renewable sources such as cornstarch, sugarcane, and other plant-based materials. This makes it a more sustainable alternative to traditional petroleum-based plastics.
- Chemical resistance: PLA is resistant to most organic solvents but is susceptible to hydrolysis, which limits its use in certain applications.
- UV stability: PLA has limited UV stability, and it tends to degrade when exposed to sunlight. However, it can be modified with various additives to improve its UV resistance **[13,14,15]**.

I.2.4. Manufacturing of poly(lactic acid)

Poly(lactic acid) (PLA) can be manufactured using various methods, depending on the specific application and the desired properties of the final product. Here are some common manufacturing methods for PLA:

- Extrusion: PLA can be extruded into various shapes and forms, such as film, sheet, and filament, using a process similar to that used for traditional plastics. The PLA pellets are melted and forced through a die to form the desired shape.
- Injection molding: PLA can also be molded into complex shapes using injection molding, which involves melting the PLA pellets and injecting the molten material into a mold under high pressure. The material then solidifies and takes the shape of the mold.
- Thermoforming: PLA can be thermoformed into various shapes and forms, such as cups, trays, and clamshells, using a process similar to that used for traditional plastics. The PLA sheet is heated and formed into the desired shape using a mold.
- Fiber spinning: PLA can be spun into fibers using a process similar to that used for traditional synthetic fibers. The PLA pellets are melted and extruded through a spinneret to form continuous fibers, which can be used for textiles and other applications.

- Additives: PLA can be modified with various additives to improve its properties, such as thermal stability, UV resistance, and impact strength. Common additives include antioxidants, UV stabilizers, nucleating agents, and plasticizers **[13,16,17]**.

I.2.5. Applications of poly(lactic acid)

Poly(lactic acid) (PLA) is a versatile and biodegradable polymer that has found numerous applications in various fields. Here are some of the most common applications of PLA:

- Packaging: PLA is used in the production of biodegradable packaging materials, such as bags, cups, and food containers.
- Textiles: PLA can be used to produce fibers that are used in the production of textiles, such as clothing, bedding, and upholstery.
- Biomedical: PLA is suitable for use in biomedical applications, such as drug delivery systems, sutures, and tissue engineering scaffolds.
- 3D printing: PLA is a popular material for 3D printing due to its biodegradability, low toxicity, and ease of processing.
- Electronics: PLA can be used in the production of electronic components, such as capacitors and sensors.
- Automotive: PLA can be used in the production of automotive components, such as interior trims and panels **[18]**.

Figure I.2. Applications of Poly(lactic acid) (PLA).

I.3. Natural Rubber

I.3.1. Background of natural rubber

Hevea brasiliensis, a tree indigenous to the tropical forests of the Amazon basin, is the only major commercial source of natural rubber (NR) **Figure I.5.** All rubber trees originate from the Hevea seeds, which were transported by Henry Wickham from Brazil to British India in 1876, where only 2000 seeds survived **[19]**. As a consequence, most modern material comes from a narrow base of a few trees that grew in the Upper Amazon region. A survey was organized under the aegis of the International Rubber Research and Development Board (IRRDB) in 1981 in Brazil to harvest plant material from different regions of the Amazon basin. Currently, the Asian continent produces 94% of global production, while the South American region produces only 2%, mainly due to the presence of South American Leaf Blight (SALB) which prevents the development of industrial rubber production **[20]**.

Figure I.3. Photographic images of Natural Rubber latex from Hevea brasiliensis tree.

I.3.2. Synthesis method of natural rubber

Natural Rubber, consisting of cis-1,4-polyisoprene **Figure I.6** as a major polymeric material, is a useful material with a high amount of production and consumption throughout the world. NR has been used as a raw material in many industries, particularly for the manufacture of rubber tires, consumer products and medical sectors, such as footwear, rubber band, rubber toys, medical gloves, etc.

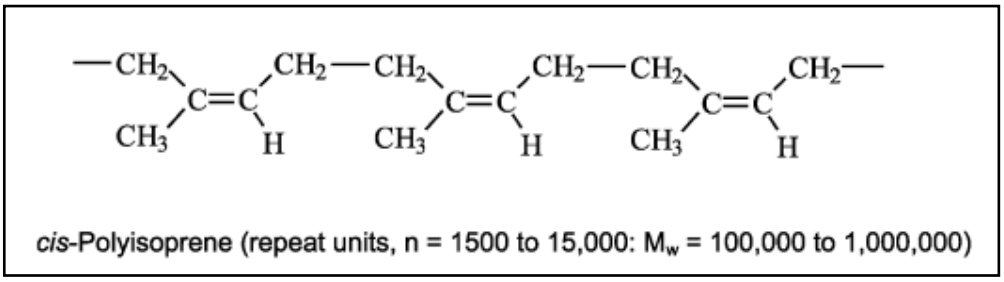

Figure I.4. Chemical structure of Natural Rubber.

The chemical structure of Natural Rubber comprises 99% of cis-1,4-polyisoprene. The remaining 1% is a mixture of non-rubber components such as protein, amino acids, sugar, fatty acids and other substances. The high content of cis-1,4-polyisoprene in NR, contributes to high degree of strain-induced crystallization as well as high mechanical properties **[21].**

I.3.3. Properties of natural rubber

Natural rubber is a type of elastomer that is derived from the sap of rubber trees. It is known for its excellent mechanical, physical, chemical, and thermal properties here are some of these properties of natural rubber:

- Elasticity: natural rubber is highly elastic, which means it can stretch and return to its original shape when the stress is removed.
- Low compression set: natural rubber can retain its original shape after being subjected to compression.
- High tear strength: natural rubber can resist tearing or ripping when subjected to stress.
- Good abrasion resistance: natural rubber can withstand wear and tear from rubbing or friction.
- Excellent resilience: natural rubber can quickly recover its original shape after being deformed.
- Good electrical insulation properties: natural rubber can resist the flow of electric current.
- Low temperature flexibility: natural rubber remains flexible and elastic even at low temperatures.
- Good chemical resistance: natural rubber has good resistance to many chemicals, including acids, bases, and alcohols.
- Low heat buildup: natural rubber can dissipate heat well and avoid overheating.
- Low permeability: natural rubber has low permeability to gases and liquids, which means it can act as a good barrier material.
- High damping capacity: natural rubber can absorb and dissipate energy effectively.
- Biodegradable: natural rubber can be broken down by natural processes and is environmentally friendly.
- High water resistance: natural rubber can resist the effects of water and moisture.
- Good adhesion properties: natural rubber has good adhesion to many surfaces, so it can form strong bonds with other materials **[22,23]**.

I.3.4. Manufacturing of natural rubber

Natural rubber is primarily produced from the latex sap of rubber trees (Hevea brasiliensis). The process of manufacturing natural rubber typically involves the following steps:

- Tapping: The rubber tree is tapped by making a small incision in the bark of the tree and collecting the latex sap that flows out. This process is usually carried out every other day and can continue for several years.
- Coagulation: Once the latex sap is collected, it is mixed with an acid or coagulating agent to cause it to solidify into a rubbery mass. This coagulated mass is then cut into small pieces.
- Washing: The coagulated rubber pieces are then washed to remove any impurities.
- Rolling: The washed rubber pieces are then rolled into sheets or pressed into blocks, depending on the intended use.
- Drying: The rubber sheets or blocks are then dried to remove any remaining moisture.
- Compounding: The dried rubber is then compounded with various additives, such as accelerators, antioxidants, and fillers, to improve its mechanical and chemical properties.
- Molding or Extrusion: The compounded rubber is then molded or extruded into the desired shape using various manufacturing processes, such as injection molding, compression molding, or extrusion.
- Vulcanization: The molded or extruded rubber is then subjected to a process called vulcanization, which involves heating the rubber with sulfur or other curing agents to cross-link the polymer chains and improve its mechanical properties **[24,25]**.

Figure I.5. The process of manufacturing natural rubber.

I.3.5. Applications of natural rubber

Natural rubber has a wide range of applications in industrial fields. Here are a few examples:

- Automotive industry: Natural rubber is used in many automotive applications, including tires, hoses, belts, and seals. Its high elasticity, tear strength, and abrasion resistance make it an ideal material for these applications.
- Construction industry: Natural rubber is used in the construction industry for applications such as roofing, flooring, and waterproofing membranes. Its low compression set, high resilience, and good adhesion properties make it well-suited for these applications.
- Medical industry: Natural rubber is used in the medical industry for applications such as surgical gloves, tubing, and seals. Its low toxicity, good biocompatibility, and good barrier properties make it a suitable material for medical devices.
- Consumer goods industry: Natural rubber is used in many consumer goods, such as footwear, toys, and household items. Its high elasticity, good grip, and low cost make it a popular material for these applications.

- Marine industry: Natural rubber is used in the marine industry for applications such as fenders, dock bumpers, and marine seals. Its high resilience, low compression set, and resistance to UV light and saltwater make it well-suited for these applications **[26]**.

Figure I.6. Applications of natural rubber (NR).

I.4. Thermoplastic elastomers from rubber/plastics blends

I.4.1. The major advantages of TPEs

TPEs offer a variety of advantages over conventional thermoset (vulcanized) rubber materials, such as the following:

- Simpler processing with fewer steps since TPEs uses the processing methods for thermoplastics, which are typically more efficient and significantly less costly so the final cost of the finished part is lower.
- Shorter fabrication times, which also lead to lower finished part costs. Since molding cycles for TPEs are typically several seconds as opposed to minutes for thermoset rubbers, the productivity of the given equipment is greatly increased.
- There is little or no compounding. The majority of TPEs is supplied fully formulated and ready for fabrication.
- The possibility of reusing scrap in the same fashion as with thermoplastics. The scrap from thermoset rubbers is very often discarded. Its amount generated may be in some cases comparable to the weight of the molded part. The TPE scrap can be reused as

a regrind frequently producing materials having the same properties as the virgin material.

- Lower energy consumption due to shorter molding cycles and simpler processing.
- Better quality control and closer tolerances of finished parts due to simpler formulations and process.
- Lower quality control costs because of greater reproducibility and consistency of properties of TPE resins.
- Since most TPEs have a lower density than conventional rubber compounds, their volume cost is often lower **[27]**.

I.4.2. Drawbacks of TPEs

The drawbacks of TPEs in comparison to conventional rubber materials include:

- Melting at elevated temperatures. This inherent property limits the use of parts from TPEs to service temperatures well below their melting point. A thermoset rubber would be probably suitable for a brief exposure to that temperature;
- A limited number of low hardness TPEs. Many TPEs are available at hardnesses about 80 Durometer A or higher. The number of materials softer than 50 Durometer A is still rather limited;
- Drying prior to processing. This step is almost never used for conventional rubber materials but is quite common in the fabrication of thermoplastics in general **[27]**.

I.4.3. Classification of TPEs

Currently, known TPEs can be classified into the following seven groups:

- Styrenic block copolymers (sbcs);
- Crystalline multiblock copolymers;
- Miscellaneous block copolymers;
- Combinations of hard polymer/elastomer;
- Hard polymer/elastomer graft copolymers;
- Ionomers;
- Polymers with core-shell morphologies **[27]**.

I.4.4. Factors affecting the properties of TPEs

The properties of TPEs are determined by a number of factors, which depend on the material properties of the rubber and plastic components.

- Dynamic shear modulus or Young's modulus. This property is a measure of the stiffness of the polymer.
- Tensile strength of the hard phase material. This property represents a limit for the strength of TPE.
- Critical surface tension for wetting. The difference between critical surface tension for wetting (for the rubber and the plastic) is a rough ostomate of the interfacial tension between the rubber and plastic during melt mixing. The interfacial tension is an important factor that determines the extent of phase heterogeneity. It has been found that blends in which the surface energies of the rubber and plastic phases are closely matched are strong and extensible.
- Crystallinity. The ultimate strength of rubber-plastic blends shows a definite dependence on the crystallinity of the plastic material component, which improves both mechanical integrity and elastic recovery.
- Melt viscosity It has been accepted that melt blending is most efficient (capable of giving the smallest particles of dispersed phase) when the viscosities of the phases are the same.
- Critical entanglement spacing: This property is measured as the number of polymer chain atoms that corresponds to the molecular weight sufficiently large for entanglements to OCCUR between molecules of undiluted polymer. It has been observed that when polymers are blended with one another, fibrous structures appear which then break up into droplets. The polymer molecules which tend to mutually entangle are found to be drawn into finer "fibers" during the early phase of mixing, to give emulsions of droplets of smaller size **[28]**.

I.5. Thermoplastic vulcanizates

Thermoplastic vulcanizates (TPVs) are prepared by a dynamic vulcanization technique by adding curative during a mixing operation. The TPVs consist of the dispersion of vulcanized rubber domains in a thermoplastic matrix, which differs from the simple blends. Dynamic vulcanization occurs through two stages: first, blending steps without crosslinking or simple blend, and second, superimposed cross-linking and mixing steps. The viscosity plays a significant role in the formation of TPV morphology. When the degree of vulcanization is high, the rubber particles may be broken into micron size of elastomeric particles. The dynamic vulcanization of the rubber phase in the plastic matrix leads to the formation of materials with improved properties of high elasticity, while thermoplastic phase provides the melt processing.

The varieties of TPVs have already found commercial applications, especially in the automotive sector **[29,30,31]**.

In the first blending step, the morphology of both phases changes to co-continuous structure **Figure I.9. (a)**. The continuous mixing leads to formation of smaller grains of co-continuous structure under the action of shear and elongational stresses on a highly viscous co-continuous structure **Figure I.9. (b)**. After addition of curatives, viscosity of the rubber phase quickly increases and the co-continuous structure is deformed by shearing process **Figure I.9. (c)**. The break-up mechanism of the highly deformed co-continuous structure happens after the blend reached a critical stress from increased viscosity, which results in dispersion of the cross-linked rubber phase in the thermoplastic matrix. With the high amount of crosslinks in rubber, the rubber phase will break up into a finely dispersed particles morphology **Figure I.9. (d) and (e)** **[29,31,32]**.

This is the moment where the co-continuous morphology is transformed into a dispersed matrix phase, which depends on blend composition, viscosity and elasticity ratio, processing condition and cross-linking condition. Therefore, TPV morphology typically consists of the cross-linked rubber particles finely dispersed in the thermoplastic matrix. However, at high content of rubber phase or rubber-rich TPV, the cross-linking is insufficient to enforce phase inversion and it is commonly difficult to separate rubber particles in rubber-rich TPV.

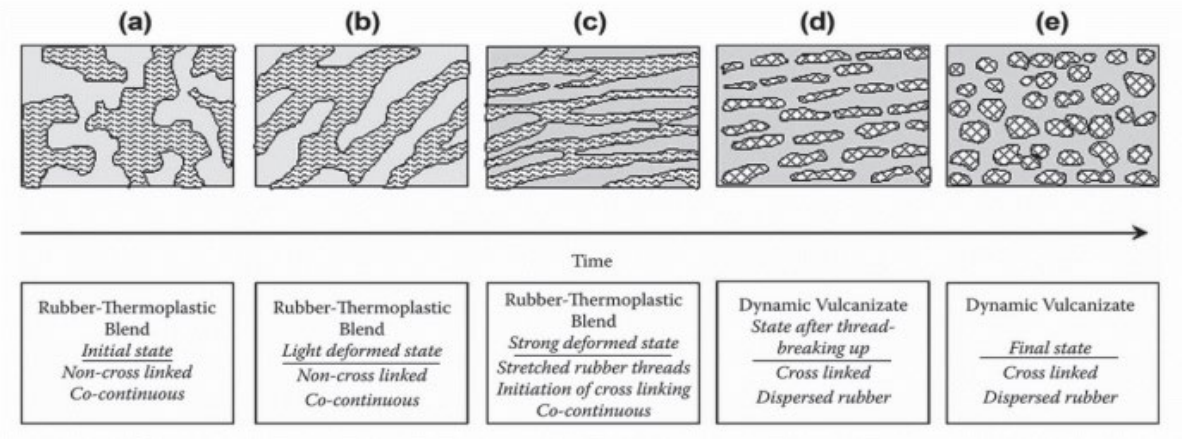

Figure I.7. Schematic diagram of morphology transformation during the dynamic vulcanization of polymer blends **[29]**.

I.6. Thermoplastic natural rubber blends

Thermoplastic natural rubber blends are a group of thermoplastic elastomers prepared by blending NR with thermoplastics in various proportions. There are several types of thermoplastics that could be used to prepare thermoplastic natural rubber blends. They include poly(lactide acid) (PLA), polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), poly(methyl methacrylate) (PMMA), and polyamide. Ect

I.6.1. Natural rubber-poly(lactic acid) blends

Natural rubber-poly(lactic acid) (NR-PLA) blends are a type of polymer blend that combines natural rubber, a renewable and sustainable biopolymer derived from the latex of rubber trees, with poly(lactic acid), a biodegradable and compostable synthetic polymer made from renewable resources such as corn starch, sugarcane, or cassava.

NR-PLA blends offer several advantages over traditional petroleum-based polymer blends, including improved biodegradability and reduced environmental impact. They also have good mechanical properties, such as high tensile strength and good elongation, making them suitable for various applications, including packaging, textiles, and biomedical devices.

However, NR-PLA blends can present some challenges due to the differences in their chemical and physical properties, such as their polarity and thermal stability. To overcome these challenges, researchers have explored various methods to improve the compatibility between the two polymers, such as the addition of compatibilizers or the modification of the polymers' surfaces **[33,34]**.

I.7. Polymer blends

Polymer blends are materials formed by the mixing of two polymers or copolymers to make a new material having synergistic properties of each polymer **[35-41]**. Polymer blending is an interesting method to develop new materials for specific applications since it is very cost effective and simple. By blending one can prepare a new material with the combined properties of each component. It is a cost-effective method for the preparation of new material with desired properties other than synthesizing a new one in the lab **[35,36,38,42-48]**. Polymer blending has many advantages, which involve the following:

- Fabrication of new materials with desired properties.

- Development of new materials in a cost-effective manner.
- Better processability of materials.
- Developing materials with combined properties of two or more polymers.
- Tuning of final properties by controlling the morphologies.
- Method of recycling of plastic waste.
- Enhances the product performance to meet the rising customer needs.
- Development of lightweight materials.
- Optimization of composition to suit the requirement.
- Enhances the properties of polymers such as strength, modulus, flame retardancy, and stress cracking resistance, etc.

Polymer blends have great importance in industrial and scientific areas. The first polymer blend was prepared by Thomas Hancock and was a mixture of natural rubber with Gutta-percha **[7]**. The blending of polymers will yield a unique product with the combined properties of the individual components. Generally, polymer blends can be defined as a physical mixture of two or more structurally different polymers with no covalent bond between them. The expected interactions are only the van der Waals forces, dipole interactions, or hydrogen bonding between the components and are useful in making a final product with various property combinations. Blending can be considered a cost-effective method for the preparation of material with specific properties required for the applications **[38,41,46,50-54]**.

I.8. Thermodynamics of binary polymer blend systems

Polymer blend is prepared by mixing two or more polymers or copolymers to obtain a new material with desired properties. Such blends may be homogeneous or heterogeneous in nature; otherwise, it can be termed miscible or immiscible respectively. Miscibility of polymer blends can be predicted using thermodynamic parameters through the Gibbs free energy of mixing, ΔG_m. For miscibility of blends following inequality must be hold for.

$$\Delta G_m = \Delta H_m - T\,\Delta S_m < 0 \qquad \text{(I.1)}$$

Where ΔG_m is the free energy of mixing per unit volume and ΔH_m and ΔS_m are enthalpy and entropy of mixing respectively. ΔH_m is a measure of energy change. The entropy of mixing for macromolecules is generally very low because of the restricted number of possible molecular configurations and so the negligible entropy of mixing makes ΔG_m become more positive due to the major contribution of the positive enthalpy of mixing. The sign of ΔG_m

depends on the value of the enthalpy of mixing, $\mathbf{\Delta H_m}$ and miscible blends can be formed if the entropic contribution exceeds the enthalpic contribution So, for the negative Gibbs free energy, there should be excellent intermolecular interactions between the components **[51]**. For miscibility, in addition to a negative value of $\mathbf{\Delta G_m}$, the following inequality must also hold **[52].**

$$\left(\frac{\partial^2 \Delta G_m}{\partial \Phi_i^2}\right) T, p > 0 \qquad (\mathbf{I.2})$$

Where ϕ_i represents the volume fraction of component, T represents the fixed temperature and p represent fixed pressure. $\mathbf{\Delta G_m}$ for a binary mixture can vary with composition. The phase diagram is shown in **Figure I.10.**

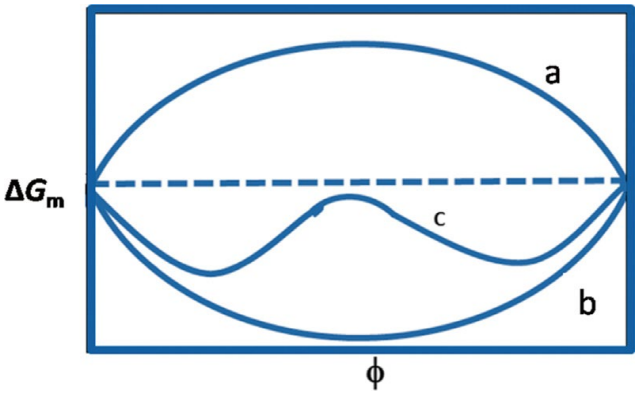

Figure I.8. Free energy of mixing for (a) completely immiscible, (b) completely miscible, and (c) partially miscible**.**

In immiscible polymer blends, Gibbs free energy of mixing is positive and does not satisfy the above two equations, which represents the curve 'a'. Curve 'b' represents a miscible system which satisfies the above equation for miscibility and curve 'c' represents a partially miscible blend system. If two polymers are mixed together, miscible polymer blends show single-phase morphology, immiscible blends show two-phase morphology, and in the case of partially miscible blends, they will show either two-phases or single-phase morphology. The miscibility of polymer components depends on several other factors such as polarity of polymer components, composition, molecular weight, processing temperature, pressure, etc..**[38]**.

Miscibility of polymer blends can be explained using a phase diagram shown in **Figure I.11**. There are three different regions and used to explain the degree of miscibility: Phase diagram explains the binodal and spinodal phase separation; spinodal curve and binodal curves are marked in the phase diagram. The position at which **Eq. (I.3)** satisfies represents the spinodal curve.

$$\text{Spinodal: } \left(\frac{\partial^2 \Delta G_m}{\partial \Phi^2}\right)_{P,T} = 0 \qquad (I.3)$$

The equilibrium phase boundary between homogeneous and heterogeneous phase (phase separated phase) region represents the binodal curve. Position of binodal curve can be expressed in terms of chemical potentials (μ) of each polymer components in the binary system.

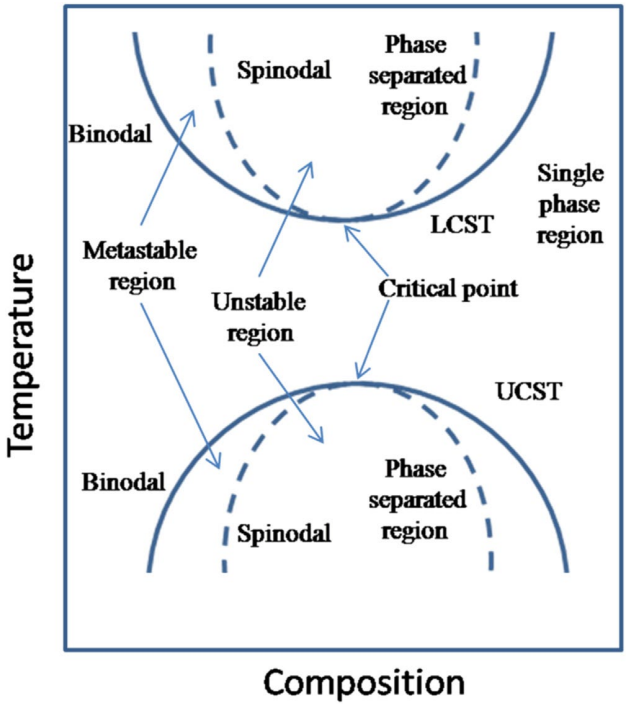

Figure I.9. Phase diagram showing the performance of polymer blends **[52].**

$$\Delta\mu_1^a = \Delta\mu_1^b \quad \Delta\mu_2^a = \Delta\mu_2^b \qquad (I.4)$$

where 1 and 2 stand for the polymer components and a, b denote the phases.

The double tangent to the free energy of mixing gives the values of binodal curve. Also at a critical point binodal and spinodal curve intersects and it can be estimated using the equation given below.

$$\left(\frac{\partial^2 \Delta G_m}{\partial \Phi^2}\right)_{P,T} = \left(\frac{\partial^3 \Delta G_m}{\partial \Phi^3}\right)_{P,T} = 0 \qquad (\mathbf{I.5})$$

With the help of a phase diagram, degree of miscibility can be explained using spinodals and binodals. Three different regions in the phase diagram can be observed, that is between the two binodals there is single-phase or miscible region (highly miscible system has single phase); between binodals and spinodals there is metastable region: and phase separated or immiscible region bordered by spinodal curves. Low-molecular-weight substances show two critical points, but in the case of high-molecular-weight substances it can show either lower critical

solution temperature (LCST) or upper critical solution temperature (UCST). Polymer blends normally show LCST **[52,56-58]**.

Flory-Huggins lattice theory is the preliminary one used to explain polymer solutions and blends and is basically an extended concept of normal solutions. According to Flory-Huggins, for binary systems, expression for free energy of mixing can be written as,

$$\Delta Gm = RT\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2\right] \qquad (I.6)$$

Here R is the universal gas constant and T is the absolute temperature. ϕ1 and ϕ2 are the volume fraction of the component 1 and 2, "r" represents the number of polymer segments (proportional to the degree of polymerization) and c is the Flory-Huggins interaction parameter **[37,51,59,60]**. In the above equation the first two terms are related to the entropy of mixing as,

$$\Delta S_m = -R\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \qquad (I.7)$$

While the third term represents the enthalpy of mixing, i.e.,

$$\Delta H_m = RT\chi\phi_1\phi_2 \qquad (I.8)$$

It is well known that entropy contribution is very small for the infinite molar masses. Hence the miscibility or immiscibility of the system mainly depends on the value of the enthalpy of mixing. If the parameter χ is negative, miscibility can be observed for the system ($\Delta H_m < 0$). Miscibility of the system occurs at $\chi < \chi_{cr}$ where χ_{cr} is χ parameter at the critical point (function of the molar masses) and it can be expressed as

$$\chi_{cr} = \frac{1}{2}\left(\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right)^2 \qquad (I.9)$$

I.9. Classification of polymer blends

Polymer blends are of different types and have different properties. They can be classified into different types on considering the number of phases/ morphologies, constituents, miscibility, and method of preparation.

I.9.1. Classification based on constituents

Based on the constituents, blends can be categorized as rubber/rubber blends, rubber/plastic, and plastic/plastic blends, some examples are listed below in **Table 1.1**.

Table I.1. Examples of polymer blends which are classified based on the constituents.

	Plastic/plastic	Plastic/rubber	Rubber/rubber
1	Polycarbonate/ polyethylene (PC/PE)	Natural rubber/ high density Polyethylene (NR/HDPE)	Ethylene-propylene- diene monomer/ butadiene rubber (EPDM/BR) blends
2	PE/polystyrene (PS)	PE/EPDM	Nitrile-butadiene rubber (NBR)/EPDM
3	PC/polypropylene (PP)	EPDM/poly vinyl chloride (PVC)	EPDM/ethylene-propylene rubber (EPR)
4	PP/poly(trimethylene terephthalate) (PTT)	PVC/NBR	Styrene-butadiene rubber (SBR)/NR
5	PE/PTT	HDPE/EPDM	NBR/SBR
6	PP/PE	NR/PP	NR/NBR (nitrile rubber)
7	Poly (ethylene terephthalate) (PET)/(PP)	Brominated butyl rubber (BIIR)/(EPDM)	EPDM/nitrile-butadiene rubber (NBR)
8	PS/PP	EPDM/PP	EPDM/NR
9	Polyamide 6 (PA6)/poly (butylene terephthalate) (PBT)	SBR/PVC	EPDM/epoxidized natural rubber (ENR)
10	PE/polyethylene oxide blends	NBR/HDPE	EPDM/SBR

I.9.2. Classification based on the miscibility

According to miscibility polymer blends can be classified into three, which are miscible blends, compatible blends, and immiscible blends.

I.9.2.1. Miscible blends

Miscible blends exhibit homogeneous morphology with only one glass transition temperature ($\mathbf{T_g}$), and is in between the $\mathbf{T_g}$***s*** of both blends.

components. In the case of miscible blends, $\mathbf{\Delta H_m < 0}$ due to specific interactions and homogeneity is observed at least on a nanometer scale **[39]**. As already discussed, for complete miscibility, blend system must satisfy the conditions given as **Eqs. (I.1)** and **(I.2)**. So it is clear that miscible blends are homogeneous in nature and are associated with a negative value of free energy of mixing. Development of miscible polymer blends depends on many factors which involves chemical nature of the polymers, polarity, viscosity ratio, surface tension, interfacial tension, and exothermic interactions such as dipole-edipole interactions, hydrogen bonding, dispersive forces, acid-ebase interactions, etc **[61]**.

For example, polystyrene/poly(phenylene oxide) (PS/PPO) blends, poly (styrene-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA) blends **[39]**.

Measurement of glass transition temperature ($\mathbf{T_g}$) can be considered as a general method to judge the miscibility of blends. As already discussed single$\mathbf{T_g}$of blend represents a miscible blend and two $\mathbf{T_g}$ represents a phase separated blend system. The main experimental techniques which are generally used to measure $\mathbf{T_g}$ of components involve differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) **[62]**.

There are some theoretical equations reported for miscible blends, which show the composition dependence of $\mathbf{T_g}$. The important equations are Fox equations, Gordon and Taylor equation, and Couchman equations and are given below,

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (\mathbf{I.10})$$

$$\ln T_g = \frac{w_1 \ln T_{g1} + k w_2 \ln T_{g2}}{w_1 + k w_2} \qquad (\mathbf{I.11})$$

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (\mathbf{I.12})$$

where **w** represents the weight fraction of each component. $\mathbf{T_{g1}}$ and $\mathbf{T_{g2}}$ represent the $\mathbf{T_g}$ of components 1 and 2, while the glass transition temperature of blend is represented by $\mathbf{T_g}$. **k** is equal to $\mathbf{\Delta}C_{p1}/\ \mathbf{\Delta}C_{p2}$ **[61-64]**.

I.9.2.2. Compatible blends

These blends can be referred to as compatible blends since they exhibit fine-phase morphology and better properties. In the case of partially Introduction 7 miscible blends, one part of the blend component is dissolved in the other. Both blend phases are homogeneous and have their own $\mathbf{T_g}$ and both the $\mathbf{T_g s}$ are shifted from the values for the pure blend components toward the $\mathbf{T_g}$ of the other blend component. Polycarbonate (PC)/acrylonitrilebutadiene-styrene blend is an example for partially miscible blend **[65]**.

I.9.2.3. Immiscible blends

Most of the polymer blends are immiscible in nature due to the negligible entropy of mixing. Polymers have a high degree of disorder, so the addition of a different polymer does not cause any significant change in entropy. Therefore, the mixing enthalpy has to be negative, to make a polymer spontaneously mix. Immiscible blends have heterogeneous morphology. If two polymers are mixed and are immiscible in nature, it shows two glass transition temperatures ($\mathbf{T_g s}$) and melting temperatures ($\mathbf{T_m s}$) corresponding to each polymeric component **[39].**

Immiscible blends possess sharp interphase and this indicates the absence of strong interactions between the two polymer components. Generally weak interactions like hydrogen bond and van der Waals attraction can be observed in immiscible blends. On the other hand, most of the useful products are made up of immiscible blends.

For example, poly (ethylene terephthalate)/poly (vinyl alcohol) (PET/ PVA) blends, polybutadiene/PS blends, poly(propylene) (PP)/PS blends, PP/poly(ethylene) (PE) blends, PC/PP, poly(trimethylene terephthalate) (PTT)/PP **[39,66]**.

I.10. Preparation methods of polymer blends

Fabrication methods have great importance since they can affect the uniform mixing, morphology, and thereby final properties of the blends and composites. The methods of solution blending, melt blending, and in-situ polymerization are broadly applied to fabricate polymer blends and their composites. In addition, solid-state shear pulverization, freeze-drying, latex blending, and coagulation spinning methods also show promise **[67]**.

I.10.1. Melt mixing/melt blending

Melt mixing is one of the main methods for the preparation of polymer blend in an economic and eco-friendly manner. In this method, the polymers are heated to form a melt, and mixing occurs under high shear forces. In the case of melt mixing, a large amount of mechanical energy can be supplied by the rotating screws for the uniform mixing of polymers. Melt mixing of two or more different polymers leads to different morphologies depending on the rheological and thermodynamic properties of the components and on processing conditions. The morphology of the fabricated blends strongly influences the final properties of the system. The melt mixing can be carried out in batch or continuous operation using a melt mixer (e.g., Brabender mixer, Haake mixer) and extruder, respectively. The melt processing is considered as a feasible choice for the preparation of polymer blends toward large-scale synthesis for industrial applications **[67,68]**.

I.10.2. Mill mixing

Mill mixing is a general method to prepare rubber-based polymer blends. Blending can be carried out in between two horizontally placed rotating hollow metal cylinders. The nip gap between the two rollers can be adjusted by varying the roller distances as per the compound consistency.

I.10.3. Solution mixing

In this method, polymers are dissolved in a common solvent, under vigorous stirring. The blend is finally recovered by solvent evaporation or by a nonsolvent. This method is only applicable to the polymers which are soluble in any solvents and is the main drawback of this technique. Also, the solvent recovery is a problem for the wide use of this solution mixing **[67,68]**.

I.11. Factors affecting properties of polymer blends

The properties of polymer blend not exactly show the combined properties of individual polymer components. Overall performance and properties of polymer blends depend on several factors such as properties of the individual polymer components (which include its structure, state, and molecular weight), method of preparation, processing temperature and time, composition of polymer components, morphology and morphological parameters (size, shape,

interfacial area, uniformity, and distribution), and distance between adjacent dispersed particles and adhesion between polymer components. **[69,70,71]**.

In the case of miscible polymer blends, its properties follow a mathematical expression as,

$$X = X_1\phi_1 + X_2\phi_2 + IX_1\phi_2 \qquad (\mathbf{I.13})$$

Where **X** is the property of interest, **ϕ** is the concentration, and I is an interaction term. If **I** value is zero, the polymer blends may behave as mixtures, If **I** is negative, an anti-synergistic effect can be observed in the properties of polymer blend, and if **I** is positive synergistic effect can be observed in the overall properties of polymer blends.

The above equation is not practicable for immiscible polymer blends; its physical properties follow another semiempirical rule and it can be expressed as,

$$P_2 = \frac{1 + AB\phi_2}{P_1 - B\psi\phi_2} \qquad (\mathbf{I.14})$$

Where $\mathbf{P_1}$ represents the continuous phase, $\mathbf{P_2}$ represents the dispersed phase, $\boldsymbol{\phi_2}$ denotes the concentration of the dispersed phase, "A" the shape and orientation of the dispersed phase, "B" the relative values of the properties $\mathbf{P_1}$, $\mathbf{P_2}$, and A, and $\boldsymbol{\psi}$ represents packing fraction (concentration term) **[72]**.

I.12. Characterization techniques: to study phase separation in blends

I.12.1. Morphological studies

From the morphological studies one can clearly get an idea regarding the type of morphology, phase separation, and degree of miscibility. The morphology of a developed polymer blend can be analyzed by various microscopic techniques such as transmission electron microscopy, SEM, atomic force microscopy, optical microscopy, fluorescence microscopy, confocal microscopy, etc. **Figure I.12.** shows the morphology of PTT/PP (90/ 10) blends analyzed by SEM and optical microscopy. From the figure it is very clear that PTT/PP blend is immiscible and phase separated system. In the images the domains represent the PP phase and PTT is the continuous phase.

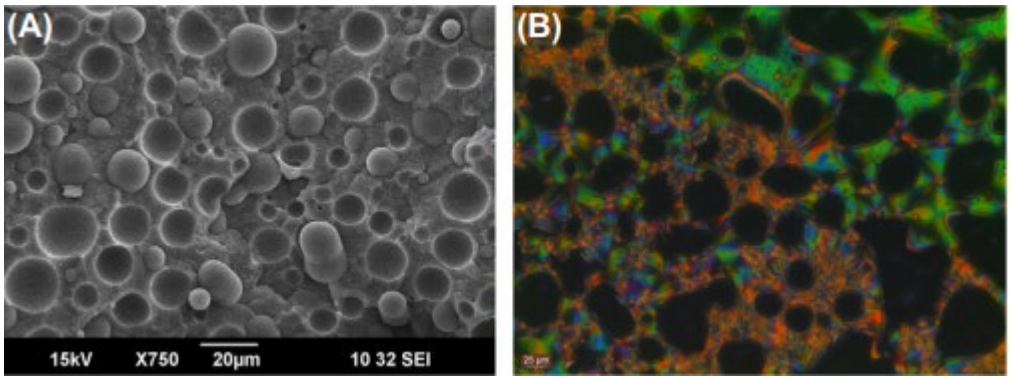

Figure I.10. (A) scanning electron microscopy image and (B) optical microscopy image of 90 poly(trimethylene terephthalate)/10 polypropylene blend**.**

I.12.2. Analysis of glass transition temperature

Other important techniques used to check the phase separation and miscibility of blend system are DSC and DMA by the analysis of the T_g of the blend. As already discussed, the analysis of T_g can be considered as a common way to evaluate the miscibility of blends. The single T_g of blend stands for a miscible blend and the possibility of two or more T_g sheds light on a phase separated blend system. The main experimental techniques generally used to measure T_g of components involve DSC and DMA Various characterization techniques used for polymer blend nanocomposites are given in **Table 1.2.**

Table I.2. Characterization techniques for polymer blends.

Characterization techniques used for polymer blends	Information
Morphology Scanning electron microscopy (SEM)	Surface roughness and morphology, particle size and distribution
Transmission electron microscopy (TEM)	Morphology and microstructure, phase separation, structural heterogeneities
Atomic force microscopy (AFM)	Phase separation, surface roughness, morphology and microstructure
Infrared (IR) spectroscopy	Component identification and analysis of interfacial interactions
Thermogravimetric analysis (TGA)	Thermal stability
Differential scanning calorimetry (DSC)	Melting and crystallization behavior, local dynamics of polymer chains

Rheometry	Flow properties, viscoelastic properties
Mechanical test	Young's modulus, tensile strength, elongation at break, impact strength, hardness
Dynamic mechanical analysis (DMA)	Viscoelastic properties
Optical	Morphology, crystallization kinetics, spherulite growth rate study
Neutron scattering	Miscibility, morphology
Ultrasound	Composition of polymer blends, measuring extrusion flow instabilities, monitoring injection-molding processes, polymer chain modification, compatibilization of immiscible blends, dispersing nanoparticles in polymer melts, morphology
Ellipsometry	Determination of interfacial thickness between two polymers, determination of glass transition temperature (thin films)
Light scattering	Phase separation studies, crystallization studies, cloud-point determination (to locate the phase boundary), evaluation of particle size
X-ray scattering techniques	Structural characterization, crystallization studies (degree of crystallinity, size of crystals)
Secondary ion mass spectrometry (SIMS) techniques, time-of-flight secondary ion mass spectrometry (ToFSIMS), and nanoscale secondary ion mass spectrometry (Nano SIMS)	Polymer surface characterization (focused especially on polymer blends and interfaces), molecular structural information (such as branching, saturation, functional groups, molecular weight distribution, segmental length, etc.)
Fluorescence microscopy	Structural analysis of polymer blend systems
Solid-state nuclear magnetic resonance (NMR) spectroscopy	Microstructures, miscibility, intermolecular interactions of polymer blends
Raman imaging	Phase morphology
Electron paramagnetic resonance (EPR) spectroscopy and forward recoil spectrometry (FRES)	Surface and interfacial properties and processes of polymer blends (especially for polystyrene-based blends)
Dielectric relaxation spectroscopy (DRS)	Degree of miscibility of polymer blends, crystallization kinetics of amorphous/ crystalline polymer blends
Positron annihilation spectroscopy (PAS)	Free-volume distributions, miscibility

I.13. Compatibilization of polymer blends

Blending is an excellent and economic way to enhance the properties of product material. But the blends of polymers usually have coarse phase morphology and poor interfacial adhesion between the blend phases. This may be so, as most polymers are immiscible. When the viscoelastic behavior of polymer blends is observed, the melt viscosity of immiscible polymer blends is found to depend on the interfacial interactions and phase morphology. Hence compatibilization by addition of an interfacial agent is needed to attain synergistic effect for making it most useful. There are several methods for the compatibilization of polymer blends, but the principle of all techniques is the homogenization of mixture of the polymer by adding a compatibilizing agent.

Compatibilizers are macromolecular in nature and bring interfacial activities in heterogeneous polymer blends. The compatibilizer, which can be added directly to the immiscible polymer blend and generated in situ during the blending process, usually has one part miscible with one polymer and the other part miscible with the second polymer. The compatibilizers mainly retard the formation of the Rayleigh disturbances, on the generated threads of polymer 1, which results in decreased interfacial tension. The lower interfacial tension stretches the threads longer, making their diameter also smaller. The smaller size of the generated droplets of polymer 1 helps to bring the average particle size to submicron level. The compatibilizer also prevents the coalescence at the surface of the generated phase. Compatibilizers can thus generate and stabilize finer blend morphology. Several strategies are reported for the compatibilization of polymer blends **[73-79]**.

I.14. Strategies for compatibilization of polymer blends

Polymer blends can be compatibilized by different methods. Industrial suitability of compatibilization techniques depends on several factors, such as cost, final performance, recyclability, and possible biodegradability.

Some of the general strategies involve the following:

- Adding previously made grafted block copolymers.
- Adding reactive polymers (advantage is the short processing time of a minute or even less).

- Addition of low-molecular-weight chemicals like peroxide activate inert polyolefins, resulting in the formation of branched copolymers, a functional chemical that forms block copolymers or a mixture of a peroxide and a functional chemical, all of which leads to the formation of branch/graft copolymers: Lack of chemical selectivity is the problem in this approach although this compatibilization method is quite simple.
- Another method used is that of interchange reactions. Here two or more poly-condensates are blended together, resulting in interchange reactions. The type of polymers, nature and concentration of the reactive groups, blending temperature, moisture content, concentration of interchange catalyst, and reaction time will influence this method.
- Mechanical mixing is one industrially viable method and requires no chemicals for compatibilization. i.e., no additional polymers or chemicals are added. In this method the polymers are melt processed in kneaders or extruders under high shear forces. Mechano-degradation is advantageous for specific polymer blends.
- Addition of selective crosslinking agents is yet another method. This method of specific interactions compatibilization is done by introducing suitable functional groups which can chemically modify the blend components, like a third polymeric or low-molecular-weight material.

Another important strategy for compatibilization of immiscible blends involves the usage of nanofillers. The various chapters in the book discusses the compatibilization of polymer blends by graft copolymers, random copolymers, micro and nanofillers, coupling agents, janus particles and shear pulverization in a detailed manner **[80]**.

I.15. Why do we need compatibilizers?

Even though polymer blends are the combinations of polymers having good properties; its applications are limited due to the immiscibility of most of the polymer blends. Majority of polymer blends are immiscible in nature due to the negligible entropy of mixing, high molar mass, difference in polarity of polymer components, viscosity ratio between components, etc.

The high interfacial tension between the polymer components will offer poor interfacial adhesion between the components and hence shows poor properties inferior to that of individual polymer components. Thus, it can be said that un-stabilized morphology, phase separation, poor interfacial adhesion between the polymeric components of immiscible polymer blend will lead to the poor physic-mechanical properties. So, it is necessary to find out a solution to overcome

the disadvantages of immiscible blends, thereby we can enhance the applications of blends into more fields.

Properties of a heterogeneous blend depend mainly on the compatibility between the polymer components. The interface between the phases in a polymer blend system can be characterized by the interfacial tension, which when approaching zero the blend becomes miscible. That is, if there are strong interactions between the polymer components, then the polymer blend will be miscible in nature. Large interfacial tension leads the phase separation and the phase separated particles possibly undergoing coalescence; this will result in large particle size for the dispersed domains. The large interfacial tension between polymer components in polymer blends can be reduced by the addition of interfacial agents known as compatibilizers; these are generally molecules that can be aligned along the interfaces between the two polymer phases, reducing the interfacial tension and thereby increasing the compatibility of the polymer blends.

Compatibilizers play a key role to improve the interfacial adhesion between the components and to reduce the interfacial tension between the components. They exhibit interfacial activities in heterogeneous polymer blends. The interfacial activities of compatibilizers help to stabilize the morphology by enhancing interfacial adhesion. Compatibilizers resist the coalescence of dispersed phases, thereby reducing the interfacial tension and the size of the dispersed domains which results in an increase of adhesion at the interface and improved properties of the final product. Commonly used compatibilizers are block, graft, or random copolymers consisting of dissimilar blocks **[81,82]**.

The high interfacial tension between the polymer components will offer poor interfacial adhesion between the components, thereby polymer blends become immiscible in nature and show poor properties inferior to that of individual polymer components. Thus, compatibilizers can be helpful for the conversion of immiscible polymer blends into useful polymeric products with improved properties. By adding compatibilizers into immiscible polymer blends one can increase the application of immiscible blends in an industrial level. The overall action of compatibilizers involves the improvement in the compatibility between the components by enhancing the interaction between the components, reducing the interfacial tension between the components, improving the interfacial adhesion between the components, etc. and the compatibilizing action of compatibilizers is similar to that of an emulsifier **[83-85]**.

I.16. Theoretical aspects of compatibilization

A good compatibilizer should migrate to the interface and reduce the interfacial tension coefficient, decreasing the dispersed phase dimensions, thereby stabilizing the blend morphology and enhancing the adhesion between phases in the solid-state. Compatibilizing agents often provide additional morphology stabilization by acting as a surfactant and decreasing the interfacial surface tension. In general, the added compatibilizers, if compatible with both phases, segregate preferentially at the interface and ensure strong interfacial adhesion **[86, 87]**.

A successfully compatibilized blend of moderate composition (up to 30 wt% minority component) exhibits spherical dispersed phases with consistent diameters, averaging on the micron and submicron scale. Such consistent morphologies can be achieved when the compatibilizing agent provides a steric hindrance to the dispersed phase coalescence. Compatibilizers which provide steric hindrances act as anchors for minority phase droplets in the matrix **Figure I.13** and also serve as repulsive "springs" when two droplets are in proximity.

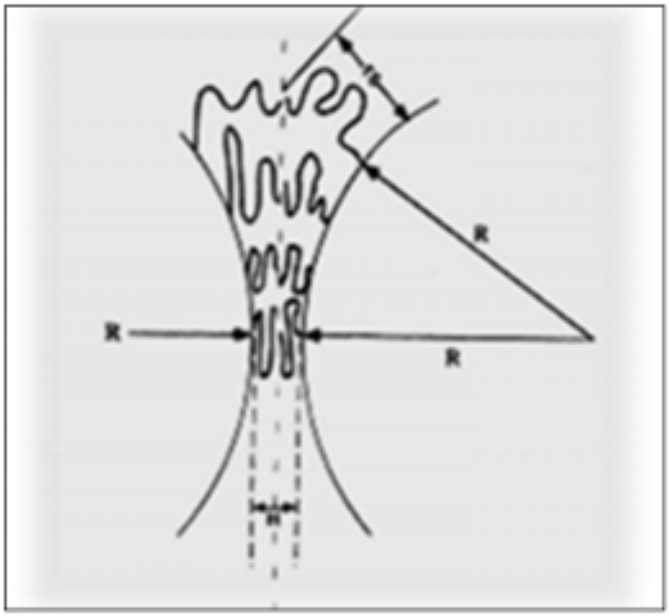

Figure I.11. Steric hindrance by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence **[88].**

From a commercial point of view, it can say that compatibilization is the method of converting a multiphase polymer mixture into a commercially useful product. In principle, a molecule can act as a compatibilizer if it has a segment that is miscible in one phase and another segment that is miscible in the other phase. And this will lead to the positioning of the compatibilizer across the interface. So, a booming compatibilizer will

- Reduce interfacial tension between components,
- Permit finer dispersion during mixing,
- Provide a measure of stability against gross separation,
- Produce ultimate product, and
- Results in improved interfacial adhesion.

I.17. Blending with a compatibilizer, a third component

I.17.1. Compatibilizer immiscible in both blended polymers

When two polymers are to be blended, but they are incompatible, then a third component or additive can be added to make the blend compatible. The compatibilizer will form at surfaces or provide an interphase. A compatibilizer is analogous to a surfactant. A surfactant can emulsify or compatibilizer oil and water dispersions by stabilizing interfaces in the micellar mechanism. Compatibilizers function in the same way; they can, however, form an interphase containing some of each component. A compatibilizer can be a small molecule or a polymer. If the compatibilizer is immiscible, but compatible with both polymers of a blend, then it will tend to reside at the interface. An inclusion of filler particles, particularly nanoparticles with their large surface area to volume ratio, can be a compatibilizer between two blended polymers **[89]**.

Nanoparticles that interact with both polymers of an incompatible blend tend to align at the blend interface to minimize surface energy. This organization of nanoparticles along an interface can be used to create nanoparticles alignment and emphasizes the properties contributed by the nanoparticles. Graphene has been oriented in blends to enhance conductivity by providing continuous pathways along the graphene even when the graphene is at low concentration; the percolation threshold is lowered. PLA and poly-caprolactone blends have been prepared with graphene trapped at the interface to obtain massive enhancement of thermal conductivity at volume fraction of graphene as low as 0.53% **[90]**. PP blends with poly(ethylene terephthalate) (PET) have been prepared with graphene mostly in the PET phase of the co-

continuous or double percolated blend that exhibited increased electrical conductivity and electromotive force shielding in the GHz frequency range **[91]**.

I.17.2. Compatibilizer mutually miscible

When the compatibilizer is mutually miscible with both blended polymers then it can form an interphase. The interphase is a region of finite thickness between the two blended polymers. The interphase is a composition or structure gradient between the two blended polymers and it may provide a functional mechanical gradient to the properties. An example is a blend of PVC with a poly(alkyl acrylate) where a plasticizer such as di-octyl phthalate has been added; this ester will be miscible in both phases and function as a plasticizer for the PVC. The poly(alkyl acrylate) may also be plasticized by the ester, but regardless it can be a toughening agent for PVC. Toughening is performed by a separate phase of a deformable polymer, not a miscible phase that gives plasticization that decreases the modulus and strength overall. PVC has been shown to be miscible with some ester and ether repeat unit polymers, such as poly(methyl methacrylate) and poly(oxyethylene) due to donor acceptor interactions between chlorines and ester or ether oxygens **[92]**. Plasticizers such as dioctyl phthalate or poly(ethylene adipate), are miscible with the host PVC and also with blended polymers used for toughening PVC, such as poly(alkyl acrylate)s or poly(alkyl methacrylate).

I.17.3. Compatibilizer miscible with one of the blended polymers

If there is miscibility with one of the blended polymers, then the compatibilizer can provide a secondary modification as a plasticizer for instance.

Since the blended polymers are incompatible, the compatibilizer can migrate from the polymer within which it is miscible to the interface. The driving force for this migration will be to reduce the interfacial energy, which will occur when the compatibilizer develops at least a monolayer at the interface. In each situation where the interfacial energy is minimized, there is opportunity for dispersed particle size reduction, which involves creation of a greater interfacial area. A greater interfacial area is thermodynamically stable when the interfacial energy is minimized.

I.18. Role of compatibilizers in blending processes

Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and a second block miscible

with the other blend component. These blocky structures can be pre-made and added to the immiscible polymer blend, but they can also be generated in-situ during the blending process. The latter procedure is called reactive compatibilization, and mutual reactivity of both blend components is required.

The role of compatibilizers in the blending process is firstly to retard the formation of the Rayleigh disturbances on the generated threads of polymer, as the result of a decreased interfacial tension.

The lower the interfacial tension, the longer the deformation tension exceeds the interfacial tension, the longer the stretching of the thread will proceed, the smaller the diameter of the resulting thread will become, and, consequently, the smaller the size of the generated droplets of polymer will be. Usually, an average particle size in the sub-micron range can be achieved. In addition, the presence of compatibilizer molecules at the surface of the small generated particles prevents coalescence from occurring during subsequent processing. Compatibilizers are thus able to generate and to stabilize a finer morphology.

Finally, provided that each block of a poly(A-b-B) compatibilizer penetrates the parent phase (A and B, respectively) deeply enough to be entangled with the constitutive chains, the interfacial adhesion is enhanced. Good interfacial adhesion is essential for stress transfer from one phase to the other one to be efficient and for cracks initiated at the interface to be prevented from growth until catastrophic failure occurs. Refinement and stabilization of the phase morphology and the enhancement of the interfacial adhesion usually upgrade an inferior and useless immiscible polymer blend to an interesting material **[93]**.

I.19. Properties of polymer blends influenced by compatibilization

Most polymer systems are thermodynamically immiscible. The enthalpy of mixture of molten polymer mixtures takes a positive value, much more than the negligible amount of entropy, which is the characteristic of macromolecules. Correspondingly, high interfacial tension among dispersed and matrix components in a polymer blend leads to immiscibility **[94]**. The use of a compatibilizer strengthens the interfacial adhesion between blend components. Commercially available compatibilizers are block or graft copolymers that can be added to a polymer blend prior to or during the mixing process. In general, the presence of compatibilizer promotes miscibility through the interfacial adhesion improvement, which is responsible for change in mechanical, rheological, thermal, and morphological characteristics of polymer

blends **[95-99]**. Addition of compatibilizer to a polymer blend allows for interfacial tension reduction, while above a critical concentration it may cause interfacial saturation **[100]**. Therefore, there were attempts to explain structure-property interrelation in binary **[101]** and ternary **[102]** polymer blends in terms of interfacial phenomena.

I.20. New challenges in compatibilized blends

When we think about the polymer blends, ease of handling, new mixing technologies, stability of blend morphology, suitability for advanced applications, and recycling are the major concerns. Compatibilization opens new windows to polymer technology and applications. Two polymers having good intrinsic properties, but are immiscible and incompatible or nonreactive can be utilized by converting them to blends using compatibilizers. As mentioned in the above sections, thermodynamic miscibility parameters play an inevitable role in compatibilization. It is demanding to select most favorite pair of polymers and ease to handle compatibilizing agents. Conventionally single compatibilizing agents have been utilized, but a mixture of more than one or a hybrid compatibilizer can be an interesting in this field. Interestingly nano-hybrids are creating a trend nowadays. New types of homogeneous compatibilizing agents will enhance the scope of the study. The interface modifiers which are added to the blend system may get inserted into the interface region and get broken down to extremely small size. This type of breaking up leads to the development of nano-structured morphology in the blends. Generally, compatibilizers are selected depending on the polymer mixture and compatibilization is somewhat a selective process. Not all the compatibilizing agents are suitable for all blend systems.

All-in-one compatibilizing agents are still a mirage in polymer research. A compatibilizing agent that suits different pairs of polymers is a challenge in development. It is most of the times the localization of the compatibilizing agent in a binary or ternary blend system is unpredictable. Tuning the localization to a particular phase is another challenge. Development of compatibilizers that can be recycled and reused is a necessary situation. Exploring new materials, technology, methods, and characterization in blending invites the researchers to hit new horizons.

I.21. Applications of compatibilized polymer blends in biomedical fields

Life expectancy among people increases along technology progression level. The future ahead of such technological advances in various fields underlines the need for new and innovative tools in accordance to people's comfort. Health is the most important issue worldwide and scientists endeavor to enhance the level of people's health, so various strategies have been developed so far to meet health requirements. Nowadays polymers are known as the building blocks of both commodity and modern stuff ranging from general purpose to sophisticated applications. In particular, polymers have been vital elements of advanced materials and systems in medical landscapes **[103]**.

As a general term, medicine is a vast field in which a proper therapy or treatment method depends on early-stage diagnosis of disease. Biomedical engineering can bridge between engineering and biology, seeking new methods and materials to enhance the health level of life, and then getting prepared for advanced health-care treatment such as therapy, diagnosis, and monitoring. The tunable microstructure of polymers paves the way for targeted design of biomedical materials and systems. Application of polymers as diagnostic system like fluorescent loaded polymeric nano-particle, as therapeutic system like drug carrier, and as regenerative scaffold in tissue engineering has been the subject of several reports **[104, 105]**.

Biocompatibility is the first requirement of a polymer to be utilized in biomedical applications. Polymers used in biomedical engineering can be categorized into two main groups including synthetic and natural polymers. Each group has some pros and cons, for instance, natural polymers like chitosan exhibit appropriate biocompatibility, but their mechanical properties are not acceptable, unless one makes them blend with polymers.

Polycaprolactone (PCL) is known as a biocompatible synthetic polymer widely used in tissue engineering, but unsurprisingly hydrophobic properties of PCL deteriorate efficacy of cell attachment emphasizing the need for blending PCL with other polymers in the quest of hydrophilicity. Various methods have been proposed to enhance PCL performance, among which grafting and blending are the most promising methods. For the sake of simplicity and affordability, blending is preferable **[106, 107]**.

Miscibility is an important factor in blending polymer pairs. Immiscible polymers are prone to phase separation which affects even the surface topology of blends, thereby governing the cell activity. A scaffold having uniform topology results in monotonic cellular growth.

There is agreement that polymer blends are hardly miscible, but they can be partially miscible by using compatibilizers. Immiscibility of polymer blends leads to non-uniform activity of cells and disintegrated cells. The use of a layer of natural polymer as compatibilizer is responsible for insufficient biocompatibility in immiscible polymer systems **[108]**. Various compatibilizers have been added to polymer blends to enhance the miscibility. Naffakh et al. employed polylactic acid (PLA)/polypropylene (PP) blends containing tungsten disulphide as a candidate for biomedical applications, but phase separation led to unsuitable properties. To overcome this drawback, PP grafted maleic anhydride (PP-g-MAH) was used as a compatibilizer **[109]**.

Calandrelli et al blended PLA with PCL to fabricate artificial liver. Addition of lactic acide-caprolactone copolymer as a compatibilizer enhanced the miscibility of PLDA and PCL in their blends, so that cell proliferation enhanced due to restricted phase separation **[110]**. It should be noticed that high concentration of the compatibilizer sometimes results in toxicity, signifying the need for optimizing compatibilizer content.

Various types of biocompatible polymer blends have been fabricated so far and utilized in biomedical applications. It is always required for bio-based polymer blends to be processed appropriately. Typically, blends are fabricated using various methods such as electro-spinning, gelation, and casting, but the final application determines the polymer blends and fabrication methods to be selected. For example, fabrication of injectable interpenetrating polymer networks has been recognized as a noninvasive method to regenerate damaged tissues. Since cells can proliferate properly on the aligned scaffold rather than random morphology, electro spinning driven nanostructures are promising to enhance cellular activity. For instance, electrospun nanofibers have been utilized in bio-sensing applications and enhanced material performance **[111,112]**. All in all, it can be concluded that there is need for profound knowledge about biocompatible polymers to select proper blends for biomedical applications.

Human health care was the main driving force behind several sorts of research and market developments in the past decades. Having this in mind, biomedical engineering received ever increasing attention and several technologies were developed to enhance the human health level. Macromolecular design/engineering enabled production of a vast variety of biomaterials for biomedical uses. Natural and synthetics polymers have been utilized in various applications such as tissue engineering, biosensors, and drug delivery pursuing such developments. Natural polymers due to the inferior mechanical properties required to be reinforced through blending with other polymers to receive credit from mechanical properties perspective. Meanwhile, due

to their acceptable mechanical characteristics, synthetic polymers were used in the form of blend with natural ones having good cellular attachment. In general, natural polymers could mimic ECM properties, while synthetic polymers could in principle enhance the mechanical properties. In this regard, fine-tuning the microstructure of bio-based polymer blends was centered to the focus and hot challenges. Though there were some evidence that natural and synthetic polymers could in the form of blend provide synergistic properties, very limited miscibility window of such blends when melted was the reason for using appropriate compatibilizer. Based on final applications, precise choice of biopolymers for blending together with a proper compatibilizer required for interfacial adhesion toward high performance encouraged having this chapter written.

References

[1] Hottle, T.A., M.M. Bilec, and A.E. Landis, Sustainability assessments of bio-based polymers. Polymer Degradation and Stability, 2013. 98(9): pp. 1898–1907.

[2] Ganguly, S. and S. Margel, Remotely controlled magneto-regulation of therapeutics from magnetoelastic gel matrices. Biotechnology Advances, 2020. 44: p. 107611.

[3] Chen, G., T. Ushida, and T. Tateishi, Scaffold design for tissue engineering. Macromolecular Bioscience, 2002. 2(2): pp. 67–77.

[4] Ganguly, S. and N.C. Das, Rheological properties of polymer–carbon composites, in carbon-containing polymer composites, 2019. Springer. pp. 271–294.

[5] Reshmy, R., et al., Advanced biomaterials for sustainable applications in the food industry: Updates and challenges. Environmental Pollution, 2021. 283: p. 117071.

[6] Ganguly, S., et al., Microwave-synthesized polysaccharide-derived carbon dots as therapeutic cargoes and toughening agents for elastomeric gels. ACS Applied Materials & Interfaces, 2020. 12(46): pp. 51940–51951.

[7] L. Avérous, Monomers, Polymers and Composites from Renewable Resources, Elsevier, Amsterdam 2008, p. 433.

[8] R. Auras, B. Harte, S. Selke, Macromol. Biosci. 2004, 4, 835.

[9] M. H. Hartmann, in Biopolymers from Renewable Resources (Ed: D. L. Kaplan), Springer, Berlin, Heidelberg 1998, p. 367.

[10] D. Garlotta, J. Polym. Environ. 2001, 9, 63.

[11] Jyotishkumar Parameswaranpillai, Suchart Siengchin, Nisa V. Salim, Jinu Jacob George, and Aiswarya Poulose. 2022 - Polylactic Acid-Based Nanocellulose and Cellulose.

[12] Koh, J. J., Zhang, X., He, C., “Fully biodegradable poly(lactic acid)/starch blends: a review of toughening strategies”, International Journal of Biological Macromolecules 2018, 109, 99–113.

[13] C. Bastioli, "Handbook of Biodegradable Polymers," Rapra Technology Limited, 2005.

[14] Y. Zhang et al., "Poly(Lactic Acid) Blends: Processing, Properties, and Applications," Progress in Polymer Science, vol. 99, pp. 101-129, 2019.

[15] J. M. Kenny et al., "Processing of Poly(Lactic Acid): Characterization of Chemical Structure, Thermal Stability and Mechanical Properties," Polymer Degradation and Stability, vol. 81, pp. 329-338, 2003.

[16] C. Peterson, "Poly(lactic Acid) Production, Processing, and Applications: A Review," Polymer-Plastics Technology and Engineering, vol. 52, pp. 713-728, 2013.

[17] Y. Zhang et al., "Poly(Lactic Acid) Blends: Processing, Properties, and Applications," Progress in Polymer Science, vol. 99, pp. 101-129, 2019.

[18] ChatGPT: Applications of poly(lactic acid), https://poe.com/ChatGPT/Applications of poly(lactic acid)

[19] Webster, C.C., Baulkwill, W. J., Eds. Rubber; Longman Scientific and Technical: Essex, UK, 1989.

[20] Vaysse, L.; Bonfils, F.; Thaler, P.; Sainte-Beuve, J. Natural Rubber, In Sustainable Solutions for Modern Economies; R. Höfer, Ed.; Chapter 9.5, pp. 339–367, RSC Publ.: Cambridge, UK, 2009.

[21] Rodgers, B., Ed.; Marcel Dekker: Rubber Compounding: Chemistry and Applications; New York, N.Y. 2004,645.

[22] Natural rubber: Properties and applications" by S. K. De, S. K. Chattopadhyay, and S. K. Debnath, in Journal of Polymer Materials, vol. 26, no. 2 (2009).

[23] ChatGPT: Properties of natural rubber (NR), https://poe.com/ChatGPT/ Properties of natural rubber

[24] Rubber processing and products by R. S. Williams and E. N. Chukwu, in Rubber Chemistry and Technology, vol. 82, no. 2 (2009).

[25] Processing of natural rubber by A. K. Bhowmick, in Rubber Science, vol. 25, no. 1 (2012).

[26] ChatGPT: Applications of natural rubber (NR), https://poe.com/ChatGPT/ Applications of natural rubber

[27] Handbook of thermoplastic elastomers 2nd edition Jiri George Drobny 2007

[28] AY. Coran. in Handbook of Elastomers. New Developments and Technology. Eds. AK Bhowmick, HL. Stephens, Marcel Dekkar. New York (1988),

[29] Radusch, H.-J. 2005. Phase morphology of dynamically vulcanized thermoplastic vulcanizates, in Micro- and Nanostructured Multiphase Polymer Blend Systems, S. Thomas, G. Groeninckx and C. Harrats,eds. CRC Press, Boca Raton.

[30] Bhadane, P.A., Virgilio, N., Favis, B.D., Champagne, M.F., Huneault, M.A. and Tofan, F. 2006. Effect of dynamic vulcanization on co-continuous morphology.AlChE J. 52, 3411-3420.

[31] Martin, G., Barrès, C., Sonntag, P., Garois, N. and Cassagnau, P. 2009. Morphology development in thermoplastic vulcanizates (TPV): Dispersion mechanisms of a pre-crosslinked EPDM phase.Eur. Polym. J. 45, 3257-3268.

[32] Antunes, C.F., Machado, A.V. and Van Duin, M. 2011. Morphology development and phase inversion during dynamic vulcanisation of EPDM/PP blends.Eur. Polym. J. 47, 1447-1459.

[33] Srithep, Y., & Supaphol, P. (2016). Natural rubber-based blends and composites: Preparation, properties, and applications. CRC Press.

[34] Gahleitner, M., & Ebner, C. (2018). Natural rubber/poly(lactic acid) blends—A review. Journal of Applied Polymer Science, 135(1), 45587.

[35] Blends P, Paul DR, Newman S. NY: Acdemic Press; 1978; 2:391.

[36] Brown SB. Reactive compatibilization of polymer blends. In: Polymer blends handbook. Springer; 2003. p. 339e415.

[37] Paul D, Barlow J. Polymer blends. J Macromol Sci Rev Macromol Chem 1980;18(1):109e68.

[38] Paul DR. Polymer blends. Elsevier; 2012.

[39] Thomas S, Grohens Y, Jyotishkumar P. Characterization of polymer blends: miscibility, morphology and interfaces. John Wiley & Sons; 2014.

[40] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; 1989.

[41] Utracki LA, Wilkie CA. Polymer blends handbook. Springer; 2002.

[42] Bahrami R, Löbling TI, Schmalz H, Müller AH, Altstädt V. Micromechanics of "raspberry" morphology in PPE/SAN polymer blends compatibilized with linear ABC triblock terpolymers. Polymer 2015;80:52e63.

[43] Chiu F-C. Poly (vinylidene fluoride)/polycarbonate blend-based nanocomposites with enhanced rigiditydselective localization of carbon nanofillers and organoclay. Polym Test 2017;62:115e23.

[44] Otero-Navas I, Arjmand M, Sundararaj U. Carbon nanotube induced double percolation in polymer blends: morphology, rheology and broadband dielectric properties. Polymer 2017;114:122e34.

[45] Wang H, Fu Z, Zhao X, Li Y, Li J. Reactive nanoparticles compatibilized immiscible polymer blends: synthesis of reactive SiO2 with long poly (methyl methacrylate) chains and the in situ formation of janus SiO2 nanoparticles anchored exclusively at the interface. ACS Appl Mater Interfaces 2017;9(16):14358e70.

[46] Utracki L. Economics of polymer blends. Polym Eng Sci 1982;22(17):1166e75.

[47] Roman C, García-Morales M, Gupta J, McNally T. On the phase affinity of multiwalled carbon nanotubes in PMMA: LDPE immiscible polymer blends. Polymer 2017;118:1e11.

[48] Jiao Q, Shen J, Ye L, Li Y, Chen H. Poly (oxymethylene)/poly (butylene succinate) blends: Miscibility, crystallization behaviors and mechanical properties. Polymer 2019;167:40e7.

[49] Métivier T, Cassagnau P. Compatibilization of silicone/fluorosilicone blends by dynamic crosslinking and fumed silica addition. Polymer 2018;147:20e9.

[50] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci 2006;31(6):576e602.

[51] Paul D, Barlow J. A binary interaction model for miscibility of copolymers in blends. Polymer 1984;25(4):487e94.

[52] Robeson LM. Polymer blends. Compr Rev 2007. ISBN-10: 3-446-22569-2 ISBN- 13: 978-3-446-22569-5.

[53] Utracki LA. Compatibilization of polymer blends. Can J Chem Eng 2002;80(6):1008e16.

[54] Rostami A, Masoomi M, Fayazi MJ, Vahdati M. Role of multiwalled carbon nanotubes (MWCNTs) on rheological, thermal and electrical properties of PC/ABS blend. RSC Adv 2015;5(41):32880e90.

[55] Polásková M. Polymer blends with microfibrillar-phase morphology. 2006.

[56] Li S, Feng L, Lu H, Feng S. From LCST to UCST: the phase separation behaviour of thermo-responsive polysiloxanes with the solubility parameters of solvents. New J Chem 2017;41(5):1997e2003.

[57] Yao W, Wang H, Cui G, Li Z, Wang J. Tuning phase behaviour of PEG-functionalized ionic liquids from UCST to LCST in alcohol-water mixtures. Phys Chem Chem Phys 2016;18(42):29192e8.

[58] Kuila A, Maity N, Chatterjee DP, Nandi AK. Phase behavior of Poly (vinylidene fluoride)-graft-poly (diethylene glycol methyl ether methacrylate) in alcohol water system: coexistence of LCST and UCST. J Phys Chem B 2016;120(9):2557e68.

[59] Ten Brinke G, Karasz FE. Lower critical solution temperature behavior in polymer blends: compressibility and directional-specific interactions. Macromolecules 1984;17(4):815e20.

[60] Tambasco M, Lipson J, Higgins JS. Blend miscibility and the Flory-Huggins interaction parameter: a critical examination. Macromolecules 2006;39(14):4860e8.

[61] Lu X, Weiss R. Relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. Macromolecules 1992;25(12):3242e6.

[62] Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A. Prediction of glass transition temperatures: binary blends and copolymers. Mater Lett 2008;62(17e18):3152e5.

[63] An L, He D, Jing J, Wang Z, Yu D, Jiang B, et al. Effects of molecular weight and interaction parameter on the glass transition temperature of polystyrene mixtures and its blends with polystyrene/poly (2, 6-dimethyl-p-phenylene oxide). Eur Polym J 1997;33(9):1523e8.

[64] Kalogeras IM, Brostow W. Glass transition temperatures in binary polymer blends. J Polym Sci B Polym Phys 2009;47(1):80e95.

[65] Tjong S, Meng Y. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile-butadiene-styrene) blends. Eur Polym J 2000;36(1):123e9.

[66] Mathew L, Saha P, Kalarikkal N, Thomas S, Strankowski M. Tuning of microstructure in engineered poly (trimethylene terephthalate) based blends with nano inclusion as multifunctional additive. Polym Test 2018;68:395e404.

[67] Moniruzzaman M, Winey KI. Polymer nanocomposites containing carbon nanotubes. Macromolecules 2006;39(16):5194e205.

[68] Khan W, Sharma R, Saini P. Carbon nanotube-based polymer composites: synthesis, properties and applications. In: Carbon nanotubes-current progress of their polymer composites. InTech; 2016.

[69] Pötschke P, Paul D. Formation of co-continuous structures in melt-mixed immiscible polymer blends. J Macromol Sci C Polym Rev 2003;43(1):87e141.

[70] George S, Ramamurthy K, Anand J, Groeninckx G, Varughese K, Thomas S. Rheological behaviour of thermoplastic elastomers from polypropylene/ acrylonitrileebutadiene rubber blends: effect of blend ratio, reactive compatibilization and dynamic vulcanization. Polymer 1999;40(15):4325e44.

[71] Gonzalez-Nunez R, Favis B, Carreau P, Lavallee C. Factors influencing the formation of elongated morphologies in immiscible polymer blends during melt processing. Polym Eng Sci 1993;33(13):851e9.

[72] Yue M, Chian K. Properties and applications of thermoplastic polyurethane blends. In: Advances in engineering fluid mechanics: multiphase reactor and polymerization system hydrodynamics. Elsevier; 1996. p. 747e61.

[73] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; 1989.

[74] Blends P, Paul DR, Newman S, vol. 2. NY: Acdemic Press;1978. p.391.

[75] Xanthos M. Interfacial agents for multiphase polymer systems: recent advances. Polym Eng Sci 1988;28(21):1392-400.

[76] Lambla M, Yu R, Lorek S. Coreactive polymer alloys. In: Multiphase polymers: blends and ionomers; 1988. p. 67-83.

[77] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. J Appl Polym Sci 1990;39(3):655-78.

[78] Xanthos M, Dagli S. Compatibilization of polymer blends by reactive processing. Polym Eng Sci 1991;31(13):929-35.

[79] Liu N, Baker W. Reactive polymers for blend compatibilization. Adv Polym Technol 1992;11(4):249-62.

[80] Cor Koning, Martin Van Duin, Christophe Pagnoulle', Robert Jerome, Strategies for compatibilization of polymer blends, Progress in Polymer Science Volume 23, Issue 4, 1998, Pages 707-757

[81] Bharati A, Wübbenhorst M, Moldenaers P, Cardinaels R. Dielectric properties of phase-separated blends containing a micro-capacitor network of carbon nano-tubes: compatibilization by a random or block copolymer. Macromolecules 2017;50(10):3855-67.

[82] Van der Donck T, Wübbenhorst M, Moldenaers PP. Tuning the phase separated morphology and resulting electrical conductivity of carbon nano-tube-filled PAMSAN/PMMA blends by compatibilization with a random or block copolymer. Polymer 2017;108:483-92.

[83] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. J Appl Polym Sci 1990;39(3):655-78.

[84] Sinha Ray S, Bousmina M. Compatibilization efficiency of organoclay in an immiscible polycarbonate/poly (methyl methacrylate) blend. Macromol Rapid Commun 2005;26(6):450-5.

[85] Yoon KH, Lee HW, Park OO. Properties of poly (ethylene terephthalate) and maleic anhydride-grafted polypropylene blends by reactive processing. J Appl Polym Sci 1998;70(2):389-95.

[86] Ajitha A.R.,Sabu Thomas, Compatibilization of Polymer Blends: Micro and Nano Scale Phase Morphologies, Interphase Characterization and Properties, Book 2020, 640 Pages

[87] Utracki LA. Commercial Polymer Blends. Chapman & Hall, London; New York. 1998

[88] Macosko, C. W., Guegan, P., Khandpur, A. K., Nakayama, A., Marechal, P., Inoue,T. Macromolecules 1996, 29, 5590-5598

[89] Salzano de Luna M, Filippone G. Effects of nanoparticles on the morphology of immiscible polymer blends e challenges and opportunities. Eur Polym J 2016;79:198-218.

[90] Huang J, Yutian Z, Lina X, Jianwen C, Wei J, Xiaoan N. Massive enhancement in the thermal conductivity of polymer composites by trapping graphene at the interface of a polymer blend. Compos Sci Technol 2016;129:160-5

[91] Sadeghi A, Yeganeh MR, Khademzadeh J. Highly conductive PP/PET polymer blends with high electromagnetic interference shielding performances in the presence of thermally reduced graphene nanosheets prepared through melt compounding. Polym Compos 2019.

[92] Subramaniam RT, Yahaya AH, Arof AK. Miscibility studies of PVC blends (PVC/ PMMA and PVC/PEO) based polymer electrolytes. Solid State Ionics 2002;148(3):483-6.

[93] Koning Cor, Van Duin Martin, Pagnoulle Christophe, Jérôme Robert, Strategies For Compatibilization Of Polymer Blends, Progress in polymer science 1998, vol. 23, iss. 4, pp. 707-757

[94] Anastasiadis SH, Gancarz I, Koberstein JT. Interfacial tension of immiscible polymer blends: temperature and molecular weight dependence. Macromolecules 1988;21(10):2980-7.

[95] Majumdar B, Keskkula H, Paul D, Harvey N. Control of the morphology of polyamide/styrene-acrylonitrile copolymer blends via reactive compatibilizers. Polymer 1994:4263-79.

[96] Koning C, Van Duin M, Pagnoulle C, Jerome R. Strategies for compatibilization of polymer blends. Prog Polym Sci 1998;23(4):707-57.

[97] Van Puyvelde P, Velankar S, Moldenaers P. Rheology and morphology of compatibilized polymer blends. Curr Opin Colloid Interface Sci 2001;6(5e6):457-63.

[98] La Mantia FP, Ceraulo M, Mistretta MC, Botta L, Morreale M. Compatibilization of polypropylene/polyamide 6 blend fibers using photo-oxidized polypropylene. Materials 2018;12(1):81.

[99] Rigoussen A, Raquez J-M, Dubois P, Verge P. A dual approach to compatibilize PLA/ ABS immiscible blends with epoxidized cardanol derivatives. Eur Polym J 2019;114:118-26.

[100] Rastin H, Saeb MR, Jafari SH, Khonakdar HA, Kritzschmar B, Wagenknecht U. Reactive compatibilization of ternary polymer blends with coreeshell type morphology. Macromol Mater Eng 2015;300(1):86-98.

[101] Kim S, Kim JK, Park C. Effect of molecular architecture of in situ reactive compatibilizer on the morphology and interfacial activity of an immiscible polyolefin/polystyrene blend. Polymer 1997;38(8):1809-15.

[102] Jazani OM, Arefazar A, Peymanfar MR, Saeb MR, Talaei A, Bahadori B. The influence of NBR-g-GMA compatibilizer on the morphology and mechanical properties of poly (ethylene terephthalate)/polycarbonate/NBR ternary blends. Polym Plast Technol Eng 2013;52(13):1295-302.

[103] Bakhshandeh B, Zarrintaj P, Oftadeh MO, Keramati F, Fouladiha H, Sohrabijahromi S, et al. Tissue engineering; strategies, tissues, and biomaterials. Biotechnol Genet Eng Rev 2017;33:144-72.

[104] Zarrintaj P, Moghaddam AS, Manouchehri S, Atoufi Z, Amiri A, Amirkhani MA, et al. Can regenerative medicine and nanotechnology combine to heal wounds? The search for the ideal wound dressing. Nanomedicine 2017;12:2403-22.

[105] Nilforoushzadeh MA, Amirkhani MA, Zarrintaj P, Salehi Moghaddam A, Mehrabi T, Alavi S, et al. Skin care and rejuvenation by cosmeceutical facial mask. J Cosmet Dermatol 2018;17(5):693-702.

[106] Nilforoushzadeh MA, Zare M, Zarrintaj P, Alizadeh E, Taghiabadi E, HeidariKharaji M, et al. Engineering the niche for hair regeneration-a critical review. Nanomed Nanotechnol Biol Med 2018;15(1):70-85.

[107] Tariverdian T, Zarintaj P, Milan PB, Saeb MR, Kargozar S, Sefat F, et al. Nanoengineered biomaterials for kidney regeneration. In: Nano-engineered biomaterials for regenerative medicine. Elsevier; 2019. p. 325-44

[108] Diban N, Stamatialis D. Polymeric hollowfiber membranes for bioartificial organs and tissue engineering applications. J Chem Technol Biotechnol 2014;89:633-43.

[109] Naffakh M, Díez-Pascual AM, Marco C. Polymer blend nanocomposites based on poly (l-lactic acid), polypropylene and WS2 inorganic nanotubes. RSC Adv 2016;6:40033-44.

[110] Calandrelli L, Calarco A, Laurienzo P, Malinconico M, Petillo O, Peluso G. Compatibilized polymer blends based on PDLLA and PCL for application in bioartificial liver. Biomacromolecules 2008;9:1527-34.

[111] Przybysz M, Zedler Ł, Saeb MR, Formela K. Structure-property relationships in peroxide-assisted blends of poly (ε-caprolactone) and poly (3-hydroxybutyrate). React Funct Polym 2018;127:113-22.

[112] Hassanpour Asl F, Saeb MR, Jafari SH, Khonakdar HA, Rastin H, Pötschke P, et al. Looking back to interfacial tension prediction in the compatibilized polymer blends: discrepancies between theories and experiments. J Appl Polym Sci 2018;135:46144.

Chapter II

Literature Review

II.1. Literature Review

It is well-known that bio-based plastics are prepared using the renewable biomass that offers sustainable alternative to the petroleum-based plastics such as poly(lactic acid) (PLA). PLA is receiving considerable attention due to its biodegradability, renewability and comparable properties with commodity plastics. Recent concerns with respect to the environmental effects have fuelled the need to explore the new alternatives as a potential candidate to compete with commodity plastics, especially from biomass. The use of nondegradable plastics for consumer goods such as packaging material has created a considerable disposal problem. Apart from the environmental issues, the cost of production has been escalated due to its dependency on oil prices. As such, polymers from renewable sources are on the verge of competing with the traditional plastics. PLA is a typical biodegradable polyester obtained by the synthesis of lactic acid (or lactide), which can be produced from renewable resources like corn or sugarcane. In general, PLA is the most promising plastic as its tensile strength and stiffness are similar to polyethylene terephthalate, but it is too brittle to be used commercially. Various types of modifications have been investigated in an effort to improve the elongation and toughness properties of the PLA, and melt blending is one of the most practical and economical methods. Therefore, it is not surprising that PLA has been blended with both nondegradable and biodegradable polymers. Typically, the blending of two different polymers leads to be incompatible blends and shows different phases of blend morphologies, that is, dispersion of one polymer in the matrix of another polymer. Generally, a compatibilizer is used in order to improve the interfacial adhesion that interacts chemically. The compatibilizer minimizes the separation of phases, delamination, agglomeration or skinning and ultimate physical failure.

As an alternative, rubber can be blended with PLA. Rubber particles can act as a stress concentrator enhancing the energy absorption of brittle polymers like PLA and so improve the toughness of the rubber materials. Natural rubber (NR) has attracted more interest than synthetic rubbers due to the fact that it is a renewable resource and has unique properties, such as high elasticity, flexibility and toughness. Nevertheless, the incompatibility between the polar PLA molecules and the non-polar NR chains remains a problem. To circumvent the phase incompatibility of NR and PLA, compatibilizers are generally required to improve the compatibility of the polymer blend.

In this part and for the sake of illustration, a brief presentation of some of the works about compatibilization of poly(lactic acid) and natural rubber (PLA/NR) has been published and which covered the different aspects of the subject. The following research works are presented in the chronological order.

For example, **P. Juntuek et al [1]** have investigated the effect of Glycidyl Methacrylate-Grafted Natural Rubber (NR-g-GMA) as a compatibilizer on the Physical, Structural, and Mechanical Properties of Polylactic Acid /Natural Rubber PLA/NR thermoplastic elastomer (TPE) Blends. Natural rubber was melted blended with polylactic acid (PLA) at various ratios using an internal mixer at the temperature of 170ºC with a rotor speed of 60 rpm for 10 minutes. Fourier transform infrared spectrometer and mechanical properties were also investigated by means of FT-IR spectroscopy, Izod impact and tensile test, respectively. From FT-IR results, it was confirmed that the epoxy group in NR-g-GMA can react with the carboxyl groups of PLA chain ends during blending. These results indicated the enhancement of the interfacial interactions as well as the compatibility between the two polymer phases (i.e: PLA, and NR). They have also found that the impact strength and elongation at break of PLA/NR blend dramatically increased with increasing NR content up to 10% (w/w). The effects of content and %grafting of NR-g-GMA on mechanical properties of PLA/NR blend were also studied. Their results showed that the addition of NR-g-GMA as a compatibilizing agent in PLA/NR TPE blend significantly improved impact strength and elongation at break of PLA/NR blend when compared with that of neat PLA and the control PLA/NR blends. The impact strength and elongation at break of PLA/NR blend increased with increasing NR-g-GMA content up to 1% (w/w).

In another study, the compatibilization of Polylactic Acid / Epoxidized Natural Rubber (PLA/ENR) thermoplastic elastomer Blends was studied by **M. Bijarimi and coworkers [2]** using Liquid Natural Rubber (LNR) as a compatibilizer. The PLA/ENR/LNR blends were melt blending in a Haake internal mixer at 180°C and a mixing speed of 50 $r.min^{-1}$ for 15 minutes. The mechanical, morphological as well as thermal properties were also investigated by means of tensile test, scanning electron microscopic (SEM) examination, and differential scanning calorimetric (DSC) analysis, respectively. They have found that the addition of LNR as a compatibilizer has improved the tensile strength and elongation at break for the compositions of the 40PLA/55ENR/5LNR compatibilized system when compared to those of the uncompatibilized PLA/ENR blends. The elongation at break for the blend with 5% of LNR which was used as a compatibilizer showed a twofold increment compared with the blend

without LNR. The increase in tensile strength as well as elongation at break was associated with the ability of LNR to promote the uniform dispersion between the natural rubber (NR) and PLA phases as observed in the SEM analysis. Moreover, the differential scanning calorimetric results indicated that the compatibilized PLA/ENR blends showed the highest degree of crystallinity and thus contributed to improving their mechanical properties.

Y. Huang et al [3] studied the effects of Dicumyl Peroxide (DCP) as a compatibilizer as well as a cross-linker agent on the thermal, and mechanical properties of PLA/NR TPE Blends. The PLA/NR/DCP blends with various DCP contents were melt blending in a Haake internal mixer at 170°C and a rotor speed of 60 rpm for 10 minutes. Their results indicated that the crystallization temperatures of PLA and PLA/ NR blends can be reduced by the introduction of DCP. An increase of the crystallinity, generated during cooling period, has been noticed while introducing enough DCP (≥0.5 wt%). Thermogravimetric analysis (TGA) results have revealed that the NR components have caused lower thermal stability of PLA/NR blends, compared to PLA. Different from NR, DCP does not affect the thermal stability of PLA and PLA/NR blends. Mechanical properties test shows that the impact strength has improved with increasing DCP. The results of the mechanical properties indicated also that the DCP could increase the compatibility of poly(lactic acid) and natural rubber. In other words, with small amount of Dicumyl peroxide, the effect on NR toughening PLA was enhanced and the tensile toughness of PLA/NR blends was improved. When the DCP content was up to 0.2 wt%, the PLA/NR blend reached the maximum elongation at break (26.21 %) which was 2.5 times compared to those of neat PLA (the elongation at break of neat PLA was 10.7 %). The mechanism of action of DCP as a compatibilizing agent involves its ability to generate free radicals upon thermal or mechanical activation. These free radicals can then react with the functional groups on the chains of the other polymer, creating a chemical bond between the two polymers and improved the interfacial adhesion between the two phases.

In another study, the effects of the Natural rubber grafted with poly(vinyl acetate) copolymer (NR-g-PVAc) as a compatibilizer on the Mechanical, Dynamic mechanical, and thermal Properties of Polylactic Acid /Natural Rubber (PLA/NR) (TPE) Blends was investigated by **W. Chumeka et al [4].** The preparation of the PLA/NR/NR-g-PVAc blends was performed in a twin screw extruder at 160 °C and a screw speed of 190 rpm. The mechanical, dynamic mechanical and thermal properties were also investigated by means of Izod impact strength, tensile test, Dynamic mechanical thermal analysis (DMTA), and differential scanning calorimetry (DSC). Characterization by tensile test, DMA and DSC showed an enhancement in

miscibility of the PLA/NR/NR-g-PVAc blends. NR-g-PVAc could be used directly as a toughening agent of PLA or a compatibilizer of the PLA/NR blend. NR mastication could be applied to the blends containing NR-g-PVAc for improvement of the impact strength and elongation at break. This could be attributed to improve the interfacial interaction and reduce the interfacial tension between the two polymer phases. The presence of PVAc in the NR-g-PVAc copolymer increased the miscibility of PLA and NR by decreasing the temperature of the maximum tan d of PLA in the blends. The higher the grafted PVAc content, the lower the temperature of the maximum tan δ peak. NR and NR-g-PVAc acted as a nucleating agent for PLA by inducing the cold crystallization and increased the crystallinity in the second heating scan.

W. D. N. Ayutthaya & S. Poompradub [5] investigated the effects of the 03/01 Phr (parts by weight per hundred parts of resin) of co-compatibilizer based on Epoxidized Natural Rubber and Poly(methyl methacrylate) (ENR/PMMA) in the mechanical, and thermal properties of 100/15 PLA/NR thermoplastic elastomer blends. The formulation of the PLA/NR/ENR/PMMA polymer blends were melt blending with an internal mixer at 200 °C and rotor speed of 80 rpm for 15 minutes. The mechanical, and thermal properties were investigated by means of tensile test, thermogravimetric analysis and differential scanning calorimetry (DSC), respectively. They have found that the elongation at break and impact strength of the 100:15 phr PLA/NR blend was significantly improved up to 1,813% and 362%, respectively. The thermal stability of the PLA/NR blend was also increased when using the co-compatibilizers. Interestingly, the PLA/NR blend containing the co-compatibilizer showed a high ultimate tensile strength after thermal aging at 100 °C for 1 h with good mechanical properties. However, the percentage of crystallinity and glass transition temperature were decreased by the added co-compatibilizer. The use of ENR/PMMA was shown to be an effective co-compatibilizer for a 100/15 phr PLA/NR blend. This may be attributed to the epoxy group of ENR could react with the carbonyl groups of PMMA via hydrogen bonding and the carbonyl groups of PMMA could induce a dipole force with the ester group of the PLA chain during processing. The π-π interaction between the double bonds of NR and ENR molecular chains could also be achieved.

In another study, the compatibilization of Polylactic Acid / Natural Rubber (PLA/NR) thermoplastic elastomer Blends was investigated by **N. N. B. Mohammad et al [6]** using Polylactic Acid grafted Maleic Anhydride (PLA-g-MA) as a compatibilizer. The preparation of PLA-g-MA was carried out using internal mixer by free radical melt grafting reaction followed by Fourier Transform Infrared Spectroscopy (FTIR) analysis to confirm the grafting reaction.

PLA was blended with different ratio of natural rubber (0 to 20 wt.%) through melt blending in a twin screw extruder. To investigate the compatibilization effect on the mechanical properties of PLA/NR blends, PLA-g-MA was added to the blends at various compositions (1 – 10 phr). The mechanical properties of the control PLA/NR as well as PLA/NR/PLA-g-MA were also reported by means of tensile test. From their results, the FTIR analysis indicated confirmation of grafted MA onto PLA. They have also found that the results of tensile strength, and young's modulus of the uncompatibilized PLA/NR blends were decreased which means the poor mechanical properties due to the interfacial tension between the two polymer phases. Supported with the addition of the compatibilizer, the mechanical properties of material were significant improved (i.e: increased in the tensile strength, young's modulus, and a decreased in the elongation at break) and 3 phr of PLA-g-MA was selected as the best content of compatibilizer in order to get higher performance and best mechanical properties of samples. These improvements can mainly be attributed to a compatibilizing effect of PLA-g-MA resulting in a more homogeneous phase distribution and excellent interfacial adhesion between the components.

In another publication, **N. N. B. Mohammad et al [7]** investigated the effects of carbon nanotube (CNT) as a reinforcement filler as well as PLA grafted Maleic Anhydride (PLA-g-MA) as a compatibilizing agent (CA) in the mechanical properties of Polylactic acid / Natural rubber (PLA /NR) TPE blends. TPE blends were prepared by melt blending method in a twin screw extruder. To investigate the effects of the reinforcement filler as well as the compatibilizer on the mechanical properties of PLA/NR blends, CNT and CA were added to the blends at various contents. The mechanical properties of the PLA/NR/PLA-g-MA/CNT blends were reported by means of tensile test. They have found that the tensile strength of the PLA/NR/PLA-g-MA without CNT showed higher mechanical properties. However, with increasing CNT content, Young's modulus and flexural modulus were increased firstly and then decreased as CNT was further added. This phenomenon could be attributed to the presence of agglomerations which caused a poor dispersion of CNT in the matrix system and its responsible also on the lack of enhancement and improvement in the mechanical properties.

In another study, **N. S. A. Sani and coworkers [8]** have studied the effects of two types of compatibilizer namely: PLA grafted maleic anhydride (PLA-g-MA) and NR grafted MA (NR-g-MA) in the thermal and mechanical properties of (PLA/NR) blends. The PLA/NR blends with compatibilizer were melt blended using a counter-rotating twin screw extruder with the mixing temperature varied between 160 to 190°C. The PLA-g-MA and NR-g-MA were added

in the control PLA/NR TPE blends at various contents (1, 3, 5 and 10 wt.%, respectively). The mechanical and thermal properties of the uncompatibilized as well as compatibilized samples were investigated by means of tensile, flexural, impact strength tests, and thermogravimetric analysis, respectively. From the results, the addition of PLA-g-MA in PLA/NR blend improved the impact strength and elongation at break of the blends as compared with neat PLA and PLA/NR blend without compatibilizer and for thermal stability, it only had a slight influence on the blends. Addition of NR-g-MA on contrary did not give improvement on mechanical properties but increasing in thermal stability.

C. Pattamaprom and coworkers [9] investigated the effects of Sorbitan Ester (SE) as a compatibilizer on the impact resistance of (PLA/NR) Blends. Their study is focused on the enhancement of impact strength of polylactic acid blended with masticated natural rubber using sorbitan ester, as a compatibilizing agent. The effects of NR mastication, compatibilizer and NR contents and the mixture's viscosity on the impact strength properties of PLA/NR blends were investigated by means of Izod impact test. In relation to the changes in the morphology, thermal behavior and impact strength of PLA/NR blends. They have found that the optimum viscosity of NR that provided the highest impact strength to the blends was achieved when NR was masticated at 40 rpm for 15 min. The highest impact strength corresponded well not only with the small NR phase size, but also with the highest crystallization rate. For the effect of compatibilizer, it was found that a small amount of SE could more than double the impact strength of the blends, where the optimum compatibilizer content was 0.5 wt%. Interestingly, the high impact strength of the blends in all cases was accompanied by short interparticle distance and slightly higher percent crystallinity.

N. N. B. Mohammad et al [10] studied the effects of the compatibilizing agent (CA) based on maleic anhydride (MA) grafted natural rubber (NR-g-MA) on the mechanical properties of PLA/NR systems. Melt blending of PLA/NR/NR-g-MA was performed in a twin screw extruder at screw speed of 100 rpm and at the range of temperature (160 ˚C to 180 ˚C). Fourier transform infrared spectrometer and mechanical properties were also investigated by means of FT-IR spectroscopy, flexural and tensile test, respectively. The effect of (CA) on the mechanical properties of PLA/NR blends was investigated with addition 3 phr of NR-g-MA. FTIR result confirmed grafting reaction occurred between MA and NR. Their results indicated also that the tensile strength and young's modulus of PLA/NR blends without (CA) were dramatically decreased. However, PLA/NR blend with NR-g-MA provided an improvement in young's modulus, elongation at break, and slightly in tensile strength compared to the control PLA/NR

samples. The impact strength of the blends was also found a significantly enhancement as expected with increasing of NR content. Overall, their results showed that the addition of NR-g-MA as a compatibilizing agent in PLA/NR TPE blend significantly improved impact strength and elongation at break of PLA/NR blend compared to those of neat PLA and the control PLA/NR blends. These results could be attributed to the enhancement of the interfacial interactions as well as the development of compatibility between the two polymer phases (i.e.: PLA, and NR).

In another study, the effects of telechelic liquid natural rubber (TLNR) as a compatibilizer on the structural, thermal, mechanical, and morphological properties of polylactic acid and natural rubber blends was investigated by **N. A. Rosli and coworkers [11]**. PLA/NR Blends were prepared by melt blending in a Brabender Plasticorder internal mixer at 170 °C for a rotor speed of 60 rpm for 12 minutes. Structural analyses, morphological examination, thermal behavior, and mechanical properties were also investigated by means of FT-IR spectroscopy, Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Izod impact and tensile tests. FT-IR analysis indicated that there are two possible chemical interactions between PLA and LNR, which was confirmed by an increase in tensile and impact strength with increasing LNR addition up to an optimum value of 6 wt% LNR. SEM micrographs revealed that morphological aspects such as interfacial adhesion and particle size are the main factors affecting the mechanical properties of the blends. The glass transition temperature (Tg) and crystallization temperature (Tc) values obtained by DSC analysis corresponded well with the results obtained by mechanical testing. On the basis of this, it is concluded that LNR is both a good nucleation agent for PLA and a good compatibilizer for PLA and NR.

N. N. B. Mohammad et al [12] reported the Influence of compatibilizers on the structure properties of Polylactic Acid/Natural Rubber Blends. Two different of compatibilizers, namely: maleated PLA (PLA-g-MA) and maleated NR (NR-g-MA) were used as coupling agents. The blends were prepared using twin screw extruder at various contents of NR. Mechanical, thermal and morphological analyses were carried by means of tensile and flexural properties, DSC, SEM analyses to evaluated the effects of compatibilizers on the PLA/NR blends. It was found a significant performance was achieved in mechanical properties particularly in elongation at break 10 wt % and impact strength up to 15 wt % of NR content by adding NR-g-MA into polymer blend. Although further increased in NR content may slightly sacrificed the polymer strength probably because of agglomeration due to higher loading of NR but still improvement in impact strength should give a wide opportunity in its applications. Glass transition

temperature (Tg) was significantly decreased approaching the glass transition temperature of neat PLA (58.06°C) by the addition of compatibilizers explained a better progress in compatibility of polymer blend between PLA and NR. Furthermore, an increment of thermal stability almost 5–10% of the compatibilized blends as compared to virgin PLA influenced by the interaction and dispersion of the components. Observation by SEM illustrated a slightly improvement in the interfacial adhesions with no formation of void and the presence of spherical NR particle were almost absent in polymer blend. No biodegradation testing had done in this study because more focusing on renewability of PLA an alternative to conventional petroleum-based polymeric materials.

The effects of compatibilizers on morphology, mechanical and thermal properties of polylactic acid (PLA)/natural rubber (NR) blends were determined with the composition of 95/5 PLA/NR and studied by **N. N. B. Mohammad et al [13].** The PLA/NR blend was incorporated with two different compatibilizers: maleated polylactic acid (PLA-g-MA) and maleated natural rubber (NR-g-MA) at various loadings (1-10 phr) and compounding was prepared using twin screw extruder. The samples were then characterized using SEM, DSC, and DMA. The SEM results showed better interfacial adhesion between PLA and NR phases was achieved upon addition of 3 phr PLA-g-MA. In all cases, further increased PLA-g-MA and NR-g-MA up to 5 phr and 10 phr, respectively in the 95/5 PLA/NR blend caused the blend stiffness to decrease as decreasing in degree of crystallinity of PLA showed in DSC analysis. DSC results revealed also that the melting points of both blends remain roughly unchanged while the crystallization temperature of the blends slightly decreased. DMA study showed that 3 phr PLA-g-MA exhibited the highest value of storage modulus and with further addition of compatibilizer, the stiffness of the blends was decreased which indicated that the elastic properties were reduced by addition of PLA-g-MA and also NR-g-MA. As the result, PLA-g-MA has played a good role as compatibilizer compared to NR-g-MA according those analyses. The effective composition of PLA-g-MA was 3 phr as it was showed better performance towards PLA properties compared to others formulations.

In another study, the effects of NR-graft-PLA as a compatibilizer on the morphological, thermal, and mechanical properties of polylactic acid and natural rubber blends was investigated by **P. Sookprasert & N. Hinchiranana [14]**. Natural rubber (NR) is expected to enhance impact strength of poly(lactic acid) (PLA). Because the polarity difference of NR and PLA leads PLA/NR blends having phase separation and poor mechanical properties. The morphological examination, thermal behavior and mechanical properties were also investigated

by means of SEM micrographs, DSC, TGA analysis and impact strength, respectively. With respect to the compatibility between PLA and NR phases in the PLA/NR blend with NR-g-PLA, SEM analysis indicated that the incorporation of NR-g-PLA reduced the size of the NR phase dispersed in the PLA/NR blend resulting in a better NR dispersion in the PLA phase. Moreover, the addition of 1–3% (w/w) NR-g-PLA into the PLA/NR blend slightly increased the Tg of the NR phase with a slight reduction of Tg for the PLA segment. This reflected that the NR-g-PLA promoted a partial compatibility between the NR and PLA constituents in the blends. Moreover, it was observed that the PLA/NR/NR-g-PLA blends exhibited the higher resistance to the thermal decomposition of the uncompatibilized one. They have also found that the addition of NR-g-PLA into PLA/NR blend increased Izod impact strength of the neat PLA due to partial miscibility of systems.

S. Pongsathit and C. Pattamaprom [15] investigated the effects of the compatibilizing agent (CA) based on maleic anhydride (MA) grafted natural rubber (NR-g-MA) on the structural, mechanical, and thermal properties of PLA/NR systems. The FT-IR spectrometer, Proton-nuclear magnetic resonance (^{1}H-NMR) analysis have confirmed successful grafting of MA onto NR. The grafted NR were then used to increase the compatibility and the impact property of PLA/NR blends. It was also found that the highest impact strength of the blends was achieved when the grafting was carried out. On the aspect of thermal properties, it was found that the thermal properties of PLA/NR blends were not affected by the presence of NR-g-MA.

In another paper, **V. Tanrattanakul et al [16]** studied the effects of Natural rubber grafted with maleic anhydride (NR-g-MA) as a compatibilizer on the structural, morphology, thermal and mechanical properties of poly(lactic acid)/natural rubber blends. PLA/NR/NR-g-MA were prepared in a twin screw extruder at temperature of 170°C with a rotor speed of 150 rpm. Mechanical, morphological, thermal and analysis were carried out by means of tensile, Izod impact, flexural tests, SEM spectroscopy, and dynamic mechanical thermal analysis (DMTA) to evaluated the effects of compatibilizer on the PLA/NR blends. NR-g-MA was a better impact modifier than NR. The PLA/NR-g-MA blends had greater impact strength and tensile properties than neat PLA and a PLA/NR blend. The presence of MA in the polymer blends reduced the average particle diameter which suggested improved miscibility in the polymer blends. The α-transition temperature of the blends was determined by dynamic mechanical thermal analysis.

J. Klinkajorn & V. Tanrattanakul [17] reported the effects of the epoxidized natural rubber grafted with maleic anhydride (ENR-g-MA) as a compatibilizer agent on the structural,

morphologies, thermal and mechanical properties of the control PLA/ENR systems. PLA/ENR/ENR-g-MA with ratio of 90/5/5 were prepared by melt-blending in an internal mixer at 170 °C using a rotor speed of 60 rpm for 10 minutes. The grafting reaction of MA onto the ENR backbone (ENR-g-MA) was successfully achieved using the heat and shearing action produced by the internal mixer. The morphological behavior, thermal, as well as mechanical properties were also investigated by means of SEM examination, DSC analysis, Izod impact, and tensile test, respectively. As a result, the interfacial adhesion between PLA and ENR was increased, which reduced the size of rubber particles in the matrix. Higher MA concentrations in ENR-g-MA produced smaller rubber particle sizes. With increments of MA concentration, the α-transition temperature of PLA decreased and the α-transition temperature of ENR increased. These results indicate that the miscibility of the PLA/ENR blends was improved. The impact strength and elongation at break were greater in the PLA/ENR-g-MA and PLA/ENR/ENR-g-MA blends than in PLA. These improvements were attributed to the small rubber particle diameter and good miscibility of the blends. PLA/ENR-g-MA showed better mechanical properties than PLA/ENR/ENR-g-MA blends. The optimal MA concentration was 0.60 phr.

In another study, the effects of compatibilizers as well as reinforcement filler on the rheological properties of PLA/NR were investigated by **N. N. B. Mohammad and coworkers [18]**. Polylactic Acid (PLA) was blended with Natural Rubber (NR) and compatibilized by PLA grafted maleic anhydride (PLA-g-MA) and NR grafted maleic anhydride (NR-g-MA) to achieve high performance of PLA/NR blends. Pristine carbon nanotube (CNT) was then added into PLA/NR blends with different CNT loading (1–8 part per hundred resin) as a reinforcement filler using melt blending technique to form nanocomposites. A systematic investigation of the rheological properties of the nanocomposites as a function of pristine CNT content were carried out using an AR2000 rheometer. Rheological analysis exhibited an enhancement in the storage and loss moduli of nanocomposites compared to those of the blends without CNT. The compatibilizers namely: PLA-g-MA and NR-g-MA have shown contrasting results in terms of rheological values. Rheological analysis showed that the both sets of nanocomposites behaved solid-like at lower frequencies. When the CNT loading was increased the nanocomposites showed no dependence of frequency.

In order to improve the interfacial adhesion between PLA and NR, **T. Udomkitpanya & K. Srikulkit [19]** studied the effects of reactive compatibilization on the PLA/NR system. Poly(acrylic acid) (PAA) was grafted onto natural rubber (NR) to enhance the compatibility of

NR and poly(lactic acid) (PLA). PLA/NR-g-PAA was prepared by an internal mixer at 170ºC with a rotor speed of 45 rpm. Fourier-transform infrared spectroscopy (FT-IR), tensile test, impact strength, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to determine the functional group, mechanical behavior and thermal properties of blends, respectively. ATR-FTIR spectra showed a peak at 1718 cm^{-1}, confirming that PAA was grafted onto NR backbone. Results showed that the addition of NR-g-PAA significantly improved the elongation, impact strength and thermal stability of blends.

S. Srisuwan et al [20] have studied the effects of triblock copolymers based on liquid natural rubber and low molecular weight poly(lactic acid) on physical properties of poly(lactic acid)/natural rubber blend. Triblock copolymers of poly(lactic acid) (PLA) and natural rubber (NR) (PLA–NR– PLA) with different lengths of PLA end blocks were produced from hydroxyl-terminated liquid natural rubber (HTLNR) and low molecular weight PLA (pre-PLA). The HTLNR with a number-average molecular weight ($\bar{M}n$) ~ 28,000 g/mol obtained from photochemical degradation of NR and pre-PLA with varying molecular weight ($\bar{M}n$ ~ 3000, ~ 6500, ~ 9700 g/mol) was subjected to condensation polymerization. The compatibilizing effect of copolymers on the physical properties of the PLA/NR system was studied using PLA/NR/PLA–NR–PLA blend ratios of 90/10/0, 90/9/1, 90/8/2 and 90/7/3 by weight percent (wt%). The mechanical properties, morphological examination, and thermal analysis of uncompatibilized as well as compatibilized PLA/NR were also investigated by means of tensile, impact tests, SEM, DSC analysis. From the tensile testing results, elongation at break of the blends increased with an increase in the amount of triblock copolymer and with the length of the PLA end block. The blend without the copolymer showed elongation at break of 60.54%, whereas the blend with 3 wt% of PLA–NR–PLA prepared from pre-PLA with $\bar{M}n$ of ~ 9700 g/mol showed elongation at break of 199.38%. This was about a 300% increase. The highest impact strength of 79.58 kJ/m^2 (400% higher than neat PLA) was also found for the blend containing 3 wt% of PLA–NR–PLA with the longest PLA end block. A reduction in the diameter and well dispersion of the rubber particles in the PLA matrix were seen in micrographs taken with a scanning electron microscope. In general, after the addition of PLA–NR–PLA into a PLA/NR blend, the Tg of NR phase shifted to a higher temperature, whereas the Tg of the PLA phase decreased. The PLA–NR–PLA triblock copolymer with the longest PLA end block is possibly used as an effective compatibilizer for the PLA/NR blend.

In another study, The effects of PLA-g-ENR on compatibility of poly(lactic acid)/epoxidized natural rubber blends were studied by **J. Klinkajorn & V. Tanrattanakul [21]**. The effect of

the epoxide content in epoxidized natural rubber (ENR) on the miscibility and compatibility with poly(lactic acid) (PLA) was also considered. PLA was blended with 10 wt% of ENRs (epoxidized at 10, 15, 20, and 25 mol%). Their study showed that the in-situ graft copolymer, PLA-g-ENR, was formed during melt blending in the blends containing 10 and 15 mol% ENR. The thermal behavior, morphologies, and mechanical properties were evaluated by means of DSC, SEM microscopy, tensile, and impact tests. They have found that the PLA-g-ENR acted as a compatibilizer, producing a partially miscible blend, indicated by an inward shift of the α-transition temperatures of PLA and ENR in the blends. PLA-g-ENR also greatly reduced the particle size of ENR and increased the impact strength, tensile strength, and elongation at break of the blends. The epoxide content of ENR changed deformation mechanisms of the blends.

In another paper, **A. Burkov and coworkers [22]** were reported the effects of epoxidized soybean oil (ESO) as a natural plasticizer and compatibilizer on the mechanical, thermal, and morphological properties of PLA/NR system. The PLA/NR/ESO were prepared by melt blending in a closed double-rotor mixer at temperature of 160 °C and a rotor speed of 60 rpm for 30 minutes. From their results, the PLA/NR/ESO demonstrated the best mechanical properties. ESO compounding in the PLA-NR blends increased the mobility of the biopolymers molecular chains and improved the thermal stability of the novel material. The size of the NR domains embedded in the continuous PLA matrix decreased with the ESO content increment. The combination of thermal analysis and scanning electron microscopy enabled the authors to determine the features of potential packaging material and the optimal content of PLA/NR/ESO for the best mechanical properties. Thus, ESO is an effective multifunctional additive in PLA-NR blends. ESO simultaneously acts as a compatibilizer and plasticizer. As a plasticizer, ESO exhibits a decrease in viscosity, an increase in segmental mobility, processability of material, and elongation at break. Its impact as a compatibilizer upon the morphology of the blends could be proven by SEM micro-photos (a decrease in the dimension for the 2nd phase).

References

[1] Juntuek, P.; Ruksakulpiwat, C.; Chumsamrong, P.; Ruksakulpiwat, Y. Effect of Glycidyl Methacrylate-Grafted Natural Rubber on Physical Properties of Polylactic Acid and Natural Rubber Blends. J. Appl. Polym. Sci. 2012, 125 (1), 745–754. https://doi.org/10.1002/app.36263.

[2] Bijarimi, M.; Ahmad, S.; Rasid, R. Mechanical, Thermal and Morphological Properties of Poly(Lactic Acid)/Epoxidized Natural Rubber Blends. Journal of Elastomers & Plastics 2014, 46 (4), 338–354. https://doi.org/10.1177/0095244312468442.

[3] Huang, Y.; Zhang, C.; Pan, Y.; Wang, W.; Jiang, L.; Dan, Y. Study on the Effect of Dicumyl Peroxide on Structure and Properties of Poly(Lactic Acid)/Natural Rubber Blend. J Polym Environ 2013, 21 (2), 375–387. https://doi.org/10.1007/s10924-012-0544-0.

[4] Chumeka, W.; Tanrattanakul, V.; Pilard, J.-F.; Pasetto, P. Effect of Poly(Vinyl Acetate) on Mechanical Properties and Characteristics of Poly(Lactic Acid)/Natural Rubber Blends. J Polym Environ 2013, 21 (2), 450–460. https://doi.org/10.1007/s10924-012-0531-5.

[5] Ayutthaya, W. D. N.; Poompradub, S. Thermal and Mechanical Properties of Poly(Lactic Acid)/Natural Rubber Blend Using Epoxidized Natural Rubber and Poly(Methyl Methacrylate) as Co-Compatibilizers. Macromol. Res. 2014, 22 (7), 686–692. https://doi.org/10.1007/s13233-014-2102-1.

[6] Mohammad, N. N. B.; Arsad, A.; Rahmat, A. R.; Talib, M. S.; Mat Desa, M. S. Z. Influence of Compatibilizer on Mechanical Properties of Polylactic Acid/Natural Rubber Blends. AMM 2014, 554, 81–85. https://doi.org/10.4028/www.scientific.net/AMM.554.81.

[7] Mohammad, N. N. B.; Arsad, A.; Rahmat, A. R.; Mat Des, S. Z.; Abdullah Sani, N. S. Effect of Carbon Nanotube on the Mechanical Properties of Compatibilized Polylactic Acid/Natural Rubber Blend. *AMM* 2014, *695*, 273–276. https://doi.org/10.4028/www.scientific.net/AMM.695.273.

[8] Abdullah Sani, N. S.; Arsad, A.; Rahmat, A. R.; Mohammad, N. N. B. Effects of Compatibilizer on Thermal and Mechanical Properties of PLA/NR Blends. MSF 2015, 819, 241–245.

https://doi.org/10.4028/www.scientific.net/MSF.819.241

[9] Pattamaprom, C.; Chareonsalung, W.; Teerawattananon, C.; Ausopron, S.; Prachayawasin, P.; Van Puyvelde, P. Improvement in Impact Resistance of Polylactic Acid by Masticated and Compatibilized Natural Rubber. Iran Polym J 2016, 25 (2), 169–178.

https://doi.org/10.1007/s13726-015-0411-7.

[10] Mohammad, N. N. B.; Arsad, A.; Rahmat, A. R.; Abdullah Sani, N. S. Effects of Maleated Natural Rubber on Mechanical Properties of Polylactic Acid/Natural Rubber Blends. *MSF* **2015**, *819*, 284–289.

https://doi.org/10.4028/www.scientific.net/MSF.819.284.

[11] Rosli, N. A.; Ahmad, I.; Anuar, F. H.; Abdullah, I. Mechanical and Thermal Properties of Natural Rubber-Modified Poly(Lactic Acid) Compatibilized with Telechelic Liquid Natural Rubber. Polymer Testing 2016, 54, 196–202.

https://doi.org/10.1016/j.polymertesting.2016.07.021.

[12] Mohammad, N. N. B.; Arsad, A.; Rahmat, A. R.; Abdullah Sani, N. S.; Ali Mohsin, M. E. Influence of Compatibilizer on the Structure Properties of Polylactic Acid/Natural Rubber Blends. Polym. Sci. Ser. A 2016, 58 (2), 177–185.

https://doi.org/10.1134/S0965545X16020164.

[13] Mohammad N.N.B.; Arsad A.; Sani N.A.; Basri M.H. Effect of Compatibilizers on Thermal and Morphological Properties of Polylactic Acid/Natural Rubber Blends. Chemical Engineering Transactions 2017, 56, 1027–1032.

https://doi.org/10.3303/CET1756172.

[14] Sookprasert, P.; Hinchiranan, N. Morphology, Mechanical and Thermal Properties of Poly(Lactic Acid) (PLA)/Natural Rubber (NR) Blends Compatibilized by NR- Graft - PLA. J. Mater. Res. 2017, 32 (4), 788–800.

https://doi.org/10.1557/jmr.2017.9.

[15] Pongsathit, S.; Pattamaprom, C. Irradiation Grafting of Natural Rubber Latex with Maleic Anhydride and Its Compatibilization of Poly(Lactic Acid)/Natural Rubber Blends. Radiation Physics and Chemistry 2018, 144, 13–20. https://doi.org/10.1016/j.radphyschem.2017.11.006.

[16] Tanrattanakul, V.; Jaratrotkamjorn, R.; Juliwanlee, W. Effect of Maleic Anhydride on Mechanical Properties and Morphology of Poly(Lactic Acid)/Natural Rubber Blend. 2020.

[17] Klinkajorn, J.; Tanrattanakul, V. Compatibilization of Poly(Lactic Acid)/Epoxidized Natural Rubber Blend with Maleic Anhydride. J. APPL. POLYM. SCI. 2019. DOI: 10.1002/app.48297

[18] Mohammad, N. N. B.; Arsad, A.; Choi, H. J.; Ngadi, N.; Mat Desa, M. S. Z. Influences of Pristine Carbon Nanotube on the Rheological Properties of Compatibilized Polylactic Acid/Natural Rubber Nanocomposite. Materials Today: Proceedings 2021, 39, 951–955. https://doi.org/10.1016/j.matpr.2020.04.211.

[19] Udomkitpanya, T.; Srikulkit, K. Properties of Poly(Lactic Acid) Blended with Natural Rubber-Graft- Poly(Acrylic Acid). KEM 2020, 845, 45–50. https://doi.org/10.4028/www.scientific.net/KEM.845.45

[20] Srisuwan, S.; Ruksakulpiwat, Y.; Chumsamrong, P. Effect of Triblock Copolymers Based on Liquid Natural Rubber and Low Molecular Weight Poly(Lactic Acid) on Physical Properties of Poly(Lactic Acid)/Natural Rubber Blend. Polym. Bull. 2021, 78 (3), 1253–1273. https://doi.org/10.1007/s00289-020-03158-8.

[21] Klinkajorn, J.; Tanrattanakul, V. The Effect of Epoxide Content on Compatibility of Poly(Lactic Acid)/Epoxidized Natural Rubber Blends. J Appl Polym Sci 2020, 137 (34), 48996. https://doi.org/10.1002/app.48996.

[22] Burkov, A.; Kraev, A.; Grishin, M.; Vesnin, R.; Fomin, S.; Iordanskii, A. Structural Features and Properties' Characterization of Polylactic Acid/Natural Rubber Blends with Epoxidized Soybean Oil. Polymers 2021, 13 (7), 1101. https://doi.org/10.3390/polym13071101.

General Conclusion

General Conclusion

In conclusion, the compatibilization of PLA/NR blends is a promising technique for improving, enhancing the properties and performance of biodegradable polymers. Blending PLA and NR can lead to materials with desirable properties, but the immiscibility of these two polymers can cause phase separation and reduced the mechanical properties. The addition of a third component called Compatibilizing Agent (CA) , can improve the interfacial adhesion and interfacial interaction between two polymer phases (i.e.: PLA ,and NR) and prevent phase separation.

By the way, various types of compatibilizers, such as **PLA-g-MA, NR-g-MA, PLA-g-NR** as well as **ENR**, have been investigated for their effectiveness in improving the compatibility of PLA/NR blends. The use of these compatibilizers has led to improve the Rheological, Mechanical, Dynamic Mechanical, Morphological, and Thermal properties, which are critical for various applications in industrial fields.

The compatibilization of PLA/NR blends has significant potential in various industries, such as packaging, automotive, and biomedical industries, where biodegradable polymers are becoming increasingly important. The development of new and effective compatibilizers is critical for the creation of high-performance materials with enhanced properties, which can be tailored for specific applications.

Overall, the compatibilization of PLA/NR blends is an important area of research that has the potential to lead to the creation of new and innovative biodegradable materials with enhanced properties and performance.

Abstract

This Master Thesis investigates the effects of various compatibilizers on the Rheology, Morphology development, Dynamic Mechanical, Mechanical, and Thermal properties of immiscible thermoplastic elastomers based on Poly (lactic acid)/Natural Rubber **(PLA/NR)** blends. The main aim of this study is focused to improve the compatibility between the two polymer phases by different strategies of compatibilization, which can lead to enhanced the mechanical properties and performance of **PLA/NR TPE** system. The results showed that the addition of compatibilizers significantly improved the compatibility between **PLA** and **NR,** leading to improve the interfacial adhesion, reduced phase separation and interfacial tension. Overall, this study demonstrates that the use of compatibilizing agents can significantly improve the properties and performance of **PLA/NR** blends which can be tailored for specific applications in various industrial fields.

Keywords Thermoplastic Elastomers, Poly (lactic acid), Natural Rubber, Blends, Immiscible, Compatibilizing Agents, Compatibility, Interfacial Adhesion.

Résumé

Ce mémoire de master étudie les effets de divers compatibillisateurs sur les propriétés Rhéologiques, Morphologiques, Mécaniques, Mécaniques et Thermiques des Elastomères Thermoplastiques non miscibles à base de poly (acide lactique) /caoutchouc naturel **(PLA/NR).** L'objectif principal de cette étude est d'améliorer la compatibilité entre les deux phases polymères par différentes stratégies de comptabilisation, ce qui peut conduire à l'amélioration des propriétés mécaniques et des performances du système **PLA/NR TPE**. Les résultats ont montré que l'ajout de compatibillisateurs a considérablement amélioré la compatibilité entre **PLA** et **NR**, ce qui a amélioré l'adhérence interfaciale, réduit la séparation de phase et la tension interfaciale. Dans l'ensemble, cette étude démontre que l'utilisation d'agents compatibillisants peut améliorer considérablement les propriétés et les performances des mélanges **PLA/NR** qui peuvent être adaptés à des applications spécifiques dans divers domaines industriels.

Mots clés Élastomères thermoplastiques, poly (acide lactique), caoutchouc naturel, mélanges, non miscibles, agents compatibillisants, compatibilité, adhésion interfaciale.

الملخص

تبحث هذه الأطروحة الرئيسية في تأثيرات مختلف الموافقات على علم الريولوجيا، وتطوير المورفولوجيا، والخصائص الميكانيكية والميكانيكية والحرارية الديناميكية للمرونات البلاستيكية الحرارية غير القابلة للانقسام القائمة على خلطات بولي (حمض اللاكتيك)/المطاط الطبيعي (**PLA/NR**). يركز الهدف الرئيسي لهذه الدراسة على تحسين التوافق بين مرحلتي البوليمر من خلال استراتيجيات مختلفة للتوافق، مما قد يؤدي إلى تعزيز الخصائص الميكانيكية وأداء نظام **PLA/NR TPE**. أظهرت النتائج أن إضافة أجهزة التوافق حسنت بشكل كبير التوافق بين **PLA** و **NR**، مما أدى إلى تحسين الالتصاق البيني، وتقليل فصل الطور والتوتر البيني. بشكل عام، توضح هذه الدراسة أن استخدام العوامل المتوافقة يمكن أن يحسن بشكل كبير خصائص وأداء خلطات **PLA/NR** التي يمكن تصميمها لتطبيقات محددة في مختلف المجالات الصناعية.

الكلمات المفتاحية مواد مطاطية بلاستيكية حرارية، بولي (حمض اللاكتيك)، مطاط طبيعي، خلطات، عوامل متوافقة، توافق، الالتصاق البيني.