STUDIES ON DEGRADABILITY OF HIGH DENSITY POLYETHYLENE (HDPE)–POLYLACTIDE (PLA) BLENDS

A Thesis

Submitted in Partial Fulfillment for the Award of Degree of

Doctor of Philosophy

By

GAURAV MADHU
(Registration No.: 901201001)

Under the Guidance of

Prof. Pramod K. Bajpai
Distinguished Professor
Department of Chemical Engineering
Thapar University, Patiala

Dr. Haripada Bhunia
Associate Professor
Department of Chemical Engineering
Thapar University, Patiala

Department of Chemical Engineering
Thapar University, Patiala 147004 Punjab
www.thapar.edu

July 2015

Dedication

Dedicated to

My parents, my wife and
the most precious inspiration of my life:
my daughters Gauri and Arushi

Declaration

The work described in this thesis was conducted at the Department of Chemical Engineering, Thapar University, Patiala, between July 2012 and June 2015. Unless otherwise stated, it is the work of the author and has not been submitted in support of any other degree.

Gaurav

(Gaurav Madhu)
Ph.D. Regn. No. 901201001
Department of Chemical Engineering,
Thapar University, P.O. Box 32,
Patiala 147004 Punjab, India

Certificate

It is certified that the work presented in the thesis entitled "Studies on Degradability of High Density Polyethylene (HDPE)–Polylactide (PLA) Blends", being submitted by Mr. Gaurav Madhu, to the Department of Chemical Engineering, Thapar University, Patiala in fulfilment of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him under our guidance and supervision and is worthy of consideration for the award of the degree of Doctor of Philosophy of the university.

01-07-2015
(Pramod K Bajpai)
Distinguished Professor,
Department of Chemical Engineering,
Thapar University, P.O. Box 32,
Patiala 147004 Punjab, India

01-07-2015
(Haripada Bhunia)
Associate Professor,
Department of Chemical Engineering,
Thapar University, P.O. Box 32,
Patiala 147004 Punjab, India

Acknowledgements

I would like to express my deepest respect and most sincere gratitude to my supervisors ***Prof. Pramod K. Bajpai*** *and* ***Dr. Haripada Bhunia*** *for providing me an opportunity to work under their guidance in the Department of Chemical Engineering,* ***Thapar University****. They provided me with the motivation, knowledge and the tools to carry out this research and for future success. I am thankful for their constant encouragement, intellectual generosity and valuable contribution of their time throughout the course of this work. It's been a great honour and privilege to work under their inspiring guidance.*

Heartily thanks are payable to ***Prof. Prakash Gopalan****, Director, Thapar University;* ***Shri Gurbinder Singh****, Registrar, Thapar University;* ***Dr. R. S. Kaler*** *and* ***Dr. Susheel Mittal****, Deputy Directors, Thapar University;* ***Dr. O. P. Pandey****, Dean of Research & Sponsored Projects, Thapar University;* ***Dr. S. S. Bhatia****, Dean of Academic Affairs, Thapar University;* ***Dr. Maneek Kumar****, Dean of Student Affairs, Thapar University for giving the necessary approvals and kind support to perform this research work.*

I would like to express the utmost appreciation to the members of the doctoral committee for my research work who were invaluable to the development and completion of this thesis. ***Dr. Raj Kumar Gupta****, Associate Professor and Head, Department of Chemical Engineering, Thapar University;* ***Dr. Sanghamitra Barman****, Assistant Professor, Department of Chemical Engineering, Thapar University; and* ***Dr. M. S. Reddy****, Professor, Department of Biotechnology, Thapar University; all provided their expertise and vast experience throughout the course of this research in a patient and encouraging manner. Their enlightening guidance has enabled me to think, explore and experience new ways to look at the work.*

*I am also grateful to **Prof. Golok B. Nando**, Professor, Rubber Technology Centre, **IIT Kharagpur**, West Bengal for his kind support and guidance in performing some part of the experimental work in his research laboratory. His constructive suggestions have been of immense value in improving the quality of my research work.*

*Also, my sincere thanks to **Prof. Veena Choudhary**, Centre of Polymer Science & Engineering, **IIT Delhi** for her guidance and encouragement at all stages of my work and for stimulating discussions.*

*I also acknowledge my thanks to **Dr. B. N. Chudasama**, Assistant Professor, School of Physics and Material Science, Thapar University; and **Dr. Rajesh Kumar**, Associate Professor, School of Chemistry and Biochemistry, Thapar University; for providing their support.*

*I express deep sense of gratitude to my colleagues **Ms. Chitrakshi Goel**, **Ms. Kimi Jain**, **Mr. Kumar Uddipto** and **Mr. Dev Kumar Mandal** for providing all the possible support, motivation and cooperation during the course of experimental work. I am thankful to my friends **Mr. Munish Kashyap**, **Mr. Shubham Kaushal** and **Sh. Sunder Singh Rana** for providing their assistance and help during laboratory work.*

*Special thanks to **Sh. Kamal Jeet Rana** for his help, support, care and generosity throughout my stay in Thapar University.*

*On a personal level, a special thank goes to my wife **Charu** who has been an unbelievable support throughout my Ph.D. Also, to my two lovely daughters, Gauri and Arushi, who have changed my life. But mostly, this thesis is dedicated to my father **Sh. G. D. Madhu** and my mother **Smt. Shakuntala Rani**, who supported me all the way.*

Finally, I would like to thank the national R&D organization ***Council of Scientific & Industrial Research (CSIR)****, Govt. of India, which funded and supported this research (Project Title: Preparation and characterization of polylactide (PLA)-polyethylene blends and its degradability studies; Scheme No.: 02(0035)/11/EMR-II.*

Abstract

Polyethylene (PE) is predominantly used for consumer packaging in the form of trash bags and other short-term flexible packaging and disposable products because they are economical and convenient. But, due to non-biodegradable nature, they cause hazardous environmental pollution and become carcinogenic for human beings, marine bodies and other living species. Hence, the major challenges and opportunities exist in developing biodegradable polyethylene blends having similar mechanical and processing properties as that of the conventional PE. The objectives of this research work were set to develop biodegradable and oxo-biodegradable blends of high-density polyethylene (HDPE) by compounding poly(lactic acid) (PLA) in varying amounts and/or pro-oxidant with/without compatibilizer maleic anhydride grafted high density polyethylene (MA-*g*-HDPE), to investigate the effect of blend composition on the performance properties and degradability and to study degradation kinetics of the polymer blends. The selection of HDPE was made due to its large use in current commercial packaging. PLA is a well known biodegradable polyester polymer having good mechanical properties, fair processability and superior recyclability; hence, emerging as a viable substitute for synthetic, semi-crystalline non-biodegradable polymers. MA-*g*-HDPE was selected as compatibilizer due to the intrinsic immiscibility between HDPE and PLA. Thin films from HDPE/PLA blends were produced through melt-compounding followed by hot-pressing. Initially, the ratios of HDPE/PLA blends were taken as 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, and 70/30 and after recognizing 80/20 blend with optimum combination of mechanical (tensile) properties and PLA content, it was further compatibilized with 2, 4, 6, and 8 parts per hundred of resin (phr) of MA-*g*-HDPE. Amongst compatibilized HDPE/PLA (80/20) blends, 4 phr quantity of MA-*g*-HDPE blends had the finest relevant mechanical properties. Subsequently, neat HDPE and selected HDPE/PLA blends were formulated with an ever-effective pro-oxidant additive cobalt stearate (CoSt) to influence the initial rates of

degradation. The characterization of the selected films was done by a number of techniques including Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA) differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and parallel-plate rheometry. Considering the importance of permeability or barrier properties for packaging of fresh produce, water vapour transmission rate (WVTR) of the optimized blend films was also determined. Further, biodegradation in terms of CO_2 gas produced by the samples (in grams) and percent mineralization was analyzed under composting conditions according to ASTM D5338 standard. An economical apparatus for measuring biodegradation was developed indigenously as per the guidelines of the ASTM standard which gave consistent and reliable results on the biodegradability of the samples. Thermal degradation kinetics and lifetime of HDPE/PLA blends were assessed by using TGA data and applying the well known isoconversional methods viz. Friedman, Kissinger and Flynn–Wall.

FTIR of 80/20 blend with compatibilizer represented different peak positions of carbonyl stretching band indicating promotion of some compatibility between the two immiscible polymers. Thermal investigation (TGA and DSC) revealed that the thermal stability of HDPE decreased with addition of PLA but still, the blends were stable enough to be used for packaging application(s). WAXD analysis revealed lesser crystallinity of the blends than pure HDPE. Through SEM, it was observed that MA-*g*-HDPE influenced the morphology of the blends and it acted as a suitable compatibilizer for HDPE/PLA blends. Rheology of the samples confirmed that the blends retain their processability as they were pseudoplastic in nature. WVTR of the optimized HDPE/PLA blends met the specified standard value for packaging applications. The biodegradability levels of the samples under composting environment were obtained as cellulose (43.2%) > $HD_{80}MA_4CoSt_{0.1}$ (10%) > $HD_{80}CoSt_{0.1}$ (9.1%) > $HD_{80}MA_4$ (3.7%) > HD_{80} (3.5%), which suggested that the blends containing pro-

oxidant were more degraded. The effect of pro-oxidant on the thermal degradation kinetics and lifetime of HDPE and HDPE/PLA blended films was observed using thermogravimetry and applying the isoconversional techniques mentioned above. It was observed that CoSt provoked the thermal degradation and biodegradation of HDPE and HDPE/PLLA blends and decreased their lifetime as well.

Publications

1. Peer-Reviewed Journals

1.1. Publications Related to Ph.D. Work

1. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. "Blends of High Density Polyethylene and Poly(L-lactic acid): Mechanical and Thermal Properties", *Polymer Engineering & Science*, 54(9): 2155-2160 (2013).
2. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. "Investigation of Physico-Mechanical Properties and Biodegradability of High Density Polyethylene/Polylactide Blends", *Journal of Polymer Materials*, 31(3): 381-395 (2014).
3. **Gaurav Madhu**, Haripada Bhunia, Pramod K. Bajpai and Veena Choudhary. "Mechanical and Morphological Properties of High Density Polyethylene and Polylactide Blends", *Journal of Polymer Engineering*, 34(9): 813-821 (2014).
4. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. "Physico-Mechanical Properties and Biodegradation of Oxo-degradable HDPE/PLA Blends", *Polymer Science Series A*, Manuscript ID: 2014/337 (*Accepted for Publication*).
5. **Gaurav Madhu**, Dev K. Mandal, Haripada Bhunia and Pramod K. Bajpai. "Thermal Degradation Kinetics and Lifetime of HDPE/PLA Blends", *Journal of Thermoplastic Composite Materials*, Manuscript ID: JTCM-15-0042 (*Accepted for Publication*).

1.2. Other Publications in the Related Area

1. Kimi Jain, **Gaurav Madhu**, Haripada Bhunia, Pramod K. Bajpai and M. S. Reddy. "Kinetics of Biodegradation of Polypropylene/Polylactide Blends", *Journal of Polymer Materials*, 31(1): 63-76 (2014).

2. Kimi Jain, **Gaurav Madhu**, Haripada Bhunia, Pramod K. Bajpai, Golok B. Nando and Mondem S. Reddy. “Physico-Mechanical Characterization and Biodegradability Behaviour of Polypropylene/Poly(L-lactide) Polymer Blends”, *Journal of Polymer Engineering*, 35(5): 407-415 (2015).

1.3. Under Review / Communicated

1. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. “Thermal degradation kinetics and lifetime of HDPE/PLLA/pro-oxidant blends”, *Journal of Polymer Engineering*, Manuscript ID: POLYENG.2015.0199.R1 (*Under review*).

2. International Conferences

1. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. “Biodegradable High Density Polyethylene – Poly(L-lactic acid) Blends and its Degradation Studies”, *International Conference on Rubber and Rubber-like Materials (ICRRM)*, Rubber Technology Centre, IIT Kharagpur. 6-9 March, 2013.
2. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. “Evaluation of Biodegradability of High Density Polyethylene and Poly(Lactic Acid) Blends”, *International Conference on Emerging Materials & Applications (ICEMA)*, IIT Roorkee, Saharanpur Campus, Saharanpur, Uttar Pradesh. 5-6 April, 2014.

3. National Conferences

1. **Gaurav Madhu**, Jasmeet Kaur, Haripada Bhunia and Pramod K. Bajpai. “Biodegradability Studies of High-Density Polyethylene and Poly(L-lactic acid) Blends”, *National Conference on Innovative Molecules for Sustainable Future (NCIMF)*, School of Chemistry and Biochemistry, Thapar University, Patiala. 24-26 October, 2013.

2. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. “Preparation and Characterization of Oxi-Degradable High Density Polyethylene/Polylactide Blends”, *Students’ Chemical Engineering Congress (SCHEMCON)*, Haldia Institute of Technology, Haldia, West Bengal. 19-20 September, 2014.
3. **Gaurav Madhu**, Haripada Bhunia and Pramod K. Bajpai. “Oxo-biodegradable HDPE/PLA Blends: Preparation, Characterization and Biodegradability”, *Indian Chemical Engineering Congress (CHEMCON)*, Panjab University, Chandigarh. 27-30 December, 2014.

Vitae

2001………………………………….. B. Tech. in Chemical Engineering from the Department of Chemical Engineering, Sant Longowal Institute of Engineering & Technology, (SLIET), Longowal, Sangrur, Punjab, India.

2003………………………………….. M. Tech. in Polymer from Dr. S. S. Bhatnagar University Institute of Chemical Engineering & Technology, Panjab University, Chandigarh, India.

2004 – 2011………………………….. Gained professional experience of 7 years (total) out of which 3 years in teaching (at SLIET, Longowal, Punjab and Shoolini University, Solan, H.P.) and 4 years in industry (at Quarkcity India Pvt. Ltd., Mohali, Punjab and Jubilant Organosys Ltd., Gajraula, Bhartiagram, J.P. Nagar, U.P.)

2012 – 2015………………………….. Research Associate and Research Scholar in the Department of Chemical Engineering, Thapar University, Patiala, Punjab, India.

Presently………………………….…. Associate Professor in the Department of Petroleum Engineering, Chandigarh University, Gharuan, Mohali, Punjab, India.

Table of Contents

List of Symbols

T	Absolute temperature
E_a	Activation energy
Å	Angstrom
ω	Angular frequency
CO_2	Carbon dioxide
$\eta*$	Complex viscosity
T_c	Crystallization temperature
Da	Dalton
χ_c	Degree of crystallinity
$f(\alpha)$	Differential function of the kinetic model
ΔH_c	Enthalpy of crystallization
ΔH_f	Enthalpy of fusion
T_f	Final degradation temperature
T_g	Glass transition temperature
β	Heating rate
T_i	Initial degradation temperature
G''	Loss modulus
T_{max}	Maximum degradation temperature
MPa	Mega pascal
T_m	Melting temperature
µm	Micrometer
$\overline{M}_n$	Number average molecular weight

A	Pre-exponential factor or frequency factor
γ	Shear strain
G'	Storage modulus
T_f	Temperature at failure
$CO_2(Th)$	Theoretical carbon dioxide
t_f	Time of failure
R	Universal gas constant
$	US dollar
$\overline{M}_w$	Weight average molecular weight
α	Weight loss

List of Abbreviations

ASTM	American Society for Testing and Materials
CAGR	Compound Annual Growth Rate
CaSt	Calcium Stearate
CoSt	Cobalt Stearate
DDR	Draw-down Ratio
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry
EB	Elongation at Break
FeSt	Iron Stearate
FTIR	Fourier Transform Infrared
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	Maleic Anhydride
MA-*g*-HDPE	Maleic Anhydride *grafted* High Density Polyethylene
MFI	Melt Flow Index
MnSt	Manganese Stearate
MW	Molecular Weight
MWD	Molecular Weight Distribution
PCL	Poly(ε-caprolactone)
PE	Polyethylene

PHA	Poly(hydroxyalkanoates)
PHB	Poly(3-hydroxybutyrate)
phr	Parts Per Hundred of Resin
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
SEM	Scanning Electron Microscopy
TG	Thermogravimetry
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
WAXD	Wide-angle X-ray Difraction
XRD	X-ray Difraction

List of Tables

List of Figures

Chapter 1 – Introduction

1.1. Polymers

Polymers are the macromolecules, which are built up from basic units, referred to as 'monomers'. These units can be extremely simple, where a simple molecule adds on to itself or other simple molecules. For example, ethylene (CH_2–CH_2) can be converted into polyethylene, of which the repeating unit is $-(-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$ where *n* is the number of repeating units.

1.2. Brief history of polymers

The word 'polymers' was although coined in the 20th century, but the polymers are in use since 15th century long before anyone understood what they were. When natural polymer was first discovered in 1496 by Columbus, 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. Amongst the first natural fibres known to mankind are silk, hair, jute and wool etc. The first synthetic plastic material 'Bakelite' was invented in 1907 by Leo Hendrik Baekeland [1]. In 1920, German chemist Hermann Staudinger suggested that polymers are actually giant molecules formed by the permanent attachment of numerous 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 (PS), polyvinyl chloride (PVC), polysulphide rubber, neoprene, and nylon. However, it was not until World War II that a significant change took place in the use of polymers as a strategic material and thus the ‘Polymer Age’ evolved. The technology to produce synthetic polymers from petroleum resources have developed rapidly, so also their applications in various fields including military and household, thus emerged the use of polymers in every field of human endeavour towards the middle of 20th century [2]. Since then, plastics have been found useful in applications ranging from transportation, packaging, building, medical appliances, agricultures and communication. Numerous varieties of plastic materials having differing properties are now created by using additives like plasticizers, fillers, antioxidants, coloring agents, flame retardants etc. which imparts desired functionalities to these products. Today, plastics have become an integral part of our lives.

1.3. Classification of polymers

Polymers are classified in a number of ways depending upon one criterion or the other viz. their origin, line structure, physical properties & applications, method of formation, crystallinity, thermal behaviour, degradability [3-5] as summarized in Figure 1.1.

1.4. Polymers in flexible packaging

The flexible packaging market is one of the most dynamic packaging markets exhibiting diversified types of packaging and materials used across the regions. The global market value for flexible packaging is projected to reach $99,621.9 million by 2018, growing at a compound annual growth rate (CAGR) of 5.1% from 2013 to 2018 driven by rising demand in major Asian markets such as India and China [6]. Flexible packaging substrates provide opportunities to reduce materials, lower package weight and cut costs. Properties of flexible packaging can be easily tailored to meet demanding specifications for a wide range of products.

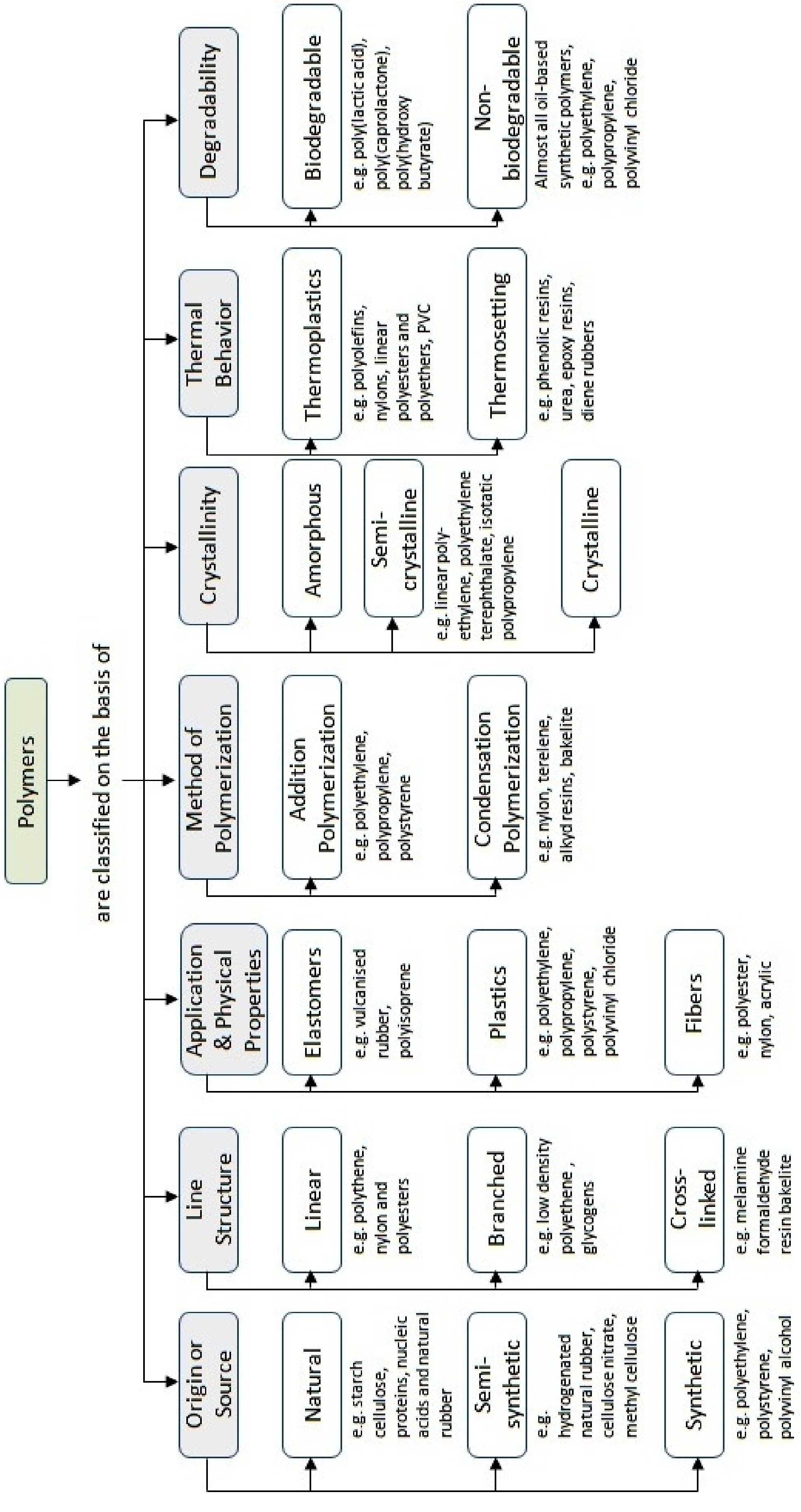


Figure 1.1. Classification of polymers [3]

Over the years, the flexible packaging market has developed from simple paper wrapping and bags to very sophisticated multilayer and multimaterial packaging for barrier protection and shelf-life extension. Figure 1.2 shows the market share of various types of materials in flexible packaging.

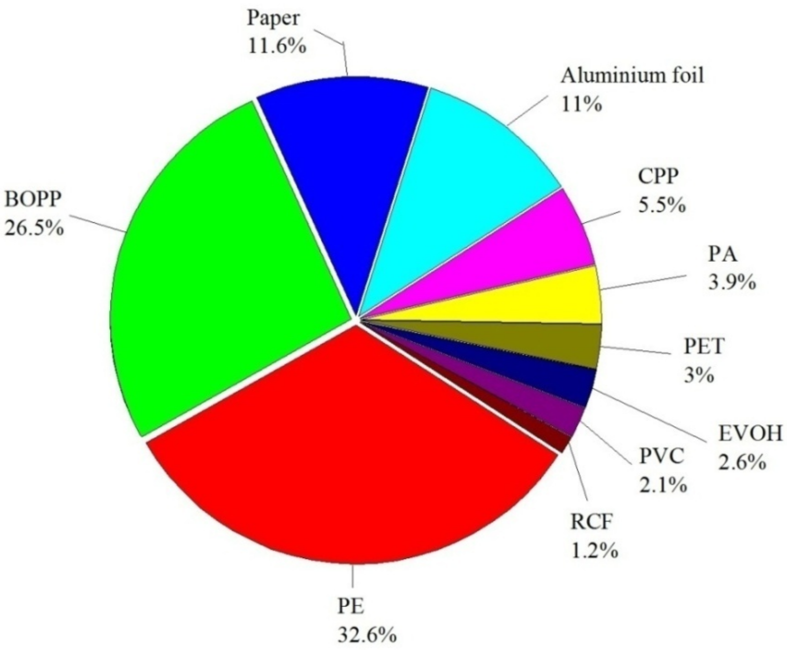


Figure 1.2. Market share of all types of flexible packaging materials [7]

Polyethylene (PE) dominates the flexible packaging market and accounted nearly 32% of the total market share in 2013. The second largest share is of biaxially oriented polypropylene (BOPP) followed by paper packaging. The other flexible packaging materials include aluminium foil, cast polypropylene (CPP) films, polyamide (PA), polyethylene terephthalate (PET), ethylene vinyl alcohol (EVOH), polyvinyl chloride (PVC) and regenerated cellulose film (RCF).

1.5. Waste generated from packaging plastics

An estimate of worldwide plastic waste generation is about 60 million metric tons annually [8]. In India, particularly, the figure of plastic waste generation was approximately 5.6

million metric tons per year in 2012, which is estimated to rise to approximately 16.5 million metric tons by 2030; trebling every 10 years [9]. India is the 3rd largest consumer market (behind US and China) for plastic goods with a consumption of 12.5 million metric tons per annum (TPA). In 2012-13, India's per capita plastics consumption was estimated as 9.7 kg [10]. Out of the total plastic waste, approx. 40% contribution is from the packaging industry. Each year, an estimated 500 billion to 1 trillion plastic bags are consumed worldwide, i.e., over 1 million plastic bags used per minute [11]. Building and construction is the second largest source with 20.3% of the total plastic waste. Automotive is the third sector with a share of 8.5%; electrical and electronic applications represent 5.6% of the plastic waste and are closely followed by agricultural applications which have a share of 4.3%. Other application sectors such as appliances, household and consumer products, furniture and medical products comprise a total of 21.7% of the plastic waste [12]. The segment-wise sources of plastic waste are shown in Figure 1.3.

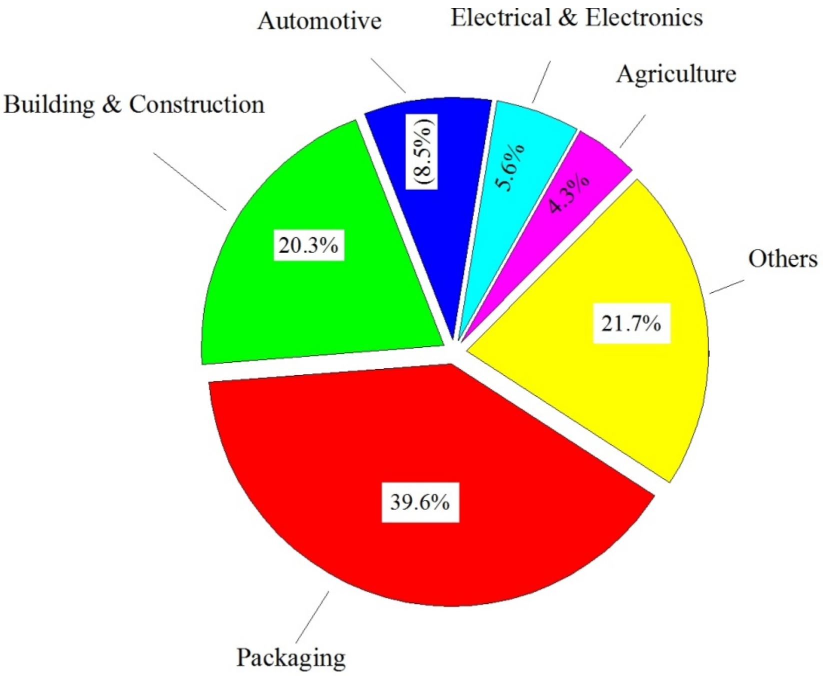


Figure 1.3. Sources of plastic waste [11]

In the terrestrial and marine coastal environment, the synthetic plastics accumulate at a rate of 25 million tons per year [13]. A recent study conservatively estimated that 2,68,940 tons plastic particles are currently in the world's oceans [14]. The plastic waste in World's oceans is shown in Figure 1.4.

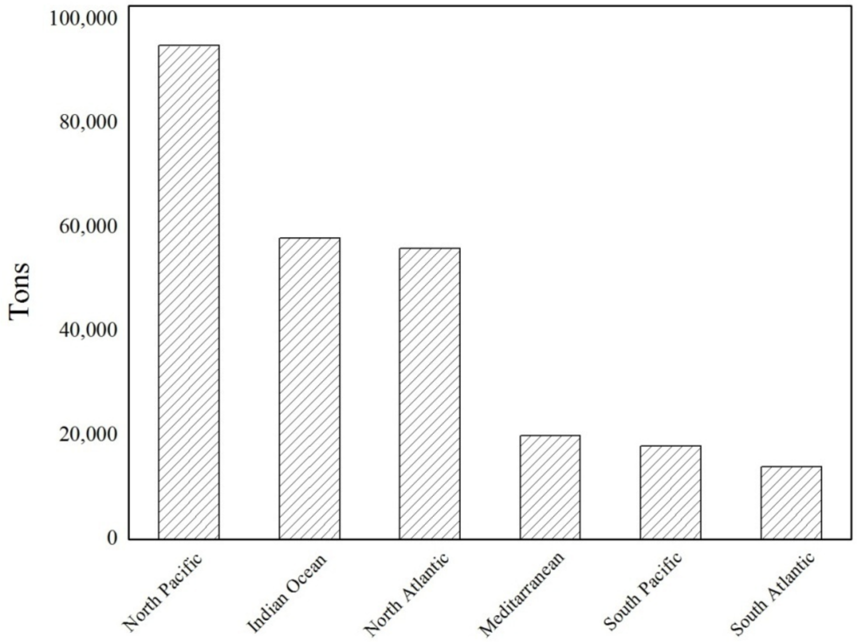


Figure 1.4. Plastic waste in world's oceans in 2014 [14]

1.6. Environmental implications from plastic waste

Looking beyond the essential services that plastics provide to humanity and their associated human health risks, evidence abounds for plastics' potential to pollute and disrupt important natural processes and quality of life [15]. The functional properties of plastics happen to be the reasons why they are a serious hazard to the environment. Since they are also buoyant, an increasing load of plastic debris is being dispersed over long distances, and when they finally settle in sediments they may persist for centuries [16]. Unfortunately, the drastic rises in the use of plastic materials have not been accompanied by a corresponding development of procedures for the safe disposal or degradation of these materials, and hence, the post consumer waste of plastics has also increased enormously. Waste plastics are often found to be as litter across cities; they are burned, buried or disposed-off in open dumps along with other waste. The amassing of these non-biodegradable plastics in the environment leading to long-term environment, economic and waste management problems is a subject of great concern [17]. Numerous hazards are caused by the discarded waste plastic products; the most affected are the marine and aquatic population. Sea turtles eat a jellyfish looking floating plastic bag which clogs their intestines due to which they miss out on vital nutrients and ultimately, starve to death. Other types of loose plastics entangle birds, fish and mammals, which too leads to their ultimate demise. Plastic bags and other plastic garbage thrown into the ocean kill as many as 1 million sea creatures every year [18]. Earlier, the abundance of plankton was about five times higher than that of plastic, but now, the mass of plastic exceeded that of plankton six fold. The second most affected species is we, i.e. human beings. We are prone to health risks when plastics are incinerated; our lives get threatened when water ways are clogged [15]. Apart from these, the waste non-biodegradable plastics are accountable for soil contamination; toxic chemical loading, air pollution through release of toxic gases when plastics are burned [19].

The most commonly observed plastic debris include thin films used for flexible packaging applications. Polyolefins, viz. high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) are widely used to make thin packaging films for various applications viz. carry bags, mulching films, and for similar other purposes. The reason of using these polymers is their low cost and high energy effectiveness together with wide range of favorable properties viz. easy processability, good mechanical properties, chemical resistance, toughness and flexibility, transparency in thin films, barrier properties against water and oxygen, odorlessness, etc. [20]. Packaging with extremely durable synthetic plastics is widespread, unnecessary, and unsustainable. The huge waste generated due to non-biodegradability of these plastics causes “white pollution”, waste management problems, perceived garbage crisis, shortage of landfills etc. Many plastic articles, e.g., throwaway cups, utensils, plastic bags, etc. have a very short useful life span, which can be measured in timescales of seconds, minutes, or hours. However, upon release into the environment, these products are known to persist and pollute for decades, centuries, or even millennia [21]. The increased production of durable plastics, with limited recyclability, for disposable and short-lived consumer products gives rises to human health risks and makes our environment unsustainable [22-24]. Moreover, the production of conventional plastics is based on petroleum and accounts for 8% of the total world oil production, out of which nearly 4% is used as feedstock and remaining 3–4% is utilized for energy requirements in manufacturing [25]. Therefore, diminishing petroleum resources have also motivated consideration of various alternatives of synthetic polymers [26].

1.7. Apparent solutions for plastic waste management

Most of the waste plastic materials are disposed-off through landfilling and incineration, which causes serious threat to our planet. Hence, this option is the least favored and placed at the bottom of Figure 1.5. The concept of the 4 R’s, i.e., reduce, reuse, recycle, re-develop, may serve as a guiding principle for consumers, industry and government for adaptive measures addressing environmental and human health issues posed by plastics. The latter verb refers to the need to consider the ways of imparting biodegradability in the conventional plastics by re-designing or re-developing the plastic production processes, assessment of life cycle of plastics from an earth systems engineering. In recycling and reuse of waste polymeric materials, it is very difficult to collect the whole plastic waste, segregate according to their types and transport it to respective type of recycling plant. According to a report, only 9% of the total plastic waste generated in 2012 was recovered for recycling. Moreover, the recycled products are of inferior quality as compared to those from virgin polymers [27, 28].

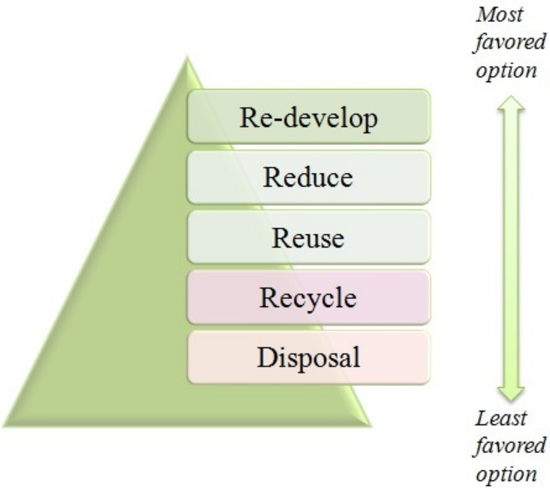


Figure 1.5. Options for handling plastic waste [29]

The reduction in using the plastic products is another favored option than recycling and reuse, but lack of society’s environmental awareness in our country hinders and dilutes this preference. Nevertheless, the government and individual’s perspective and to address systematically at the policy and governance level the unsustainable use of plastics, may be helpful in overcoming these hurdles. The most favored option is to re-develop or re-design the plastics production process and it has become demand of the situation [30].

The mixture of biodegradable plastics and conventional synthetic polymers is a simple and practical way of making innovative materials with functional properties. Films produced by blending two or more polymers usually possess different physical and mechanical properties than the initial components. Furthermore, because synthetic polymers are easily obtained and have low production costs, the mixture of biodegradable and synthetic (oil-based) polymers may improve the performance-cost ratio of the resulting films [31]. In recent times, investigations have been increased concerning the total or partial substitution of synthetic plastics by biodegradable materials, viz. poly(lactic acid) (PLA) [32], poly(ε-caprolactone) (PCL) [33], poly-β-(hydroxybutyrate) (PHB), poly-β-(hydroxybutyrate-*co*-β-valerate) (PHB-V) [34], poly(butylene adipate-*co*-terephthalate) (PBAT) [35], etc. The major issue in incorporating bio-polymer into conventional synthetic polymer is their compatibility. Bio-based polymers are usually hydrophilic whereas synthetic polymers are hydrophobic in nature. The resultant blend of these two types of polymers is generally immiscible. The interfacial compatibility between biodegradable polymer and the thermoplastic matrix is a critical requirement for obtaining good mechanical properties in these composites. Many researchers have proposed the use of compatibilizers to improve the interfacial adhesion between the polymers. For immiscible binary mixtures, polymers grafted with maleic anhydride shows good results in promoting compatibility between the polymers.

1.8. Biodegradable polymers

From last two decades, there has been a significant research interest on compostable and/or biodegradable polymers in order to alleviate solid waste disposal problems related with petro-based plastics [36]. These biodegradable polymeric materials are increasingly used today in packaging, agricultural, medical, pharmaceutical, and other areas. Biodegradable plastics with functionalities ester, amide, or ether and processabilities comparable to traditional petrochemical-based plastic have been developed for packaging applications [37]. Interest in biodegradable plastic packaging arises primarily from their use of renewable raw materials (crops instead of crude oil) and end-of-life waste management by composting or anaerobic digestion to reduce landfilling [38]. Two main classes of biodegradable polymers can be distinguished [39]: (i) *Natural biodegradable polymers* produced from feedstocks derived from biological or renewable resources available in large quantities; and (ii) *Synthetic biodegradable polymers* produced from feedstocks derived from non-renewable petroleum resources. Figure 1.6 shows a classification of biodegradable polymers according to their origin.

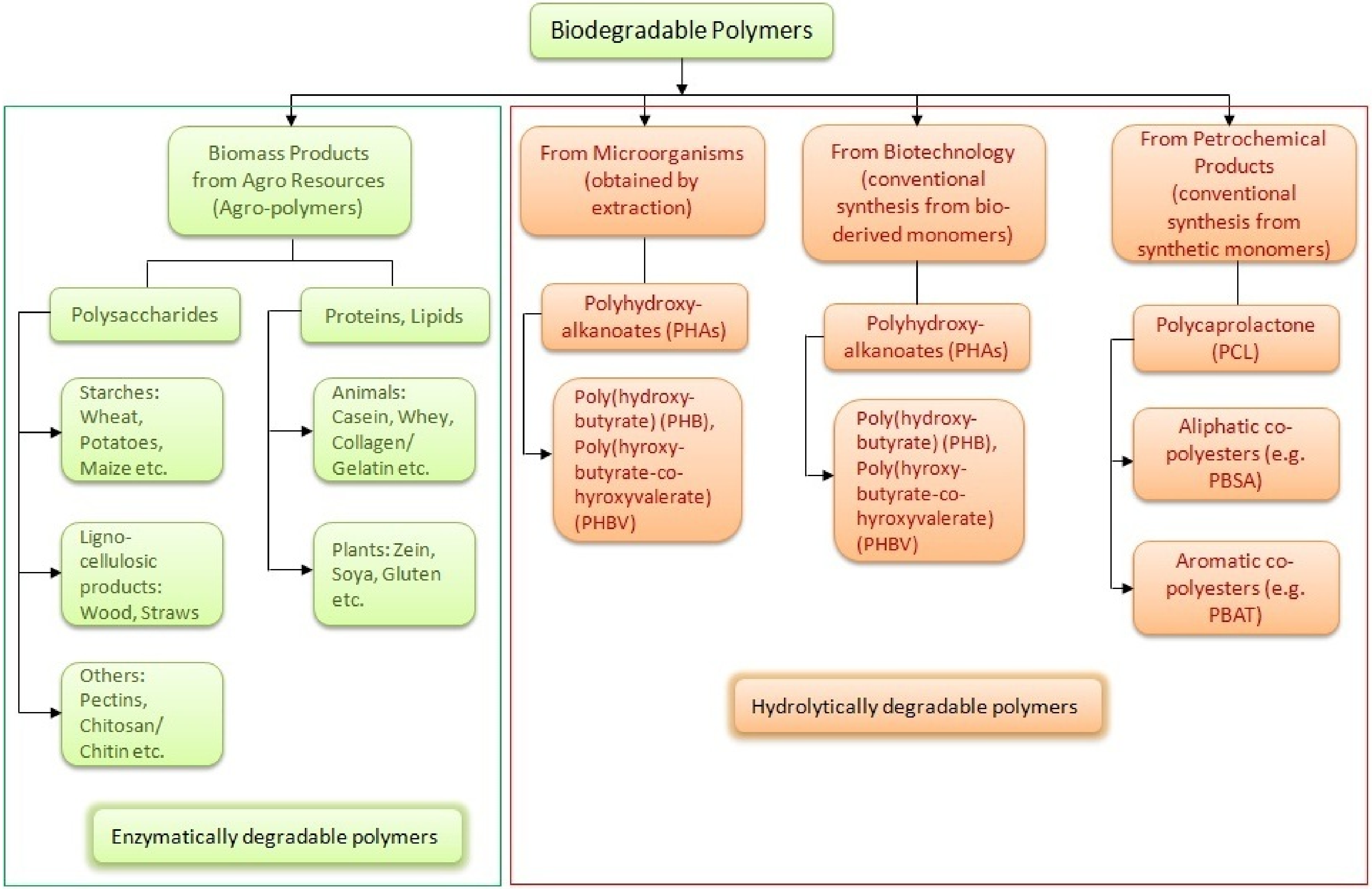


Figure 1.6. Classification of the most known biodegradable polymers [39]

Agro-polymers include polysaccharides, like starches found in potatoes or wood, and proteins, such as animal based whey or plant derived gluten. Polysacharides consist of glycosidic bonds, which take a hemiacetal of a saccharide and bind it to an alcohol via loss of water. Proteins are made from amino acids, which contain various functional groups. These amino acids come together again through condensation reactions to form peptide bonds, which consist of amide functional groups. Examples of biopolyesters include polyhydroxybutyrate and polylactic acid.

The most commercialized biodegradable polymers are starch based thermoplastics and poly(lactic acid) (or polylactide). Considering their good thermal and mechanical properties, these polymers are potential alternatives to conventional thermoplastic polymers of petrochemical origin, such as polyolefins, the scale of production worldwide is still very low [40]. Moreover, there has been little research on the extent to which these materials truly degrade and/or biodegrade over the time scale of waste management systems such as composting facilities and anaerobic digestion or in natural settings [41].

Biodegradable polymers from renewable resources such as wheat, potatoes, corn, sugar cane, etc. stand out as a reliable alternative to commodities in packaging applications, as most of them are hydrolytically degradable polymers. These polymers can reduce the dependence on fossil sources and open new fields of research and may also contribute to mitigate uncontrolled disposal of plastics worldwide. Nowadays, bioplastics (including biodegradable and non-biodegradable polymers from renewable sources) represent around 0.3% of the World’s plastic production (724,000 tons in 2010) [40, 42]. Within the overall bioplastics production, the biodegradable polymers represented 59% share in 2011 [7]. The largest production of biodegradable polymers is occupied by starch based thermoplastic (SBT), poly(lactic acid) (PLA), and poly(hydroxyalkanoates) (PHAs). Figure 1.7 shows the distribution of bioplastics production worldwide.

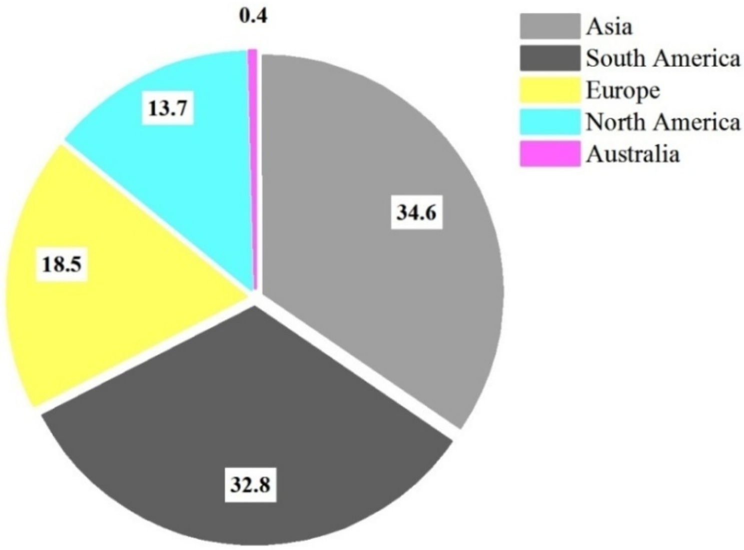


Figure 1.7. Bioplastic production in the world in 2011 [7]

The penetration of biodegradable polymers into the market relies on offering products favorable to the environment. The added value of these products is based on several features: a lower energy demand in processing than ordinary plastics, the release of CO_2 and water only after degradation, potential use as compost and the possibility to incorporate exclusively renewable raw materials in the production process.

The type of polymer raw material (renewable or non-renewable) for making the plastic products and the way of their disposal (controlled or uncontrolled) can make a huge difference on environmental impact. Figure 1.8 schematically summarizes the interrelations between the different raw plastic sources, the polymer transformation and the disposal options when plastic is used for packaging. If the plastics made from non-renewable sources (petroleum) are disposed-off in uncontrolled manner, they accumulate in environment causing plastic pollution which unfavorably affects lands, waterways and oceans.

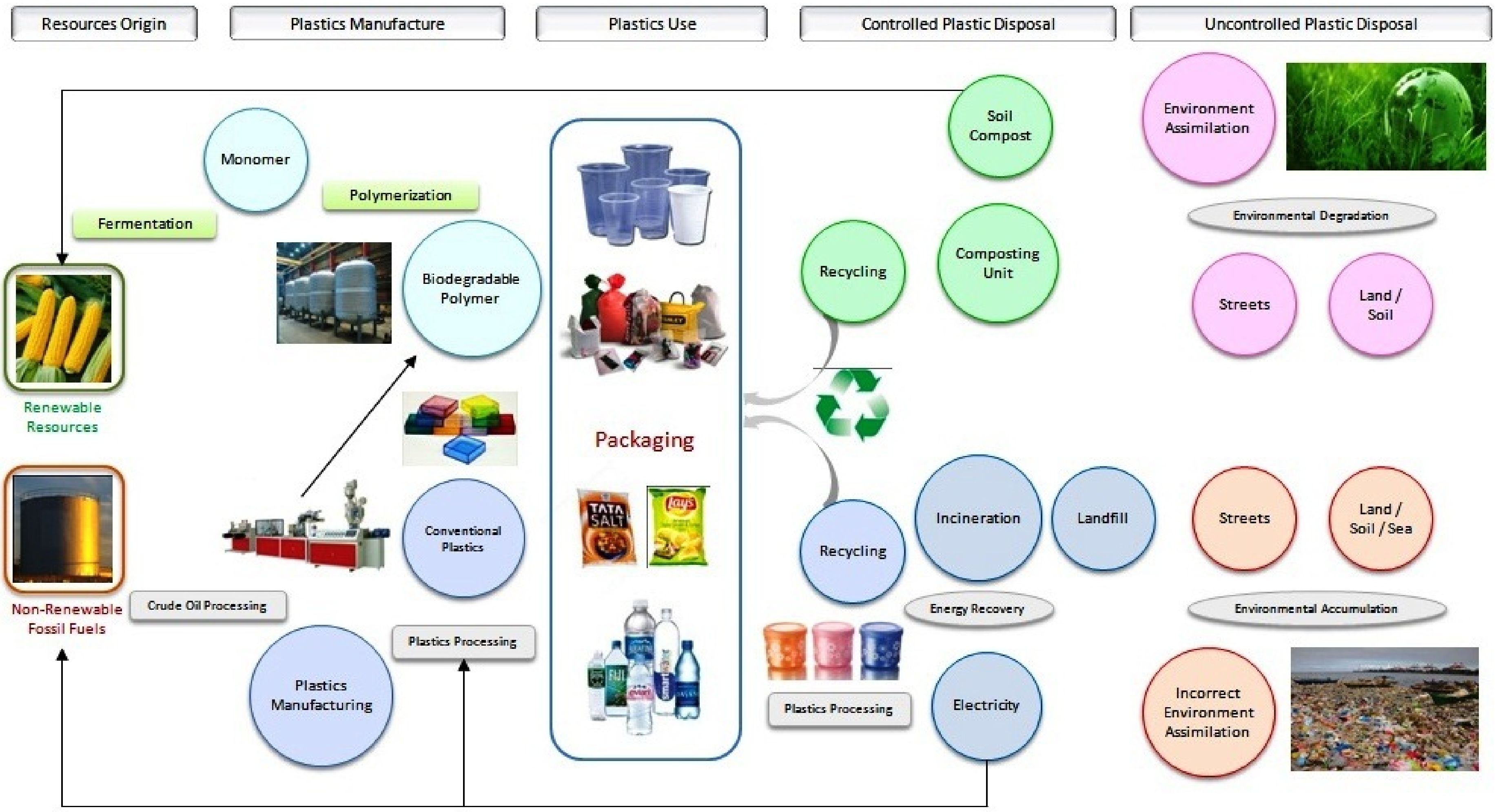


Figure 1.8. Lifecycle of plastics from different resources used in packaging [40]

1.9. Poly(lactic acid) at a glance

PLA belongs to the family of aliphatic polyesters usually made from α-hydroxy acids, which also include, for example, polyglycolic acid (PGA). It is easy to modify the stereochemical structure of PLA and obtaining low or high molecular weight and amorphous or semi-crystalline product by polymerizing a controlled mixture of L and D isomers. Thus, the properties of PLA can be altered by varying the ratio of isomers (L/D ratio) and the relative quantity of homo and (D,L) copolymers. Moreover, the performance properties of this polymer can be tailored by different formulations including addition of plasticizers, fillers, other biopolymers, etc. [43]. For lactide, three optical arrangements are available (L-lactide, D-lactide, and *meso*-lactide); while for lactic acid, two optical arrangements are obtainable, viz. L-lactic acid, D-lactic acid. Hence, there are several notable primary structures for PLA resulting in a variety of highly ordered crystalline structures. The simplest is the isotactic homopolymer poly(L-lactide) (PLLA) or its opposite enantiomer poly(D-lactide) (PDLA) where all of the monomers in the chain are of the same optical composition. Since the commercial production of lactic acid has been predominantly L-lactic acid, therefore a greater amount of research has been done on PLLA [43, 44]. As long as the renewable resources (carbohydrates) are used to produce lactic acid (the basic monomers of PLA) by fermentation, PLA is essentially classified as an environment friendly material and complies with the rising worldwide concept of sustainable development.

PLA is a biodegradable and biocompatible polymer. The former feature is mainly adapted for short-term packaging and the latter for biomedical applications. PLA can be easily degraded by abiotic degradation, i.e., simple hydrolysis of the ester bond without requiring the presence of enzymes to catalyze it. In the second step during biodegradation process (biotic degradation), the enzymes degrade the residual oligomers till final mineralization [44].

PLA is one of the most widely used materials in the manufacture of disposable and biodegradable plastic products. It is produced from cassava, corn, rice-derived dextrose or from bacterially-fermented starch obtained from food waste, such as potato peelings. PLA is more expensive than many polymers based on petroleum; however, PLA using corn has become cheaper as the scale of production increases due to the higher demand [45]. It is water-insoluble, can be either transparent or semi-transparent depending on polymer crystallinity, and optically active. It can be processed as a conventional thermoplastic polymer [46]. However, PLA does have limitations, which includes poor mechanical properties and high cost. It has a high glass transition temperature (60-65 °C) and limited thermal processing. This means that the polymer tends to be brittle and has a narrow window of melt processing conditions. Therefore, a great number of investigations have been performed on PLA to improve its mechanical properties and to reduce its price for use in the market. To achieve these points, blending techniques by solvent or melting and also co-polymerisation have been widely investigated to modify the physical properties. However, the blending techniques are more significant for practical use than the synthesis of the new copolymers because they can be useful in the market.

1.10. Degradation of polymers

In general, degradation is the process where the deterioration in the properties of the polymer takes place due to different factors like light (UV radiation), heat, mechanical stress, microbes, etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties resulting in embrittlement, cracks, discoloration, etc. and the life of the material becomes limited [47]. Thus, any polymer or its composite which is to be used in outdoor applications must be highly resistant to all the environmental conditions. Conventionally, the term degradation is taken to mean a reduction in the molecular weight of the polymer [48]. The main degradation processes are described in the following sections.

1.10.1. Photo-oxidative degradation

Exposure to ultraviolet (UV) radiation may cause significant degradation of many materials. UV radiation causes photo-oxidative degradation which results in breaking of the polymer chains, produces radicals and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after an unpredictable time [49]. 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 1.9. The cycle is terminated when two radicals combine or recombine to form a non-radical product.

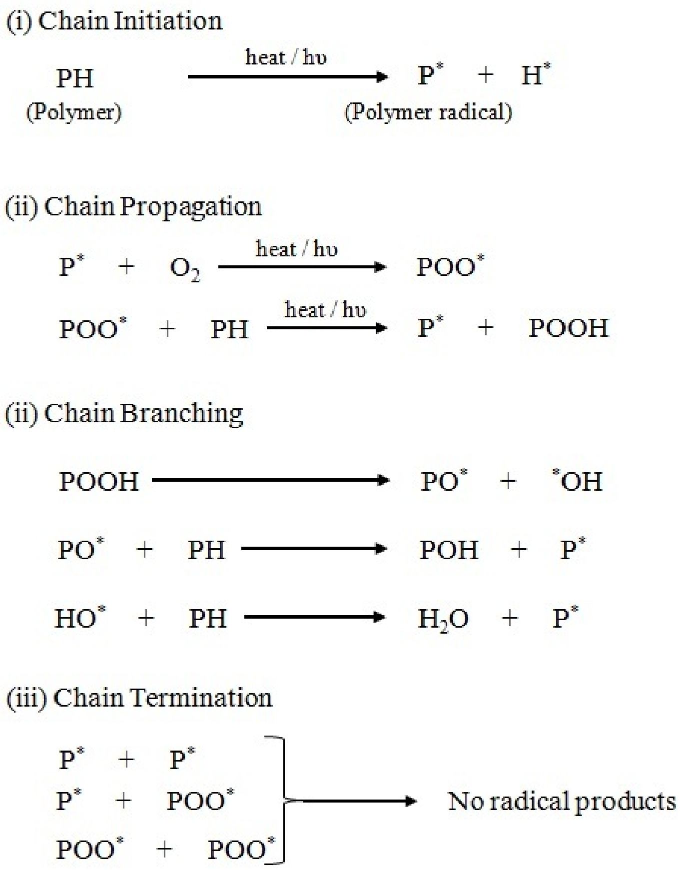


Figure 1.9. General photo-oxidative degradation in polymers [49]

1.10.2. Thermal degradation

All polymers can be thermally degraded by the influence of heat. Long term exposure to elevated temperature causes a deleterious effect on mechanical, thermal and morphological properties of polymers. However, the fundamentals of degradation mechanisms of polymers are based on the same principles for both the thermal and photo-oxidative degradation; the only exception is that photo-oxidative degradation proceeds at a faster rate than thermal degradation and hydroperoxides are thermally cleaved to reactive radicals in thermal degradation [50].

1.10.3. Chemical degradation

Chemical degradation of polymer materials occurs via hydrolysis or enzyme-catalysed hydrolysis, which can also result in their degradation or main chain scission [51]. Polymers such as polyamides, polycarbonates, polyacetals can be degraded by hydrolysis under acidic conditions present in the environment. Hydrolytic degradation takes place when polymers containing hydrolysable groups are exposed to moisture. If hydrolysis is achieved enzymatically, then the process is often referred to as biodegradation, meaning that the degradation is mediated at least partially by a biological system [52].

1.10.4. Mechanical degradation

Sometimes, mechanical degradation also occurs in polymers if they are subjected to mechanical stress higher than permissible. For example, during processing in a screw extruder, the polymers are subjected to high shear stress due to which micro alkyds are formed leading to accelerated oxidation.

1.10.5. Radiation induced degradation

X-rays and γ-rays are the high energy radiations which degrade polymers to a larger extent than that by UV radiation. Like UV, γ-rays are also electromagnetic radiations but their energy level is much higher than those of UV rays.

1.10.6. Degradation due to environmental stress cracking

When a polymer material deteriorates and/or develops cracks due to stress by the external environment viz. in presence of detergent chemicals, polar vapours of liquids, etc., it is termed as environmental stress cracking (ESC).

1.10.7. Biodegradation

Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles. It can only occur within the biosphere as microorganisms play a central role in the biodegradation process [53]. While synthetic polymers are not attacked by microorganisms, some additives incorporated in these polymers may act as host to initiate their biodegradation. Enhanced photo-oxidation of polymers may also increase their biodegradability. In Figure 1.10, general mechanism of biodegradation of polymeric materials is presented. During the microbial degradation stage, most of the abiotic oxidation products (low molecular weight compounds) are utilized by the microbes. An important aspect during this stage of biodegradation is the sustained growth of microorganisms and decrease in the number of carbonyl groups. In case of polyolefin polymers, significant biodegradation in a reasonable time period is achieved when the carbonyl groups from original oxidation products (such as ketones, esters and lactones) are consumed and the average molecular weight of polymer is decreased to 5000 Da only. [54].

This indicates that the microorganisms are growing and eventually the microorganisms degrade the smaller segments of polyolefin to form carbon dioxide and water as end products.

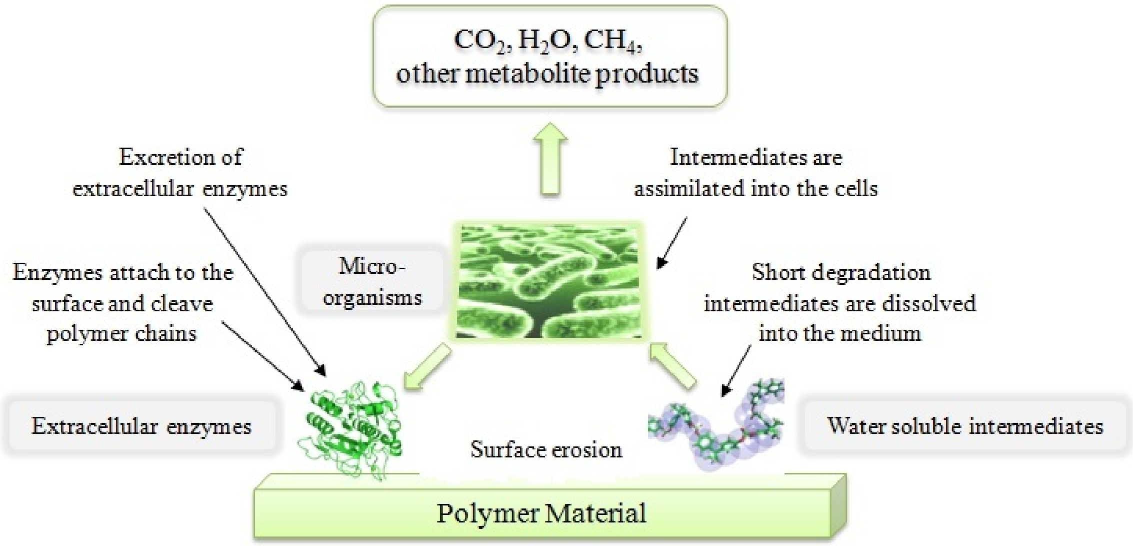


Figure 1.10. General mechanism of biodegradation of polymeric materials [55]

Biodegradation of polymer materials predominantly takes place as a result of enzymatic action of microorganisms and believed to occur in two major steps [56] – in first step, the polymer's molecular weight is reduced due to various factors viz. hydrolysis, oxidative reaction, heat, light, etc. resulting in short polymer chains. In second step, the low molecular weight oligomers are used by microorganisms yielding degradation products. During aerobic biodegradation, the carbon present in polymer molecules is converted by microorganisms into gaseous carbon dioxide, water, biomass (or humus), and carbon residues as shown in Eq. 1.1 [57].

$$C_{polymer} + O_2 \rightarrow CO_2 + H_2O + C_{biomass} + C_{residue} \qquad (1.1)$$

Therefore, the degree of aerobic biodegradation can be determined by measuring the total amount of CO_2 evolved from the polymer and expressed as percentage biodegradation (or mineralization), which is the ratio of cumulative CO_2 actually generated by the test sample to the theoretical CO_2 evolved from the material. Complete biodegradation occurs when no residue remains, i.e., when the original polymer material gets completely converted into gaseous products and salts. The percent biodegradation can be determined by either elemental analysis, or calculation from chemical composition according to ASTM D5338 [58] and ISO 14855 [59] standards.

1.11. Degradable polymer blends

To overcome the environmental hazards from non-biodegradable polymers and inferior mechanical properties of biodegradable polymers, preparing and using the blends of these two types of polymers makes sense. But, neat biodegradable polymers have limited uses because of a lack of mechanical properties and/or physical properties; thus, polymer-polymer blending techniques are used to remedy this shortcoming, instead of trying to synthesise a new polymer, which is more difficult. In addition to better mechanical properties of biodegradable polymers, blending these with conventional polymers reduces their cost of production also. As an example, polyolefin-starch blends commonly used in the packaging industry have better mechanical properties compared to starch, and enhanced biodegradability in relation to pure polyolefin [60, 61]. In general, the miscibility of biodegradable and non-biodegradable polymers is very low; therefore, compatibilizers viz. grafted maleic anhydride is utilized to enhance the compatibility between the two polymers [62].

Chapter 2 – Literature Review

It is estimated that 15,342 tons per day (TPD) of plastics waste is generated in India only, i.e., approximately 9% of 0.17 million TPD of total municipal solid waste (MSW) in the country resulting in widespread littering on landscape, which not only affects environment but also human beings [63]. Asia's top plastic waste market is India's National Capital Delhi, in which the daily handling and trading is over 1,000 tons [64, 65]. Amongst all the plastic wastes, PE films used in flexible packaging applications and disposable materials share the largest amount. Globally, the plastic waste accumulate in the environment at a rate of 60 million tons per year [8]. This "white pollution" caused by huge amount of plastic waste have an undesirable influence on the environment. Thus, there is a tendency to substitute such polymers with those which undergo biodegradation processes.

An effective method of preparation of biodegradable polymeric materials for packaging applications is to blend synthetic polymers with biodegradable polymers. The advantage of blending is that the produced polymer material will have the requisite physical and mechanical properties during its useful life after which it will be degraded biologically under environmental and/or composting conditions.

2.1. Polymer blends in general

A polymer blend is a macroscopically homogeneous mixture of two or more different polymers, which can be binary, ternary, or quaternary depending on the number of constituents in the blend. The method used to mix polymers together to create a new material with different physical properties is called polymer blending.

In initial stages during the development of polymer science, studies in polymer physics were involved with the understanding of the basic properties of homopolymers. Variations of the basic polymer structure leading to copolymers and graft copolymers were quickly followed by the detailed studies of the physical nature of these variations. More recently, detailed studies of the physics of polymer blends have been emphasized in both academic and industrial research laboratories [66].

There are a few blending techniques to prepare polymer blends, however, melt blending process was used in this work. Polymer blends can be broadly divided into three categories; miscible polymer blends, immiscible polymer blends, and compatible polymer blends [67]. According to International Union of Pure and Applied Chemistry (IUPAC), the definitions of these three categories [68] are as follows:

- A *miscible polymer blend* or homogeneous polymer blend is a blend that is thermodynamically stable or metastable.
- An *immiscible polymer blend* or heterogeneous polymer blend is a polymer blend that exhibits immiscibility.
- A *compatible polymer blend* is an immiscible polymer blend that exhibits macroscopically uniform physical properties throughout its whole volume. The macroscopically uniform properties are usually caused by sufficiently strong interactions between the component polymers.

The final properties of polymer blends depend on the chemical structure of the original components, mixing ratio of the constituent polymers, interaction between the components, and the processing steps to which they are subjected.

2.2. Polyethylene-based biodegradable blends

Polyethylene (PE) is highly stable and takes very long time to degrade in the environment, where the degradation process can span many decades. Moreover, the PE which is used for flexible packaging, cannot be properly recycled [69]. Thus, if PE products are made biodegradable which degrade in a shorter time, their environmental impact could be minimized. An effective method of tuning biodegradability in conventional PE is to blend it with biodegradable polymers, such as cellulose, starch, aliphatic polyesters like PLA, PCL, PHB, etc. and/or by incorporating special additives to the mixture, which accelerate the degradation process, e.g. stearate (St) complexes of transition metals like manganese (MnSt), cobalt stearate (CoSt), etc. [70]. Presence of any biodegradable polymer as a blend will affect the behaviour of the PE in outdoor weathering and will act as an initiator for their oxidative degradation by heat, light and microbes. One of the obvious advantages of blending biodegradable polymer with the conventional PE is that the blend will have the requisite physical and mechanical properties during its useful life after which it will be degraded biologically under environmental and/or composting conditions. These types of blends have been considered a promising avenue for preparing polymers with “tailor-made” properties (functional physical properties and biodegradability).

2.2.1. Polyethylene with natural biodegradable polymers

Blending of natural polymer with synthetic one is a strategy to enhance biodegradation. The natural polymers include starch, cellulose, chitin, chitosan etc. The percentage of natural polymer added in the blend affects the physical and mechanical properties of the synthetic polymer. Shelf life of such blends decrease since the rate of degradation of the natural polymer used as filler is several orders of magnitude larger than that of the synthetic polymer. The final properties of the blend depend on the type and amount of blend material that is added, its morphology, interaction between the blend material and the polymer, crystallinity of the polymer and processing conditions for preparing the blends [71]. Starch provides higher oxygen permeability as it is consumed by microorganisms. Higher permeability helps in the release of degradation products from the sample, thus making the matrix hollow, increasing the surface to volume ratio [72]. Many researchers have blended starch in traditional plastics (based on the Griffin technology), particularly in polyolefin [73-78]. E. Chiellini *et al.* [79, 80] performed extensive research on biodegradable blends of polyethylene-starch and analyzing their oxidative degradability. Upon blending with starch, PE films biodeteriorate on exposure to a soil environment [81, 82]. The microbial consumption of the starch component, in fact, leads to increased porosity, void formation, and the loss of integrity of the plastic matrix. Generally, starch is added at fairly low concentrations [83]; and the overall disintegration of these materials is achieved by the use of transition metal compounds, soluble in the thermoplastic matrix, as pro-oxidant additives which catalyse the photo and thermo-oxidative process [84-86]. However, PE and starch are immiscible because of their differences in polarity; that is, starch is hydrophilic whereas PE is hydrophobic. To improve their compatibility, various attempts have been made to modify either starch or PE [87-90]. It was found that plasticizers, coupling agents, or modified starch only partially improved the dispersion of starch in PE and their interfacial properties because of their limited interaction. Another approach was to use poly(ethylene-*co*-acrylic acid), poly(ethylene-*co*-vinyl alcohol), or oxidized PE as a compatibilizer in PE–starch composites, but the composites had unsatisfactory mechanical properties [91, 92]. The inferior mechanical properties were a result of weak interaction (e.g., hydrogen bonding) between starch and compatibilizer and limited opportunities for compatibilizer to interact with PE. Biodegradation of polyolefin-cellulose blends have also been reported using soil organism and soil compost [93, 94]. It was found that polyethylene-cellulose blend having 5% to 15% of cellulose failed to show any significant increase in biodegradation, whereas when the amount of cellulose was increased up to 30%, the degradation of the blends started after 14 weeks under composing conditions. However, the increasing cellulose amount in the polymer affects its physical property considerably making it unsuitable in many applications.

Chitin is an essential part of the carbohydrate skeleton of the fungal cell wall and is a molecule that is not represented in humans and other vertebrates [95]. Next to cellulose, chitin is the second most abundant polysaccharide in nature [96]. Chitosan is the deacetylated product of chitin and has been used widely as a food packaging material because of its antimicrobial action [97-99]. However, there are some limitations to the application of chitin and/or chitosan film for packaging, because of their high sensitivity to moisture. Blending chitosan with synthetic biodegradable polymers, for example, poly(3-hydroxybutyric acid) (PHB) [100] and poly(ε-caprolactone) (PCL) [101], has been used to modify its water sensitivity properties. Another interesting option is to blend chitosan with poly(lactic acid) (PLA) [102] to improve its water vapour barrier of chitosan. However, this purpose was achieved but on the cost of tensile strength and elastic modulus due to immiscibility of chitosan and PLA. To best of our knowledge, only one research group [31, 103] has carried out studies on blending chitosan with polyethylene. They reported that the presence of chitosan in PE accelerates the degradation of the blended films significantly. In addition, the compatibilizer polyethylene-*graft*-maleic anhydride (PE-*g*-MA) also accelerated the photo-oxidation rate of their films.

2.2.2. Polyethylene with synthetic biodegradable polymers

Nowadays, synthetic biodegradable polymers, such as aliphatic polyesters, have become attractive alternatives to natural biodegradable polymers for preparing blends with conventional polymers because the chemical modifications of synthetic biopolymers are easier [104]. Ammala *et al.* [70] stated that the aim of degradable polyolefin design is to retain functionality as a commodity plastic for the required service life but degrade to nontoxic end products in a disposal environment. Several researchers [105-108] have proven the usefulness of conventional polyolefin (from environment point of view) after blending with biodegradable polymer(s). In general, these blends are immiscible or partially miscible and suitable compatibilizers are required to increase their interfacial adhesion and thus miscibility. Likewise, blending PLA with conventional polymers including polyethylene, poly(ethylene oxide), poly(ethylene glycol), poly(vinyl acetate), poly(4-vinylphenol), and polyacrylates can substantially modify the mechanical and thermal properties, degradation rate, and permeability [109-113]. Some other research groups have done investigation on isolation of polymer degrading bacteria [82, 114-116].

Wang and Hillmyer [117] prepared PLLA/LDPE binary blends and PLLA/LDPE/PE-*b*-PLLA (polyethylene-poly(L-lactide) diblock copolymer) ternary blends by solution blending followed by precipitation and compression moulding and found that PE-*b*-PLLA is a good compatibilizer for PLLA/LDPE blends. Rezende *et al.* [118] prepared low-density polyethylene (LDPE) / poly(ε-caprolactone) (PCL) blends and investigated the effect of addition of a pro-oxidant calcium stearate (CaSt) on their properties. They found that the enzyme lipase showed its specificity on PCL, and the addition of CaSt delayed the degradation of PCL and 75/25 PCL/LDPE blend, but accelerated the degradation of the blends 50/50 and 25/75. Because of the difference in their chemical structures, PE and PLA should be immiscible and exhibit weak interfacial adhesion in their binary blends, which, in general, leads to poor mechanical properties [119]. Hence, for immiscible polymer blends, adding a suitable compatibilizer can increase the morphological stability and interfacial adhesion, and improve the ultimate mechanical properties [120-122]. Singh *et al.* [123-125] studied the physico-mechanical properties and degradability behaviour of LLDPE/PLLA blends and reported that compatibilized 80/20 (LLDPE/PLLA) blend gives the optimum combination of mechanical properties and PLLA content. They also noticed faster degradation of blended films in composting environment. A review on polyethylene and biodegradable mulches for agricultural applications was published by Kasirajan *et al.* [126] in which they mentioned the successful preparation and application of PE blends with starch or other biodegradable polymers viz. PVA, PCL, PLA etc. Omura *et al.* [127] prepared blends of PLLA and LLDPE and analyzed their thermal degradation behaviour with MgO catalyst. They demonstrated that the thermal degradation of the PLLA ingredient in a PLLA/LLDPE 20:80 (wt/wt) blend proceeded randomly to give not only L,L-lactide but also *meso*lactide and cyclic oligomers, while the PLLA ingredient in a PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite depolymerised according to the unzipping reaction to produce the L,L-lactide dominantly.

2.3. Enhancing biodegradability of polymers with pro-oxidants

Pro-oxidants are transition metal ion complexes and they are added to polyethylene in the form of either stearates or other organic ligand complexes to catalyze the degradation process of the PE. The most commonly used pro-oxidants are Fe^{3+}, Mn^{2+}, and Co^{2+} stearates [128, 129]. The catalytic effect is stronger for pro-oxidants based on metal combinations capable of yielding two metal ions of similar stability and with oxidation number differing by one unit only [128]. Among the mentioned pro-oxidants, Fe^{3+} initiates photooxidative degradation, whereas Mn^{2+} and Co^{2+} initiate a thermooxidation process (i.e., oxidation without the influence of light intensity). Abrusci *et al.* [130, 131] studied thoroughly the effect of metal stearates as pro-oxidant additives on biodegradation of LDPE mulching films and found the sequence of effectiveness in biodegrading the film as $Co^{2+} > Mn^{2+} > Fe^{2+}$. Similar outcome was obtained by Fontanella *et al.* [132, 133]. Benítez *et al.* [20] also investigated the influence of a pro-oxidant additive on the accelerated and environmental LLDPE and LDPE films and found that the pro-oxidant additive induced oxidation of PE samples promoting the formation of polar groups, increasing crystallinity and reducing the molecular weight leading to a depletion of the intervening amorphous layers between crystalline hard domains. Kyrikou *et al.* [134] examined the behaviour of experimental mulching photodegradable LLDPE films with pro-oxidants under real field cultivation conditions and in laboratory. Their results indicated that with pro-oxidants, a rapid (rather abrupt) degradation of the films occurs and at much shorter time as compared to conventional LLDPE mulching films. Similarly, Corti *et al.* [135, 136] probed the effects of outdoor exposure to natural sunlight on the oxo-biodegradation behaviour of LLDPE samples containing proprietary pro-degradant additives. They claimed that the LLDPE containing pro-degradant additive can accelerate oxidative degradation when film samples are submitted to outdoor exposure. The combination of different environmental factors such as oxygen, temperature, sunlight and action of living microorganisms are responsible for the degradability/biodegradability of LLDPE containing pro-degradant additives. Pablos *et al.* [137] tried another pro-oxidant calcium stearate for photodegradation of polyethylenes and compared its effect with that of iron stearate. They revealed the higher efficiency of Fe-stearate compared to Ca-stearate in decomposing hydroperoxides, leading to higher degradation during processing.

2.4. Measurement of biodegradation

A biodegradable polymer is capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, and biomass from the action of naturally occurring microorganisms such as bacteria, fungi and algae [138]. The predominant mechanism is the enzymatic action of microorganisms, which can be measured by standard tests over a specific period of time, reflecting available disposal conditions. The end-products are CO_2, new biomass, and water (in the presence of oxygen) or methane (in the absence of oxygen). Therefore, the degree of aerobic biodegradation can be determined by measuring the total amount of CO_2 evolved from the polymer and expressed as percentage biodegradation, which is the ratio of cumulative CO_2 actually generated by the test sample to the theoretical CO_2 evolved from the material. Standard test methodologies have been developed and published by international standards authorities namely American Society for Testing and Materials (ASTM) www.astm.org; Bureau of Indian Standards (BIS) www.bis.org.in; European Committee for Standardization (CEN) www.cen.eu; German Institute for Standardization (DIN) www.din.de; International Organization for Standardization (ISO) www.iso.org; to assess the rate of polymer degradation under simulated (in-lab) and real-time exposure (field test) conditions.

ASTM D5338 [58] and ISO 14855 [59] are used for determining aerobic biodegradation of plastic materials under controlled composting conditions by analysis of evolved carbon dioxide. According to these, the theoretical CO_2 content of the material can be determined by either elemental analysis or calculation from chemical composition by standard methods. Depending on the type of standard to follow, different composting conditions (humidity and temperature cycle) must be realized to determine the compostability level [139]. Microbial population, moisture, temperature and oxygen are the key elements that control the rate of degradation [140]. Emo Chiellini and his research group presented a fantastic review [141] on standard techniques and criteria established by different standardization bodies with basic interpretation of degradation of plastics.

Only a few studies deal with the biodegradation study of polymer and/or polymer blends in terms of CO_2 evolution and measurement. Uematsu *et al.* [142] carried out evaluation of microbial-degradability of cellulosic material with Microbial Oxidative Degradation Analyzer (MODA) apparatus in a laboratory scale. They found that the cellulose degraded by over 70% in 45 days of test period. Moura *et al.* [143] evaluated the aerobic biodegradability of aliphatic polyesters blends with HDPE by microbial growth in polymeric films and biochemical oxygen demand methods. The results obtained by them have shown biodegradability of the blends (by the biochemical oxygen demand method) ranging from 22% for 30/10/60 (HDPE/PE-*g*-MA/PLA) blend to 52% for 30/10/60 (HDPE/PE-*g*-MA/Mater-Bi) blend (Mater-Bi® is a brand name of a broad family of innovative bioplastics produced and marketed by Novamont S.p.A., Novara, Italy). They concluded that the studied samples were not "readily biodegradable" according to the Organisation for Economic Co-operation and Development (OECD) standards. Goncalves and Martins-Franchetti [144] investigated the biodegradation of 70/30 (PP/PHBV) blend films in soil, monitoring the evolution of CO_2 using the respirometric method. The polymeric films were incubated at 28±2 °C for 180 days in biometer flasks, and the sequence of biodegradation percentage obtained was 70/30 (PP/PHBV) > PP, that is, 15% and 0%, respectively. Li *et al.* [145] studied the biodegradation of native starch granules, thermoplastic starch (TPS) with a high concentration of glycerol plasticizer and its blends with PLA and LDPE under composting conditions. They correlated their results with the morphologies and continuity behaviour of the various blend systems and found that thermoplastic starch degrades more rapidly than native starch. They also reported that blending TPS with LDPE and PLA in a co-continuous morphology at a 50/50 composition provides a significant increase in TPS surface area, which increases the biodegradation rate for the blends as compared to pure TPS. The percent mineralization of 30/70 (TPS/LDPE) was 50% approximately. Sangwan *et al.* [146] presented first report on molecular investigation of biodegradation of three different PLA/ organically modified layered silicates (OMLS) nanocomposites under aerobic composting conditions according to Australian standard (AS ISO 14855). They found that after 60 days of degradation, the total degradation of PLA/TSA, PLA/ODA, PLA/DDA nanocomposites and the neat PLA samples was approximately 35, 32, 30 and 31% respectively. Recently, Ruka *et al.* [147], from the same group of researchers, measured the biodegradation of PHB/ bacterial cellulose blends using the precise method of CO_2 evolution. In their work, both PHB and bacterial cellulose were found to degrade rapidly, with bacterial cellulose initially having the highest rate of degradation of the samples.

2.5. Scope of the present work

Plastic is a relatively cheap, durable and versatile material. Plastic products have brought benefits to society in terms of economic activity, jobs and quality of life. However, plastic waste also imposes negative environmental externalities. It is usually non-biodegradable and therefore can remain as waste in the environment for a very long time; it may pose risks to human health as well as the environment; and it can be difficult to reuse and/or recycle in practice. Previous sections of this study have shown that plastic packaging not only makes up the largest share of plastic consumption, it also accounts for the largest fraction of plastic waste generated. Moreover, the limited reserves of crude oil, from which conventional plastics are manufactured, has generated sparking interest in development and use of biodegradable polymers. Today, public concerns about the environment, climate change and limited fossil fuel resources are important drivers for governments, companies and scientists to find alternatives of non-biodegradable polymers. For example, the ban on the use of plastic carry bags of a certain quality by governments and civic bodies across the country is an opportunity for the development of biodegradable plastic. Biodegradable plastics may offer significant contributions by reducing the dependence on fossil fuel and the related environmental impact. Hence, there are ample prospects to explore the escalation of biodegradable polymers which are of low cost and eco-friendly as well. Biodegradable polymers due to its environmental benefits have gained a widespread attention of the researchers in academia as well as in industry. However, high materials cost of biodegradable polymers are the main culprit for hindering its application at commercial level.

The recommendation of using biodegradable polymers is triggered by the problem of limited waste management capacities and therefore, the feature of these polymers is their usefulness during their shelf life and extent of biodegradability after their disposal.

To make a balance between the well known properties of conventional polymers and need of using biodegradable plastics, blending of these two classes of materials seems the most popular and explored option, especially in flexible packaging applications. The ratio of these polymers and addition of additives, which will give the desired and optimum results, is extremely important and therefore, requires extensive research.

In terms of volume, HDPE is the third-largest commodity plastic material in the world, after poly(vinyl chloride) and polypropylene. Blow moulding and injection moulding films & sheets account for approximately 66% of the world market for HDPE, most of it being in packaging. Hence, if we succeed in making this material as degradable, it will be a great contribution in reducing plastic waste and sustainable environment. As the most economic and practical way to achieve this is to blend an appropriate biodegradable polymer in HDPE, therefore, we chose poly(lactic acid) (PLA), which is an eco-friendly bioplastic with excellent biocompatibility and processability, for the purpose. By using this polymer in blending with HDPE, it was reckoned that the drawbacks of PLA, viz. brittleness and low thermal stability etc. will be overcome and at the same time, biodegradability will be introduced in HDPE if these two polymer phases were made to be compatible by using a suitable compatibilizer. Additionally, it is very important to characterize these blended products which will help the manufacturers in setting the various parameters for production. The estimation of degradation rate with respect to the disposal of HDPE/PLA blends is also critical, as polyethylene takes enormous time to degrade in natural environment whereas PLA degradation is very fast, which makes difficult to predict the lifetime of their blends.

If ultimately successful, the reconstruction of the packaging industry using bio-based feedstocks will have a major impact and can be seen as another industrial revolution.

2.5.1. Aim and objectives

The ultimate aim of the project was to develop degradable HDPE by blending with PLA/pro-oxidant additives for packaging applications. To attain this, following specific objectives were planned:

1. Compounding of HDPE with varying amounts of PLA/pro-oxidant in absence/presence of compatibilizer.
2. Optimizing the blend composition, for flexible packaging applications, based on mechanical properties which should be comparable with the conventional packaging films.
3. Characterization of the selected blend samples and investigating the effect of blend composition on the performance properties and processability.
4. Determination of thermal degradation kinetics and estimating the lifetime of the polymer blends.
5. Measuring biodegradation of new polymeric blends using the guidelines of ASTM D5338 standard for determining aerobic biodegradation under controlled composting conditions.

Chapter 3 – Experimental Methods

3.1. Scheme of the research work

The overall strategy of the present research work is summarized in Figure 3.1. Firstly, several blends of HDPE/PLA with/without MA-*g*-HDPE and CoSt in predetermined ratios were prepared by using melt blending technique. Thereafter, films from these blends were produced by compression moulding technique. Numerous characterizations of the prepared blend films were performed to investigate the effect of blend composition on the performance properties and degradability. For biodegradability measurement, a low-cost biodegradability measuring apparatus is developed, which is of significant importance in this research work. Finally, the kinetic studies and lifetime assessment of the blend samples were performed.

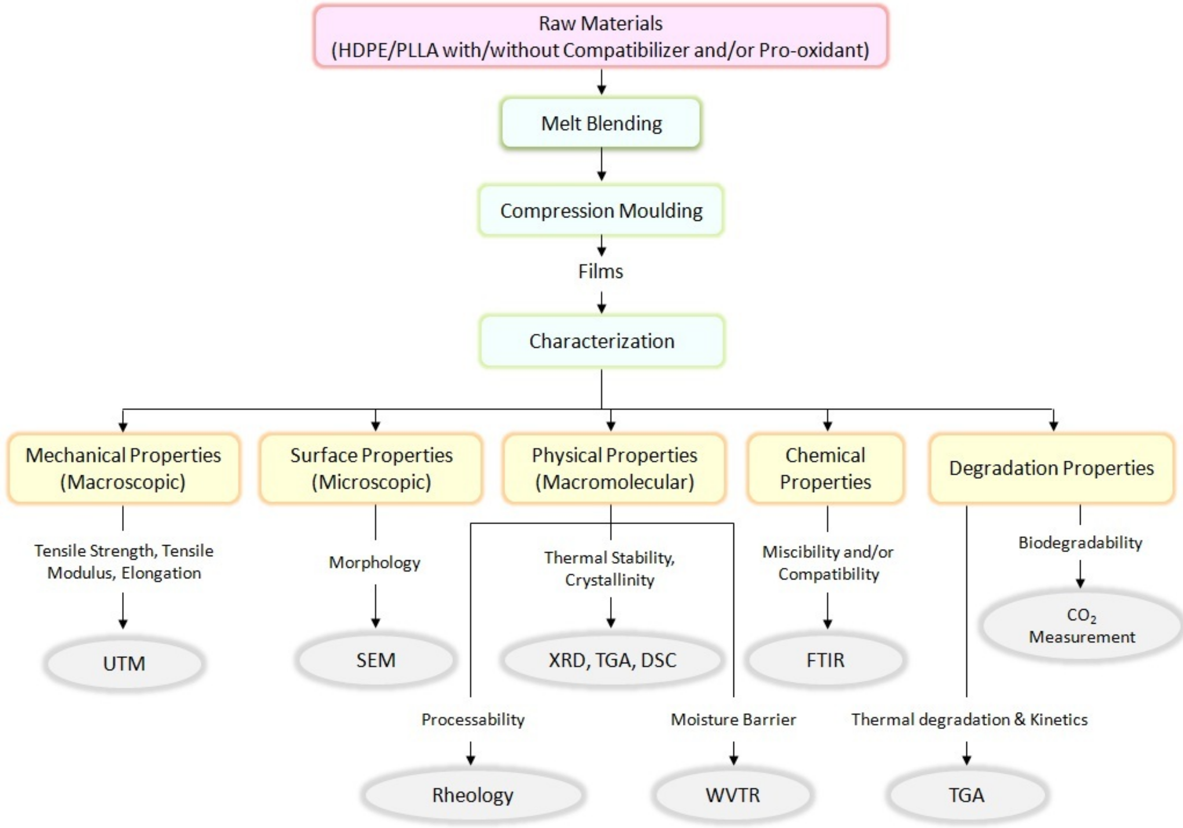


Figure 3.1. Summary of the methodology applied for the research work

3.2. Materials

HDPE of film grade having trade name F5400 was supplied in pellet form by Haldia Petrochemicals Limited, India. It was having the density of 0.954 g/mL and melting temperature (T_m) of 131 °C. PLA pellets with trade name L9000 was kindly supplied by Biomer Forst-Kasten-Str Kailling, Germany, with 2% (w/w) D-isomer content, and having weight average molecular weight $\left(\overline{M}_w\right)$ of 200 and number average molecular weight $\left(\overline{M}_n\right)$ of 101. This grade of Biomer PLA is semi-crystalline polymer with relatively slow nucleation and crystallization rates. As a result, the extruded products from this grade such as film or sheet are completely amorphous after normal quenching operations. The compatibilizer maleic anhydride grafted high density polyethylene, MA-*g*-HDPE (trade name Fusabond® E100) was kindly supplied by DuPont, India. It was having the density of 0.95 g/mL and melting temperature (T_m) of 134 °C. Cobalt(II) stearate (CoSt) in pellet form was purchased from Alfa Aesar, Johnson Matthey Chemicals India Private Limited. It was having the molecular weight of 625.89, density 1.71 g/mL, and cobalt content of 9-10% (w/w).

For biodegradability testing, the mature compost (digested municipal solid waste) was obtained from a compost plant at Okhla, New Delhi (Delhi Jal Board, India). It was screened through a 10 mm mesh sieve to separate outsized inert substances (stones, glass pieces, metallic parts, etc.). Moisture content of the compost was determined by drying it in a vacuum oven at 105 °C for 5-6 hours, and weighed before and after drying. The properties of this compost are given in Table 3.1.

Microcrystalline cellulose powder of thin-layer chromatography grade with a particle size of less than 20 μm was procured from Sigma-Aldrich, India.

Barium hydroxide octahydrate, $Ba(OH)_2.8H_2O$, having molecular weight of 315.46 and hydrochloric acid (HCl), having 35% concentration, were purchased from Hi-Media Laboratories Pvt. Ltd., India.

Table 3.1. Properties of matured compost

Property	**Value**
Moisture content (%)	60-65
Total dry solids (%)	65
Volatile matter (%)	20
pH of wet compost	7.3
Total organic carbon (dry weight basis, %)	34
Total Kjeldahl nitrogen (dry weight basis, %)	2.2
C/N ratio	15.45

3.3. Methods

3.3.1. Mechanical testing

The mechanical tests – tensile strength (at yield), tensile modulus, and percent elongation (at break) were performed at room temperature on a Zwick-Roell Universal Testing Machine – Model Z010, Zwick-Roell, Germany (shown in Figure 3.2), according to the procedure of ASTM D 882 using rectangular shaped specimens. The grip to grip separation of the samples having 25.4 mm gauge length was 100 mm at the start position. A crosshead speed of 50 mm/min was maintained. At least 3 specimens of each blend were tested and the average values were taken for analysis.

Figure 3.2. Zwick Roell universal testing machine used for performing mechanical testing of the samples

3.3.2. Fourier transform infrared (FTIR) spectroscopy

In order to identify the formation of new functional groups or disappearance of existing functional groups in the prepared blends and to determine the miscibility of the blends, FTIR spectroscopic studies by attenuated total reflectance (ATR) were carried out on the film samples using a FTIR spectrophotometer (model BX-II, PerkinElmer, Shelton, USA) with a zinc selenide crystal. A total of 16 scans per sample were taken, with a resolution of 4 cm^{-1} and the obtained spectrum was analyzed with the spectrum software (LX100627-I, PerkinElmer).

3.3.3. Wide-angle X-ray diffraction (WAXD)

In order to understand the chemical composition and crystallographic structure of a material, Wide angle X-ray diffraction (WAXD) is a versatile and non-destructive technique. The WAXD patterns were recorded at room temperature using a Philips Xpert diffractometer (Almelo, Netherlands) with monochromatic CuK$_\alpha$ radiation (λ = 1.5418 Å) operating at 40 kV and 20 mA. Monochromatic X-rays were applied to identify the interplanar spacing in any unknown substance. During the test, the scanning speed was kept at 5° per min and the diffraction angle (2θ) was 0°-60°.

3.3.4. Differential scanning calorimetry (DSC)

The melting and crystallization behaviour of HDPE/PLA blends was evaluated by differential scanning calorimetry performed with DSC 200F3 Maia apparatus (Netzsch, Germany) under nitrogen atmosphere. For repeated heating–cooling cyclic measurements, samples of 5-10 mg were taken and heated from -50 °C to 200 °C at 30 °C/min and kept at 200 °C for 1 min to erase thermal history. Cooling was then performed at 10 °C/min from 200 to -50 °C followed by a second heating from -50 °C to 200 °C at the same rate. The transition temperatures and peak areas of the samples were determined by using the data obtained by the software and the standard graphical analysis tools. The degree of crystallinity (χ_c) was calculated according to equation 3.1 as follows:

$$\chi_c = (\Delta H_f^{cal} / \Delta H_f^{std}) \times 100 \qquad (3.1)$$

where ΔH_f^{cal} is the calculated heat of fusion and ΔH_f^{std} is standard heat of fusion for 100% crystalline HDPE (287 J/g) [148] or PLA (93 J/g) [149].

3.3.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA), which is used to measure the change in weight during heating and thus analyzing thermal stability, was performed on a TGA Q-500 (TA Instruments Inc., USA). The experiments were conducted under flowing atmosphere of nitrogen at a purge rate of 50 mL/min. The weight of each sample was between 5-10 mg, and was heated from room temperature to 600 °C maintaining a programmed heating rate of 20 °C/min. Onset degradation temperature at 5% weight loss (T_{onset}), and maximum degradation temperature at 95% weight loss (T_{max}) were recorded during the TGA courses.

3.3.6. Scanning electron microscopy (SEM)

The scanning electron microscope JSM5800 (JEOL, Japan) operating at a 20 kV accelerating voltage, was used to observe blend morphology. The surfaces taken from cryofractured samples were examined. In order to prepare cryofractured samples, the films were plunged in liquid N_2 into a stable, insulated vessel while holding with tweezers. The films were removed after the bubbling stopped and then broken into two pieces. The samples were then coated with 50 μm thin layer of gold using a sputtering coater before putting them into the microscope. Finally, the SEM micrographs of the cryofractured surfaces were analyzed to characterize the microstructures of the samples.

3.3.7. Rheological properties

Shear rheology of the blends and neat polymers was studied using a dynamic oscillatory rheometer Anton-Paar MCR 302 (Anton-Paar GmbH, Austria). The parallel plate diameter was 25 mm, and the distance between the plates was 1 mm. The samples were placed between the parallel plates and heated up to 190 °C under nitrogen blanket. The shear strain was varied from 0.01% to 100%. Frequency sweep was conducted between 0.1 to 628 rad/s with 20 data points per decade to measure storage modulus (G'), loss modulus (G") and viscosity.

3.3.8. Water vapour transmission rate (WVTR)

Water vapour permeability was measured using a MOCON Permatran-W®3/33 (Modern Control, Inc., Minneapolis, MN, USA) apparatus as per ASTM F1249. Prior to testing, the specimens were conditioned for at least 48 hours at 50% RH and 23 °C. The calibration was performed using Mylar LB92 supplied by MOCON, which has a WVTR of 12.5 g/m^2 per d at 25 °C and 100% RH. Samples, with a test area of 50 cm^2, were masked using aluminium foil fixed by an adhesive backing. The nitrogen flow rate during the test was set to 100 mL/min. Measurements were carried out at 25 °C under 90% RH and finished after values of WVTR reached a steady state, usually after 6–8 h.

3.3.9. Biodegradability test

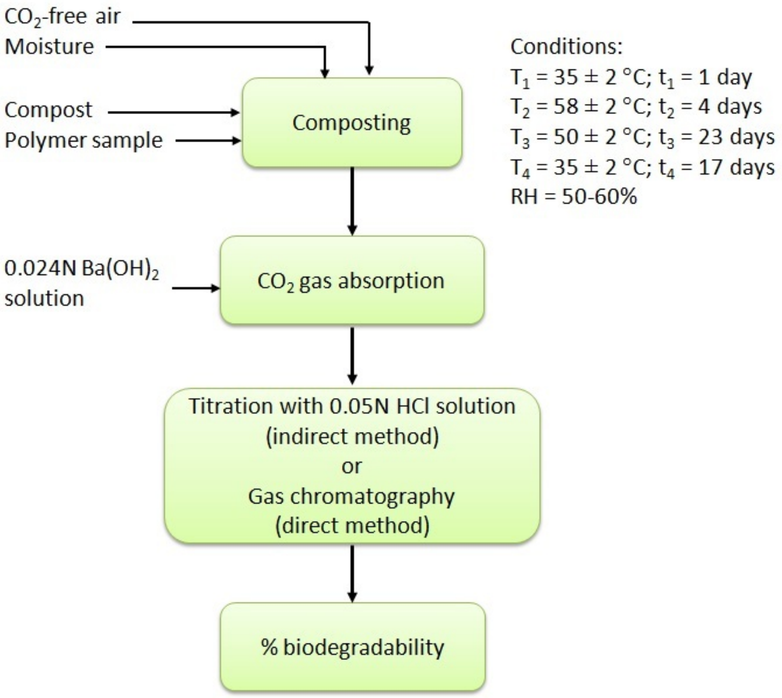
Biodegradation of the film samples was studied under composting condition according to ASTM D5338 [58] standard guidelines in an indigenously designed and developed apparatus. The film samples were cut into 2 x 2 cm size and were concealed inside composting vessels containing 300 g of compost.

3.4. Biodegradability testing apparatus

The designing of biodegradability testing apparatus was the most challenging as well as interesting task and breakthrough of this research work.

3.4.1. Concept

A biodegradability testing apparatus is a gadget used for measuring CO_2 evolution by respiration activity of living microorganisms while utilizing carbon as their energy source. As per the guidelines of ASTM D5338, the apparatus should consist of following components: (a) supply arrangement of CO_2-free air (also known as zero-air); (b) Composting chamber with temperature control mechanism inside which composting vessels may be placed; and (c) CO_2 absorbing vessels to quantify the amount of CO_2 release. The composting vessel, in which the polymer sample will be exposed to composting conditions, should be air-tight. The temperature controlling mechanism should be such that the temperature profile, as mentioned in the protocol, could be maintained throughout the testing period. The process which should be followed for measuring biodegradability, as per ASTM D5338 standard, is shown in Figure 3.3.



T = temperature, t = time, RH = relative humidity

Figure 3.3. Methodology of measuring percent biodegradability as per ASTM D5338

3.4.2. Transformation of concept in realistic apparatus

Considering the theoretical steps mentioned in the standard, the apparatus was assembled with the following components:

(a) Supply arrangement of CO_2-free air

(b) Composting vessels (or bioreactors)

(c) Composting chamber with temperature control mechanism containing composting vessels.

(d) CO_2 absorbing vessels to quantify the amount of CO_2 release.

The different parts of the apparatus were considered separately and the accuracy, compactness, reliability, and of course, the economy etc. were the main factors which were taken care of while designing.

The apparatus consisted of 12 composting vessels placed in 3 level partitions (4 vessels on each stage) of the temperature controlled chamber. On each stage, the first vessel was taken as blank (containing compost only); the second one was taken as positive control (containing microcrystalline cellulose); third as the negative control (containing pure HDPE); and the last one was taken as the test (containing the test sample). The CO_2 gas evolved from each bioreactor was absorbed in three vessels (in series) containing barium hydroxide solution. The flow diagram for the process followed for evaluation of biodegradability of polymer samples is shown in Figure 3.4.

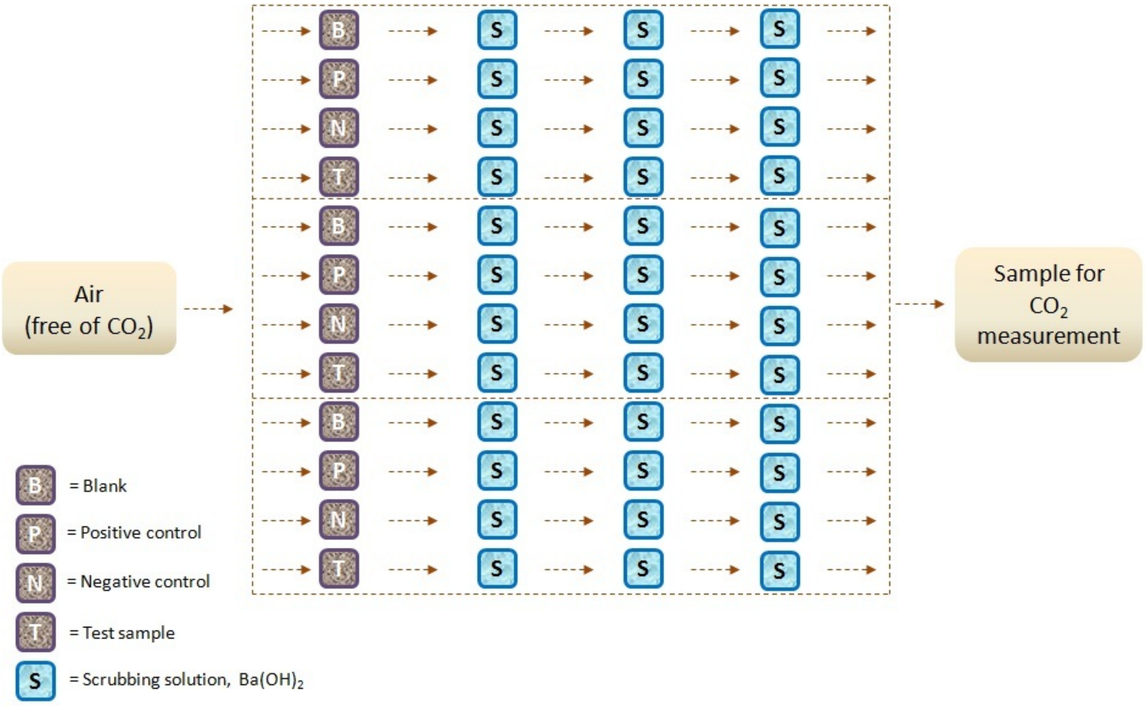


Figure 3.4. Flow diagram for evaluation of biodegradability of polymer samples [58]

3.4.3. Supply arrangement of CO_2-free and flow measuring mechanism

The supply of CO_2-free air from a cylinder was connected to a common inlet point of rotameters from where it was distributed to the respective composting vessels. The rotameters were designed to have flow-rate capacity from 0 to 100 mL/min. The connecting pipes were silicon tubes having 6 mm inner diameter (ID) and 8 mm outer diameter (OD).

3.4.4. Composting vessels

The glass vessels of 1 L total volume were used as composting vessels. These vessels have an opening arrangement at the top and fitted with an air-tight mechanism in-between the main body (lower part) the upper part to prevent any leakage of air and/or CO_2. An inlet port for the incoming air (CO_2-free) was provided near the bottom where it was filled with an appropriate quantity of water so that the air may acquire the required humidity before entering the compost zone. The inlet was designed to have openings at equal intervals for uniform distribution of air. A stainless steel screen was placed on the support made near the inlet port of the composting vessel to prevent dropping of the compost particles. The outlet (for CO_2 gas) was provided at the top of the upper part, which was connected to the respective CO_2 absorbing flasks through the silicon tubes. All the 12 composting vessels were placed in a temperature controlled chamber.

3.4.5. CO_2 gas absorbing vessels

The CO_2 gas absorbing vessels were conical in shape of 500 mL volume. The CO_2 evolved from each composting vessel was absorbed in $Ba(OH)_2$ solution contained in the conical vessels (three in series). The inlet pipe to the gas absorbing vessel was deep enough so as to absorb the gas in the solution, and the outlet was short so that only the gas from the headspace of the vessel carried forward to the next vessel.

Chapter 4 – Preparation and Optimization of HDPE/PLA Blends

4.1. Introduction

In this chapter, the techniques adopted for preparation of blends (and films from the blends) and the basis of optimization of HDPE/PLA ratio is described in detail. Here, the "optimization" signifies the finest combination of mechanical properties and biodegradable PLA content, keeping in view the standards required for flexible packaging applications. Further, the appropriate quantity of compatibilizer MA-*g*-HDPE, suitable to be blended along with HDPE and PLA was found. Finally, effect of adding pro-oxidant, cobalt stearate (CoSt) on the mechanical properties of the blends is described.

4.2. Preparation of HDPE/PLA blends

Blends of HDPE/PLA were prepared by melt compounding technique and then, films from these blends were produced by compression moulding method. The detailed procedures followed for these two methods are explained in the following sections.

4.2.1. Melt blending

The equipment used for preparing HDPE/PLA blends was HAAKE PolyLab OS measuring mixer and extruder system; RD 7 version coupled with Rheomix 600 mixer (Thermo Scientific, USA). The materials were previously dried with de-moisturized air at 60 °C for 4 hours. The ingredients were weighed at a prescribed ratio and manually mixed before being loaded into the mixer for melt blending. The melt mixing was performed at 190°C with 50 rpm rotor speed for 4 min. The blended polymer material in semi-solid state was then passed through a two roll mill (Schwabentan, Berlin, Germany) with a nip gap of 2 mm. The melt mixing equipment and the two roll mill are shown in Figures 4.1 and 4.2 respectively.

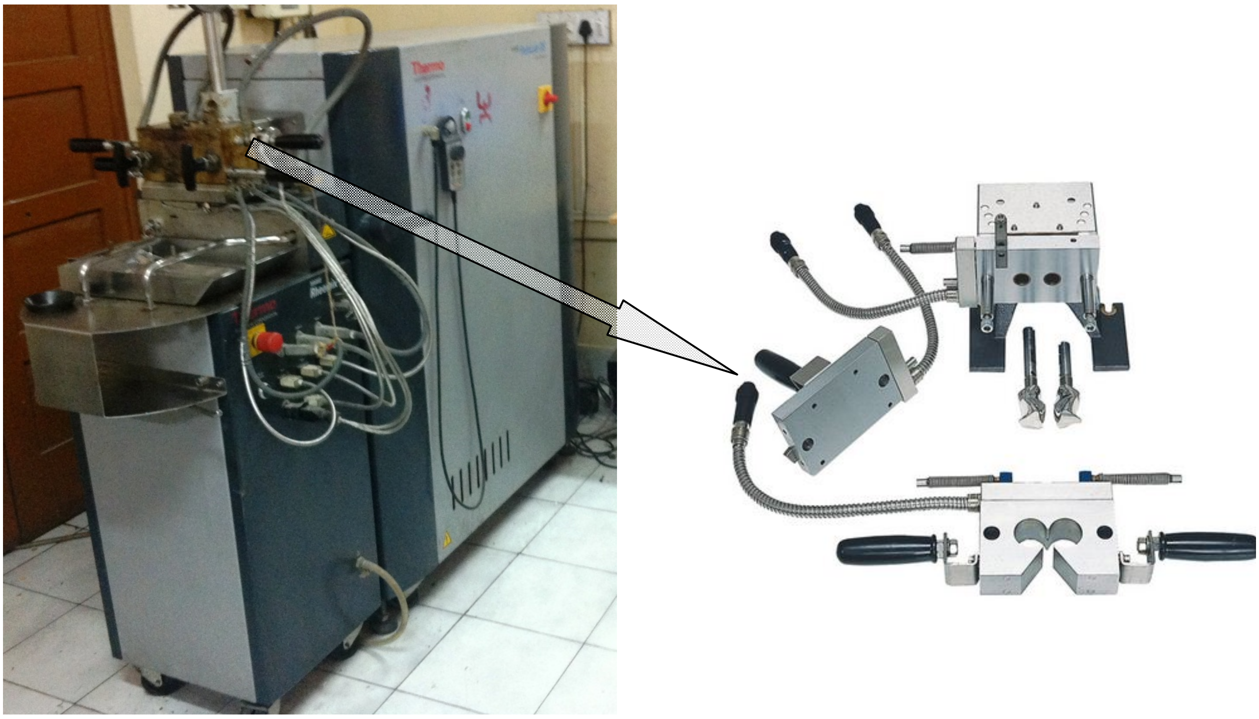


Figure 4.1. HAAKE PolyLab apparatus used for performing melt mixing

Figure 4.2. Two-roll mill used for preparing blends

4.2.2. Compression moulding

The blends were then molded into films at 190°C and 5 MPa in a compression moulding press (George E. Moore Press, UK) for 2 min to obtain 40-50 µm thick films. Teflon sheets were kept in between the mold plates to prevent the molten material sticking to it. Film samples were then quenched through the platens at the same pressure to maintain the dimensional stability of the films. The compression moulding machine used for preparing the films is shown in Figure 4.3.

The thickness of the prepared films was measured using a dial thickness gauge 7301, Mitutoyo, Japan at an accuracy of ±5 µm.

Figure 4.3. Compression moulding machine (hot press) used for preparing film samples

Initially, the ratio of HDPE/PLA was varied as 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, and 70/30 (Table 4.1).

Table 4.1. Formulations of HDPE/PLA blends without MA-*g*-HDPE and CoSt

Sr. No.	Sample Name	Composition	
		HDPE (wt%)	PLA (wt%)
1.	HD_{100}	100	0
2.	HD_{95}	95	5
3.	HD_{90}	90	10
4.	HD_{85}	85	15
5.	HD_{80}	80	20
6.	HD_{75}	75	25
7.	HD_{70}	70	30

4.3. Optimization of HDPE/PLA ratio based on mechanical properties

Mechanical properties of polymers are considered as most important of all the physical and chemical properties for most applications. For polymer blends, there are three structure components: dispersed phase, continuous phase, and interface. Good bonding between blend components, usually achieved by introducing compatibilizer, assures that the applied force is transmitted into the dispersed inclusions. Here, the mechanical properties viz. tensile strength, tensile modulus, and percent elongation of the prepared HDPE/PLA blends were estimated in order to find out the best possible combination of these properties and the PLA content.

4.3.1. Optimization of HDPE/PLA ratio without any additive (compatibilizer)

Firstly, the objective was to identify the blend which has the best combination of mechanical properties and the expensive PLA content, therefore, the mechanical testing (tensile strength at yield, tensile modulus and the breaking elongation) of HDPE/PLA blends (without compatibilizer) was performed and the results are summarized in Table 4.2.

Table 4.2. Mechanical properties of HDPE/PLA blends without compatibilizer

Sr. No.	Sample Name	Film Thickness (µm)	Mechanical Properties		
			Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation (%)
1.	HD_{100}	44±3	33.51 ± 1.72	1474 ± 29	481 ± 24.05
2.	HD_{95}	42±2	31.04 ± 1.28	1280 ± 25	445 ± 22.25
3.	HD_{90}	43±2	30.61 ± 1.56	1265 ± 24	313 ± 19.65
4.	HD_{85}	40±1	28.43 ± 1.14	1210 ± 25	254 ± 16.70
5.	HD_{80}	41±2	25.27 ± 1.03	1181 ± 23	256 ± 17.80
6.	HD_{75}	42±3	19.32 ± 1.17	986 ± 14	177 ± 11.85
7.	HD_{70}	46±3	15.15 ± 1.39	712 ± 19	92 ± 9.60

The tensile properties of the blended film samples showed a decreasing trend with increasing PLA content. It was observed that the decrease in the tensile properties was comparatively smaller up to 20% PLA addition in the HDPE matrix. It may be endorsed to the interfacial adhesion and chain entanglement PLA with HDPE during melt blending and curing of the specimen. However, with further increasing the amount of PLA, this brittle polymer turned out to be more prevailing resulting in drastically declining of these properties. Figure 4.4

shows the changes in tensile strength at break and tensile modulus by varying PLA composition in HDPE and Figure 4.5 represents the changes in elongation at break with the corresponding variation in PLA content in the blend.

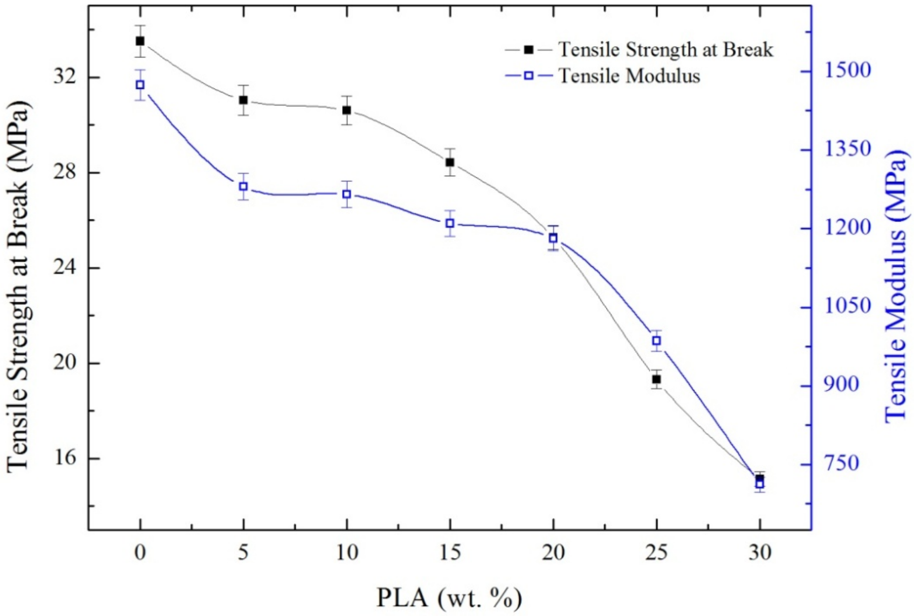
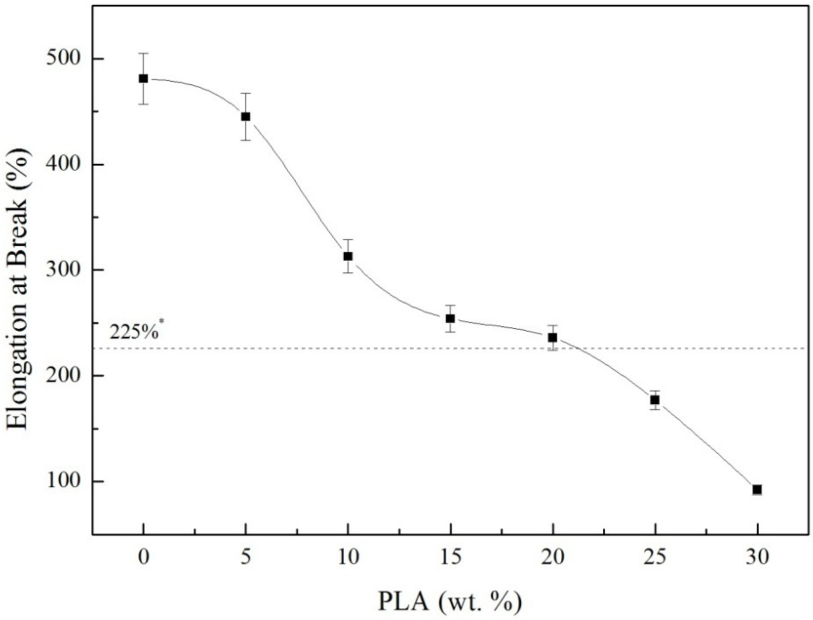


Figure 4.4. Tensile strength and tensile modulus of HDPE/PLA blends with increasing proportion of PLA



**lower limit for flexible packaging applications*

Figure 4.5. Percent elongation (at break) of HDPE/PLA blend with varying amounts of PLA

A sharp decrease in percent elongation was noted with increasing amount of PLA addition, but for HD_{80} blend, it was 245% which is well above the minimum requisite value prescribed for flexible packaging applications. Hence, in view of better retention of mechanical properties, we selected HD_{80} blend for further study. Consequently, the compatibilized blends of 80/20 (HDPE/PLA), using the compatibilizer MA-*g*-HDPE in varied amounts ranging from 2-8 phr, were prepared and films from those blends were obtained following the same methodology as mentioned in section 4.2. The compatibilized blends' formulations and their names are shown in Table 4.3.

Table 4.3. Formulations of HDPE/PLA blends with MA-*g*-HDPE

Sr. No.	Sample Name	Composition		
		HDPE (wt%)	PLA (wt%)	MA-*g*-HDPE (phr)
1.	$HD_{80}MA_2$	80	20	2
2.	$HD_{80}MA_4$	80	20	4
3.	$HD_{80}MA_6$	80	20	6
4.	$HD_{80}MA_8$	80	20	8

4.3.2. Optimization of compatibilizer quantity

The objective of compatibilization was to improve the interfacial adhesion between the two polymer phases and thus finding the blend with optimized mechanical properties. All the results of mechanical properties of the compatibilized blends are summarized in Table 4.4. It was observed that the tensile strength and modulus increased with increase in compatibilizer up to 6 phr. The tensile strength of $HD_{80}MA_4$ increased from 20.27 MPa to 22.64 MPa as compared to HD_{80}. This may be attributed to the better interfacial interaction and improved plasticity of the blend by assimilation of the compatibilizer. Additionally, the compatibilizer interacted with the polymer chains distributing itself uniformly within the polymer, hence creating additional free volume.

Table 4.4. Mechanical properties of HDPE/PLA blends with compatibilizer

Sr. No.	Sample Name	Film Thickness (μm)	Mechanical Properties		
			Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation (%)
1.	$HD_{80}MA_2$	41±1	18.76	1225 ± 15	217 ± 12.34
2.	$HD_{80}MA_4$	42±1	20.33	1240 ± 12	232 ± 10.64
3.	$HD_{80}MA_6$	40±3	20.42	1253 ± 18	195 ± 11.90
4.	$HD_{80}MA_8$	43±2	20.64	1072 ± 15	179 ± 8.58

However, on further increasing the quantity of MA-*g*-HDPE, the value of these two properties decreased which may be due to increased heterogeneity of the blend resulting in phase separation. The elongation at break of HD_{80} increased a little up to 4 phr of the compatibilizer, but decreased with its further addition. Figure 4.6 shows the changes in tensile strength and tensile modulus of HD_{80} blend with increasing proportion of compatibilizer and Figure 4.7 shows the variation in percent elongation of that by varying MA-*g*-HDPE composition. As can be seen from Figure 4.7, percent elongation of $HD_{80}MA_4$ is 242% and that of $HD_{80}MA_8$ is 189% only. Brittle nature of PLA and incapability to impart plasticity by MA-*g*-HDPE might be the reasons behind this phenomenon. However, 6 and 8 phr addition of the compatibilizer increased the tensile strength and modulus values, but 4 phr compatibilizer was taken as optimum because of meeting the criteria of minimum required value of elongation at break, i.e. 225% for flexible packaging plastic materials. Hence, the blends HD_{80} (without compatibilizer) and $HD_{80}MA_4$ (with compatibilizer) showed acceptable mechanical properties for packaging applications.

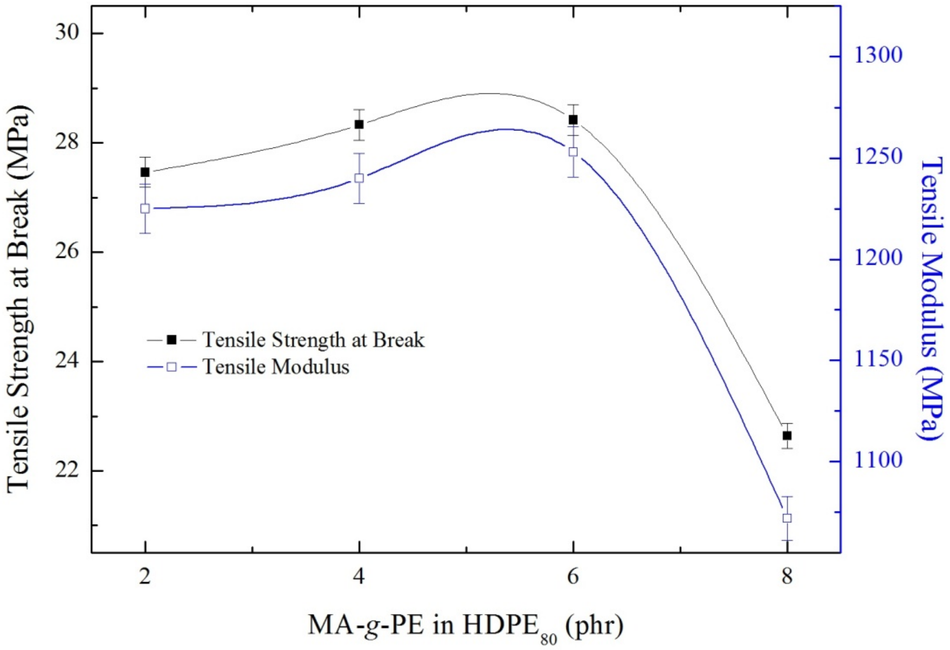


Figure 4.6. Tensile strength and tensile modulus of HD_{80} with varying amounts of MA-*g*-HDPE

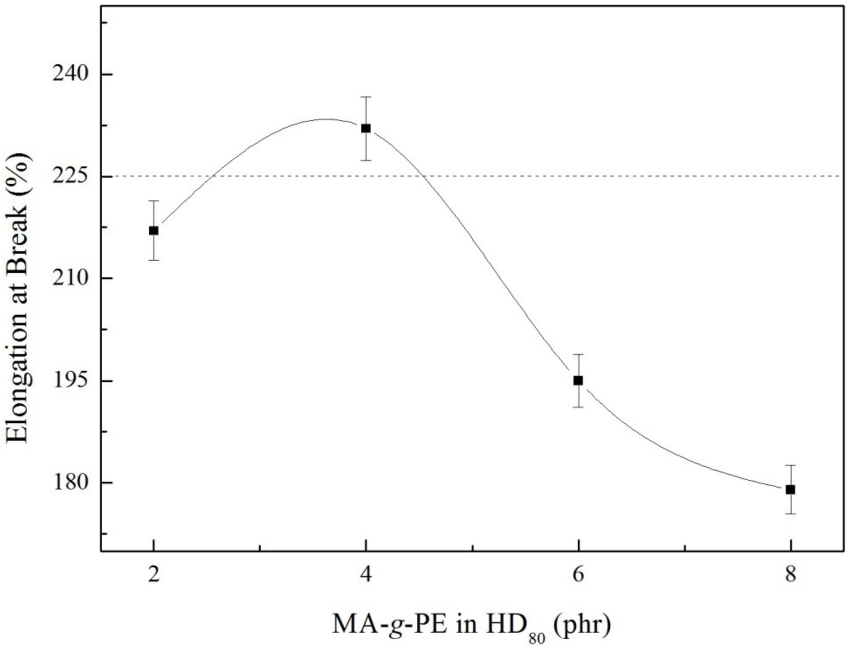


Figure 4.7. Percent elongation (at break) of HD_{80} with varying amounts of MA-*g*-HDPE

4.3.3. Addition of pro-oxidant in optimized blends

To impart oxo-biodegradability in 80/20 (HDPE/PLA) blends, trace amounts of CoSt was blended with/without compatibilizer. The pro-oxidant was blended in neat HDPE also to compare the results with the former blends. The blend formulations with pro-oxidant are shown in Table 4.5.

Table 4.5. Compositions of HDPE and HDPE/PLA blends with CoSt

Sr. No.	Sample Name	Composition			
		HDPE (wt%)	PLA (wt%)	MA-*g*-HDPE (phr)	CoSt (phr)
1.	$HD_{80}CoSt_{0.1}$	80	20	0	0.1
2.	$HD_{80}CoSt_{0.2}$	80	20	0	0.2
3.	$HD_{80}MA_4CoSt_{0.1}$	80	20	4	0.1
4.	$HD_{80}MA_4CoSt_{0.2}$	80	20	4	0.2
5.	$HD_{100}CoSt_{0.1}$	100	0	0	0.1
6.	$HD_{100}CoSt_{0.2}$	100	0	0	0.2

The mechanical properties of the above mentioned blended film samples were analyzed, which are given in Table 4.6 and graphically shown in Figures 4.8 and 4.9. As expected, the outcomes revealed that both the tensile strength and modulus of the blend decreased by the addition of pro-oxidant (Figure 4.5). However, the reduction in these properties with 0.1 phr pro-oxidant is lesser as compared to 0.2% addition. Interestingly, the blends which contained compatibilizer showed better tensile properties than the uncompatibilized ones. As shown in Figure 4.9, a major decline in percent elongation of $HDPE_{80}$ is noticed when pro-oxidant was added. The elongation of $HD_{80}CoSt_{0.1}$ was 148% and that of $HD_{80}CoSt_{0.2}$ was 110% only as compared to 256% of HD_{80}. There values, however, recovered by the addition of 4 phr MA-*g*-HDPE to a considerable extent.

Table 4.6. Mechanical properties of HDPE/PLA blends with/without compatibilizer and pro-oxidant (cobalt stearate)

Sr. No.	Sample Name	Film Thickness (µm)	Mechanical Properties		
			Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)
1.	$HD_{80}CoSt_{0.1}$	45±4	19.53 ± 1.16	736 ± 11	148 ± 7.48
2.	$HD_{80}MA_4CoSt_{0.1}$	41±2	20.68 ± 0.93	781 ± 17	180 ± 9.13
3.	$HD_{80}CoSt_{0.2}$	44±2	12.95 ± 0.87	710 ± 10	110 ± 5.50
4.	$HD_{80}MA_4CoSt_{0.2}$	42±1	16.14 ± 1.29	729 ± 14	125 ± 6.25

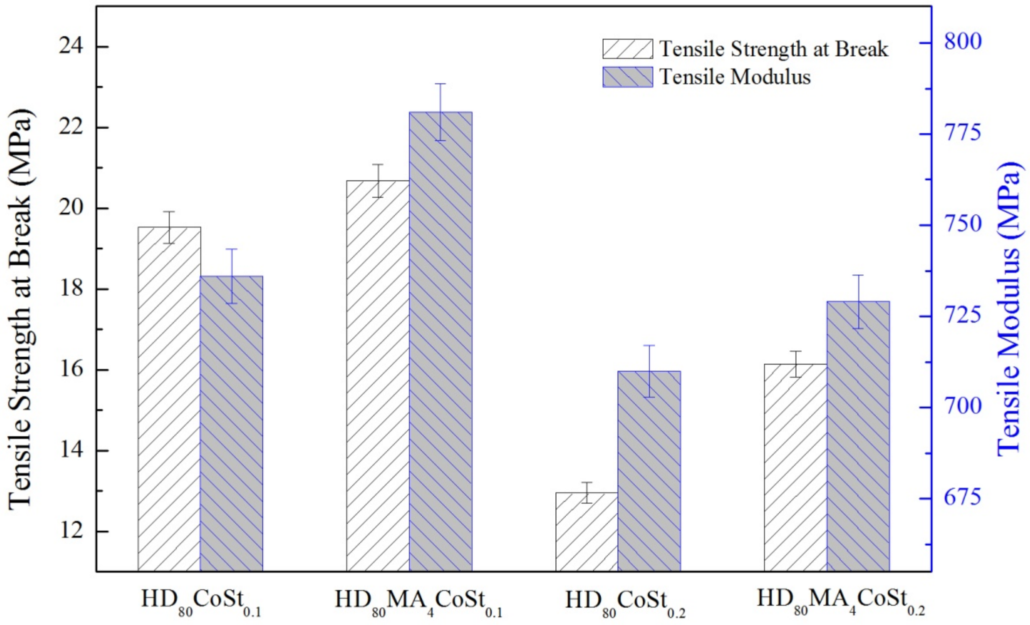


Figure 4.8. Tensile strength and tensile modulus of HD_{80} containing pro-oxidant (cobalt stearate) with and without MA-*g*-HDPE

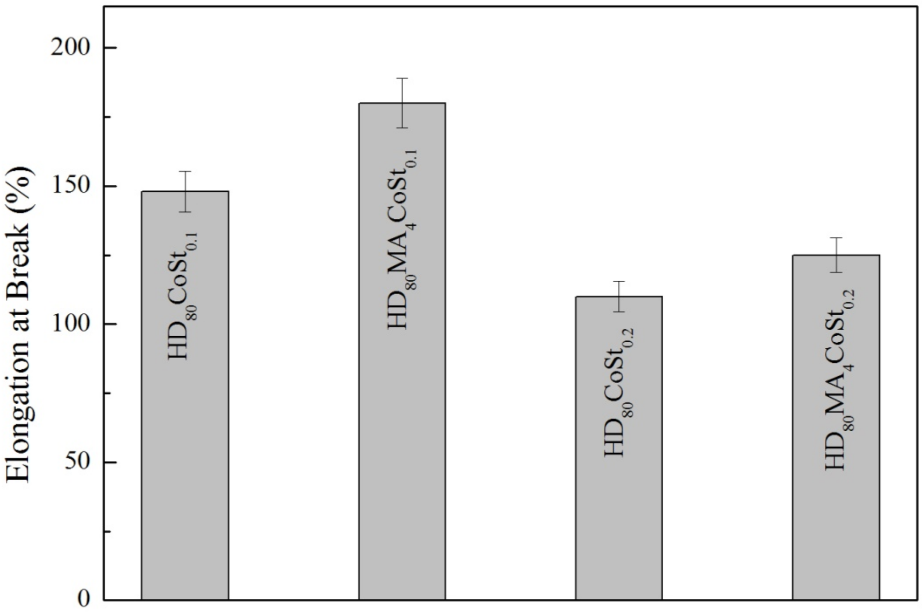


Figure 4.9. Percent elongation (at break) of HD_{80} containing pro-oxidant (cobalt stearate) with and without MA-*g*-HDPE

After examining the mechanical properties of all the prepared blends, we preferred to investigate the other relevant properties of the following blends with reference to the neat polymers:

i. HD_{80} (80/20 HDPE/PLA blend)
ii. $HD_{80}MA_4$ (80/20 HDPE/PLA blend with 4 phr compatibilizer)
iii. $HD_{80}CoSt_{0.1}$ (80/20 HDPE/PLA blend with 0.1 phr pro-oxidant)
iv. $HD_{80}MA_4CoSt_{0.1}$ (80/20 HDPE/PLA blend with 0.1 phr pro-oxidant and 4 phr compatibilizer)

Chapter 5 – Characterization of HDPE/PLA Blends

5.1. Introduction

Since degradability of polymer blends is affected by the components miscibility and crystallinity, their molecular structure, hydrophobic-hydrophilic balance, melting temperature, composition ratio etc. [45, 106, 150, 151], therefore, it is necessary to be familiar with the various relevant physicochemical characteristics of the polymer blends in order to better understand the mechanism of their degradation. Therefore, in this chapter, these parameters have been evaluated through various characterization techniques viz. FTIR, WAXD, DSC, TGA, SEM, rheology and WVTR measuring apparatus. The results are presented and discussed here.

5.2. FTIR analysis

FTIR spectroscopy was used to determine the interactions between HDPE, PLA and other ingredients. The FTIR spectra of the selected samples including that of neat polymers are depicted in Figure 5.1. The typical spectra in the 600–3600 cm^{-1} range are illustrated in which the bands located in the range 2882–2926 cm^{-1} can be assigned to $–CH_3$ and $–CH_2$ stretching vibrations groups of HDPE [152]. For neat PLA sample, a strong absorption band centered at 1747.9 cm^{-1} is also observed due to carbonyl vibration [153]. The absorption peak due to crystalline carbonyl vibration of PLA, expected at 1755 cm^{-1} [154, 155] could not be identified since the polymer was amorphous. In PLA spectrum, a wide halo commencing peak centered at 1086 cm^{-1} was also detected which is due to C–O–C stretching. The ratios of peak intensities of HDPE and PLA bands are dependent on measurement points in both blends. In the 80/20 HDPE/PLA blends, the spectra of many spots are similar to the semi-crystalline HDPE spectrum. The formation of a new C–O stretching frequency at 2361 cm^{-1}

assigned to stretching vibration of –OH are not seen in the neat HDPE, which indicates incorporation of oxygen in the polymer chain.

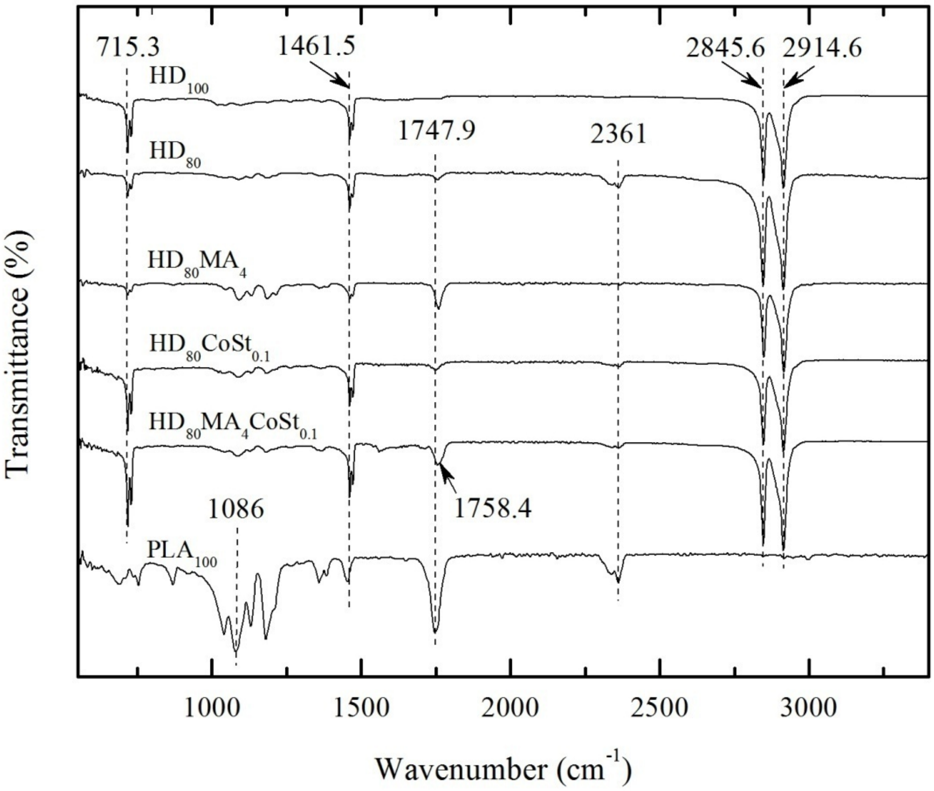


Figure 5.1. FTIR spectra of neat HDPE, neat PLA and HDPE/PLA blends

The spectra of the HD_{80} and $HD_{80}CoSt_{0.1}$ blends are very similar to that of neat HDPE, which indicates that HDPE and PLA are immiscible in these blends, and there are no strong molecular interactions between them. However, the blends in which compatibilizer was mixed, i.e., $HD_{80}MA_4$ and $HD_{80}MA_4CoSt_{0.1}$ the carbonyl stretching band at 1758.4 cm^{-1}, associated with the amorphous carbonyl stretching of PLA, has a different peak position compared with that of pure PLA at 1747.9 cm^{-1}. These results indicate that, although HDPE and PLA are generally immiscible, there is an interaction between these two polymers in these blends due to the compatibilizing effect by the MA-*g*-HDPE. It was also noticed that the pro-oxidant content has very insignificant effect on the FTIR spectra of HDPE/PLA blends.

5.2. Wide angle XRD analysis

The wide angle X-ray diffraction scans of HDPE/PLA blends and the homopolymers as a function of Bragg angle (2θ) are displayed in Figure 5.2. Two visible crystal diffraction peaks were seen at around 2θ = 21.6° and 23.9° in neat HDPE, which correspond to the crystal plane 1 1 0 and 2 0 0 of PE. Neat PLA presented a smooth curve with a bump at 16.6° which corresponds to interplanar spacing of 5.9 Å. The diffraction peaks did not appear in the entire spectrum of PLA but only a broad band, which is an evidence of its amorphous characteristic. In 80/20 HDPE/PLA blends, two scattering peaks of low intensity appears at 2θ = 16.6° and 19°, which stand for the amorphous portion due to PLA addition.

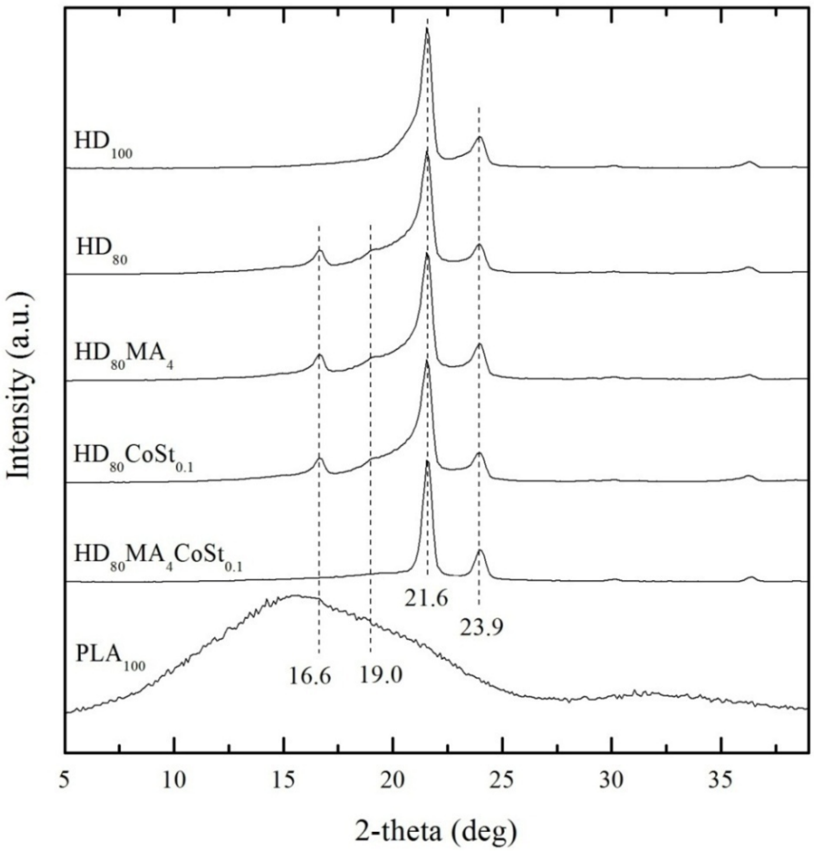


Figure 5.2. WAXD Spectra of neat HDPE, neat PLA, and HDPE/PLA blends

5.3. DSC analysis

With the help of DSC analysis, following parameters were determined from the melting endotherms and crystallization exotherms of the samples:

1. Crystalline melting point (T_m) corresponding to first and second heating, °C;
2. Onset temperature (T_{onset}) of melting and crystallization, °C;
3. Crystallization temperature (T_c) analogous to first and second cooling, °C;
4. Enthalpy of crystallization (ΔH_c), evaluated from the area under the exotherm, J/g;
5. Enthalpy of fusion (ΔH_f) measured from the area under the endotherm, J/g;

The typical DSC curves obtained by first and second heating cycles of the neat polymers and their blends are shown in Figure 5.3. Table 5.1 shows the melting temperature (T_m) and crystallinity values for HDPE, PLA, and their blends. The crystallization melting point (T_m) of neat HDPE and neat PLA was 134.9 and 171.7 °C respectively. The glass transition temperature (T_g) of PLA was visible in neat PLA sample only as the blends contained very small amount of it as compared to HDPE. The onset temperatures of melting and crystallisation (T_{onset}) of individual polymers were not much affected by blending, which shows that HDPE and PLA were immiscible. No crystallization temperature was noted for neat PLA which depict that the PLA was amorphous in nature. However, it was interesting to note that as compared to pure HDPE, the enthalpy of fusion (ΔH_f) for 80/20 blend was slightly higher, but when compatibilizer was added in the blend, it showed a fall in value of ΔH_f. Consequently, a higher degree of crystallinity was observed for HD_{80} and lower for $HD_{80}MA_4$ blend. Similar results were seen in case of enthalpy of crystallization (ΔH_c). The probable reason of this phenomenon was that HDPE and PLA were immiscible, but in presence of compatibilizer, a little degree of mixing and interaction between the polymer interfaces was attained.

Table 5.1. Melting and crystallization behaviour of HDPE/PLA blends

Blend	T_m of HDPE and PLA (°C)		T_g of HDPE and PLA (°C)		T_{onset} of HDPE and PLA (°C)		T_c of HDPE and PLA (°C)		$-\Delta H_c$ (J/g)	ΔH_f (J/g)		χ_c (%)	
	First heating	Second heating	First heating	Second heating	Melting	Crystallization	First cooling	Second cooling		HDPE	PLA	HDPE	PLA
HD_{100}	135.5	134.9	---	---	123.2	100.7	110.8	111.2	187.7	191.8	---	66.8	---
HD_{80}	136.1 175.3	135.4 170.2	--- 64.1	--- 61.6	123.2 164.6	100.1 ---	110.7 ---	110.8 ---	201.3 ---	207.5	12.7	72.3	13.7
$HD_{80}MA_4$	134.2 173.7	134.7 173.3	--- 63.5	--- 61.2	123.3 167.7	100.4 ---	110.9 ---	110.8 ---	184.5 ---	163.9	8.8	57.1	9.5
$HD_{80}CoSt_{0.1}$	135.3 170.1	133.7 167.8	--- 63.9	--- 61.2	121.5 159.4	100.0 ---	111.1 ---	111.0 ---	192.6 ---	203.9	10.2	69.2	10.3
$HD_{80}MA_4$ $CoSt_{0.1}$	134.0 169.9	134.2 170.5	--- 63.2	--- 61.4	122.1 163.4	101.2 ---	111.6 ---	111.3 ---	180.4 ---	160.5	7.1	57.8	9.0
PLA_{100}	170.9	171.7	61	65.9	163.6	---	---	---	---	---	47.27	---	---

T_m = *crystallization melting point*
T_g = *glass transition temperature*
T_{onset} = *onset temperature*
T_c = *crystallization temperature*
ΔH_c = *heat of crystallization*
ΔH_f = *heat of fusion*
χ_c = *crystallinity*

In general, a semi-crystalline polymer compromises or even loses its crystallinity after crosslinking and accordingly, the crystallization temperature decreases due to a reduction in chain mobility [156-158]. Amorphous PLA gained some crystallinity upon blending with HDPE, which was probably due to the stress-induced crystallization of PLA with HDPE during film formation by compression moulding. It was also noticed that the presence of pro-oxidant CoSt did not significantly altered the T_m of the blend samples. When cooled from the melt, the maximum crystallization temperature (T_c) for HDPE and HDPE/PLA blends was almost the same, i.e., ≈111 °C which is due to immiscibility of the two polymer phases. However, the enthalpy of crystallization increases for HD_{80} and $HD_{80}CoSt_{0.1}$ blends, which decreases to some extent and become closer to that of neat HDPE in the presence of MA-*g*-HDPE, showing some compatibilization effect. PLA sample showed no sharp crystallization peak which is due to its amorphous nature. Figure 5.4 shows DSC curves corresponding to the cooling scans of HDPE, PLA and their blends. It is noticed from the data shown in Table 5.1, that the percent crystallinity of neat HDPE was 66.8% and increased to 72.3% when 20 wt% PLA was blended in it. However, this value decreased to 57.1% in presence of 4 phr compatibilizer. Neat PLA, having no crystallinity so far, gained crystallinity upon blending with HDPE, which went upto 13.7% for HD_{80} blend, probably due to stress-induced crystallization of PLA with HDPE during melt blending and compression molding. Upon addition of cobalt stearate, a little change (increase) in crystallinity of HDPE and PLA was observed in absence of MA-*g*-HDPE. Hence, it was clear that reorganization of polymer chains occurred when PLA and/or cobalt stearate was added in the blends.

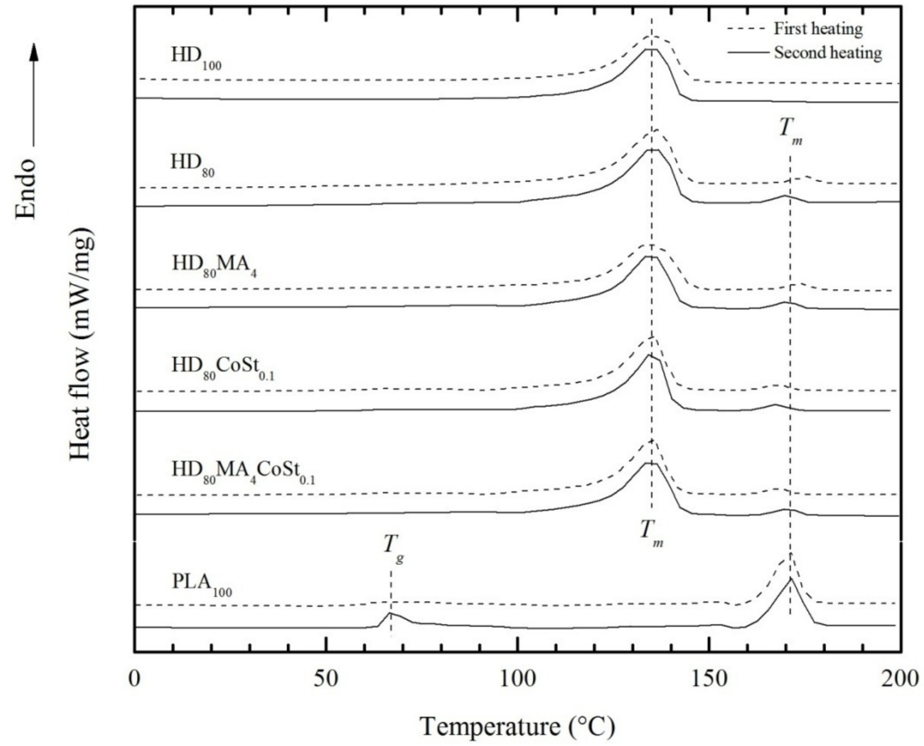


Figure 5.3. DSC heating curves of neat HDPE, neat PLA and HDPE/PLA blends

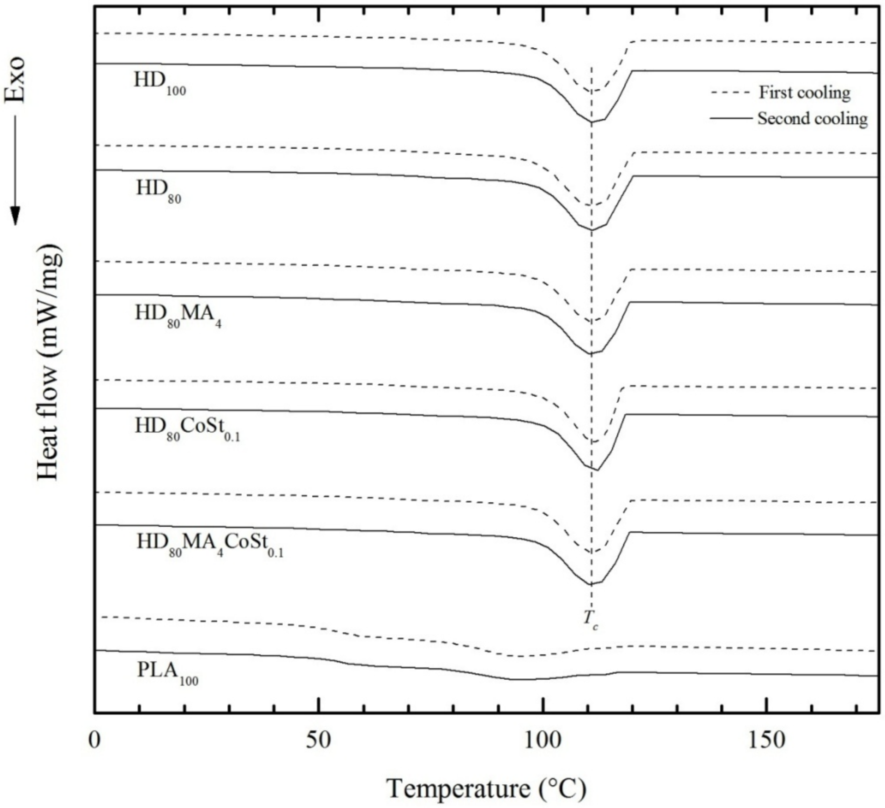


Figure 5.4. DSC cooling curves of neat HDPE, neat PLA and HDPE/PLA blends

5.4. TG analysis

Integral thermogravimetric traces can be difficult to show the differences between several materials at the same time when they decompose at close temperatures [159]. Therefore, in addition to the simple thermogravimetric (TG) curves of HDPE/PLA blends in nitrogen atmosphere (Figure 5.5), 1^{st} derivative thermogravimetric (DTG) curves are also presented in Figure 5.6 to compare their thermal behaviour. It is observed that HDPE is much stable than PLA, obviously due to higher molecular weight. Among HDPE/PLA blends, those which contain CoSt are comparatively less stable than those which do not contain the pro-oxidant. The maximum rate of decomposition (DTG peak) of PLA in the blends shifted to higher temperatures. On the other hand, the DTG peaks of HDPE in the blends remain almost similar. Decomposition of single components (neat polymers) occurred in a single degradation step, whereas the profile of binary and tertiary blends showed two-stage degradation process. In the temperature range 250–420 °C, there is a decrease in the weight of the HDPE/PLA blends which is not noticed in the case of neat HDPE. This first degradation stage of the blends is due to water evaporation from the decomposition of hydroxyl groups. In the blends containing pro-oxidant, this degradation may also be caused by oxidative stress generation function of the same. The second degradation stage between 420 and 525 °C is due to chain scission of the carbon–carbon bonds in the main chain. Neat polymers show only one DTG maxima; HDPE at around 495 °C and PLA at around 395 °C. The two separated DTG maxima in the blends indicate that a separation phase has occurred between the HDPE and PLA components. The onset degradation temperature (T_{onset}) of 5% weight loss, maximum degradation temperature (T_{max}) of 95% weight loss deviation from the base line and the percentage residual weight were used as the indicator of the samples' thermal stability, which are depicted in Table 5.2.

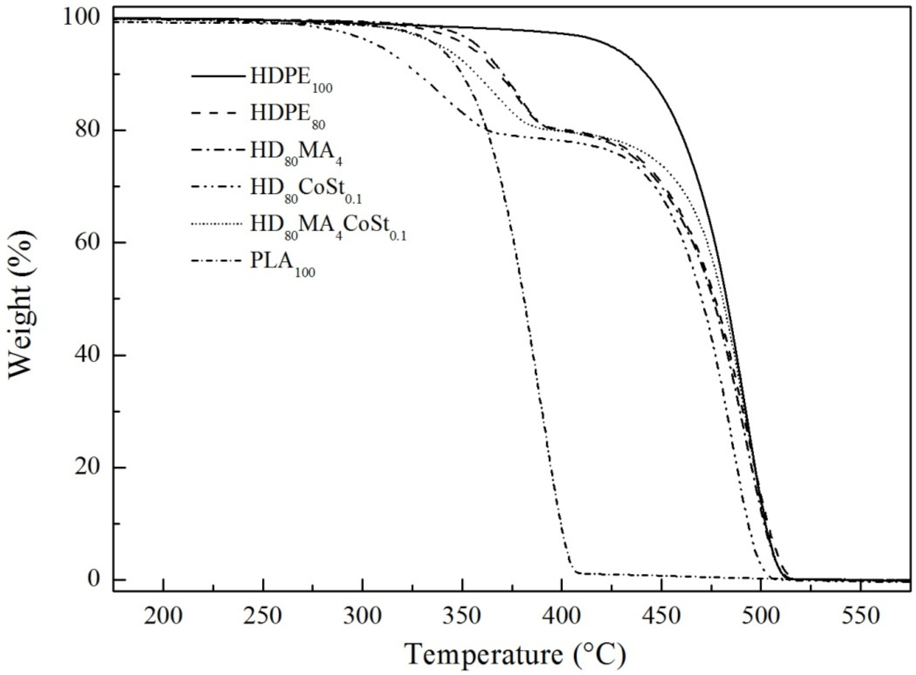


Figure 5.5. TG curves of HDPE/PLA blends

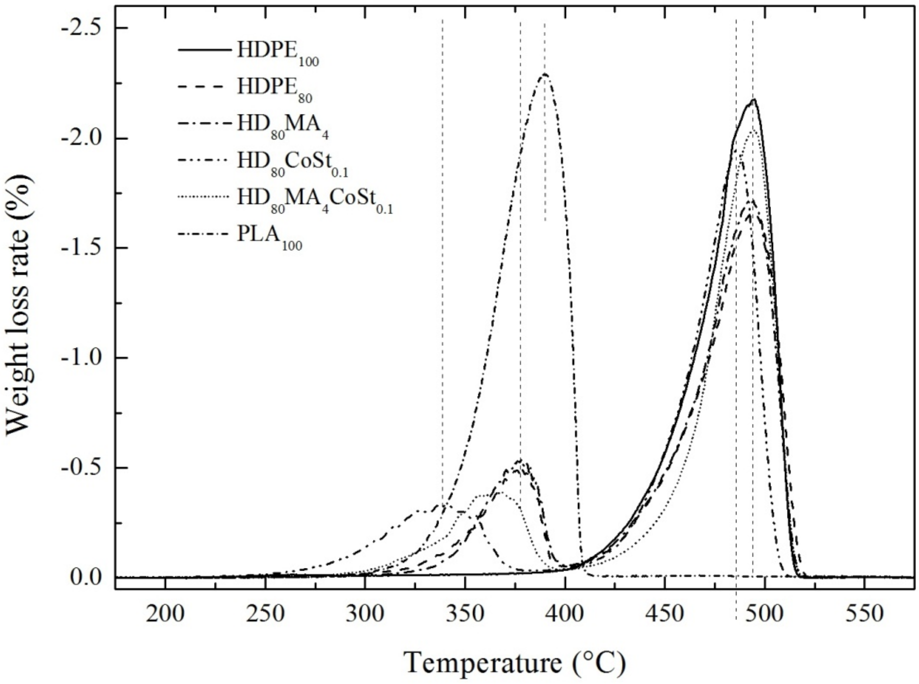


Figure 5.6. DTG curves of HDPE/PLA blends

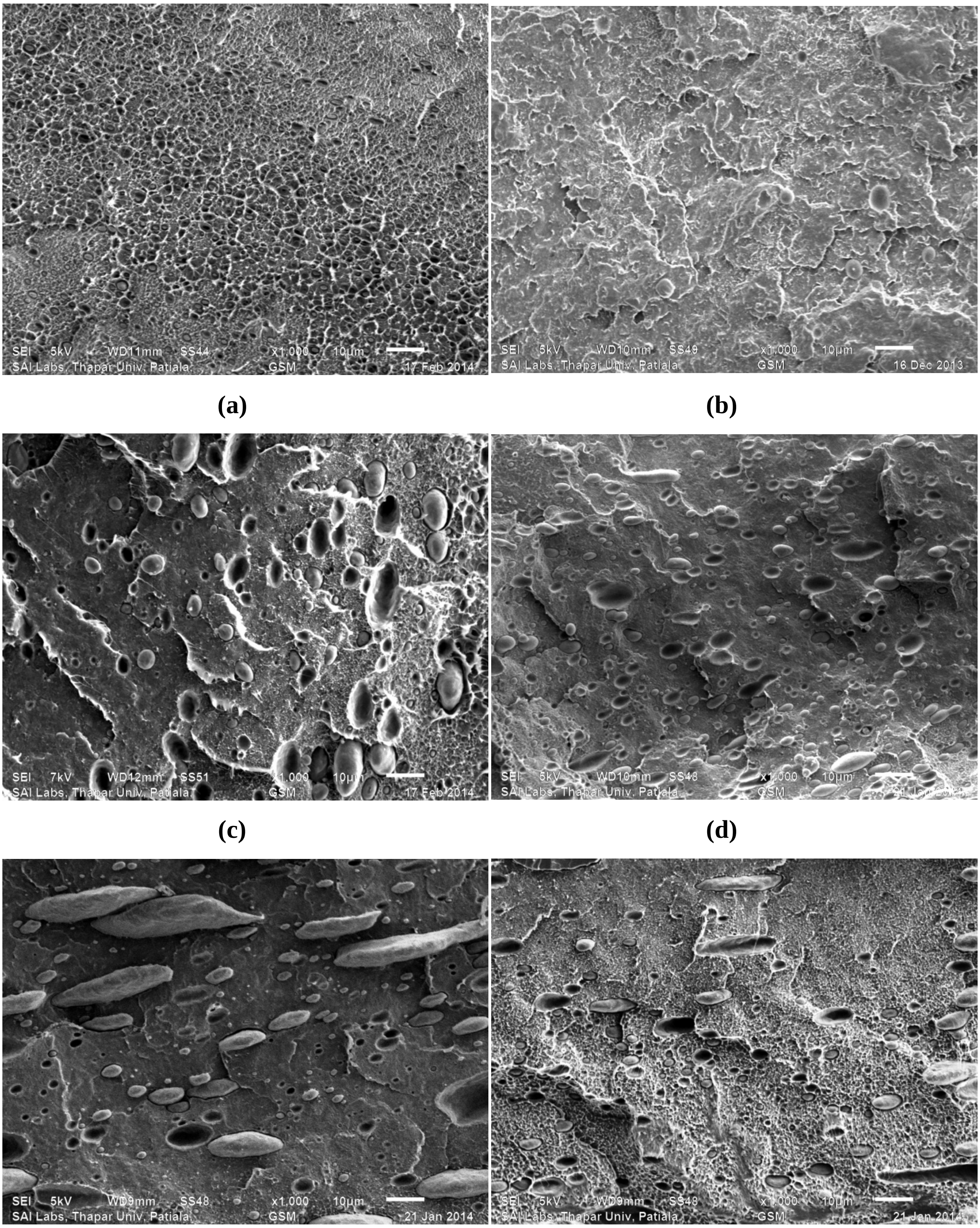
Table 5.2. TGA data of neat HDPE, PLA and HDPE/PLA blends

Sample	Max. degradation temperature (T_{max}) (°C)	Onset degradation temperature (T_{onset}) (°C)	Residual weight (%)
HD_{100}	505.72	424.78	1.214
HD_{80}	507.65	353.06	0.856
$HD_{80}MA_4$	505.62	358.13	1.073
$HD_{80}CoSt_{0.1}$	497.35	308.44	0.037
$HD_{80}MA_4CoSt_{0.1}$	505.29	338.82	0.119
PLA_{100}	402.67	337.59	0.105

The T_{max} of blends is almost the same as that of pure HDPE. This means that addition of PLA to HDPE does not adversely affect the thermal stability of HDPE in the blends. However, the onset degradation temperature decreased by addition of PLA which improved a little in presence of compatibilizer. The residual weight decreases as the PLA content is increased. The addition of PLA along with pro-oxidant has decreased the thermal stability of virgin HDPE, since some portion of polymer (HDPE) is replaced with less thermally stable material (PLA and pro-oxidant). This is a common trend and generally approved that addition of pro-oxidants will reduce thermal stability of the polymer matrix [160]. Interestingly, the compatibilized blend containing pro-oxidant showed a little higher thermal stability than the uncompatibilized one. This could probably be due to improved bonding between HDPE and PLA through MA-*g*-HDPE. However, the decreased thermal stability of 80/20 HDPE/PLA blend with 0.1% pro-oxidant shall help developing biodegradability in it, as can be seen in the biodegradation test results (Chapter 7). Percent residual weight loss was also noted minimum in $HD_{80}CoSt_{0.1}$ blend. Thus, it is clear that there is a very different trend in the degradation of HDPE/PLA blends from that of neat HDPE and neat PLA, which indicates that PLA affected the degradation process of the blends due to its low thermal stability and biodegradable nature.

5.5. Morphological properties

The phase morphology of the HDPE and PLA blends taken on the specimens' fractured surfaces is shown in Figure 5.7. It was observed from the Figure that the HDPE gradually changed from a continuous phase to a dispersed phase with addition of 20 wt% PLA content. However, phase separation indicates an immiscible behaviour between the HDPE and PLA and the sharp phase boundary implies a weak interfacial adhesion between the two components. An *in situ* compatibilization [161] was generated after addition of the compatibilizer where MA-*g*-HDPE copolymers and/or HDPE-crosslink-PLA networks are formed at the interfaces. The effect of the addition of 0.1% pro-oxidant on the morphology of 80/20 HDPE/PLA blend without compatibilizer and with compatibilizer are shown in Figure 5.7(e) and (f) respectively. It can be observed that CoSt additive was not homogeneously distributed within the HDPE matrix and open spaces between the domains were apparent due to the poor adhesion of the dispersed particles of CoSt. The morphology of the 80/20 (HDPE/PLA) blend with 0.1 wt% amount of pro-oxidant ($HD_{80}CoSt_{0.1}$) showed increased formation of cavities, rough surface with large holes and increased droplet radius, whereas in the same blend with 4 phr compatibilizer ($HD_{80}MA_4CoSt_{0.1}$), the domain size of polymers was reduced obviously ascribing to the *in situ* compatibilization, meanwhile the phase boundary became unclear indicating an enhanced interfacial adhesion and improved compatibility between the HDPE and PLA phases. From the results of mechanical properties and morphology of the neat polymers and 80/20 (HDPE/PLA) blends, it is suggested that MA-*g*-HDPE (4 phr) acts as a fine compatibilizer for the blends.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 5.7. SEM images of **(a)** $HDPE_{100}$, **(b)** PLA_{100}, **(c)** HD_{80}, **(d)** $HD_{80}MA_4$, **(e)** $HD_{80}CoSt_{0.1}$, and **(f)** $HD_{80}MA_4CoSt_{0.1}$

5.6. Rheology

Rheology is the study of deformation and flow of matter. Rheological characterization is of special interest for those materials which do not follow the Newton's law of viscosity. Newtonian materials flow in usual manner, whereas non-Newtonian materials flow in an unusual way, exhibiting various interesting and peculiar flow phenomena. Polymers consist of long chain macromolecules, which largely determine their non-Newtonian flow behaviour. They are further defined as viscoelastic materials, which means that their behaviour is somewhere between that of elastic solids and viscous fluids.

In order to understand and manage the melt processing of polymers, we need to understand their rheological behaviour. Rheology plays significant role in determining melt processability of polymers as well as the physical properties of the processed end products [162]. In case of polymer blends, it is important to know their structure-property relationship which can be obtained through their rheological behaviour.

The viscoelastic properties of HDPE, PLA and their blends are measured using dynamic oscillatory rheometer, equipped with parallel plate geometry. Linear viscoelastic range (LVER) measurements have been carried out for all samples by performing an amplitude sweep prior to carrying out their dynamic rheological measurements. The moduli initially are independent of stress, giving a plateau known as the linear viscoelastic region. Hence, linear viscoelastic range refers to the region in which the internal structure of the polymer would not be affected by shear forces; storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) is independent of imposed strain within this region. From the amplitude sweep test, stress or strain must be selected from the LVER and incorporated into subsequent oscillation.

5.6.1. Linear viscoelastic range (LVER) measurements

The linear viscoelastic range (LVER) of pure polymers, i.e. neat HDPE and neat PLA was detected, which is characterized by the onset of their shear strain (γ) dependent behaviour. Figures 5.8 and 5.9 show the selected amplitude (strain) sweeps for HDPE and PLA respectively. The storage modulus (G′) measures the stored energy, representing the elastic portion, and the loss modulus (G″) measures the energy dissipated as heat, representing the viscous portion [163]. Both, G′ and G″ of neat HDPE polymer increased initially with increase in shear strain, remained constant up to approx. 10% and then decreases radically on further increasing the strain. In case of neat PLA (Figure 5.9), G′ and G″ remained constant and parallel over the entire range of the investigated strain. Hence, to be on a safer side, the strain of 5 % was chosen as constant for the dynamic frequency sweeps of all the blended samples. A comparison between G′ and G″ indicated that the loss modulus is higher than the storage modulus.

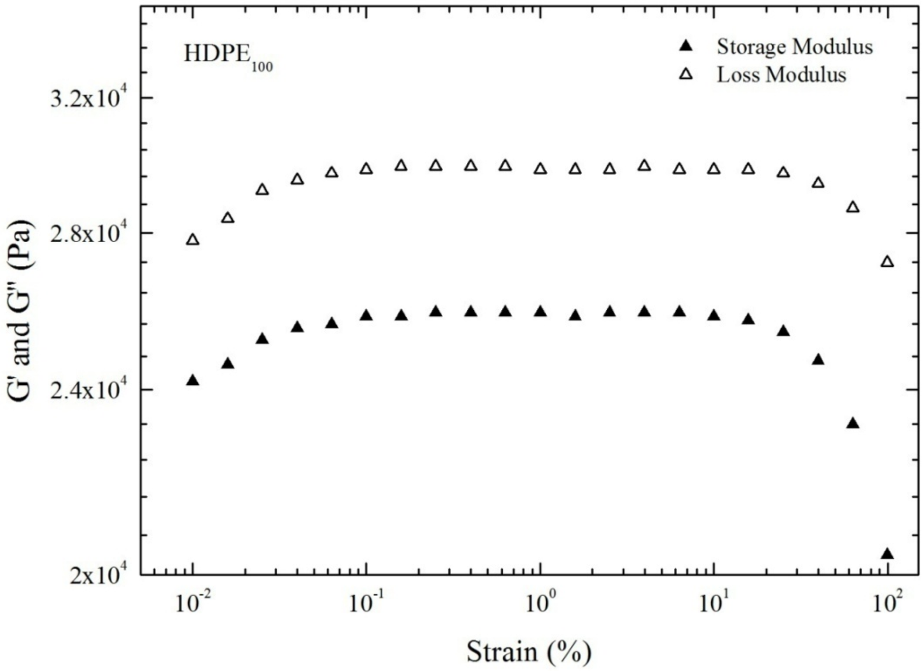


Figure 5.8. Storage modulus (G′) and loss modulus (G″) versus strain for neat HDPE

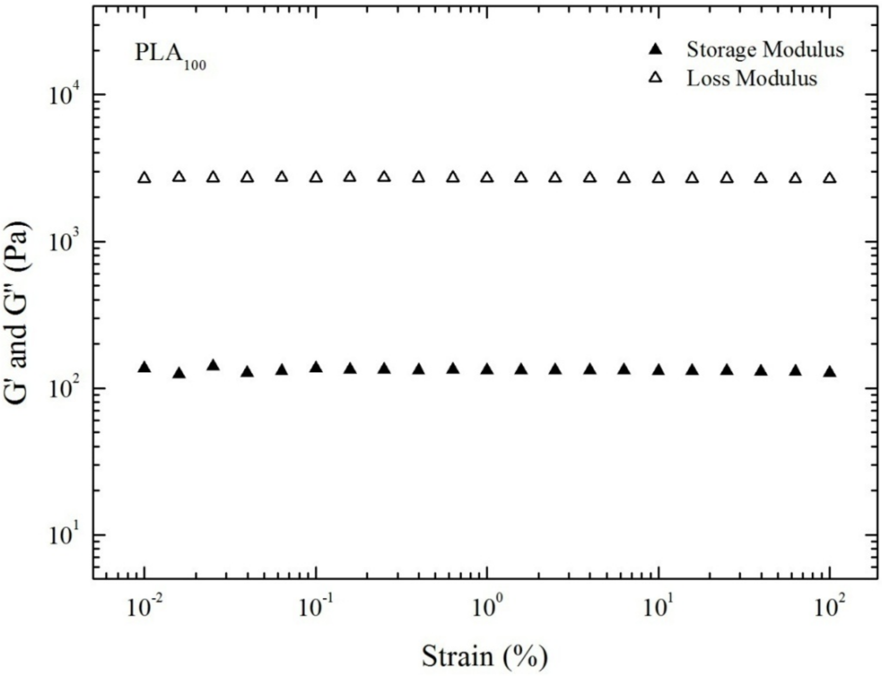


Figure 5.9. Storage modulus (G′) and loss modulus (G″) versus strain for neat PLA

5.6.2. Variation of complex viscosity with angular frequency

The effect of blending PLA and adding compatibilizer and/or pro-oxidant on the complex viscosity (η*) of HDPE as a function of angular (or oscillation) frequency (ω) at 190 °C is shown in Figure 5.10. The dynamic complex viscosity of neat HDPE (HD_{100}) was considerably higher than that of neat PLA (PL_{100}) and decreased with increasing frequency, which was due to the strong shear thinning behaviour and thermal degradation of the polymer at the molten state. The η* of PLA was extremely low (of the order of 10^2 only) and remained almost constant over the investigated frequency range, thus, exhibiting almost Newtonian behaviour. For all HDPE/PLA blends, there was a steady decrease in complex viscosity with increased shear rate (frequency); which means that the blends exhibited shear thinning behaviour (pseudo plasticity). The η* of the compatibilized blend containing the pro-oxidant ($HD_{80}MA_4CoSt_{0.1}$) was fairly lower than HD_{100}, while all other HDPE/PLA blends showed exactly the same behaviour as neat HDPE, i.e. shear thinning. This behaviour can be attributed to some degree of HDPE-PLA interaction, which requires higher shear stress and longer relaxation times for the blends to flow. Entanglements between branches and chain segments of HDPE and PLA may occur randomly, modifying the entanglement density of these blends under shear flow. Consequently, a nonlinear rheological behaviour is observed. It is known that the increased viscosities of the blends depict the increased compatibility between the dispersed and continuous phases [164]. Hence, the compatibilized 80/20 (HDPE/PLA) blend without pro-oxidant was attested as the best miscible blend amongst all from the rheological behaviour point of view. However the η^* of all the blends was low in high frequency zone, which indicated that the HDPE/PLA blends retain their melt processability even after immiscible behaviour between them. It has also been observed that HDPE is much more viscous than PLA and the complex viscosity of the blends are close to that of the pure HDPE. In case of neat PLA, the values of complex viscosity remained low at approximately entire range of angular frequency; however, it decreased a little bit at the frequency higher than 10^2 rad/s.

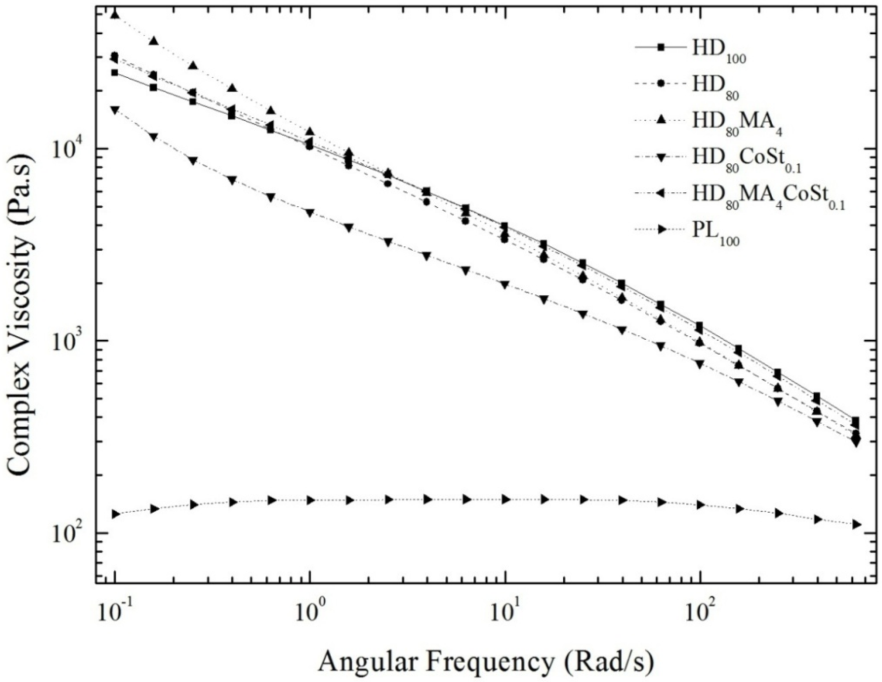


Figure 5.10. Complex viscosity (η^*) vs. angular frequency (ω) for HDPE/PLA blends

The viscosity curves between η^* and ω could be used to determine the power law parameters and to explain shear thinning behaviour of the polymer blends. For the frequency sweep data, power law expression is written as

$$\eta^* = k\omega^n \qquad (5.1)$$

where k is a sample specific pre exponential factor; and n is the shear thinning exponent; these could be directly determined from the logarithmic plot of η^* versus ω as follows:

$$\log(\eta^*) = \log\ k + n\ \log(\omega) \qquad (5.2)$$

Here, n can be obtained by calculating the slope of straight line between log (η^*) versus log (ω). This parameter n can also be considered as the degree of exfoliation. In this study, power law model was applied to complex viscosity curves of the samples in low-frequency region of 10^{-1}–10^{1} rad/s. HDPE/PLA and HDPE/PLA/MA-*g*-HDPE blends show significant shear thinning behaviour, resulting in a shear thinning exponent n = -0.33. This value indicates a strong exfoliated structure for these blends and confirms that these blends are pseudoplastic in nature.

The storage modulus of PLA was extremely lower than that of HDPE and increased significantly at higher frequencies. Similar to the viscosity, the storage modulus of 80/20 (HDPE/PLA) blends remained almost analogous to that of HDPE. However, the G′ of compatibilized blend containing pro-oxidant remained lower and thus different from other 80/20 (HDPE/PLA) blends. As frequency increased, the storage modulus differences decreased between blend samples compared with that in the low frequency.

5.6.3. Variation of storage modulus with angular frequency

The storage modulus of HDPE and HDPE/PLA blends increases gradually with the increase in frequency at the same pace approximately, whereas that of PLA increases very sharply (Figure 5.11). The analysis indicates that addition of PLA in HDPE affected the restriction of the polymer chain mobility but addition of low amount of MA-*g*-HDPE has very limited effect on the same.

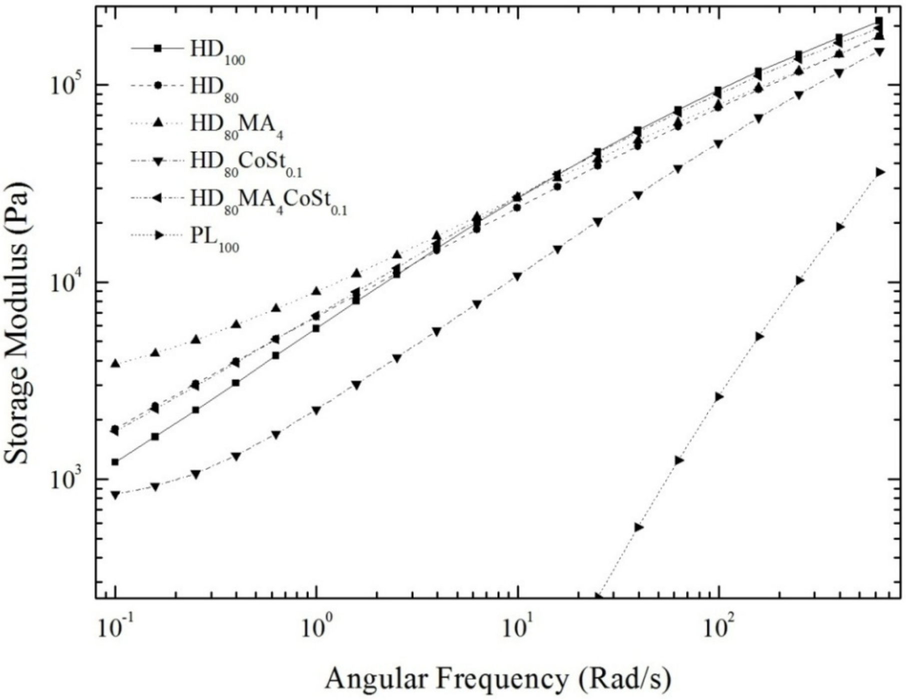


Figure 5.11. Storage modulus (G′) vs. angular frequency (ω) for HDPE/PLA blends

5.6.4. Variation of loss modulus with angular frequency

The effect of blending PLA and adding compatibilizer and/or pro-oxidant on the loss modulus (G″) of HDPE as a function of angular (or oscillation) frequency (ω) at 190 °C is shown in Figure 5.12. The loss modulus results are very similar to the storage modulus outcome. The loss modulus depends on the energy dissipated as heat due to internal friction between the constituent phases [165]. The values of G″ for HDPE/PLA blends are somewhat similar to those of pure HDPE which may be due to the balancing effect of pseudolubricating and amorphization of HDPE. For the compatibilized blend of HDPE/PLA along with pro-oxidant ($HD_{80}MA_4CoSt_{0.1}$), the G″ values were slightly lower than those of HDPE and other blends which may be due to enhanced slippage of HDPE chains facilitated by an extent of degradation of MA-*g*-HDPE under dynamic loading conditions. Thus, there is a little (but important) sensitivity of HDPE/PLA blends towards cobalt stearate content and it is evident from the rheology test results that $HD_{80}MA_4CoSt_{0.1}$ blend has lower G′ and G″ values, hence is more useful from biodegradability point of view.

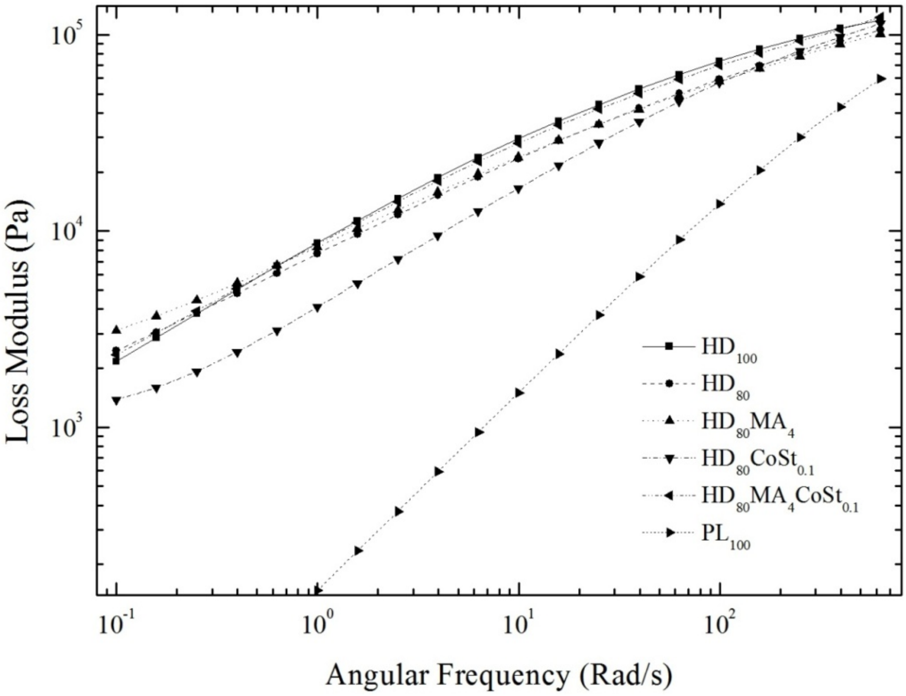


Figure 5.12. Loss modulus (G″) vs. angular frequency (ω) for HDPE/PLA blends

5.7. Water vapour transmission rate

It is well known that barrier properties of packaging films against moisture and oxygen are crucial and these values must be low for proper protection of the packaged material. The results of the WVTR test for HDPE/PLA blends are presented in Figure 5.13.

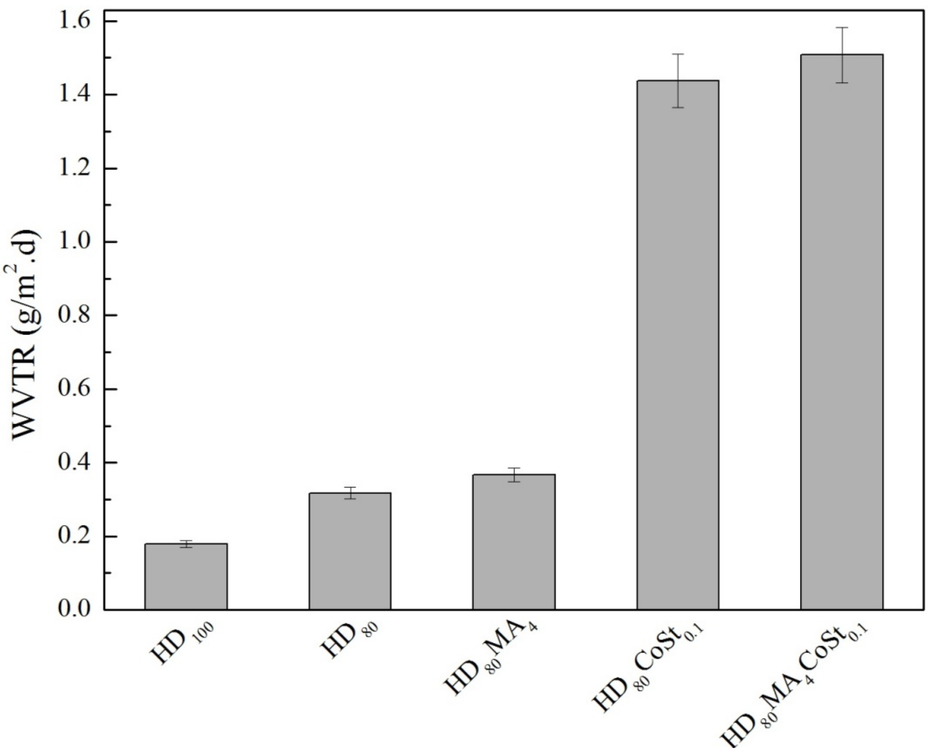


Figure 5.13. WVTR values of HDPE/PLA blends

WVTR for neat HDPE film was observed to be 0.179 g/m^2.d and blending PLA in HDPE increased this value. The WVTR values of the HDPE/PLA blended films were as follows: 0.317 g/m^2.d for HDPE$_{80}$, 0.367 g/m^2.d for HD$_{80}$MA$_4$, 1.437 g/m^2.d for HD$_{80}$CoSt$_{0.1}$, and 1.508 g/m^2.d for HD$_{80}$MA$_4$CoSt$_{0.1}$. The increase in water vapour permeability with increasing PLA content is due to the reason that HDPE is more hydrophobic than PLA. The WVTR values of HDPE/PLA films containing cobalt stearate were increased by 78% approx. as compared with the neat HDPE film. The increase in WVTR of HDPE/PLA films containing the pro-oxidant is believed to be due to the degradation of the polymer backbone chains caused by cobalt stearate making the films more susceptible to water vapours. The WVTR values of the films containing pro-oxidant are higher than the neat HDPE film, but still lower than the minimum required for flexible packaging applications [166]. This analysis revealed that HDPE becomes sensitive to water vapours (or moisture) when biodegradable polymer PLA is added; and even more when trace amount of pro-oxidant is blended.

5.8. Conclusions

According to the results obtained from the experiments, the following conclusions can be drawn:

1. FTIR and WAXD studies suggested that the blends gained some compatibility in presence of MA-*g*-HDPE.
2. DSC examination showed lower values of the enthalpy of fusion and crystallinity for those blends in which the compatibilizer was added during preparation, hence, some degree of mixing and interaction between the polymer interfaces was attained with MA-*g*-HDPE.
3. The thermal stability is highest for neat HDPE, lower for HDPE/PLA blends followed by that of neat PLA, and least for the HDPE/PLA blend with cobalt stearate.
4. The thermograms of neat polymers illustrate one stage degradation process whereas for the blends, it showed two-stage degradation.
5. SEM also indicated that the two polymers were incompatible but gained some extent of compatibility in the presence of compatibilizer.
6. HDPE becomes sensitive to water vapours (or moisture) when biodegradable polymer PLA is added; and even more when trace amount of pro-oxidant is added.
7. At 5% strain, which was considered as LVER for both polymers HDPE and PLA, the complex viscosity (η^*) of HDPE/PLA blends decreased with increase in frequency which means that the blends were pseudo-plastic in nature and exhibited shear thinning behaviour.
8. The storage modulus and loss modulus of HDPE and HDPE/PLA blends increases gradually with the increase in frequency at the same pace approximately, whereas that of PLA increases very sharply.

9. The values of both, G′ and G″ for $HD_{80}CoSt_{0.1}$ were lower as compared to neat HDPE and compatibilized blends of HDPE/PLA, which may be helpful in accelerating the thermal- and/or bio-degradation of the blend.

Chapter 6 – Thermal Degradation Kinetics of HDPE/PLA Blends

6.1. Introduction

Thermogravimetry (TG) is most commonly used technique for quickly analysing the thermal degradation kinetics of polymer materials because of its simplicity, accuracy and detailed information provided by a simple thermogram [167]. It expresses the dependence of change in mass on the temperature which gives information about sample composition, product formed after heating, and kinetic parameters [168], however, the experimental procedures and/or conditions, temperature range, heating rate, quantity of sample etc. may vary as per the requirement. The mechanism of polymer degradation reaction is a very complex radical chain mechanism, which involves initiation, propagation and termination stages [169]. The kinetic modeling of the thermal decomposition process of a polymer or polymer blend plays an important role in accurately predicting its behaviour under different environments. Therefore, a precise prediction requires information of the kinetic parameters namely, activation energy (E_a), frequency factor [$\ln(A)$] and the reaction model, $f(\alpha)$ [167]. This latter parameter, also known as conversion function, is an algebraic expression associated with the physical model which describes the kinetics of a solid-state reaction.

Several methods for the calculation of kinetic parameters of the thermal degradation by TG measurements have been developed. They can be classified into three groups: integral, differential, and direct-solution methods based on the ways of solution of Eq. 6.1 [170].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (1-\alpha)^n A \exp\left(-E_\mathrm{a} / RT\right) \qquad (6.1)$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the weight-loss rate, A is the pre-exponential (or frequency) factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Another way of classifying the methods of calculating the kinetic parameters is: single heating-rate method and multiple heating-rate method. In single heating-rate method, such as Friedman [171, 172], Freeman–Carroll [173] and Coats–Redfern [174], the kinetic parameters can be calculated from only one TG and one DTG curves obtained at a single heating rate, whereas the multiple heating-rate methods, Flynn–Wall [175, 176], Ozawa [177, 178], Reich [179], Kim–Park [180] and Kissinger [181], allow calculation of the kinetic parameters from thermograms obtained at various heating rates. Friedman method can be considered as both, single heating-rate method and multiple heating-rate method [170]. The multiple heating-rate Friedman method is based on a comparison of weight-loss rates (dα/dt) for a fractional weight loss, determined at different heating rates. The third classification of methods for the analysis of kinetic parameters is either model-fitting or model-free methods [182]. Both the methods can be performed under isothermal and non-isothermal conditions and are presented in Table 6.1 [183].

Table 6.1. Methods for studying solid-state kinetics [183]

Model-free		Model-fitting	
Isothermal	Non-isothermal	Isothermal	Non-isothermal
a. Standard	a. Friedman (Differential) b. Kissinger c. Flynn-Wall-Ozawa d. Vyazovkin e. Kissinger-Akahira-Sonuse	a. Conventional	a. Freeman-Carroll b. Coats-Redfern c. Kennedy-Clark

The model-free methods require several kinetic curves to perform the analysis. Calculations from several curves at different heating rates are performed on the same value of conversion, which allows calculating the activation energy for each conversion point. The best known representatives of the model-free approach are the isoconversional methods. Model-fitting methods consist of fitting different models to the TGA data so that a model is chosen when it gives the best statistical fit as the model from which the kinetic parameters are calculated.

Since the thermal degradation of the polymers is a very complex reaction, the choice of a reliable model or a combination of kinetic models is extremely important. Historically, model-fitting methods were widely used for solid-state reaction because of their ability to directly determine the kinetic parameters from a single TGA measurement but in recent years, the use of isoconversional or model-free methods has been increased [184-186]. The reason behind poor status of model-fitting methods is that the deriving kinetic parameters for an assumed model from a single heating rate produces unreliable and sometimes nonsensical results [187]. Following this, some advanced isoconversional methods like Vyazovkin [188], which have their roots in the Friedman and Flynn–Wall–Ozawa methods of the 1960's, have become increasingly popular. Criado and Morales [189, 190] claimed that a single α vs. T curve recorded at a certain heating rate can be satisfactorily described by some different kinetic triplets. But, due to the inherent experimental errors, discrimination of the correct kinetic triplet was unattainable by applying a statistical criterion. This observation led to the main conclusion from some recent research articles [191-195], that the correct kinetic analysis of non-isothermal data corresponding to a heterogeneous process can be only performed by making use of the experimental data recorded at several heating rates. For more accurate assessment, model-free methods may be applied to assess the dependence of activation energy on the degree of conversion, which can be correlated with the investigated process mechanism. The advantages of the model-free analysis are found in its simplicity and avoidance of errors connected with the choice of a kinetic model and modelistic assumptions [196]. The only disadvantage of these methods is that a series of measurements at different heating rates which must be made at the same sample mass and the same volumetric flow of inert gas and their fluctuation can cause errors [197, 198]. Application of model-fitting methods for non-isothermal data gives higher values of kinetic parameters [183]. This method has recently declined in favor of model-free (or isoconversional) methods. These methods allow estimates of E_a at specific extent of conversion, α for an independent model. Repeating this procedure at different conversion values, we obtain a profile of the E_a as a function of α. The principal assumption in model-free methods is that the reaction model, $f(\alpha)$, is identical at a given α for a given reaction under different conditions [199]. Some researchers have performed single heating rate or multiple heating rate experiments and described thermal degradation process through power law equation [200-203]. Depending on the heating rate, amount of sample and methods with predetermined kinetic models used for calculations, the kinetic parameters show significant variations for similar polymer or polymer blends [204].

Keeping in view the above mentioned information, we performed the kinetic analysis of the selected HDPE/PLA blends with the application of model-free methods suggested by Friedman, Kissinger and Flynn–Wall. These methods only assume that the reaction model is the same for all the heating rates at a given value of the conversion degree [205]. The thermal degradation process was studied by TGA and the thermal analysis curves were recorded at several linear heating rates. The results obtained by these methods are compared and the effect of heating rate on decomposition is also studied.

Each sample, weighing around 5 mg, was heated from room temperature to 650 °C at four heating rates (5, 10, 15 and 20 °C/min) under nitrogen atmosphere with a flow rate of 50 mL/min. The time interval of each sample for recording sample weight loss was 1 s.

6.2. Theoretical considerations for thermal kinetic calculations

In general, the rate of degradation or conversion with temperature or time, dα/dt, is calculated in terms of weight loss, i.e.

$$\alpha = \frac{w_\mathrm{i} - w_\mathrm{t}}{w_\mathrm{i} - w_\mathrm{f}} \qquad (6.2)$$

where w_i, w_t and w_f are the initial weight, actual weight at time t, and the final weight respectively. The final weight is measured at the end of the degradation.

The rate of thermal degradation, based on chemical reaction (solid state) is usually based on a single step kinetic equation [206]

$$r = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\, f(\alpha) \qquad (6.3)$$

where r is the rate of reaction (degradation), $f(\alpha)$ is the reaction model, and k is the temperature dependent rate constant, which is generally assumed to follow the Arrhenius equation.

$$k = A \exp\left(-E_\mathrm{a} / RT\right) \qquad (6.4)$$

Combining Eq. (6.3) and (6.4), the rate of degradation can be expressed as

$$r = A \exp\left(-E_\mathrm{a} / RT\right) f(\alpha) \qquad (6.5)$$

In TGA, if the heating rate is shown as β, which is equal to dT/dt, the degree of conversion α can be expressed as the function of the temperature, which is further dependent on the heating time. Therefore,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\mathrm{d}\alpha}{\mathrm{d}T}\times\frac{\mathrm{d}T}{\mathrm{d}t}=\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} \qquad (6.6)$$

From Eq. (6.5) and (6.6), the following expression may be obtained:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp\left(-E_{\mathrm{a}}/RT\right)f\left(\alpha\right) \qquad (6.7)$$

Integrating both sides of above equation, it becomes,

$$g\left(\alpha\right)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f\left(\alpha\right)}=\frac{A}{\beta}\int_0^{T}\exp(-E_{\mathrm{a}}/RT)dT \qquad (6.8)$$

where $g(\alpha)$ is the integral function of α.

The degradation process of polymer materials generally follows the sigmoidal or deceleration functions, which can be used to analyze the reaction mechanism imitated by the dynamic thermogravimetry curves [207].

6.2.1. Friedman method

Friedman method is a differential method and was one of the first isoconversional methods based on basic Arrhenius equation. The following expression was given by Friedman [172] for calculation of thermal degradation kinetics:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)=\ln\left(A\right)+n\ \ln\left(1-\alpha\right)-\frac{E_{\mathrm{a}}}{RT} \qquad (6.9)$$

From the linear plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ versus $(1/T)$, E_{a} can be obtained from its slope, which is equal to $(-E_{\mathrm{a}}/R)$. Similarly, E_{a}/ nR can be calculated from the linear plot of $\ln(1-\alpha)$ versus $1/T$.

6.2.2. Kissinger method

The Kissinger method [181] is a model-free isoconversional multiple heating rate technique, in which there is no need to calculate E_a for each conversion value in order to evaluate kinetic parameters. The equation of this method is expressed as

$$\ln\left(\frac{\beta}{T_\mathrm{m}^2}\right)=\ln\left[\frac{n\left(1-\alpha_\mathrm{m}\right)^{n-1}}{E_\mathrm{a}}AR\right]-\frac{E_\mathrm{a}}{RT_\mathrm{m}} \tag{6.10}$$

Here, E_a value can be calculated from the slope of the plot between $\ln(\beta/T_\mathrm{m}^2)$ and ($1/T_\mathrm{m}$) at the maximum weight-loss rate. The intercept (I) of the plot is given as

$$I=\ln\left[\frac{n\left(1-\alpha_\mathrm{m}\right)^{n-1}}{E_\mathrm{a}}AR\right] \tag{6.11}$$

The value of n can be obtained from the following equation:

$$n=\left(1-\alpha_\mathrm{m}\right)E_\mathrm{a}\left[(I)\right]\frac{\left\{\exp\left(-E_\mathrm{a}/RT_\mathrm{m}\right)\right\}}{\beta R\left(d\alpha/dt\right)} \tag{6.12}$$

6.2.3. Flynn–Wall method

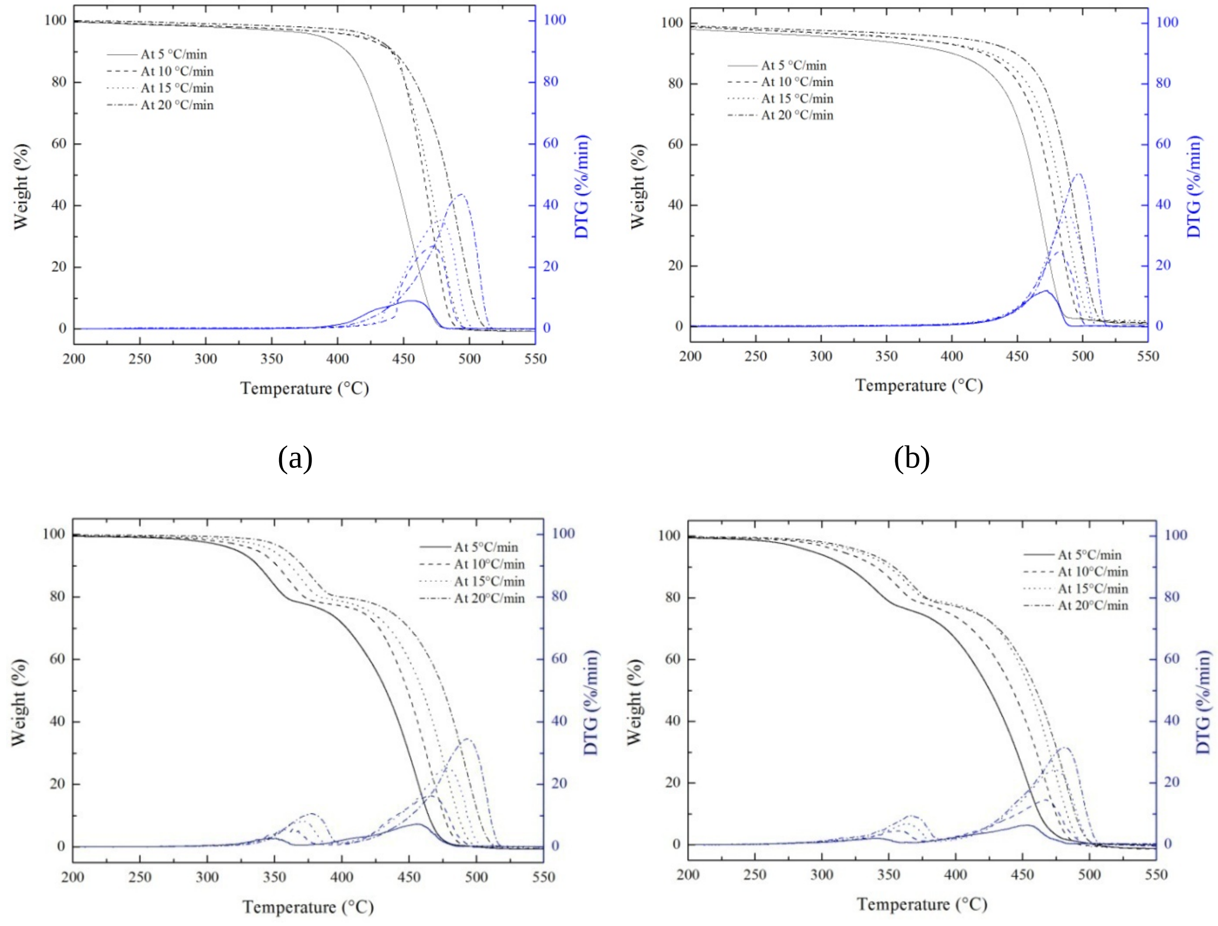
The multiple heating-rate method proposed by Flynn–Wall [175] uses the following approximate equation at a constant weight loss in a thermal degradation process.

$$\ln\beta=\ln\left(\frac{AE_\mathrm{a}}{R}\right)-\ln f\left(\alpha\right)-0.4567\frac{E_\mathrm{a}}{RT} \tag{6.13}$$

From this equation, E_a can easily be calculated based on the slope of a plot of $\ln\beta$ versus $1/T$ at a fixed weight loss.

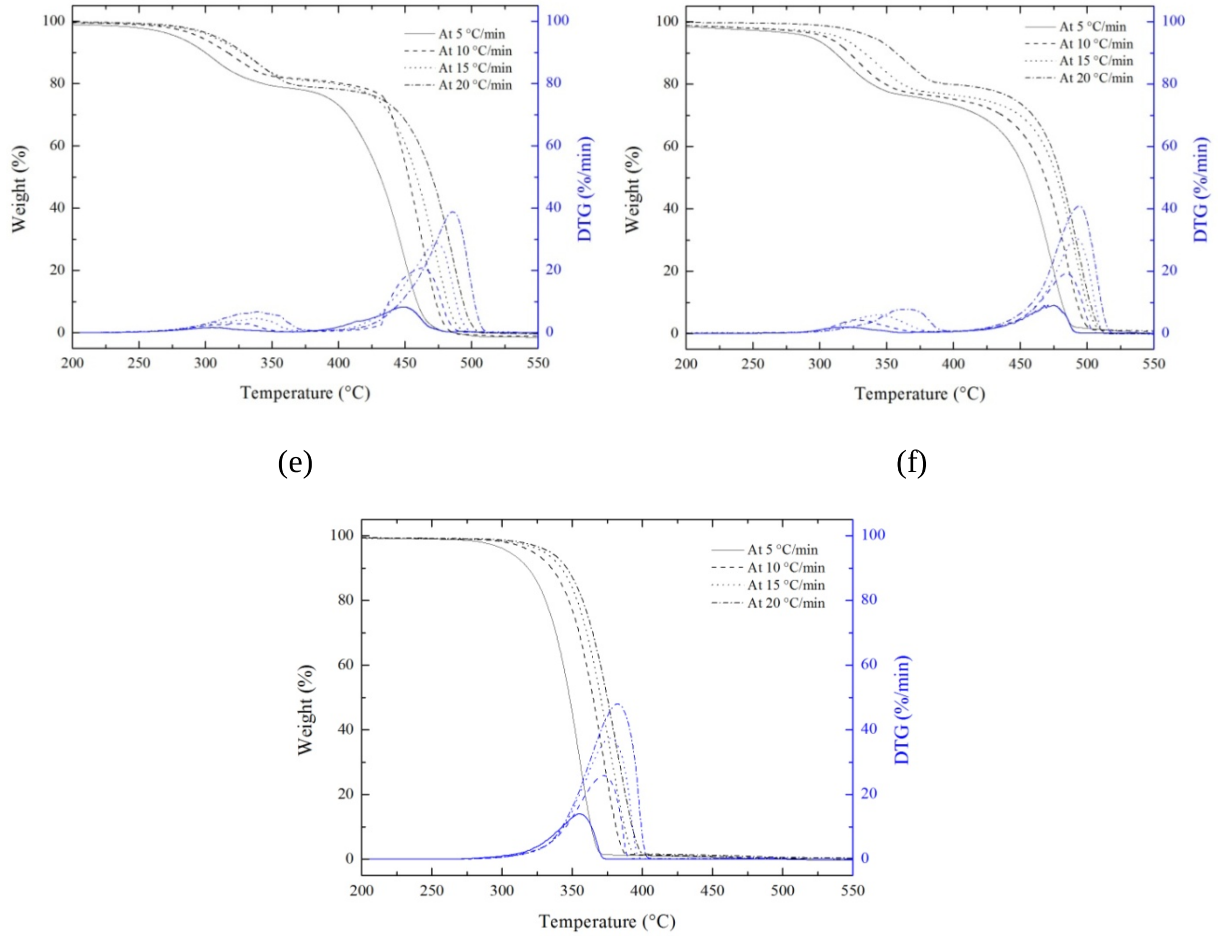
6.3. TGA and DTG analysis

TGA was conducted under nitrogen atmosphere flowing at a rate of 50 mL/min. Figure 6.1 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for (a) neat HDPE (HD_{100}); (b) HDPE containing 0.1 phr of pro-oxidant cobalt stearate ($HD_{100}CoSt_{0.1}$); (c) 80/20 (HDPE/PLA) blend (HD_{80}); (d) 80/20 (HDPE/PLA) blend containing 4 phr of compatibilizer MA-*g*-HDPE ($HD_{80}MA_4$); (e) 80/20 (HDPE/PLA) blend containing 0.1 phr of cobalt stearate ($HD_{80}CoSt_{0.1}$); (f) 80/20 (HDPE/PLA) blend containing 4 phr of compatibilizer MA-*g*-HDPE and 0.1 phr of cobalt stearate ($HD_{80}MA_4CoSt_{0.1}$); and (g) neat PLA (PL_{100}) at four different heating rates (5, 10, 15 and 20 °C/min).



(a) (b)

(c) (d)



(e) (f)

(g)

Figure 6.1. TG and DTG curves of (a) HD_{100}, (b) $HD_{100}CoSt_{0.1}$, (c) HD_{80}, (d) $HD_{80}MA_4$, (e) $HD_{80}CoSt_{0.1}$, (f) $HD_{80}MA_4CoSt_{0.1}$, and (g) PL_{100}

The TG curves of HD_{100}, $HD_{100}CoSt_{0.1}$, and PL_{100} samples exhibit single step decomposition over a relatively short temperature range. In inert atmosphere, random scission has been reported to be the primary pathway for degradation in polyethylene [208]. It is observed that the degradation temperature is increased with increase in the heating rate (β), which is in agreement with the principle of time–temperature superposition. At a faster heating rate, a particular sample requires lesser time to reach the assigned temperature. The TG curves of all the 80/20 (HDPE/PLA) blends, i.e., HD_{80}, $HD_{80}MA_4$, $HD_{80}CoSt_{0.1}$, and $HD_{80}MA_4CoSt_{0.1}$ reflected a two-step degradation process, showing degradation process of the HDPE and PLA components individually. The range of each degradation temperature corresponded to that of

HDPE or PLA homopolymers, and the ratio of weight loss in every step was similar to the composition ratio of each ingredient. These observations imply that the HDPE and PLA ingredients did not significantly influence the degradation temperatures of each other. The initial degradation temperature (T_i), temperatures at the maximum rates of thermal decomposition and final temperature of degradation (T_f) calculated at different heating rates are shown in Table 6.2.

It is observed that T_i shifts to lower temperatures with increase in the concentration of cobalt stearate, which also results in larger ΔT (difference of T_i and T_f). This also indicates that the degradation requires relatively longer time periods. At 5 °C/min heating rate, HDPE starts to degrade at 403.9 °C, while HDPE containing 0.1% CoSt starts degrading at much lower temperature (323.4 °C) which may be attributed to the pro-oxidative nature of the cobalt stearate added in HDPE. If we look upon the data of 80/20 (HDPE/PLA) blends, the T_i of binary blend is 292.8 °C, which reduces to 279 °C in presence of 0.1% CoSt in the blend. However, the initial degradation temperature of 80/20 (HDPE/PLA) blend increases when compatibilizer MA-*g*-HDPE was added, whether it is with pro-oxidant or without pro-oxidant. It might be due to complicated arrangement and increased interfacial adhesion (or cross-linking) of polymer chains, which affects their movements and decomposition with temperature. These results indicate that the compatibilizer introduced some interfacial adhesion and compatibility between HDPE and PLA resulting in increased thermal stability of the blend. It is interesting to see that the T_i of $HD_{80}CoSt_{0.1}$ and $HD_{80}MA_4CoSt_{0.1}$ are lower than neat PLA, which is favourable for their environmental degradation. Similar results were obtained at higher heating rates.

The degradation temperatures of different blend samples in proportion to their conversion are summarized in Table 6.3.

Table 6.2. TGA data for HDPE, PLA, and their blends at different heating rates

Blend Name	HDPE/PLA/MA-*g*-HDPE/CoSt Ratio	T_i (°C)	T^1_{max} (°C)	T^2_{max} (°C)	T_f (°C)
β = 5 °C/min					
HD_{100}	100:0:0:0	403.9	-	471.9	483.8
$HD_{100}CoSt_{0.1}$	100:0:0:0.1	323.4	-	472.6	484.0
HD_{80}	80:20:0:0	292.8	349.2	470.1	480.7
$HD_{80}MA_4$	80:20:4:0	321.2	359.0	469.8	482.4
$HD_{80}CoSt_{0.1}$	80:20:0:0.1	279.0	305.9	447.9	464.1
$HD_{80}MA_4CoSt_{0.1}$	80:20:4:0.1	293.2	320.5	474.9	485.0
PL_{100}	0:100:0:0	304.7	-	355.1	366.2
β = 10 °C/min					
HD_{100}	100:0:0:0	411.9	-	481.0	492.9
$HD_{100}CoSt_{0.1}$	100:0:0:0.1	364.6	-	482.2	495.5
HD_{80}	80:20:0:0	314.2	363.4	479.9	490.5
$HD_{80}MA_4$	80:20:4:0	336.1	370.6	480.4	491.4
$HD_{80}CoSt_{0.1}$	80:20:0:0.1	295.5	320.9	462.7	476.8
$HD_{80}MA_4CoSt_{0.1}$	80:20:4:0.1	305.0	326.0	484.2	496.3
PL_{100}	0:100:0:0	321.6	-	372.3	383.9
β = 15 °C/min					
HD_{100}	100:0:0:0	432.5	-	492.9	504.6
$HD_{100}CoSt_{0.1}$	100:0:0:0.1	381.4	-	489.1	502.7
HD_{80}	80:20:0:0	325.6	374.2	487.5	502.0
$HD_{80}MA_4$	80:20:4:0	347.8	381.3	490.6	503.4
$HD_{80}CoSt_{0.1}$	80:20:0:0.1	305.4	335.6	473.4	485.7
$HD_{80}MA_4CoSt_{0.1}$	80:20:4:0.1	314.7	344.1	492.1	503.3
PL_{100}	0:100:0:0	329.1	-	377.2	390.1
β = 20 °C/min					
HD_{100}	100:0:0:0	458.2	-	502.9	515.4
$HD_{100}CoSt_{0.1}$	100:0:0:0.1	407.2	-	497.0	509.9
HD_{80}	80:20:0:0	331.0	376.4	493.5	510.1
$HD_{80}MA_4$	80:20:4:0	358.1	390.1	505.6	514.7
$HD_{80}CoSt_{0.1}$	80:20:0:0.1	308.4	338.4	485.3	497.3
$HD_{80}MA_4CoSt_{0.1}$	80:20:4:0.1	320.3	352.4	495.9	508.0
PL_{100}	0:100:0:0	333.9	-	382.5	395.8

Table 6.3. Thermal degradation temperatures corresponding to progressive conversion at different heating rates

Conversion (%)	Degradation Temperature (°C)						
	HD_{100}	$\mathrm{HD}_{100}\mathrm{CoSt}_{0.1}$	HD_{80}	$\mathrm{HD}_{80}\mathrm{MA}_{4}$	$\mathrm{HD}_{80}\mathrm{CoSt}_{0.1}$	$\mathrm{HD}_{80}\mathrm{MA}_{4}\mathrm{CoSt}_{0.1}$	PL_{100}
β = 5 °C/min							
10	421.8	401.0	318.9	337.8	299.7	311.5	318.4
20	439.0	436.6	346.7	358.2	343.1	349.0	331.0
30	449.3	448.8	392.3	403.6	406.7	419.1	338.3
40	456.4	456.2	411.7	420.5	421.0	444.2	343.6
50	461.9	461.7	425.5	432.9	431.4	455.5	348.1
60	466.5	466.5	436.6	442.2	439.3	463.2	351.9
70	471.0	470.8	445.8	449.9	445.8	469.3	355.5
80	475.2	475.1	453.9	456.9	451.9	475.0	359.1
90	480.2	480.2	462.6	464.4	458.8	481.0	363.2
β = 10 °C/min							
10	433.2	423.9	340.3	351.9	316.4	322.1	335.1
20	449.2	441.3	365.7	372.1	402.6	418.9	347.6
30	458.5	452.0	411.6	427.7	439.9	436.4	354.7
40	465.3	458.8	430.4	439.9	446.9	458.2	360.0
50	471.2	464.0	442.8	448.8	452.5	468.7	364.8
60	476.1	468.5	452.4	456.3	457.7	475.8	369.0
70	480.5	472.6	460.4	462.7	462.6	481.4	372.8
80	485.1	476.7	467.5	468.9	467.4	486.6	376.8
90	490.1	481.9	474.9	475.7	473.0	492.4	381.2
β = 15 °C/min							
10	435.8	429.2	350.2	361.8	326.7	333.4	341.8
20	465.3	457.6	376.4	383.9	415.8	421.7	353.1
30	472.5	468.7	430.9	435.1	448.9	452.7	360.4
40	478.8	475.4	445.9	449.8	450.7	468.2	365.8
50	483.7	480.7	455.9	459.9	458.8	477.4	370.2
60	488.2	485.2	463.6	467.5	465.2	483.9	374.5
70	493.4	489.4	470.2	474.1	470.7	489.2	378.7
80	496.6	493.7	476.6	480.0	476.0	494.2	382.8
90	501.5	498.9	483.2	486.4	481.8	499.6	387.2
β = 20 °C/min							
10	470.2	448.9	353.5	370.7	328.5	339.4	346.0
20	481.6	469.4	377.9	399.1	422.9	433.6	357.5
30	487.3	478.1	432.0	450.1	456.7	462.5	364.7
40	492.2	484.2	448.9	465.6	461.0	471.7	370.1
50	496.7	489.0	460.2	475.7	470.2	481.2	374.9
60	500.4	493.4	468.7	483.1	477.1	487.8	379.4
70	503.7	497.3	475.9	489.4	483.2	493.3	383.5
80	507.8	501.5	482.4	495.2	487.5	498.3	387.8
90	512.2	506.4	489.2	501.6	492.8	504.0	392.6

The results show the shifting of TGA peaks towards the higher temperature region with the increase of heating rate. At a lower heating rate, the equilibrium reaches swiftly at the prescribed point with an increase in temperature. However, when the heating rate is high, the equilibrium reaches slowly and consequently, higher degradation temperature is observed, probably due to the slower diffusion of heat [209]. At the heating rate of 5 °C/min, the thermal degradation temperature of $HD_{100}CoSt_{0.1}$ sample at 10% conversion was observed as 401 °C, whereas at 20 °C/min, it was noticed as 448.9 °C.

6.4. Kinetics of thermal degradation

6.4.1. Friedman method

Using Friedman method, the calculated results of kinetic parameters for thermal degradation of all the samples at four heating rates are given in Table 6.4 and a representative plot for $HD_{80}CoSt_{0.1}$ blend sample is shown in Figure 6.2. The graphs are obtained by plotting $\ln(d\alpha/dt)$ versus $(1/T)$ with the slope (E_a/R) for calculating the values of E_a. The linear plots of $\ln(1-\alpha)$ versus $(1/T)$ give the numerical values of $(E_a/(nR))$, from which n is determined. With the help of E_a and n values, $\ln(A)$ is calculated by using Eq. (6.9) at different heating rates. The kinetic parameters of a particular blend are different at different heating rates. The order of the reaction (n) for HD_{100} sample varied from 1.4 to 2.3 when heating rate was varied from 5 °C/min to 20 °C/min. The E_a values increased from 193.90 kJ/mol to 293.28 kJ/mol as the heating rate was increased from 5 °C/min to 20 °C/min. For $HD_{80}CoSt_{0.1}$, the E_a at 5 °C/min heating rate is 122.71 kJ/mol, which is lower than that of $HD_{80}MA_4CoSt_{0.1}$ (130.56 kJ/mol) and neat PLA (PL_{100}) sample (134.83 kJ/mol) at the same heating rate. Similar trend for E_a is observed when the calculations are performed for heating rates of 10, 15, and 20 °C/min. These results show that the calculated kinetic parameters depend on the heating rates and on the fraction of constituent in the blend.

Table 6.4. Kinetic parameters of degradation of HDPE/PLA blends at different heating rates calculated by Friedman technique

Sample	β = 5 °C/min			β = 10 °C/min			β = 15 °C/min			β = 20 °C/min		
	E_a (kJ/mol)	n	ln(A)	E_a (kJ/mol)	n	ln(A)	E_a (kJ/mol)	n	ln(A)	E_a (kJ/mol)	n	ln(A)
HD_{100}	193.90	1.4	19.6	226.13	1.5	22.6	266.09	2.0	30.5	293.28	2.3	35.7
$HD_{100}CoSt_{0.1}$	191.22	1.4	19.3	222.46	1.4	21.5	265.14	1.9	26.7	274.32	2.3	28.1
HD_{80}	140.54	0.5	14.7	149.57	0.6	17.2	154.01	0.6	18.6	156.98	0.7	19.3
$HD_{80}MA_4$	184.43	1.0	16.8	195.81	1.2	19.2	202.97	1.2	20.6	204.87	1.3	20.8
$HD_{80}CoSt_{0.1}$	122.71	1.0	5.4	131.83	1.0	7.1	147.26	0.9	10.2	151.33	0.9	12.2
$HD_{80}MA_4CoSt_{0.1}$	130.56	0.9	7.1	139.9	0.9	10.0	156.72	0.9	15.4	162.50	0.8	19.6
PL_{100}	134.83	0.4	13.1	146.63	0.6	16.6	150.33	0.6	18.0	155.69	0.7	18.9

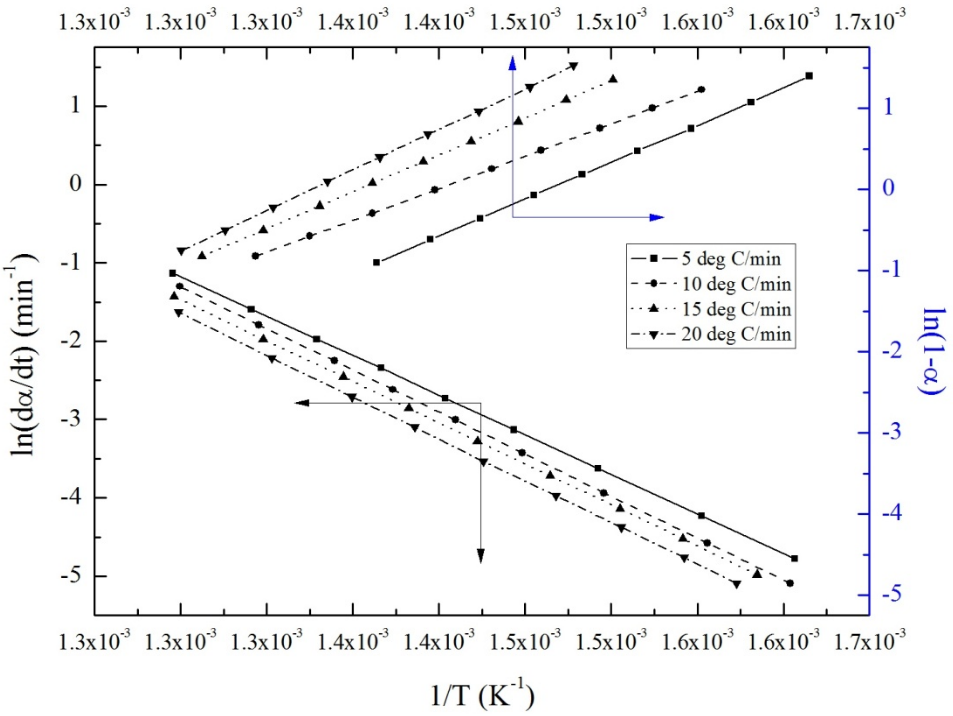


Figure 6.2. Friedman plots for calculating kinetic parameters for the thermal degradation of $HD_{80}CoSt_{0.1}$ at four different heating rates

6.4.2. Kissinger method

Considering the first Kissinger technique, the kinetic parameters for the thermal degradation of HDPE/PLA blends are calculated and summarized in Table 6.5. The observations about E_a and ln(A) are similar to those from the previous techniques except that n remains more or less same for all the polymer samples. The E_a values for neat HDPE and neat PLA are 222.7 and 151.2 kJ/mol respectively. For HDPE containing CoSt, the values of E_a are in between those of pure polymers whereas for $HD_{80}CoSt_{0.1}$ and $HD_{80}MA_4CoSt_{0.1}$ blends, this value is 102.5 kJ/mol and 135.3 kJ/mol respectively. Figure 6.3 shows the plots obtained from the correlation between $\ln(\beta / T_m^2)$ and ($1/T_m$) at the heating rates of 5, 10, 15 and 20 °C/min.

Table 6.5. Kinetic parameters for thermal degradation of HDPE/PLLA blends calculated by Kissinger technique

Sample	At maximum rate of conversion		
	E_a (kJ/mol)	n	ln(A)
HD_{100}	222.7	1.2	35.3
$HD_{100}CoSt_{0.1}$	218.4	1.2	33.5
HD_{80}	198.5	1.1	23.9
$HD_{80}MA_4$	210.0	1.2	27.4
$HD_{80}CoSt_{0.1}$	102.5	1.0	11.6
$HD_{80}MA_4CoSt_{0.1}$	135.3	1.0	14.2
PL_{100}	151.2	1.0	15.8

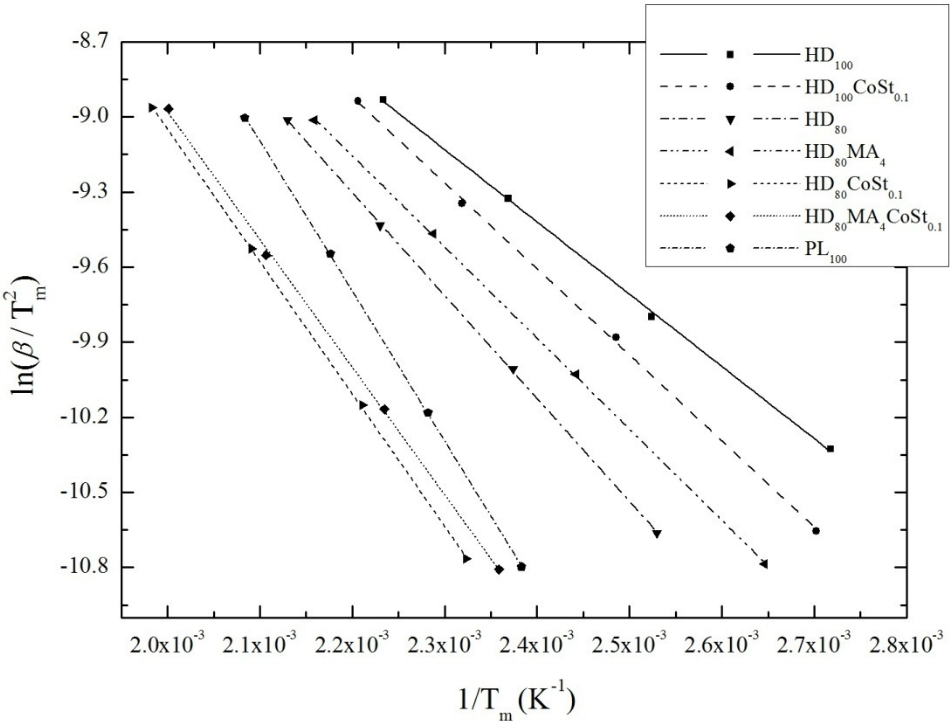


Figure 6.3. The plots of First Kissinger techniques for all investigated samples

6.4.3. Flynn–Wall method

The values of kinetic parameters obtained from non-isothermal isoconversional multiple heating rate Flynn–Wall method at progressive percentage of conversion (5, 10, 15, 20, 25%) are shown in Table 6.6. The variation of kinetic parameters at different conversion rates is quite clear. It is found that the E_a for HD_{100} increases from 195.8 kJ/mol (at 5% conversion) to 203.3 kJ/mol (at 25% conversion) whereas for PL_{100}, the values are 148.1 and 153.2 kJ/mol, respectively. For HDPE containing CoSt, these values are lower than HD_{100} and for HDPE/PLA (80/20) blends containing CoSt, E_a and ln(A) values are much lower than HD_{100}. $HD_{80}CoSt_{0.1}$ blend shows higher values in presence of MA-*g*-HDPE, which indicates that higher activation energy is required for this blend due to increased compatibility. Figure 6.4 shows the plots obtained from the correlation between $\ln(\beta)$ and (1/T) at 5% conversion of all samples.

Table 6.6. Kinetic parameters for thermal degradation of HDPE/PLLA blends calculated by Flynn-Wall technique

Sample	Conversion (%)									
	5		10		15		20		25	
	E_a (kJ/mol)	ln(*A*)	E_a (kJ/mol)	ln(*A*)	E_a (kJ/mol)	ln(*A*)	E_a (kJ/mol)	ln(*A*)	E_a (kJ/mol)	ln(*A*)
HD_{100}	195.8	21.2	198.0	22.4	202.5	22.8	202.9	23.5	203.3	23.7
$HD_{100}CoSt_{0.1}$	189.6	21.0	195.2	21.6	200.7	21.9	201.4	22.4	202.0	23.2
HD_{80}	173.4	18.5	175.8	18.9	179.4	19.3	180.1	20.0	180.6	20.2
$HD_{80}MA_4$	182.6	20.9	184.2	22.3	185.7	23.5	186.3	23.9	187.0	24.1
$HD_{80}CoSt_{0.1}$	123.5	8.1	124.1	8.3	126.4	9.0	126.9	9.5	128.0	9.8
$HD_{80}MA_4CoSt_{0.1}$	137.2	9.8	137.9	10.0	139.4	10.5	141.5	10.9	143.4	12.6
PL_{100}	148.1	13.3	150.5	13.9	151.8	14.2	152.5	14.8	153.2	15.0

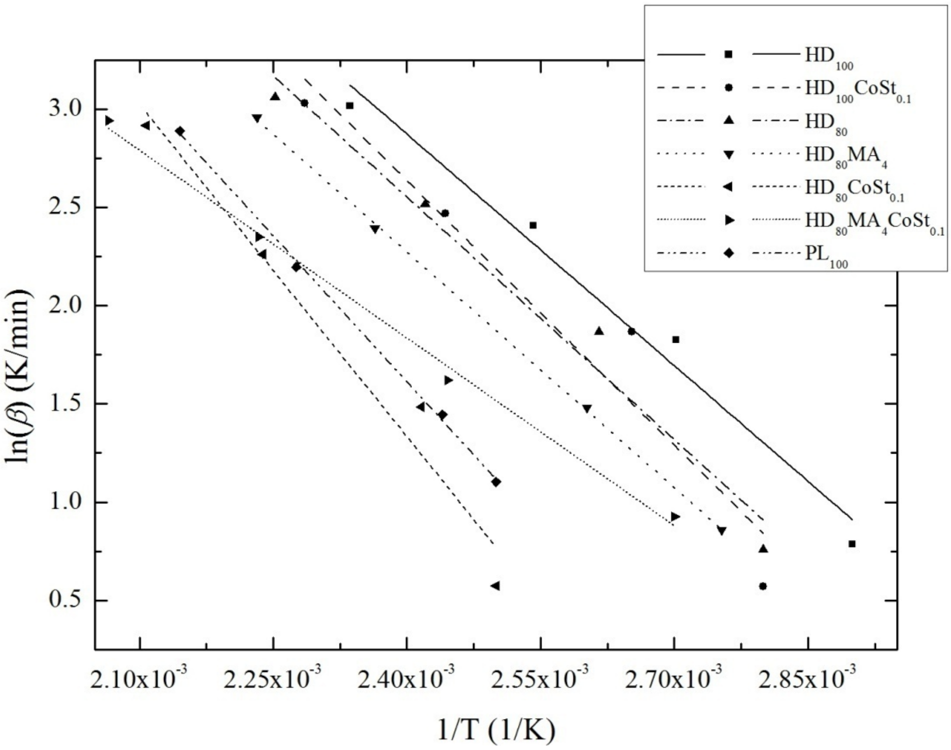


Figure 6.4. Flynn–Wall Plots for all the blend samples

The degradation kinetic parameters are affected by different mechanisms at initial and final stages and at initial stage, the degradation occurs at comparatively weaker bonds. Therefore, low activation energies are associated with the initial decomposition stage. But, HDPE is a linear polymer containing little branches; hence, the rate limiting step of thermal degradation of HDPE caused by random scission, which requires higher activation energy. The values of E_a and A were found to decrease with increasing concentration of CoSt, which signifies that the pro-oxidant is able to catalyze the degradation process of HDPE through a different route of degradation. It has been reported that during processing of PE in the presence of CoSt, some intermediate products may be formed which require low activation energy and hence decompose at early stages [210]. Further, the polymeric structure of PE decomposes during the carbonization process generating smaller intermediate objects, which can further react and produce low molecular weight hydrocarbon molecules, liquids and gases [211-213]. However, this process is not followed by each and every bond broken in the polymer chain. Only small fragments could be evaporated at that particular temperature and then, weight loss happens which is recorded and shown by the balance. Hence, the rate of weight change of the polymer and degradation kinetics is influenced by both physical as well as chemical processes [214, 215].

The variations of rate constant with temperature for all the samples are calculated considering the kinetic parameters obtained at the conversion levels of 5, 10, 15, 20 and 25% and are shown in Figure 6.5. At low temperatures, the rate constant values are same for all the samples, but after a particular temperature, it increases exponentially with increase in temperature. However, the trend for all the blends is same throughout the degradation region, but the threshold value of the rate constant is different for different samples. The rate constants for $HD_{100}CoSt_{0.1}$ and $HD_{100}CoSt_{0.2}$ are similar to that for HD_{100} at a particular temperature but slightly higher for $HD_{80}CoSt_{0.1}$ and $HD_{80}MA_4CoSt_{0.1}$ at that temperature. For

PL_{100}, the exponential increase in rate constant occurs at much lower temperature than all the other samples.

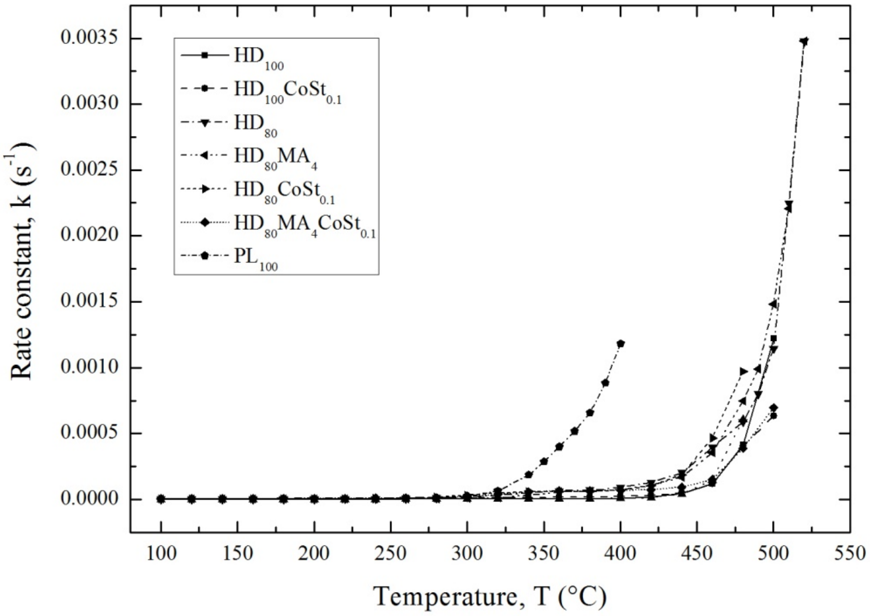


Figure 6.5. Rate constant versus temperature plot for all samples

Further, for better understanding of degradation of HDPE and HDPE/PLA blends in presence of pro-oxidant, the percent conversion (α) is plotted against time at temperatures 250, 300, 350 and 400 °C. Figure 6.6 (representative plot) shows the percent conversion versus time plots for all the blend samples at 300 °C. It is shown that the pure polymers achieve complete conversion very soon after reaching their initial degradation temperature, but for HDPE/PLA blends, it takes much longer time for complete conversion. The probable reason behind this phenomenon is immiscibility between the two polymers. Figure 6.6 signifies that each constituent of the blend influences the rate of degradation.

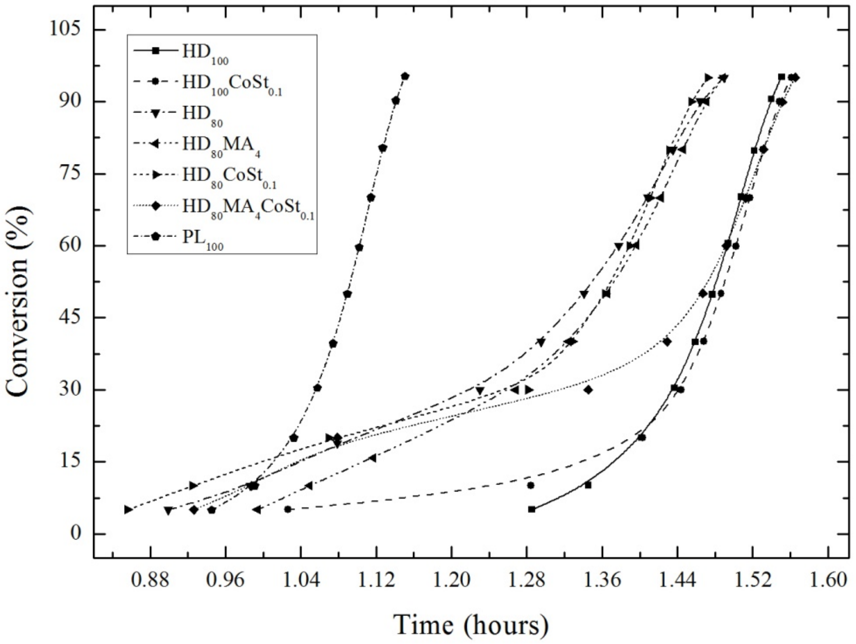


Figure 6.6. Conversion versus time plots for all samples

On the basis of the results mentioned above, it is understood that the PLA ingredient in the HDPE/PLA blended film samples must be degraded randomly according to the many kinds of well-known degradation reactions to give not only L,L-lactide but also diastereoisomers and cyclic oligomers. The degree of conversion for HDPE/PLA blends, at both initial and final degradation stages depends on the rate of heating.

6.5. Lifetime prediction

The approximate lifetimes of HDPE, PLA, and their blends are calculated to envisage the stability of their films in temperature range of 50–250 °C. On the basis of the average values E_a, n, and $\ln(A)$ listed in Table 6.4 and Table 6.5, the lifetime estimates for pure HDPE, pure PLA, and the blends generated from the conversion (weight loss) of 5% are constructed by using Eq. 6.14 given by Toop [216] and subsequently applied by Paik and Kar [203].

$$\ln t_{\mathrm{f}} = \left(\frac{E_{\mathrm{a}}}{2.303RT_{\mathrm{f}}} \right) + \ln \left[\frac{E_{\mathrm{a}}}{qR} p\left(X_{\mathrm{f}} \right) \right] \qquad (6.14)$$

where t_f is approximated time of failure, T_f is the temperature at failure, and $p(X_f)$ is a function whose value depends on the E_a at the failure temperature.

The results of lifetime prediction are shown in Figure 6.7. It is seen that the lifetime of all the blends depends on temperature and decreases exponentially with increase in temperature. Moreover, incorporation of PLA and/or CoSt in HDPE helps in lowering its lifetime at a particular temperature. For example, the lifetime of neat HDPE at 65 °C (as per the calculation performed using Eq. 6.14) is 5240 years; and upon addition of 0.1 phr CoSt, it is reduced to 2010 years at the same temperature, i.e., 65 °C. For 80/20 HDPE/PLA blend, it is 65 years only; which further reduced to 9 years when CoSt is added in the same blend. The possible reason behind lower lifetime or environment stability of PLA and HDPE/PLA films is their low molecular weight as compared to HDPE. Hence, blending PLA with HDPE along with CoSt as pro-oxidant additive significantly reduces the lifetime of HDPE.

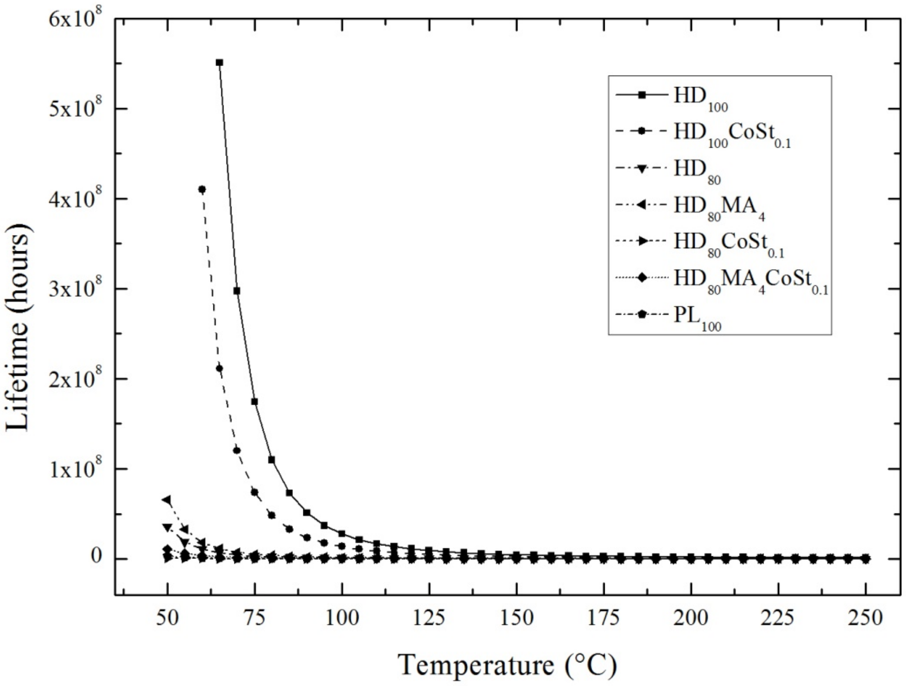


Figure 6.7. Lifetime of HDPE, PLA and their blends with temperature

6.6. Conclusions

Single-step thermal degradation process is observed for pure HDPE and pure PLA polymer samples, whereas two-step degradation is noticed for HDPE/PLA blends. The stability of HDPE decreases a little upon addition of trace amount of CoSt. The film sample containing HDPE, PLA, and cobalt stearate is least stable, even lesser than neat PLA. Addition of compatibilizer MA-*g*-HDPE increases the thermal stability of the HDPE/PLA blend probably due to the increased interfacial adhesion and interaction between the polymer chains of the two polymers. The variation in the degradation trends shown by the data of different samples is obviously due to the difference in degradation reaction mechanism, sample composition, and the micro-structural features of the polymers and polymer blends. The values of activation energy for HDPE/PLA blends are lower than those of neat HDPE, possibly due to radical character of degraded PLA derivatives, which affects the initial thermal degradation reaction. However, the complexity of the degradation reaction mechanism is due to the practical dependence of activation energy on the extent of conversion. The values of kinetic triplet E_a, n and $\ln(A)$ of the blends are constituent dependent. Additionally, these parameters are significantly affected by the heating rates and calculation methods. The E_a values calculated by Friedman, Kissinger, and Flynn–Wall techniques are in good agreement with each other. The lifetime of all the samples decreases drastically with increase in temperature. Addition of PLA and cobalt stearate results in reduced lifetime of HDPE.

Chapter 7 – Biodegradability of HDPE/PLA Blends

7.1. Introduction

Biodegradation of polymer products occur in two major steps: (a) primary degradation and (b) secondary (or ultimate) degradation (Figure 7.1). In primary degradation, chain scission of the ester groups in the polymer's backbone occurs due to hydrolysis, oxidative reaction, heat, light, etc. Due to chain scission, the polymer backbone breakdowns into several shorter chains resulting in reduction of its molecular weight. In secondary (or ultimate) degradation, the low molecular weight oligomers from primary degradation are used by microorganisms yielding degradation products, i.e. carbon dioxide, water, biomass and residue.

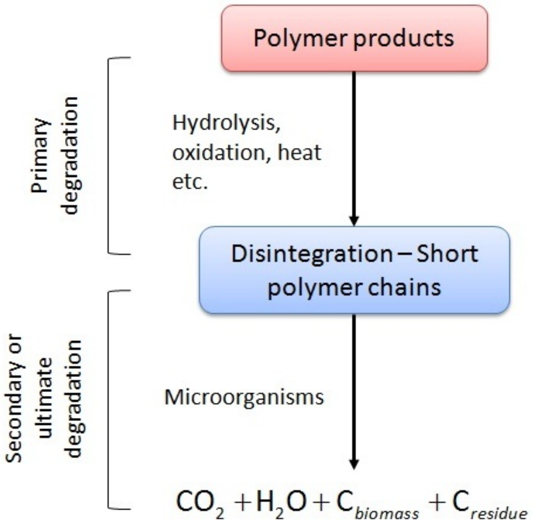


Figure 7.1. Biodegradation of polymer products

Biodegradable polymer in a blend with a non-biodegradable polymer will act as an initiator for their oxidative degradation. As novel materials, biodegradable polymer blends make claims to be environmentally friendly. Consequently, it must be proved by using scientifically based and generally accepted methods. Moreover, it is critical to investigate how long biodegradation would take in conditions that are relevant to real world situations. Biodegradability of polymeric materials is determined by several abiotic and biotic factors such as climatic conditions, microbial diversity, and composition of the material [217, 218]. There is a wide variety of methods currently available for measuring the biodegradability of polymer materials [219]. The loss of weight of materials is commonly used, however this method can be problematic, as degrading materials can absorb moisture which alters their weight, or the materials could disintegrate into smaller fragments, causing difficulty in recovering the materials to determine the weight loss. Moreover, this is not enough to prove its biodegradability because these observations do not quantify the fraction of the material that can be consumed by the micro-organisms over a definite period of time. The biodegradable components of a polymer product should eventually be mineralized into CO_2 and H_2O (under aerobic conditions) by enzymatic action of the microorganisms present in compost, therefore, measurement of carbon dioxide (CO_2) production or oxygen consumption provides a quantitative measure of degradation. Moreover, the use of such respirometric data can allow the calculation of the degree and rate of biodegradation during aerobic composting process itself, which is very convenient [147]. In these methods, usually, the polymeric matrix is exposed to controlled environmental conditions (e.g., soil, sludge compost).

Standards developed by American Society for Testing and Materials (ASTM) and International Organization for Standardization (ISO) are used to assess the biodegradability of biodegradable plastics in different environments. ASTM D5338 is a method used to assess biodegradability of plastics under simulated or controlled composting conditions which correlates biodegradability to the total mineralization of organic carbon (CO_2 evolved) in the polymer [58]. In this chapter, assessment of biodegradation of the selected HDPE/PLA blends by ASTM D5338 (modified) standard are shown and discussed. The term ‘modified’ is used here as the apparatus is also developed indigenously (as described in Chapter 3) following the guidelines of the mentioned ASTM standard.

7.2. Preparations prior to biodegradability test

7.2.1. Preparation and standardization of $Ba(OH)_2$ and HCl solutions

0.024N barium hydroxide solution was prepared by dissolving 4.0 g $Ba(OH)_2.8H_2O$ per liter of distilled water. The normality of the solution was verified by standardizing it against HCl. As HCl is a secondary standard, it was standardized with the primary standard sodium carbonate (Na_2CO_3) prior to use. The $Ba(OH)_2$ solution, thus prepared, standardized with HCl prepared earlier was filtered and then stored in an air-tight glass vessel to prevent the absorption of atmospheric CO_2.

7.2.2. Blank, positive and negative controls

The blank consisted of the inoculum (compost only), whereas for positive control and negative control references, microcrystalline cellulose powder (MCC) and pure HDPE film sample respectively were taken.

7.3. Biodegradation test

7.3.1. Procedure

The composting vessels (bioreactors) were filled up with three different mixtures: blank (compost only), test (compost + test polymer), and positive reference (compost + MCC), each in triplicate. The test was initiated with an air (CO_2-free) flow rate of 60 mL/min and 50-60% relative humidity (RH). The composting vessels were placed inside a biodegradability testing apparatus for 45 days using a temperature profile as mentioned in the protocol [58] to ensure favourable conditions for compost microorganisms involved in biodegradation process. The contents of all bioreactor were shaken twice a week to ensure uniform distribution of air throughout the compost. From each composting vessel, the evolved CO_2 was absorbed in flasks containing $Ba(OH)_2$ solution (0.024 N). The retrieved $Ba(OH)_2$ solution was titrated with 0.05 N HCl and the amount of CO_2 produced was determined by calculating the difference (in mL of titrant) between the test substance and blank $Ba(OH)_2$ traps. The measurement was taken once a day, at time intervals of about 24 hours, for 45 days.

7.3.2. Calculations

The theoretical amount of CO_2 produced by the total oxidation of the test sample was calculated by using Eq. 7.1.

$$CO_2(Th) = W_{sample} \times C_{sample} \times \frac{44}{12} \qquad (7.1)$$

where W_{sample} is the mass of total dry solids in the test sample initially added to the composting vessels (g); C_{sample} is proportion of total organic carbon (TOC) in the sample (g/g); 44 and 12 are the molecular weights of carbon dioxide and carbon, respectively (g/mol). TOC of the samples was determined with a carbon analyzer (TOC-V CPH SSM 5000A, Shimadzu, Japan).

The mean value (from the three replicates) of the net CO_2 produced by controlled composting of the test substances was determined by subtracting the mean CO_2 production from the blank composting vessel, i.e., the compost only. The % biodegradation was calculated by using Eq. 7.2.

$$\%\, biodegradation = \frac{CO_2(test) - CO_2(blank)}{CO_2(Th)} \times 100 \qquad (7.2)$$

where CO_2 *(test)* is the cumulative amount of carbon dioxide evolved from each composting reactor containing a test sample (g) and CO_2 *(blank)* is the cumulative amount of carbon dioxide evolved from the blank reactor (g).

7.3.3. Statistical analysis

Each measurement was done in triplicate and the mean and standard deviation of the experimental results were calculated using Origin 8.0.

7.3.4. Results

The analyses of total organic carbon (TOC), carried out on the different samples, in order to make it possible to calculate the theoretical carbon dioxide [$CO_2(Th)$], is shown in Table 7.1.

Table 7.1. Total organic carbon (%) and theoretical CO_2 (g) evolution from polymers and blend samples

Sample	TOC (%)	Wt. of carbon in 1 g of polymer (g)	Th. CO_2 evolution (g)
Compost	20.1	0.20	0.737
Microcrystalline cellulose (MCC)	42.8	0.43	1.569
HD_{100}	49.1	0.49	1.800
HD_{80}	49.7	0.50	1.822
$HD_{80}MA_4$	50.2	0.50	1.841
$HD_{80}CoSt_{0.1}$	48.2	0.48	1.767
$HD_{80}MA_4CoSt_{0.1}$	48.5	0.49	1.778

7.3.4.1. Example calculation for theoretical CO_2

$$CO_2\ (Th)\ \text{for}\ HD_{80}\ \text{sample} = 1 \times 0.5 \times \frac{44}{12} = 1.822\ \text{g}$$

The values of CO_2 produced (in grams) and the percent biodegradation of each sample were calculated using Eq. 7.2, which are shown in Table 7.2.

Table 7.2. Calculation of biodegradation for all the samples

Sample	Th. CO_2 evolution (g)	Vol. of $Ba(OH)_2$ taken (mL)	mmol of $Ba(OH)_2$ taken	Vol. of HCl used (mL)	mmol of HCl used	mmol of CO_2 produced	grams of CO_2 produced	Cumulative CO_2 produced in 45 days (g)	% Bio-degradation (after 45 days)
Compost	0.737	30	0.36	10.8	0.540	0.090	0.004	0.070	9.5
Microcrystalline cellulose (MCC)	1.569	30	0.36	6.5	0.325	0.198	0.009	0.748	43.2
HD_{100}	1.800	30	0.36	12.4	0.620	0.050	0.002	0.080	0.6
HD_{80}	1.822	30	0.36	9.7	0.485	0.118	0.005	0.134	3.5
$HD_{80}MA_4$	1.841	30	0.36	9.9	0.495	0.113	0.005	0.138	3.7
$HD_{80}CoSt_{0.1}$	1.767	30	0.36	9.1	0.455	0.133	0.006	0.299	9.1
$HD_{80}MA_4CoSt_{0.1}$	1.778	30	0.36	8.9	0.445	0.138	0.006	0.477	10.0

7.3.4.2. Example calculation for percent biodegradation

Vol. of $Ba(OH)_2$ taken = 30 mL

Normality of $Ba(OH)_2$ = 0.024

Therefore, molarity of $Ba(OH)_2$ = $\frac{0.024}{2} = 0.012$ [as the acidity of $Ba(OH)_2$ is 2]

Hence, mmols of $Ba(OH)_2$ taken = 30 x 0.012 = 0.36 mmoles

And,

Vol. of HCl used = 9.7 mL

Normality of HCl = 0.05

Molarity of HCl = 0.05 [as the basicity of HCl is 1]

Hence, mmols of HCl used = 9.7 x 0.05 = 0.485 mmoles

Now,

$$\text{mmoles of CO}_2\text{ produced} = \text{mmoles of Ba(OH)}_2 \text{ at start} - \frac{\text{mmoles of HCl}}{2}$$

$$= 0.36 - \frac{0.485}{2} = 0.118 \text{ mmoles}$$

We know that,

1 mol of CO_2 = 44 g/L

Therefore, 1 mmol of CO_2 = 44 x 10^{-3} = 0.044 g/L

Hence, grams of CO_2 produced = 0.118 x 0.044 = 0.005 g

In this way, the readings were taken on daily basis for 45 days and the cumulative sum of CO_2 produced for HD_{80} sample was 0.134 grams.

Finally, using Eq. 7.2, we get

$$\% \text{ biodegradation} = \frac{0.134 - 0.07}{1.822} \times 100 = 3.5\%$$

As expected, the maximum carbon dioxide is evolved from the cellulose (0.748 g). Among the tested blend samples, $HD_{80}MA_4CoSt_{0.1}$ produced 0.477 g of CO_2 followed by $HD_{80}MA_4$ blend (0.138 g) and HD_{80} (0.134 g). A little amount of CO_2 from neat HDPE sample (0.08 g) also was produced.

The day-wise percent biodegradation of each sample, calculated from the theoretical CO_2, actual CO_2 and CO_2 evolved from blank, is shown in Figure 7.2. From the degradation curves, it is possible to distinguish a short lag phase (day 0-5), where the adaptation of the microbial inoculum to the test substance occurs, a more or less important degradation phase (day 5-30) in which the bacteria use the test substances as food and grow and finally, a plateau phase (day 30 to the end of tests at day 45), in which degradation has ended.

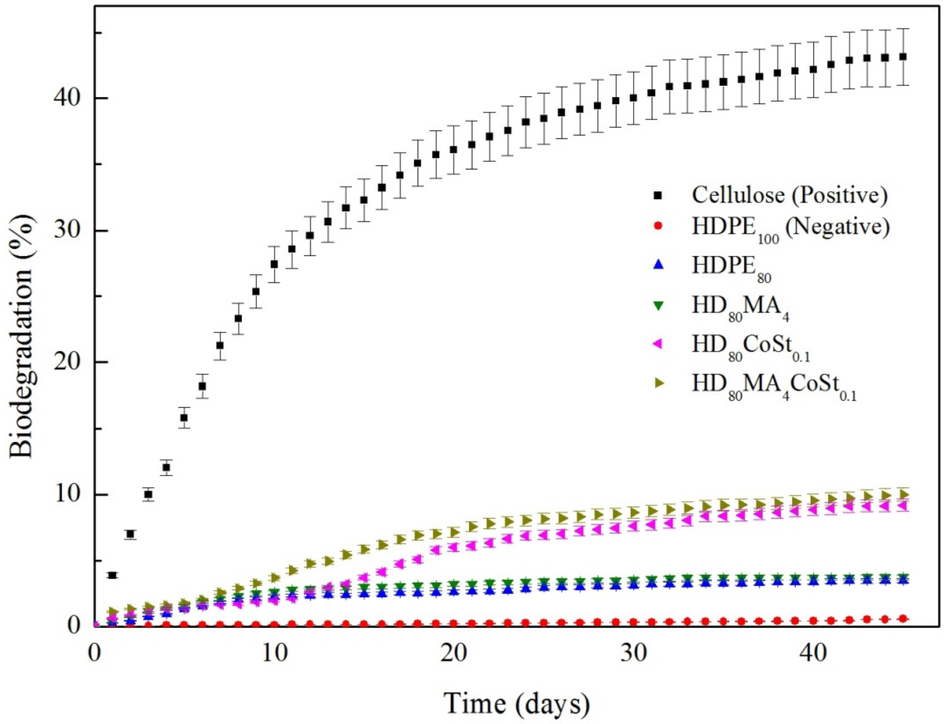


Figure 7.2. Percent biodegradation (day-wise) of HDPE/PLA blends

Among the tested samples, the blend which degraded the most is $HD_{80}MA_4CoSt_{0.1}$. Indeed, after 45 days of incubation, it is degraded to 10%. $HD_{80}CoSt_{0.1}$ is also well degraded to 9.1%. $HDPE_{80}$ is degraded much less with only 3.5% and neat HDPE is almost not degraded, only to 0.6%. The percent biodegradation of each sample after 45 days of test period is shown in Figure 7.3.

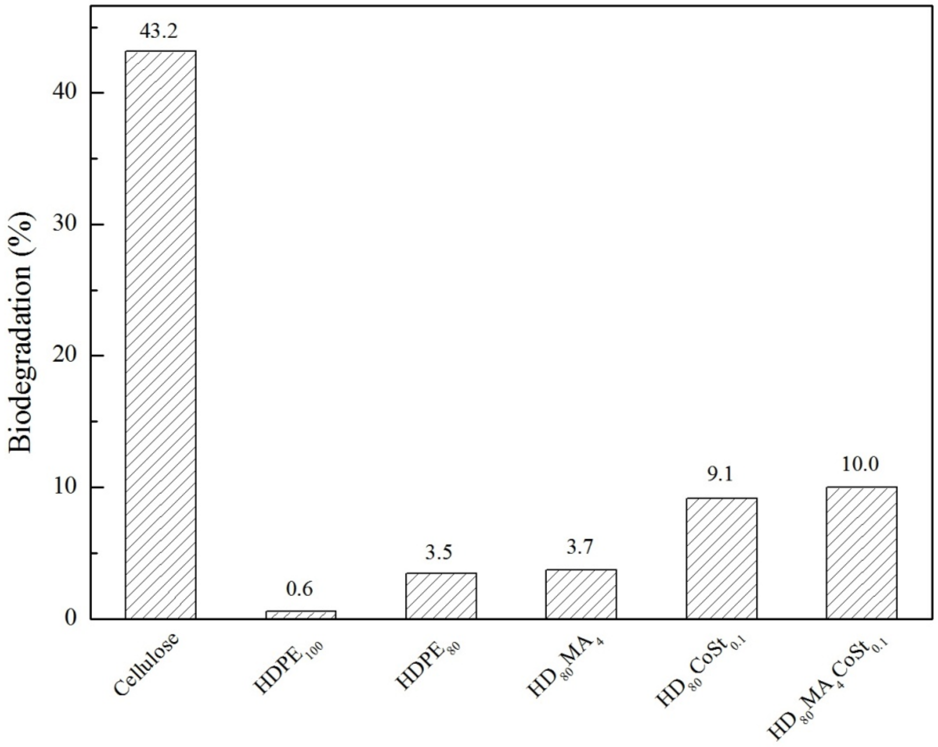


Figure 7.3. Percent biodegradation of HDPE/PLA blends after 45 days of composting

The results obtained with the blends containing pro-oxidants suggests that the pro-oxidant, in combination with the given amount of compatibilizer additive, leads to fast degradation under the combined effect of microorganisms and oxidation. The initiation and propagation of biodegradation of the pro-oxidant samples was also faster than those without pro-oxidant. This is due to the photo-oxidation of the blends containing pro-oxidant as the cleavage at the weak links of these blends occurs predominantly which have lower bond energies leading to the formation of free radicals resulting in drastic reduction of the molecular weight of the polymer blend samples. Some of the carbon atoms in respective samples get converted to carbon dioxide by microorganisms and the others into microbial biomass.

7.4. Conclusions

The samples which do not contain cobalt stearate showed somewhat lower degree of biodegradation but still significant to be considered for producing biodegradable packaging films of HDPE. The results also suggested that the microcrystalline cellulose is highly biodegradable material which required no induction time for its biodegradation since cellulose can be directly degraded by enzymes such as cellulases. The biodegradation of 80/20 (HDPE/PLA) blends without MA-*g*-HDPE was accelerated after a small lag phase, as the samples have to undergo hydrolytic chain scission prior to starting the biodegradation process. Better degradation of these samples is attributed to a diminutive interaction of HDPE and PLA phases mediated by the compatibilizer, leading to break-down of some carbon atoms of HDPE too, by the enzymatic reaction. Biodegradation of neat HDPE was very little, probably due to the inhibited activity of microorganisms.

Chapter 8 – Conclusions and Recommendations for Future

8.1. Conclusions

The mechanical properties of the blends are dependent on the ratio of HDPE and PLA components and the amount of the additives used. The maximum amount of PLA blended with HDPE and retaining the minimum requisite mechanical properties for flexible packaging application is 20% (w/w). The mechanical properties increase with addition of compatibilzer and 4 phr is found to be optimum amount of the same. However, when pro-oxidant is blended in the 80/20 (HDPE/PLA) blend, the tensile properties decrease drastically. Some recovery in the mechanical properties is possible by compatibilizing the blend.

On analyzing the FTIR results of the blends and comparing the same with those of neat polymers, the compatibilized blends show different peak positions showing some compatibility between the two immiscible polymers. Similarly, the peaks of the blends in WAXD are of lower intensity, hence verifying the compatibility between the two polymer components.

Immiscibility and phase separation between the two polymers are seen clearly from SEM images. However, these immiscible blends become compatible in presence of maleic anhydride grafted high density polyethylene. Therefore, the compatibilizer is suitable to introduce and enhance compatibility between the selected polymers.

The heat of fusion and crystallization of the compatibilized blends (obtained from DSC results) are lower than those without compatibilizer. This indicates that some degree of mixing and interaction between the polymer interfaces is possible through the compatibilizer.

The blends containing pro-oxidant have lower thermal stability (TGA results), which should help in propagating their biodegradation. The neat polymers followed one-stage degradation while the blends tracked two-stage degradation, which is an indication of separate degradation of the two polymer components analogous to their individual thermal degradation temperature.

The test for water vapours (or moisture) barrier property revealed that HDPE becomes sensitive to water vapours when biodegradable polymer PLA is added; and even more when trace amount of pro-oxidant is blended. But, water vapour permeability of the selected blends is found to be satisfactory for packaging applications.

The viscoelastic response of all the blend samples was monitored by the storage modulus (G′) and the loss modulus (G″) versus angular frequency. All the blends show a shear thinning behaviour. The good observation is that the processability of the targeted blends is good for producing films, as studied from their rheology.

An important feature of this research work is the development of a low-cost apparatus for measuring biodegradability of polymer materials as per the guidelines of ASTM D5338 standard (modified) and its fabrication. The apparatus has been developed successfully which is giving the consistent and reliable results on the biodegradability of the samples.

The biodegradability test of the prepared blends under composting conditions for 45 days shows the order of percent biodegradation as cellulose (43.2%) > $HD_{80}MA_4CoSt_{0.1}$ (10%) > $HD_{80}CoSt_{0.1}$ (9.1%) > $HD_{80}MA_4$ (3.7%) > HD_{80} (3.5%). Neat HDPE is the least, only 0.6% biodegradable. Clearly, the blends containing pro-oxidant are degraded to a significant extent.

Overall, it can be said that semi-biodegradable / partial biodegradable and oxo-biodegradable HDPE/PLA films have been developed with optimized composition and physico-mechanical properties along with remarkable degree of biodegradation, which may replace non-biodegradable films in flexible packaging applications.

8.2. Recommendations for future work

The scientific and technological development is a never ended journey. Each concluded research project opens up a new range of questions and avenues that can be further explored in multiple directions. However, some areas for future work are recommended as follows:

1. The fate of non-biodegradable part of the blends be investigated. Non-toxicity of the resultant fragmented product(s) need to be verified by conducting several eco-toxicological tests as per the ASTM guidelines.
2. The relative biodegradability of novel polymer blends can be studied under all possible circumstances of degradation, viz. synergistic effect of photo- and bio-degradation, and characterization of effect of these degradations on the structure of the polymers.
3. Some other analytical techniques may also be applied to study the degradation behaviour, e.g. chromatography, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF), nuclear magnetic resonance (NMR), etc.
4. It would be interesting to develop HDPE based biodegradable blends with other biodegradable polymers like PHB along with inorganic fillers like nanoclay and study their physical, mechanical, structural, thermal properties, and biodegradability.
5. The positive outcomes of the research shall be tested firstly on pilot scale and then on commercial scale.

References

[1] Utracki L; History of commercial polymer alloys and blends (from a perspective of the patent literature). Polymer Engineering & Science 35 (1995) 2-17.

[2] Feldman D; Polymer history. Designed Monomers and Polymers 11 (2008) 1-15.

[3] Fried JR; Polymer Science and Technology: 3rd edition (2014). Prantice Hall of Inida, New Delhi, India.

[4] Chanda M; Introduction to Polymer Science and Chemistry: A Problem-Solving Approach: 2nd edition (2013). CRC Press, Florida, USA.

[5] Gowariker VR, Viswanathan NV, Sreedhar J; Polymer Science: 2nd edition (2015). New Age International, New Delhi, India.

[6] Rohan; Market research report entitled "Flexible Packaging Market worth $99,621.9 Million by 2018". Dallas, Texas, USA. Available online at http://www.marketsandmarkets.com/PressReleases/flexible-packaging.asp

[7] Frequently asked questions on bioplastics (2015). Europian Bioplastics e.V., Berlin, Germany. Available online at http://en.european-bioplastics.org/press/faq-bioplastics/

[8] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL; Plastic waste inputs from land into the ocean. Science 347 (2015) 768-771.

[9] Sarker M, Rashid MM, Rahman MS; Conventional naphtha chemical produced from municipal solid low density polyethylene (LDPE) waste plastic. International Journal of Applied Chemistry 8 (2012) 153-163.

[10] Singh S; Study: Plastic consumption to double in India by 2016. Plastic News (2013). Available online at http://www.plasticsnews.com/article/20131204/NEWS/131209962/study-plastic-consumption-to-double-in-india-by-2016

[11] Clapp J, Swanston L; Doing away with plastic shopping bags: international patterns of norm emergence and policy implementation. Environmental Politics 18 (2009) 315-332.

[12] Mader FW; Plastics waste management in Europe. Makromolekulare Chemie Macromolecular Symposia, Wiley Online Library 57 (1992) 15-31.

[13] Sharma SK, Mudhoo A, Clark JH; A Handbook of Applied Biopolymer Technology: Synthesis, Degradation and Applications: 1st edition (2011). Royal Society of Chemistry, Cambridge CB4 0WF, UK.

[14] Eriksen M, Lebreton LCM, Carson HS, Thiel M, Moore CJ, Borerro JC, Galgani F, Ryan PG, Reisser J; Plastic pollution in the world's oceans: More than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PloS one 9 (2014) e111913.

[15] Halden RU; Plastics and health risks. Annual Review of Public Health 31 (2010) 179-194.

[16] Derraik JG; The pollution of the marine environment by plastic debris: a review. Marine Pollution Bulletin 44 (2002) 842-852.

[17] Orhan Y, Hrenovic J, Buyukgungor H; Biodegradation of plastic compost bags under controlled soil conditions. Acta Chimica Slovenica 51 (2004) 579-588.

[18] Patel GBS, Fagan SS, Julie M; A research study on "Bring your own bag and help saving plastic bags". Rutgers University Community Repository (2011), Rutgers University, New Jersey, USA. Available online at https://rucore.libraries.rutgers.edu /rutgers-lib/42560/

[19] Sepúlveda A, Schluep M, Renaud FG, Streicher M, Kuehr R, Hagelüken C, Gerecke AC; A review of the environmental fate and effects of hazardous substances released from electrical and electronic equipments during recycling: Examples from China and India. Environmental Impact Assessment Review 30 (2010) 28-41.

[20] Benítez A, Sánchez JJ, Arnal ML, Müller AJ, Rodríguez O, Morales G; Abiotic degradation of LDPE and LLDPE formulated with a pro-oxidant additive. Polymer Degradation and Stability 98 (2013) 490-501.

[21] Barnes DKA, Galgani F, Thompson RC, Barlaz M; Accumulation and fragmentation of plastic debris in global environments. Philosophical Transactions of the Royal Society B: Biological Sciences 364 (2009) 1985-1998.

[22] Hopewell J, Dvorak R, Kosior E; Plastics recycling: challenges and opportunities. Philosophical Transactions of the Royal Society B: Biological Sciences 364 (2009) 2115-2126.

[23] Song JH, Murphy RJ, Narayan R, Davies GBH; Biodegradable and compostable alternatives to conventional plastics. Philosophical Transactions of the Royal Society B: Biological Sciences 364 (2009) 2127-2139.

[24] Thompson RC, Moore CJ, Vom Saal FS, Swan SH; Plastics, the environment and human health: current consensus and future trends. Philosophical Transactions of the Royal Society B: Biological Sciences 364 (2009) 2153-2166.

[25] Raju P; Plastic waste a deadly threat to earth. Urban Update Magazine (2015). New Delhi, India. Available online at http://urbanupdate.in/environment/plastic-waste-deadly-threat-earth

[26] Sailaja RRN, Chanda M; Use of maleic anhydride–grafted polyethylene as compatibilizer for HDPE–tapioca starch blends: effects on mechanical properties. Journal of Applied Polymer Science 80 (2001) 863-872.

[27] Dintcheva NT, Mantia FPL; Recycling of the “light fraction” from municipal post-consumer plastics: effect of adding wood fibers. Polymers for Advanced Technologies 10 (1999) 607-614.

[28] Gironi F, Piemonte V; Bioplastics and petroleum-based plastics: strengths and weaknesses. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 33 (2011) 1949-1959.

[29] Lazarevic D, Aoustin E, Buclet N, Brandt N; Plastic waste management in the context of a European recycling society: comparing results and uncertainties in a life cycle perspective. Resources, Conservation and Recycling 55 (2010) 246-259.

[30] Konduri MKR, Koteswarareddy G, Rohini Kumar D, Venkata Reddy B, Lakshmi Narasu M; Effect of pro-oxidants on biodegradation of polyethylene (LDPE) by indigenous fungal isolate, *Aspergillus oryzae*. Journal of Applied Polymer Science 120 (2011) 3536-3545.

[31] Quiroz-Castillo JM, Rodríguez-Félix DE, Grijalva-Monteverde H, del Castillo-Castro T, Plascencia-Jatomea M, Rodríguez-Félix F, Herrera-Franco, PJ; Preparation of extruded polyethylene/chitosan blends compatibilized with polyethylene-graft-maleic anhydride. Carbohydrate Polymers 101 (2014) 1094-1100.

[32] Anderson KS, Hillmyer MA; The influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends. Polymer 45 (2004) 8809-8823.

[33] Rutkowska M, Jastrzębska M, Janik H; Biodegradation of polycaprolactone in sea water. Reactive and Functional Polymers 38 (1998) 27-30.

[34] Savenkova L, Gercberga Z, Nikolaeva V, Dzene A, Bibers I, Kalnin M; Mechanical properties and biodegradation characteristics of PHB-based films. Process Biochemistry 35 (2000) 573-579.

[35] Brandelero RPH, Yamashita F, Grossmann MVE; The effect of surfactant Tween 80 on the hydrophilicity, water vapor permeation, and the mechanical properties of

cassava starch and poly (butylene adipate-co-terephthalate)(PBAT) blend films. Carbohydrate Polymers 82 (2010) 1102-1109.

[36] Lim L-T, Auras R, Rubino M; Processing technologies for poly (lactic acid). Progress in Polymer Science 33 (2008) 820-852.

[37] Queiroz AUB, Collares-Queiroz FP; Innovation and industrial trends in bioplastics. Journal of Macromolecular Science Part C: Polymer Reviews 49 (2009) 65-78.

[38] Murphy R, Bartle I; Summary report, biodegradable polymers and sustainability: insight from life cycle assessment. A report in National Non-Food Crops Centre (2004), NNFCC, Biocentre, York, UK. Available online at http://www.nnfcc.co.uk/tools/biodegradable-polymers-and-sustainability-insights-from-lca

[39] Kfoury G, Raquez J-M, Hassouna F, Odent J, Toniazzo V, Ruch D, Dubois P; Recent advances in high performance poly (lactide): from “green” plasticization to super-tough materials via (reactive) compounding. Frontiers in Chemistry 1 (2013) 1-46.

[40] Blasco LS; Contribution to the study of thermal, biological and photo degradation of polylactide. Ph.D. Thesis (2012), Polytechnic University of Valencia, Valencia, Spain.

[41] Edwards KH; "Sorting through the latest names, claims and performance of degradable additives and how they impact compostable plastics" in US Composting Council Annual Meeting (2013), Bethesda, Maryland, USA.

[42] Bajpai PK, Bhunia, H; Bioplastics in the Waste Stream (2012). Smithers Rapra Publishing, Akron, Ohio, USA.

[43] Henton DE, Gruber PR, Lunt J, Randall J; Polylactic acid technology. Natural Fibers, Biopolymers, and Biocomposites 1 (2005) 527-77.

[44] Drumright RE, Gruber PR, Henton DE; Polylactic acid technology. Advanced Materials 12 (2000) 1841-1846.

[45] Bastioli C; "Biodegradable material for various applications" in Biopolymers: General Aspects and Special Applications, Steinbiichel A (Ed), Wiley-VCH Verlag GmbH, Germany (2003) pp. 61-70.

[46] Gérard T, Budtova T, Podshivalov A, Bronnikov S; Polylactide/poly (hydroxybutyrate-co-hydroxyvalerate) blends: Morphology and mechanical properties. Express Polymer Letters 8 (2014) 609-617.

[47] Singh G; Studies on degradable polymeric blends based on poly(lactic acid). Ph.D. Thesis (2010), Thapar University, Patiala, Punjab, India.

[48] Anna Dilfi KF; Linear Low density polyethylene-biodegradability using bacteria from marine benthic environment and photodegradability using ultraviolet light. Ph.D. Thesis (2011), Cochin University of Science & Technology, Kochi, India.

[49] Yousif E, Haddad R; Photodegradation and photostabilization of polymers, especially polystyrene: Review. Springer Plus 2 (2013) 398-460.

[50] Beyler CL, Hirschler MM; "Thermal decomposition of polymers" in SFPE Handbook of Fire Protection Engineering (2002) 110-131.

[51] Göpferich A; Mechanisms of polymer degradation and erosion. Biomaterials 17 (1996) 103-114.

[52] Salamone JC; Concise polymeric materials encyclopedia. Vol. 1 (1998), CRC Press, Taylor & Francis Group, London, UK.

[53] Chandra R, Rustgi R. Biodegradable polymers. Progress in Polymer Science 23 (1998) 1273-335.

[54] Reddy MM, Deighton M, Gupta RK, Bhattacharya SN, Parthasarathy R; Biodegradation of oxo-biodegradable polyethylene. Journal of Applied Polymer Science 111 (2009) 1426-1432.

[55] Müller RJ; "Biodegradability of polymers: regulations and methods for testing" in Biopolymers: General Aspects and Special Applications, Steinbiichel A (Ed), Wiley-VCH Verlag GmbH, Germany (2003) pp. 365-374.

[56] Leejarkpai T, Suwanmanee U, Rudeekit Y, Mungcharoen T; Biodegradable kinetics of plastics under controlled composting conditions. Waste Management 31 (2011) 1153-1161.

[57] Grima S, Bellon-Maurel V, Feuilloley P, Silvestre F; Aerobic biodegradation of polymers in solid-state conditions: A review of environmental and physicochemical parameter settings in laboratory simulations. Journal of Polymers and the Environment 8 (2000) 183-195.

[58] ASTM D5338: Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions (1998). West Conshohocken, Pennsylvania, USA.

[59] ISO 14855-1. Determination of the ultimate aerobic biodegradabilty and disintergration of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide (1999). Geneva, Switzerland, Europe.

[60] Psomiadou E, Arvanitoyannis I, Biliaderis CG, Ogawa H, Kawasaki N; Biodegradable films made from low density polyethylene (LDPE), wheat starch and soluble starch for food packaging applications Part 2. Carbohydrate Polymers 33 (1997) 227-242.

[61] Taghizadeh A, Sarazin P, Favis BD; High molecular weight plasticizers in thermoplastic starch/polyethylene blends. Journal of Materials Science 48 (2013) 1799-1811.

[62] Imre B, Pukánszky B; Compatibilization in bio-based and biodegradable polymer blends. European Polymer Journal 49 (2013) 1215-1233.

[63] Sharholy M, Ahmad K, Mahmood G, Trivedi R; Municipal solid waste management in Indian cities–A review. Waste Management 28 (2008) 459-467.

[64] Misra V, Pandey S; Hazardous waste, impact on health and environment for development of better waste management strategies in future in India. Environment International 31 (2005) 417-431.

[65] Sarkar P; "Solid waste management in Delhi–a social vulnerability study" in Proceedings of the Third International Conference on Environment and Health, York University, Ontario, Canada (2003) pp. 451-464.

[66] Olabis O; Polymer-polymer Miscibility. Academic Press (2012), Elsevier, Atlanta, Georgia, USA.

[67] Juikham S; Design and characterisation of novel blends of poly (lactic acid). Ph.D. Thesis (2012) Aston University, Birmingham, England, UK.

[68] Jones RG, Wilks ES, Metanomski WV, Kahovec J, Hess M, Stepto R, Kitayama T; Compendium of Polymer Terminology and Nomenclature: IUPAC Recommendations, 2008. Royal Society of Chemistry, Cambridge CB4 0WF, UK, 2009.

[69] Montagna LS, de Camargo Forte MM, Santana RMC; Induced degradation of polypropylene with an organic pro-degradant additive. Journal of Materials Science and Engineering 3 (2013) 123-131.

[70] Ammala A, Bateman S, Dean K, Petinakis E, Sangwan P, Wong S, Yuan Q, Yu L, Patrick C, Leong KH; An overview of degradable and biodegradable polyolefins. Progress in Polymer Science 36 (2011) 1015-1049.

[71] Ołdak D, Kaczmarek H, Buffeteau T, Sourisseau C; Photo-and bio-degradation processes in polyethylene, cellulose and their blends studied by ATR-FTIR and Raman spectroscopies. Journal of Materials Science 40 (2005) 4189-4198.

[72] Rutkowska M, Heimowska A, Krasowska K, Janik H; Biodegradability of polyethylene starch blends in sea water. Polish Journal of Environmental Studies 11 (2002) 267-272.

[73] St-Pierre N, Favis B, Ramsay B, Ramsay J, Verhoogt H; Processing and characterization of thermoplastic starch/polyethylene blends. Polymer 38 (1997) 647-655.

[74] Goheen S, Wool R; Degradation of polyethylene–starch blends in soil. Journal of Applied Polymer Science 42 (1991) 2691-2701.

[75] Sastry PK, Satyanarayana D, Mohan Rao D; Accelerated and environmental weathering studies on polyethylene–starch blend films. Journal of Applied Polymer Science 70 (1998) 2251-2257.

[76] Raj B; Low density polyethylene/starch blend films for food packaging applications. Advances in Polymer Technology 23 (2004) 32-45.

[77] Sharif A, Aalaie J, Shariatpanahi H, Hosseinkhanli H, Khoshniyat A; Study on the structure and properties of nanocomposites based on high-density polyethylene/starch blends. Journal of Polymer Research 18 (2011) 1955-1969.

[78] Vieyra H, Aguilar-Méndez M, Martín-Martínez S; Study of biodegradation evolution during composting of polyethylene–starch blends using scanning electron microscopy. Journal of Applied Polymer Science 127 (2013) 845-853.

[79] Chiellini E, Cioni F, Solaro R, Vallini G, Corti A, Pera A; Starch-filled polyethylene in a composting environment: Evidence for polyethylene matrix oxidation. Journal of Environmental Polymer Degradation 1 (1993) 167-70.

[80] Chiellini E, Solaro R, Corti A, Picci G, Leporini C, Pera A, Vallini G, Donaggio, P; Degradation of starch-filled polyethylene films in a composting environment. La Chimica e l'Industria 73 (1991) 656-663.

[81] Bastioli C; Biodegradable materials—present situation and future perspectives. Macromolecular Symposia, Wiley Online Library, 1998 pp. 193-204.

[82] Muthukumar T, Aravinthana A, Dineshram R, Venkatesan R, Doble M; Biodegradation of starch blended high density polyethylene using marine bacteria associated with biofilm formation and its isolation characterization. Journal of Microbial & Biochemical Technology 6 (2014) 116-122.

[83] Thakore I, Iyer S, Desai A, Lele A, Devi S; Morphology, thermomechanical properties, and biodegradability of low density polyethylene/starch blends. Journal of Applied Polymer Science 74 (1999) 2791-2802.

[84] Sharma N, Chang L, Chu Y, Ismail H, Ishiaku U, Ishak ZM; A study on the effect of pro-oxidant on the thermo-oxidative degradation behaviour of sago starch filled polyethylene. Polymer Degradation and Stability 71 (2001) 381-393.

[85] Muthukumar T, Aravinthan A, Mukesh D; Effect of environment on the degradation of starch and pro-oxidant blended polyolefins. Polymer Degradation and Stability 95 (2010) 1988-1993.

[86] Chiellini E, Corti A, D'Antone S; Oxo-biodegradable full carbon backbone polymers–biodegradation behaviour of thermally oxidized polyethylene in an aqueous medium. Polymer Degradation and Stability 92 (2007) 1378-1383.

[87] Evangelista RL, Sung W, Jane JL, Gelina RJ, Nikolov ZL; Effect of compounding and starch modification on properties of starch-filled low-density polyethylene. Industrial & Engineering Chemistry Research 30 (1991) 1841-1846.

[88] Parandoosh S, Hudson SM; The acetylation and enzymatic degradation of starch films. Journal of Applied Polymer Science 48 (1993) 787-791.

[89] Sagar AD, Merrill EW; Properties of fatty-acid esters of starch. Journal of Applied Polymer Science 58 (1995) 1647-1656.

[90] Aburto J, Thiebaud S, Alric I, Borredon E, Bikiaris D, Prinos J, Panayiotou C; Properties of octanoated starch and its blends with polyethylene. Carbohydrate Polymers 34 (1997) 101-112.

[91] Willett J; Mechanical properties of LDPE/granular starch composites. Journal of Applied Polymer Science 54 (1994) 1685-1695.

[92] Prinos J, Bikiaris D, Theologidis S, Panayiotou C; Preparation and characterization of LDPE/starch blends containing ethylene/vinyl acetate copolymer as compatibilizer. Polymer Engineering & Science 38 (1998) 954-964.

[93] Johnson KE, Pometto AL, Nikolov ZL; Degradation of degradable starch-polyethylene plastics in a compost environment. Applied and Environmental Microbiology 59 (1993) 1155-1161.

[94] El-Shafei HA, El-Nasser NHA, Kansoh AL, Ali AM; Biodegradation of disposable polyethylene by fungi and Streptomyces species. Polymer Degradation and Stability 62 (1998) 361-365.

[95] Lenardon MD, Munro CA, Gow NA; Chitin synthesis and fungal pathogenesis. Current Opinion in Microbiology 13 (2010) 416-423.

[96] Rathke TD, Hudson SM; Review of chitin and chitosan as fiber and film formers. Journal of Macromolecular Science, Part C: Polymer Reviews 34 (1994) 375-437.

[97] Wong DW, Gastineau FA, Gregorski KS, Tillin SJ, Pavlath AE; Chitosan-lipid films: microstructure and surface energy. Journal of Agricultural and Food Chemistry 40 (1992) 540-544.

[98] El Ghaouth A, Arul J, Ponnampalam R, Boulet M; Chitosan coating effect on storability and quality of fresh strawberries. Journal of Food Science 56 (1991) 1618-1620.

[99] Ghaouth A, Arul J, Ponnampalam R, Boulet M; Use of chitosan coating to reduce water loss and maintain quality of cucumber and bell pepper fruits. Journal of Food Processing and Preservation 15 (1991) 359-368.

[100] Ikejima T, Inoue Y; Crystallization behaviour and environmental biodegradability of the blend films of poly (3-hydroxybutyric acid) with chitin and chitosan. Carbohydrate Polymers 41 (2000) 351-356.

[101] Olabarrieta I, Forsström D, Gedde U, Hedenqvist M; Transport properties of chitosan and whey blended with poly (ε-caprolactone) assessed by standard permeability measurements and microcalorimetry. Polymer 42 (2001) 4401-4408.

[102] Suyatma NE, Copinet A, Tighzert L, Coma V; Mechanical and barrier properties of biodegradable films made from chitosan and poly (lactic acid) blends. Journal of Polymers and the Environment 12 (2004) 1-6.

[103] Rodríguez-Félix DE, Quiroz-Castillo JM, Grijalva-Monteverde H, Castillo-Castro T, Burruel-Ibarra SE, Rodríguez-Félix F, Madera-Santana T, Cabanillas RE, Herrera-Franco, PJ; Degradability of extruded polyethylene/chitosan blends compatibilized with polyethylene-graft-maleic anhydride under natural weathering. Journal of Applied Polymer Science 131 (2014) DOI: 10.1002/app.41045.

[104] Tian H, Tang Z, Zhuang X, Chen X, Jing X; Biodegradable synthetic polymers: preparation, functionalization and biomedical application. Progress in Polymer Science 37 (2012) 237-280.

[105] Rosa DS, Grillo D, Bardi MAG, Calil MR, Guedes CGF, Ramires EC, Frollini E; Mechanical, thermal and morphological characterization of polypropylene/ biodegradable polyester blends with additives. Polymer Testing 28 (2009) 836-842.

[106] Jayasekara R, Harding I, Bowater I, Lonergan G; Biodegradability of a selected range of polymers and polymer blends and standard methods for assessment of biodegradation. Journal of Polymers and the Environment 13 (2005) 231-251.

[107] Basu D, Datta C, Banerjee A; Biodegradability, mechanical properties, melt flow index, and morphology of polypropylene/amylose/amylose-ester blends. Journal of Applied Polymer Science 85 (2002) 1434-1442.

[108] Jana SC, Prieto A; On the development of natural fiber composites of high-temperature thermoplastic polymers. Journal of Applied Polymer Science 86 (2002) 2159-2167.

[109] Anderson KS, Hillmyer MA; Melt preparation and nucleation efficiency of polylactide stereocomplex crystallites. Polymer 47 (2006) 2030-2035.

[110] Zhang J, Jiang L, Zhu L, Jane JL, Mungara P; Morphology and properties of soy protein and polylactide blends. Biomacromolecules 7 (2006) 1551-1561.

[111] Soni S, Gupta H, Kumar N, Nishad DK, Mittal G, Bhatnagar A; Biodegradable biomaterials. Recent Patents on Biomedical Engineering 3 (2010) 30-40.

[112] Nagarajan S, Reddy BSR; Bio-absorbable polymers in implantation-an overview. Journal of Scientific and Industrial Research 68 (2009) 993-1009.

[113] Gupta AP, Kumar V; New emerging trends in synthetic biodegradable polymers - Polylactide: A critique. European Polymer Journal 43 (2007) 4053-4074.

[114] Watanabe T, Ohtake Y, Asabe H, Murakami N, Furukawa M; Biodegradability and degrading microbes of low-density polyethylene. Journal of Applied Polymer Science 111 (2009) 551-559.

[115] Orr IG, Hadar Y, Sivan A; Colonization, biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. Applied Microbiology and Biotechnology 65 (2004) 97-104.

[116] Hadad D, Geresh S, Sivan A; Biodegradation of polyethylene by the thermophilic bacterium *Brevibacillus borstelensis*. Journal of Applied Microbiology 98 (2005) 1093-1100.

[117] Wang Y, Hillmyer MA; Polyethylene-poly (L-lactide) diblock copolymers: Synthesis and compatibilization of poly (L-lactide)/polyethylene blends. Journal of Polymer Science Part A: Polymer Chemistry 39 (2001) 2755-2766.

[118] Rezende M *de* L, Rosa D *dos* S, Guedes C *das* GF, Fechine GJM, Nóbrega JA; Investigation of the effect of addition of calcium stearate on the properties of low-density polyethylene/poly (ε-caprolactone) blends. Journal of Materials Science 49 (2014) 1544-1555.

[119] Sheng J, Ma H, Yuan XB, Yuan XY, Shen NX, Bian DC; Relation of chain constitution with phase structure in blends: compatibility of two phases in blends of polyamide with low-density polyethylene and its ionomers. Journal of Applied Polymer Science 76 (2000) 488-494.

[120] Nair LS, Bender JD, Singh A, Sethuraman S, Greish YE, Brown PW, Allcock HR, Laurencin CT; Biodegradable poly [bis (ethyl alanato) phosphazene]-poly (lactide-co-glycolide) blends: miscibility and osteocompatibility evaluations. MRS Proceedings: Cambridge University Press 844 (2004). DOI: 10.1557/PROC-844-Y9.7.

[121] Biresaw G, Carriere C; Compatibility and mechanical properties of blends of polystyrene with biodegradable polyesters. Composites Part A: Applied Science and Manufacturing 35 (2004) 313-320.

[122] Sabet SS, Katbab A; Interfacially compatibilized poly (lactic acid) and poly (lactic acid)/polycaprolactone/organoclay nanocomposites with improved biodegradability and barrier properties: effects of the compatibilizer structural parameters and feeding route. Journal of Applied Polymer Science 111 (2009) 1954-1963.

[123] Singh G, Bhunia H, Bajpai PK, Choudhary V; Thermal degradation and physical aging of linear low density polyethylene and poly(l-lactic acid) blends. Journal of Polymer Engineering 32 (2012) 59-66.

[124] Singh G, Bhunia H, Rajor A, Choudhary V; Thermal properties and degradation characteristics of polylactide, linear low density polyethylene, and their blends. Polymer Bulletin 66 (2010) 939-953.

[125] Singh G, Kaur N, Bhunia H, Bajpai PK, Mandal UK; Degradation behaviours of linear low-density polyethylene and poly (L-lactic acid) blends. Journal of Applied Polymer Science 124 (2012) 1993-1998.

[126] Kasirajan S, Ngouajio M; Polyethylene and biodegradable mulches for agricultural applications: a review. Agronomy for Sustainable Development 32 (2012) 501-529.

[127] Omura M, Tsukegi T, Shirai Y, Nishida H, Endo T; Thermal degradation behaviour of poly (lactic acid) in a blend with polyethylene. Industrial & Engineering Chemistry Research 45 (2006) 2949-2953.

[128] Jakubowicz I; Evaluation of degradability of biodegradable polyethylene (PE). Polymer Degradation and Stability 80 (2003) 39-43.

[129] Albertsson AC, Karlsson S; The three stages in degradation of polymers—polyethylene as a model substance. Journal of Applied Polymer Science 35 (1988) 1289-1302.

[130] Abrusci C, Pablos JL, Corrales T, López-Marín J, Marín I, Catalina F; Biodegradation of photo-degraded mulching films based on polyethylenes and stearates of calcium and iron as pro-oxidant additives. International Biodeterioration & Biodegradation 65 (2011) 451-459.

[131] Abrusci C, Pablos J, Marín I, Espí E, Corrales T, Catalina F; Comparative effect of metal stearates as pro-oxidant additives on bacterial biodegradation of thermal-and

photo-degraded low density polyethylene mulching films. International Biodeterioration & Biodegradation 83 (2013) 25-32.

[132] Fontanella S, Bonhomme S, Koutny M, Husarova L, Brusson J-M, Courdavault J-P, Pitteri S, Samuel G, Pichon G, Lemaire J; Comparison of the biodegradability of various polyethylene films containing pro-oxidant additives. Polymer Degradation and Stability 95 (2010) 1011-1021.

[133] Fontanella S, Bonhomme S, Brusson J-M, Pitteri S, Samuel G, Pichon G, Lacoste J, Fromageot D, Lemaire J, Delort A-M; Comparison of biodegradability of various polypropylene films containing pro-oxidant additives based on Mn, Mn/Fe or Co. Polymer Degradation and Stability 98 (2013) 875-884.

[134] Kyrikou I, Briassoulis D, Hiskakis M, Babou E; Analysis of photo-chemical degradation behaviour of polyethylene mulching film with pro-oxidants. Polymer Degradation and Stability 96 (2011) 2237-2252.

[135] Corti A, Sudhakar M, Chiellini E; Assessment of the whole environmental degradation of oxo-biodegradable linear low density polyethylene (LLDPE) films designed for mulching applications. Journal of Polymers and the Environment 20 (2012) 1007-1018.

[136] Corti A, Muniyasamy S, Vitali M, Imam SH, Chiellini E; Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. Polymer Degradation and Stability 95 (2010) 1106-1114.

[137] Pablos J, Abrusci C, Marín I, López-Marín J, Catalina F, Espí E, Corrales T; Photodegradation of polyethylenes: comparative effect of Fe and Ca-stearates as pro-oxidant additives. Polymer Degradation and Stability 95 (2010) 2057-2064.

[138] Chiellini E, Corti A, Swift G; Biodegradation of thermally-oxidized, fragmented low-density polyethylenes. Polymer Degradation and Stability 81 (2003) 341-351.

[139] Steinbüchel A. Biopolymers: General Aspects and Special Applications (2005), Wiley-VCH Verlag GmbH, Germany.

[140] Orhan Y, Büyükgüngör H; Enhancement of biodegradability of disposable polyethylene in controlled biological soil. International Biodeterioration & Biodegradation 45 (2000) 49-55.

[141] Krzan A, Hemjinda S, Miertus S, Corti A, Chiellini E; Standardization and certification in the area of environmentally degradable plastics. Polymer Degradation and Stability 91 (2006) 2819-2833.

[142] Uematsu S, Murakami A, Hiyoshi K, Tsukamoto Y, Saida H, Tsuji M, Hoshino A; Accurate and easy evaluation of aerobic microbial-degradability of biodegradable plastics under controlled soil. Polymer Preprints-America 43 (2002) 930-931.

[143] Moura I, Machado AV, Duarte FM, Nogueira R; Biodegradability assessment of aliphatic polyesters-based blends using standard methods. Journal of Applied Polymer Science 119 (2011) 3338-3346.

[144] Gonçalves S, Martins-Franchetti S; Respirometric evaluation of the biodegradability of films of PE/PHBV Blends. International Journal of Material Science 3 (2013) 54-60.

[145] Li G, Sarazin P, Orts WJ, Imam SH, Favis BD; Biodegradation of thermoplastic starch and its blends with poly (lactic acid) and polyethylene: influence of morphology. Macromolecular Chemistry and Physics 212 (2011) 1147-1154.

[146] Sangwan P, Way C, Wu DY; New insight into biodegradation of polylactide (PLA)/clay nanocomposites using molecular ecological techniques. Macromolecular Bioscience 9 (2009) 677-686.

[147] Ruka DR, Sangwan P, Garvey CJ, Simon GP, Dean KM; Biodegradability of poly-3-hydroxybutyrate/bacterial cellulose composites under aerobic conditions-measured via evolution of carbon dioxide, spectroscopic and diffraction methods. Environmental Science & Technology (2015) DOI: 10.1021/es5044485.

[148] Na B, Zhang Q, Fu Q, Zhang G, Shen K; Super polyolefin blends achieved via dynamic packing injection molding: the morphology and mechanical properties of HDPE/EVA blends. Polymer 43 (2002) 7367-7376.

[149] Auras RA, Harte B, Selke S, Hernandez R; Mechanical, physical, and barrier properties of poly (lactide) films. Journal of Plastic Film and Sheeting 19 (2003) 123-135.

[150] Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo J-E; Polymer biodegradation: Mechanisms and estimation techniques–A review. Chemosphere 73 (2008) 429-442.

[151] Eubeler JP, Zok S, Bernhard M, Knepper TP; Environmental biodegradation of synthetic polymers I. Test methodologies and procedures. TrAC Trends in Analytical Chemistry 28 (2009) 1057-1072.

[152] Kopčilová M, Hubáčková J, Růžička J, Dvořáčková M, Julinová M, Koutný M, Tomalová M, Alexy P, Bugaj P, Filip J; Biodegradability and mechanical properties of poly (vinyl alcohol)-based blend plastics prepared through extrusion method. Journal of Polymers and the Environment 21 (2013) 88-94.

[153] Di Lorenzo ML, Rubino P, Cocca M; Miscibility and properties of poly (l-lactic acid)/poly (butylene terephthalate) blends. European Polymer Journal 49 (2013) 3309-3317.

[154] Zhang JF, Sun X; Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. Biomacromolecules 5 (2004) 1446-1451.

[155] Langelaan H, de Boer AP; Crystallization of thermotropic liquid crystalline HBA/HNA copolymers. Polymer 37 (1996) 5667-5680.

[156] Dong W, Ma P, Wang S, Chen M, Cai X, Zhang Y; Effect of partial crosslinking on morphology and properties of the poly (β-hydroxybutyrate)/poly (d, l-lactic acid) blends. Polymer Degradation and Stability 98 (2013) 1549-1555.

[157] Abdolrasouli MH, Nazockdast H, Sadeghi GMM, Kaschta J; Morphology development, melt linear viscoelastic properties and crystallinity of polylactide/polyethylene/organoclay blend nanocomposites. Journal of Applied Polymer Science 132 (2015) DOI: 10.1002/app.41300.

[158] Maiti P, Nam PH, Okamoto M, Hasegawa N, Usuki A; Influence of crystallization on intercalation, morphology, and mechanical properties of polypropylene/clay nanocomposites. Macromolecules 35 (2002) 2042-2049.

[159] Baral D, De P, Nando GB; Thermal characterization of mica-filled thermoplastic polyurethane composites. Polymer Degradation and Stability 65 (1999) 47-51.

[160] Bohlmann GM; "General characteristics, processability, industrial applications and market evolution of biodegradable polymers" in Handbook of Biodegradable Polymers, Rapra Technology Ltd, Shawbury, UK (2005) pp. 183-212.

[161] Mishra AK, Chattopadhyay S, Nando GB; Effect of modifiers on morphology and thermal properties of novel thermoplastic polyurethane-peptized laponite nanocomposite. Journal of Applied Polymer Science 115 (2010) 558-569.

[162] Sadeghi F, Ajji A, Carreau PJ; Analysis of row nucleated lamellar morphology of polypropylene obtained from the cast film process: effect of melt rheology and process conditions. Polymer Engineering & Science 47 (2007) 1170-1178.

[163] Eshtiaghi N, Markis F, Yap SD, Baudez J-C, Slatter P; Rheological characterisation of municipal sludge: A review. Water research 47 (2013) 5493-5510.

[164] Jose S, Aprem A, Francis B, Chandy M, Werner P, Alstaedt V, Thomas S; Phase morphology, crystallisation behaviour and mechanical properties of isotactic polypropylene/high density polyethylene blends. European Polymer Journal 40 (2004) 2105-2115.

[165] Kwak G, Inoue K, Tominaga Y, Asai S, Sumita M; Characterization of the vibrational damping loss factor and viscoelastic properties of ethylene–propylene rubbers reinforced with micro-scale fillers. Journal of Applied Polymer Science 82 (2001) 3058-3066.

[166] Massey LK; Permeability properties of plastics and elastomers: a guide to packaging and barrier materials. 2nd edition (2003) William Andrew, New York, USA.

[167] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N; ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta 520 (2011) 1-19.

[168] Kalbende PP, Tarase MV, Zade AB; Preparation, characterization, and thermal degradation studies of p-nitrophenol-based copolymer. Journal of Chemistry 2013 (2012) 1-9.

[169] Chrissafis K, Paraskevopoulos K, Pavlidou E, Bikiaris D; Thermal degradation mechanism of HDPE nanocomposites containing fumed silica nanoparticles. Thermochimica Acta 485 (2009) 65-71.

[170] Li XG; Thermogravimetric kinetics of thermotropic copolyesters containing p-oxybenzoate unit by multiple heating-rate methods. Journal of Applied Polymer Science 74 (1999) 2016-2028.

[171] Friedman HL; Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. Journal of Polymer Science Part C: Polymer Symposia: Wiley Online Library 6 (1964) 183-195.

[172] Friedman HL; Kinetics and gaseous products of thermal decomposition of polymers. Journal of Macromolecular Science-Chemistry 1 (1967) 57-79.

[173] Freeman ES, Carroll B; The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. The Journal of Physical Chemistry 62 (1958) 394-397.

[174] Coats A, Redfern J; Kinetic parameters from thermogravimetric data. Nature 201 (1964) 68-69.

[175] Flynn JH, Wall LA; A quick, direct method for the determination of activation energy from thermogravimetric data. Journal of Polymer Science Part B: Polymer Letters 4 (1966) 323-328.

[176] Flynn JH, Wall LA; General treatment of the thermogravimetry of polymers. Journal of Research of the National Bureau of Standards 70 (1966) 487-523.

[177] Ozawa T; A new method of analyzing thermogravimetric data. Bulletin of the Chemical Society of Japan 38 (1965) 1881-1886.

[178] Ozawa T; Kinetic analysis of derivative curves in thermal analysis. Journal of Thermal Analysis and Calorimetry 2 (1970) 301-324.

[179] Reich L; A rapid estimation of activation energy from thermogravimetric traces. Journal of Polymer Science Part B: Polymer Letters 2 (1964) 621-623.

[180] Kim S, Park JK; Characterization of thermal reaction by peak temperature and height of DTG curves. Thermochimica Acta 264 (1995) 137-156.

[181] Kissinger HE; Reaction kinetics in differential thermal analysis. Analytical Chemistry 29 (1957) 1702-1706.

[182] Šimon P; Isoconversional methods. Journal of Thermal Analysis and Calorimetry 76 (2004) 123-132.

[183] Khawam A; Application of solid-state kinetics to desolvation reactions. Ph.D. Thesis (2007) University of Iowa, Iowa, USA.

[184] Vyazovkin S, Wight CA; Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochimica Acta 340 (1999) 53-68.

[185] Yu Y, Wang M, Gan W, Tao Q, Li S; Polymerization-induced viscoelastic phase separation in polyethersulfone-modified epoxy systems. The Journal of Physical Chemistry B 108 (2004) 6208-6215.

[186] Premkumar T, Govindarajan S, Coles AE, Wight CA; Thermal decomposition kinetics of hydrazinium cerium 2, 3-pyrazinedicarboxylate hydrate: a new precursor for CeO_2. The Journal of Physical Chemistry B 109 (2005) 6126-6129.

[187] Burnham AK, Dinh L; A comparison of isoconversional and model-fitting approaches to kinetic parameter estimation and application predictions. Journal of Thermal Analysis and Calorimetry 89 (2007) 479-490.

[188] Vyazovkin S; Thermal analysis. Analytical Chemistry 74 (2002) 2749-2762.

[189] Ado JM, Morales J; Defects of thermogravimetric analysis for discerning between first order reactions and those taking place through the Avrami-Erofeev's mechanism. Thermochimica Acta 16 (1976) 382-387.

[190] Criado J, Morales J; Thermal decomposition reactions of solids controlled by diffusion and phase-boundary processes: possible misinterpretation of the mechanism from thermogravimetric data. Thermochimica Acta 19 (1977) 305-317.

[191] Sinfronio F, Santos J, Pereira L, Souza A, Conceição M, Fernandes Jr V; Kinetic of thermal degradation of low-density and high-density polyethylene by non-isothermal thermogravimetry. Journal of Thermal Analysis and Calorimetry 79 (2005) 393-399.

[192] Lomakin S, Rogovina S, Grachev A, Prut E, Alexanyan CV; Thermal degradation of biodegradable blends of polyethylene with cellulose and ethylcellulose. Thermochimica Acta 521 (2011) 66-73.

[193] Budrugeac P; Theory and practice in the thermoanalytical kinetics of complex processes: Application for the isothermal and non-isothermal thermal degradation of HDPE. Thermochimica Acta 500 (2010) 30-37.

[194] Yang R, Liu Y, Yu J, Wang K; Thermal oxidation products and kinetics of polyethylene composites. Polymer Degradation and Stability 91 (2006) 1651-1657.

[195] Santana O, Rodríguez C, Belzunce J, Gámez-Pérez J, Carrasco F, Maspoch ML; Fracture behaviour of de-aged poly (lactic acid) assessed by essential work of fracture and J-Integral methods. Polymer Testing 29 (2010) 984-990.

[196] Opfermann J, Kaisersberger E, Flammersheim H; Model-free analysis of thermoanalytical data-advantages and limitations. Thermochimica Acta 391 (2002) 119-127.

[197] Khawam A, Flanagan DR; Role of isoconversional methods in varying activation energies of solid-state kinetics: II. Nonisothermal kinetic studies. Thermochimica Acta 436 (2005) 101-112.

[198] Khawam A, Flanagan DR; Role of isoconversional methods in varying activation energies of solid-state kinetics: I. Isothermal kinetic studies. Thermochimica Acta 429 (2005) 93-102.

[199] Zhou D, Schmitt EA, Zhang GG, Law D, Vyazovkin S, Wight CA; Crystallization kinetics of amorphous nifedipine studied by model-fitting and model-free approaches. Journal of Pharmaceutical Sciences 92 (2003) 1779-1792.

[200] Zhang L, Ma J, Zhu X, Liang B; Kinetics of thermal degradation of thermotropic poly (p-oxybenzoate-co-ethylene-2,6-naphthalate) by single heating rate methods. Journal of Applied Polymer Science 91 (2004) 3915-3920.

[201] Kumar S, Kumar M, Lal S, Kumar S, Arora S; Model free multiple heating rate degradation kinetic studies of modified celluloses. Chemical Science Transactions 4 (2015) 181-193.

[202] Paik P, Kar KK; Thermal degradation kinetics and estimation of lifetime of polyethylene particles: effects of particle size. Materials Chemistry and Physics 113 (2009) 953-961.

[203] Paik P, Kar KK; Kinetics of thermal degradation and estimation of lifetime for polypropylene particles: Effects of particle size. Polymer Degradation and Stability 93 (2008) 24-35.

[204] Ceamanos J, Mastral J, Millera A, Aldea M; Kinetics of pyrolysis of high density polyethylene. Comparison of isothermal and dynamic experiments. Journal of Analytical and Applied Pyrolysis 65 (2002) 93-110.

[205] Sbirrazzuoli N, Vincent L, Mija A, Guigo N; Integral, differential and advanced isoconversional methods: complex mechanisms and isothermal predicted conversion–time curves. Chemometrics and Intelligent Laboratory Systems 96 (2009) 219-226.

[206] Brown ME, Dollimore D, Galwey AK; Reactions in the solid state. Vol. 22, 1st edition (1980) Elsevier, USA.

[207] Núñez L, Fraga F, Nunez M, Villanueva M; Thermogravimetric study of the decomposition process of the system BADGE (n=0)/1, 2 DCH. Polymer 41 (2000) 4635-4641.

[208] Hinsken H, Moss S, Pauquet J-R, Zweifel H; Degradation of polyolefins during melt processing. Polymer Degradation and Stability 34 (1991) 279-293.

[209] Tang W, Li XG, Yan D; Thermal decomposition kinetics of thermotropic copolyesters made from trans-p-hydroxycinnamic acid and p-hydroxybenzoic acid. Journal of Applied Polymer Science 91(2004) 445-454.

[210] Roy P, Surekha P, Rajagopal C, Choudhary V; Thermal degradation studies of LDPE containing cobalt stearate as pro-oxidant. Express Polymer Letters 1 (2007) 208-216.

[211] Kiran N, Ekinci E, Snape C; Recyling of plastic wastes via pyrolysis. Resources, Conservation and Recycling 29 (2000) 273-283.

[212] Heikkinen J, Hordijk J, De Jong W, Spliethoff H; Thermogravimetry as a tool to classify waste components to be used for energy generation. Journal of Analytical and Applied Pyrolysis 71 (2004) 883-900.

[213] Domınguez A, Blanco C, Barriocanal C, Alvarez R, Díez M; Gas chromatographic study of the volatile products from co-pyrolysis of coal and polyethylene wastes. Journal of Chromatography A 918 (2001) 135-144.

[214] Koo J-K, Kim S-W; Reaction kinetic model for optimal pyrolysis of plastic waste mixtures. Waste Management & Research 11 (1993) 515-529.

[215] McCoy BJ; Distribution kinetics for temperature-programmed pyrolysis. Industrial & Engineering Chemistry Research 38 (1999) 4531-4537.

[216] Toop DJ; Theory of life testing and use of thermogravimetric analysis to predict the thermal life of wire enamels. IEEE Transactions on Electrical Insulation E1-6 (1971) 2-14.

[217] Lugauskas A, Levinskait L, Pečiulyt D; Micromycetes as deterioration agents of polymeric materials. International Biodeterioration & Biodegradation 52 (2003) 233-242.

[218] Kijchavengkul T, Auras R, Rubino M, Selke S, Ngouajio M, Fernandez RT; Biodegradation and hydrolysis rate of aliphatic aromatic polyester. Polymer Degradation and Stability 95 (2010) 2641-2647.

[219] Pagga U; Testing biodegradability with standardized methods. Chemosphere 35 (1997) 2953-2972.