STUDIES ON DEGRADABLE POLYMERIC BLENDS BASED ON POLY(LACTIC ACID)

Thesis submitted
for the award of the degree
of

DOCTOR OF PHILOSOPHY

by

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ਹਮ ਮੂਰਖ ਅਗਿਆਨ ਗਿਆਨੁ ਕਿਛੁ ਨਾਹੀ ॥

ਸਤਿਗੁਰ ਤੇ ਸਮਝ ਪੜੀ ਮਨ ਮਾਹੀ ॥

ਹੋਹੁ ਦਇਆਲੁ ਕ੍ਰਿਪਾ ਕਰਿ ਹਰਿ ਜੀਉ ਸਤਿਗੁਰ ਕੀ ਸੇਵਾ ਲਾਈ ਹੇ ॥੧੪॥

ਮਾਰੂ (ਮਃ ੪) ਗੁਰੂ ਗ੍ਰੰਥ ਸਾਹਿਬ - ਅੰਗ ੧੦੭੦

I am foolish and ignorant; I have no wisdom at all.

From the True Guru, I have obtained understanding in my mind.

O Dear Lord, please be kind to me, and grant Your Grace; let me be committed to serving the True Guru. ||14||

CERTIFICATE

This is to certify that thesis entitled **"Studies on Degradable Polymeric Blends Based on Poly(Lactic Acid)",** being submitted by Mr. Gursewak Singh, to the Department of Chemical Engineering, Thapar University, Patiala for the award of degree of **DOCTOR OF PHILOSOPHY**, is a record of bonafide research work carried out by him. Mr. Gursewak Singh has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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PREFACE

This research work was carried out by the author under the guidance of Dr. Veena Choudhary, Professor, (Centre for Polymer Science and Engineering, Indian Institute of Technology, New Delhi) and Dr. Haripada Bhunia, Assistant Professor, (Chemical Engineering Department, Thapar University, Patiala).

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5. Navleen Kaur, **Gursewak Singh**, P. K. Bajpai and H. Bhunia, “Biodegradability assessment of linear low density polyethylene and poly(L-lactic acid) blends”, *International Conference on Chemical Industry in India: Opportunities and Challenges*, 5-6 March, 2010, SLIET, Sangrur, India.
6. **Gursewak Singh**, P. K. Bajpai and H. Bhunia, “Thermal and morphological studies of linear low density polyethylene (LLDPE) and polylactide (PLLA)”, *Conference on Polymer Science and Engineering: Emerging Dimensions*, 26-27 November, 2010, Punjab University, Chandigarh, India.
7. **Gursewak Singh**, P. K. Bajpai and H. Bhunia, “Preparation of linear low density polyethylene and poly (L-lactic acid) blends and its biodegradation study”, *11th International Conference on Polymer and Advance Materials*, 14-16 December, 2010, IIT, Delhi, India.

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List of Symbols

Symbol	Description	Unit
a	Approximation Integral	
b	Approximation Derivative	1/K
E_A	Refined Arrhenius Activation Energy	kJ/mol
K_{TO}	Thermo-Oxidation Coefficient	
R	Gas Constant	8.314 J/mol °K
T	Temperature at Constant Conversion	°K
T_c	Crystallization Temperature	°C
T_f	Final Degradation Temperature	°C
T_F	Failure Temperature at Given Value of Conversion	°K
t_f	Thermal Life at a Given Value of Conversion	hr
T_g	Glass Transition Temperature	°C
T_i	Onset Temperature of Degradation	°C
T_m	Melting Temperature	°C
X_c	Degree of Crystallinity	%
T_{max}	Maximum Degradation Temperature	°C
β	Heating Rate	°K /min
$\bar{M}_w$	Weight Average Molecular Weight	kDa
$\bar{M}_n$	Number Average Molecular Weight	kDa

List of Abbreviations

Abbreviations	**Description**
AFM	Atomic Force Microscope
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
DSC	Differential Scanning Calorimetry
DP	Degree of Polymerization
FTIR	Fourier Transform Infra Red
GA	Glycolide
GPC	Gel Permeation Chromatography
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	Maleic Anhydride
MA-g-LDPE	Maleic Anhydride grafted LDPE
MD	Machine Direction
MFI	Melt Flow Index
MSW	Municipal Solid Waste
phr	Parts per Hundred of Resin
PCL	Polycprolactone
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PLLA	Poly(L- lactic acid)
PP	Polypropylene

PS	Polystyrene
PVC	Poly(vinylchloride)
RTI	Relative Thermal Index
SEM	Scanning Electron Microscopy
TD	Transverse Direction
TEM	Transmission Electron Microscopy
TGA	Thermogravimetry Analysis
XRD	X Ray Diffraction

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Abstract

Melt blending of linear low density polyethylene (LLDPE) and poly(L-lactic acid) (PLLA) was performed in an extrusion mixer with post extrusion blown film attachment with and without compatibilizer i.e. maleic anhydride grafted low density polyethylene. The blend compositions were optimized for tensile properties as per ASTM D 882-91. Based on this, blend sample having 80 wt % LLDPE and 20 wt % PLLA i.e. sample LLDPE 80 and 80 wt % LLDPE, 20 wt % PLLA and 4 parts compatibilizer per hundred parts of resin i.e. sample M-g-L 80/4 were found to have an optimum composition of performance properties; the effect of blending on the mechanical, thermal and morphological characteristics was done. The blends were characterized using mechanical, thermal and morphological behavior. Morphological characteristics of film surface and fracture surface of polymer blends in absence and presence of compatibilizer were examined using scanning electron microscopy. It has been observed that the dispersion of PLLA in LLDPE matrix improved in presence of compatibilizer. FTIR reveals that the presence of compatibilizer shifts carbonyl peak indicating some increase in interaction between LLDPE and PLLA. Thermogravimetric (TG) analysis of blends showed that the M-g-L 80/4 blend has highest thermal stability as compared to LLDPE/PLLA blends of varying composition. The thermogravimetric profile and thermal endurance of these blends were characterized as per ASTM E1641-07 and E1877-05. The effect of physical aging on mechanical and thermal properties of these blends was evaluated. PLLA showed the highest Arrhenius activation energy, relative thermal index and strongest thermal endurance of all samples followed by M-g-L 80/4 and LLDPE 80. The thermo-oxidation coefficient improved with addition of compatibilizer in the blends. With increasing pH, hydrolytic degradation of the blend films increased, while both the tensile strength and the elongation at break of the blend films decreased. The degradation study under different pH of soil composting indicates that alkaline conditions and presence of compatibilizer favors the degradation. From this studies it can be concluded that such films based on LLDPE/PLLA with 20% of PLLA and in presence of compatibilizer (4phr) may find application in the field of packaging as biodegradable material.

1: INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

1.1.1 Background

Life on earth has emerged nearly 3.5 billion years ago. Human life has advanced from the "Stone Age" through the "Bronze Age, Iron Age and Steel Age" to its current Electronic Age, also considered as the 'Age of Polymers' because this is an age in which natural and synthetic polymers are the material of choice and will continue to do so for centuries to come. The word 'polymer' was although coined in the 20th century, but the polymers are in use since 15th century long before anyone understood what they were. When Columbus first imported natural polymer in 1496, the European explorer as a material obtained from the exudates of a tree (*Heavea brasiliensis*).

The first natural plastics known to mankind were shellac, rosin, cobweb, animal glue and tortoise shell. The first natural fibers known to human kind are silk, hair, jute etc. The first synthetic plastic material 'Bakelite' was invented in 1907 by Leo Hendrik Baekeland. In 1920, German chemist Hermann Staudinger made his macromolecular hypothesis, suggesting that polymers are actually giant molecules formed by the permanent attachment of countless smaller molecules. But the concept was not fully accepted until the work of W. H. Carothers, the inventor of nylon in 1929. As decades passed, stability and durability of these thermoplastics have improved continuously, thus these groups of materials are now considered as synonym to materials being resistant to the environmental influences. In 1930s, several important new polymers were developed, including polyolefins, polystyrene, poly (vinyl chloride), polysulphide rubber, neoprene, and nylon. However, it was not until World War II that significant change took place in the use of polymers as a strategic material and thus the ‘Polymer Age’ evolved.

The technologies to produce synthetic polymers from petroleum resources have developed rapidly, so also their applications in various fields including military and household. Polymers have now become indispensable to humankind not only in the industrial world but also in household goods, upholstery, civil constructions, aerospace engineering, defense, marine engineering, biomedical engineering and packaging industry. The proportion of their utilization is growing exponentially in every field in day-to-day life and they have a vast potential for exciting new application areas in the foreseeable future too. The use of polymer has spread into such diverse areas as: conduction and storage of electricity, heat and light, molecular based information storage and processing, molecular composites, unique separation membranes, revolutionary new forms of food processing and packaging, health, housing and transportation. The utilitarian values of plastics are ubiquitous and immensely varied by any known material such as metals, paper and glass. Their widespread use attests their versatility, quality and economic advantage over other materials.

Unfortunately, as the consumption of plastics grew up, these post consumer waste of plastics also increased more so in the packaging and food processing industry. Thus, plastics and plastic products are under scrutiny and cause a great concern to the industrialists and environmentalists because of the huge waste it generates, threatening the environment. Population explosion has demanded huge quantities of these materials in day to day life and this instrumented a rapid expansion in utilization volume of polymer products in daily life. Because of their high durability, they accumulate in the environment at a rate of 25 million tons per year [1]. Polyethylene, particularly as thin films, has found widespread use as a packaging material primarily because of its excellent mechanical properties, barrier properties against water borne microorganisms, low-cost and high energy effectiveness [1, 2]. However, this property of recalcitrance to microorganisms, which had once made polyethylene a popular choice as a packaging material, has now made it a subject of much criticism. Most of the polyethylene, after serving its useful life as a packaging film, finds its way to the landfill sites, where it simply refuses to degrade because of its non-biodegradable nature. While plastics are undoubtedly superior materials in terms of their costs, processability and functional properties, they are biologically inert and not readily assimilated by the various ecosystems upon disposal.

1.1.2 Plastics and Their Impact on Environment

All the synthetic polymers are made from mineral oil or gas, and the main constituent of all these materials is the petroleum resource. The monomers which bulid the structure of the polymers are different for every kind of plastic. Many harmful additives are often used to produce plastic goods with specific end use property and some of them are released during the production stage as well as during service life of the products. When they are dumped, disposed or burnt to generate fuel, the additive substances are converted into various by products and even toxic gases are emitted. The demand for products from plastics and elastomers has been growing exponentially in India and rest of the world. The global plastic production is currently 250 million tonnes and is increasing in a staggered manner by 5% to 9% annually that generates huge amount of polymer waste as a part of Municipal Solid Waste (MSW) [3].

The handling of this huge polymeric waste generated from different streams is problematic and raises unsolved questions in front of environmentalists and polymer scientists. Polymers, especially commodity thermoplastics like PE, PET, PP, PVC and PS are highly inert in nature and their use in huge quantities cause tremendous waste disposal concern. These polymers come into the waste streams either as industrial scrap or as post consumer waste. It creates voluminous littering of non-biodegradable plastic bags and bottles into the beautiful landscapes of cities. On a longer term, neither the land filling nor the incineration solves the problem of waste disposal, because the suitable and safe depots are expensive, and the incineration stimulates the growing emission of harmful and greenhouse gases e.g. NO_x, SO_x, CO_x etc. Hence, bio-based polymers have a crucial role in mitigating the burden of polymer waste in the MSW. The effectiveness of polymer material development and modification such as blending technology is indicative of the extent to which the method succeeds in reducing the environmental impact due to polymer wastes.

1.1.2.1 Plastics waste scenario in India

Waste management is one of the essential obligatory functions of our country [4]. This service is still a linear system of collection and disposal and hence, falling too short of the desired level of efficiency and satisfaction resulting in problems to health, sanitation and environmental pollution. Urban India is likely to face massive waste disposal problems in the coming years. India will probably see a rise in waste generation from less than 40,000 metric tonnes per year in the current situation to over 125,000 metric tonnes by the year 2030 (Indiastat.com, 2008). MSW management strategies, through recycling and reduction adopted in many countries, have produced a significant influence which can lead to the ultimate goal of zero waste in the surroundings [5]. In the Indian context, it is seen that the growth of the plastic industries is phenomenal. Polymer demand in India has consistently recorded double-digit growth rates, trebling very 10 years. Per capita polymer consumption is at a low 5 kg in India, only 20% of the global average. The government is aiming for a rise in per capita polymer consumption to 12 kg by 2012. Polymer production is set to rise from 5.33 million tonnes (MT) per annum in 2006 to 11.1 MT per annum by 2012. New investments are expected to add an additional 6.29 MT per annum of polymer production capacity by 2012, leaving a deficit of 1 MT. Polyolefins account for the major share of 60% in the total plastic consumption in India. Packaging is the major plastic consuming sector, with 42% of the total consumption, followed by consumer products and the construction industry [6].

According to the ‘Environment Agency Report’, the world wide distribution of post consumer polymer waste is as follows; 80% goes to the landfill, 8% incinerated and only 7% is recycled [7]. However, in India, about 60% of the plastic wastes generated are recycled which is the highest in the world. On the other hand, the remaining 40% of the plastic waste remains uncollected, un-segregated, strewn on the ground, littered around in open drains or in unmanaged garbage dumps. The collection of such soiled waste including the one which has been recycled thrice or even four times earlier is not only uneconomical for recovery of material but also unhygienic and undermines the environmental benefits of materials recycling. These indiscriminately disposed solid plastic wastes are of concern for clogging of municipal sewers, blocking of the storm water run-off in drains particularly in hilly areas, causing deaths to many animals, like, cows which fed on the garbage food thrown in polythene bags.

1.1.3 Bio-based Polymers: Need and Limitations

There are several options to reduce the environmental impacts related to polymer production and use, many of which are also relevant for other bulk materials. Important strategies are:

- increased energy efficiency and material efficiency (yields) in all processes in the production chain leading to polymers,
- increased end-use material efficiency, i.e., ensuring the same product service by lower amounts of material (e.g. by use of thinner plastic films),
- improved waste management by recycling of materials, re-use of product components, energy recovery in waste-to-energy facilities (incineration) and in the case of biodegradable polymer digestion (with energy recovery) and composting,
- replacement of petrochemical feedstocks by bio-based feedstocks.

The latter option, which in principle, offers wide scope for change since bio-based polymers now account for less than 0.1% of the total production of polymers in the world. Bio-based polymers have been attracting more and more attention in the last few years. Although, the policy on renewable resources was until recently typically limited to energy supply issues, the use of renewable raw materials for the production of bio-based materials was taken into account in future. Several Government agencies are actively involved in making the policies and promoting the research in renewable resources.

1.1.4 Renewable Resources

Resources are often classified into renewable and non-renewable. Renewable resources are generally those resources which can restock themselves at approximately the rate at which they are extracted. Non-living renewable natural resources include water, wind, tides and solar radiation – considered as renewable energy. In general, renewable resources are totally natural resources, not depleted when used by human beings. Plastics, gasoline, coal and other items produced from fossil fuels are non renewable, because the resource is depleted and can be used only once.

1.1.4.1 Importance of renewable resources

The benefits of naturally occurring polymers for material applications are many, most importantly their environmental compatibility. In addition, the use of renewable resources provides an incentive to extend non renewable petrochemical supplies. The agriculture industry produces sufficient supplies of some agricultural products that could be used as renewable sources for polymer feed stocks. Biodegradability is an additional benefit of renewable polymers. These polymers are not designed for high temperature and therefore their uses are limited to normal ranges of biological functions found in the biosphere. The innovation in the development of materials from biopolymers are the preservation of fossil-based raw materials, complete biological degradability, the reduction in volume of garbage and compostability in the natural environment as well as the application possibilities of agricultural resources for the production of biomaterials. This has attracted great interest not only from academic point of view but also for industrial applications.

1.1.5 Classification of Bio-based Polymers

The bio-based polymers are mainly classified into seven emerging groups. Starch polymers and poly(lactic acid) [PLA] are now clearly the most important types of polymers. Starch polymers have been the front runners in the bio-based polymer business. At the global level, PLA might be about to overtake starch polymers due to Cargill Dow's large-scale plant. Some of the other bio-based polymers that are not yet manufactured commercially are rather close to industrial production (PTT and PHA). The remaining polymers have been mentioned but it is often unclear how far from commercialization they might be. It should be noted that there may be further bio-based polymers belonging to these groups which, however, were deemed to be less important.

As shown in Table 1.1, the seven groups of bio-based polymers belong to four polymer categories, namely **polysaccharides, polyesters, polyurethanes and polyamides**.

(i) The **polysaccharides** generally represent modified natural polymers (see Table 1.1). Bacterial cellulose, is an exception since it is produced by a natural or genetically modified organism. Chitin (a polysaccharide, mainly produced from shellfish waste), proteins (such as collagen, casein and zein, the latter two are mainly used for non-plastic applications), amino acids (e.g. polyaspartic acid, mainly used for non-plastics) and natural fibres.

(ii) In the case of **polyesters**, the monomer (which may be an alcohol or an acid) is generally produced by fermentation from a renewable feedstock. The polyester may be composed of only one type of monomer, wherever this is not the case, the copolymer is a petrochemical product (Table 1.1). Poly(hydroxyl alkanoates) (PHA) represent a special case since they can be either produced by fermentation or in a genetically modified crop e.g. potatoes.

(iii) In case of **polyurethanes**, polyols used are bio-based while the isocyanate component is synthesized by petrochemical processes.

(iv) Three representatives of the fourth group, i.e. **polyamides**, are produced by fermentation or by conventional chemical transformation of a crop-derived feedstock (depending on the type).

1.1.5.1 PLA substitution potential and its future applications

PLA has high odour and flavour barrier. It also has high resistance to grease and oil, thus finding application in the packaging of viscous oily liquids. It is also suitable for packaging of dry products and short shelf-life products. In comparison to starch polymers, PLA is superior in terms of moisture barrier, whereas the gas barrier is inferior [8]. PLA exhibits good chemical resistance to aliphatic molecules such as mineral oils and turpenes. The resistance to solvents, acids and bases is average to poor. Having a linear aliphatic structure, PLA has good UV resistance. This is in contrast to aromatic polymers such as PET, which are highly sensitive to UV. Since PLA is a polar material, it has a high critical surface energy and is thus easy to print, metallise and dye. Its printability is similar to PET and better than PE and PP. It is possible to print PLA using natural dyes and pigments which are heavy metal free. PLA's potential for packaging applications (especially for food) is very high due to its transparency, good mechanical properties and suitable moisture permeability for packaging of foods sensitive o moisture such as bread as PLA has a better moisture barrier properties as compared to starch.

Table 1.1: Classification of bio-based polymers

S.No.	Bio-based polymer	Type of polymer	Production process
1	Starch polymers	Polysaccharides	Modified natural polymer
2	Poly(lactic acid) (PLA)	Polyester	Bio-based monomer (lactic acid) by fermentation, followed by polymerisation
3	Other polyesters from bio-based Intermediates	Polyester	
a	Poly(trimethylene terephthalate) (PTT)	-	Bio-based 1,3-propanediol by fermentation plus petrochemical terephthalic acid (or DMT)
b	Poly(butylene terephthalate) (PBT)	-	Bio-based 1,4-butanediol by fermentation plus petrochemical terephthalic acid
c	Poly(butylene succinate) (PBS)	-	Bio-based succinic acid by fermentation plus petrochemical terephthalic acid (or DMT)
4	Poly(hydroxyl alkanoates) (PHAs)	Polyester	Direct production of polymer by fermentation or in a crop (usually genetic engineering in both cases)
5	Polyurethanes (PURs)	Polyurethanes	Bio-based polyol by fermentation or chemical purification plus petrochemical isocyanate
6	Nylon	Polyamide	
a	Nylon 6	-	Bio-based caprolactum by fermentation
b	Nylon 66	-	Bio-based adipic acid by fermentation
c	Nylon 69	-	Bio-based monomer obtained from a conventional chemical transformation from oleic acid via azelaic (di)acid
7	Cellulose polymers	Polysaccharides	a) Modified natural polymer b) Bacterial cellulose by fermentation

1.1.5.2 Limitations of bio-based polymers

The major limitation for widespread use of totally bio-based polymers is its high cost. This is due to two factors: viz use of costly monomers and/or requirement of expensive additives or compatibilizers. Also, additional processing such as mixing the ingredients with a mechanical mixing mill or an extruder is necessary. The possibility of replacing commercial polymers such as polyethylene, polypropylene, poly (vinyl chloride), nylons and polyesters etc. by totally biodegradable polymers for clean environment is remote. Attainment of high performance of the former by the latter is not yet possible. Secondly, biodegradable polymers are meant for single use i.e. these are to be thrown to the garbage after only one time use. These polymers, therefore, should be cheap. To overcome this limitation, partially biodegradable polymers will be developed as a compromise between cost and performance.

1.2 DEGRADABILITY OF PLASTICS

In general, degradation is the process where the deterioration in the properties of the polymer takes place due to different factors like, light, heat, mechanical action, etc. Because of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties, the article becomes brittle, and the life of the material becomes limited. Thus, any polymer or its blend, which is to be used in outdoor applications, must be highly resistant to all the environmental conditions. Thus, the degradation study is necessary for the new material or developed blends.

Three main degradation processes are as follows:

1.2.1 Photodegradation

Photodegradation begins with the production of macro-radical ($P^{\bullet}$) in the amorphous regions of polymer substrate. This radical rapidly reacts with oxygen to give a macroperoxy radical ($POO^{\bullet}$) which abstracts a hydrogen atom from the polymer backbone to produce a hydroperoxide (POOH).

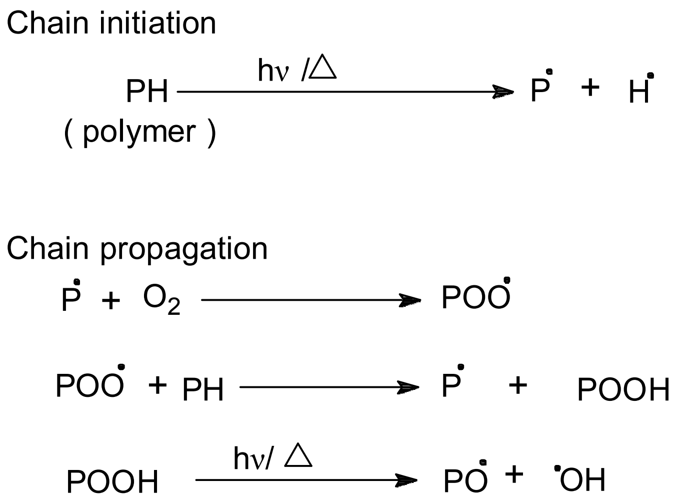


Figure 1.1: Mechanism of polymer photo-degradation

The hydroperoxide group is photolytically cleaved to produce the highly reactive radicals, which continue the cycle of chain degradation by the mechanism shown in Figure 1.1. The cycle is terminated when two radicals combine or recombine to form a non-radical product.

1.2.2 Thermal Degradation

The fundamentals of degradation mechanism of polymers are based on the same principles both for thermal and photodegradation. The only exception is that photodegradation proceeds at a faster rate than thermal degradation and hydroperoxides are thermally cleaved to reactive radicals in thermal degradation.

1.2.3 Biodegradation

The definition of biodegradation is not always clear and is open to a large diversity of interpretations. Here are the definitions of some key words according to the American Society for Testing and Materials i.e. ASTM D20-96:

1.2.3.1 Degradable plastic

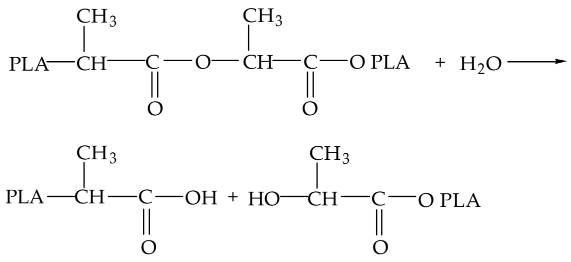
A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and its applications in a period of time.

1.2.3.2 Biodegradable plastic

A degradable plastic is one in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae. Biodegradability is the ability of material to be utilized as a carbon source by microorganisms and converted safely into carbon dioxide, biomass and water. Microbial attack is started where the carbonyl group is found. A general mechanism of biodegradation in non degradable polyolefins was described by Albertsson et al. [9] in 1987, according to which that biodegradation can be initiated by photooxidation where carboxylic acid parts, generated through Norrish type-I and II mechanisms during oxidation process, can be consumed by microbial attack.

1.2.4 Hydrolytic Degradation

Degradation of PLA is primarily due to the hydrolysis of ester linkages, which occurs more or less randomly along the backbone of the polymer. It requires the presence of water according to the following reaction:



$$\text{PLA}-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{O}{\|}}{C}-O-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{O}{\|}}{C}-O\ \text{PLA} + H_2O \longrightarrow$$

$$\text{PLA}-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{O}{\|}}{C}-OH + HO-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{O}{\|}}{C}-O\ \text{PLA}$$

The rate of hydrolysis is determined by its intrinsic rate constant, water concentration, acid or base catalyst, temperature and morphology.

1.2.5 Enzymatic Degradation

Several enzymes have been shown to catalyze PLA hydrolysis. Enzymatic hydrolysis of PLLA with varied crystal morphologies was studied using proteinase K by Tsuji and Miyauchi [10]. It was concluded that the enzymatic degradation proceeded via mainly a surface erosion mechanism. Amorphous regions hydrolyzed more readily than the crystalline regions. Tie chains degraded more readily than folds or restricted amorphous chains.

1.2.6 Miscellaneous

There are several means of polymer degradation other than thermal, photo and biodegradation. High molecular weight polymers undergo chain scission during treatment with ultrasonic waves. X-rays, gamma and beta rays can also cause the degradation of polymers and degradation with these high-energy radiations is much more massive than degradation caused by ultraviolet light (a radiation of low energy). Polymer chains having ester, amide and acetal functional groups in their backbone undergo degradation by the hydrolysis at a defined pH.

Many high molecular weight elastomers can be degraded by ozone and generate low molecular weight oligomers and/or liquid polymers those are useful in many applications. Figure 1.2 described all the possible degradation pathways of polymeric material.

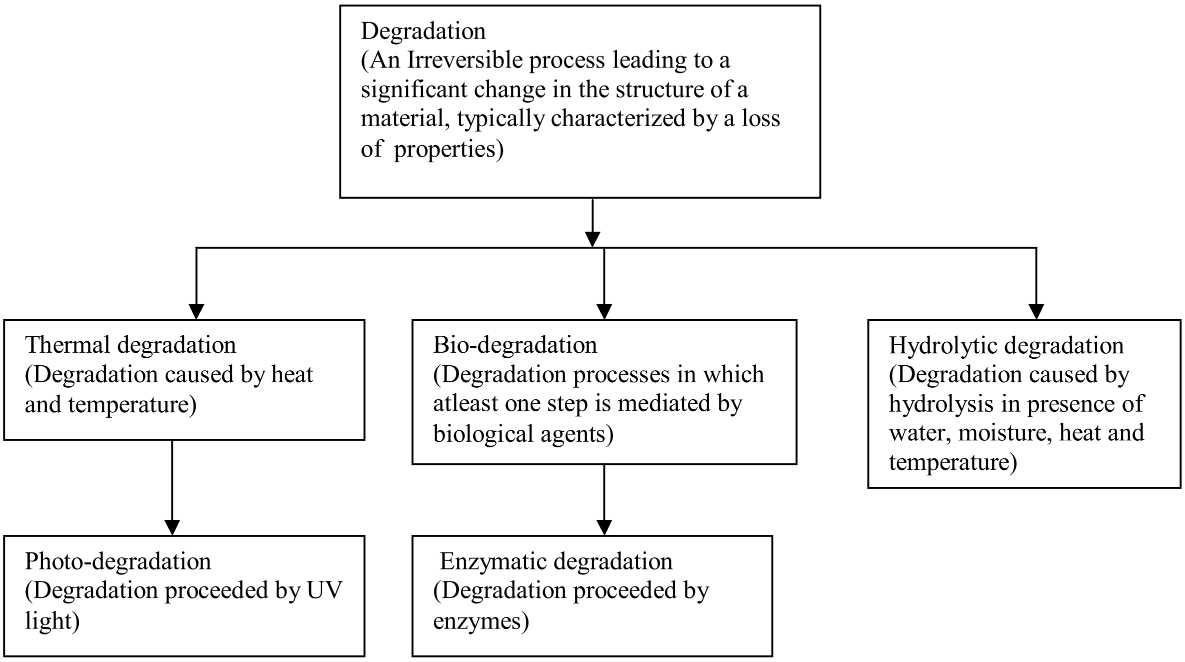


Figure 1.2: The possible degradation pathways of polymeric material

1.2.7 Evaluation Methods

The most applicable and popular measurement methods for blend characteristics and degradation in thermoplastics are summarized in Figure 1.3. Thermal degradation can be tested under inert as well as in presence of oxygen in a heating oven. The biodegradation can be studied by several means and countries have their own practice to determine the biodegradability in polymeric materials.

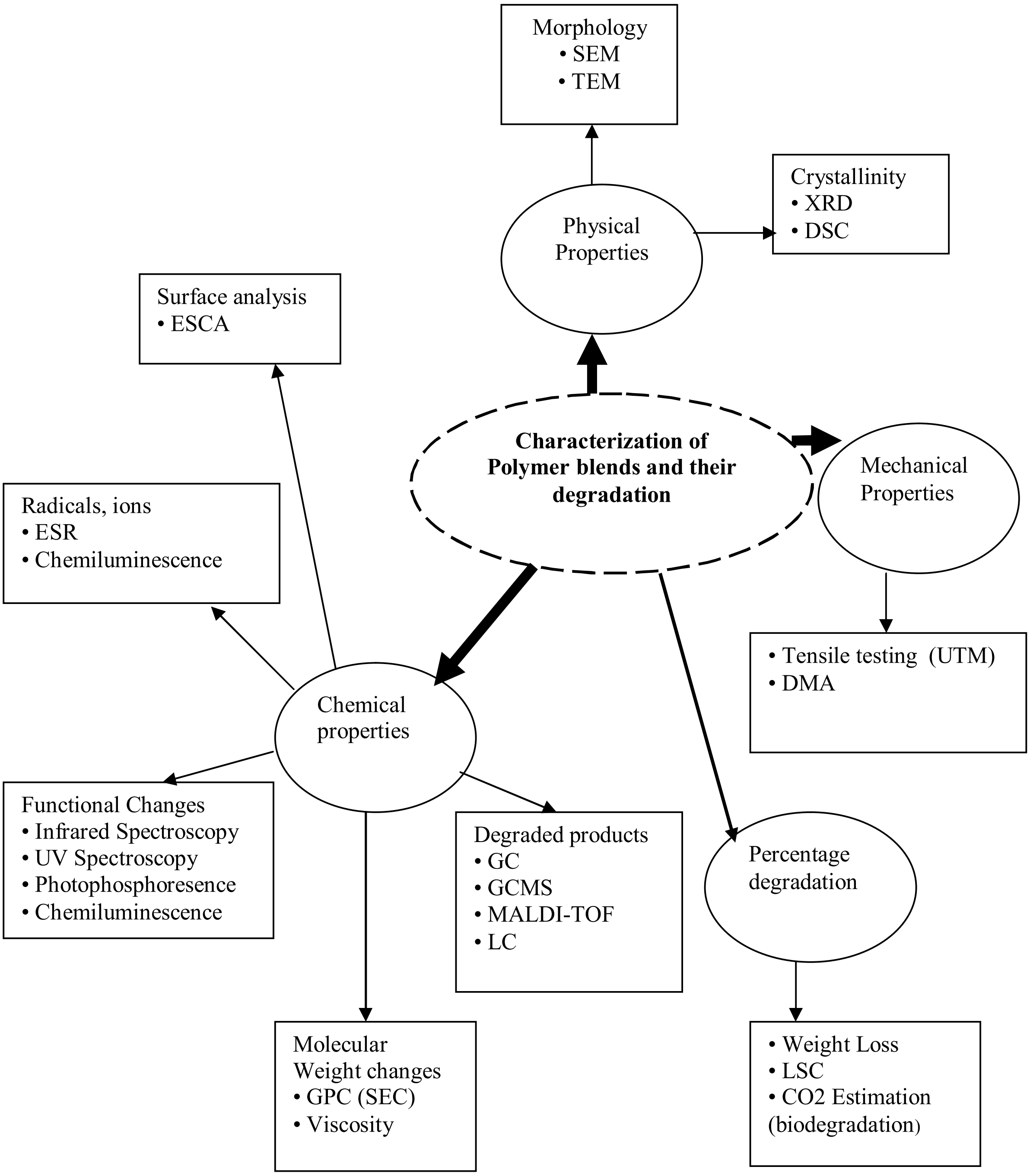


Figure 1.3: Different evaluation methods for degradability

1.3 LITERATURE REVIEW

The chemical and phase structures are the major determinants of the properties of biodegradable polymers. These structures and thereby the chemical and physical properties of lactic acid based polymers can be adjusted through changes in polymerization and processing conditions, by copolymerization and variation of the copolymer composition as well as through other chemical modification such as by blending with other polymers, and by compounding with additives like fillers, plasticizers, dyes and stabilizers. The methods for modification of PLA polymers are discussed below.

1.3.1 Polymerization

Polycondensation of lactic acid is usually performed in bulk by distillation of condensation water, with or without catalyst, while vacuum and temperature are progressively increased. Although high molecular weight polyesters with good physical properties are not easy to obtain, the properties of lactic acid oligomers, which can be further used as intermediates in the synthesis of polyurethanes, can be controlled by the use of different catalysts and functionalization agents and by varying the polymerization conditions [11, 12].

Ring-opening polymerization of lactide can be carried out in melt, bulk, or in solution and by cationic, anionic and coordination-insertion mechanisms depending on the catalyst [13, 14]. The choice of initiator system, co-initiators as chain control agents, catalyst concentration, monomer to initiator ratio, polymerization temperature and time significantly affect the material properties. These properties, such as the molecular weight, degree of crystallinity and residual monomer content, in turn affect the physico-mechanical properties and maximum temperature usage of the polylactides and its copolymers [15-19]. The role of racemization and the extent of transesterification in the polymerization and copolymerization process are also decisive for the enantiomeric purity and chain microstructure of the resulting polymer [20-24]. Many current PLA polymerization methods employ stannous octoate as the catalyst since it has been shown to be very effective, causes a low degree of racemization at high temperature [25], as low toxicity and is accepted by the US Food and Drug Administration (FDA) [26].

1.3.2 Copolymerization

Copolymerization of lactic acid or lactide with other monomers has been recognized as a valuable tool in modifying the properties of homopolymers. Although PLA polymers appear very versatile, in general the properties of homopolymers can only be slightly modified by varying the molecular weight or crystallinity and copolymers are required to provide materials with a wider range of properties. The PLA copolymers can present all the classical structures, namely random, diblock or multiblock, star, etc., with all the consequent variation in properties one can predict from such differences [19].

Only a few monomers have been shown to increase the glass transition temperature (T_g) of poly(lactic acids). Fukuzaki and co-workers [27, 28] have used α-hydroxy acids containing aromatic rings as the side groups or in the main chains to stiffen the oligomer chain. L-lactic acid was polycondensed with aromatic hydroxy acids such as p-hydroxybenzoic acid, p-hydroxyphenylacetic acid and p-3-(hydroxyphenyl) propionic acid, or monomers having aromatic rings as side-group residues, e.g. DL-mandelic acid and L-3-phenyllactic acid. Copolymerizations of L-lactide with incorporation of glycine/salicylic acid resulting in an improvement in T_g [29].

Another approach is to lower T_g and improve low temperature properties by increasing the flexibility of PLA. Copolymers of lactide and glycolide (GA) have found wide-spread use as biomedical materials due to increased hydrophilicity and enhanced degradation [30, 31]. In all copolymerizations of L-lactic acid or L-lactide, the length of crystallizable LA sequences is greatly reduced as compared with homopolymerizations, it can therefore be expected that, as the amount of comonomer increases, the crystallinity and the melting temperature of the copolymer will reduce. The L-LA/GA copolymers in the composition range of 25-65 wt.% GA are fully amorphous. Similarly, in stereocopolymers of L-lactide and D- or DL-lactide, melting temperature of the semicrystalline copolymers decreases as the content of D-units increases [32]. Incorporation of a small amount of lactide enantiomer of opposite configuration has been utilized in varying the degradation profile, but it has also been the most widely used method for improving PLA processability [33-35]. Copolymers of lactide and ε-caprolactone (CL) have a wide variety of mechanical properties, ranging from elastomeric to rigid, depending on the composition and the average sequence length [16, 36]. The chemical microstructure of such copolymers varies from random to diblock arrangement, depending on the polymerization and the type of initiator used.

Transesterification, i.e., the exchange reaction of ester groups between different chains, generates the redistribution of sequences in the polyester chain, thus changing its microstructure [37]. Lactic acid derivatives [38], lactone [27, 39-41] and ether lactone [13, 42] monomers, as well as trimethylene carbonate [34, 43, 44] and its dimethyl derivatives [45] have also been widely studied as comonomers to obtain copolymers with versatile properties.

Modifications to the degradation kinetics of PLA, especially in drug release systems, have been of interest. The incorporation of flexible water soluble polyethers, such as poly(ethylene glycol) and poly(propylene glycol) or their respective monomers, to form random and block copolymers, enables variation of hydrophilicity, biodegradation rate, and of course the final mechanical properties [46-48]. In addition, poly(orthoester) and poly(anhydride) have been reported as bioerodible materials, and thus the PLA copolymers with corresponding monomers have shown surface erosion behaviour [26, 49]. On introduction of functional side groups by copolymerization, variation in the physical properties can be achieved. PLA copolymers with pendant side-chain amino groups of the lysine [50, 51] and di-hydroxyl [52] groups will provide a functional handle to attach bioactive molecules and to prepare graft copolymers. The free carboxylic acid groups, obtained from the copolymerization of maleic acid, [48, 53, 54] can also be further functionalized to manipulate the material properties. These groups are thought to have a catalytic effect on the hydrolytic scission of the ester bonds, increasing the degradation rate. Copolymers with polydepsipeptides having pendant carboxyl and amino, or thiol groups have also been reported [55]. In addition, Chen et al. [47] have copolymerized a cyclic carbonate monomer, which has a cyclohexene group with L-lactide to introduce C=C functional groups. This provides opportunities to introduce other functionalities or free radical crosslinking.

1.3.3 Crosslinking

The crosslinking of homo- and copolymers of linear polylactones would provide further possibilities for modifying the physical and mechanical properties of these materials. According to Nijenhuis et al. [56], a tetrafunctional monomer, 5,5'-bis(oxepane-2-one), is an excellent lactone crosslinker for improving the impact and tensile strength. Spiro-bis-dimethylene-carbonate has been used in the crosslinking of poly(lactide) chains to influence thermal properties, without necessarily leading to deterioration in the mechanical properties [57]. Peroxide crosslinking with dicumyl peroxide proved to be an effective in the crosslinking of PLLA. The crosslinking resulted in a ductile material [56].

1.3.4 Chain Linking of Lactic Acid Oligomers

Chain coupling of low molecular weight oligomers is not only an alternative route for synthesizing PLA polymers, but it also offers the possibility of introducing different functional groups into the polymer chain. Improved mechanical properties and flexibility in the manufacture of copolymers are also associated with the use of chain extending agents. Typical extenders for polyesters that contain -OH and -COOH groups are diisocyanates, diepoxides, bisoxazolines, dianhydrides and bisketeneacetals. Polyurethanes are a unique class of polymers, with a broad range of properties which can be tailored by varying the type and amount of their components. Linear poly(ester urethanes) have been synthesized by reacting either lactic acid or lactide based polyol with different diisocyanates [58, 59]. In poly(D,L-lactide-urethane) networks, the physical properties were further enhanced with increasing crosslinking density. This was attributed to a higher degree of hydrogen bonding provided by the urethane segments [60]. The chemical make-up of the polyester polyol enabled the design of physical properties in lactide and ε-caprolactone based polyurethanes [61, 62]. A poly(ester-amide) structure was presented by Tuominen and Seppälä [63, 64], where polycondensed carboxyl terminated lactic acid prepolymers were chain extended with 2,2'-bis(2- oxazoline). The mechanical properties appeared to be slightly better than for the corresponding urethanes.

1.3.5 Rubber Toughening

In general, semi-crystalline and amorphous poly(lactic acid) is a relatively brittle polymer with low impact resistance. One successful route for improving the impact resistance of polymers is rubber toughening. In this process, rubber modification is achieved by phase separation in the blend, when typically between 3 and 20 wt.% rubber is incorporated as a dispersed phase into a continuous matrix phase. Phase separation between hard and flexible components is important because a rubber that is miscible with the matrix acts as a plasticizer. Secondly, the adhesion between the phases at the rubber-matrix interface is an important parameter in rubber toughening, and therefore the rubber is ideally neither completely compatible nor completely incompatible. The resulting blends show significant improvements in impact strength, elongation at break, work to break and fracture toughness, with only slight reductions in modulus and tensile strength. Factors affecting rubber modification include the chain structure of matrix; phase separation and interfacial adhesion of matrix and rubber; particle size, shape, volume fraction and type of rubber [65, 66].

Grijpma and co-workers [67-70] have studied the rubber toughening of poly(L-lactide) and amorphous non-crystallizable lactide stereocopolymers with several hydrolytically degradable rubbers. Rubber modification with poly(trimethylene carbonate), poly(trimethylene carbonate/ε-caprolactone), or poly(L-lactide/ε-caprolactone) rubbers resulted in increased impact strengths, lower yield strengths and higher elongations. Randal et al. [71] have prepared poly(lactide) composites with improved impact resistance, using epoxidized natural rubber elastomer as a second phase. In order to improve compatibility of the phases, they have used a reactive compatibilizing agent. In addition, Sinclair and Preston [72] have used non-biodegradable rubber in rubber toughened poly(lactide) blends.

1.3.6 Fillers and Plasticizers

Fillers are usually solid additives mixed with plastics to improve material properties, to introduce specific characteristics, or to reduce the cost of the compound. In the case of mass volume biodegradable polymers, cost reduction has practical importance beside improvement in the mechanical properties. Fillers are inorganic or organic materials, and each group consists of fibrous and nonfibrous types. Individual fillers are available in a number of grades differing in average particle size and size distribution, particle shape and porosity, chemical nature of the surface, and impurities. As a result of the presence of filler, hardness and stiffness are increased while impact and tensile strengths are usually decreased [73-75]. Thakur et al. [76] have found that talc, which is commonly added as a filler, also acts as a nucleating agent for poly(lactide) and increases the number of spherulites in crystallization. Kolstad [35] concluded that 6 wt.% talc gives a 500-fold increase in the nucleation density. Hiljanen-Vainio et al. [77] have enhanced the mechanical properties of lactic acid based poly(ester-urethane) via the addition of organic and inorganic fillers. Primarily, plasticizers are added to polymers to achieve flexibility and processability, although many other properties are also modified. Typically, when plasticizers, such as citrate esters, poly(ethylene glycol), glucose monoesters and fatty acid esters, have been used with poly(lactic acid), the increase in plasticizer content has caused a corresponding reduction in modulus, tensile strength, and softening temperature, whereas elongation at break and toughness have been improved [78, 79]. Poly(lactic acid) is also plasticized with its own monomer and oligomers [80, 81]. The use of a plasticizer such as lactide or lactic acid is beneficial in producing more flexible materials, but due to the fast migration of rather small molecules, it results in unevenness in films and sticking during processing [77, 82]. Sinclair and Preston [81] have also used unreacted monomer and oligomers for impact modification of poly(lactide).

1.3.7 Processing

Poly(lactic acid) are thermoplastics that can readily be processed by conventional means, including extrusion, injection molding, and film blowing. One major disadvantage of PLA is that it belongs to the group of polymers which are relatively sensitive to thermal degradation. Molecular weight decrease under processing conditions has an extensive effect on the properties of the final products [83]. Postulated thermal degradation reactions in poly(lactide) are intramolecular transesterification from the end of the chain (back-biting) or in the middle of chain, intermolecular transesterification, hydrolysis and pyrolytic elimination [84]. The parameters that have been reported to influence thermal stability include molecular weight, end-groups, moisture, residual or hydrolyzed monomers and oligomers, impurities, and residual metals [85-92]. Since the degradation rate under processing conditions is strongly dependent on the nature and amount of metal catalyst used, the thermal stability of polylactides is remarkably enhanced when the ring-opening polymerization is initiated by aluminium isopropoxide rather than stannous octoate [93]. In addition to this, obvious methods for the removal of any organometallic compound are solvent extraction or solvating and selective precipitation of the polyester [94, 95]. Industrially, the more reasonable and straightforward strategy is the post-polymerization quenching of the metal catalyst by deactivating agents, including various types of peroxides [96-99], boron compounds [100], tropolone [101] and phosphite-containing or phenolic compounds [82]. These compounds are supposed to deactivate the catalyst and to decrease its activity in transesterification reactions [93]. However, the use of a free-radical promoter, such as benzoyl peroxide, tends to induce chain branching and crosslinking reactions. Acetylation of end-groups has also led to an increase in thermal stability [88].

The intrinsic properties of PLA polymers have also been modified for a specific application by processing techniques. Törmälä et al. [102, 103] have introduced the self-reinforcing technique, where poly(L-lactic acid) rods are reinforced with highly oriented fibres of the same polymers, achieving higher strength materials for fixation devices in orthopedic applications. In addition, high strength fibres for general medical applications have been prepared using melt or solution spinning processes, which involve orientation of the chains by cold- and/or hot-drawing [104, 105]. PLA films can be draw-oriented up to about 8 times before showing strain whitening, but considerable enhancement of properties can be achieved with nominal draws of 3 to 5 times [81].

1.3.8 Polymer-polymer Blends

Chemical modification is not the only method for changing the properties of polymers. In many cases, this can be performed more rapidly and cost-effectively by mixing available polymers using existing processing equipment rather than through the development of new chemistry. The final properties of these blends depend on the chemical structure of original components, the mixing ratio of the constituent polymers, the interaction between the components and the processing steps to which they are then subjected. In polymer-polymer blends of PLA, the primary problem has been to find polymers that exhibit at least some degree of miscibility or compatibility. Most of the blends were found to be immiscible, including a phase-separated morphology and yielding blends with poor mechanical properties. In addition, the second component must also be biodegradable, which makes the process less economically attractive in some cases. However, several blend systems containing PLA have been investigated, such as blends of PLA with poly(ε-caprolactone) [106-110], poly[(R)-3-hydroxybutyrate] [111-113], poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] [114], poly(ethylene oxide) [115-118] and poly(vinyl acetate) [119].

An interesting phenomenon in blends of poly(L-lactide) and poly(D-lactide) is the formation of a stereocomplex. The PLA stereocomplex is found to possess a racemic crystalline structure, where PDLA and PLLA chains are packed side by side with a D monomer unit to L monomer unit in the ratio of 1:1. One of the most interesting findings in PLLA/PDLA stereocomplexation studies is that the melting temperature of the stereocomplex is 230°C, approximately 50°C above that of the corresponding homopolymer. This enantiomeric polymer blend also exhibits substantially higher tensile properties and better thermal stability and hydrolysis resistance than the polylactides from which the blends are prepared [120, 121].

Blending PLA with other polymers can substantially modify the mechanical and thermal properties, degradation rate and permeability. PLA/ poly (ε-caprolactone) (PCL) blends have been extensively studied [108, 122-133]. Various compatibilizers such as Poly(LA-co-CL) copolymer were used to improve the miscibility between PLA and PCL [108, 123-126]. The blends displayed good dispersion of PCL (minor phase) in the PLA matrix, resulting in better mechanical properties compared to those of neat PLA. Experiments found that the addition of compatibilizers led to a highly homogeneous structure, while phase separation occurred in the absence of compatibilizers. In the PEU/poly(L-lactic acid-co-ε-caprolactone-urethane) blend, poly(L-lactic acid-co-ε-caprolactone-urethane) increased the impact strength of the blend [64, 134]. Particulate or fibrous fillers such as wollastonite, kaolinite and wood fibre added as a third component increased the stiffness [135-143].

Biodegradable blend membranes based on chitosan with PLA have also been studied [144-146]. The main goal of these blends was to improve the water vapor barrier of chitosan by blending it with a hydrophobic biodegradable polymer from renewable resources. The incorporation of PLA with chitosan improved the water barrier properties and decreased the water sensitivity of chitosan film. Blending of PLA with starch has been studied by several researchers [147, 148] and they characterized blends of starch and PLA in the presence of different water contents. Initial moisture content of the starch was found to have no significant effect on its mechanical properties, but had a significant effect on the water absorption of the blends. The thermal and crystallization properties of PLA in the blend were not affected by moisture content. The blends prepared by compression molding had higher crystallinity than those prepared by injection molding. However, the blends prepared by injection molding had higher tensile strength, elongation and lower water absorption values than those made by compression molding. The crystallinity of blends increased greatly with annealing at the PLA second crystallization temperature (155^{o}C). The decomposition of PLA indicated that PLA degraded slightly in the presence of water under the processing conditions.

Blends of different stereoisomeric PLAs have also been studied [149-152]. Mechanical properties and melting temperature were found to increase due to the formation of stereocomplex crystallites which acted as intermolecular links. On the contrary, neat PLA had larger-sized spherulites of less contacting area with the surrounding spherulites [153-156]. PLA was also blended with other non biodegradable polymers, including polyethylene, poly(ethylene oxide), poly(ethylene glycol), poly(vinyl acetate), poly(4-vinylphenol) and polyacrylates [53, 157-167]. Varying degrees of property modifications of PLA were achieved by blending with these polymers. Many of these blends are immiscible or only partially miscible and may need compatibilizer to increase their compatibility [168-170].

1.3.9 Degradation Study

The environmental degradation of PLA occurs by a two-step process [171]. During the initial phases of degradation, the high molecular weight polyester chains hydrolyze to lower molecular weight oligomers. The hydrolysis of PLA has been studied using at least four experimental designs: melt hydrolysis to simulate extrusion conditions, solution hydrolysis of PLA dissolved in various solvents and two types of solid-state hydrolysis methods. The first type of solid-state hydrolysis experiment utilizes solid samples suspended in aqueous media. The second type utilizes exposure of solid samples to humidity. Since the product of the hydrolysis reaction is also a catalyst for further reaction, the hydrolysis of PLA is autocatalytic. Melt hydrolysis, solution hydrolysis and solid exposure to humidity experimental designs generally give rise to homogeneous hydrolysis. In contrast, exposure of solid samples suspended in water or aqueous buffers gives rise to inhomogeneous hydrolysis. This is due to differences in hydrolysis rate as a function of depth within the sample and it is caused by extraction of PLA oligomers from the surface of the sample into the aqueous medium. It is the chain end groups of the PLA oligomers that catalyze the rate of hydrolysis, and therefore the inside of the sample actually hydrolyzes faster than the surface for thick samples submersed in water [172].

Hydrolytic degradation of PLA is autocatalytic due to the production of carboxylic acid end groups that catalyze further hydrolysis [173]. An effect of this is that for a thick sample immersed in a buffer (7.4 pH) at 37°C, bulk hydrolysis occurs faster than surface hydrolysis [174]. The pH of surface remains 7.4 i.e. pH of buffer whereas the pH of the bulk sample is reduced due to the accumulation of PLA acid end groups and the inability of the oligomers to quickly diffuse into the buffer medium. Vert et al. [175] summarized the literature on the hydrolytic stability of solid, suspended PLA and captured several key points including autocatalysis and leaching effects. In addition, morphology and structure were addressed. The rate of degradation is strongly influenced by the number average molecular weight [176]. PLA having lower number average molecular weight (M_n) degraded faster as did PLA with higher levels of oligomers. The presence of lactide also increased the rate of hydrolytic degradation [177]. Effects of M_n, oligomers and lactide can all be attributed to autocatalysis. PLA's amorphous domains are more susceptible to hydrolysis than the crystalline domains. This is due to the ability of water to permeate within the amorphous phase but not the crystalline phase, and leads to differences in water concentration throughout the article on the microscale. Hydrolysis of the crystalline domain occurs mainly by a surface erosion mechanism.

Grizzi et al. [174] used the fact that surface hydrolysis is slow compared to bulk hydrolysis, therefore PLA can be stabilized towards hydrolysis simply by using small dimensions. By suspending PLA samples of varying size in water and determining the rates of hydrolysis, they showed that leaching could be used to slow down the rate of solid-state hydrolysis. They estimated that the skin, which was formed due to the leaching of catalytic oligomers, was about 200 to 300 μm in thickness. Samples smaller than this size were found to degrade much more slowly than large samples.

The heterogeneity of process makes it difficult to determine hydrolysis kinetic constants for solids suspended in aqueous media. Translation of data from these kinds of studies to other environments is suspect for this reason.

In alkaline media, Iwata and Doi [178] studied the change in morphology and crystalline state of solution-grown single crystals of PLLA. Samples were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM) and gel permeation chromatography (GPC). As hydrolysis proceeded, the molecular weight of degraded crystals corresponded to the value calculated from lamellar thickness measured by AFM. The explanation for this is that PLA first degrades in the more loosely packed chain folding regions. In the later stages of hydrolysis, the more persistent crystalline region's molecular weight approaches that of the lamellar thickness and the degradation mechanism will change to that of surface erosion.

Tsuji and Nakahara [179] tested PLLA films in HCl solution & D,L-lactic acid solution (pH=2.0), phosphate buffer (pH=7.4) and NaOH solution (pH=12.0). While the alkaline media, samples degraded faster than the neutral pH, the samples in acid media degraded at about the same rate as at the neutral pH control. Using microcapsules suspended in buffer solutions, Makino et al. [180] showed that PLA degrades slowest at pH 5.0 and increases in acidic and alkaline solutions. The activation energy of hydrolysis at pH 7.4 and ionic strength 0.15 was 19.9 kcal/mol for PDLLA microcapsules and 20.0 kcal/mol for PLLA microcapsules when the initial M_w was about 100,000 for both polymers.

The degradation characteristics of PLA in seawater are important for certain applications and potential disposal routes. Yuan et al. [181] tested PLLA fibers in saline buffer at 37°C for molecular weight loss and mechanical properties. The results suggested that the tensile properties of PLLA fibers were stable for 35 weeks, even though their molecular weights decreased remarkably and obvious spotty defects appeared on their surfaces. Tsuji and Suzuyoshi [182] showed that PLA degraded faster in natural seawater than controlled static seawater, although the rate of molecular weight loss is slow. Makino et al. [180] showed that $AlCl_3$, $CaCl_2$, and KCl had no or little effect on the degradation rate.

The degradation rate of PLA increased substantially above the glass transition temperature. Tsuji et al. [183] tested PLLA films in buffers at 97°C and showed that the hydrolysis takes place predominantly and randomly at the chains in the amorphous region. Amorphous samples crystallized while degrading and higher initial crystallinity slightly slowed the rate of hydrolysis.

In extreme case showing the effect of morphology fibers drawn to a draw ratio of about 8X using a solution spinning approach were examined. These fibers possessed few defects (chain folds, microvoids) together with high crystallinity, low fractional free volume and small cross-sectional dimension [173]. The PLLA fiber was very stable over a 5-year period immersed in water at room temperature under a static load and lost 10% of its diameter and less than 25% of its tensile strength. The perfection of morphology was thought to reduce the penetration and diffusion of water into the fiber. Effects of processing conditions were also examined by Iannace et al [184]. Samples of PLLA crystallized under isothermal and nonisothermal conditions were prepared. Initial morphology developed during the isothermal crystallization affected the rate of hydrolysis in buffer solutions. Larger crystals developed at higher T_c were more resistant to erosion compared to less perfect and smaller crystals developed at higher degrees of supercooling.

Tsuji and Suzuki [179] also studied stereocomplex degradation over the course of 30 months in buffer solution (pH=7.4) using 1:1 blend and neat films prepared from PLLA and PDLA. Change in properties such as tensile strength, crystallization, morphology and molecular weight (DSC, SEM, optical polarizing microscopy, XRD and GPC) was investigated as a function of degradation. The rate of molecular weight loss, tensile strength, Young's modulus, melting temperature and mass remaining of the films in the course of hydrolysis was more stable for the stereocomplex film than for the neat films.

Solution hydrolysis is generally thought to occur by random scission of the ester linkages in PLA [185]. It has been reported, however, that base and neutral hydrolysis occur by random chain scission but acid hydrolysis occurs by a mixture of two mechanisms, random and chain-end scission, with chain-end scission being the faster [186]. This was determined in dioxane/water solution with ^{1}H NMR and GPC using a statistical method where the level of lactic acid produced by hydrolysis is compared to the degree of degradation across the entire molecular weight distribution. The chain-end scission is sometimes referred to as "unzipping."

PLA solution hydrolysis was also studied in acetone/water by Zhang et al. [187] and acetonitrile/water by Siparsky et al [188]. The latter solvent had a much higher dielectric constant ($\mathcal{E}$=36) than acetone ($\mathcal{E}$=21) or dioxane ($\mathcal{E}$=2) so that the carboxylic acid groups were more ionized, as in water ($\mathcal{E}$=79). Autocatalysis was observed in acetonitrile whereas it was not in the lower dielectric solvents due to a lower extent of ionization of the carboxylic acid.

Samples exposed to temperature and humidity best simulate the shelf-life environment for many PLA applications. The equilibrium moisture level as a function of humidity is known for PLA at room temperature. It has not been as thoroughly studied for elevated temperatures. Hydrophilic impurities such as lactide and carboxylic acid end groups, whose concentration increase as degradation proceeds, increase the level of moisture. Sharp et al. [189] measured the water uptake of PDLLA using a quartz crystal microbalance in humid environments at various temperatures. Kinetics of water adsorption and equilibrium concentrations were measured and the Flory Huggins interaction parameter X was found to be 3.5 at 20°C using binary mixing theory. The equilibrium swell level of water in PLA increases with decreasing molecular weight due to the strong affinity of acid and hydroxyl end groups for water. It was also shown that the T_g of high molecular weight PLA was depressed by 11°C at 7000 ppm water (the highest level of swelling studied) compared to zero ppm water.

The crystalline regions of PLA were found to hydrolyze very slowly [173, 185]. The rate of molecular weight loss follows a two-step process, the first occurring very fast (interpreted as loss of the amorphous phase) and the second occurring much slowly (interpreted as loss of the crystalline phase). The apparent percentage of crystallinity increases during the amorphous phase hydrolysis, consistent with the interpretation. The molecular weight of the remaining PLA after the amorphous phase degradation was about 5000 to 9000 (DP = 70 to 125), roughly that of the fold length of the lamella [190]. Crystalline injection-moulded samples lost physical properties faster than amorphous samples, although the rate of Mw loss was similar between them [185]. This was interpreted as the loss of amorphous tie chains between the crystals causing catastrophic failure of the system. Also, chain folds and tie chains connecting crystallites are thought to hydrolyze preferentially because they are stressed due to a “reeling in” force [191]. These observations may be the result of chain end groups and catalysts concentrating in the amorphous regions.

Morphology also affects water permeation in another way. Microvoids or porosity allow water to migrate more freely into the material and thereby enhance the rate of hydrolysis. This is probably a small effect for samples exposed to humidity because the rate of hydrolysis is slow compared to the water diffusion rate, as discussed above. Localized regions of high water absorption may cause mechanical stresses due to increased osmotic pressure.

The inherent resistance of polyethylene to biological attack can be attributed to its hydrophobic nature (carbon-only backbone), high molecular weight and the absence of functional groups recognizable by microbes. The major strategy to facilitate the disintegration and subsequent degradation of the polymeric polyethylene chain is focused on direct incorporation of carbonyl groups within the backbone or its in-situ generation by introduction of pro-oxidant at the processing stage. Typical pro-oxidants include UV activators like aromatic ketones and/or transition metal based complexes [168, 192, 193]. Polyethylene appears to be one of the most inert plastic materials. Indeed, in a long-term study on the biodegradation of ^{14}C-labelled polyethylene, Albertsson and Karlsson [194] found that after 10 years of incubation in soil, <0.5% carbon (as CO_2) by weight was evolved from an UV-irradiated polyethylene sheet. Non-irradiated polyethylene emitted <0.2% carbon dioxide during the same time. Furthermore, no signs of deterioration could be observed in a polyethylene sheet that had been incubated in moist soil for 12 years [195] and only partial degradation was observed in a polyethylene film buried in soil for 32 years [196].

From a chemical perspective, we would expect polyethylene to be biodegradable, as linear alkenes are usually subject to biodegradation. However, for polyethylene there is an inverse relationship between molecular weight and biodegradability. Linear hydrocarbon oligomers with molecular weights lower than 620 support microbial growth, while those having higher molecular weights are not utilized [195, 197]. It is widely accepted that the resistance of polyethylene to biodegradation stems from its high molecular weight, its three-dimensional structure and its hydrophobic nature, all of which interfere with its availability to microorganisms. Nevertheless, several studies have demonstrated partial biodegradation of polyethylene after UV irradiation [198], thermal treatment [199] or oxidation with nitric acid [200, 201]. Furthermore, a synergistic effect has been found between photo-oxidation and biodegradation of polyethylene [202]. Apparently, the biodegradation of polyethylene is enhanced by oxidation pretreatment, which increases surface hydrophilicity by the formation of carbonyl groups that can be utilized by microorganisms [203-205].

Biodegradation resulting from the utilization of polyethylene as a nutrient (i.e. a carbon source) may be more efficient if the degrading microorganism forms a biofilm on the polyethylene surface. However, the hydrophobicity of polyethylene interferes with the formation of a microbial biofilm. Attempts to facilitate colonization of polyethylene by adding nonionic surfactants to the culture medium promoted the biodegradation of polyethylene [206]. Presumably, the surfactant increased the hydrophilicity of polyethylene surface and thus facilitated the adhesion of bacteria to the polymer.

The ability of this bacterium to form a biofilm on polyethylene was attributed to the hydrophobicity of its cell surface [207, 208]. Addition of a small amount (0.05%) of mineral oil to the culture medium increased both biofilm formation and the subsequent biodegradation of polyethylene, presumably by increasing the hydrophobic interactions between the bacterial biofilm and the polymer [207]. A thermophilic bacterium *Brevibaccillus borstelensis* strain 707 (isolated from soil) utilized branched low-density polyethylene as the sole carbon source and degraded it [209].

Abiotic degradation in the presence of pro-oxidants generally leads to the formation of functional macromolecules, which can thermally or photochemically cleave repeatedly to low molecular weight oxygenated fragments. These include aliphatic carboxylic acids, alcohols, aldehydes and ketones, which can support microbial growth and in turn get consumed by microorganisms [210-212]. There have been some studies on the biodegradation of pro-oxidant activated polyethylene in soil, waste water, sludge and compost [1, 202, 213]. This approach offers several advantages, like diverse microbial inoculum or close relation to the real conditions in the nature and in waste treatment processes.

The degradation of abiotically aged low-density polyethylene (LDPE) films containing trace quantities of a representative pro-oxidant (cobalt stearate) were investigated in the presence of well-defined enriched microbial strains namely, *Bacillus pumilus*, *Bacillus halodenitrificans* and *Bacillus cereus* in nutrients medium. The films were initially subjected to an abiotic treatment comprising UV irradiation, and subsequently inoculated with the bacterial strains. The degradation in the polymeric chain was monitored by changes in the mechanical, morphological, structural and thermal properties [168, 214-216].

1.4 SCOPE OF THE PRESENT WORK

Lactides and lactic acid monomers are obtained from the fermentation of crop like corn starch and sugar feed stocks. Polymerization of lactic acid into PLA produces biodegradable thermoplastic polyester with good biocompatibility and physical properties, such as high mechanical strength, thermoplasticity and fabricability. PLA has mostly been used for biomedical applications such as drug delivery systems and controlled release matrices for fertilizers, pesticides and herbicides. The advantages of PLA are numerous and include: (1) production of the lactide monomer by fermentation of a renewable agricultural source (corn); (2) fixation of significant quantities of carbon dioxide, the leading greenhouse gas; (3) significant energy savings; (4) the ability to recycle back to lactic acid (nontoxic, naturally occurring metabolite) by hydrolysis or alcoholysis; (5) capability of producing hybrid paper-plastic consumer packaging that is compostable; (6) reduction in landfill volumes; (7) improvement of nation's farm economy; and (8) the ability to tailor physical properties through material modifications. During the literature survey, the following technological gaps are observed.

Despite its good properties, the applications are limited due to its low flexibility and low impact strength.

- PLA is presumed to be biodegradable, although the role of hydrolysis versus enzymatic depolymerization in this process remains open to debate.
- The polymeric blends of PLA are immiscible resulting in poor mechanical properties and biodegradation rate. There is limited information on miscible PLA blends.
- PLA is more expensive than the majority of commodity polymers.

- Processibility of PLA is rather poor and its biodegradation is not easy to control.
- Much less is known about the plasticizing effect of plasticizer on PLA and its blends.
- Little research has been conducted on blending PLA with non biodegradable polymers.

Because none of the PLA blends are commercially available at present, blending PLA with other polymers needs to be explored to obtain products with properties which are currently not attainable. Therefore, it is proposed to study on PLA polymeric blends. The research outcome will help as a step in developing the low-cost and eco-friendly material.

1.4.1 Objectives and Outlines

To develop degradable polymer blends having optimum performance properties based on poly(lactic acid) [biodegradable] and non-biodegradable polymers.

To attain these objectives, the following studies were planned.

- Investigating the effect of blend composition and compatibilizer content on the physico-mechanical properties of blends.
- Degradation study of polymeric blends under different environmental conditions.

2: MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Linear Low Density Polyethylene (LLDPE)

Commercial grade linear low density polyethylene (LLDPE) [Trade name Halene-L, 71601S, melt flow index (MFI) 1.0 g/10 min @2.16 kg; 190^0C] was obtained from Haldia Petrochemical Ltd, Haldia, India.

2.1.2 Poly (L-lactic acid) (PLLA)

Commercial grade poly (L-lactic acid) [Trade name Biomer L 9000, $\bar{M}_w$ = 20 kDa, $\bar{M}_n$ =10.1 kDa, MFI 3.0 g/10 min @2.16 kg; 190^0C] was procured from Biomer Forst-Kasten-Str Kailling, Germany.

2.1.3 Maleic Anhydride Grafted Low Density Polyethylene [MA-g-LDPE]

The commercial grade compatibilizer, maleic anhydride grafted low density polyethylene [Trade name OPTIM E142, MFI 4.0 g/10 min @2.16 kg; 190^0C, density 0.925 (g/cm^3), melting point (T_m) 103^0C] was obtained from Pluss Polymes Pvt. Ltd, New Delhi, India. It contains maleic anhydride 0.9 to 1.3%. In the following text, this grafted copolymer is abbreviated as M-g-L.

2.1.4 Soil Compost

Soil compostage consisted of 23% loamy silt, 23% organic matter (cow manure), 23% sand, and 31% distilled water (w/w). Calcium hydroxide was added to provide pH values of 7, 9, and 11.

2.2 METHODS

2.2.1 Blend Preparation

The PLLA can degrade by hydrolysis of the ester bond therefore drying of PLLA pellets was done at 80°C under vacuum for 24 h before processing. Before blending, the polymer granules of LLDPE, PLLA and compatibilizer were mixed by tumbler mixing

Table 2.1: Details of sample preparation and their degradation

Blend designation	Amount of		
	LLDPE (g)	PLLA (g)	M-g-L (g)
LLDPE 100	100	0	0
LLDPE 95	95	5	0
LLDPE 90	90	10	0
LLDPE 85	85	15	0
LLDPE 80	80	20	0
LLDPE 75	75	25	0
LLDPE 70	70	30	0
LLDPE 65	65	35	0
LLDPE 60	60	40	0
LLDPE 55	55	45	0
LLDPE 50	50	50	0
M-g-L 80/2	80	20	2
M-g-L 80/4	80	20	4
M-g-L 80/6	80	20	6
M-g-L 80/8	80	20	8
M-g-L 80/10	80	20	10
M-g-L 65/2	65	35	2
M-g-L 65/4	65	35	4
M-g-L 65/6	65	35	6
M-g-L 65/8	65	35	8
M-g-L 65/10	65	35	10

in the desired compositions (shown in Table 2.1) followed by melt blending in extruder fitted with blown film attachment. The melt blending was performed at 200°C and screw speed of 30 rpm in a Haake PolyLab extrusion mixer with post extrusion blown film attachment (Thermo Haake, Karlsruhe,Germany). It was not possible to prepare the film by blowing process using higher amounts of PLLA because of its brittle nature.

2.2.2 Degradation Evaluation Procedures

2.2.2.1 Thermo-oxidative ageing

Thermo-oxidative ageing studies were performed according to BS 7646 -93. The samples were placed in an air oven and aged at 70°C for 72 h. The thermo-oxidation coefficient was calculated according to the physico-mechanical properties (the tensile strength and elongation at break) before and after the thermo-oxidation ageing.

The thermo-oxidation coefficient (K_{TO}) was calculated using the following equation.

$$K_{TO} = \frac{\text{The value of }\left(\text{tensile strength or elongation at break}\right)\text{ after testing}}{\text{The value of }\left(\text{tensile strength or elongation at break}\right)\text{ before testing}}$$

2.2.2.2 Hydrolytic degradation

The blend films (12 samples each) were immersed in NaOH solution of pH 7, 9 and 11 at 50°C. The NaOH solution was exchanged every 4 days. After the interval of 2, 6, 10 and 14 days, the three samples were taken out and washed intensively with distilled water at room temperature, followed by vacuum drying for at least 24 h at 30°C. Then mechanical properties of the films were determined as per ASTM D 882-91 and average of three samples was taken into account.

2.2.2.3 Measurement of degradability in soil compostage of varying pH

The films of LLDPE 100, LLDPE 80 and M-g-L 80/4 blends were weighed and buried, in triplicate, in soil compostage of pH 7, 9 and 11. Five samples of each were buried in a row in their respective trays. Biodegradation was monitored after every 30 days for approximately 12 months by measuring the residual mass. For this, the buried samples were recovered, washed with distilled water, and dried at room temperature before being weighed. The residual mass was calculated as the ratio between the final and the initial weight.

2.3 ANALYTICAL PROCEDURES

The materials obtained following the above procedure was then characterized to know the initial structure and transformation during melt blending. The changes in the characteristic properties like tensile, thermal and morphological were investigated. For the analysis of above properties, the obtained blend samples were characterized for tensile properties (UTM), structural (FTIR-ATR), crystallinity (XRD), melting behavior (DSC), thermal stability (TGA) and blend morphology (SEM). The details of these techniques are given below:

2.3.1 Tensile Testing

Physical properties such as tensile strength and elongation at break were measured according to ASTM D 882-91 procedure in Zwick Universal testing machine (model Z010 Zwick/Roell, Germany, at room temperature [25°C] and relative humidity of 50%) at a cross-head speed of 50 mm/min. Five replicates were run for each composition and the average values have been reported.

2.3.2 Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out using differential scanning calorimetry (DSC-2, Perkin Elmer, Shelton, USA). All measurements were performed under nitrogen. DSC measurements were carried out by heating from room temperature to 300^0C at a rate of 10^0C /min and were controlled by compatible computer running the Perkin Elmer (STAR SW900) instrument software. The software collected data and provided graphical analysis tools to determine transition temperatures and peak areas. DSC studies revealed the significant thermal properties of the samples, such as transition temperature (T_g) and melting temperature (T_m).

2.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a helpful tool to characterize thermal degradation (amount and rate of mass loss), thermal stability and the lifetime behavior of polymeric materials. Such characterizations provide valuable information for selection of material, prediction of product performance, and product quality.

The thermal stability of the polymer blends was determined by using TGA (Perkin Elmer Pyris, diamond TG/DTA) under a nitrogen flow of 50 ml/min. Samples weighing 3 ± 1 mg were heated from 50 to 500^0C, at a heating rate of 1, 2, 5 and 10^0C/min. The Arrhenius activation energy (E_A) was determined according to ASTM method E1641-07. The temperatures at 5, 10, 15 and 20% decomposition from each heating rate were used for calculation of E_A. These E_A values were used to generate a thermal endurance curve (lifetime) according to ASTM method E1877-05.

2.3.4 X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials.

X-ray diffraction patterns were recorded at room temperature using Philips Xpert diffractometer using monochromatic CuK_α radiation (λ = 1.5418 Å) operating at 40 kV and current 20 mA. Monochromatic x-rays are used to determine the interplanar spacing of the unknown samples. During the experiment, the scanning speed and diffraction angle were 5°/min and 5° to 100° (2θ) respectively. Percent crystallinity was calculated by using software High Score provided by Xpert.

2.3.5 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. The electrons interact with atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and morphology of crystalline phases. The types of signals produced by SEM include secondary electrons (SE), back scattered electrons (BSE), characteristic x-rays, light (cathodoluminescence), specimen current and transmitted electrons. These types of signals require specialized detectors for their detection that are not usually present on a single machine. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the present study, scanning electron micrographs of the selected samples were taken by SEM in order to understand the effect of compositions on morphology of blends.

Scanning electron micrographs of the films were taken with a scanning electron microscope (JEOL, Model JSM 5800). The accelerating voltage was 15 kV. The specimens were coated with 50 nm thick gold film in an automatic sputter coater (Polaron) to avoid charging under an electron beam prior to SEM studies.

2.3.6 Fourier Transform Infrared (FTIR) Attenuated Total Reflectance (ATR) Spectroscopy

Infrared spectroscopy is very important technique for materials analysis in the laboratory for over several decades. An infrared spectrum represents a fingerprint of a sample with absorption peaks, which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each material is a unique combination of atoms, no two compounds produce the exact by same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, intensity of signals in a spectrum gives quantitative information about the various groups presents or generated. With modern software algorithms, infrared is an excellent tool for quantitative analysis, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

Fourier transform infrared-attenuated total reflectance (FT-ATR) spectroscopic studies were carried out on film samples using a Perkin Elmer FT-IR spectrophotometer (Model BX-II, www.perkinelmer.com) in the horizontal ATR mode, using a zinc-selenide crystal. An optical layout of a typical FTIR spectrometer is shown in fig. 2.1.

A total of 16 scans were taken with a resolution of 4 cm^{-1}. The spectra were analyzed using spectrum software (LX100627-I).

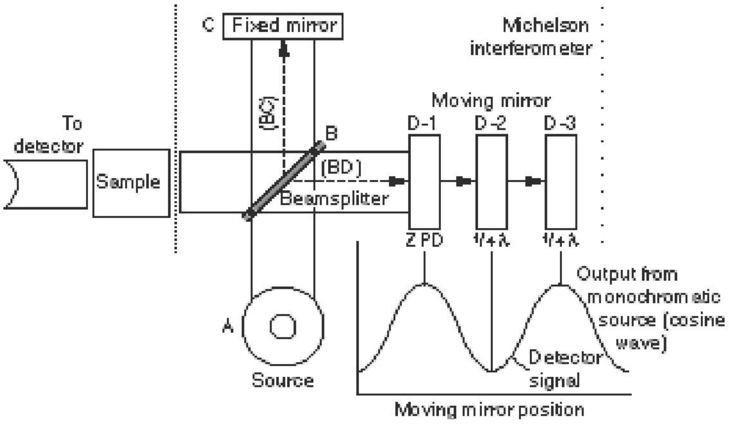


Figure 2.1: Simplified optical layout of a typical FTIR spectrometer

3: PREPARATION AND CHARACTERIZATION OF PLLA/LLDPE BLENDS

3.1 INTRODUCTION

Mixing of two or more polymers to produce blends by common processing steps is today a well-established approach for obtaining suitable materials for specific end-uses. Specific applications of biodegradable blends have drawn marked attention in offering an attractive route to further improve environmental waste management [217]. In the last few years, studies concerning the partial substitution of synthetic plastics by biodegradable materials have been increasing steadily and have proven a very useful in finding solution of plastic solid waste management problem, at least to some extent [185, 218, 219]. The systematic study of preparation of blown films which are commonly used for packaging, has not received much attention. To the best of our knowledge, no study has been done so far to investigate the effect of properties of PLLA/LLDPE blends at various PLLA loadings. Previous investigation on PLLA and LLDPE blends were primarily on toughening of PLLA [220]. Although it seems that the use of LLDPE, a non biodegradable polymer, as a blend component for PLLA may defeat the purpose of developing a ‘green’ polymer, the potential application from this research is for utilization of PLLA in structural applications especially when petroleum based commodity plastics becomes more scarce and expensive. This chapter demonstrates the investigation on blend extrusion blow film process optimization and the mechanical, thermal and morphology of PLLA/LLDPE blends having varying amounts of LLDPE.

3.2 PLLA AND LLDPE BLENDS

3.2.1 Optimization of Processing Conditions

3.2.1.1 Effect of processing temperature and screw rpm on blend preparation

PLLA is moisture sensitive and is not easy to prepare film by extrusion blown film blending technique because of poor melt stability. Therefore, their was a need to optimize the processing conditions to have better film characteristics. For this purpose, three blends samples i.e. PLLA/LLDPE 30/70, 60/40 and 90/10 were chosen. Film samples were parepared by varing temperature for 190°C to 220°C and screw rpm from 25 to 40. The films formed were optimized by using tensile properties and film forming characteristics of blend. It has been observed that because of PLLA's inherent brittle nature, the blowing was not possible for blends having 60 and 90 weight % of PLLA under these conditions. Films prepared at high temperature (above 200°C) and high shear (above 30 rpm) have poor mechanical properties (Table 3.1). This could be due to the degradation of PLLA whereas at low temperature and low shear then also gave samples with inferior mechanical properties. From these studies, optimum conditions for processing chosen for further work i.e. Temperature =200°C and screw rpm =30.

3.2.1.2 Effect of predrying on blend preparation

Table 3.1 shows that the predrying has little effect on the tensile strength of the films. Film samples of LLDPE/PLLA (70/30 w/w) blends were prepared after drying and without predrying. The tensile properties of films prepared from samples (dried before processing) and without predrying were compared. It is well reported in literature that polyesters are sensitive to hydrolytic degradation if not dried properly before processing. However in the present work we did not observe any effect on the properties of films prepared from granules after drying. Since the granules were stored under dry condions and atmospheric humidity during summer is negligible, therefore predying was not required.

Table 3.1: Optimization of processing conditions for LLDPE/PLLA (70/30 w/w) blends

Temperature °C	Screw rpm	Tensile Strength (MPa) (MD)	
		PLLA30 (After predrying)	PLLA30 (Without predrying)
190	25	6.42	6.36
200	25	7.27	7.01
210	25	7.90	7.29
220	25	6.23	6.02
190	30	8.23	7.96
200	30	10.46	10.25
210	30	9.56	9.35
220	30	7.40	7.12
190	35	6.54	6.20
200	35	8.26	7.29
210	35	8.59	8.21
220	35	8.20	7.95
190	40	6.98	6.25
200	40	8.59	8.25
210	40	7.56	7.46
220	40	6.36	6.23

3.2.2 Blend Preparation at Optimized Conditions

The details of the blend preparation and their designation are given in Table 3.2. All the blend films were prepared using optimized processing conditions i.e. 200^{o}C and 30 screw rpm.

Table 3.2: Details of blend preparation and their sample designation

Blend designation	Amount (g)	
	LLDPE	PLLA
LLDPE 100	100	0
LLDPE 95	95	5
LLDPE 90	90	10
LLDPE 85	85	15
LLDPE 80	80	20
LLDPE 75	75	25
LLDPE 70	70	30
LLDPE 65	65	35
LLDPE 60	60	40
LLDPE 55	55	45
LLDPE 50	50	50

3.2.3 Mechanical Properties

3.2.3.1 Tensile properties

The results of tensile strength and elongation at break for LLDPE 100 and its blends are shown in the Figure 3.1a and 3.1b. It has been observed that with increase of PLLA content in blends, tensile strength decreases, as PLLA is brittle in nature and acts as filler when it is dispersed in LLDPE.

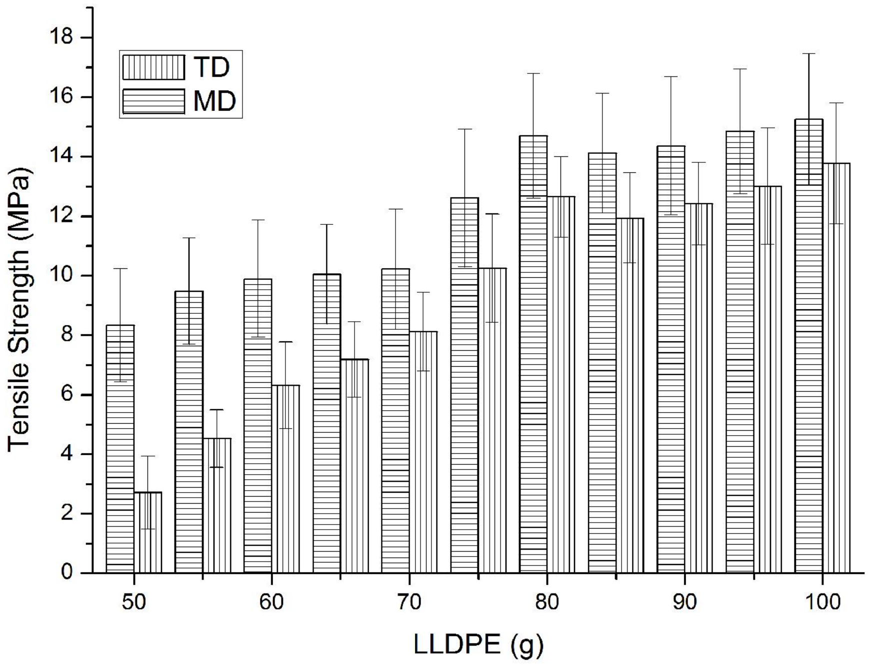


Figure 3.1a: Effect of PLLA content on tensile strength of LLDPE/PLLA blends

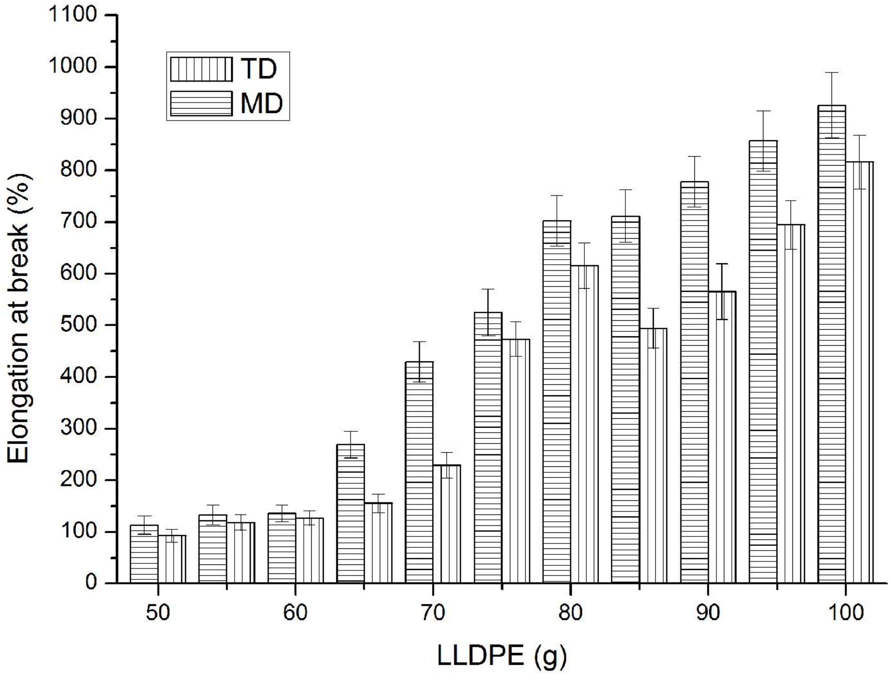


Figure 3.1b: Effect of PLLA content on elongation at break of LLDPE /PLLA

It has been observed that up to 20 % PLLA addition to the LLDPE matrix (i.e. sample LLDPE 80); tensile strength showed a marginal decrease. It may be attributed to the interaction, chain entanglement and stress induced crystallization behavior of PLLA with LLDPE during post extrusion biaxial oriented blown film in melt blending. LLDPE 80 may have maximum interfacial entanglements that would be trapped upon melt crystallization of LLDPE and PLLA. But with further increase of PLLA, the effect was nullified and PLLA polymer plays a dominant role and hence decrease in mechanical properties was observed. Therefore, we have selected LLDPE 80 for further study considering better retention of mechanical properties as well as relatively low proportion of expensive PLLA. The values of tensile strength and elongation at break for packaging application required are 11.7 MPa, and 225 % in machine direction (MD) and 8.8 MPa, and 350% in transverse direction (TD) respectively (ASTM D 4635) irrespective of thickness. Thus studies clearly shows that film preparations by using up to 25% of PLLA satisfy the requirements of packaging applications as per ASTM D 4635 [Figure 3.1a and 3.1b].

3.2.4 FTIR Spectroscopy

FTIR spectra of PLLA, LLDPE 100 and LLDPE 80 blend are shown in Figure 3.2. The FTIR spectra for the films in the study were obtained in the region 500-4000 cm^{-1}. In this FTIR spectra of PLLA, strong peaks due to -C=O- strech, -CH$_3$- bending, -C-O- bending were observed at 1760 cm^{-1}, 1465 cm^{-1}, 1362 and 1165 cm^{-1} respectively.

It is well reported in the literature that due to hydrogen bonding or some interaction in the component material, one observe a shift in absorption band. In this present work, we took FTIR spectra of PLLA, LLDPE and their blends. No shift in the absorption band of PLLA upon blending with varing amounts of LLDPE clearly show that two polymers behave independently in the polymer blends.

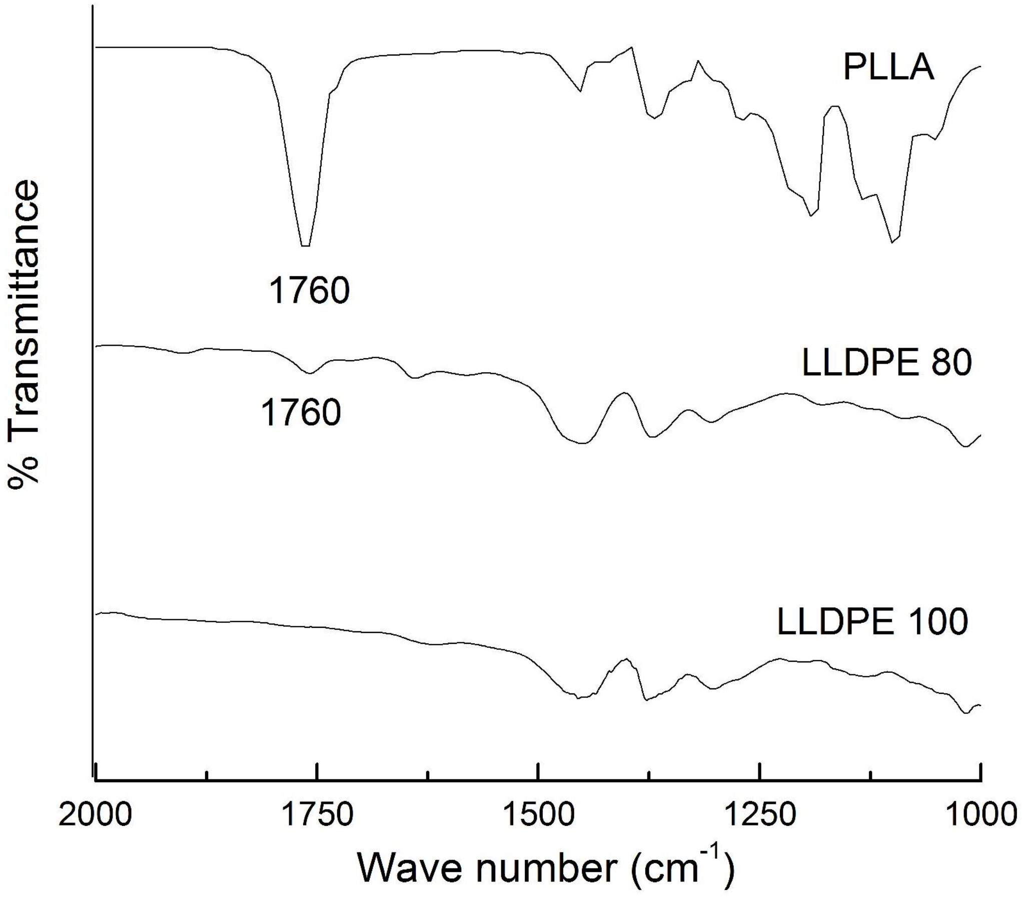


Figure 3.2: FTIR spectra of PLLA, LLDPE 100 and LLDPE 80

3.2.5 Thermal Properties

Figure 3.3 show the DSC traces of PLLA, LLDPE 100 and LLDPE 80 (blend of LLDPE/PLLA 80/20). In the DSC trace of LLDPE 100, an endothermic peak due to melting was observed which corresponds to melting peak at 125.36^{0}C. In the DSC trace of PLLA, an endothermic shift which corresponds to glass transition temperature (T_g) was observed at 64.69^{0}C followed by melting endotherm with a peak at 169.79^{0}C was observed. In the DSC trace of LLDPE 80 blend, an endothermic shift in baseline corresponding to T_g of PLLA i.e. 56.29^0C and two melting endotherms with a peaks at 123.43^0C (due to LLDPE) and 169.19^0C (due to PLLA) was observed.

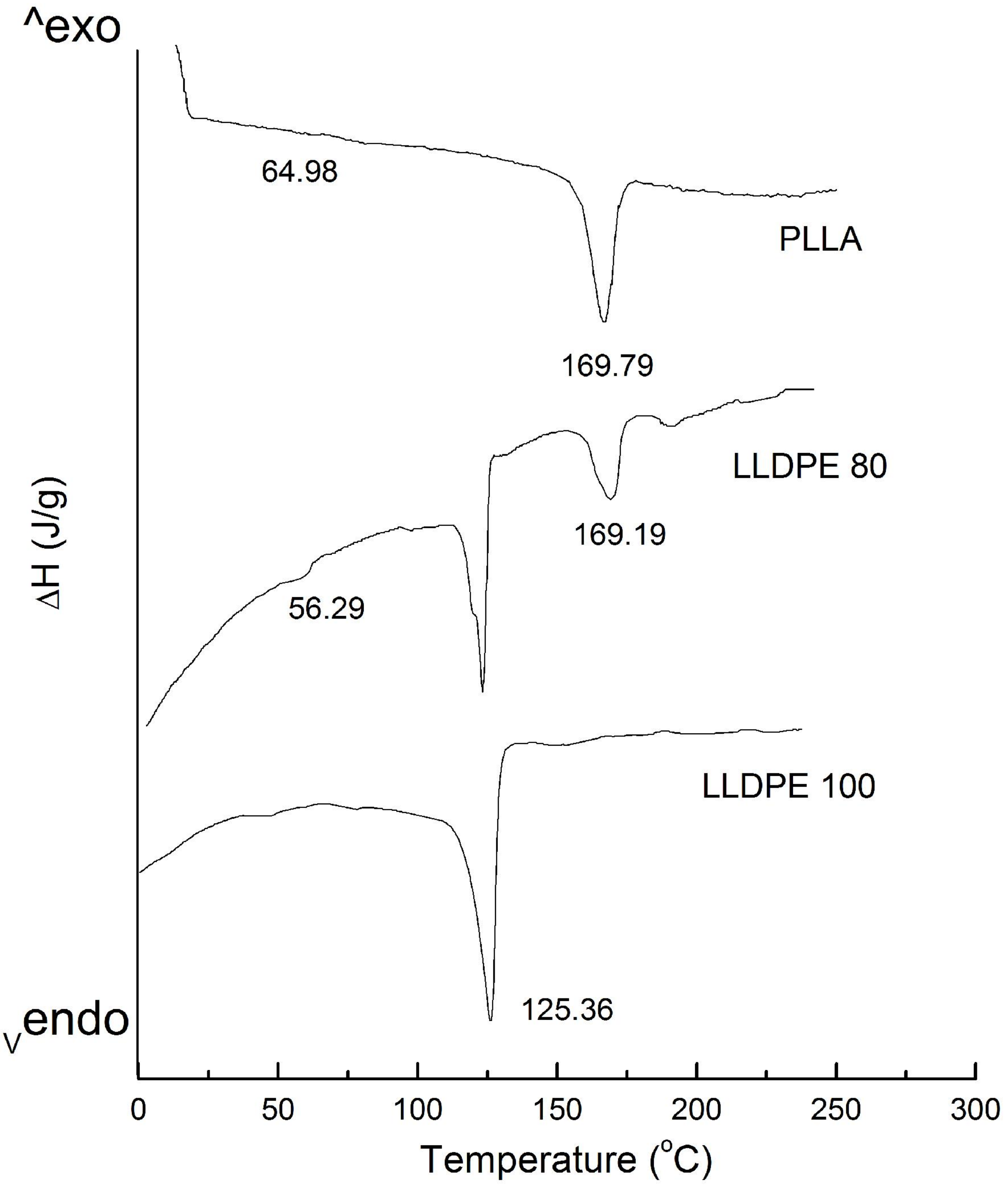


Figure 3.3: DSC traces of PLLA, LLDPE 100 and LLDPE 80

Table 3.3: Endothermic peaks of DSC scans of PLLA, LLDPE 100 and LLDPE 80

Blends/component	T_g (^{0}C)	T_m(^{0}C)
PLLA	64.69	169.79
LLDPE 100	-	125.36
LLDPE 80	56.29	123.43, 169.19

The results of DSC scans are summarized in Table 3.3. The results clearly show the shift in T_g of PLLA, However melting point does not change significantly. The decrease in T_g of PLLA upon blending could be due to the softening of PLLA phase by blending with LLDPE phase.

3.2.6 X-Ray Diffraction Analysis

Figure 3.4 shows the diffraction pattern of LLDPE 100, LLDPE 80 and LLDPE 65 blend. All samples were crystalline. In case of LLDPE 100, diffraction peaks were at 2θ of 8.98^0, 21.0^0 and 28.16^0. The diffraction angle 2θ remains unchaged with addition of PLLA suggests crystalline structure does not change after blending. The area under curve has been calculated by software High Score, gives degree of crystallization (X_c) of the LLDPE 100, LLDPE 80 and LLDPE 65 were 41%, 43% and 32% respectively. The small increase in degree of crystallization in LLDPE 80 can be attributed to the interaction, chain entanglement and crystallization behavior of PLLA phase with LLDPE phase during post extrusion blown film blending. Degree of crystallization further decreases in LLDPE 65 blend may be due to more brittle PLLA phase, which restricts crystallization.

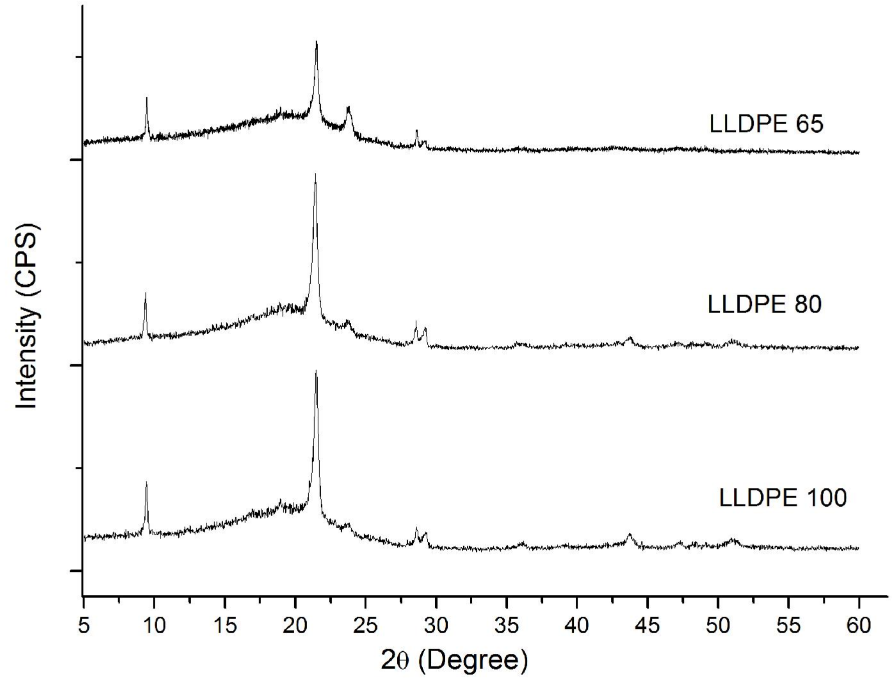
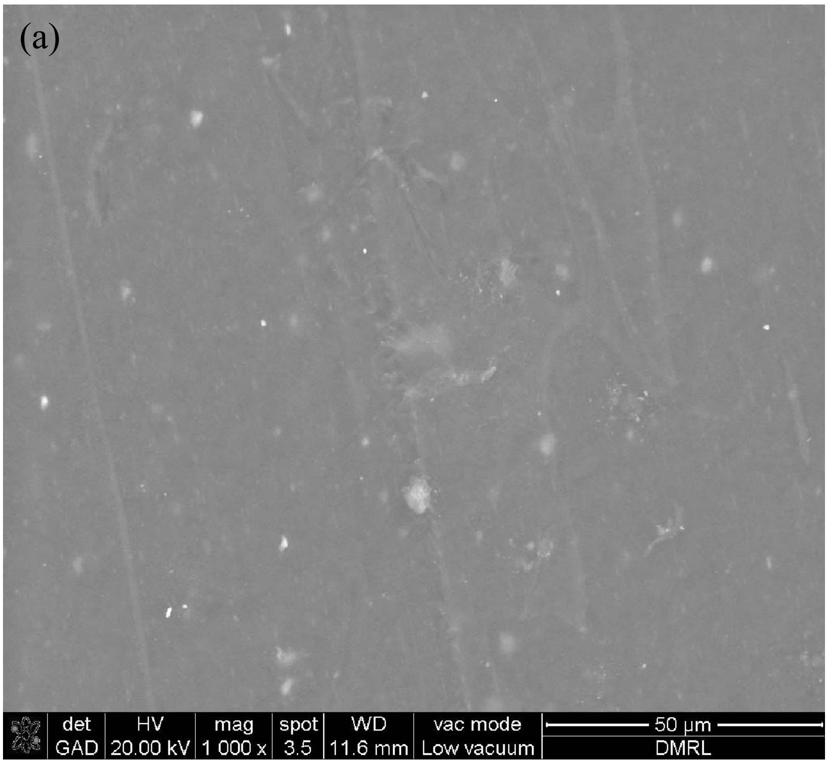
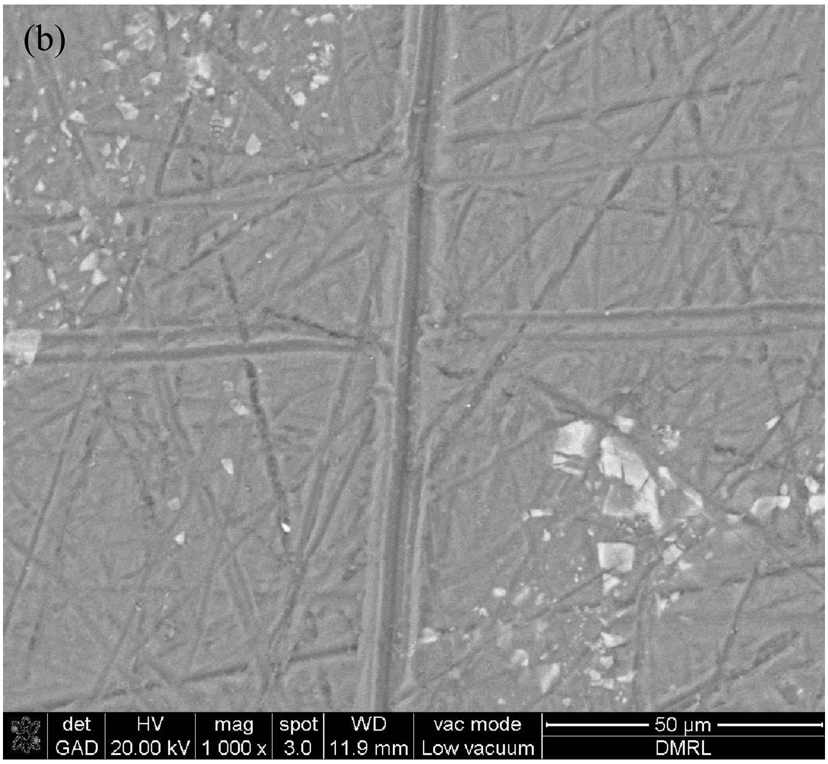


Figure 3.4: XRD patterns for LLDPE 100, LLDPE 80 and LLDPE 65

3.2.7 Morphological Characteristics

Scanning electron microscopy was used to characterize the morphology of LLDPE films before and after blending. As expected LLDPE film surface smooth (Figure 3.5a) whereas in case of LLDPE 80 and LLDPE 65 two phase morphology was clearly seen . (Figure 3.5b and 3.5c). PLLA was dispersed in the LLDPE matrix in a non-uniform manner. PLLA form large narrow and non-uniform channels, suggesting that LLDPE forms a continuous phase and PLLA a separated coarse phase. The boundary between the PLLA and LLDPE is very clear and sharp indicating strong incompatibility and weak interfacial adhesions.


(a)
det GAD
HV 20.00 kV
mag 1 000 x
spot 3.5
WD 11.6 mm
vac mode Low vacuum
50 µm
DMRL


(b)
det GAD
HV 20.00 kV
mag 1 000 x
spot 3.0
WD 11.9 mm
vac mode Low vacuum
50 µm
DMRL

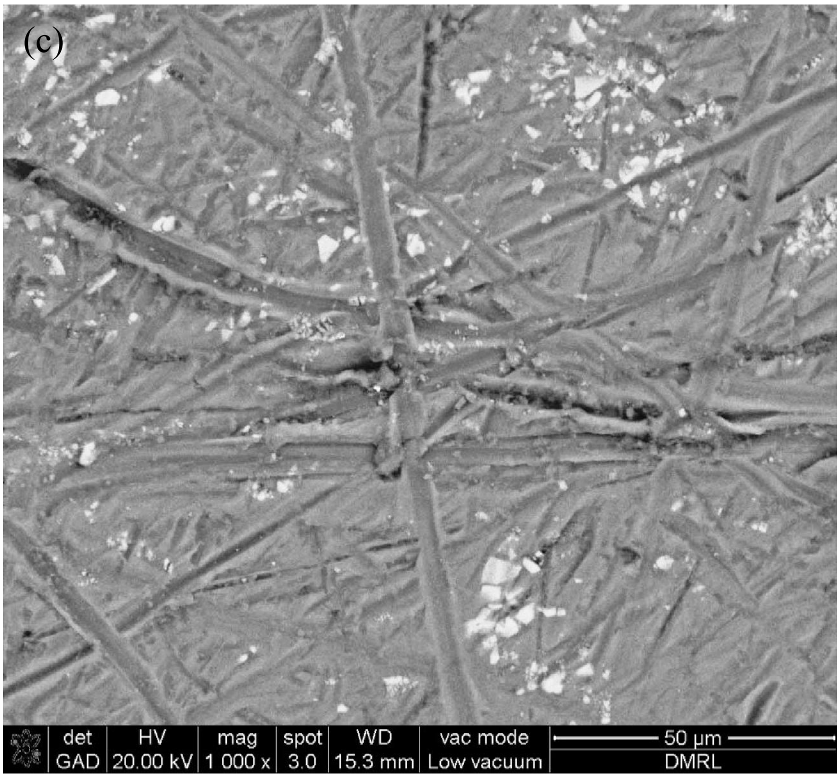


Figure 3.5: Scanning electron micrographs of the LLDPE 100 and its blends:
(a) LLDPE 100, (b) LLDPE 80 and (c) LLDPE 65

3.3 CONCLUSION

The polymer blends LLDPE/PLLA were prepared successfully by melt blending using single screw extruder fitted with post extrusion blown film attachment. The mechanical properties of LLDPE/PLLA blend decreases with increase of PLLA content. Among the investigated samples, the blend LLDPE 80 had optimum tensile strength and elongation at break. The FTIR analysis indicated that there is no specific interaction in the blends. DSC and XRD study support the some interaction between LLDPE/PLLA blends. Morphological studies indicate that the composition of PLLA has influenced the morphology of the LLDPE/PLLA blends. Investigated samples of LLDPE/PLLA blends were found to be incompatible over whole range of compositions.

4: PREPARATION AND CHARACTERIZATION OF PLLA/LLDPE BLENDS WITH COMPATIBILIZER

4.1 INTRODUCTION

Blending of PLLA with variety of polymers is well reported in the literature and most of the blends based on PLLA are incompatible. Compatibilization of such blends is required to have an optimum combination of properties. The development of miscible blends improves its physical properties and extends its applications; however, it is very difficult to obtain a miscible blend of non-polar polymers like polyolefins and polar polyesters. The LLDPE is the non-polar and PLLA is a polar polymer. Thus, the strategy for developing compatible blend should be the use of third component which has polar functionalization and grafted on non-polar component of the blend. This will act as a bridge between two components. The functionalized polyethylene via grafting reaction with polar unsaturated monomers in solution, melt, or solid state, has attracted much attention due to its application in polymer blends and composites. Among these unsaturated monomers, maleic anhydride (MAH) is widely used [221, 222].

On basis of literature report, it was therefore considered of interest to investigate the effect of compatibilizer i.e. LDPE-g-MA on the properties of LLDPE/PLLA blends. For this purpose, we choose LLDPE 80 [LLDPE/PLLA 80/20] and LLDPE 65 [LLDPE/PLLA 65/35] which should be an optimum combination of properties (chapter 3 of thesis).

4.2 PREPARATION OF LLDPE/PLLA BLENDS IN PRESENCE OF COMPATIBILIZER

The details of sample preparation alongside sample designation are given in Table 4.1. Several samples were prepared by taking 2, 4, 6, 8 and 10 phr of M-g-L and samples based on LLDPE/PLLA 80/20 blend have been designated as M-g-L 80/2, M-g-L 80/4, M-g-L 80/6, M-g-L 80/8 and M-g-L 80/10 respectively. M-g-L represents

LLDPE/PLLA in presence of compatibilizer, 80 represents wt% of LLDPE and numeral 2, 4, 6, 8 and 10 represents phr of compatibilizer. Similarly the samples based on LLDPE/PLLA 65/35 were designated.

Table 4.1: Details of formulations along with sample designation (temperature 200^{o}C and 30 screw rpm)

Blend code	Amount (g)		
	LLDPE	PLLA	M-g-L
M-g-L 80/2	80	20	2
M-g-L 80/4	80	20	4
M-g-L 80/6	80	20	6
M-g-L 80/8	80	20	8
M-g-L 80/10	80	20	10
M-g-L 65/2	65	35	2
M-g-L 65/4	65	35	4
M-g-L 65/6	65	35	6
M-g-L 65/8	65	35	8
M-g-L 65/10	65	35	10

4.2.1 Mechanical Properties

The stress-strain curves of the LLDPE 100, LLDPE 80 and M-g-L 80/4 films in both machine direction (MD) and transverse direction (TD) are also shown in the Fig. 4.1a and 4.1b. The maximum force required for break decreased by 5N and 11N in case of LLDPE 80 and M-g-L 80/4 respectively as compared to LLDPE 100. The decrease in elongation at break and yield stress could be due to brittle nature of PLLA or higher MFI comapatibilzer. The mechanical properties of the LLDPE 100 and its blends with

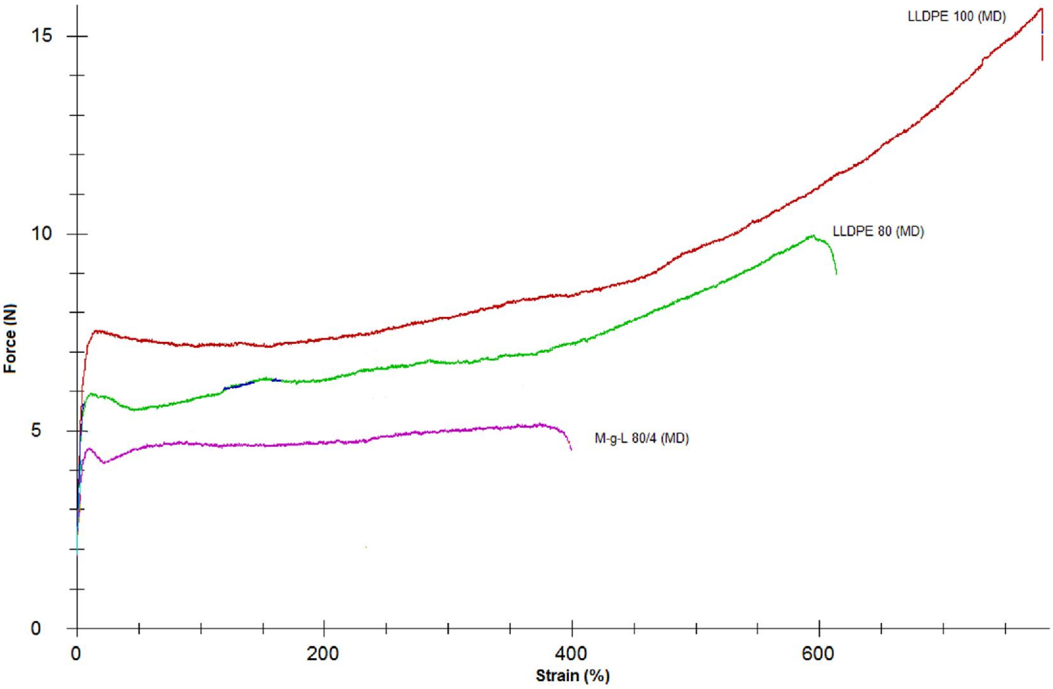


Figure 4.1a: Stress-strain curves (MD) for LLDPE 100, LLDPE 80 and M-g-L 80/4

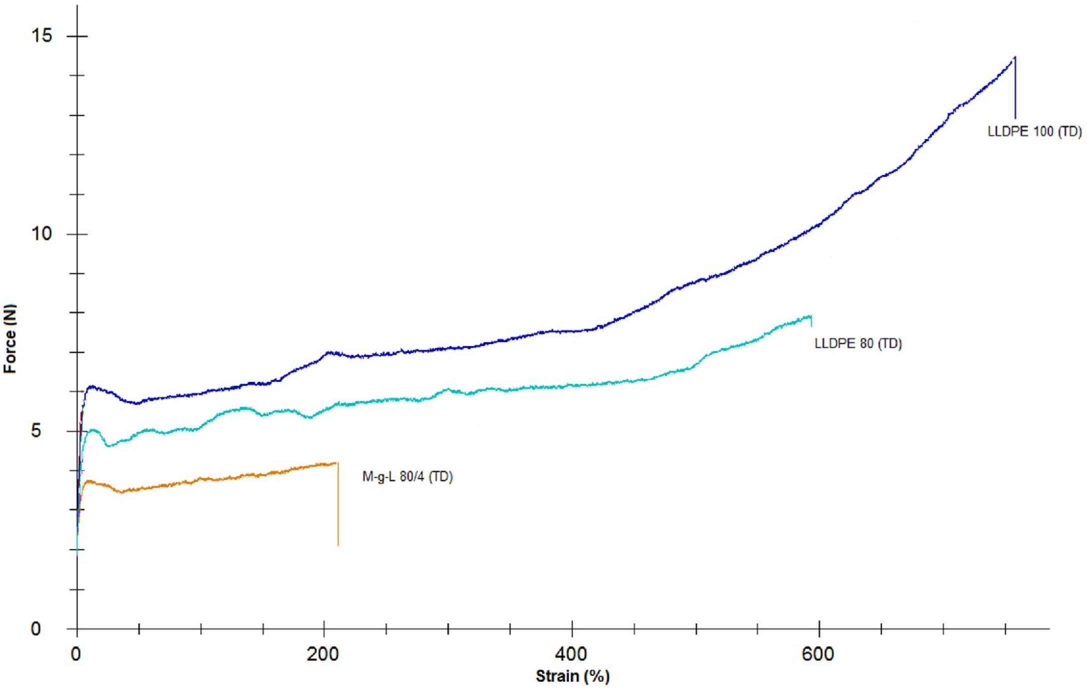


Figure 4.1b: Stress-strain curves (TD) for LLDPE 100, LLDPE 80 and M-g-L 80/4

and without compatibilizer are given in Table 4.2. The Figure 4.2a & 4.2b shows tensile strength as well as elongation at break of the PLLA/LLDPE blends. The two blend samples i.e. LLDPE 80 and LLDPE 65 were chosen to investigate the effect of compatibilizer M-g-L. The amount of compatibilizer was viewed for 2-10 phr and several samples were prepared. The addition of compatibilizer decreases the tensile strength as well as elongation at break of blends (Figure 4.3a, 4.3b, 4.3c & 4.3d). One would have expected an improvement in the mechanical properties in presence of compatibilizer. However, the observed decrease in tensile properties could be due to the low molecular weight of M-g-L (MFI=4) which may act as plasticizer and resulted in a overall decrease in tensile properties. Tensile strength was highest for blends in presence of 4 phr compatibilizer. The blends LLDPE 80 and M-g-L 80/4 with relatively better mechanical properties were selected for further studies as these blend materials can be used in packaging applications.

4.2.2 FTIR Spectroscopy of Optimized Blend Films

FTIR spectra of LLDPE 100, LLDPE 80, M-g-L 80/4, PLLA and M-g-L are shown in Figure 4.4. The FTIR spectra for the study were shown in the region 1000-2000 cm^{-1}. The strongest peaks observed in the case of PLLA at 1760 (-C==O), 1465 (-CH-), 1362 and 1265 (-C-O-). M-g-L exhibits absorptions at 1864-1860 cm^{-1} {the asymmetric stretching of carbonyl ν_{as}(C=O)}, 1786-1784 cm^{-1} {the symmetric stretching of carbonyl ν_s(C=O)}, 1224 cm^{-1} {the asymmetric ring stretching ν(=C-O-C=)}, and 1064 cm^{-1} and 1051 cm^{-1} {the symmetric ring stretching ν(=C-O-C=)}, characteristic of cyclic ethers [223]. In many compatible blends polymer containing carbonyl group usually undergo some interaction such as hydrogen bonding and a shift this peak is observed.

Table 4.2: Mechanical properties of LLDPE, PLLA/LLDPE and PLLA/LLDPE/M-g-L blends

S. No.	Blend Code	Tensile Strength (MPa)		Elongation at Break (%)	
		TD	MD	TD	MD
1	LLDPE 100	13.78 (2.03)	15.25 (2.21)	816.00 (52)	926.00 (63)
2	LLDPE 95	13.01 (1.96)	14.85 (2.09)	694.00 (47)	857.00 (58)
3	LLDPE 90	12.42 (1.39)	14.36 (2.32)	565.00 (54)	778.00 (49)
4	LLDPE 85	11.43 (1.52)	13.92 (2.01)	494.00 (38)	711.00 (51)
5	LLDPE 80	12.65 (1.35)	14.69 (2.09)	615.60 (44)	702.00 (49)
6	LLDPE 75	10.25 (1.82)	12.62 (2.31)	473.20 (33)	525.00 (45)
7	LLDPE 70	8.12 (1.32)	10.22 (2.02)	228.80 (25)	429.20 (39)
8	LLDPE 65	7.19 (1.26)	10.05 (1.67)	155.80 (18)	269.20 (26)
9	LLDPE 60	6.32 (1.46)	9.90 (1.96)	127.20 (14)	136.00 (16)
10	LLDPE 55	4.53 (0.97)	9.48 (1.78)	118.20 (15)	133.00 (19)
11	LLDPE 50	2.72 (1.22)	8.34 (1.91)	93.00 (12)	113.60 (18)
12	M-g-L 80/2	4.77 (1.56)	5.02 (1.39)	102.00 (15)	356.00 (25)
13	M-g-L 80/4	7.02 (1.68)	8.55 (1.27)	206.40 (20)	446.80 (35)
14	M-g-L 80/6	3.98 (1.02)	4.13 (1.26)	95.80 (13)	303.00 (42)
15	M-g-L 80/8	3.67 (1.23)	3.88 (1.02)	70.60 (5)	249.60 (29)
16	M-g-L 80/10	3.15 (1.02)	3.80 (1.32)	50.20 (9)	186.00 (24)
17	M-g-L 65/2	4.20 (1.33)	6.56 (1.69)	10.60 (4)	249.00 (32)
18	M-g-L 65/4	6.98 (1.47)	7.12 (1.45)	16.00 (3)	349.00 (43)
19	M-g-L 65/6	4.93 (1.95)	5.25 (1.25)	11.20 (4)	251.60 (32)
20	M-g-L 65/8	4.45 (1.52)	5.99 (1.02)	12.00 (6)	239.00 (29)
21	M-g-L 65/10	3.88 (1.26)	5.28 (1.24)	12.80 (4)	224.00 (26)

Values within parenthesis represents standard deviations

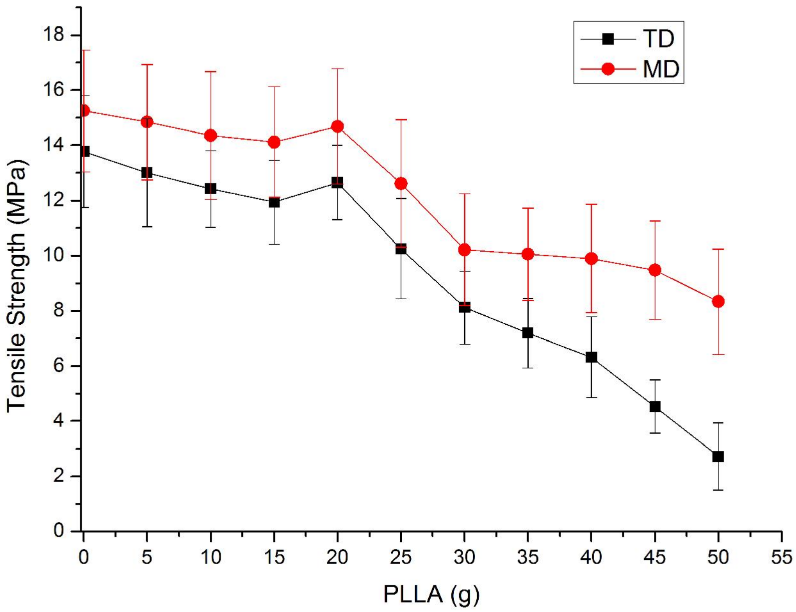


Figure 4.2a: Tensile strength and elongation at break of blends: Change in tensile strength by varying PLLA composition in blend

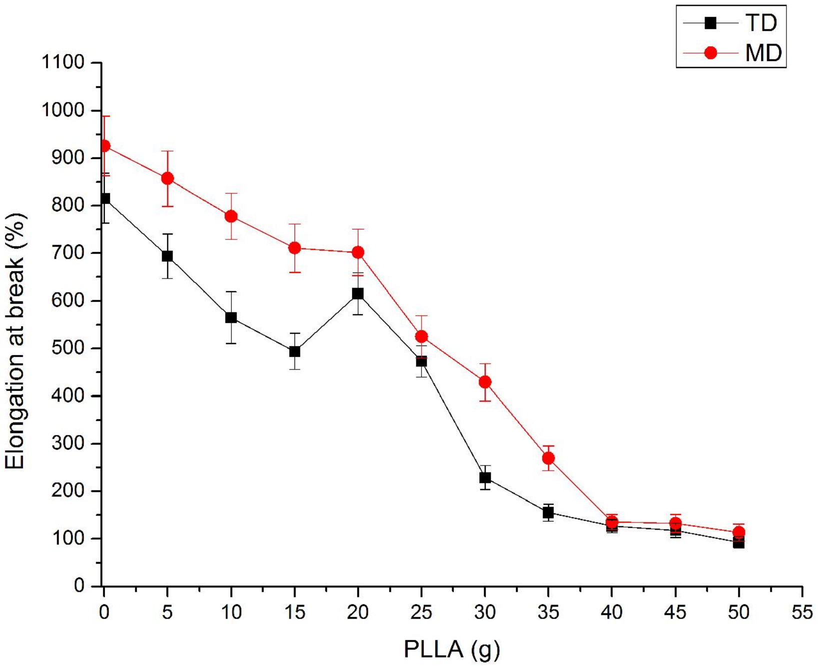


Figure 4.2b: Tensile strength and elongation at break of blends: Change in elongation at break by varying PLLA composition in blend

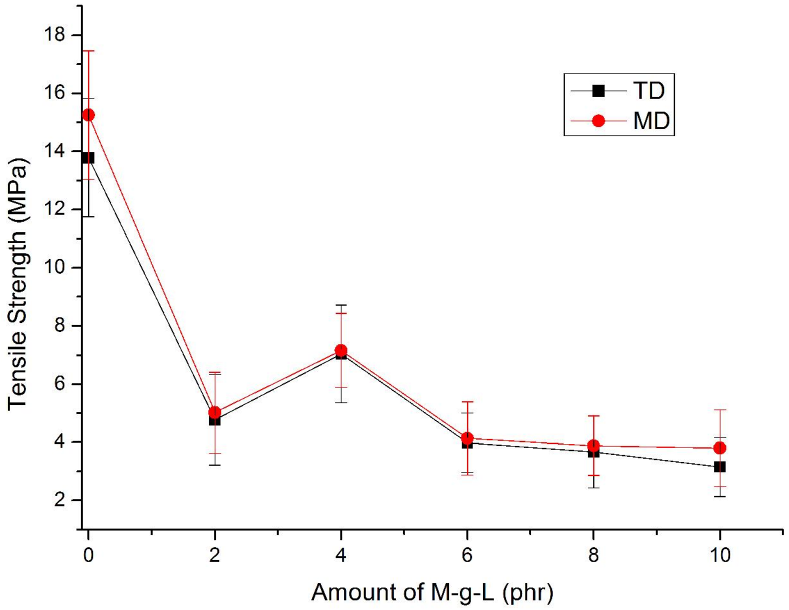


Figure 4.3a: Effect of M-g-L content on tensile strength of LLDPE 80 [PLLA/LLDPE 20/80] blend

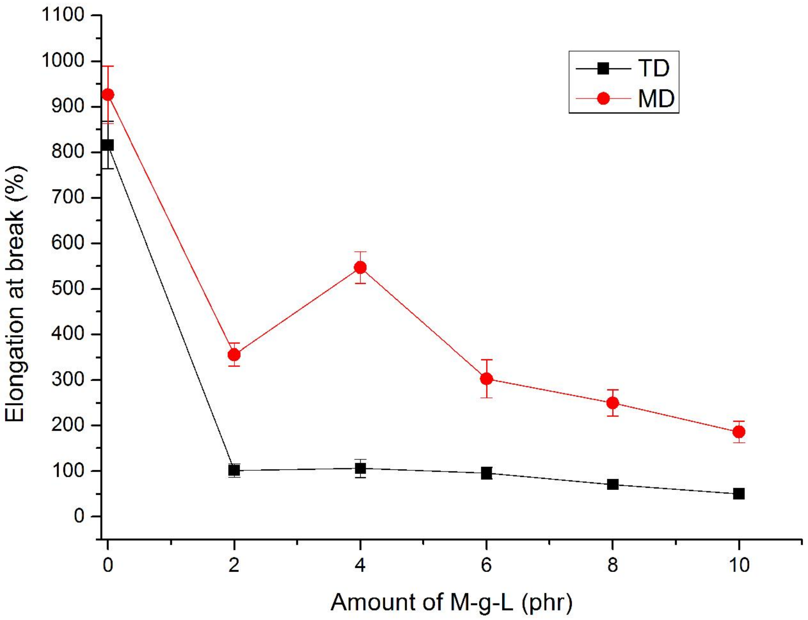


Figure 4.3b: Effect of M-g-L content on elongation at break of LLDPE 80 [PLLA/LLDPE 20/80] blend

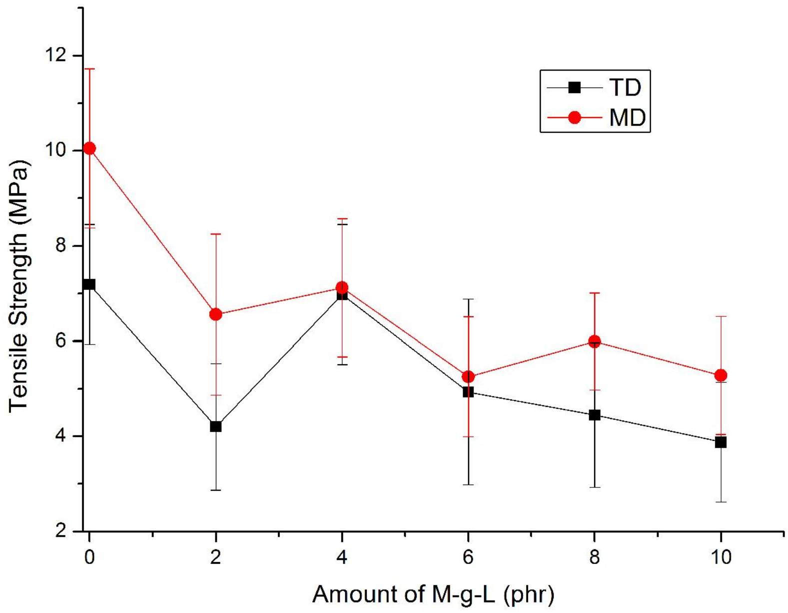


Figure 4.3c: Effect of M-g-L content on tensile strength of LLDPE 65 [PLLA/LLDPE 35/65] blend

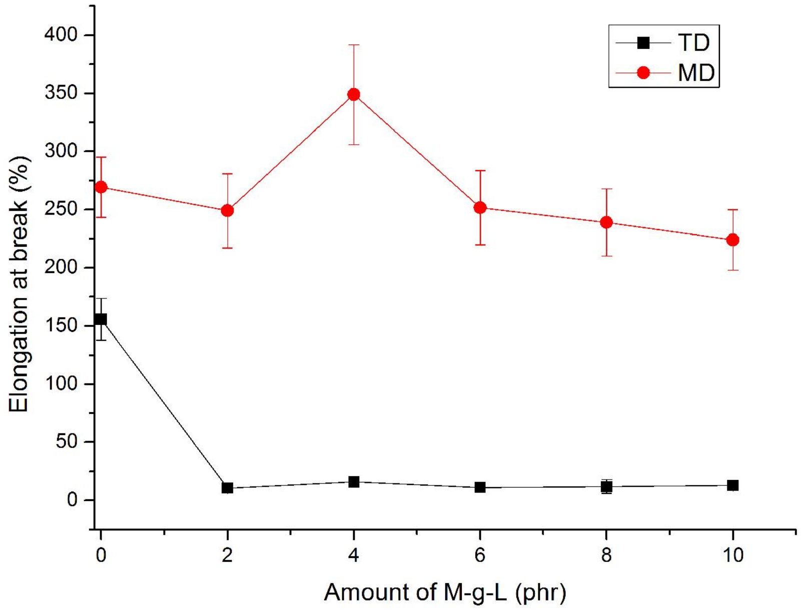


Figure 4.3d: Effect of M-g-L content on elongation at break of LLDPE 65 [PLLA/LLDPE 35/65] blend

In PLLA the peak centered at 1760 cm^{-1} is attributed to the carbonyl group and is of interest because any interactions would shift peak positioning. However no significant shift in this peak was observed in the blend LLDPE 80.

The peaks observed in the M-g-L 80/4 spectra at 1784 and 1742 cm^{-1} are assigned as carbonyl peak of M-g-L and PLLA respectively. The 18 cm^{-1} shift in peak can be attributed to the blend M-g-L 80/4 which may be due to hydrogen bonding interaction in the two phases of PLLA and LLDPE in the presence of compatibilizer. This indicates that the two polymers are incompatible but in the presence of compatibilizer shows some extent of compatibility.

4.2.3 X-Ray Diffraction Analysis

Figure 4.5 shows XRD patterns of films of LLDPE 100 and their blends in presence and absence of compatibilizer. All samples were crystalline. The diffraction peaks for LLDPE were at $2\theta = 8.98^0$, 21.0^0 and 28.16^0. These peaks were still evident after addition of the PLLA and compatibilizer M-g-L. It suggests that crystalline structure does not change after addition of the compatibillizer.

The degree of crystallization (X_c) of the LLDPE 100, LLDPE 80 and M-g-L 80/4 were 41%, 43% and 44% respectively has been calculated by the software High Score. The small increase in degree of crystallization has been observed in M-g-L 80/4 as compared to LLDPE 80. The addition of compatibilizer and its interaction may have packed crystals in more uniform manner. The crystallization of blends has been influenced marginally by the presence of compatibilizer.

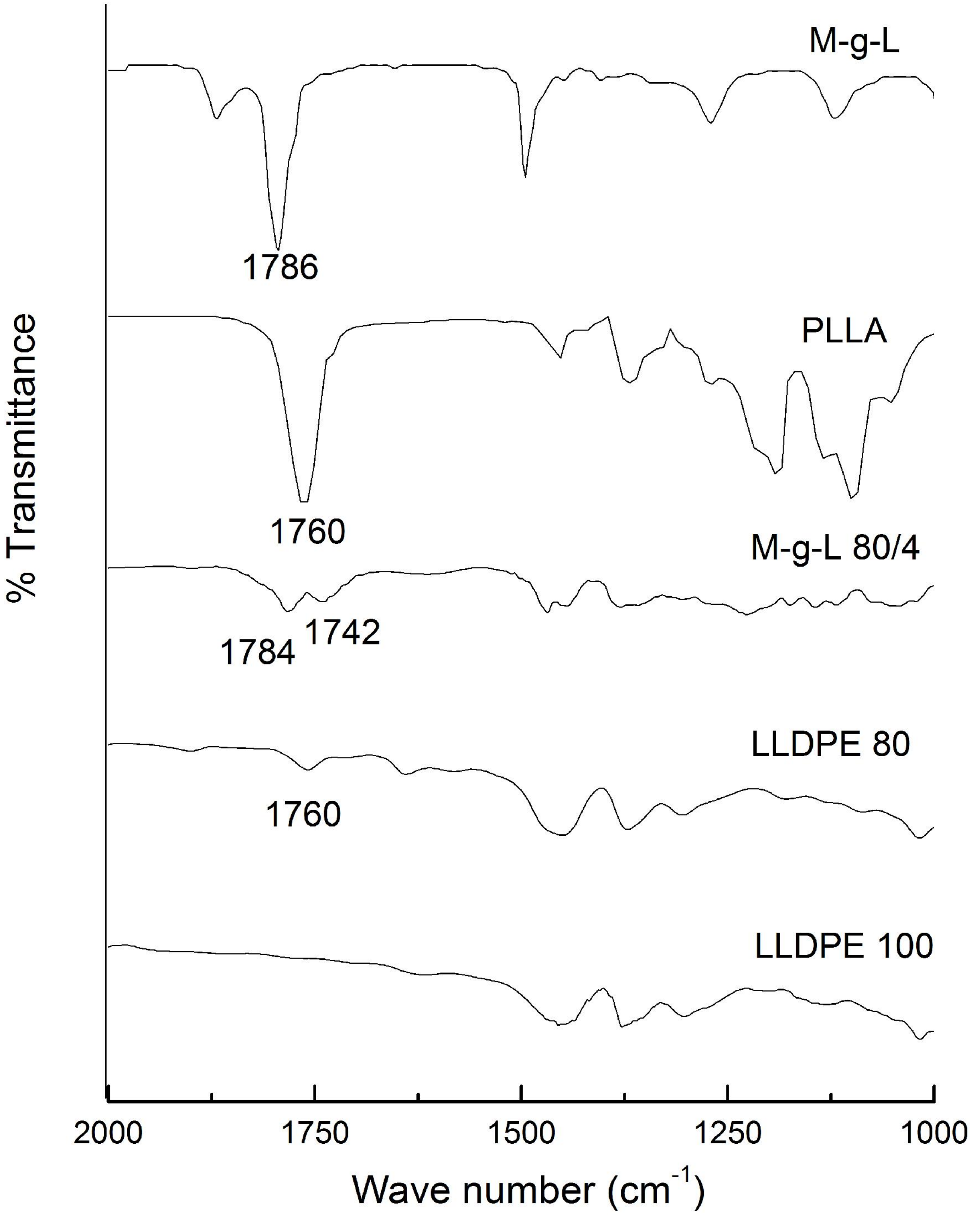


Figure 4.4: FTIR spectra of PLLA, M-g-L, LLDPE 100, LLDPE 80 and M-g-L 80/4

Table 4.3 Characteristic FTIR peaks of blends

Blend Code	-O-H#	-CH-#	-C=O- #	$-CH_3$ *	-C-O-#	-O-H *	-C-C- #
PLLA	3571	2997	1760	1456	1179	1047	874
LLDPE 100		2951		1455	1165	1016	864
LLDPE 95		2977	1761	1454	1156	1078	865
LLDPE 90		2978	1759	1453	1180	1080	865
LLDPE 85		2940	1761	1451	1158	1070	868
LLDPE 80		2975	1760	1455	1153	1056	866
LLDPE 75		2940	1758	1442	1161	1054	865
LLDPE 70		2944	1762	1445	1156	1047	867
LLDPE 65		2932	1760	1467	1160	1070	869
LLDPE 60		2944	1761	1446	1178	1078	870
LLDPE 55		2938	1759	1456	1155	1070	875
LLDPE 50		2932	1761	1467	1147	1056	876

# indicates stretch and * indicates bend

Table 4.4 Comparison of characteristic FTIR peaks of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

Blend Code	-O-H#	-CH-#	-C=O- #	$-CH_3$ *	-C-O-#	-O-H *	-C-C- #
PLLA	3571	2997	1760	1456	1179	1047	874
LLDPE 100		2951		1455	1165	1016	864
LLDPE 80		2975	1760	1455	1153	1056	866
M-g-L 80/4		2937	1784/1742	1468	1227	1025	865

# indicates stretch and * indicates bend

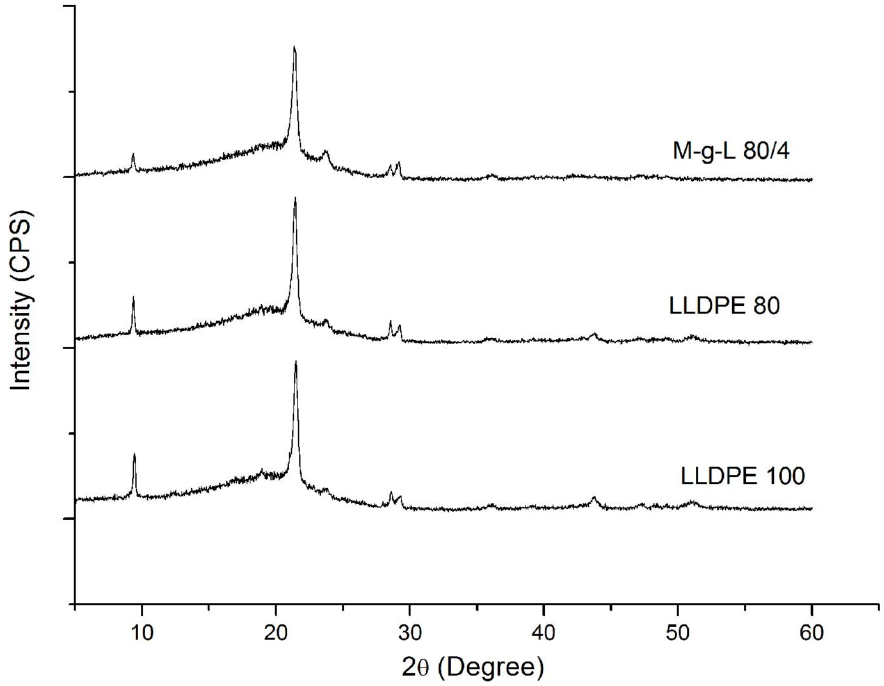


Figure 4.5: XRD patterns for LLDPE 100, LLDPE 80 and M-g-L 80/4

4.2.4 Morphological Properties of Optimized Blend Films

4.2.4.1 Surface morphology

Figure 4.6 show the scanning electron micrographs of LLDPE 100 and its blends. The Figure 4.6a of LLDPE100 surface appears uniform and smooth. Figure 4.6b show LLDPE 80 blend. The PLLA was dispersed in the LLDPE matrix in a non-uniform manner. PLLA form large narrow and non-uniform channels, suggesting that LLDPE forms a continuous phase and PLLA a separated coarse phase. Hence with addition of the PLLA there was decrease in tensile strength. The boundary between the PLLA and LLDPE is very clear and sharp indicating strong incompatibility.

Once the compatibilizer was added to the LLDPE 80 blend the PLLA was uniformly dispersed in LLDPE matrix as shown in Figure 4.6c. It indicates that the compatibilizer has influenced the morphology of the LLDPE/PLLA blends. The particle size of PLLA phase decreased with addition of compatibilizer as reported in the literature [224].

4.2.4.2 Fracture surface morphology

Figure 4.7 shows the scanning electron micrographs of the LLDPE 100 and its blends fracture surface. Figure 4.7a of LLDPE 100 tensile fracture surface is showing stretch fibrils. This stretch fibrils accounts for relatively high ductility as well as high toughness since considerable amount of energy consumed in the process. Figure 4.7b and 4.7c show fracture surface of LLDPE 80 and M-g-L 80/4 blend films.

The addition of PLLA, a brittle material has influenced the morphology of LLDPE 80. The mix of river and fibrils like pattern gives brittle mechanism of fracture. The M-g-L 80/4 shows same type of pattern with relatively lower river pattern indicating that the compatibilizer has influenced the morphology of LLDPE/PLLA blends. This fracture morphology can also be related to brittle fracture. The break pattern of LLDPE 80 and M-g-L 80/4 indicates that brittle break gives more river pattern in LLDPE 80 as compared to M-g-L 80/4 where break is comparatively ductile. The compatibilzer has influenced the break pattern, elongation may have decreased but because of compatibilization, it required more energy at break.

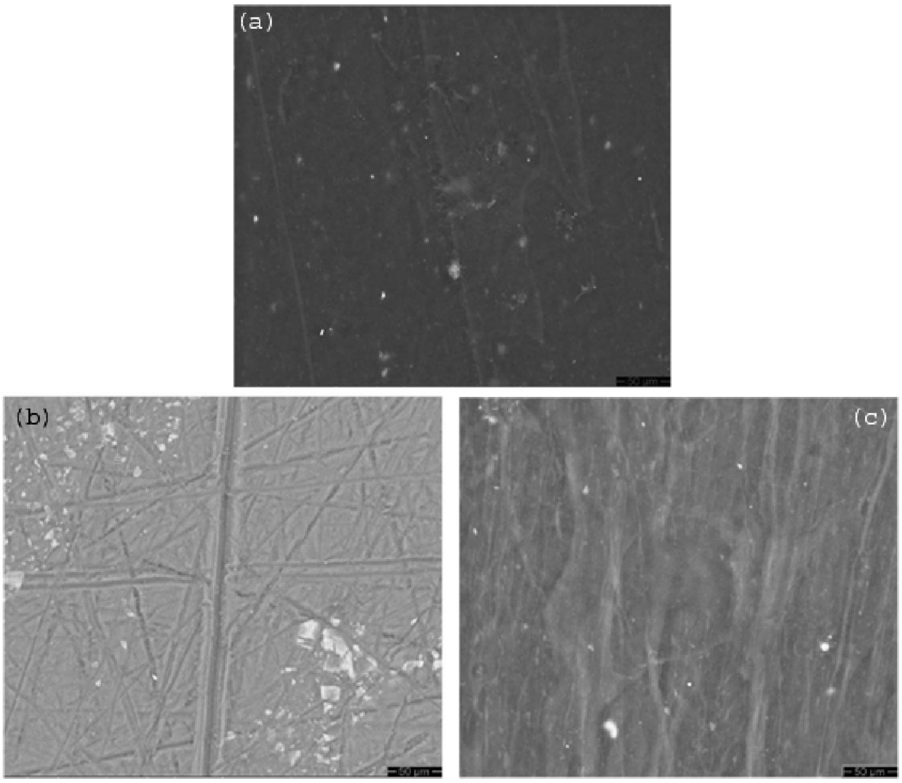


Figure 4.6: Scanning electron micrographs of surface: (a) LLDPE 100 (b) LLDPE 80, and (c) M-g-L 80/4

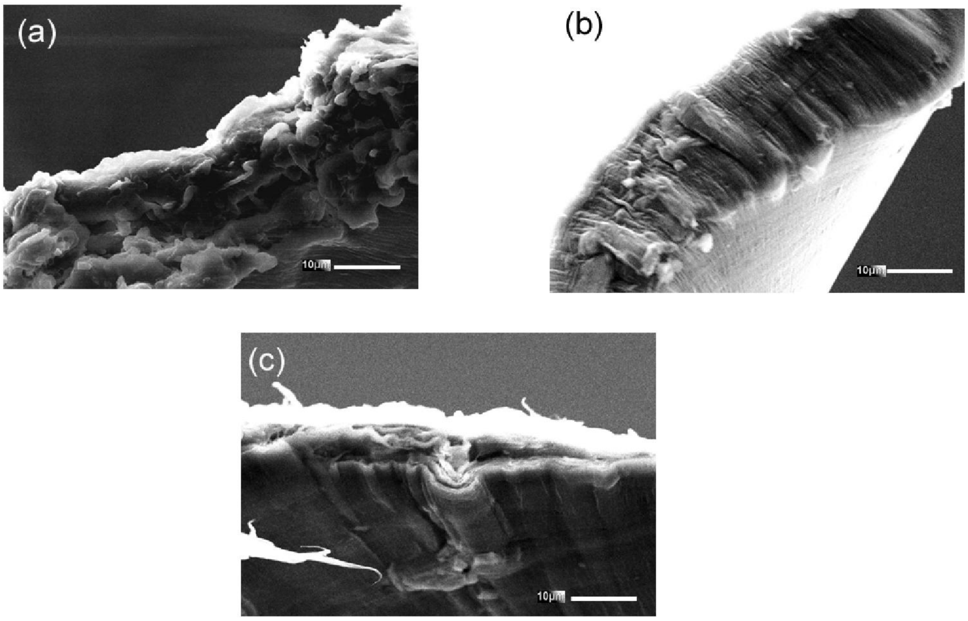


Figure 4.7: Scanning electron micrographs of tensile fracture surface (a) LLDPE 100 (b) LLDPE 80 and (c) M-g-L 80/4

4.2.5 Thermal Properties

4.2.5.1 DSC

Miscible polymer pairs show a single glass transition (T_g) intermediate between those of pure polymers which makes DSC a well known method to study the miscibility of polymer blends. The DSC traces of LLDPE 100, LLDPE 80, M-g-L 80/4, and PLLA and M-g-L are shown in Fig. 4.8. PLLA, is a semi crystalline polymer and the major features of its DSC curve are the T_g at 64.98°C and its melting peak (T_m) at 169.79°C. LLDPE is semi crystalline and the T_m is 125.36°C. The transitions shown at 45.00°C and 72.00°C can be attributed to chemical composition distribution of copolymer components of pure material. This transition does not appear in the blends LLDPE 80 and M-g-L 80/4. This may be due to reaction or interaction between the PLLA and LLDPE components. The compatibilizer (M-g-L) is also semi crystalline polymer and its T_m is 107.56°C. The blend LLDPE 80 shows the decrease of T_g from 64.98°C to 56.29°C, and T_m show negligible change. It may be due to interaction between the two polymer interfaces. The T_m which does not change significantly may be because of stress induced crystallization. In M-g-L 80/4 blend, there is further decrease in T_g to 52.98°C. This can be attributed to the plasticizing effect of the compatibilizer. There may be more uniform dispersion which increases the interfacial interaction which is also supported by SEM micrograph and FTIR spectroscopy analysis.

4.2.5.2 Thermal stability analysis of blend films

The weight loss behavior during the thermal degradation of the PLLA, LLDPE 100, M-g-L, LLDPE 80 and M-*g*-L80/4 films has been studied. The thermally stable material shows resistance to weight loss up to processing temperatures. This directly gives the idea about the processing conditions and applications of the blends.

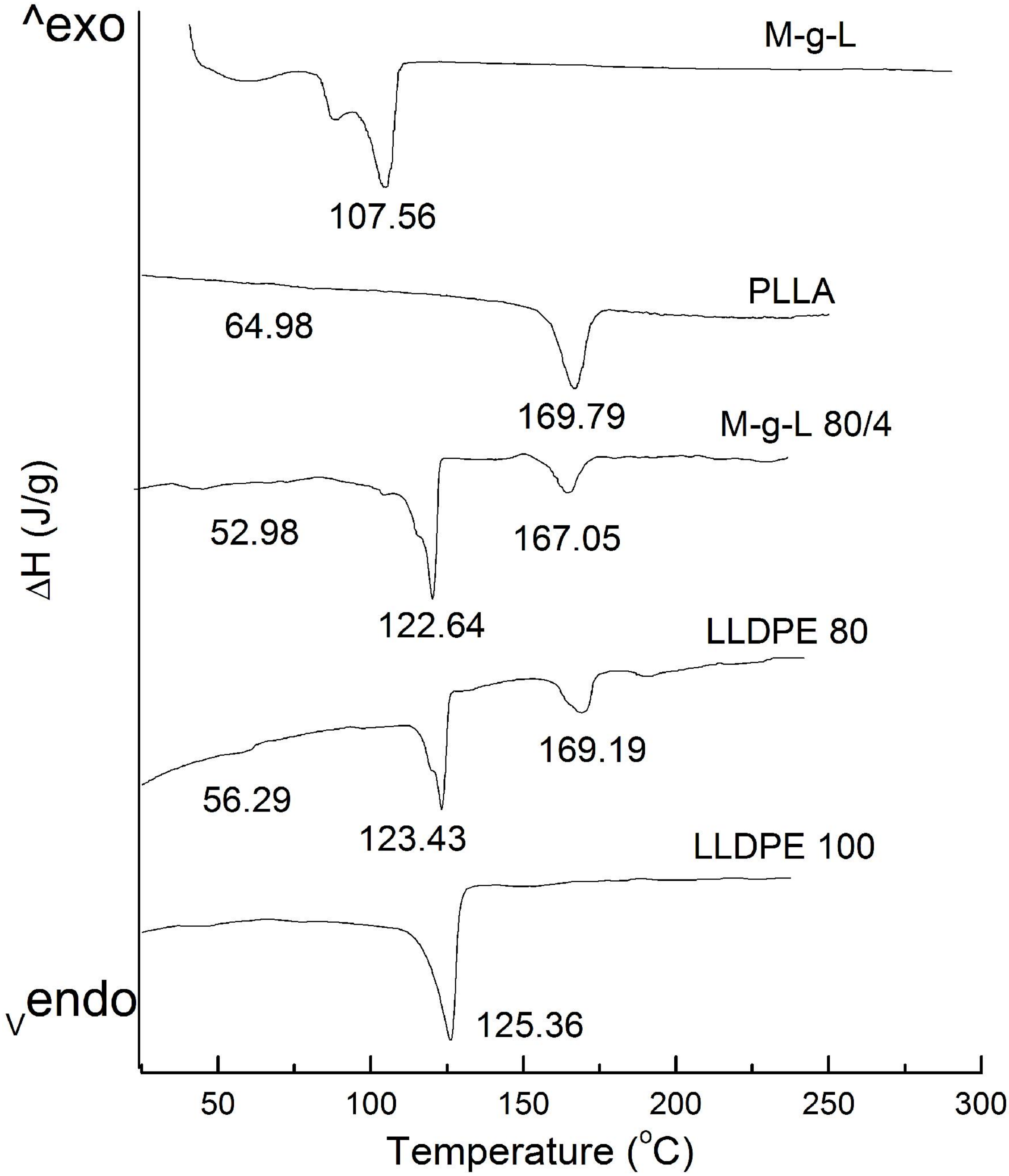


Figure 4.8: DSC thermograms of PLLA, M-g-L, LLDPE 100, LLDPE 80 and M-g-L 80/4

Thermogravimetric (TG) curves of PLLA, M-g-L, LLDPE 100, LLDPE 80 and M-g-L 80/4 blend films are illustrated in Figure 4.9 and results are summarized in Table 4.5 which shows the thermal degradation initiation temperature (T_i), maximum temperature (T_{max}), final temperature (T_f) and percent weight loss. The initial degradation temperature (T_i), corresponding to 1% weight loss of the polymer sample. T_{max} is measured from the mid point of the TGA curve which is showing major degradation (perpendicular line drawn at X axis between mid point of T_i and T_f.). The final degradation temperature (T_f) corresponds to 1% residual left after which no appreciable loss is possible. The thermal degradation of LLDPE 100 appears to be in three steps. This can be explained as formation of intermediate products due to crosslinking and branched chains that compete with the back bone cleavage reaction. The degradation of LLDPE is not a single step decomposition process but seems to follow a more complex degradation pattern [225]. The addition of PLLA improves the thermal stability as shown in TGA curve of LLDPE 80. There must be some interaction between the intermediate component of LLDPE and PLLA. It shows a two-step degradation process, clearly reflecting each degradation process of PLLA and LLDPE ingredients. Each degradation temperature range was in the same temperature range with that of PLLA or LLDPE homo polymer films, and the weight loss ratio in each step was compatible with the composition ratio of each ingredient. These results suggest that the degradation of PLLA and LLDPE ingredients proceeded independently; that is, they did not influence each other [226]. The M-g-L 80/4 blend shows single stage degradation which reflects that miscibility improves with compatibilizer as result the thermal stability further improves with addition of the compatibilizer.

Table 4.5: TG analysis of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80 showing thermal degradation

Sample	T_i (^{0}C)	T_{max} (^{0}C)	T_f (^{0}C)	Weight loss (%)
PLLA	280	350	385	100
LLDPE 100	80	250	425	100
M-*g*-L	152	381	440	100
LLDPE 80				
1st stage degradation	84	153	253	18
2nd stage degradation	253	320	460	82
M-g-L 80/4	240	375	465	100

T_i: initial temperature; T_{max}: maximum temperature; T_f : final temperature.

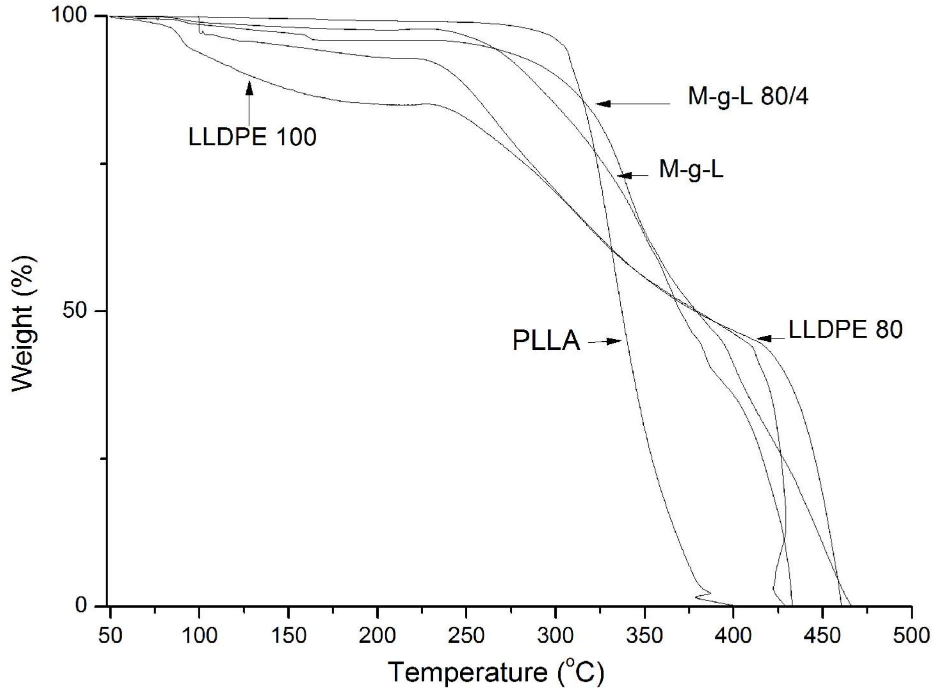


Figure 4.9: Thermogravimetric traces of PLLA, M-g-L, LLDPE 100, LLDPE 80 and M-g-L 80/4

4.3 CONCLUSIONS

The polymer blends LLDPE/PLLA with and without compatibilizer, using maleic anhydride grafted low density polyethylene, were prepared by melt blowing using extrusion mixer with post extrusion blown film attachment. The mechanical properties of the polymer blends depended on the component polymer ratios and the compatibilizer content. Among the investigated sample, the polymer blend LLDPE 80 and M-g-L 80/4 had the optimum tensile strength and elongation at break. The FTIR analysis indicated that there was specific interaction of carbonyl group (C=O) in the blend in presence of compatibilizer. DSC study support the some interaction between LLDPE/PLLA blends. Thermal properties show that the PLLA gives higher thermal stability compared to all blends. It has been also observed that the addition of the compatibilizer enhances the thermal stability of blend due to more uniform dispersion of PLLA in the LLDPE matrix. The M-g-L 80/4 blend shows greater thermal stability compared to LLDPE 80 blend.

5: DEGRADATION STUDIES OF BLENDS

5.1 INTRODUCTION

In general, degradation is the process where deterioration in the properties of polymer takes place due to different factors like, light, heat, mechanical etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties and the article becomes brittle and the life of the material becomes limited. Biodegradation of polymers may be achieved by two major paths (1) design of a polymer from monomers which are vulnerable to micro-organisms and (2) incorporation of biodegradable components/additives in the non-biodegradable polymer [217]. Polymers obtained from biodegradable monomers such as poly-L-lactic acid or poly-b-hydroxybutyrate contains hydrolysable linkages. The biodegradable component in the partial biodegradable polymer blends contains some hydrolysable groups or linkages such as ester, hydroxyl, amide and urea etc. Such hydrolysable groups are hydrolysed under microbial attack as shown below.

$$\text{Polymers} \xrightarrow[\text{Microbial attack}]{\text{Hydrolysis}} \text{Hydrolyzed product} \xrightarrow[\text{Microbial attack}]{\text{Oxidation}} CO_2 + H_2O$$

In this study the path chosen was to incorporate the biodegradable component (PLLA) in non biodegradable component (LLDPE). The preparation and characterization of blends is given in chapter 3 and 4.

This chapter demonstrates the investigation on degradation studies of blends and their effect on mechanical, thermal, and morphology of PLLA/LLDPE blends in the absence/presence of compatibilizer.

5.2 ABIOTIC DEGRADATION STUDIES

5.2.1 Thermo-Oxidative Degradation

The degradable plastics exposed to heat may be subject to many types of physical and chemical changes. Short exposure times at elevated temperatures generally serve to shorten the induction period of oxidatively degradable plastics. Physical properties, such as tensile strength and elongation may change during this induction period. However, these changes are generally not due to molecular-weight reduction but are merely a temperature dependent response, such as loss of mechanical properties due to embrittlement.

The thermo-oxidative stability of blends was studied by calculating the loss of mechanical properties before and after ageing (K_{TO}) of blend films as shown in Table 5.1.

Table 5.1: Results of Thermo-oxidation coefficient (K_{TO}) of LLDPE 100 and LLDPE blends in presence and absence of M-g-L

Blend code	K_{TO} according to tensile strength	K_{TO} according to elongation at break
LLDPE 100	0.94	0.96
LLDPE 80	0.81	0.83
M-g-L 80/4	0.89	0.90
LLDPE 65	0.72	0.73
M-g-L 65/4	0.80	0.82

It has been observed that with increasing % of PLLA in blends without compatibilizer the thermo-oxidative stability decreases. K_{TO} was much higher for LLDPE 100 as compared to LLDPE 65. This could be due to the presence of PLLA, which is more prone to deterioration in presence of heat and oxygen. However, in presence of compatibilizer, thermo-oxidative stability of blend increased. This could be due to increase in resistance to oxidative diffusion of LLDPE in compatibilized blends which prevent the diffusion of atmospheric oxygen into molecular chains of polymer blends.

5.2.2 Thermal Degradation Under Inert Medium

Thermogravimetric (TG) traces of PLLA, M-g-L, LLDPE 100 and their blend films are illustrated in Figure 4.9. The thermal stability has been discussed in chapter 4. The thermal decomposition kinetics was studied by using thermogravimerty decomposition data. The determination of kinetic parameters, Arrhenius activation energy and pre exponential factor has been calculated. The calculation of thermal endurance of blends was also performed as per the procedure given in ASTM E1641 and ASTM E1877. The observations from these have been discussed below:

5.2.2.1 Thermal-endurance of blends

The activation energies were calculated from Arrhenius plot of heating rates and temperatures of constant conversions using equation (1)

$$E_A = -\left(R/b\right)\frac{\Delta \log \beta}{\Delta \frac{1}{T}} \qquad (1)$$

Where,

E_A = Refined Arrhenius activation energy (kJ/mol)

R = Gas constant (8.314 J/mol-K)

b = Approximation derivative (1/K)

β = Heating rate (K/min)

T = Temperature at constant conversion (K)

$\frac{\Delta \log \beta}{\Delta \frac{1}{T}}$ = Slope of the Arrhenius plot

Activation energy calculated from these plots was highest for PLLA (230.1 kJ/mol) and lowest for LLDPE 100. PLLA/LLDPE (80/20) blend and M-g-L 80/4 had activation energy of 172.2 and 192.1 kJ/mol respectively. The calculated activation energies for thermal degradation of pure polymers and their blends are presented in Fig. 5.1.

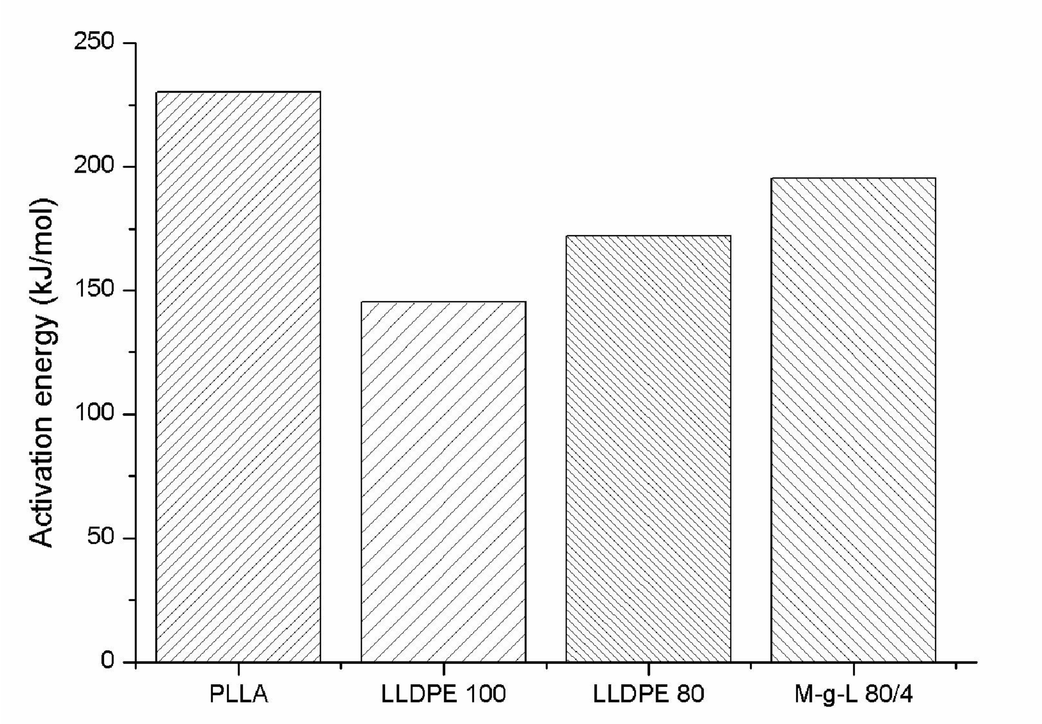


Figure 5.1: Activation energies (E_A) for thermal degradation of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

From the knowledge of activation energy, The Arrhenius activation energies obtained are used to develop a thermal endurance curve using equation (2).

$$T_F = \frac{E_A}{2.303R[\log t_f - \log(E_A / R\beta) + a]} \qquad (2)$$

T_F = Failure temperature (K) at given value of conversion

t_f = Thermal life (hr) at a given value of conversion

a = Approximation integral

The thermal - endurance curves, which estimate the lifetime (duration) of a material exposed at a certain temperature, are shown in Figure 5.2. A greater value of E_A for PLLA indicates that a larger amount of energy is needed to decompose the matter. Indeed, PLLA showed the greatest thermal endurance of all samples. The effect of its greater activation energy could be noticed on TGA plots also. It has been observed that PLLA took longer to start decomposing than did PLLA/LLDPE blends (with or without compatibilizer). The closeness of E_A values for LLDPE 100, LLDPE 80 and M-g-L 80/4 blends (145.1, 172.2 and 192.1 kJ/mol, respectively) reflects the similarity of their TGA plots. But, this small difference becomes clearly noticeable on their thermal-endurance curves. The M-g-L 80/4 blend showed greater thermal endurance than that LLDPE 80.

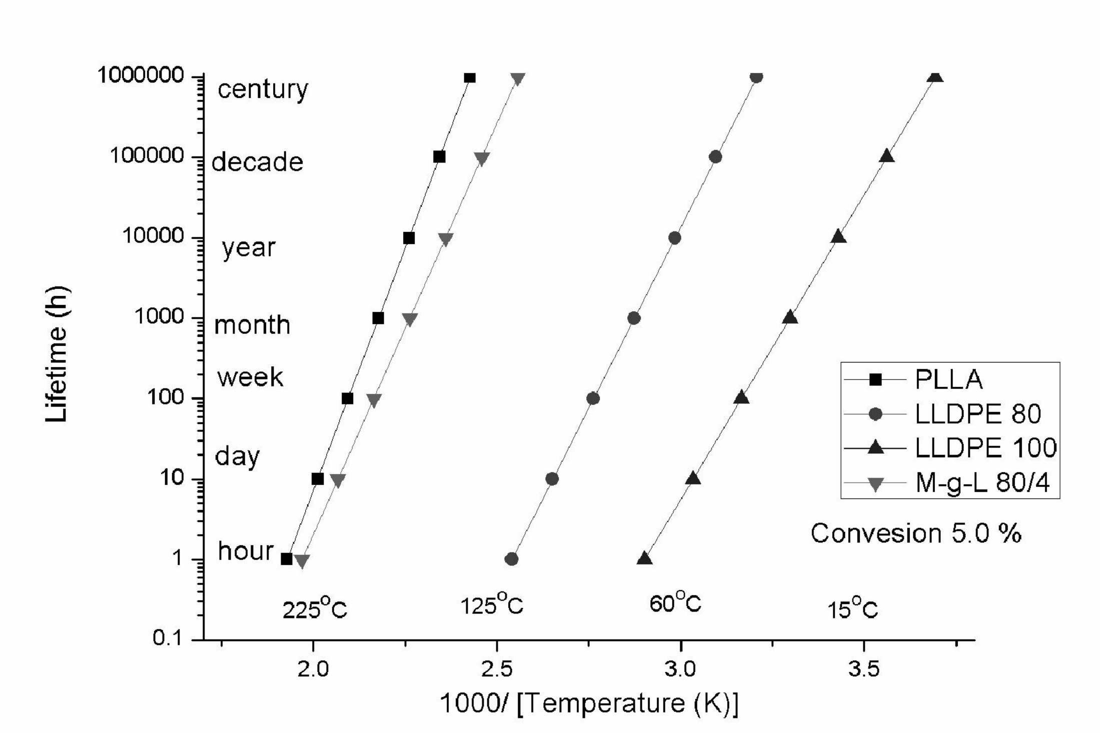


Figure 5.2: Thermal endurance curves of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

This difference might be caused by the enhancing effect of compatibilizer i.e., uniform dispersion of PLLA in LLDPE matrix which would require a larger amount of energy to decompose the blend.

5.2.2.2 Relative thermal index (RTI)

Relative thermal index is a measure of the thermal endurance of a material when compared with that of a control with proven thermal endurance characteristics. The RTI is also considered to be the maximum temperature below which the material resists changes in its properties over a defined period of time. In the absence of comparison data for a control material, a time-to-failure of 60000 hr has been arbitrarily selected for measuring RTI.

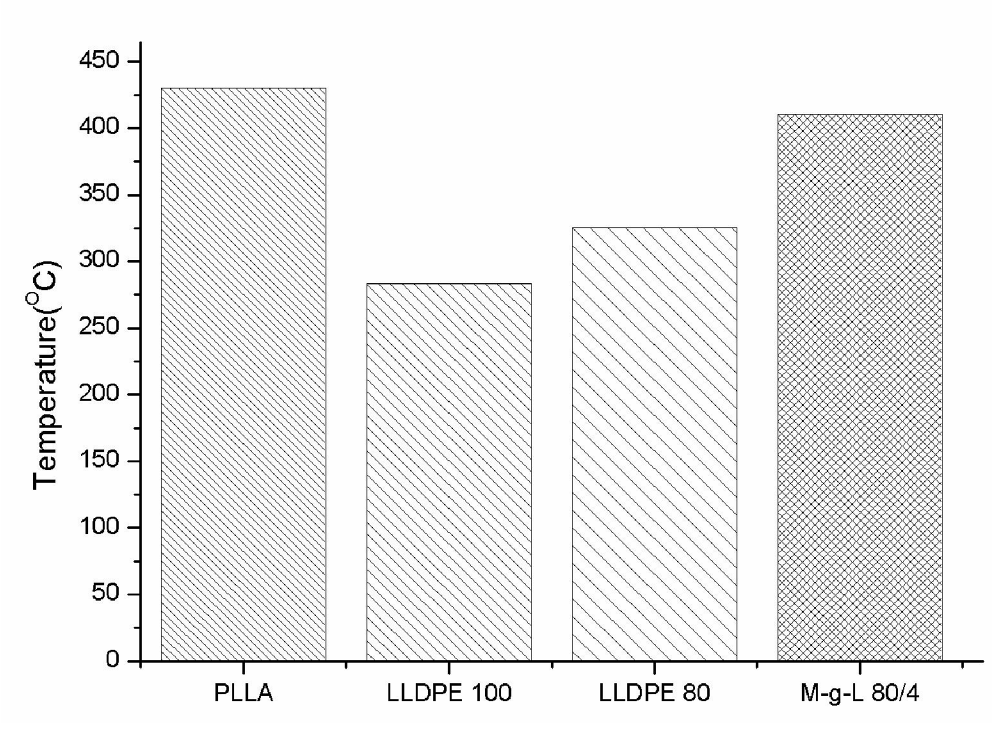


Figure 5.3: Relative thermal index (RTI) of PLLA, LLDPE 100, LLDPE 80 and M-g-L 80/4

RTI is therefore, the failure temperature (RTI_f), obtained from the thermal endurance curve. The relative thermal indices of LLDPE 100, LLDPE 80 and M-g-L 80/4 are shown in Figure 5.3. With addition of PLLA to LLDPE, there is a significant increase in RTI due to higher stability of PLLA as compared to LLDPE. Addition of the compatibilizer shows relatively higher RTI (410.4^{0}C) due to improved dispersion of PLLA in LLDPE matrix.

5.2.3 Hydrolytic Degradation

The hydrolytic degradation has also been studied by comparing the mechanical properties loss after and before exposure to acidic and basic media. Figure 5.4a, 5.4b and 5.4c shows the mechanical properties of LLDPE 100, LLDPE 80 and M-g-L 80/4 at different pH levels (7, 9 and 11) respectively. Being a hydrolytically stable material, LLDPE100 showed insignificant drop in tensile strength at all pH levels. LLDPE 80 showed some drop in tensile properties probably due to degradation of PLLA. Whereas, M-g-L 80/4 showed maximum drop in mechanical properties over the pH range investigated. However, maximum degradation was observed under alkaline condition i.e. pH 11, as indicated by loss of strength (Figure 5.4c). Alkaline pH has been reported to favour the hydrolytic degradation [227]. The loss of mechanical properties can be attributed to surface erosion of amorphous phase and hence the change in the crystalline phase and molecular weight.

5.2.3.1 Morphological characteristics

Figure 5.5a and 5.5b shows the SEM images of the M-g-L 80/4 blend before and after hydrolytic degradation respectively. The before hydrolytic degradation image is shown for reference. There is a uniform dispersion of different phases before the degradation. The change in the uniformity after the degradation can be seen by the white spots, indicating that the surface erosion has taken place due to degradation of PLLA phase

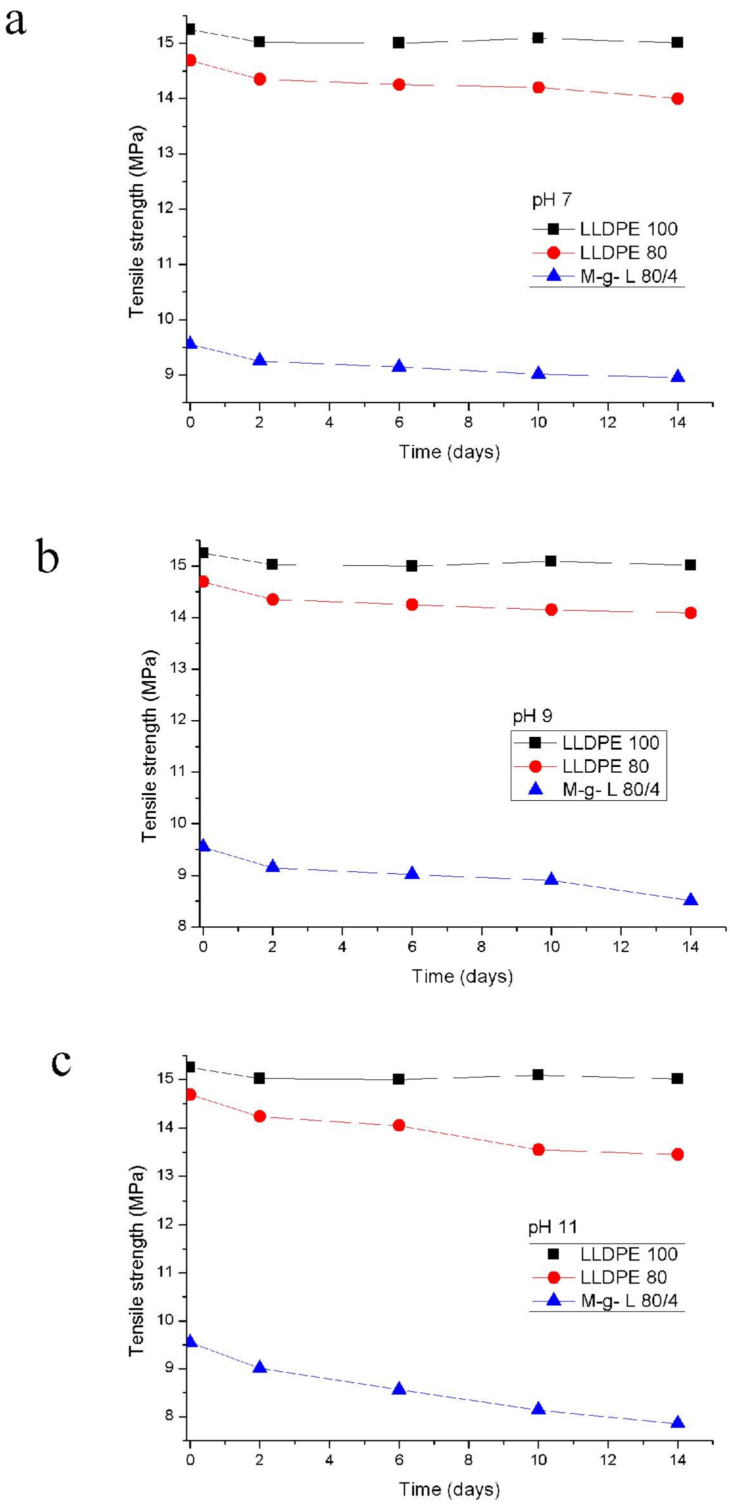


Figure 5.4: Tensile strength variations during hydrolytic degradation of LLDPE 100, LLDPE 80 and M-g-L 80/4 at different pH levels: (a) pH 7, (b) pH 9, and (c) pH 11

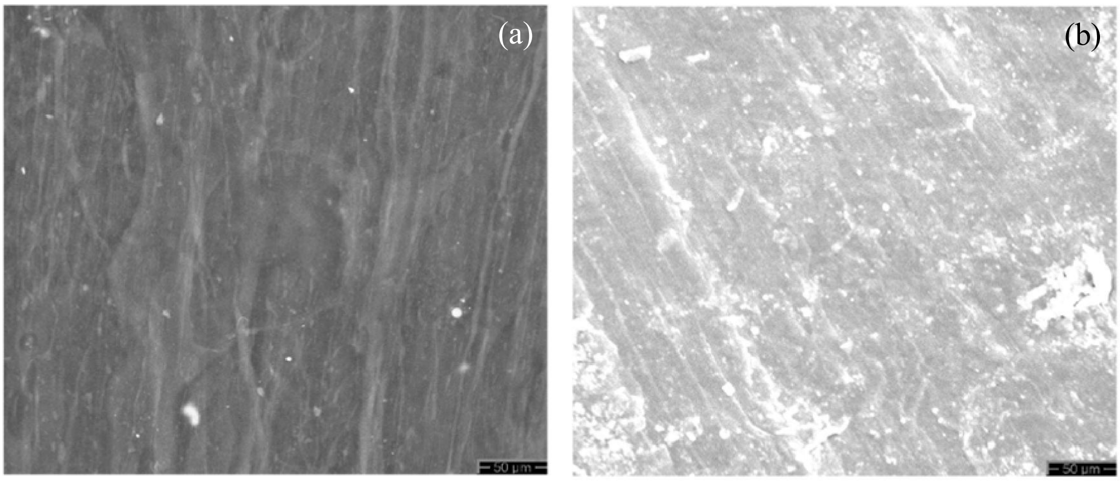


Figure 5.5: Scanning electron micrographs of the M-g-L 80/4 blend : (a) before, and (b) after hydrolytic degradation at pH 11

which would loosen the grip within the matrix resulting in loss of mechanical properties.

5.3 BIOTIC DEGRADATION STUDIES

5.3.1 Degradation Characteristics of Blends in Soil Compost

The degradation of polymeric blends especially under environmental conditions is very important parameter form commercialization point of view. Any inert packaging material if converted into smaller particle size it will resolve the solid waste management problem. If the one component i.e. PLLA degrades from the blend matrix, the films changes into eroded surface having very less mechanical properties. The partial degradation study of blends also gives the idea how the new material perform in soil. Therefore, the degradation was evaluated in alkaline soil compost at pH (7, 9 and11). The degradation at alkaline pH was selected because the polymers are more susceptible to hydrolysis in alkaline medium [228]. The degradation behavior of LLDPE 100, LLDPE 80 and M-g-L 80/4 at pH 7, 9, and 11 are shown, respectively, in Figure 5.6a, 5.6b and 5.6c. It has been observed that PLLA showed some degradation, whereas LLDPE did not. For the LLDPE 80 blend, the mass loss was maximum after aging in soil compostage for around 210 days, showed 10% degradation compared to LLDPE. The degradation was favored by alkaline soil compostage, as shown by the maximum loss of mass at pH 11. The M-g-L 80/4 blend had the highest degradation, because the presence of M-g-L increases the dispersion of PLLA in LLDPE matrix which leads to faster degradation.

5.3.1.1 Change in morphological properties after degradation

Figure 5.7a and 5.7b shows the SEM images of the M-g-L 80/4 blend before and after degradation of 360 days respectively. The before degradation image is shown for reference. There is a uniform dispersion of different phases before the degradation. The change in the uniformity after the degradation can be seen by spots, indicating that the surface erosion has taken place due to degradation of PLLA phase which would loosen the grip within the matrix resulting in weight loss.

5.3.1.2 XRD analysis

Figure 5.8 shows x-ray diffraction patterns of LLDPE 100, LLDPE 80 and M-g-L 80/4 taken before and after degradation. Table 5.4 summarized the degree of crystallization of LLDPE 100, LLDPE 80 and M-g-L 80/4 calculated before and after degradation. There is an increase in crystallanity in LLDPE 80 and M-g-L 80/4 by 10.13 and 12.81% respectively. This may be due to the assimilation of the amorphous part of the polymer by the bacteria and thus only crystalline region of is left behind leading to increase in the crystallanity. The negligible change in LLDPE 100 indicates there was no effect of soil compost on pure LLDPE films. The results are in support of the SEM.

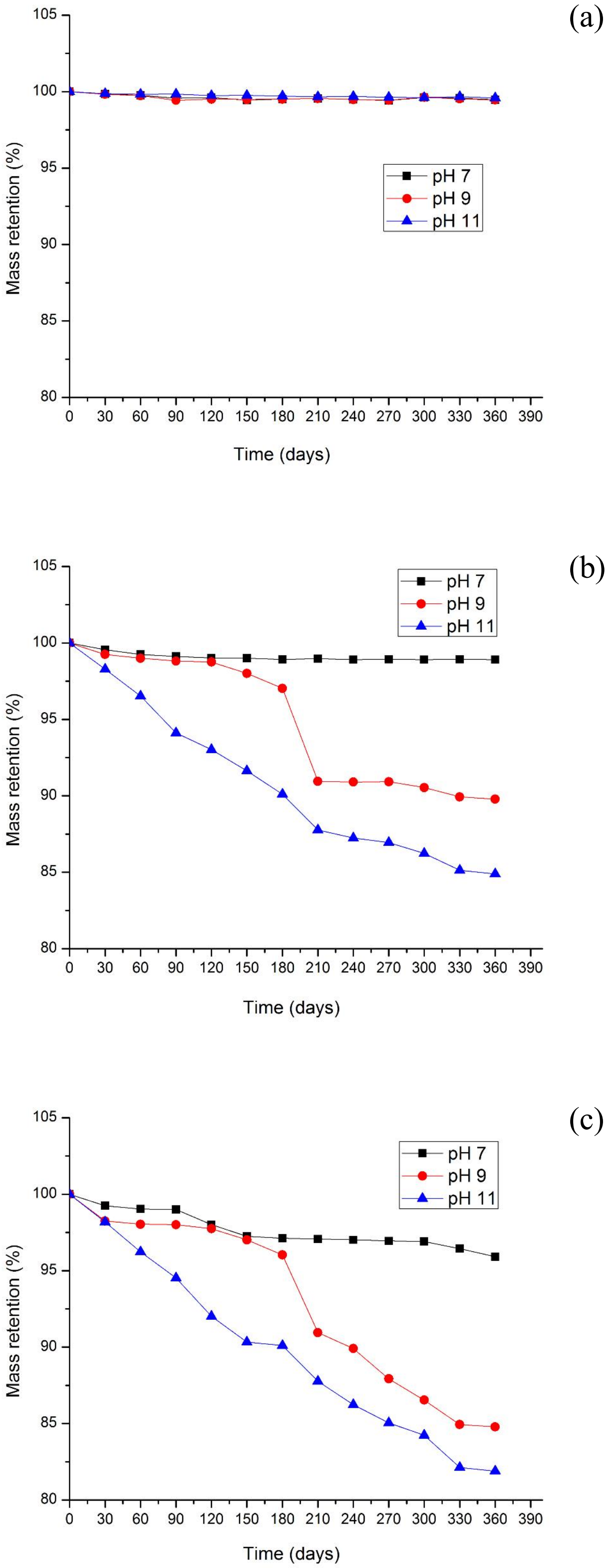


Figure 5.6: Degradation in soil compost: mass retention of (a) LLDPE 100 (b) LLDPE 80 (c) M-g-L 80/4 at different pH levels: (■) pH 7, (●) pH 9, and (▲) pH 11

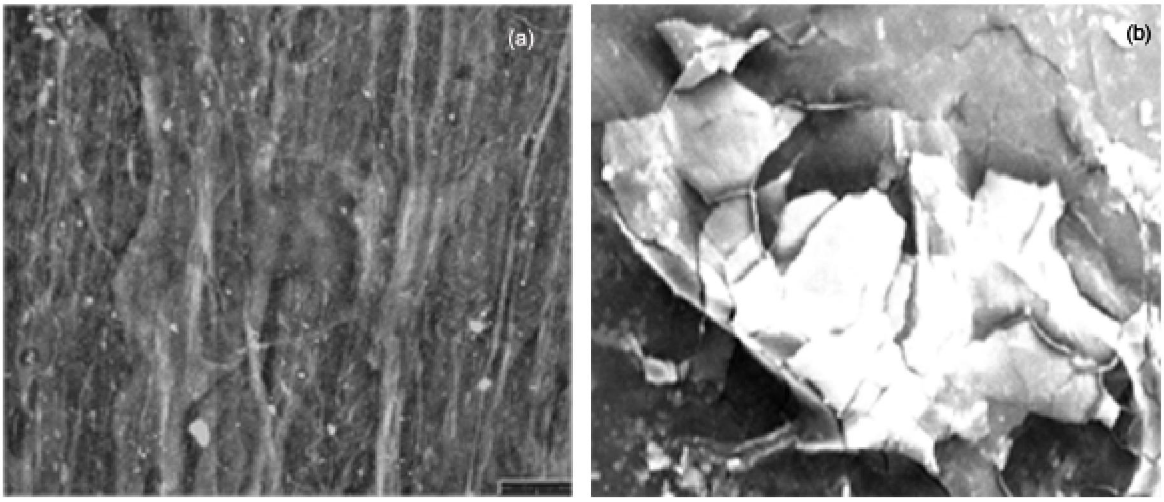


Figure 5.7: Scanning electron micrographs of the M-g-L 80/4 blend: (a) before and (b) after soil compost

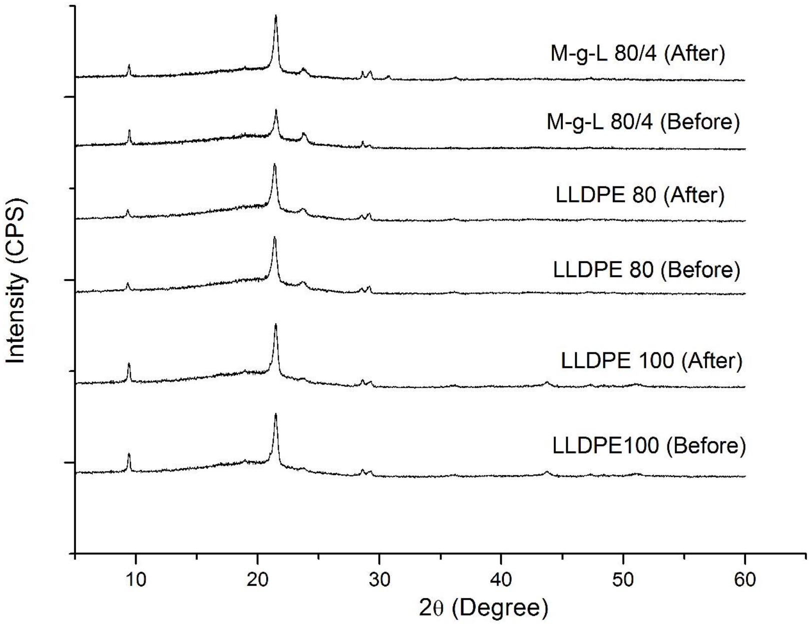


Figure 5.8: XRD patterns of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil compost

Table 5.2: Crystallanity (%) of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil compost

Sample	Crystallanity (%) (Before)	Crystallanity (%) (After)	Change (%)
LLDPE 100	40.61	40.79	0.18
LLDPE 80	43.06	53.19	10.13
M-g-L 80/4	43.78	55.59	12.81

5.3.1.3 Thermal behaviour

The change of crystallinity after soil composting was also confirmed by DSC thermograms. The changes of melting enthalpy indicated changes of crystalline degree of blend samples. In Table 5.5, melting enthalpies of crystalline phase is presented.

Table 5.5: Changes of melting enthalpy ΔH (J/g) of LLDPE 100, LLDPE 80 and M-g-L 80/4 before and after soil composting

Samples	Changes of melting enthalpy ΔH (J/g)	
	Before soil composting	After soil composting
LLDPE 100	61.63	61.85
LLDPE 80	52.07	65.33
M-g-L 80/4	53.78	64.07

The changes of melting enthalpy ΔH (J/g) of films after composting can be seen very clearly. The increase in crystallinity was confirmed by an increase of melting enthalpy of the crystalline phase of polymer blends, because the amorphous phase was degraded first the overall crystallinity has been increased.

5.3.1.4 Thermogravimetric behaviour

The TGA of LLDPE 80, M-g-L 80/4 films before and after the biotic exposure are presented in Figure 5.9 Surprisingly, an increase in the T_{20} from 266.47 ^{0}C to 328.66 ^{0}C for LLDPE 80 and T_{20} from 326.07 ^{0}C to 394.920 ^{0}C for M-g-L 80/4 was observed. This increase could be attributed to the preferential bioerosion of the amorphous regions and fragments generated during the biotic exposure of the films as they are recognizable by the microbial enzymes [200].

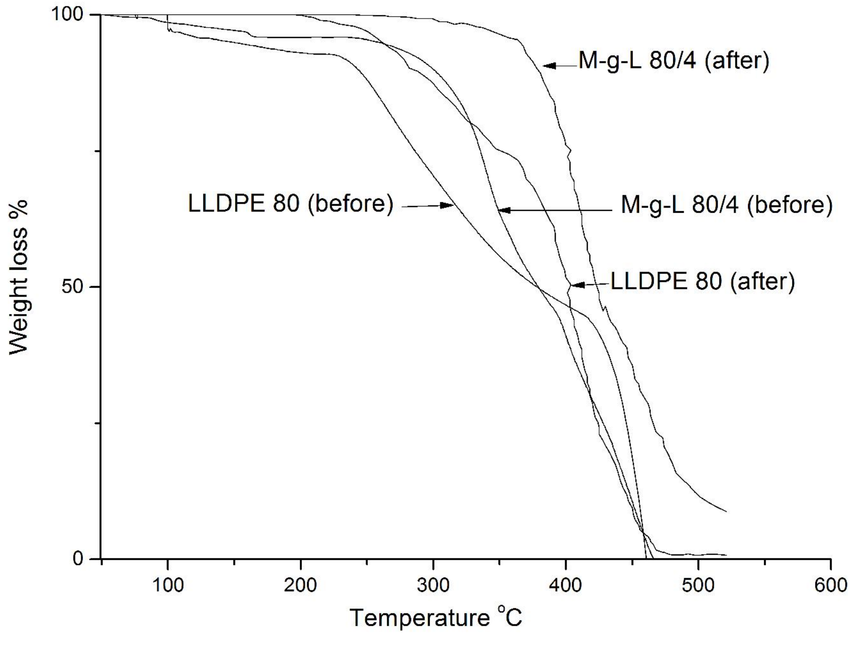


Figure 5.9: Change in the thermal behaviour of LLDPE 80 and M-g-L 80/4 before and after soil composting

5.4 CONCLUSIONS

LLDPE/PLLA blends with and without compatibilizer, using grafted low-density polyethylene maleic anhydride, were prepared at melting condition in an extrusion mixer with post extrusion blown film attachment. Thermal properties show that the PLLA gives higher thermal stability compared to all blends. It has been also observed that the addition of the compatibilizer enhances the thermal stability of blend due to more uniform dispersion of PLLA in the LLDPE matrix. The M-g-L 80/4 blend shows greater thermal endurance and relative thermal index compared to LLDPE 80 blend. Thermo-oxidation stability of LLDPE is higher than that of PLLA. In the presence of compatibilizer, thermo-oxidation resistance increases largely due to filling of the incompatible gaps of LLDPE/PLLA blends with the compatibilizer, which prevents the diffusion of atmospheric oxygen into molecular chains of polymer blends. The M-g-L 80/4 shows maximum tensile strength loss at pH 11.

6: CONCLUSIONS AND FUTURE RECOMMENDATIONS

6.1 CONCLUSIONS

Based on the experiments conducted in the present study, the following conclusions have been drawn.

1. Films based on LLDPE/PLLA blends were prepared successfully at melting condition in an extrusion mixer with post extrusion blown film attachment.
2. The conditions for film preparations were optimized i.e. temperature 200^0C and screw speed 30 rpm.
3. It was not possible to prepare blown films from LLDPE having PLLA content more than 50% (w/w).
4. The mechanical properties of the LLDPE/PLLA polymer blends depended on the amount of PLLA and optimized combination of properties seen in case of the blends having 20% (w/w) PLLA.
5. Structural, thermal and morphological characteristics using FTIR, DSC, XRD and SEM analysis showed that LLDPE/PLLA blends were incompatible over the whole compositions range investigated.
6. Films based LLDPE having 20% and 35% (w/w) PLLA were successfully prepared using 2%, 4%, 6%, 8%, and 10% of compatibilizer i.e. MA-g-LDPE.
7. The compatibilizer content also affected the mechanical properties of films and tensile strength and elongation at break was highest for sample having 4 phr of M-g-L i.e. sample M-g-L 80/4.
8. FTIR analysis indicated specific interaction of carbonyl group (C=O) in LLDPE/PLLA blends in presence of compatibilizer. Those specific interaction of absorption peak of C=O group in blends may be the driving force for compatibilzation.

9. DSC scans shows decrease of T_g of PLLA in presence of compatibilizer in LLDPE/PLLA blends. This indicates some interactions and softening of PLLA phase in presence of compatibilizer.
10. PLLA showed highest thermal stability, activation energy, thermal endurance and relative thermal index compared to all.
11. Thermal stability, activation energy, thermal endurance and relative thermal index showed an increase upon compatibilization. The M-g-L 80/4 blend show higher thermal stability, activation energy, thermal endurance and relative thermal index compared to LLDPE 80 blend.
12. Incorporations of varying amount of M-g-L in LLDPE/PLLA (80/20, 65/35) blends clearly show the interactions between two phases.
13. Thermo-oxidation stability of LLDPE is higher than that of PLLA. In the presence of compatibilizer, thermo-oxidation resistance increases to a great extent due to filling of the incompatible gaps of LLDPE/PLLA blends with the compatibilizer which prevents the diffusion of atmospheric oxygen into molecular chains of polymer blends.
14. Hydrolytic degradation increased in presence of compatibilzer and alkaline medium. The M-g-L 80/4 shows maximum tensile strength loss at pH 11 as compared to LLDPE 80.
15. Biotic degradation under soil compost increases in presence of compatibilizer and alkaline soil compost. The M-g-L 80/4 shows maximum mass loss at pH 11 as compared to LLDPE 80.

6.2 RECOMMENDATIONS FOR FUTURE WORK

1. To increase our knowledge about biodegradation of LLDPE, we need to put more efforts into identifying LLDPE-degrading microorganisms isolated from the compost. An understanding of the mechanisms of both natural and synthetic polymer degradation by microorganisms and enzymes will open new prospects in the field of biodegradable plastics.
2. Composting according to ASTM D5338 needs more detailed study to know the fate of these organic polymers in the environment and the time required for their total mineralization to CO_2 have yet to be fully understood.
3. Composting under controlled conditions needed to be studied.
4. In the case of pure culture, other cultures which are available for the degardation of polyethylene can be tested upon and the results can be compared with *Brevibacillus borstelensis.*

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