BIODEGRADABLE POLYMER BLENDS/COMPOSITES, WITH HIGH-PERFORMANCE CHARACTERISTICS, FOR PACKAGING APPLICATION

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2021

AUCKLAND, NEW ZEALAND

Biodegradable Polymer Blends/Composites, with High-Performance Characteristics, for Packaging Application

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A thesis submitted to the Auckland University of Technology

In fulfillment of the requirements for the degree of

Doctor of Philosophy (Ph.D.)

May 2021

Faculty of Design & Creative Technology

School of Engineering

Auckland University of Technology

Auckland, New Zealand

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Acknowledgments

I want to thank my Primary Supervisor Dr. Maximiano Ramos, Senior Lecturer - Mechanical and Production, Institute of Biomedical Technologies (IBTec), Auckland University of Technology (AUT) University, Auckland, for providing an opportunity to experience independent research. I would also like to thank my Secondary Supervisor, Professor Ahmed Al- Jumaily, Director, IBTec, AUT, Auckland, for his support and encouragement throughout the years in this research. I thank Yelena Dumanovic, Administrative & Research Assistant, IBTec, AUT, for her constant support. I want to thank Dr. G. Sasikumar for sharing his expertise. I would also like to acknowledge Professor Owen Yong, food science & microbiology, AUT, and Dr. Adrian Owens, Senior Technician, applied science, AUT, for their mechanical test support. I must appreciate Mr. Jim Crosson & the team who helped me prepare the required experimental mold. Following that, I want to thank Noemi Gutierrez-Maddox, senior lecturer, food science, for helping me with the experiments related to microbiology. I appreciate Yuan Tao for her support for sem analysis.

I thank my parents Govindan Rengan and Sasikala Govindan, for their blessings and prayers throughout my life. Finally, I thank my lovable wife, Priyadharshini Srinivasan, and my dear son, Pranav Krishna Srinivasan, for their support and encouragement.

Abstract

This research project focuses on developing biodegradable polymer films for flexible packaging applications with high-performance characteristics.

During this research, three biodegradable polymers, namely, Polybutylene succinate (PBS), Polyhydroxybutyrate (PHB), and Polylactic acid (PLA), were selected and investigated to improve their performance.

Three strategies were adopted for improvement; namely, i) by blending with Polycaprolactone (PCL), a highly biodegradable polymer, ii) by plasticization with three plasticizers, and iii) by the fabrication of nanocomposites/ by incorporating nanomaterials such as nano-cellulose and nano-clay.

Polymer films of various compositions were fabricated by injection molding, followed by hot-pressing and carried out an investigation of the tensile properties, water vapor transmission rate (WVTR)/ barrier properties, and biodegradability characteristics (in-home compost & seawater medium) of polymer films, and analyzed the effect of blending, plasticization, and nanomaterials.

The investigation carried out on blending of PBS, PHB, and PLA with PCL (with 10, 20, 30, and 40 wt% PCL) demonstrated enhancement of tensile elongation (ε), improvement in water vapor barrier property (decrease in WVTR), and increase in the biodegradation rate (in-home compost and seawater), with the addition of PCL, though with a slight decrease in tensile strength (σ). It was concluded from the studies on blending that polymer blending with approximately 10-20wt % PCL offer overall enhancement of polymer properties.

Studies carried out on plasticization of PBS-PCL20, PHB-PCL20, and PLA-PCL20 blends, with three plasticizers, [GTA, a monomeric plasticizer P1; Ultramoll, a polymeric plasticizer P2; and mixed plasticizer P3 (1: 1 mix of P1 and P2)], with 5 wt% plasticizer loading, indicated, a substantial increase in elongation at break and biodegradability, with the addition of all the three plasticizers, though with a decrease in tensile strength (σ) and water vapor barrier property. It was

concluded from the plasticization study that mixed plasticizer P3 offers the best overall performance enhancement.

An investigation carried out on nanocomposites of PBS, PHB and PLA, prepared by incorporating nano cellulose and nano clay (1, 3, and 6 wt%) in plasticized blends, (PBS-PCL20-P3, PHB-PCL20-P3, and PLA-PCL20-P3) demonstrated improved water vapor barrier properties (decrease in WVTR), improved tensile strength (except for PLA), and higher biodegradation rate with the addition of both nano cellulose and nano clay. Though a decrease in elongation at break was observed with nanomaterials' addition to the plasticized blends, the cumulative improvement was observed for neat polymers.

Studies on nanomaterial content's effect indicated that the best performance was obtained with 1wt % nano cellulose and 6% nano clay, which differ only slightly in properties.

The nanocomposites with nano cellulose (1wt%), namely PBS-PCL20-P3-nCell1, PHB-PCL20-P3- nCell1, and PLA-PCL20-P3- nCell1 was found to have improved properties, such as higher tensile elongation by 50%, 168%, and 494%; higher water vapor barrier properties (lesser WVTR) by 59%, 46% and 48%; higher biodegradation rate in home compost media by 56%, 13%, and 93%; and higher biodegradation rate in seawater media (after 180 days) by 79%, 10%, and 92% respectively, compared to neat PBS, PHB and PLA. The nanocomposites with 6 wt% nano clay were found to have slightly higher tensile strength and water vapor barrier properties, though slightly lower ductility and biodegradability. Hence nanocomposites with 1% nano cellulose or 6% nano clay may be used depending on the application requirement.

The present investigation thus demonstrated the overall performance improvement of PBS, PHB, and PLA polymers through blending, plasticization, and nanomaterials.

The present investigation has also generated valuable data on biodegradation of PBS, PHB and PLA polymers, PCL blends, plasticized blends, and nanocomposites under ambient temperature/ home composting conditions and marine environment, which will be of great help for future researchers.

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Abbreviations

AS	Australian Standard
ASTM	American Society for Testing and Materials International
ATBC	Acetyl o-tributyl citrate
$BaCl_2$	Barium chloride
$BaCO_3$	Barium Carbonate
BC	Bacterial Cellulose
BD - C	Biodegradation compost
BD - S	Biodegradation Seawater
CF	Cellulose fibers
CH_4	Methane
CNC	Cellulose nanocrystals
CNC-g-PCL	PCL grafted CNC
CNC-g-PLLA	PLA grafted CNC
CNF	Carbon nanofibrils
CNT	Carbon nanotubes
CO_2	Carbon dioxide
CW	Cellulose whisker
DMA	Dynamic mechanical analysis
DMTA	Dynamic mechanical, thermal analysis
DOA	Bis(2-ethylhexyl) adipate
DSC	Differential scanning calorimetry
D_t	% Biodegradation
EB	Elongation at break
EC	Ethylcellulose
EIS	Electrochemical impedance spectroscopy
ESBO / ESO	epoxidized vegetable oils / epoxidized soybean oil
expt	experiment
Fig	Figure
FTIR	Fourier-transform infrared spectroscopy
GONS	Graphene oxide nanosheets.
GPa	Giga Pascal
GPC	Gel permeation chromatography
GTA	Triacetin/ glycerol triacetate
H_2O	Water
HCl	Hydrogen chloride

HDPE	High-density Polyethylene
HDT	Heat distortion temperature
ISO	International Standards Organization
K_2CO_3	Potassium carbonate
KCl	Potassium chloride
KH_4Cl	Potassium dihydrogen phosphate
KN	Kilo newton
KOH	Potassium hydroxide
kv	Kilovolts
LDPE	Low-density polyethylene
LOI	Loss of ignition
MCC	Microcrystalline cellulose
MD	Machine direction
MFR	Melt flow rate
mL	Millilitre
MLO	Maleinized linseed oil
Mol wt / Mw	Molecular weight
MPa	Mega Pascal
mPCL	Modified Polycaprolactone
MWCNT	Multiwalled carbon nanotubes
Nano – $CaCO_3$	Nano calcium carbonate
nCell	Nano cellulose
nClay	Nano clay
NF T 51-800	French standard
NH_4Cl	Ammonium chloride
nm	Nanometer
NMR	Nuclear Magnetic Resonance Spectroscopy
NY11	nylon 11
O_2	Oxygen
OLA	Lactic acid oligomer
OM	Organic matter
OMLS	Organically Modified Layered Silicates
OMMT	Organically modified montmorillonite clay
OTR	Oxygen transmission rate
P(BS-co-CL)	Poly (butylene succinate-co-caprolactone)
P1	Monomeric Plasticizer
P2	Polymeric Plasticizer
P3	Mixture of monomeric and polymeric Plasticizer
PA	Polyamide

PBAT	Poly (butylene adipate-co-terephthalate)
PBS	Polybutylene succinate
PBS - PEG	Phosphate-buffered saline solution – Polyethylene glycol
PBSA	Polybutylene succinate adipate
PCL	Polycaprolactone
PDLA	Poly-D-lactic acid
PDLLA	Poly-DL-lactic acid
PE	Polythene
PEG	Polyethylene glycol
PEO-PPO-PEO	Poly (ethylene oxide)-block-poly(propylene oxide)-block poly(ethylene oxide)
PES	Polyethylene succinate
PET	Polyethylene terephthalate
PGA	Polyglycolic acid
pH	Potential of hydrogen or power of hydrogen
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Poly (3-hydroxybutyrate-co-3 hydroxy valerate
PHV	Polyhydroxyvalerate
PLA	Polylactic acid
PLA-b-PEG	Poly(D, L-lactide)-b-poly(ethylene glycol) copolymers
PLLA	poly-L-lactic acid
PP	Polypropylene
ppt	Parts per thousand
PS	Polystyrene
PVC	Polyvinyl chloride
PVOH	Polyvinyl Alcohol
RH	Relative humidity
S - CNC	Surfactant - modified Cellulose nanocrystals
SEM	Scanning Electron Microscopy
SN	Starch nanocrystals
TB	Glyceryl tributyrate
TBC	Tributyl citrate
T_d	High decomposition temperature
TEC	Triethyl citrate
T_g	Glass transition temperature

$ThCO_2$	Theoretical amount of CO2 evolved from the test sample/reference sample
TiO_2	Titanium oxide
T_m	Melting Temperature
TOC	Total organic carbon of the sample
TR	Transmission rate
TS	Tensile strength
TSM	Thermoplastic soy meal protein
UM	Ultramoll IV
UV	Ultraviolet
V_{final}	ml of HCl to titrate unreacted KOH
V_{HCl}	ml of HCl corresponding to KOH reacted with CO_2
$V_{initial}$	ml of HCl needed to titrate fresh KOH
WHC	Water holding capacity
WVTR	Water vapor transmission rate
XRD	X-ray diffraction
YM	Youngs modulus
ZnO	Zinc oxide

Symbols

˚C	Degree Celsius
˚F	Fahrenheit Celsius
A	Area
B	Blank
C	Carbon
cc	Cubic centimeter
cm	Centimeter
D	Diffusion coefficient
d	Day
ε	Tensile elongation / elongation at break
g	Gram
H	Hydrogen
h	Hour
I	Interaction factor
J	Joule
kg	kilogram
l	Thickness
L	Litre
m	Meter/ Mass
mil	One-thousandth of an inch
ml	Milli liter
mm	Millimeter
mol	Mole
N	Normality
O	Oxygen
OH	Hydroxide
p	Pressure
P	Property / permeability
ϕ	Volume fraction
Pa	Pascal
Q	Quantity
S	Solubility coefficient
s	Seconds
t	Time
T	Test samples
V	Volume
V_B	Blank Vessels
V_R	Reference vessels

V_T	Test vessels
w	Weight
δ	Solubility factor
Δp	partial pressure difference
Δp	Partial pressure
µl	Micro liters
µm	Micrometre
Σ	Cumulative
σ	Tensile strength

Chapter 1 Introduction

This chapter provides a broad overview of the present investigation. It also gives an outline of the remaining chapters and summarizes the way the thesis has been organized.

1.0 Background

Polymers/ plastics have become an indispensable material of our everyday life. They are being used in almost all the industrial sectors, including packaging, construction, electrical, electronics, medical, aerospace, and transportation [1-4]. The packaging is the most extensive application of polymers/ plastics among the various sectors, with a market share of more than 40%, as illustrated in Fig 1.1 [5, 6]. The most commonly used polymers/ traditional plastics include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), and polyamide (PA).

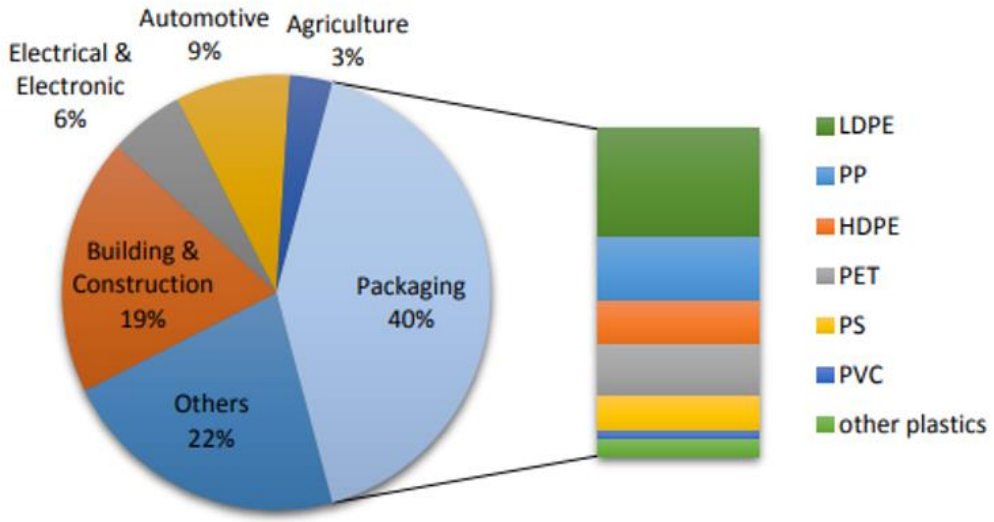

Fig 1. 1 Global market share of plastics, by application [5]

Though the introduction of polymers has revolutionized the progress of all the industries and transformed our lives in many positive ways, excessive use of traditional polymers has created many environmental pollution issues [7-10].

1.1 Environmental issues with traditional plastics & Need for biodegradable polymers-for packaging

Every year, more than 300 million tons of traditional plastics are being produced globally, and the rate of consumption is increasing very fast [11]. Plastics production was 7 million tonnes in 1960 and is expected to rise to 540 million tonnes by 2020 [12]. Wastes generated from these polymers decompose very slowly and take hundreds of years for degradation, or in other words, they are considered non-biodegradable [13, 14]. It is estimated that more than 60% of plastic waste is discarded in the environment (a small percentage is incinerated and only a small percentage is recycled), and hence the cumulative plastic waste accumulation in natural environment/ landfills by the year 2050 will be about 12,000 million metric tons, as illustrated in Fig.1.2. [6].

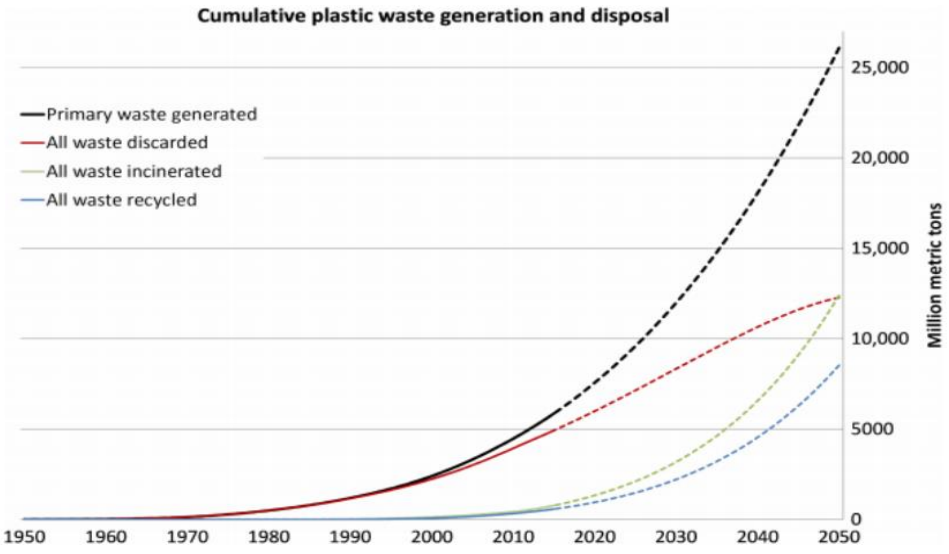

Fig 1. 2 Cumulative plastics waste generation and disposal[6]

Many plastic wastes are discarded /littered on the land and are often eaten by land animals, causing danger to their health, or may lead to death. Discarded plastic materials are often carried away to the sea and pose a significant danger to marine animals, birds, and humans [15]. It is estimated that approximately about 4.8 to 12.7 million tonnes of this plastic waste get into the ocean in a year [16]. The waste plastic materials are eaten by marine animals and birds, leading to poisoning or death, and they often cause entanglement leading to severe injuries. A large portion of plastic waste materials breaks down into tiny particles known as micro-plastics (<5nm), which are eaten

by marine animals and enter our food chain. Microplastics have been reported in marine and freshwater samples from most continents [17], which may cause very harmful effects on all species that drink the water contaminated with plastics. The impact of plastic pollution on animals is illustrated in Fig. 1.3.

Fig 1. 3 Impact of plastic pollution

As described above, extensive use and improper disposal of traditional, non-degradable plastics have led to our environment's pollution and have posed a challenge to sustainability. Hence, for a sustainable future, there is an urgent need for environment-friendly, "biodegradable polymers" [18, 19], especially for packaging applications, since packaging materials contribute to the maximum generation of plastic waste [20].

1.2 Biodegradable polymers

Biodegradable polymers are degraded by naturally occurring microorganisms such as bacteria, fungi or algae, to result in natural by-products such as gases (CO_2), water, biomass, and inorganic salts. [21].

1.2.1 Classification and examples of Biodegradable polymers

There are a large number of biodegradable polymers, both natural (polymers found in nature) and synthetic (human-made), and are classified in many ways [22, 23]. Based on origin, biodegradable polymers may be classified as i) Bio-based polymers and ii) Petroleum-based /fossil-based polymers, as indicated in Fig.1.4, and as described below:

i) **Bio-based biodegradable polymers:**

This include,

a) Natural polymers found in nature of
   - plant origin (such as cellulose, starch, alginates),
   - animal origin (such as chitin/chitosan, collagen, albumin), and
   - microbial origin, (collectively called Polyhydroxyalkonates (PHA) polymers), such as:

   Polyhydroxybutyrate (PHB),
   Polyhydroxyvalerate (PHV),
   Poly hydroxybutyrate-valerate (PHBV) etc.,

b) Synthetic polymers, produced using natural, bio-based monomers (or mixed monomers from biomass and petroleum) such as,
   Polylactic acid (PLA),
   Polyglycolic acid (PGA),
   Polybutylene succinate (PBS) etc.

ii) Petroleum-based /fossil-based biodegradable polymers

This include biodegradable polymers, synthesized from petroleum/ fossil resources, such as,
   Polycaprolactone (PCL),
   Polybutylene succinate (PBS),

Polyethylene succinate (PES),

Polybutylene succinate adipate (PBSA),

Poly(butylene adipate-co-terephthalate) (PBAT),

Polyvinyl Alcohol (PVOH) etc.

(It may be noted that Polybutylene succinate (PBS) is included in both the groups since it is being produced commercially from biobased as well as from petroleum-based chemicals.

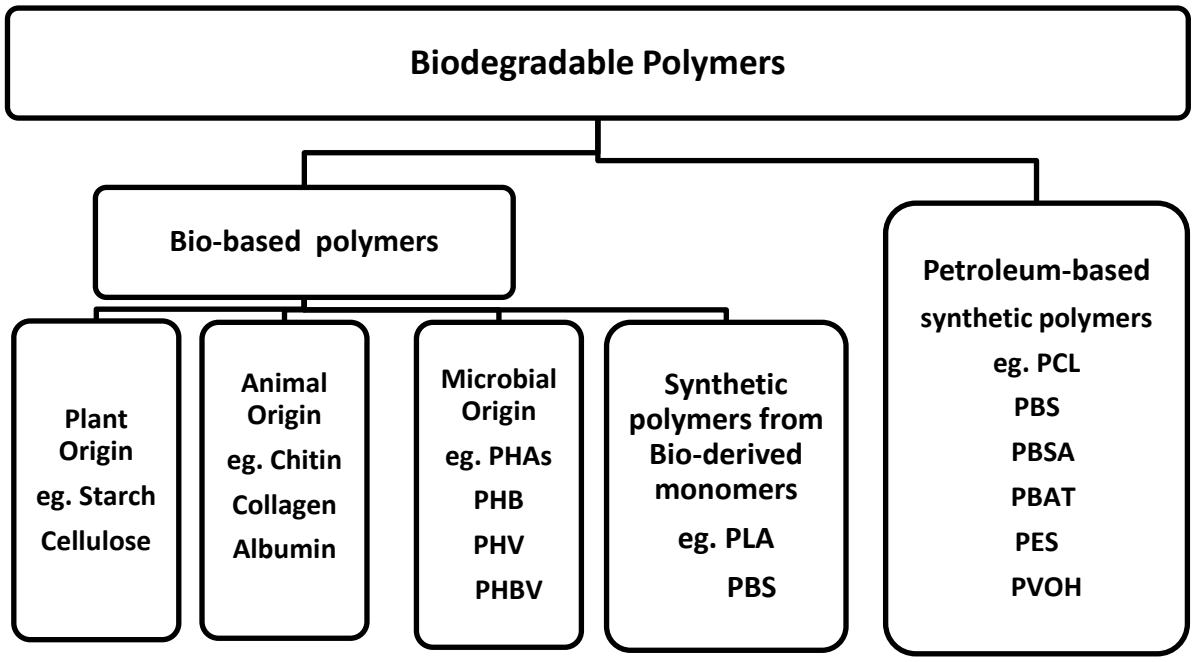

Fig 1. 4 Classification and examples of biodegradable polymers

It should also be noted that bio-based origin does not guarantee biodegradability [24]. For example, bio-based polymers such as bio-polythene (PE), bio-based nylon 11 (NY11), bio-PET, etc., are derived from bio-based feedstocks, are not biodegradable.

The term ‘bio-plastics’ is often used for the group of polymers (Fig. 1.5) comprising of bio-based biodegradable polymers, bio-based non-biodegradable polymers, and biodegradable polymers of petroleum origin [25-27]. Biodegradable polymers may be considered as a subset of the larger bioplastics.

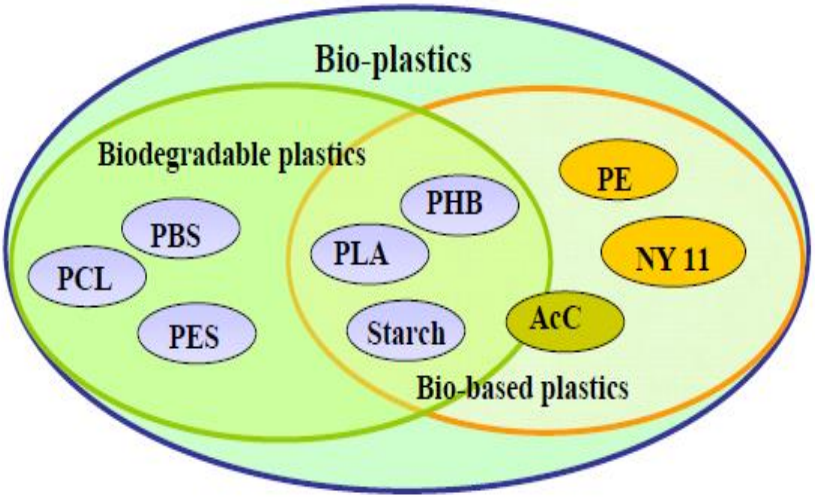

Fig 1. 5 Bioplastics, Bio-based plastics, and Biodegradable plastics (Tokiwa 2009).

Among the biodegradable polymers, the essential biodegradable polymers belong to the family of i) Polysaccharides (starch, cellulose) and ii) Polyesters (PLA, PCL, PHAs (PHB, PHBV), PBS, PBSA, PBAT) [28, 29], and all these polymers are being produced on a commercial scale.

The world consumption of biodegradable polymers is indicated in Fig 1.6, which indicates that the global biodegradable market is dominated by starch-based polymers and polylactic acid (PLA) polymers. It also indicates that biodegradable polymers' total consumption is only about 1 million tonnes per annum (0.87 million tonnes for 2017), which is very low compared to more than 300 million tonnes of plastics produced annually [11].

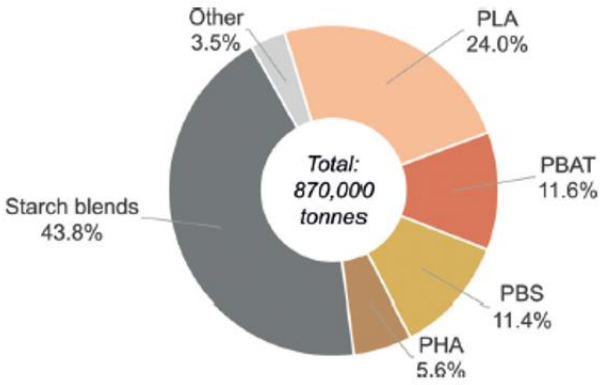

Fig 1. 6 World consumption of biodegradable polymers for 2017 [7].

The lower consumption of biodegradable polymers, as indicated above, is mainly due to their lower performance and higher cost compared to traditional polymer materials. Hence it is essential

to carry out further research and develop new polymer materials with higher performance characteristics.

The performance requirements of biodegradable polymer materials for packaging application is very complex, and an outline of the requirement is given below:

1.3 Performance requirement of packaging materials

Packaging is employed in almost all industrial sectors and has become very important in our modern lifestyle. The package helps contain the products and mainly protects the materials, improves shelf life, facilitates storage, transport, and market the products efficiently.

Packaging can be classified into two types i) rigid packaging and ii) flexible packaging. Rigid packaging includes bottles, cans, drums, boxes, etc. Flexible packaging includes pouches, sachets, bags, etc. The current trend is towards flexible packaging, especially in food, beverages, healthcare, hygiene products, etc. Since flexible packaging is very more convenient, it consumes less space and is more efficient. Currently, polythene (HDPE, LDPE) and polypropylene (PP) are the most commonly used materials for flexible packaging.

The desirable characteristics of plastics for packaging application is briefly described below. Packaging material should have good/optimum material characteristics related to i) environment-friendly/ biodegradation characteristics ii) mechanical properties iii) thermal properties iv) barrier properties v) optical properties, as indicated in Figure 1.7. In addition to the above, there are many other requirements and may vary depending on the type of packaging and nature of the product contained. More information on biodegradation requirements, mechanical and barrier properties of packaging materials are provided in the next chapter.

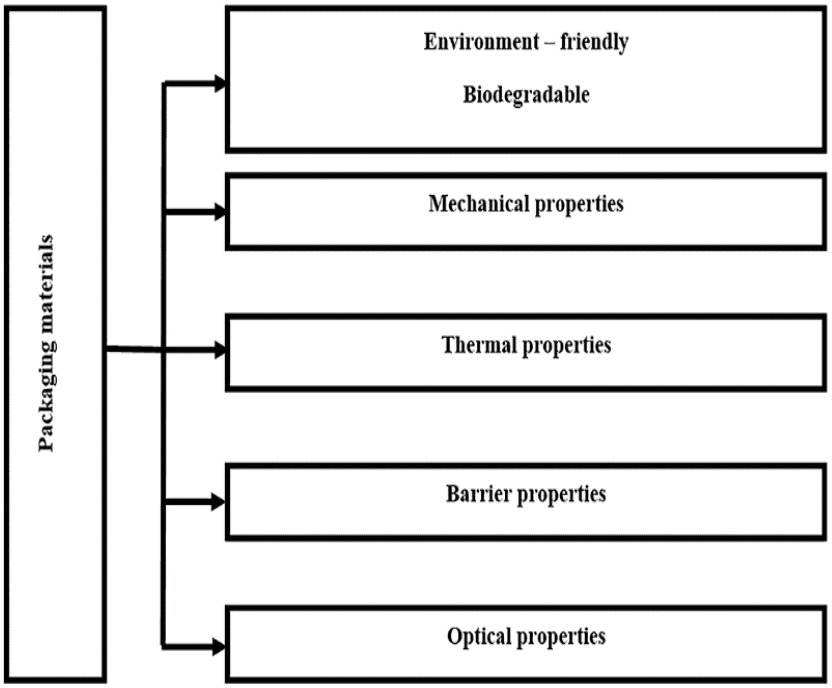

Fig 1. 7 Performance requirements/ Desirable properties of Packaging materials

The present research work deals with developing/investigating flexible packaging films based on biodegradable polyesters such as PLA, PHB, PBS, and PCL, developing high-performance packaging films.

1.4 The motivation for the present research

During the past few decades, many advances have been made on biodegradable polymers, and few products have been introduced into the market for packaging application. However, conventional plastics/polymers are still being used extensively, creating environmental pollution. This is mainly because most commercially available plastic products are marketed as biodegradable, but they have many limitations.

- Many of the commercially available biodegradable products are not truly biodegradable. They have been found to disintegrate into small fragments only and do not degrade fully, in a reasonable timeframe, in the natural environment [30]. Some packaging materials marketed as a solution to plastic pollution, such as "Oxo-degradable," would confuse the customers. They are based on conventional plastics such as LDPE or HDPE with various additives, some

of which are harmful to the environment, which contributes to micro plastic pollution, and hence they cannot be considered as a solution to plastic pollution [31, 32].

- Many of the biodegradable/ compostable products available commercially require a temperature of more than 50^{o}C for biodegradation [27]. Hence, they will not undergo biodegradation in home composting conditions / at ambient temperature. They will biodegrade only in industrial composting conditions, which operates at >50˚C, and such an industrial composting facility is not available in all waste processing sites.
- Data on biodegradation under home composting conditions (ambient temp) is not available for many polymers and polymer blends/composites since most biodegradation studies are carried out at 58˚C only, under industrial composting conditions. One of this research's motivations is to create additional knowledge on these aspects, which will help future research.
- The barrier properties (especially concerning water vapor and oxygen gas) of most packaging biodegradable polymer blends/composites available commercially are not satisfactory/ needs improvement.
- Multi-layer packaging films, metal. (aluminium) and metal oxide coated films are commonly used for packaging since most of the polymer blends/composite films do not have the required barrier properties (mainly water vapor and oxygen gas) for some applications. Multi-layer packaging poses a difficulty for waste segregation, recycling, and biodegradation [33].
- Most of the commercially available biodegradable products available in the market are more expensive than conventional materials.

Thus, there is a need to develop biodegradable polymers with improved performance and lower cost for the widespread application of biodegradable polymers for packaging applications [33, 34]

1.5 Aim of the research work

The present research focuses on biodegradable “polyesters” such as PLA, PHB, PBS, PCL and their blends/nanocomposites, since “polyesters” are considered the most promising biodegradable polymers. [28, 29, 35].

The present research's broad aim is “development and characterization of biodegradable polymer films for flexible packaging application with high-performance characteristics.”

1.6 Organization of the thesis

This thesis is organized as detailed below:

Chapter 1 provides the background of the present investigation. It outlines traditional plastics/ polymer materials' issues and explains biodegradable polymers' needs, especially packaging applications. It also provides a broad aim of the research along with a motivation for undertaking the present investigation.

Chapter 2 deals with the literature survey on biodegradable polymers, with particular reference to packaging application. It indicates the research gaps identified based on the literature survey and presents the present research work's specific objectives.

Chapter 3 gives information on the various materials used and the methodology adopted during the present investigation. It also provides information on the equipment used, test methods, and experimental details.

Chapter 4 deals with studies on PBS-PCL blends/composites to improve its performance characteristics. It presents polymer blend/ nanocomposites preparation by injection molding, preparation of polymer films by hot pressing, and evaluating mechanical, morphological, barrier, and biodegradation characteristics.

Chapter 5 deals with the preparation and characterization of PHB-PCL blend/ nanocomposite films. It covers PHB blend/ nanocomposite film preparation and evaluation of mechanical, morphological, barrier and biodegradation characteristics.

Chapter 6 deals with the investigation of PLA-PCL blend/ nanocomposites films. It covers information on the preparation of polymer blend/ nanocomposite films by injection molding

followed by hot-pressing and evaluation of mechanical, morphology, water barrier properties, and biodegradation characteristics.

Chapter 7 provides the summary and discussion of the research outcomes on PLA-PCL, PHB-PCL, and PBS-PCL blend/ nano-composite films and provides discussions on the future direction of the research work on biodegradable polymers.

Chapter 2 Literature Review

2.0 Introduction

A detailed literature survey was carried out on biodegradable polymer blends/composites for packaging application, with a view to understand the status and to identify the research gaps for the development of flexible biodegradable packaging materials with high-performance characteristics.

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It has been reported that, among the biodegradable polymers, aliphatic polyesters are the most promising biodegradable polymer materials for practical applications [28, 29, 35]. Hence for the present research on packaging materials, four commercially available, biodegradable aliphatic polyesters were chosen, as listed below:

- Polybutylene succinate (PBS)
- Polyhydroxybutyrate (PHB),
- Polylactic acid (PLA), and
- Polycaprolactone (PCL)

As mentioned in Chapter1, packaging material should have good characteristics related to

i) biodegradation
ii) barrier properties,
iii) mechanical properties
iv) thermal properties
v) optical properties etc.

2.1 Biodegradation characteristics

Biodegradation (within a reasonable time frame) is a prime requirement for modern, sustainable polymer packaging materials. In general, polymer degradation occurs due to the photo, mechanical, thermal, chemical, and biological actions in the environment. [21]. Degradation of polymers is defined as / manifested as a detrimental change in its appearance, mechanical properties, physical properties, and chemical structure [36]. Biodegradation may be considered

chemical degradation, brought about by naturally occurring microorganisms, via enzymatic action. [37]. The biodegradation rate and degradation pathway and the outcome depend very much on the process conditions, especially on oxygen availability.

The biodegradation process can be classified into two, depending on the presence or absence of oxygen during the biodegradation process, as follows:

i) aerobic biodegradation and

ii) anaerobic biodegradation

When oxygen is present under aerobic conditions, biodegradable polymers are converted into carbon dioxide, water, and biomass. In the absence of oxygen, i.e., under anaerobic conditions, methane is formed, and the above products [38].

Aerobic biodegradation: Polymer + O_2 -> CO_2 + H_2O + biomass+ residue

Anaerobic biodegradation: Polymer -> CO_2 + CH_4 + H_2O + biomass+ residue

2.1.1 Mechanism of biodegradation

The general mechanism of biodegradation is indicated in Figure 2.1 [7, 35] and is described below: Biodegradation of polymers takes place mainly in four stages/ steps: bio-deterioration, depolymerization, bio-assimilation, and mineralization. During the initial stage, microorganisms start growing on the materials' surface, form a biofilm, and lead to material fragmentation. Microorganisms secrete extracellular enzymes, which act as a catalyst for the long polymer chains' depolymerization, cause random chain or chain-end scission resulting in reduced molecular weight/polymer chain length and formation of oligomers, dimers, or monomers. This stage plays an essential role because large polymers cannot pass through living cells' outer membranes. During the bio-assimilation stage, the small-sized molecules get into the microbial cell, biochemical reactions take place inside the cell, and small polymer fragments get metabolized. In the last mineralization stage, end products such as water, carbon dioxide, methane (in the case of anaerobic degradation), and new biomass are produced [35]. The conversion of organic substances to naturally occurring gases and or inorganic substances is called mineralization [39]. Complete biodegradation occurs when no residue remains other than the biomass. Complete mineralization is established when all the biodegradable materials and biomass are consumed, and all the carbon

is converted to carbon dioxide [40]. Biodegradation of a polymer substrate can rarely reach 100% because a small portion of the polymer will be always incorporated into microbial biomass, humus, and other natural products [41, 42]. The biomass yield is typically between 10% to 40% depending on the substrate, which is converted [43].

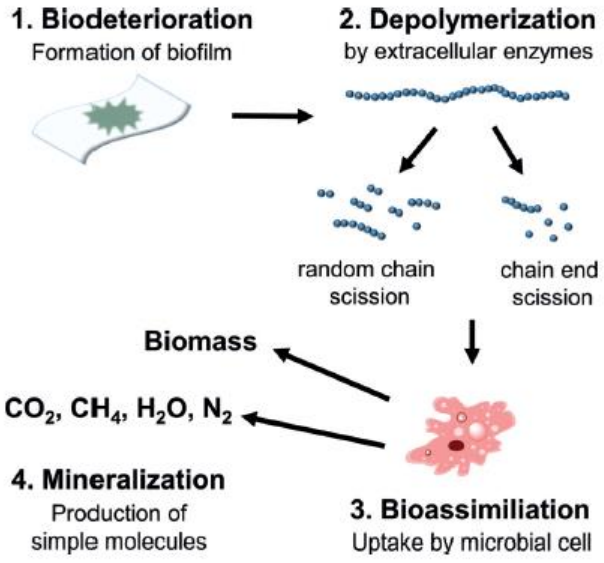


Fig 2. 1 Steps involved in plastics/polymer biodegradation [7].

2.1.2 Factors affecting biodegradation

The biodegradation of polymers depends on many factors. [44-46]. Broadly, it depends on a) polymer characteristics b) environment/exposure conditions, as indicated in Figure 2.2

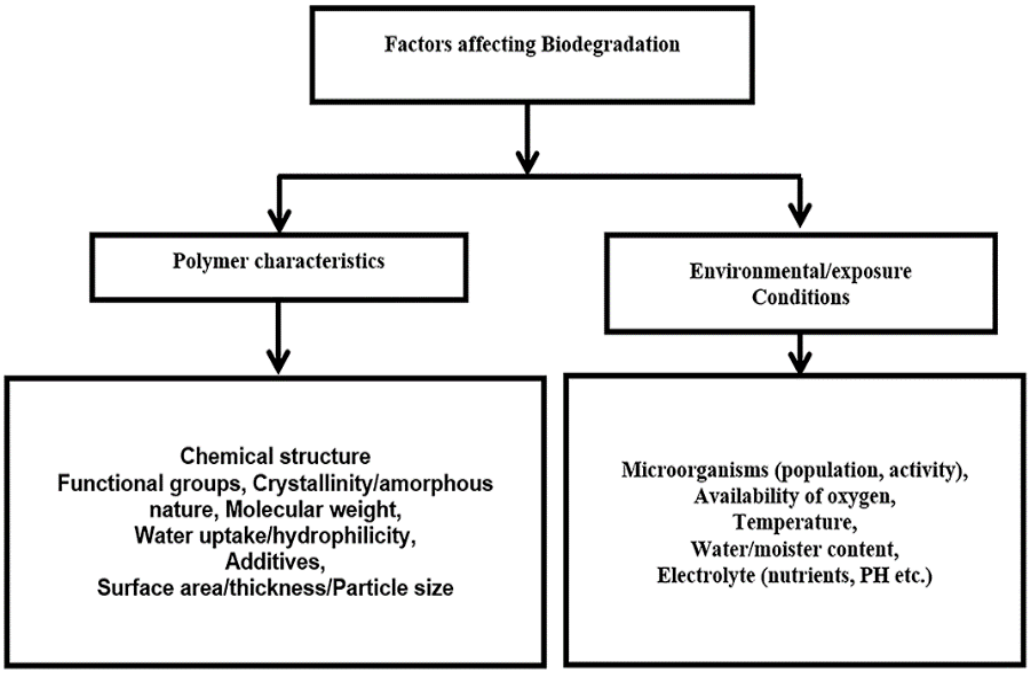


Fig 2. 2 Major Factors affecting biodegradation

a) Polymer characteristics & biodegradability

Both physical and chemical properties of polymer influence the biodegradation rate. The polymer's chemical structure is the most critical factor, which affects biodegradability, which includes type of functional groups, types of bonds, branching, cross-linking, etc. Polymers with hydrolyzable linkages and easily oxidizable functional groups on the polymer chain are susceptible to biodegradation by microorganisms. The molecular weight is an essential factor for biodegradability as it determines the physical properties of the polymer. An increase in the molecular weight decreases biodegradability. The degree of crystallinity is also a crucial factor affecting biodegradability since enzymes mainly attack the polymers' amorphous domains. The molecules in the amorphous region are loosely packed, and thus make it more susceptible to degradation. The crystalline part of the polymers is more resistant than the amorphous region. In other words, polymers with higher crystallinity will have a slower rate of biodegradation. Hydrophilicity is another factor, which influences biodegradability. Polymers containing hydrophilic groups are more biodegradable than hydrophobic polymers of comparable molecular weight. Hydrophilicity in a polymer helps better penetration of microorganisms in the polymer.

Other polymer-related factors that influence biodegradability are the flexibility of polymer chains, additives, surface area/ thickness of polymer material, etc.

b) The environmental conditions and biodegradability

The environmental factors that influence biodegradation include microorganisms, microbial population, microbial activity, availability of oxygen, amount of water/moisture, temperature, chemical environment (pH, electrolytes) etc. [43]. The various environments in which biodegradation of polymer waste can occur include soil, freshwater, marine water, landfills, home composting, industrial composting, etc, and organic materials biodegrade at different rates in these environments. The order of aggressivity of various environments for biodegradation is given in Figure 2.3.

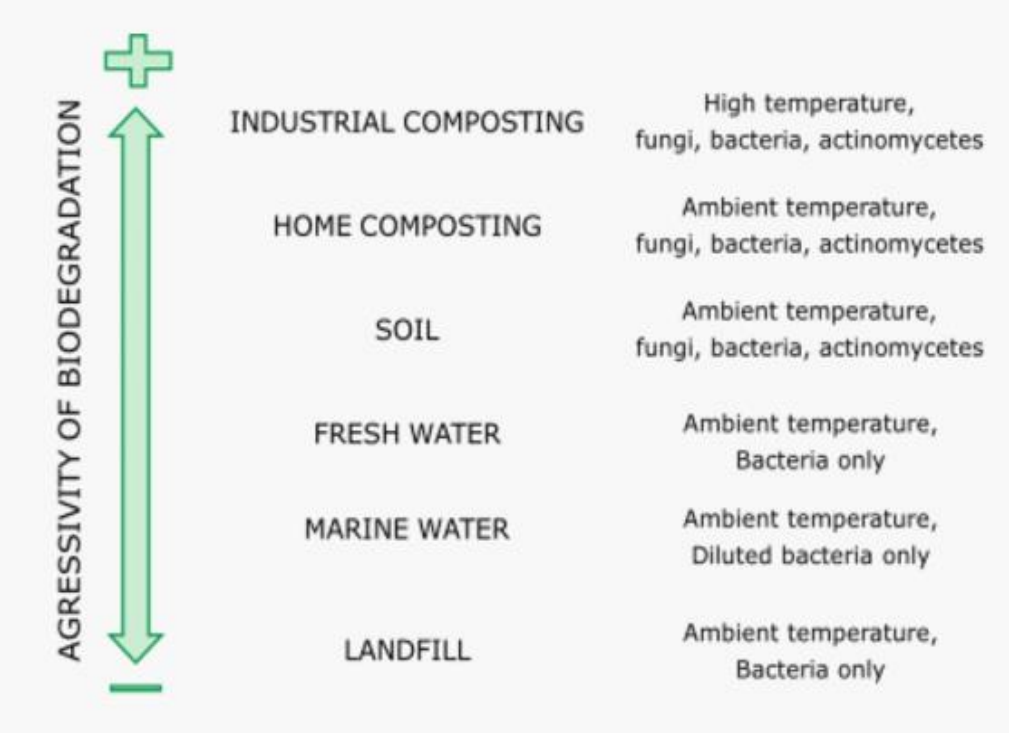


Fig 2. 3 Environment and aggressivity of biodegradation [47]

The above figure indicates that industrial composting is the most aggressive environment for biodegradation, and landfill is the least aggressive environment. Hence, composting may be considered as the best method for organic solid waste disposal.

Composting is an accelerated degradation process of treating waste organic matter by a mixed microbial population in a moist, warm, aerobic environment under controlled conditions [48-50] Composting produces "compost", a humus-like material, which can be used to improve the soil structure, moisture holding capacity, organic matter and nutrient supply to the soil [51]. Composting of waste materials at home (home composting) is usually carried out at ambient temperatures, and industrial/commercial composting is carried out at higher temperatures, typically at about $60^{\circ}C$. Though industrial composting is more conducive compared to home composting for biodegradation, its availability is limited in many countries. [52]

2.1.3 Biodegradable vs compostable plastics

The terms biodegradable and compostable are often used interchangeably, but there is a lot of difference between them. All compostable products are biodegradable, but not all the biodegradable materials are compostable. The term biodegradable only indicates that the material will decompose in the natural environment within a reasonable amount of time but does not indicate any time frame for biodegradation. In other words, biodegradability alone is not enough for environmental sustainability. The term "compostable" adheres to strict standards with respect to biodegradation rate, disintegration rate, and compost quality.

2.1.4 Standard test methods & Standard specifications for biodegradable plastics:

For testing biodegradation, there are mainly four common approaches available [53], and they are as follows:

- Monitoring microbial growth
- Monitoring the depletion of substrates
- Monitoring reaction products
- Monitoring changes in substrate properties

Based on the above general approaches, some of the test methods/ techniques reported for monitoring/testing biodegradability are listed below [43, 54-56]

- CO_2 gas evolution test (for the aerobic process)
- O_2 consumption test
- Changes in mechanical properties, such as tensile strength (σ), tensile elongation/ elongation at break (ε).etc.
- Changes in thermal properties, such as changes in Tg
- Changes in chemical properties
- Changes in crystallinity
- Changes in molecular weight
- Weight loss method
- Morphological changes/visual methods
- EIS method-Changes in electrochemical impedance characteristics
- Radiolabelling method
- Enzymatic methods
- Agar plate test- Clear zone formation test

The carbon dioxide evolution method and oxygen consumption method are the most widely used test methods for biodegradability testing, and the former method (CO_2 method) is described in detail in chapter 3

Various international bodies such as American Society for Testing and Materials International (ASTM), International Standards Organization (ISO), and European Committee for Standardization have laid down few standard test methods for biodegradability/composability testing for various test environments (soil, compost, seawater, etc.). Also, these bodies have laid down standard specifications/ requirements for biodegradable/ compostable plastics. The list of standard test methods and standard specifications prescribed by ASTM for the compost and marine environment is given in Table 2.1

Table 2. 1 ASTM test standards & specifications for biodegradation of plastics

Environment	ASTM No.	Title
Composting (Aerobic)	ASTM D6400-19 Specification	Standard Specification for Labelling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities.
	ASTM D5338-15 Test method	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures.
Marine (Aerobic)	ASTM D7081-05, Specification	Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment
	ASTM D6691-17 Test method	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Seawater Inoculum.
	ASTM D7991-15 Test method	Standard Test Method for Determining Aerobic Biodegradation of Plastics Buried in Sandy Marine Sediment under Controlled Laboratory Conditions.

For the biodegradation under composting environment, ASTM's standard test method is described in the ASTM D5338-15 method. The ASTM standard specification/ requirements for certifying / labeling biodegradable plastics as compostable plastics are provided in the ASTM D6400-19 standard. This standard specification stipulates criteria with respect to biodegradation rate (mineralization), disintegration rate (physical degradation), and compost quality (toxicity) for compostable plastics / for biodegradation in a composting environment. As per the above standard specification, the requirement for biodegradation/mineralization for a single polymer (homopolymer) is a minimum of 60% in 180 days, and for polymer blends, the requirement is a minimum of 90% biodegradation/ mineralization in 180 days test period. The above specification is about industrial composting, where the temperature is around 58°C. Currently, there is no

international standard specification for ambient temperature/ home compostable plastics, although there are few national standards, such as the standards established by Austria (AS 5810), France (NF T 51-800) and Belgium (Vinçotte OK compost home certification scheme).

There are mainly two ASTM test standards for biodegradation under marine conditions, namely ASTM D6691-17 (test conditions simulating to open sea) and ASTM D7991-15 (test conditions simulating sandy tidal zone). The standard specification/ requirement for the biodegradable plastics in the Marine environment is provided in ASTM D7081-05 standard (under revision). This specification for biodegradable plastics in the marine environment stipulates a minimum of 30% biodegradation in 180 days when tested with the ASTM D6691 test method. [49, 57-59]

2.2 Barrier property

Barrier property is one of the critical requirements for packaging material, which significantly influences the product quality and shelf life of the packed items [30]. Packaging materials made from thermoplastic polymers are permeable to small molecules, and the barrier property of material represents its ability to control the permeation of air/ oxygen, moisture/water, carbon dioxide, aroma etc. through the material. Loss or gain of oxygen, water vapor, carbon dioxide, aroma, etc., can adversely affect the taste, flavor, color, texture, etc., of food and beverage items. Barrier property is inversely related to permeability: a lower value of permeability implies better barrier property.

2.2.1 Permeability

The general mechanism of permeation/transport of gases across a polymer film mainly involves three steps (Fig. 2.4), as given below

i) Absorption of gas by the polymer film (by solubility);

ii) Diffusion of gas inside the polymer film and

iii)Desorption of gas at the side of lower penetrant concentration;

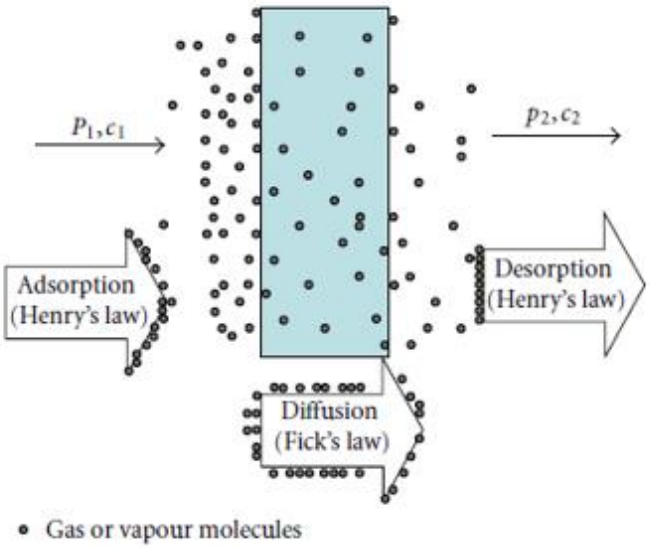


Fig 2. 4 General mechanism of gas permeation through a plastic film [60]

An expression for the quantity (Q) of penetrant gas diffusing through a polymer film, under steady-state conditions can be derived [60], based on Fick's law of diffusion and Hendry's law and is given below:

$$Q = \frac{DS(p1 - p2)At}{l} \qquad (2.\ 1)$$

Where Q is the quantity of gas or vapor permeating, t is the time, l is the thickness of the film, A is the surface area, p1 and p2 are the gas/ vapor pressure on both sides of the film (p1 > p2), D is the diffusion coefficient and S the solubility coefficient of the permeant. In the above equation, DS, the product of the diffusion coefficient D and the solubility coefficient S is referred to as the permeability coefficient or simply permeability P. Therefore, permeability coefficient P can be expressed by the following equation:

$$P = DS = \frac{Ql}{At(p1 - p2)} \qquad (2.\ 2)$$

$$P = \frac{(\text{amount of penetrant})(\text{film thickness})}{(\text{area})(\text{time})(\text{pressure drop across film})} \quad (2.3)$$

The SI unit of permeability is $kg.m.m^{-2}.s^{-1}.Pa^{-1}$. Permeability of a gas/ vapor through a polymer depends on many factors [61, 62] such as the chemical structure of the polymer and the permeant, polymer morphology, crystallinity, polarity, degree of cross-linking, hydrogen bonding, intermolecular forces/ polymer chains interactions, humidity, temperature etc. In general, permeability depends on the amount of free volume and how well the free volume is connected.

2.2.2 Water vapor transmission rate (WVTR) & Oxygen transmission rate (OTR):

Instead of permeability, the term transmission rate (TR) is used to describe the permeation/ barrier property of films, especially in the packaging industry. The transmission rate property for water vapor and oxygen is of prime importance and is called water vapor transmission rate (WVTR) and oxygen transmission rate (OTR).

The transmission rate is described as the quantity of permeant passing through a film, per unit of area, per unit of time, under steady-state conditions, under specified conditions of temperature and pressure/ humidity, and is given by the formula below:

$$\text{TR (WVTR or OTR)} = \frac{Q}{At} \quad (2.4)$$

Q is the amount of permeant passing through the polymer, A is the surface area, and t is the time. It is essential to specify the film's thickness, the temperature, and the partial pressure difference of the gas or water vapor.

Transmission rates, such as WVTR or OTR, can be converted to permeability by multiplying by the film's thickness (l) and dividing by the partial pressure difference Δp.

$$\text{Permeability} = \text{Transmission rate x } \frac{l}{\Delta p} \qquad (2.5)$$

Water vapor transmission rate (WVTR) has the unit of g $m^{-2}d^{-1}$ and is usually reported at a temperature of 25˚C or 37.8˚C/100˚F, and relative humidity of 100% or 90% or 75% RH. Oxygen transmission rate (OTR) is usually expressed in the unit of cc $m^{-2}d^{-1}$.

Since WVTR or OTR values varies with the film thickness, normalized- WVTR, i.e., values for a specific film thickness of 25 µm or 1 mil or 1 mm or 100 µm (0.1mm) etc. is often reported [63, 64]. Normalized WVTR or OTR for a 25 µm film is obtained from the WVTR or OTR for a film thickness of l µm by multiplying the non-normalized WVTR by $l/25$:

$$\text{Normalized WVTR (or OTR)} = \text{Non} - \text{normalized WVTR (or OTR) x} \frac{l}{25} \qquad (2.6)$$

Barrier materials may be classified as low, medium, high barrier films depending on the WVTR and OTR values [65], as indicated in Table 2.2

Table 2. 2 Barrier films classification based on normalized OTR and WVTR values [65]

Classification	OTR, $cm^3/m^2/d$	WVTR,$gms/m^2/d$
Low	>100	>100
Medium	6-100	6-100
High	1-5	1-5
Very High	<1	<1

The barrier requirements vary considerably depending on the product inside the packaging. Microporous, breathable, low barrier films are used for the packaging of fruits, fresh vegetables etc. However, medium and high barrier packaging films are required for most food and medical packaging [66]. A typical barrier requirement for a few food and pharmaceutical items is shown in Figure 2.5 [67, 68]. The barrier requirement for electronics, solar panels, LCD, LED items are more stringent [66, 69, 70].

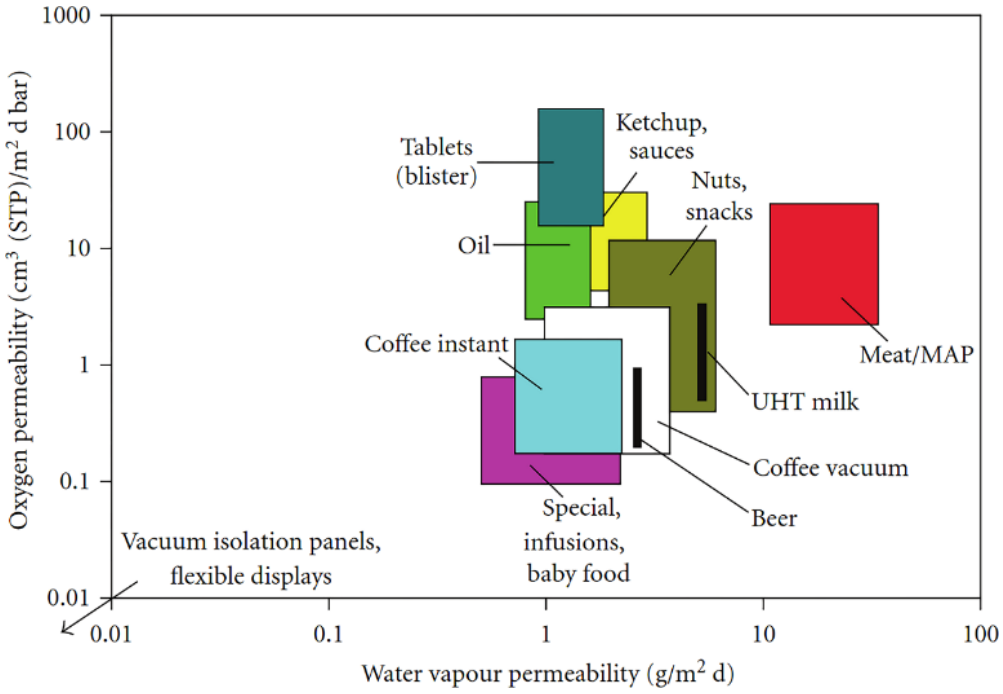


Fig 2. 5 Barrier requirements of few food and pharmaceutical items [67]

2.3 Mechanical, thermal, and optical characteristics

The packaging materials should have good mechanical properties to protect the materials enclosed from damage during handling, processing, transportation, storage etc. [71, 72]. It is essential to have good mechanical properties such as tensile properties, impact strength, burst strength, tear strength, and puncture resistance.

Tensile property may be considered as one of the most important mechanical properties of packaging materials. Tensile properties indicate how the material will react to forces being applied in tension. Tensile properties include a) tensile strength, b) tensile modulus/ Young's modulus, and c) tensile elongation/ elongation at break (ε). For tensile testing of thin films, a test specimen in the form of a rectangular strip (15mm x150mm) is clamped between two grips/fixtures and is stretched by moving the grips apart at a constant rate. Load vs extension is recorded, stress vs strain plot is generated, and the tensile parameters are calculated. Typical stress vs strain plot is given in Fig.2.6

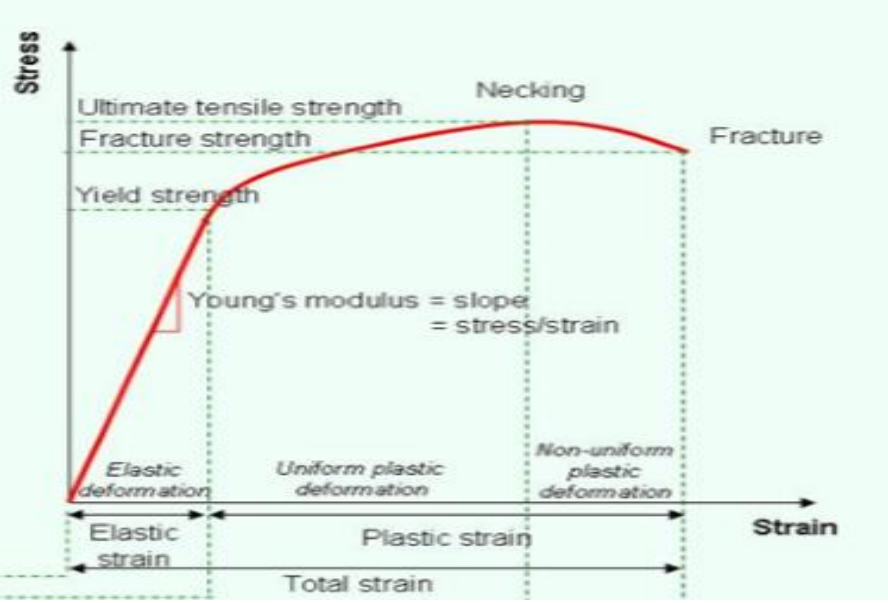


Fig 2. 6 Typical stress-strain curve

- **Tensile strength:**

The tensile strength of a material is the maximum amount of tensile stress that it can take before failures, such as breaking or permanent deformation. It is expressed in the unit of mega Pascal (MPa). There are three types of tensile strength, as indicated in the stress vs strain curve: i) ultimate strength – it is the maximum stress a material can withstand ii) Fracture strength or breaking strength – it is the stress corresponding to the point of rupture of the material and iii) yield strength – it is the lowest stress a material can withstand without permanent deformation.

- **Tensile Modulus or Young's Modulus:**

Tensile modulus/Young's modulus is the ratio of stress along an axis to the strain along that axis (in the range of stress in which Hook's law holds) and is a measure of the stiffness of the material. It is obtained from the initial linear region of the stress-strain curve in the elastic region. It is expressed in mega Pascal (MPa) or Giga Pascal (GPa).

- **Elongation at break:**

Tensile elongation is the ratio between changed length and initial length when a material is stretched, at the point of breakage of the material. It is calculated by dividing elongation at the point of rupture by the initial length of the material and multiplying by 100 and is expressed as %

elongation at break. A low value of % elongation denotes a brittle material, while a high % elongation indicates that the material is ductile.

The thermal properties of the packaging materials are essential for significant tolerance to environmental temperature changes. Some of the critical thermal properties relevant for packaging materials are melting temperature (Tm), glass transition temperature (Tg), decomposition temperature etc. Melting temperature is the property of crystalline material, and the glass transition temperature is the property of the amorphous materials. Most of the polymers are semi-crystalline, they are composed of both amorphous and crystalline regions, and thus they have both the glass transition temperature and the melting temperature. Melting temperature refers to the temperature at which the crystalline solid transitions to liquid. Glass transition temperature (Tg) is the temperature at which the polymer changes from a glassy to rubbery state. Above Tg, the material will be soft and flexible, and below Tg, the material will be hard and brittle. This temperature will determine whether the polymer material will be hard/brittle or soft/ flexible at the temperature of interest. Optical properties such as transparency and color are also important for aesthetics, protection from light etc.

2.4 Modification of polymer properties-by blending, plasticization, nanomaterials:

Neat polymers are rarely used for commercial applications since they cannot fulfill all the required characteristics. Several strategies have been reported in the literature for improving/ modifying the properties of polymers,

- by blending with other polymers,
- by the application of additives such as plasticizers (plasticization),
- by the use of nanomaterials, by preparing polymer nanocomposites.

2.4.1 Polymer blending:

A polymer blend is a mixture of two or more polymers analogous to metal alloys, without any chemical bonding. Blending is a moderately simple and cost-effective method to produce polymer materials with desired properties [73]. Generally, polymer blends will have unique physicomechanical properties, usually not present in their components. During polymer blending,

it is essential to understand how the material properties will change due to the composition. The semi-empirical relationship can write the property (P) of a binary polymer blend,

$$P = P_1 \phi_1 + P_2 \phi_2 + I\phi_1 \phi_2$$

Where ϕ is the volume fraction in the blend, and I is the interaction factor that may be negative, zero, or positive, depending on the interaction between the components. If there is no interaction between the components, i.e., if I is zero, the blend's property will vary linearly, as per the simple rule of mixtures. However, there will be interaction between components in practice, i.e., I may be positive or negative, and the property concentration plots are very rarely linear. Thus in some cases, during blending, the synergic effect may result in blends with improved properties than the constituent polymers [74]. Fig.2.7 shows three possible plots of property versus concentration.

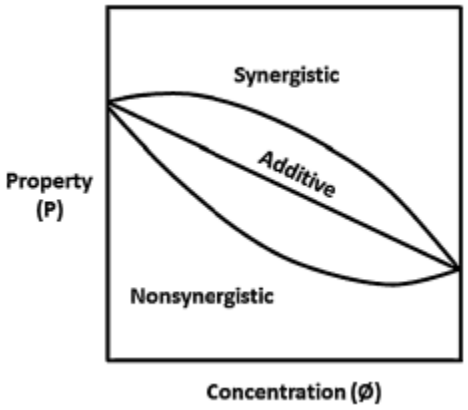


Fig 2. 7 Property-concentration relationships for a polymer blend [75]

- **Polymer blends can be classified into three types:**

i) Miscible blends (Homogeneous blend): In this polymer blend, homogeneity is observed at least on a nanometre scale, if not on the molecular level. Polymers with similar chemical structures may result in a homogeneous polymer blend. This type of blends will have a single-phase structure, with only one glass transition temperature (Tg), and will have properties between blend components, depending on the blend composition.

ii) Partially miscible blends: In partially miscible blends, a small part of one of the blend components is dissolved in the other part and will have two phases. Both blend phases will be homogeneous and will have their Tg values. However, the components' Tg s will be shifted from the values as in with that of the pure components.

iii) Immiscible blends (Heterogeneous blend): Fully immiscible blend will have at least two phases and result when there is poor adhesion between the blend phases. These blends will exhibit different Tgs corresponding to the component polymers' Tg since the components are phase-separated. Compatibilizers are often added for improving the miscibility of polymer blends. Some of the factors which influence miscibility and immiscibility of polymer blends include polarity, specific group interaction, molecular weight, crystallinity, blend ratio etc.

- **Blend Morphology:**

The polymer blends' properties depend very much on the phase morphology (shape, size, and spatial distribution of the phases) of the blends. The morphology depends very much on the phases' melt viscosity, interfacial properties, blend composition, and processing conditions.

Two major types of morphologies are seen in a binary two-phase blend: isolated droplets-dispersed in-matrix morphology and a co-continuous morphology, as shown in Fig.2.8 a, b, c. In the blends with former morphology, the blends' properties are mainly controlled by the matrix properties. In the blends with co-continuous morphology, the phases will be interconnected throughout the blending volume, and each phase will contribute to blend properties. The blend morphology depends very much on the composition. As shown in Fig 2.8, when polymer A's concentration is higher, droplets of B will be dispersed in matrix A, and with an increase in the concentration of B, it will transform to co-continuous morphology and then to morphology with droplets of polymer A in polymer B matrix.

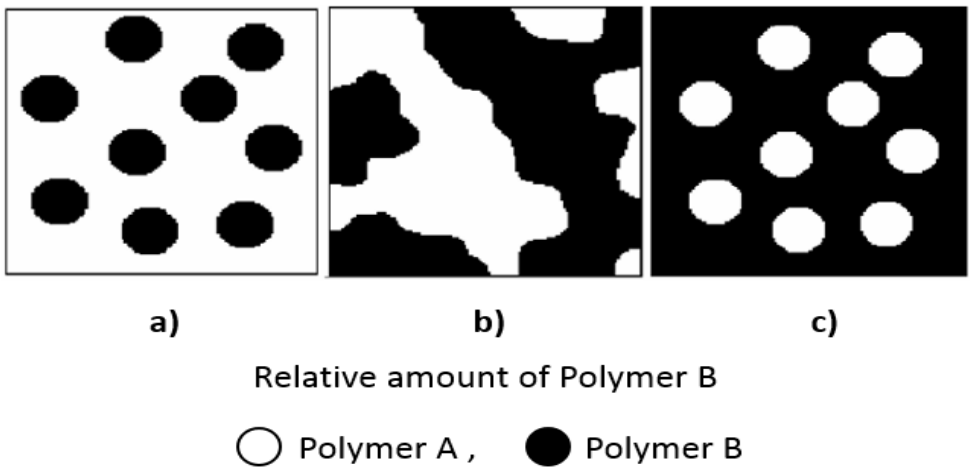


Fig 2. 8 Different morphologies of immiscible polymer blends a) & c) droplets-dispersed in-matrix, b) co-continuous morphology [76]

Different methods are used for the preparation of polymer blends. The most common methods are melt mixing and solution blending. Melt mixing is the most widely used method of polymer blend preparation. In this method, the blend components are mixed in the molten state in extruders or batch mixers. In the solution blending method, the blend components are dissolved in a solvent, and the polymer blend is prepared by evaporation of the solvent or by precipitation from the solution. This method is generally used for the preparation of polymer blends on a laboratory scale only.

2.4.2 Plasticizers:

Plasticizers are the most widely used additives in the plastic industry and are mainly added to improve polymers' flexibility and processability by lowering the glass transition temperature [77]. They are generally low molecular weight, non-volatile liquids. Plasticizers alter the polymers' mechanical properties, such as elongation at break, tensile strength, and toughness, and also may influence other properties such as the degree of crystallinity, optical clarity, electric conductivity, bio-degradation etc. [78]. The use of plasticizers may sometimes adversely affect barrier properties and other properties [79], and hence the right choice of plasticizer is essential. The choice of

plasticizers to be used depends on the application. For food packaging applications, only non-toxic substances approved for food contact must be used as a plasticizer.

Various theories describe the action of plasticizers, such as lubricity theory, gel theory, free volume theory, etc., as illustrated in Fig.2.9 [80].

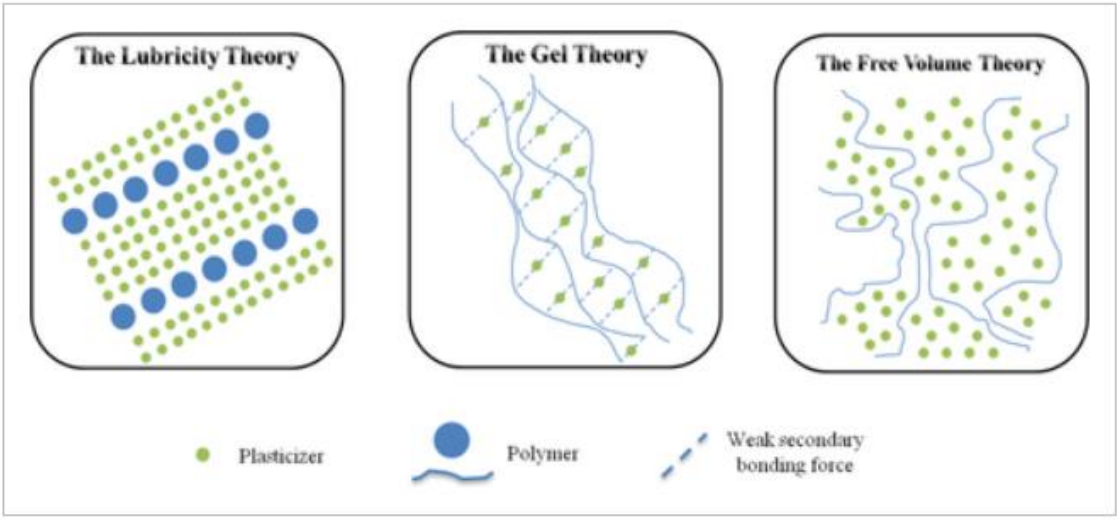


Fig 2. 9 Plasticizers – Mechanism of action [80]

According to "Lubricity theory," the plasticizer diffuses into the polymer, inserts into the polymer chains, and reduces the intermolecular frictions. Then, the plasticizer lubricates the molecules' movement, reducing their internal resistance to sliding and preventing the rigid matrix's reformation.

The gel theory assumes that the plasticizer molecules break up the polymer-polymer interaction by getting in between the polymer chains, masking the polymer molecules' interaction sites, and preventing their reformation.

According to free volume theory, a plasticizer increases the free volume, the internal space available within a polymer. With the increase in the free volume, the polymer becomes soft and rubbery, increasing polymer molecules' motion.

The compatibility between polymers and plasticizers is essential to obtain plasticized materials with the desired properties. The plasticizer should be compatible with the polymer and should be stable at the elevated processing temperature, and should not undergo migration to the surface with time. [81]. Some of the parameters that influence polymer and plasticizer compatibility include the polarity, chemical groups, molecular weight, etc.

Several empirical ways for predicting plasticizer/ polymer compatibility and one of the most used predictors is the "Hildebrand solubility parameter (HSP)" δ, which is available for many plasticizers and polymers. The solubility parameter (δ) provides a numerical estimate of the degree of interaction or solubility between materials, and the materials with similar values of δ are likely to be miscible [80]. The solubility parameter is expressed in the unit of $(J/cm^3)^{1/2}$ or $MPa^{1/2}$. Fig.2.10 below indicates the solubility parameters of some polymers and plasticizers.

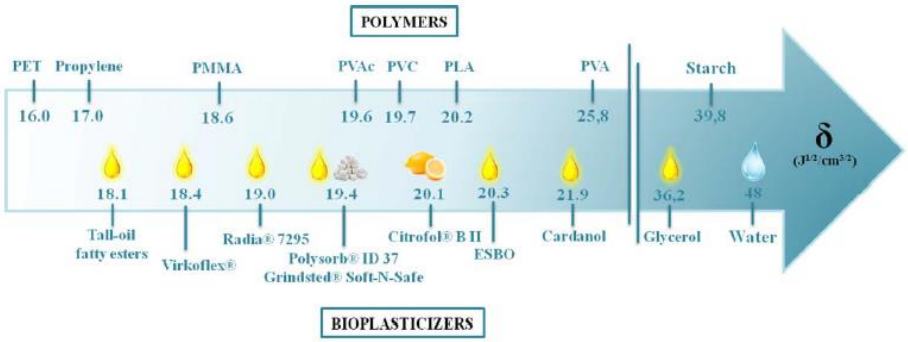


Fig 2. 10 Solubility parameters of some polymers and plasticizers[80]

For good compatibility between polymers and plasticizers, the difference in the solubility parameters should be small. However, materials having the same δ are not always compatible. A complementary way to predict materials compatibility is to analyze the chemical structures [80].

Esters of phthalic, phosphoric, adipic, sebacic, citric, and ricinoleic acids are commonly used as plasticizers. Nowadays, there is increasing interest in using bio-based plasticizers with better biodegradability, low toxicity [77], and polymeric plasticizers with lower chances of plasticizer migration. Some of the common bio-based, biodegradable plasticizers include glycerol esters such as Triacetin/ glycerol triacetate (GTA), alkyl citrates, such as triethyl citrate (TEC), tributyl

citrate (TBC), acetyl tributyl citrate (ATBC), epoxidized vegetable oils / epoxidized soybean oil (ESBO) etc.

2.4.3 Polymer nanocomposites

Various nanomaterials are often added to polymers to produce 'polymer nano-composites' for enhancing the polymer/ blend characteristics. They influence all the properties of the polymers, including mechanical, barrier, and biodegradation characteristics.

Incorporation of nano-materials influences the barrier properties by altering the diffusion pathways for oxygen/water /gas-penetrant molecules. These nanofillers make the diffusing pathways longer and more tortuous throughout the nanocomposite film, as indicated in Fig.2.11, resulting in reduced permeability/ improvement in barrier properties.

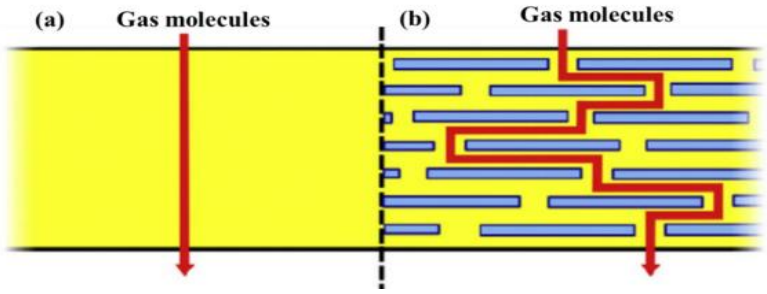


Fig 2. 11 "Tortuous pathway" created by the incorporation of nanoplatelets into a polymer matrix. a). Polymer film without filler b). Nanocomposite film [82].

Various nano-materials, organic as well as inorganic nanofillers, are used for the preparation of nanocomposites. The ideal nano-particle should be bio-based and biodegradable [83] material. Some of the inorganic fillers commonly used include metal oxide nanoparticles (nano-ZnO, nano-TiO_2 etc.) and various types of clay such as montmorillonite, saponite, hectorite, etc. [84]. Among the above nanofillers, silicate clays have been used most extensively by various researchers to prepare polymer nanocomposites, due to their low cost and easy availability. These silicate clays are usually organically modified to alter the hydrophilic characteristics for increased miscibility with the polymer. Some of the commonly used organic nanofillers include cellulose nanomaterials (such as cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), cellulose nanowhiskers), chitin nanofibrils, and starch nanocrystals. [85-87]. Carbon nanotubes (CNT), graphene, graphene oxide, etc. are some of the other nanoscale fillers used in nanocomposites to improve the gas barrier properties of polymers [82, 88].

2.5 Characteristics of traditional polymers used for packaging application

The most used plastics/ polymers for packaging application include polyethylene (LDPE, HDPE), polypropylene (PP), polystyrene (PS), polyamides/ nylon (PA), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). The mechanical, thermal, and barrier characteristics of these traditional polymers are given below, in Table 2.3, for ready reference and comparison with biodegradable polymer materials. All these polymers are non-biodegradable, as mentioned earlier.

Table 2. 3 Properties of traditional plastics/ polymers [89-91]

Polymer	Melting temp Tm (°C)	Glass transition temp Tg (°C)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	OTR $ml.m^{-2}day^{-1}$ (23˚C, 0% RH)	WVTR $g\ m^{-2}\ day^{-1}$ (25˚C, 100% RH)
PET	265	69	2800–4100	48–72	30–300	55	20
LDPE	115	-110	300–500	8–20	500–1000	7400	12.50
HDPE	137	-90	1080	22-31	10-1200	1600	3.70
PVC	212	87	2410-4140	41-52	40-80	27-120	17.5-32
PP	176	-18	1000–2000	30–40	400–900	1550-3040	5.00 -8.2
PS	240	100	3000–3500	34–50	3–5	9800	-

Among the above polymers, polythene (HDPE and LDPE) characterized by high ductility /elongation and low glass transition temperature, is the most preferred polymer for flexible packaging applications. Other polymers, PP, PS, PET, PVC, PA, are used for rigid packaging, while PP is used for flexible and rigid packaging. In practice, to meet the actual packaging requirements, multi-layer packaging, consisting of layers of many polymers, or metalized films,

metal oxide coated films, etc. However, these multi-layer films/ coated films make the manufacturing process complicated/ expensive and create difficulty in polymer/plastic waste segregation. Monolayer films based on biodegradable polymer blends/composites are more desirable than multi-layer films/ coated films.

2.6 Characteristics of Important biodegradable polyesters- PBS, PHB, PLA, and PCL

A brief description of the characteristics of critical biodegradable polyesters, such as Polybutylene succinate (PBS), Polyhydroxybutyrate (PHB), Polylactic acid (PLA), and Polycaprolactone (PCL) polymers is presented below:

2.6.1 Poly butylene succinate (PBS):

PBS is a very attractive aliphatic polyester because of its high biodegradability, relatively excellent mechanical properties, and thermal properties [92]. PBS is synthesized by the condensation polymerization of 1,4-butanediol and succinic acid. The above raw materials/ monomers are obtained from biobased chemicals as well as from petroleum-based chemicals. Earlier it was produced from petroleum-based chemicals only. Currently, it is being produced from bio-based monomers on a commercial scale by many manufacturers. The chemical structure of PBS is given below in Fig 2.12

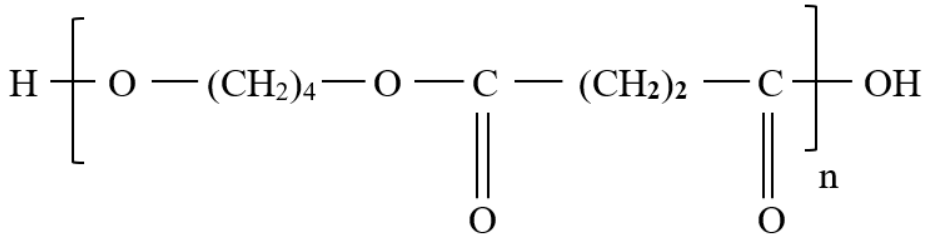


Fig 2. 12 Chemical structure of PBS

2.6.1.1 Properties of PBS

Essential properties of PBS are given in Table.2.4, and more details about its mechanical, thermal, barrier, and biodegradability characteristics are described below:

Table 2. 4 Typical Properties of PBS [89] & Datasheet from supplier

Specific gravity	1.26
Melt temperature Tm (˚C)	115
Glass transition temperature Tg (˚C)	-32
Heat distortion temperature (˚C)	97
Melt flow rate MFR (g/10 min)	22
Young's Modulus (MPa)	645
Tensile Strength (MPa)	35
Elongation at Break %	170
OTR mL m^{-2} day^{-1} (23˚C/0% RH)	403
WVTR g m^{-2} day^{-1} (25˚C/100% RH)	330

Mechanical properties:

The mechanical properties of PBS are comparable to LDPE, HDPE, and PP. The Young's modulus of PBS (645MPa) is in between LDPE and HDPE. The tensile strength of PBS (35 MPa) is in between PE and PP. PBS's tensile elongation (170-560 %) is comparable to that of PE and PP.

Thermal properties:

The thermal characteristics of PBS are between polyethylene and polypropylene. The glass transition temperature (T_g) of PBS is around -32˚C, which is in between the values for polyethylene (T_g -120˚C) and polypropylene (T_g -10˚C). PBS has a medium melting temperature (115˚C), close to that of PE.

Barrier properties:

PBS's OTR value is 403 mL m^{-2} $day^{-1,}$ and WVTR is 330 g m^{-2} day^{-1} for 1 mil film. Thus, PBS has better oxygen barrier property than LDPE, HDPE, and PP, but inferior to PVC, PET, etc. The water barrier property of PBS is inferior to all traditional polymers.

Biodegradability:

PBS has good biodegradability characteristics [93, 94]. PBS is biodegradable in compost, soil, lake, and seawater [95]. However, the biodegradation rate is not very high due to the high crystallinity of PBS [96-98]. Calabia et al. (2013) [99] reported a comparatively reasonable biodegradation rate of about 60% in 60 days through a study conducted, by CO_2 measurement, in compost medium, at 58°C.

2.6.1.2 Properties of PBS with additives (plasticizers & nanomaterials) & PBS blends

Many studies have been reported on modifying PBS properties using additives such as plasticizers and nanomaterials and by blending with other biodegradable polymers. A brief account of the investigations reported with plasticizers, nanomaterials (nano-clay, nano-cellulose), and blends with PCL polymer is presented below:

- **Properties of PBS with plasticizers (Plasticized PBS)**

Only a few studies have been reported on the use of plasticizers with PBS.

Zhao et al. (2012) [100] reported the usage of Epoxidized soybean oil (ESO) as a plasticizer for improving the mechanical and thermal properties of PBS. They observed 15 times improvement in elongation at break than that for pure PBS when the ESO loading was 5 wt%, though the tensile strength and tensile modulus for the blends were lower than those for pure PBS.

Liu et al. (2016) [101] also used epoxidized soybean oil (ESO) as a plasticizer/compatibilizer for PBS/lignin, and they studied the effects of ESO on the mechanical, rheological properties and morphology of PBS composite. Their studies indicated that ESO's use has a plasticizing effect and resulted in an increase in elongation at break by about 27.83% at 8 wt% ESO loading, though the tensile strength got reduced to some extent.

Liminana et al. (2018) [102] and Liminana (2019) [103] have used a vegetable oil-derived, maleinized linseed oil (MLO), as a plasticizer cum compatibilizer for modifying the properties of PBS-almond shell flour (ASF) composite and resulted in enhancement of mechanical properties, such as elongation at break and tensile modulus of the PBS-ASF composite, and 4.5-10 wt % of MLO was found to give the best overall performance.

- **Properties of PBS with nano-materials (Nano-composites of PBS)**

Ray et al. (2002) [104] prepared nanocomposites of PBS by melt extrusion of PBS and organically modified montmorillonite clay (OMMT) and reported remarkable improvement of mechanical properties compared to neat PBS.

Okamoto et al. (2003) [105] investigated nanocomposites of PBS with three types of organically modified montmorillonite (OMMT) clays and reported improved oxygen barrier properties and tensile modulus, though tensile strength was decreased. The biodegradability studies carried out by them in compost (58ºC) and soil medium indicated almost the same or slightly higher biodegradability for the nanocomposites. Though more cracks were observed in nanocomposite samples recovered after testing, molecular weight loss (determined by gel permeation chromatography) was almost the same for all samples, indicating the extent of PBS hydrolysis in the pure state or OMLS-filled systems is the same.

Lin et al. (2011) [106] prepared nanocomposites based on PBS, using two types of polysaccharide nanocrystals, cellulose whisker (CW) and starch nanocrystals (SN), with different loading levels, up to 20 wt%. They investigated Morphology, Mechanical, Thermal, and structural properties of the nanocomposites, which indicated enhanced mechanical properties (at lower concentrations) and higher crystallinity with CW and SN.

Phua et al. (2011) [94] prepared nanocomposites of PBS with 2 wt% organically modified montmorillonite (OMMT) clays and studied its mechanical properties, and also studied the effect of rolling. The tensile tests conducted by them indicated enhanced tensile strength, young's modulus, and elongation at break for the nanocomposites compared to neat PBS. They also observed that when the nanocomposite sheets were subjected to uniaxial cold rolling, tensile

strength along the machine direction (MD) increased substantially due to the increased molecular orientation after cold rolling.

Huang et al. (2014) [107] prepared nanocomposites of PBS with nano-TiO_2 at different loadings up to 10 wt% and studied the effect of TiO_2 content on properties, such as mechanical, thermal, morphology, etc. The studies demonstrated that TiO_2 could be uniformly distributed in the PBS matrix, the addition of TiO_2 has no effect on melting behavior, and it improves the mechanical/ flexural properties of PBS. The tensile strength decreased with TiO_2 loading. Tensile strength of the composite with 10% TiO_2 decreased to 25.5 MPa from 37.2 MPa for pure PBS. However, the tensile modulus increased with increasing TiO_2 loading, it increased by 15.5% with 10 wt% TiO_2 loadings. The PBS - TiO_2 composite exhibited increased UV resistance.

Chen et al. (2015) [108] studied the properties of nanocomposites of PBS with nano-$CaCO_3$ and observed increased thermal stability nanocomposites, though there were no changes with $CaCO_3$ content. Also, there were no changes in crystallization and melting behavior with $CaCO_3$ addition to PBS.

Luduena et al. (2016) [109] prepared nanocomposites films from PBS-PEG (80/20) and cellulose nanocrystals (CNC), with 0, 2, 4, and 6 wt% CNC. Their studies on mechanical properties indicated an increase in elongation at break and decreased tensile strength with an increase in CNC loading. The elongation at break increased from 283% (for PBS-PEG) to 320, 329, and 482, while the tensile strength decreased from 36 MPa (for PBS-PEG) to 32.3 MPa, 31.6 MPa, and 26.8 MPa, respectively with 2, 4, and 6 wt% CNC loading. The Youngs modulus increased up to 4% CNC content. Overall, they observed that the nanocomposite with 4% CNC was found to have the best overall mechanical performance.

- **Properties of PBS-PCL blends**

PBS is relatively rigid /mechanical flexibility is relatively low due to its high crystallinity, limiting its use for 100% PBS based flexible packaging products. [110-112]. PCL is one of the attractive polymers for blending with PBS [92] because of its high elasticity, low Tg, and high biodegradability, and a brief overview of the studies reported on PBS-PCL blends is given below:

John et al. (2002) [113] prepared Polybutylene succinate (Bionolle)- Polycaprolactone (PBS-PCL) blends of different compositions (and also blends with another polyester Eastar) and carried out studies on tensile properties, thermal behavior by DSC, crystallinity by DSC and XRD, morphology by SEM, FTIR studies and examined compatibility between the polymers. They reported synergic interaction, with an increase in tensile strength (~31% increase) and elongation at break (~124% increase) and crystallinity with an increase in PCL concentration up to 30% and then a decrease up to 50% PCL. They observed two different melting temperatures (Tm) and two different glass transition temperatures (Tg) for the blends indicating the blends' immiscible nature. However, they observed a slight shift in Tg and changed the position of peaks in the FTIR spectrum compared to neat polymers, indicating little interaction between them.

Qiu Z et al. (2003) [114] prepared PBS/PCL blends ranging from 80/20 to 20/80 by co-dissolving the two polyesters in chloroform and casting and investigated miscibility and crystallization behavior through DSC and optical microscopy studies, and they observed independent composition Tg, indicating low miscibility.

Reddy et al. (2012) [115] prepared blends of PBS, PCL along with thermoplastic soy meal protein (TSM) and investigated mechanical, thermal, morphology of the ternary blends. With an increasing amount of PCL in the blend, they observed improved mechanical properties such as % elongation, toughness, and impact strength, though there was a decrease in tensile strength.

Can et al. 2014 [116] carried out studies on PBS-PCL blends (10–40 wt.% PCL), with and without a compatibilizer, namely poly(ethylene oxide)-block-poly(propylene oxide)-block poly(ethylene oxide) (PEO-PPO-PEO). They investigated mechanical, thermal, and morphological properties and also degradation of the blends in a buffer solution. SEM studies of PBS-PCL blends carried out by them indicated that the PCL was dispersed in the PBS matrix as spherical domains and that the addition of compatibilizer resulted in a decrease in the PCL spherical domain size, indicating better compatibility between the PBS and PCL. However, the spherical PCL domains disappeared in the blends with high PCL content (40% PCL), in blends with and without compatibilizer. Their studies indicated that, with increasing PCL content, the PBS-PCL blends' total crystallinity was

unchanged at 10–20 wt.% PCL and then decreased at a higher amount of PCL. The degradation studies (in buffer solution) of PBS-PCL blends indicated an increased degradation rate compared to PBS.

Liu et al. (2015) [117] investigated the use of poly(butylene succinate-co-caprolactone) P(BS-co-CL) as a compatibilizer on PBS-PCL (80/20) blends. They studied effects of the amount of P(BS-co-CL) polymer on morphology, crystallization behavior, and mechanical properties of PBS/PCL blends through DSC, SEM, XRD etc. and reported a dramatic increase in mechanical properties such as modulus of elasticity, yield stress, and fracture strain with the addition of (5 wt%) compatibilizer.

Huang et al. (2016) [118] carried out degradation studies of PBS-PCL blends of various compositions in soil culture and compost culture solutions by a weight-loss method and also studied changes in structure, crystallinity, and morphology through FTIR, XRD, and microscopic studies respectively. They observed a higher degradation rate in both soil and compost culture for the PBS-PCL blends than PBS and found that the degradation rate follows the order PBS-PCL blend > PCL > PBS. Through FTIR studies, they indicated interaction and possible hydrogen bonding between PBS and PCL. They observed an increase in polymer blends' crystallinity after exposure to soil/ compost culture solutions, suggesting that the microorganisms first degrade the non-crystalline and low-density areas before degrading the crystalline part.

Fenni et al. (2019) [119] carried out studies on morphology by SEM and Crystallization behavior/kinetics by DSC. Their studies indicated the immiscible nature of PBS-PCL blends, with sea-island morphology in which the minor phase is dispersed as droplets (0.5 to 2 μm) inside the matrix of the significant phase. SEM images indicated cavities in different blends due to debonding between the polymer phases during the cryogenic fracture, indicating immiscibility and poor adhesion between the different components of binary blends.

Gumede et al. (2019) [120] prepared PBS-PCL blends with 30 and 70% PCL, with and without additives. They carried out studies on morphology, tensile, thermal, and crystallization behaviour. Their tensile tests indicated a decrease in both tensile strength and elongation at break with the

addition of 30% PCL, and they observed an increase in elongation at break only at very high PCL content (70% PCL).

A brief summary of the Investigations on PBS is given in Table 2.5-2.7

Table 2. 5 Summary of investigations on PBS with Plasticizers

Year	Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2012	Zhao	PBS+ ESO	Mechanical & Thermal	Improvement in elongation at break by 15%, at 5 wt% ESO.
2016	Liu	PBS+ESO	Mechanical, Rheological & Morphology	Improvement in elongation at break by 27.83%, at 8 wt% ESO.
2018 And 2019	Liminana (2018) and Liminana (2019)	PBS composite + MLO	Mechanical	MLO acts as a plasticizer and as a compatibilizer Increased elongation and modulus with MLO, Optimum 4.5-10 wt% MLO

Table 2. 6 Summary of investigations on PBS with Nanomaterials

Year	Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2002	Ray, Okamoto	PBS + OMMT clay	Mechanical	Improvement of mechanical properties
2003	Okamoto, Ray	PBS + OMMT clay (3 types)	Mechanical Barrier (OTR) & Biodegradation	Improved oxygen barrier properties and tensile modulus,

				No significant change in biodegradability
2011	Lin	PBS+CW PBS+SN up to 20 wt%	Morphology, Mechanical, Thermal & Crystallinity	Enhanced mechanical properties, Enhanced tensile strength, elongation at lower wt % of CW and SN. Enhanced crystallinity
2011	Phua	PBS+OMMT 2wt%	Mechanical & Effect of Rolling	Improvement in tensile strength with rolling. Enhanced tensile strength, Young's modulus, and elongation at break for the nanocomposites.
2014	Huang	PBS+TiO_2 0.5, 1, 2, 5, 10%	Mechanical & Thermal	TiO_2 has no effect on melting behavior, Improves UV resistance. Improves the mechanical/ flexural properties of PBS. Tensile strength (TS) decreases, and young's modulus (YM) increases with an increase in TiO_2 loading.
2015	Chen	PBS + Nano $CaCO_3$	Thermal & Rheological	Increased thermal stability

2016	Luduena	PBS+PEG+ CNC (2, 4, 6 wt%)	Mechanical	Elongation at break EB increases with CNC content. TS decreases with CNC loading YM increases up to 4%CNC.

Table 2. 7 Summary of investigations on PBS –PCL blends

Year	Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2002	John	PBS-PCL 0, 15, 30, 50, 70, 100 % PCL	Tensile, Thermal, Crystallinity& Morphology	Increase in TS & EB and crystallinity up to 30% PCL and then decrease to 50% PCL. -Immiscible nature of blends.
2003	Qiu Z	PBS/PCL blends	Miscibility and Crystallization behavior	Composition independent Tg, indicating low miscibility.
2012	Reddy	PBS-PCL-TSM (thermoplastic soy meal)	Mechanical, Thermal& Morphology	Increase in % elongation, Toughness, and impact strength with increased PCL content. A decrease in TS.
2014	CanE	PBS-PCL (10-40%PCL), +PEO-PPO-PEO compatibilizer	Mechanical, Thermal, Morphology& Degradation in buffer solution.	The addition of PEO-PPO-PEO improves Compatibility between PBS and PCL. Increased degradation rate (in buffer solution) for PBS-PCL blends compared to PBS.

2015	Liu.	PBS-PCL+ P(BS-co-CL) compatibilizer	Mechanical Morphology & crystallization	Increase in the mechanical properties
2016	Huang	PBS-PCL	Degradation studies in soil and compost, morphology	Higher degradation rate in both soil and compost culture. -Order of degradation PBS-PCL blend >PCL>PBS. -Interaction, hydrogen bonding between PBS and PCL.
2019	Fenni	PBS-PCL-PLA Binary and ternary blends	Morphology and Crystallization kinetics	Observed sea-island morphology for PBS-PCL blends, indicating immiscibility.
2019	Gumude	PBS-PCL-MWCNT	Tensile tests, Morphology, Thermal & crystallization behavior	Decrease in both tensile strength and elongation at break with the addition of 30% PCL, and the increase in elongation at break at very high PCL content (70% PCL).

2.6.2 Polyhydroxyalkanoates (PHAs: e.g., PHB, PHV, PHBV)

Polyhydroxyalkanoates (PHA) are a family of biodegradable polyesters produced by bacteria [121]. They are stored in the form of granules in the bacterial cells, as carbon and energy storage materials. PHAs are commercially produced by bacterial fermentation of renewable materials [122, 123] such as glucose, lipids etc., under imbalanced nutritional conditions, followed by extraction with solvents. Poly(3-hydroxybutyrate) (PHB) is the most widespread and best-characterized PHA polymer family member. PHB is a semi-crystalline material with a high degree of crystallinity (> 50). Other members of the family include polyhydroxy valerate (PHV), Poly (3-hydroxybutyrate-co-3-hydroxy valerate (PHBV), etc. The chemical structure of PHB is given below in Fig. 2.13

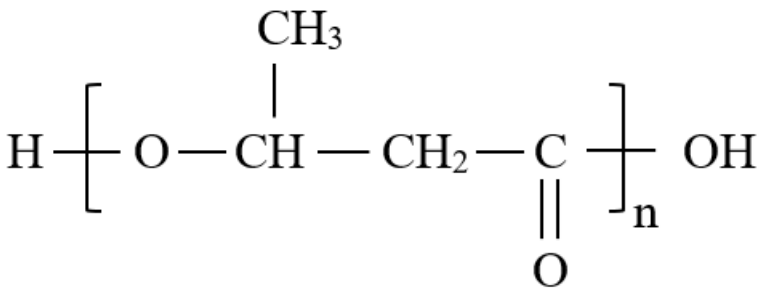


Fig 2. 13 Chemical structure of PHB

2.6.2.1 Properties of PHB

Essential properties of PHB is given in Table.2.8, and more details about its mechanical, thermal, barrier, and biodegradability characteristics are described below:

Table 2. 8 Typical Properties of PHB [89]& Datasheet from supplier

Specific gravity	1.25
Melt temperature Tm (°C)	178
Glass transition temperature Tg (°C)	4
Heat distortion temperature (°C)	135-145
Melt flow rate MFR (g/10 min)	8-15
Young's Modulus (MPa)	1000–2000
Tensile Strength (MPa)	25–40
Elongation at Break %	5-8
OTR mL m^{-2} day^{-1} (23°C/0% RH)	269–410
WVTR g m^{-2} day^{-1} (25°C/100% RH)	158–217

Mechanical properties:

PHB has many mechanical properties comparable to that of polypropylene. It has a relatively high Youngs modulus (1-2 GPa) and tensile strength (40 MPa) like PP. However, PHB is relatively brittle. It has a low elongation at break of 5-8 %, which is very much less than PP, LDPE, and HDPE.

Thermal properties:

PHB has a high melting temperature (178°C), which is very close to that of PP. The glass transition temperature of PHB is 4°C, but higher than (-18°C) for PP. One of the disadvantages of PHAs is that its thermal decomposition temperature (210ºC), is just above its melting temperature, therefore leaving a narrow temperature window for processing.

Barrier properties:

The OTR value of PHB is in the range of 269-410 mL m^{-2} day^{-1}, which is lesser than that of LDPE, HDPE, PP / thus, the oxygen barrier properties of PHB are better than PE and PP [89]. However, the water vapor barrier properties of PHB are inferior to that of PE and PP. The WVTR value of PHB is about 158-217 g m^{-2} day^{-1}, which is higher than that for traditional polymers.

Biodegradability:

PHAs are fully biodegradable in both anaerobic and aerobic conditions without forming any toxic products [34, 124]. Poly(hydroxy alkanoates) are quite resistant to moisture, but they are rapidly biodegraded by a wide range of microorganisms that are widely distributed in the environment [125]. The biodegradation of PHB has been reported in various environments such as in the compost, soil, freshwater, and seawater [126]. PHAs are reported to be compostable over a wide range of temperatures, even at a maximum of around 60°C, with moisture levels at 55%. PHA has been reported to degrade in aquatic environments such as Lake Lugano of Switzerland within 254 days, even at temperatures not exceeding 6°C [34]. Polyhydroxyalkanoates (PHAs) are gaining increasing attention in the biodegradable polymer market due to its many attractive features, especially its biodegradability characteristics in different environments [34]. The high production cost of PHAs has limited their market penetration, despite the advantages [123].

2.6.2.2 Properties of PHB with additives (plasticizers & nanomaterials) & PHB blends

Many studies have been reported on modification of PHB properties either by using additives such as plasticizers and nanomaterials or by blending with other biodegradable polymers. A brief account of the investigations reported with plasticizers, nanomaterials (nano-clay, nano-cellulose), and blends with PCL polymer is presented below:

- **Properties of PHB with plasticizers (Plasticized PHB)**

The effect of plasticizer PEG on the properties of PHB was studied by Parra et al. [2006] [127] with reported reduced tensile strength and increased elongation at break of pure PHB, with the addition of PEG. They also observed an increase in water vapor permeability and enzymatic biodegradation with the addition of PEG.

Rapa et al. (2015) [128] studied plasticization of poly(3-hydroxybutyrate) (PHB) using triethyl citrate (TEC), acetyl o-tributyl citrate (ATBC), and tributyl citrate (TBC) with 10-30% Plasticizer and reported the effect of plasticizer content on the melt viscosity, thermal properties (DSC), spectral characteristics (FTIR), tensile properties and water permeability. They found that the effect of plasticizer on WVTR was dependent on the type and content of plasticizer. They also reported that incorporating plasticizers into PHB decreased tensile strength and Young's modulus but increased elongation at break. The results indicated that acetyl tributyl citrate (ATBC) and tributyl citrate (TBC) are the most compatible and efficient plasticizers for PHB to improve the thermal, mechanical, and barrier properties of PHB.

Farris et al. (2014) [129] prepared plasticized PHB with polyethylene glycol plasticizer having a different molecular weight (400, 1500, and 4000) and with 10-20% by weight of plasticizer content, and studied the tensile properties. They observed that the property was found to vary with molecular weight and concentration. PEG 400 and PEG1500 was found to have good miscibility and was found to be most suitable for plasticizing PHB. PEG 1500, at 15 wt % concentration, was found to have the highest tensile elongation at break.

- **Properties of PHB with Nano-materials (Nanocomposites of PHB)**

Maiti et al. 2003 [130]carried out studies on nano-composites of PHB using three types of nano-clays, and results indicated improvement in mechanical properties/ Youngs modulus (by about 40%) in nanocomposites, compared to the neat polymers. Biodegradation studies indicated that the decomposition rate varies with the type of nano-clay/ surface hydroxyl groups present in the clay.

Tanase et al. (2015) [131] prepared nano-composites by blending PHB with adipate plasticizer proviplast (Bis[2-(2-butoxyethoxy)ethyl] adipate) along with 2,5 and 10% cellulose fibers and carried out studies on thermal and barrier properties (WVTR). The studies indicated a reduction of melting temperature, crystallinity, and reduction in water barrier properties (increase in WVTR) with cellulose fibers.

Seoane et al. (2017) [132] investigated nano-composite films based on PHB, incorporated with two types of nano-cellulose (2, 4 wt%), bacterial cellulose (BC) or cellulose nanocrystals (CNC), and plasticized with tributyrin or a polymeric plasticizer poly (adipate diethylene). They studied morphology, thermal properties, and disintegration under composting conditions. Their studies indicated a higher disintegration rate with plasticizers and a slower disintegration rate with nano-cellulose.

Akin et al. (2018) [133] prepared nano-composite films based on PHB and PHBV using different loadings of organo-modified montmorillonite (OMMT-Cloisite 10A) clay and studied mechanical, thermal, and water vapor permeability properties. They observed that the composite films' properties were highly dependant on the concentration/ and dispersion of clay in the polymer matrix. They observed enhanced water vapor barrier properties/ reduction in WVTR by 41% for PHB based composite films. They also observed an improvement in mechanical properties, tensile strength and reported that the elongation at break increased by 152.3% and 77.4%, respectively, with 3% nano-clay.

Seoane et al. (2019) [134] investigated nano-composites of PHB incorporated with two types of cellulose (cellulose nanocrystals-CNC and bacterial cellulose-BC) along with two types of

plasticizers (glyceryl tributyrate-TB and a polymeric plasticizer poly[di(ethylene glycol) adipate). They reported that the plasticized PHB nanocomposites prepared by the addition of CNC and BC nanoparticles were macroscopically more homogeneous and that bacterial cellulose was not as uniformly dispersed as CNC, probably because of its large aspect ratio. The plasticized nanocomposites' tensile properties were not much different from that of pristine PHB due to the opposing influence of plasticizer and nanoparticles. They observed that plasticizers' addition reduced barrier properties, which was partly countered by the improved barrier property with nano cellulose. However, there was a net increase in WVTR compared to neat PHB.

- **Properties of PHB-PCL blends**

Though Poly hydroxybutyrate (PHB) is an attractive polymer with high biodegradability characteristics, it has few shortcomings. High cost, poor thermal stability, relatively low impact resistance, low elongation at break, challenges in processing PHB into thin, flexible films are a few of the factors that have prevented its widespread application. Its high melting point and low degradation temperature limit the possibility of preparing PHB films by thermal processing. PHB films have been prepared by solvent casting process, which involves dissolving the polymer in a suitable solvent such as chloroform, acetic acid etc, and evaporating the solvent. However, the solvent casting process has many disadvantages. Solvent casting may produce pores during solvent evaporation, and traces of solvent may remain in the film's polymer, which could prove to be a health risk. [135]

PHB is often blended with other polymers to control and improve its overall performance [136]. Blends of PHB with polycaprolactone (PCL) have attracted much interest because PCL is also highly biodegradable. These two polymers display entirely different mechanical and thermal properties, thus blending them to tailor the final properties to satisfy different applications.

Antunes, M. C. M., & Felisberti, M. I. (2005) [137] prepared PHB-PCL blends of composition from 0 to 30 wt% of PCL by melt mixing and characterized the blends with DSC, DMA, and SEM. They found that the blends were immiscible with no interaction and that the morphology indicated PHB as the matrix and PCL as the dispersed phase.

Lovera, D. et al. (2007) [138] prepared two types of PHB-PCL blends, one using high molecular weight and another using low molecular weight/ modified mPCL, and studied morphology, crystallization, and enzymatic degradation of the blends by DSC, polarized light optical microscopy, SEM, H NMR, and weight loss measurements. They reported improved miscibility and lower degradation in PHB-mPCL blends, while higher degradation than individual polymers was reported in PHB-PCL blends.

Garcia-Garcia, D. et al. (2016) [139] prepared PHB blends PCL to improve the high intrinsic fragility of PHB by melt compounding in a twin-screw extruder followed by injection molding. They studied the mechanical and thermal properties and miscibility, and morphology of the blends as a blend composition function. They observed a slight increase in tensile elongation with an increase in the PCL content up to 50 wt% but observed a very rapid increase with more than 50 wt% PCL. Tensile elongation increased from 8.1% (raw PHB) up to 17.6% for PHB-PCL blends with 50 wt% PCL and up to values over 1000% for a blend with 75 wt% PCL. Dynamic mechanical, thermal analysis (DMTA) studies indicated very low miscibility between PHB and PCL polymers with Tg at around -53 ˚C and -7 ˚C for the PCL-rich phase and PHB-rich phase, respectively.

Chen, J et al. (2017) [140] prepared PHB-PCL composites using microcrystalline cellulose (MCC) particles and ethyl cellulose (EC) and studied the phase morphology and mechanical properties. They reported that the addition of MCC and EC increased the tensile strength and impact strength of PHB/ PCL (50/50) blend, due to enhanced miscibility of the components, with nano-cellulose.

Correa, J. P et al. (2017) [141] prepared PHB-PCL blends and organo - nano clay composite films and studied tensile, thermal, water vapor barrier properties and observed improved barrier properties and degradation temperature. The above films, which were activated with nisin, were effective against Lactobacillus /showed potential for their application in processed meat packaging.

Garcia-Garcia, D., et al. (2018) [142] prepared PHB-PCL blend films, with a composition of 75 wt% PHB and 25 wt% PCL (PHB75/PCL25) and prepared composite films with different loads

(3, 5 and 7 wt%) of cellulose nanocrystals (CNCs), by solvent casting followed by melt compounding and then thermo-compression. They studied the effect of CNCs loading on the mechanical, thermal, optical, wettability, and disintegration in controlled compost conditions. They reported the best dispersion of CNCs in the PHB/PCL blends and best-balanced properties in mechanical, thermal, optical, and wettability, at a loading of 3 wt% CNC. They reported enhanced transparency and improved disintegration with CNC's addition to the PHB/PCL blend films.

A brief summary of the Investigations on PHB is given in Table 2.9 - 2.11

Table 2. 9 Summary of investigations on PHB with Plasticizers

Year	Reference Author	Blend composition	Investigation carried out	Research findings/ Remarks
2006	Parra	PHB +PEG 0-40 wt%	Thermal Mechanical Permeability and Biodegradation	Reduction in tensile strength and Increased elongation at break, Increase in WVTR Increased biodegradation with PEG.
2014	Farris	PHB+PEG Mol wt 400, 1500, 4000 10-20 wt%	Mechanical	PEG 400 and PEG1500 was found to be most suitable for plasticizing PHB.
2015	Rapa	PHB + TEC, ATBC, TBC	Thermal Mechanical and WVTR	Decreased tensile strength and Young's modulus, increased elongation at break. ATBC and TBC most efficient plasticizers for PHB.

.

Table 2. 10 Summary of investigations on PHB with Nanomaterials

Year	Reference Author	Blend composition	Investigation carried out/	Research findings/ Remarks
2003	Maiti	PHB- nano clay	Mechanical Biodegradation- compost	Improved mechanical properties BD depends on the type of nano-clays, surface hydroxyl groups present in the clay.
2015	Tanase	PHB-Plasticizer-CF (2,5 10%)	Barrier (WVTR) properties & Thermal	Reduction of melting temperature, crystallinity, and reduction in water barrier properties (increase in WVTR)
2017	Seoane	PHB-Plasticizer-nano-cellulose (BC, MCC)	Morphology, Thermal & Biodegradation	Higher disintegration rate with plasticizers and a slower disintegration rate with nano-cellulose.
2018	Akin	PHB-Clay (0, 1, 2, 3%)	Mechanical & Barrier (WVTR)	Improvement in barrier properties and mechanical properties. WVTR reduced by 41% tensile strength increased by 152.3% elongation at break increased by and 77.4%

2019	Seoane	PHB+Plasticizers (TB, A) *Nano cellulose (CNC, BC) *glyceryl Tributyrate — TB) and (polydi(ethylene glycol) adipate) A)	Mechanical Barrier	The tensile properties not different from that of pristine PHB due to the opposing influence of plasticizer and nanoparticles. The addition of plasticizers reduced barrier properties, which was partly countered by the improved barrier property with nano cellulose. However, there was net increase in WVTR, compared to neat PHB.

Table 2. 11 Summary of Investigations on PHB-PCL blends

Sl No	Reference	Blend composition	Investigation carried out	Remarks
2005	Antunes,	PHB-PCL 0-30wt %PCL	Miscibility morphology	Blends immiscible with no interaction.
2007	Lovera,	PHB-PCL high and low mol wt PCL	Morphology enzymatic degradation.	Improved miscibility with low mol weight PCL, but lower degradation.
2016	Garcia	PHB-PCL 25, 50, 75% PCL	Mechanical, thermal morphology.	Improved tensile elongation with >50%PCL.
2017	Chen	PHB-PCL + MCC cellulose	morphology mechanical .	Improved miscibility /compatibility

2017	Correa	PHB-PCL + organoclay	Mechanical thermal, Barrier	Improved barrier properties.
2018	Garcia	PHB-PCL+ CNC CNC 3,5, 7 wt%	Mechanical, thermal, disintegration in compost	balanced properties with 3 wt% CNC

2.6.3 Polylactic acid (PLA)

Polylactic acid (PLA), also known as Polylactide, dominates the biodegradable polymers' word market, as it has many attractive features. PLA is chemically synthesized from lactic acid (or its cyclic di-ester lactide), obtained from renewable resources, by the bacterial fermentation of agricultural by-products such as corn starch or other starch-rich substances like maize, sugar, or wheat. Since lactic acid monomer exists as two optical isomers, i.e., D and L forms, several forms of polylactic acid exist poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and poly-DL-lactic acid (PDLLA). PLLA and PDLA are semi-crystalline polymers, while PDLLA is amorphous. Most commercially available PLA are predominantly in the L form (PLLA), with small amounts of PDLA and PDLLA [143]. The chemical structure of PLA is given in Fig. 2.14.

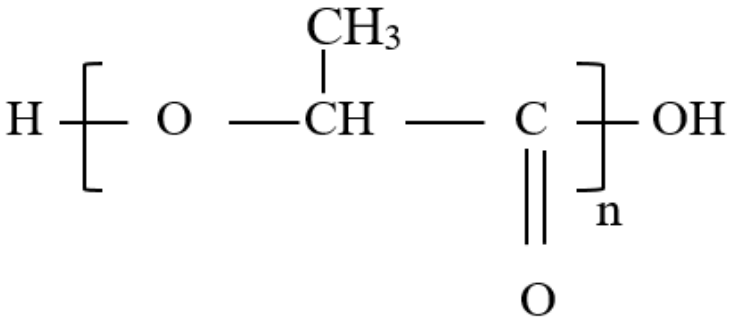


Fig 2. 14 Chemical structure of PLA

2.6.3.1 Properties of PLA

Essential properties of PLA are given in Table.2.12, and more details about its mechanical, thermal, barrier, and biodegradability characteristics are described below:

Table 2. 12 Typical Properties of PLA. Datasheet from supplier & [89]

Specific gravity	1.24
Melt temperature T_m (°C)	152
Glass transition temperature T_g (°C)	58
Heat distortion temperature (°C)	55
Melt Flow rate MFR (g/10 min)	14
Young's Modulus (MPa)	2050
Tensile Strength (MPa)	40-63
Elongation at Break %	9
OTR mL m^{-2} day^{-1} (23°C/0% RH)	800
WVTR g m^{-2} day^{-1} (25°C/100% RH)	172

Mechanical properties:

PLA's mechanical properties are comparable to conventional plastics/polymers such as polystyrene (PS) and polyethylene terephthalate (PET). PLA has comparatively a high Youngs/tensile modulus (> 2000MPa) and tensile strength (40-63MPa) like PET and PS, which is higher than that of PP, LDPE, HDPE . The elongation at break of PLA is very low (9%) like PS and is considered one of PLA's disadvantages.

Thermal properties:

PLA has a very high glass transition temperature (Tg) of 58°C, much higher than LDPE, HDPE, and PP. PLA's melting temperature is 152°C, which is very much lower than those of PET and PS, which makes PLA better for thermal processing such as through extrusion and thermoforming [144]. However, its thermal stability is poor [145].

Barrier properties:

The oxygen transmission rate (OTR) of PLA is 800 ml/m^2/d, the barrier property of PLA for oxygen is inferior to traditional polymers such as PVC, PET, etc. [89]. However, the oxygen barrier property of PLA is better than LDPE, HDPE, PS, PP. The water vapor transmission rate (WVTR)

of PLA is 82-172 g/m^2. Thus, PLA's water vapor barrier property is inferior compared to all traditional polymers such LDPE, HDPE, PP, PET, and PS., and is comparatively superior/ value of WVTR for PLA is lower than other biodegradable polymers such as PHB, PBS PCL etc.

Biodegradability:

Regarding biodegradability, PLA is fully biodegradable but requires an elevated temperature of about 58°C for the initial hydrolysis step. It is biodegradable when composted in an industrial composting facility, where the temperatures are usually above 60˚C. However, such a composting facility is not available in all waste disposal sites. PLA does not degrade in landfills (anaerobic conditions) and in-home compost conditions. PLA is mostly resistant to attack by microorganisms in soil or sewage under ambient conditions. PLA degrading microorganisms are not widespread in the environment [125].

Itavaara et al. (2002) [146] reported biodegradation studies of PLA in the aquatic medium and compost medium. The aquatic medium's biodegradation studies were carried out by CO_2 evolution method, at various temperatures from 25˚C to 60˚C, using microbial inoculum prepared by mixing household waste compost with mineral salts solution and filtering. The maximum temperature for the biodegradation studies in compost medium was about 70˚C. Their studies indicated that the temperature is a significant factor for biodegradation of PLA and that that the PLA polymer structure must be hydrolyzed before microorganisms can utilize it as a nutrient source. They observed very slow mineralization of PLLA at room temperature, only 10% biodegradation observed in 210 days, at ambient/mesophilic temperatures (25° and 37˚C). At temperatures close to the glass transition temperature (55˚C), under thermophilic conditions, they observed a rapid increase in biodegradation/ mineralization rate and observed more than 90% mineralization for PLA in aquatic medium and compost medium.

Ho et al. (1999) [147] studied biodegradation of commercial PLA samples in soil under laboratory conditions, by respirometric method, at three different temperatures, 28°, 40°, and 55°C, for 182 days. They observed a prolonged biodegradation rate for PLA in the soil at a temperature below 40˚C and a drastic increase in biodegradation rate at 55˚C. The average % biodegradation rate observed by them was 27%, 45%, and 75%, respectively, at 28˚C, 40˚C, and 55˚C, respectively.

Satti et al. (2018) [148]investigated biodegradation of PLA films soil matrix under mesophilic conditions and found that the rate of mineralization was prolonged and biodegradation was only about 10% after 150 days. They carried out studies on increasing the biodegradation rate 'bioaugmentation' with previously isolated PLA-degrading bacteria and 'bio-stimulation' by stimulating the native microbial community with 0.2% sodium lactate addition, and they observed enhanced mineralization rate of PLA to 22 and 24%, respectively, at 150 days.

Greene et al. (2018) [149] carried out biodegradation studies of commercially available PLA and other packaging materials under industrial composting conditions, marine, and anaerobic conditions ASTM D5338, ASTM D6691, and ASTM D5511 standard test methods, respectively.

They found that the biodegradation of PLA was above 90% under industrial composting conditions (at 58°C), thus meeting the ASTM D-6400 standard's degradation requirement. However, under marine conditions, at 30°C, there was very low/ practically no biodegradation for the PLA samples in seawater even after 180 days. Under the same marine conditions, cellulose reference had 32% biodegradation.

2.6.3.2 Properties of PLA with additives (plasticizers & nanomaterials) & PLA blends

Many studies have been reported on modification of PLA properties using additives such as plasticizers and nanomaterials and by blending with other biodegradable polymers. A brief account of the investigations reported with plasticizers, nanomaterials (nano-clay, nano-cellulose), and blends with PCL polymer is presented below:

- **Properties of PLA with plasticizers (Plasticized PLA)**

Baiardo et al. (2003) [150]carried out studies on the effect of plasticizers such as acetyl tributyl citrate (ATBC) and polyethylene glycol (PEG) to improve the thermal and mechanical properties of PLA. Both ATBC and PEG were found to be suitable plasticizers for PLA. Both were effective in lowering the glass transition (Tg) of PLA, enhancing elongation at break of PLA, however, at

the expense of tensile strength. The plasticizing efficiency of PEG was found to increase with decreasing molecular weight of PEG.

Murariu [2008] [151]studied the effect of three plasticizer bis(2-ethylhexyl) adipate (DOA), triacetin/ glycerol triacetate (GTA), and tributyl acetyl citrate (ATBC) on PLA and observed that GTA has the best plasticizer efficiency, about a reduction in glass transition temperature ductility etc.

Lemmouchi et al. (2009) [81] reported plasticization of PLA with tributyl citrate (TBC) along with low molecular weight poly(D,L-lactide)-b-poly(ethylene glycol) copolymers (PLA-b-PEG) of different molecular weights. They observed improvement in the plasticized blends' thermo-mechanical properties, with Tg below 30ºC and high strain at break (>220%). They also reported higher biodegradation of PLA, in composting conditions, with plasticizers to PLA.

Courgneau, C et al. 2011 [152] studied plasticization of PLA with acetyl tributyl citrate (ATBC) and polyethylene glycol (PEG-300) and reported a decrease in barrier properties which varies with the type of plasticizer and amount of plasticizer.

Arrieta et al. carried out studies on PLA-PHB blends with and without plasticizer limonene [153]. They also reported that the plasticizer limonene decreased the Tg and improved the biodegradation of PLA-PHB under composting conditions.

Arrieta et al. [2014] also carried out studies on PLA-PHB blends using plasticizers polyethylene glycol (PEG) and acetyl-tri-n-butyl citrate (ATBC) [154]and observed that PHB slowed down the PLA biodegradation, while plasticizers speeded it up.

Armentano et al. [2015] [155] prepared PLA-PHB blends plasticized with a lactic acid oligomer (OLA). They demonstrated a significant decrease in their glass transition temperatures and improvements in the barrier properties attributed to higher crystallinity of the plasticized PLA-PHB blends.

Maiza, M.et al. (2015) [156] investigated the effect of plasticizers triethyl citrate (TEC) and acetyl tributyl citrate (ATBC) on thermomechanical properties of PLA and migration of plasticizer from the PLA. They reported that the addition of both TEC and ATBC resulted in a decrease in glass transition temperature (T_g) and that Tg reduction was the largest, with the plasticizer having the lowest molecular weight (TEC). TGA studied by them indicated that ATBC and TEC promoted a decrease in the PLA's thermal stability. They also reported thermally induced migration/ leaching of the plasticizer from the product.

- **Properties of PLA with Nanomaterials (Nanocomposites of PLA)**

Ray et al. (2003) [157]prepared nanocomposites of PLA using 4 different types of organically modified layered silicate clays (OMLS) (containing 4 wt % of OMLS) and studied biodegradability in compost medium at 58˚C, by CO_2 evolution measurement, using an attached FT-IR spectrometer. They observed improvement in biodegradability and other properties such as mechanical (flexural) properties, thermal property (HDT), oxygen gas permeability, etc., compared to those of pure PLA.

Sinha Ray et al. (2003) [158] carried out studies on PLA-organically modified layered silicate clay (OMLS) nanocomposites of 3 different compositions (4, 5, and 7 wt%), and they reported significant improvement in crystallization behavior, mechanical properties, heat distortion temperature, and O_2 gas permeability when compared with pure PLA, with the addition of nano clay.

Petersson, L., & Oksman, K. (2006) [159] prepared two types of nanocomposites of PLA using bentonite clay and microcrystalline cellulose (MCC), using 5 wt% of nanomaterial, by solution casting and compared the effect of both nanomaterials. The bentonite clay nanocomposite showed more improvements in tensile modulus, yield strength. Bentonite nanocomposite also showed a reduction in the oxygen permeability, but not the MCC nanocomposite. The effect on elongation at break was found to be more satisfactory for MCC compared to the bentonite. They reported an increase in oxygen permeability with the addition of cellulose to PLA.

Ozkoc and Sebnem Kemaloglu (2009) [160] prepared nanocomposite films of PLA and plasticized PLA containing 20% PEG, with 0, 3, and 5 wt% nano clay and carried out biodegradation studies in compost at 58˚C, by weight loss measurements and also studies on mechanical properties. They found that nano clay retards the biodegradation rate of nano-composites, and order of biodegradation rate observed by them was PLA > PLA/PEG > 3% Clay/ PLA/PEG > 5% Clay/PLA/PEG > 3% Clay/PLA. Tensile tests conducted by them indicated that the addition of 3% clay to PLA and plasticized PLA enhances the nanocomposites' tensile modulus compared to neat-PLA and PLA/PEG blend. Also, the addition of clay to the plasticized resulted in a reduction in the elongation at break.

Bhatia et al. [2010] [161]prepared a nanocomposite consisting of PLA-PBS-organically modified montmorillonite clay (OMMT) and studied the barrier properties. They observed significant improvement / about 26% decrease in oxygen permeability up to 3 wt % OMMT clay. They also observed an increase in tensile strength and Young's modulus, but a decrease in elongation at break, with the addition of clay.

Fortunati, E., et al. 2012 [162]prepared PLA-cellulose nanocomposites using pristine cellulose nanocrystals (CNC) and surfactant-modified cellulose nanocrystals (s-CNC), at two different loadings of 1wt% and 5 wt%, by solvent casting and studied the effect of the cellulose modification and content of nanomaterial. Surfactant modified s-CNC exhibited good dispersion. Good oxygen barrier properties were observed for both modified and un-modified cellulose nanocrystals. However, surfactant modified s-CNC showed higher water permeability.

Duan et al. 2013 [163] prepared PLA nanocomposites containing 1 to 6 wt% of montmorillonite layered silicate clay and studied morphology and water barrier properties. They reported a decrease in WVTR with increasing nano clay content, up to a value of 5 wt%.

PLA nanocomposites were prepared by Tenn et al. [164], using 5% organically modified montmorillonite layered silicate clay, acetyl triethyl citrate ester plasticizer and reported that the nanocomposite films showed a 48% improvement in oxygen barrier properties, a 50% improvement in water vapor barrier properties in comparison to the neat PLA. They also observed slightly increased

biodegradation rates in the soil for the PLA/clay nanocomposite than the pure PLA, though the improvement in biodegradation was only very marginal.

Arrieta et al. (2014) [83] prepared nanocomposite films based on PLA and PLA- PHB blends with 5 wt% cellulose nanocrystals (CNC) and surfactant modified cellulose nanocrystals (s-CNC) by melt extrusion followed by film-forming and studied mechanical, optical, barrier, wettability properties and disintegration in compost medium, by monitoring the weight changes with time, as per ISO 20200 method. They observed enhanced mechanical properties such as stiffness & film stretchability, improved oxygen barrier properties & water resistance, and higher disintegration in the composites' compost.

Huang, H. D et al. (2014) [107]prepared PLA-graphene oxide nanocomposites by dispersing exfoliated graphene oxide nanosheets (GONS) in PLA and studied barrier properties. With a very low loading of 1.37 vol% GONS, they reported a massive decline in O_2 and CO_2 permeability of PLA films, by about 45% and 68%, respectively.

Freitas et al. (2017) [165] studied the effect of montmorillonite (OMMT) clay, closite 20A on the biodegradation of PLA/ PBAT blend in the soil medium, by CO_2 method, and they found that OMMT delayed biodegradation of PLA/PBAT blend.

Castro-Aguirre et al. (2018) [166] studied the effect of nano clays on biodegradation of PLA by preparing nanocomposites with three different nano clays (1 % 5 wt%) and carried out biodegradation in compost medium by CO_2 measurement. They reported significantly higher mineralization of the films containing nano clay than the pristine PLA during the first three to four weeks of testing, mainly attributed to the reduction in the lag time / early starting of the biodegradation phase films containing nano clay, compared to neat PLA.

Mayekar et al. (2020) [167] investigated biodegradation of nanocomposites of PLA using organomodified montmorillonite (OMMT), unmodified montmorillonite (MMT) and an organomodifier (surfactant) for MMT (QAC), by measurement of CO_2 evolved in a respirometric system, at 58˚C, for 180 days. Hydrolysis experiments were also conducted separately to decouple

the abiotic/hydrolysis of PLA. Their studies showed no significant variation in the mineralization of PLA nanocomposites compared to pristine PLA / the addition of nano clays did not enhance the biodegradability of PLA.

Flynn et al. (2020) [168] prepared PLA composites using OMMT nano-clay (organo-modified montmorillonite nano clay - Cloisite® 25A) and mineral matter from coal Extraction (NTM), with 5, 10, and 20 wt % loadings and studied the biodegradation under composting conditions in a respirometer/ by CO_2 measurement as per ASTM D5338, at 60˚C reported enhanced the mineralization rate/ biodegradation rate of PLA composites by 3- to 4-fold compared to neat PLA. Their studies also indicated improved mechanical properties up to 10% OMMT.

- **Properties of PLA-PCL blends**

The use of PLA as a film is limited [169], mainly because of its high brittleness, and efforts have been reported on PLA modification by blending with other biodegradable polymers (such as PCL, PBS, PHB, starch etc.) and by incorporating additives such as plasticizers, compatibilizers, nano-materials etc. A brief account of the research work reported on PLA-PCL blends, with and without additives, is given below:

Tsuji et al. (1998) [170] prepared PLA-PCL blends, with different PCL contents (0, 25, 50, 75 and 100% PCL), by solution casting and carried out biodegradation studies in soil, by monitoring the weight loss, by monitoring changes in tensile properties and by monitoring molecular weight changes (by gel permeation chromatography-GPC), for a period up to 20 months. Their studies indicated higher biodegradation with higher PCL content and the studies revealed preferential enzymatic degradation of PCL and insignificant attack to PLA in the blends.

Suman et al. (2011) [171] prepared PLA-PCL blends and observed an increase in the percentage of elongation at break and impact strength with the addition of PCL, up to 20% PCL, and a decrease in the above two properties with higher % of PCL.

Chavalitpanyaa and Siriwan Phattanarudee [2013] [172] investigated the compatibilizer effect on phase miscibility in PLA/PCL blends. They prepared PLA/PCL blends with PEG-PPG compatibilizer, and they observed improved miscibility of PCL in PLA with compatibilizer, and observed significant improvement in elongation at break, with a slight decrease in tensile strength.

Urquijo et al. (2015) [173] prepared PLA-PCL blends by injection molding method, a hot pressing method, and investigated the effect of the processing method on morphology and mechanical properties of the blend. They observed that the injection method produced smaller PCL particles compared to hot pressing. They observed that elongation at break of the hot-pressed specimens was lower, most likely due to the larger size of the PCL particles. They also found that the effect on some other properties, such as stiffness was independent of the processing method. The impact strength of the blends improved by approximately 350% with 40% PCL.

Ferri et al. [2016] [174] carried out degradation studies of PLA and PLA/PCL blends under composting Conditions, at 58˚C, according to the ISO 20200 method and indicated a higher disintegration rate for PLA-PCL blends with lower percentages of PCL, up to 22.5% PCL and a lower degradation rate at very high PCL contents[175].

Navarro-Baena et al. (2016) [176] prepared PLA-PCL blends with various PCL contents (0, 30, 50, 70, and 100% PCL) and carried out studies on the disintegration of the PLA blends in the compost medium (at 58˚C), by monitoring the weight loss, as per ISO 20200-2015, and also degradation tests under hydrolytic conditions, in phosphate buffer solution[175].

They studied the samples' disintegration by monitoring the weight loss, by monitoring the changes in molecular weight by Gel permeation chromatography (GPC), and by FTIR studies. GPC studies indicated lesser disintegration/ lesser decrease in molecular weight for the PLA-PCL blends with higher PCL content. In other words, they concluded that the PCL addition prevents the degradation of PLA under composting conditions. The FTIR studies indicated that PCL degrades by chain scission of the end groups, with a slight decrease in weight, and maintaining almost the same molecular weight while PLA degrades by chain scission of polymer chains with a higher decrease of molecular weight but without much weight loss.

Sun et al. (2017) [177] prepared PLA-PCL blend films, by solvent casting, with TBC as a compatibilizer and studied tensile and barrier properties. They observed an increase in elongation at break of the PLA/PCL films and improved barrier properties of the blend films (OTR and WVTR) with PCL and TBC.

Ahmadzadeh et al. (2018) [178] prepared PLA-PCL blends containing 2, 4, and 6 wt% of nano zinc oxide (ZnO) and studied the effect of ZnO on the morphology and degradation behavior in phosphate-buffered saline solution. Their studies indicated accelerated degradation of the PLA/PCL blends, with the addition of ZnO nanoparticles

Jeong et al. (2018) [179] prepared PLA-PCL blend films containing 1-7 wt% PCL films by solvent casting/ solution casting. They prepared films with the addition of tributyl citrate (TBC) and observed improvement of the film's mechanical properties (ductility and impact strength). They indicated that TBC's addition helps to improve the properties of PLA/PCL by causing crosslinking reactions between PLA and PCL.

Luyt et al. (2018) [180] prepared PLA/PCL nanocomposites containing TiO_2 nanoparticles. Luyt et al. studied the influence of TiO_2 on the morphology and tensile properties, and they observed a reduction in the elongation break with the addition of TiO_2. They observed that the TiO_2 nanoparticles were well dispersed only in the PLA phase, with only a few on the interface and the PCL phase.

Sessini et al. (2018) [169] studied the disintegration of nanocomposites of PLA-PCL (70/30) blend, incorporated with 1 wt% of three types of nano cellulose materials, namely cellulose nanocrystals (CNC), PLA grafted CNC (CNC-g-PLLA), and PCL grafted CNC (CNC-g-PCL). They studied the disintegration in compost medium at 58°C, by monitoring weight changes with time, as per ISO 20200 method, and reported a higher disintegration rate for all the nanocomposites than neat PLA.

A summary of the Investigations on PLA is given in Table 2.13 – 2.15

Table 2. 13 Summary of investigations on PLA with Plasticizer

Year	Author/ Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2003	Baiardo, M.,	PLA + ATBC, PEG	Thermal and mechanical properties	Both ATBC and PEG effective as plasticizers for PLA. The plasticizing efficiency increased with lower molecular weight PEG.
2008	Murariu	PLA+ GTA, ATBC, DOA plasticizer	Thermal and mechanical	GTA has best plasticizer efficiency with PLA
2009	Lemmouchi	PLA + TBC+ PLA-PEG copolymers	Thermal and mechanical Biodegradation	improvement of the thermo-mechanical properties plasticizers accelerate the degradation of the PLA matrix
2011	Courgneau, C	PLA+ ATBC, PEG-300,	Barrier properties	decrease in barrier properties
2014	Arrieta	PLA-PHB+ limonene	Thermal and mechanical Biodegradation	plasticizer limonene decreased the Tg, and improved biodegradation
2014	Arrieta	PLA-PHB + PEG, ATBC	Biodegradation	Higher biodegradation with ATBC,

2015	Armentano	PLA-PHB+ lactic acid oligomer (OLA)	Thermal and mechanical Barrier	Decrease of Tg with OLA. Improvements in the barrier properties due to higher crystallinity.
2015	Maiza, M.	PLA+TEC, ATBC	Thermal mechanical migration of plasticizer	Improved thermal properties. Reported migration/ leaching of the plasticizer.

Table 2. 14 Summary of investigations on PLA with Nanomaterials

Year	Author/ Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2003	Ray	PLA-OMLS clay (4 wt%)	Morphology Barrier Biodegradation	Improved mechanical, Higher thermal / HDT properties Improved barrier /Lower OTR properties. Improvement in biodegradability in compost.
2003	Ray	PLA-OMLS clay (4, 5, 7%)	Morphology Barrier	Improvement in crystallization behavior, mechanical, H propert HDT, and O_2 gas permeability
2006	Petersson,	PLA+ clay and PLA+ MCC (5 wt%)	mechanical, thermal and barrier properties	The effect on EB was more for MCC Reported an increase in O_2 permeability with MCC
2009	Ozkoc	PLA-PEG-Nano clay	Mechanical Thermal Biodegradation	Improvement in tensile modulus, Reduction in EB. Reduction in biodegradation with nano-clay.

2010	Bhatia	PLA-PBS + OMMT clay 3 wt%	Mechanical barrier/ O_2 gas permeability	Increase in TS, Y, decrease in EB 26% decrease in oxygen permeability
2012	Fortunati, E.,	PLA + CNC, s-CNC 1 & 5 wt%	Barrier Cellulose modification	Improved O_2 barrier. Higher water permeability with surfactant modified s-CNC
2013	Duan	PLA+ OMMT clay 1-6wt%	Barrier WVTR Morphology	Decrease in WVTR upto 5 wt% clay
2013	Tenn	PLA+ OMMT +acetyl triethyl citrate plasticizer	Barrier Biodegradation	Improved O_2 barrier 48% Improved water barrier Higher biodegradation in soil
2014	Arrieta	PLA+PHB+ cellulose nano crystals-based films	Mechanical Barrier Biodegradation	Higher disintegration. Improved barrier properties, lesser OTR.
2014	Huang, H.	PLA+graphene oxide nanosheet(GONS)	Barrier property- O_2 and CO_2	Large decrease in O_2 and CO_2 permeability, by 45% and 68% respectively, with very low loading of 1.37 vol% GONS.
2017	Freitas	PLA+PBAT+ OMMT	Thermal Morphology Biodegradation	Lower biodegradation rate with clay.
2018	Castro-Aguirre	PLA+ nano clay 1.5, 5, 7.5% clay	Thermal Biodegradation in compost	Higher mineralization/ biodegradation with nano-clay reduction in the lag time / early starting of the biodegradation phase

2019	Mayekar	PLA/ OMMT, MMT, and QAC surfactant	Biodegradation	No significant variation in the biodegradation / addition of nano clays did not enhance the biodegradability of PLA.
2020	Flynn	PLA / OMMT / mineral matter from coal (NTM)	Thermal Morphology Biodegradation	Improved mechanical properties up to 10% OMMT. Enhanced, 3 to 4 times higher biodegradation

Table 2. 15 Summary of investigations on PLA-PCL Blends

Year	Author/ Reference	Blend composition	Investigation carried out	Research findings/ Remarks
2011	Suman,	PLA-PCL	Mechanical properties	Increase in % EB and TS with PCL addition up to 20% PCL and then a decrease with higher % of PCL.
2013	Chavalitpanyaa,	PLA-PCL + PEG-PPG	Mechanical properties, compatibility improvement.	Improved miscibility of PCL in PLA, and improvement in EB, with decrease in TS.
2015	Urquijo	PLA-PCL	Effect of processing method	Processing method greatly influence blend properties. Injection molding method produced smaller PCL particles compared to hot pressing.
2016	Ferri	PLA-PCL	Degradation in compost conditions, 58˚C	Higher degradation for PLA-PCL blends with PCL< 22.5% PCL and

				a lower degradation at higher PCL contents.
2016	Navarro-Baena	PLA-PCL	Mechanical, Morphology, Degradation in compost, 58˚C	Lesser degradation for PLA-PCL blend with the addition of PCL
2017	Sun	PLA-PCL +TBC	Mechanical, Barrier properties. compatibility improvement.	Increase in EB of the PLA/PCL films, and improvement in barrier properties of the blend films (OTR and WVTR) with the addition of PCL and TBC.
2018	Ahmadzadeh	PLA-PCL +ZnO	Morphology, Degradation in phosphate buffer solution	Accelerated degradation of the PLA/PCL blends, with the addition of nano ZnO.
2018	Jeong	PLA-PCL +TBC	Mechanical properties, compatibility improvement.	Improvement in ductility and impact strength of the film with TBC.
2018	Luyt	PLA-PCL +TiO_2	Morphology, mechanical	Reduction in the elongation break with the addition of TiO_2
2018	Sessini	PLA-PCL-CNC	Disintegration at composting conditions @58ºC	Higher disintegration rate with the addition of CNC compared to neat PLA.

2.6.4 Polycaprolactone (PCL)

PCL is a petroleum-based biodegradable polyester and is of great interest as it can be obtained by the polymerization of a relatively cheap monomer 'ε-caprolactone.' It is a semi-crystalline polymer with a degree of crystallinity of about 50% and is non-toxic. PCL exhibits several interesting properties not found among the other aliphatic polyesters. The chemical structure of PCL is given below in Fig. 2.15

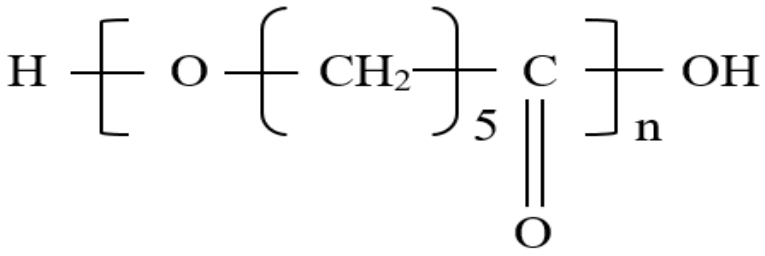


Fig 2. 15 Chemical structure of PCL

2.6.4.1 Properties of PCL

Essential properties of PCL is given in Table.2.16, and more details about its mechanical, thermal, barrier, and biodegradability characteristics are described below:

Table 2. 16 Typical Properties of PCL. [89] & Datasheet from supplier

Specific gravity	1.15
Melt temperature Tm (°C)	65
Glass transition temperature Tg (°C)	-61
Heat distortion temperature (°C)	_
Melt flow rate MFR (g/10 min)	28
Young's Modulus (MPa)	190
Tensile Strength (MPa)	14
Elongation at Break %	700

OTR mL m^{-2} day^{-1} (23°C/0% RH)	3600
WVTR g m^{-2} day^{-1} (25°C/100% RH)	177

Mechanical properties:

PCL has a relatively very low Youngs modulus (190MPa), and a low tensile strength (14 MPa) compared to other polymers. It has a very high elongation at break of 500 % to 700% [181].

Thermal properties:

PCL has a low melting temperature of 65°C and a shallow glass transition temperature of -61°C. Thus, PCL is always in a rubbery state at room temperature. Another interesting property of PCL is its high thermal stability. It has a high decomposition temperature (T_d) of 350°C, whereas other aliphatic polyesters have decomposition temperatures between 235°C and 255°C [182].

Barrier properties:

PCL has a high OTR value of 3600 mL m^{-2} day^{-1} [91]. Thus, PCL's oxygen barrier property is inferior to most of the traditional polymers, except LDPE and PS. The water barrier property of PCL is inferior to all the traditional polymers. However, the WVTR value of PCL (177 mg m^{-2} day^{-1}).

Biodegradability:

PCL may be degraded by many microorganisms, including bacteria and fungi, widely spread in soils and water bodies [125]. It undergoes biodegradation under different environments, in compost, soil, lake waters, seawater [183], sewage sludge, and abiotically in phosphate buffer solution.

2.7 Research gaps, Research questions, and Hypothesis

During the past few decades, considerable progress has been made in improving the properties of biodegradable polymers. However, biodegradable polymers are not being used widely, mainly because these improvements are not enough for practical applications.

2.7.1 Research gaps:

Literature survey on biodegradable polymers indicated many research gaps/knowledge gaps with respect to biodegradable polymers, and these are listed below:

- Though many studies have been carried out on PBS, PHB, and PLA polymers, only a minimal number of studies have been carried out on blends of these polymers with PCL. The scope of most of the existing studies on PBS-PCL, PHB-PCL, and PLA-PCL blends are limited to studies on morphology, crystallization behavior, mechanical and thermal characteristics. A limited number of studies have been reported on barrier properties and biodegradation characteristics of these polymer blends. Also, the results reported in some of the papers, such as the effect of PCL content on specific properties (e.g., Tensile properties, biodegradation), are different/ contradictory to each other.

- Only very few studies have reported on modification of PBS-PCL blends, PHB-PCL blends, and PLA-PCL blends with plasticizers, especially polymeric plasticizers. A comparative study on the effects of polymeric vs monomeric plasticizers on these polymer blends is lacking.

- Nano-cellulose is an attractive biodegradable material for the preparation of nanocomposites of biodegradable polymers. However, only a minimal number of papers have successfully developed nanocomposites of biodegradable polymers using nano cellulose. Most of the researchers have reported the use of organically modified nano-clay for the preparation of nanocomposites. A comparative evaluation of nano-cellulose vs nano-clay based nanocomposite is desirable. Only very few investigations have been reported on nanocomposites based on PBS-PCL, PHB-PCL, and PLA-PCL blends.

- Most of the existing studies on the biodegradation of polymers in compost medium are reported at industrial composting conditions (58˚C). There is a need to understand biodegradable polymers' biodegradation at ambient composting conditions (home composting conditions).

- Only very few studies have been reported on the biodegradation of PBS blends, PHB blends, and PLA blends/ composites under marine conditions.

The present study aims at filling the above research gaps.

2.7.2 Research questions:

Based on the research gaps identified, few research questions emerged with respect to the modification/ improvement of polymer properties and are given below:

- Research question #1: How do the tensile properties, barrier properties, and biodegradability characteristics of PBS, PHB, and PLA polymers get altered by blending with PCL, a polymer with high tensile elongation, low Tg, and high biodegradability.

- Research question #2: What is the comparative performance effects of monomeric vs polymeric plasticizers on tensile properties, barrier properties, and biodegradability of PBS-PCL, PHB-PCL, and PLA-PCL blends and nanocomposites?

- Research question #3: What is the comparative effects of nano-clay and nano-cellulose on the barrier properties of PBS-PCL, PHB-PCL, and PLA-PCL blends and also on tensile properties and biodegradability.

2.7.3 Research Hypotheses

For addressing the above research questions, a set of testable hypotheses have been proposed/ formulated and are given below:

- Hypothesis#1: Blending of PLA, PBS, and PHB with PCL polymer would enable the development of packaging films with improved performance, especially tensile elongation, and

higher biodegradability. Also, the blending of PBS with PCL would improve the water vapor barrier property.

- Hypothesis #2: Plasticization of PLA-PCL, PBS-PCL, and PHB-PCL blends with the right choice of plasticizer (Polymeric) would improve the compatibility of the blend components and thereby improve the performance of the polymer blend with respect to tensile properties, barrier properties, and biodegradation properties.

- Hypothesis # 3: Incorporation of suitable nanomaterials (nano-cellulose) in PLA-PCL, PBS-PCL, and PHB-PCL polymer blends would enable the development of packaging films with improved barrier properties and also may result in enhancement of tensile properties and biodegradability.

2.8 Research Objectives:

The overall objective /main objective of the research is "development and characterization of biodegradable polymer films for flexible packaging application, with high-performance characteristics."

The sub-objectives of the research are as follows:

- To fabricate polymer blend films of PBS, PHB, and PLA, with different concentrations of PCL, by injection molding followed by hot-pressing, and investigate to understand the effect of PCL content on tensile properties, barrier properties (WVTR), and biodegradation characteristics in compost media (at ambient temperature) and in marine media/ seawater.

- To develop plasticized blend films of PBS-PCL, PHB-PCL and PLA-PCL, using monomeric and polymeric plasticizers and carry out an investigation to understand the comparative performance/ influence of monomeric and polymeric plasticizers on tensile properties, barrier properties (WVTR), and biodegradation characteristics in compost media (at ambient temperature) and in seawater.

- To optimize process parameters and fabricate nanocomposite films by incorporating different loadings of nano-cellulose and nano-clay in plasticized PBS-PCL, PHB-PCL, and PLA-PCL blends and carry out an investigation to understand the comparative performance of nano-cellulose and nano-clay and the effect of different loading levels of nano-materials on the tensile properties, barrier properties (WVTR) and biodegradation characteristics in compost media (at ambient temperature) and in seawater.

Chapter 3 Methodology and Materials

3.0 Introduction

This chapter provides information regarding the materials used, experimental methods, and instrumentation techniques employed during the present investigation.

3.1 Materials used

a) Polylactic acid (PLA):

The PLA resin (Ingeo™ Biopolymer 3052D), manufactured by Natureworks, USA, was purchased from Clariant Limited, New Zealand. It is a polymer resin for injection molding, having a melting point (T_m) in the range of 45-160˚C, glass transition température (Tg) 55-60 ˚C, with a molecular weight (Mw) of 116,000 g/mol.

b) Polyhydroxybutyrate *(*PHB*) :*

The PHB resin (ENMAT Y3000P PHB), having a melting temperature of 175-180 ˚C, glass transition temperature(T_g) of 4˚C, and Mw = 350000 g/mol, was obtained from *TianAn Biologic* Materials Co., China.

c) Polybutylene succinate (*PBS*)

The PBS resin (Grade: FZ71), having a melting temperature of 115˚C, glass transition température (Tg) of -33˚C, and molecular weight (Mw) of 129000 g/mol, was purchased from *PTT MCC* Biochem Company Limited.

d) Polycaprolactone *(*PCL*)*

The PCL resin (Capa 6500), having a melting temperature of 60-62˚C, glass transition temperature (Tg) of -60˚C, and weight average molecular weight (Mw) of 84500 g/mol, was supplied by Pertstrop, USA.

e) Plasticizers

Plasticizers such as Triacetin (99%), of molecular weight: 218.20 was purchased from Sigma Aldrich, New Zealand. Lanxess, Australia supplied Ultramoll IV, a polymeric plasticizer based on an adipic acid polyester.

f) Nanomaterials

Nano-materials such as nano cellulose (Cellulose nanofibrils CNF), having a diameter of 20-60 nm and length of few micrometers, was purchased from Cellulose lab, Canada.

Nano clay, Dellite 72T, an organically modified montmorillonite clay, was purchased from Laviosa chimica mineraria SpA , Italy

3.2 Experimental details/ Methodology

3.2.1 Polymer film preparation

The following sequence of operations prepared various polymer blend films/ composite films:

a) Polymer blending,
b) Injection molding- Thick sheet preparation
c) Hot-pressing- Thin film preparation

a) Polymer blending

Polymer blends were prepared by melt blending the polymer resins in a hot blender, using a slow speed stirrer. Before blending, the polymers were dried in an air oven at 50˚ for 12 h to avoid hydrolysis during thermal processing. Temperature for blending was maintained at about 5-10°C above the melting temperature of polymers. Polymer blends with different compositions were prepared.

b) Injection Molding - Thick sheet preparation

Thick circular sheets of polymer blends, of thickness 2.5 mm, were prepared by injection molding of hot blended resins. A benchtop Injection Molding Machine, Model B-100, from Galomb Inc,

USA, was used for injection molding. Fig.3.1. indicates the features/ parts of the injection molding machine.

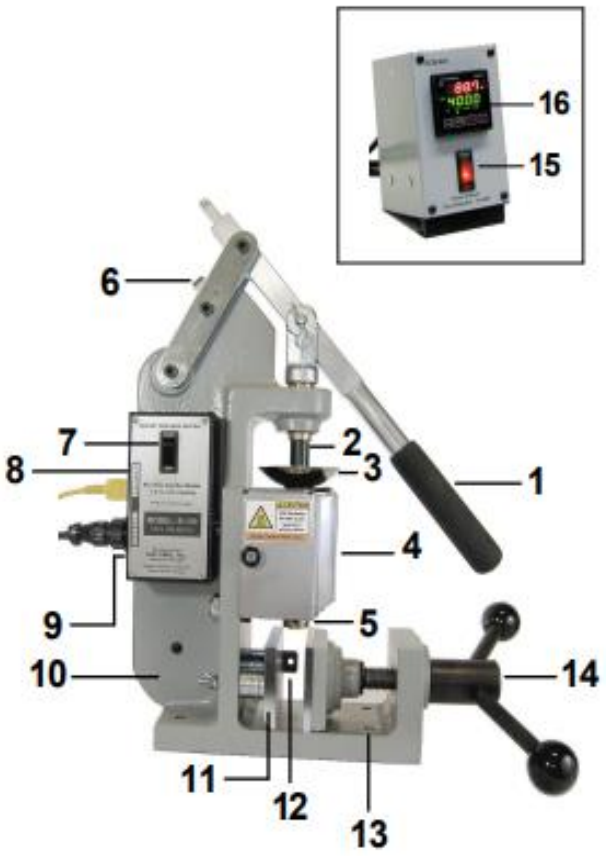


Fig 3. 1 Benchtop Injection Molding Machine, Model B-100 (Galomb Inc, USA)

Features	
1.	Cushioned handle grip
2.	Injection ram (with non-stick coating)
3.	Pellet tray (chrome-plated)
4.	Protective enclosure (stainless steel)
5.	Injection nozzle (removable)
6.	Handle lock
7.	Power switch (with built-in thermal breaker)
8.	Sensor input jack (Type K thermocouple)
9.	Power input jack
10.	Support frame (cast iron / powder coated)
11.	Back plate (adjustable position)
12.	Mold stop
13.	Mounting holes
14.	Vise handle
15.	Power switch (with built-in thermal breaker)
16.	P.I.D. - (dual digital display)

A mold with a circular cavity of diameter 38mm and a depth of 2.5mm was fabricated from aluminum plates for preparing thick circular sheets of 2.5mm thickness. The temperature for injection molding was maintained slightly above the melting temperature of polymers.

c) Hot Pressing- Thin film preparation

Thin polymer films (0.25mm /~ 10 mils thickness) were prepared from the thick sheet prepared above by the hot-pressing method. A stainless steel “thin-film mold” with an outer dimension of 170mm x170mm x 20mm, having a circular cavity of depth 0.25mm and a diameter of 150 mm was fabricated. The thick polymer sheets were taken in a mold, heated, and then pressed in a hydraulic press with a precision temperature control unit. Hot pressing was done at a temperature near the polymer's melting temperature, at a pressure of approximately 1MPa, and was then cooled to room temperature. The steps involved in thin-film sample preparation is schematically shown in Fig.3.2

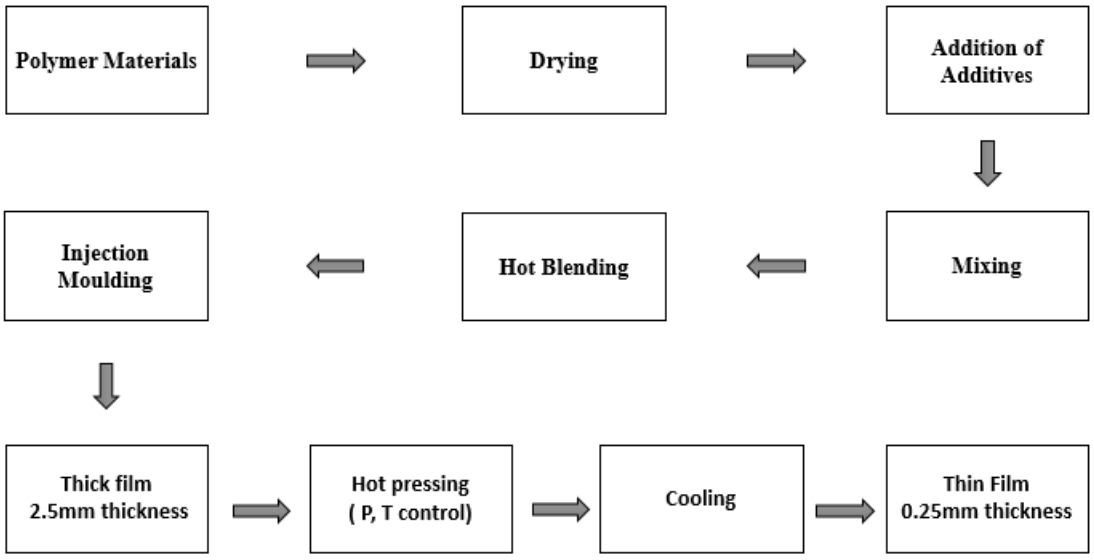


Fig 3. 2 Schematic of Thick film making by Injection molding machine and Thin film making by hot pressing

3.2.2 Characterization

A brief description of various test methods that were employed for the evaluation/characterization of polymer materials is given below:

3.2.2.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) scans the sample with a high-energy beam of electrons. The electrons interact with the sample and produce secondary electrons, backscattered electrons, and characteristic X-rays. Detectors collect these signals to form SEM images, and these images provide information on topography, morphology, composition, the orientation of grains, crystallographic information, etc., of a material [184].

In the present study, Hitachi SU-70 scanning electron microscope (SEM) instrument (Fig.3.3) was used to record the SEM images of polymer blend/ nanocomposite samples. The samples were cryo-fractured and coated with platinum to enhance the sample's electron conductivity and reduce the heat accumulation before fixing the sample holder. SEM images were recorded at an accelerated voltage of 10 kV to understand the polymer samples' morphology.

Fig 3. 3 Hitachi SU-70 scanning electron microscope (SEM) instrument

3.2.2.2 Tensile Testing

In a tensile test, tensile force (pulling) is applied to the material and measures the specimen's response to the stress. The stress-strain curve generated tensile parameters such as tensile strength, elongation at break, and Young's modulus can be calculated. Tensile strength is calculated by dividing the maximum load by the original cross-sectional area of the specimen. The result is expressed in force per unit area, usually megapascals (MPa). Elongation at break (%) is calculated by dividing the extension at the moment of the specimen's rupture by the specimen's initial gauge length and multiplying by 100.

During the present study, tensile testing was carried out using a TA.XT PLUS tensile machine (Fig.3.4), equipped with 5 KN load cells. According to the ASTM D882 method (ASTMD882-18, 2018), the polymer samples' tensile properties were determined with slight modifications. Polymer films of 0.25mm thickness, cut into rectangular strips of dimensions 10 mm x 100mm, were used as a specimen for testing (Fig 3.5). The initial distance between the two grips was set at 50mm, and the crosshead speed of the test was set at 2 mm/Sec. Tensile strength and elongation at breaking were calculated. Five identical specimens were tested in each case, and the average value was reported.

Fig 3. 4 Tensile Test - TA.XT Plus machine

Fig 3. 5 Tensile Test Sample (10 mm x 100mm)

3.2.2.3 Water vapor transmission rate (WVTR) -by ASTM E96 Method / gravimetric method/ cup method

The water vapor transmission rate is the mass of water vapor transmitted through the unit area of the packaging film material in unit time (one day), at steady-state conditions, under specified conditions of temperature and humidity, and has the units of g m^{-2} day^{-1}.

Water vapor transmission rate (WVTR) was determined by a gravimetric method, as per ASTM E96 [185], also called a cup method. ASTM E96 describes two cup methods, a desiccant method

and the water method. In the desiccant method, a desiccant is taken in the cup, while in the water method, distilled water is taken in the cup, and the test specimen film is sealed to the open mouth of a test cup, and the cup assembly is then placed in a controlled environment of relative humidity and temperature.

We have followed the water cup method during the present investigation. Few numbers of WVTR cup assemblies were designed and fabricated from an aluminum block. The WVTR cup assembly had a cup portion, with a cavity of diameter 35mm and a volume of approximately 15 cc, a metal gasket, and a threaded cap with a central hole of the same diameter as the inner diameter of the cup mouth 10 cc of distilled water was taken inside the cup. A circular specimen sample of the polymer film, 55mm diameter, was cut out using a circular cutter fabricated from an aluminum block. Fig.3.6 (a) and (b) indicates the aluminum cutter and the specimen of polymer film for WVTR expt. The polymer film's thickness was measured using a screw gauge and then placed carefully at the cup's mouth. The metal ring was placed above the polymer film, and the film was sealed to the cup by placing the threaded cap above and tightening it. The portion of the film Fig. 3.6 (c) and Fig 3.6 (d) indicates the photograph of the WVTR cup in the dismantled condition and in the assembled condition respectively.

The initial weight of the cup assembly was noted using a precision electronic balance and then placed in a desiccator (Fig 3.6 (e)) having about 100 grams of silica gel (pre-dried at 200 to 210°C for 6 hours). Thus, the relative humidity of 100 % was maintained below the membrane, and 0% relative humidity was maintained above the polymer film, and water vapor gets permeated through the polymer film, from the bottom side to the top side of the film. The desiccator with the cup assembly was placed in a chamber, and the test temperature was monitored and maintained at about 25°C.

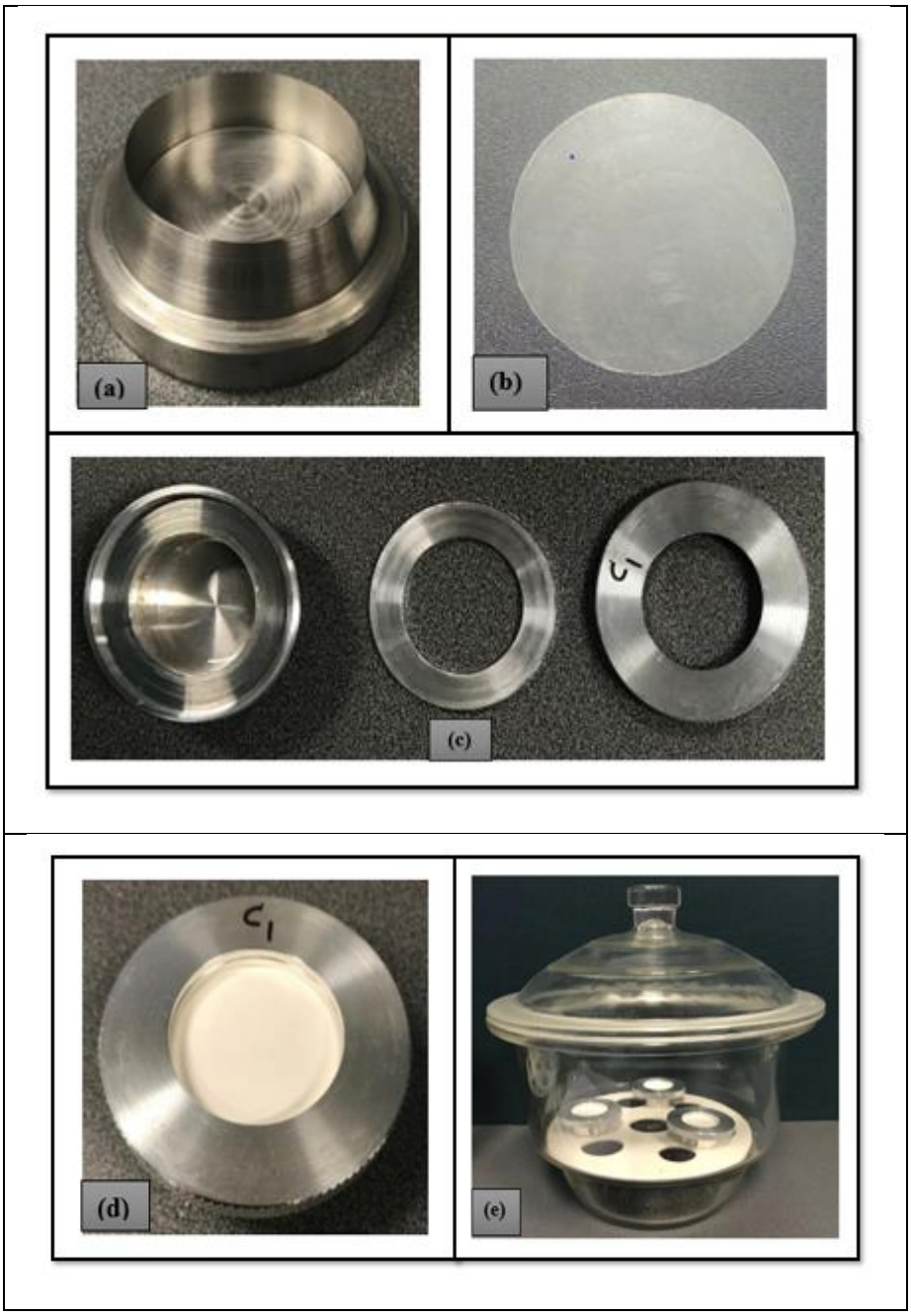


Fig 3. 6 Photograph of WVTR Experimental setup (a) Cutting tool (b) Polymer Specimen c) Dismantled WVTR Cup assembly- with cup portion, metal gasket, and threaded cap d) Assembled WVTR cup assembly (e) WVTR cup assembly placed in a desiccator

The cup assembly's weight was noted periodically (after every 24 hours) and continued until the weight change rate is a constant/ till a steady state is reached. The cumulative change in mass of

cup assembly was then plotted against time. From the slope of the straight-line portion of the plot (Q/t), and area A (in meters) of film exposed WVTR was calculated using the equation

$$\mathrm{WVTR} = \mathrm{Q}/\mathrm{At} \qquad (3.\ 1)$$

In cases where the test temperature deviated from 25°C, temperature correction for WVTR was done to calculate the WVTR at 25°C, as reported elsewhere. [186]

Since the thickness of films varies, the WVTR value is often reported to a film of a specific thickness [63], and the specific or "normalized" WVTR, for a film of 1 mil or 25 µm thickness is sometimes written with the unit of $g.mil.m^{-2}d^{-1}$ or $g.25\mu m.m^{-2}d^{-1}$. "Normalised WVTR," i.e., the value of WVTR for a film 25 µm thickness was calculated from the WVTR for test film of actual thickness, l µm, using the equation below:

$$\text{Normalized WVTR} = \text{Non} - \text{normalized WVTR} * (\frac{l}{25}) \qquad (3.\ 2)$$

3.2.2.4 Biodegradability studies

Biodegradation studies were carried out in i) compost medium and in ii) seawater/ marine environment, both under aerobic conditions and at ambient temperature/ 25±5°C.

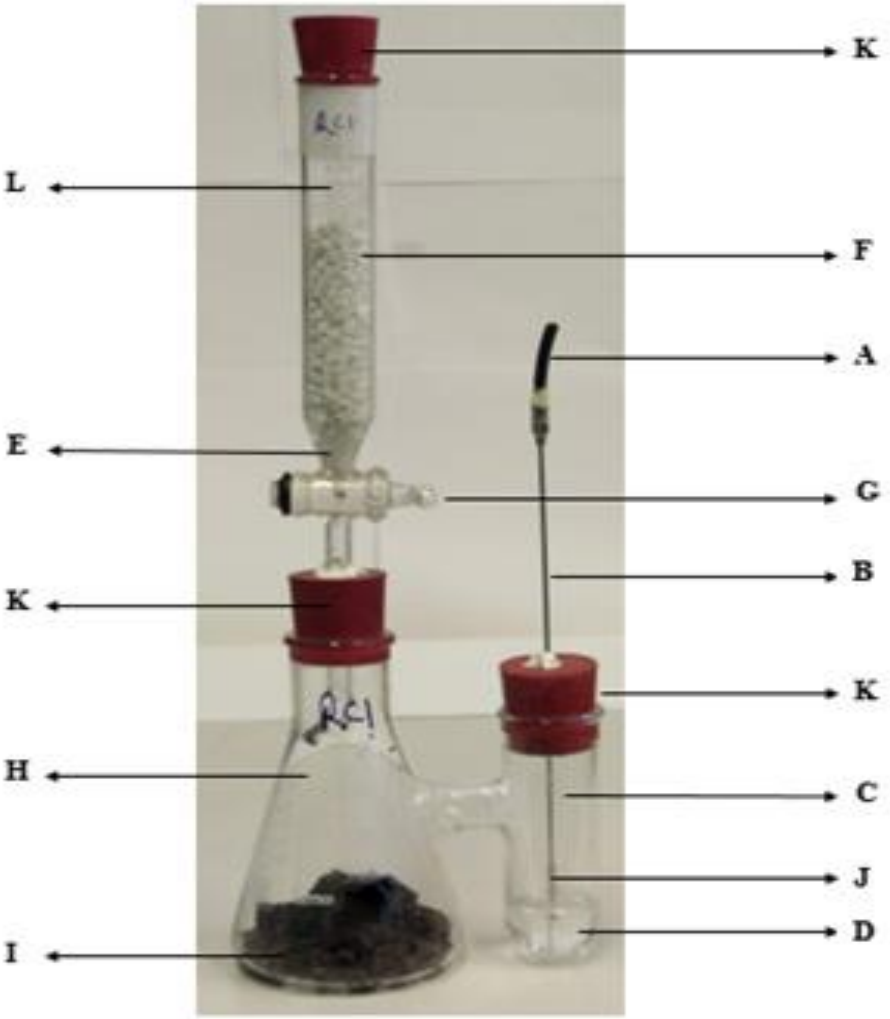
3.2.2.4.1 Biodegradation studies in the compost media

Biodegradation studies in the compost media were carried out as per the ASTM D5338-15 method guidelines, with slight modifications, such as temperature for testing [187].

Polymer test samples were exposed to inoculum derived from compost, and the samples could degrade under aerobic composting conditions at a controlled temperature, humidity, and aeration conditions. Carbon dioxide generated by the bacterial decomposition of polymer samples was measured at various intervals, by absorption in KOH followed by titration [188], for a period up to 180 days, and from the above data, the rate of biodegradation and the percentage of conversion of carbon in the sample to carbon dioxide were estimated. Compared with a biodegradable reference standard such as cellulose, the results were tested under the same conditions.

a) Composting apparatus:

In the present study, biodegradation studies were performed in 500cc biometer flasks. As indicated in Fig 3.7, the biometer flask has a conical flask portion and a sidearm portion. The conical portion is provided with a rubber stopper through which a cylindrical funnel is inserted. The sidearm portion is also provided with a rubber stopper through which a long needle with a plastic cap is inserted. A polythene/ silicone tube is attached to the bottom of the needle to touch the sidearm portion's bottom.



Features			
A	syringe cap	G	Stop cock
B	Syringe needle	H	Conical flask portion
C	Side tube portion	I	Compost + sand+ test sample
D	KOH	J	Plastic tube
E	Glass wool	K	Cork on conical flask Cork on side tube Cork on funnel
F	Soda-lime	L	Funnel

Fig 3. 7 Composting apparatus

b) Compost inoculum:

Compost (2-4 months old, well-aerated samples) supplied by Daltons, New Zealand, was used as the inoculum. Before starting the biodegradation studies, compost was tested for essential parameters such as dry solids/ moisture content, volatile solids/ organic matter, pH, compost activity etc., as per the standard test methods, as briefly given below [189]:

i) **Moisture content % (dry solids):** The compost's moisture content was determined by heating a known weight of fresh compost sample in an air-oven at 105˚C for 24 hrs and weighing the dry mass. The moisture content of the compost was calculated using the formula below:

$$\text{Moisture content (\%)} = \frac{(\text{wet mass} - \text{dry mass}) * 100}{\text{wet mass}} \qquad (3.\ 3)$$

ii) **Volatile solids/ organic matter:** Volatile solids/ organic matter (OM) in compost was estimated by the loss on ignition (LOI) method. A known weight of the pre-dried compost sample was heated in a muffle furnace at 550ºC for 2 hours, and the weight of the dry sample/ash left behind was noted. Volatile solids were calculated by the formula given below [190]:

$$\text{Volatile solids (\%)} = \frac{(\text{mass of dry sample} - \text{mass of ash}) * 100}{\text{mass of the dry sample}} \qquad (3.4)$$

iii) **pH:** The pH of the compost was determined by mixing a known weight of dry compost sample with 5 times of water (1:5 ratio by weight) and measuring the pH of the suspension using an electronic pH meter.

iv) **Compost activity:** The compost inoculum activity was tested by measuring the amount of CO_2 evolved for10 days [191]. The inoculum activity was adjusted to within the acceptable limits of 50-150 mg CO_2 /g of volatile solids, in the inoculum, for 10 days. (If the production of carbon dioxide is too high, compost should be stabilized by aeration for several days before using it in a new test. If CO_2 is too low, the inoculum should be replaced by another one.

After quality checking, the compost was sieved through a screen of less than 10mm, to remove big lumps, any stones etc, and the sieved compost was used for studies. The gravimetric water content of the compost was maintained at about 50% (wet basis) by adding distilled water (if low) or by drying gently (if high) by aerating the compost with dry air.

Sea sand is generally added to the compost (approximately equal volumes) for a better aerobic environment inside the compost. Sea sand was prepared by collecting the sand from the seashore, washing with tap water to remove suspended impurities, draining off the water and drying the sand at about 105°C, sieving through 20 mesh screen (0.85 mm opening) to remove oversized particles, and then adding 15% water (equal to the water holding capacity of sea sand).

c) Preparation of test material and reference material:

Whatman filter paper (cellulose) was used as the reference material/ as a positive control. Polymer films and cellulose paper were cut to a size of < 2cm x 2cm for testing. For each test, 2 grams of the test material/ reference material was used.

d) Starting up the test:

For each sample, a total of 9 biometer flasks/ composting vessels were taken for the biodegradability evaluation; three test vessels for the test specimen (vessel $V_{T1,}$ $V_{T2,}$ V_{T3}), three vessels for testing reference material (vessel $V_{R1,}$ $V_{R2,}$ V_{R3}), and three vessels for blank controls (vessel $V_{B1,}$ $V_{B2,}$ V_{B3}), which is shown in fig 3.8. The starting up of the test involved the following steps:

- Biometer flasks were thoroughly cleaned to remove any organic or toxic matter.
- 24 grams of wet compost (50% humidity) and 72 g wet sand of 15% humidity, was added to all the biometer vessels ($V_{T1,}$ $V_{T2,}$ $V_{T3,}$ $V_{R1,}$ $V_{R2,}$ $V_{R3,}$ $V_{B1,}$ $V_{B2,}$ V_{B3}), and the contents were mixed well.
- An additional water quantity was added to adjust the mixture's water content to about 90% of its water holding capacity (WHC).

Water holding capacity (WHC) of the compost-sand mixture was determined (and an additional quantity of water to be added was calculated) as follows [192]:
A known weight of the compost-sand mixture (w1) was dried in an oven at 105ºC till there is no significant weight change. (From the above, grams of water/gram of dry mixture was noted) The weight of the dried mixture (w2) was noted, and it was placed in a beaker and allowed to soak in excess water for two days. The excess water was then allowed to drain off under gravity through whatman#2 filter paper placed on a funnel. The weight of the water-saturated, water drained mixture (w3) was noted. 100% Water holding capacity (g water/g dry material) was calculated from the above, as follows:

$$\mathrm{WHC} = \frac{\mathrm{w3} - \mathrm{w2}}{\mathrm{w2}}\ \mathrm{g\ water/g\ dry\ material} \qquad (3.5)$$

$$\text{Water already present} = \frac{\mathrm{w1} - \mathrm{w2}}{\mathrm{w2}}\ \text{grams of water/g of the dry mixture} \qquad (3.6)$$

$$\text{Additional quantity of water to be added} = \frac{(\text{WHC} * \text{w2} * 90)}{100} - (\text{w1} - \text{w2}) \text{ g or ml} \quad (3.7)$$

Or

$$\text{Additional quantity of water to be added} = (\text{w3} - \text{w2}) * (90/100) - (\text{w1} - \text{w2}) \text{ g or ml} \quad (3.8)$$

- To the vessels $V_{T1,}$ $V_{T2,}$ and $V_{T3,}$ 2 gram of polymer test sample, cut to < 4 cm^2 was placed in the compost-sand mixture containing 12 grams of compost on a dry basis, ensuring a ratio of 1: 6 for polymer: inoculum weight ratio on a dry matter basis. It was mixed manually until a homogeneous blend was obtained.
- To the vessels, $V_{R1,}$ $V_{R2,}$ and $V_{R3,}$ 2 grams of cellulose reference samples were placed in the compost-sand mixture instead of polymer samples.
- The vessels $V_{B1,}$ $V_{B2,}$ and V_{B3} containing compost-sand mixture were used as blank, without any test or reference sample.
- The flasks were closed with the rubber stopper having a cylindrical funnel with a glass stopcock at the bottom. The sidearm portion was also closed.
- Stop cock was kept in the closed position/ horizontal position, and soda-lime (CO_2 absorbent) was taken inside the cylindrical funnel after placing glass wool at the bottom. The funnel mouth was then closed with a stopper.
- The stopcock at the bottom of the funnel was kept open for about 30 minutes to remove any carbon dioxide present in the flask.
- 50 ml of 0.5N KOH was then introduced into the biometer vessel's sidearm portion, through the needle, using a syringe. After removing the syringe, the needle was closed with the cap.
- Then the funnel stopcock was closed.
- The composting vessels were placed in a dark cabinet at about 25°C.

Fig 3. 8 Photograph of Experimental setup for biodegradation studies

Carbon dioxide evolved due to biodegradation, gets absorbed in KOH, and becomes potassium carbonate, as per the following reaction

$$2KOH + CO_2 = K_2CO_3 + H_2O \quad (3.9)$$

After the end of every 5 - 15 days, the quantity of carbon dioxide evolved from each vessel was found out by taking out KOH from the biometer flask and titrating with standard 0.1N HCl. fresh CO_2-free air was drawn into the biometer flask, through soda lime. Also, the contents of the composting vessels were mixed every week.

e) Estimation of CO_2 evolved- Titration procedure

The titration procedure adopted for estimating CO_2 evolved is described below:

- A 25ml burette was clamped on a burette stand.
- The burette was filled with 25ml of standard 0.1N HCl.
- The stopcock (G) was kept in the open position/ vertical position (to avoid an airlock).

- The needle cap was removed, and a syringe was attached to the needle, and KOH inside the sidearm was taken out.
- The KOH from the biometer flask was then transferred to a titration vessel and placed under the burette.
- About 2 ml of 0.5N Barium chloride ($BaCl_2$) was added to the KOH and stirred to convert potassium carbonate into insoluble barium carbonate, as per the following equation.

$$BaCl_2 + K_2CO_3 = BaCO_3 + 2KCl \qquad (3.10)$$

- About 2 drops / 10 micro-liters (µl) of Phenolphthalein was added to KOH.
- The burette valve was slowly opened, and the HCl could dip into KOH.
- The titration flask was slightly swirled while HCL was added.
- HCl addition was stopped/ burette valve was closed when the pink color changed to colorless.
- The volume of 0.1N HCL required to neutralize KOH (after CO_2 absorption) taken out from all the biometer flasks was noted, denoted as V_{final}.
- The volume of 0.1N HCL required to neutralize fresh KOH (before CO_2 absorption) was also determined, by titrating 50 ml of fresh KOH with 0.1N HCL, denoted as $V_{initial}$.
- The amount (mg) of CO_2 evolved from each flask (for 5 days/ 15 days) was calculated from the above by multiplying the volume of 0.1N HCl corresponding to KOH reacted with CO2 (V_{HCl}) by the normality of HCl (0.1) and by the molar mass of CO_2 (44g/mole).

  Amount (mg) of CO_2 evolved= V_{HCl} x Normality of HCl x 44/2 = V_{HCl} x 2.2 (for 0.1N HCL)

  where

  $V_{HCl} = V_{initial} - V_{final}$

  V_{HCl}= ml of HCl corresponding to KOH reacted with CO_2

  $V_{initial}$ = ml of HCL needed to titrate fresh KOH

  V_{final} = ml of HCl to titrate unreacted KOH
- The actual amount of CO_2 evolved from the test sample/ reference sample alone (excluding CO_2 from the compost inoculum) at various time intervals (for 5 - 15 days) was calculated by subtracting the amount of CO_2 evolved from the empty flask $(CO_2)_B$ from the CO_2 evolved from test/ reference sample flask $(CO_2)_T$.

  The actual amount of CO_2 from the test sample alone = $(CO_2)_T$ - $(CO_2)_B$

The cumulative amount of CO_2 evolved from the start of the test to the time t, denoted as ΣCO_2, was also calculated by adding up the CO_2 evolved from the start to time t.

f) % Biodegradation / degree of mineralization

- Theoretical amount of CO_2 evolved from the test sample/reference sample **(**$ThCO_2$**)** was calculated from the mass (m) of the sample taken in grams, and the carbon content / total organic carbon (TOC) of the sample (in %), calculated from the chemical composition of the material:

$$ThCO_2 = (m * (TOC/100) * (44/12)) \ g\,CO_2 \qquad (3.\ 11)$$

- % Biodegradation/ degree of mineralization D_t of the test material for various measurement intervals was calculated by dividing the cumulative CO_2 evolved (ΣCO_2) from the test sample alone by the theoretical CO_2 evolved, as per the equation given below

$$D_t = \frac{\Sigma(CO_2)_T - \Sigma(CO_2)_B}{ThCO_2} * 100\% \qquad (3.\ 12)$$

Where

D_t is the % Biodegradation

$\Sigma(CO_2)_T$ is the cumulative amount of carbon dioxide evolved in each composting vessel containing test material/reference, in grams, from the start to test time t.

$\Sigma(CO_2)_B$ is the cumulative amount of carbon dioxide evolved in the empty vessel, in grams, from the start to test time t.

$ThCO_2$ is the theoretical CO_2 evolved from the test material, in grams.

The biodegradation curves were drawn by plotting the cumulative amount of carbon dioxide in the composting vessel containing test material, blank or reference material as a function of time. Biodegradation curves were also drawn by plotting the % biodegradation as a function of time for the test material and the reference material, and the results were analyzed.

3.2.2.4.2 Biodegradation studies in seawater/ marine medium

There are three test standards for degradation/biodegradation in the marine environment, namely

i) ASTM D6691- 17 [57], which studies biodegradation of plastics in seawater by CO_2 measurement

ii) ASTM D7473-12 [193], which studies weight loss of non-floating plastics buried in the sediment underwater,

iii) ASTM D7991-15 [58], which studies biodegradation of plastics in a combination of water and sediment by CO2 measurement, and this method simulates the environment found in the sandy tidal zone [194].

We have carried out biodegradation studies of polymer samples in the seawater/ marine medium, by the ASTM D6991-17 [57], under an anaerobic environment, at ambient temperature 25±5^{o}C. The test involves the following steps: i) preparation of test samples, ii) preparation of inoculum, iii) exposure of materials to the inoculum, iv) determination of degradation as a function of time and assessment the degree of degradation/ biodegradability.

1. **Preparation of test samples:**

Whatman filter paper (cellulose) was used as the reference material/ as a positive control. Polymer films and cellulose paper were cut to a size of < 2cm x 2cm for testing. For each test, 4 grams of the test material/ reference material was used.

2. **Preparation of inoculum:**

Seawater was collected from the Browns Bay in Auckland, New Zealand, and was transported to the laboratory in sterilized plastic containers. It had a pH of 8 and a salinity of 33.45 ppt [195]. The seawater was amended with inorganic nutrients such as 0.5 g/L of NH_4Cl and 0.1 g/L of $KH_2(PO)_4$) [57, 196, 197].

3. Exposure of test materials to the inoculum;

Biodegradation studies were performed in 500cc biometer flasks. For each sample, a total of 9 biometer flasks were taken for the biodegradability evaluation, three test vessels for the test specimen, three vessels for testing reference material, and three vessels for blank controls. 400 ml of seawater was taken in all the flasks [149]. Four grams of polymer sample was taken in three of the flasks, four grams of cellulose reference was taken in another three vessels, and nothing was added in the remaining three empty vessels. The temperature of all the vessels was measured and was maintained at about 25°C. Carbon dioxide generated due to biodegradation was absorbed in 0.5N KOH solution, and the amount of CO_2 was estimated by titration with 0.1N HCL, which is explained earlier. Two-thirds of the seawater in the flask was changed every 15 days by a side tube fitted via a conical flask cork. [198] % biodegradation at various intervals was calculated from the cumulative amount of CO_2 generated, which is explained earlier

Chapter 4 - Experimental Results and discussion PBS-PCL blends/composites

4.0 Introduction

This chapter presents the principal outcomes of the experimental work carried out on Polybutylene succinate (PBS) – Polycaprolactone (PCL) blends, plasticized PBS-PCL blends, and nanocomposites of PBS-PCL, incorporated with nano-cellulose (nCell) and nano-clay (nClay). The composition and designation of these polymer samples are given below in Table 4.1

Table 4. 1 Composition and designation of PBS-PCL Blends/nanocomposites prepared

Designation	**PBS content (wt%)**	**PCL content (wt%)**	**Plasticizer (wt%) With respect to PBS – PCL Blends**	**Nanomaterial (wt%) With respect to PBS – PCL Blends**
PBS – PCL Blends				
PBS	100	0	0	0
PBS-PCL10	90	10	0	0
PBS-PCL20	80	20	0	0
PBS-PCL30	70	30	0	0
PBS-PCL40	60	40	0	0
Plasticized PBS-PCL Blends				
PBS-PCL20-P1	80	20	5 % Glyceryl Triacetate (GTA/Triacetin)	0
PBS-PCL20-P2	80	20	5% Ultramoll IV (UM)	0
PBS-PCL20-P3	80	20	5% (GTA – UM (50/50))	0
Nanocomposites of PBS-PCL				
PBS-PCL20-P3 - nCell 1	80	20	5% (GTA – UM (50/50))	1 % Nano cellulose

PBS-PCL20-P3- nCell 3	80	20	5% (GTA – UM (50/50))	3% Nano Cellulose
PBS -PCL20-P3 - nCell 6	80	20	5% (GTA – UM (50/50))	6% Nano Cellulose
PBS-PCL20-P3 - nClay 1	80	20	5% (GTA – UM (50/50))	1% Nano Clay
PBS-PCL20-P3 - nClay 3	80	20	5% (GTA – UM (50/50))	3% Nano Clay
PBS-PCL20-P3 - nClay 6	80	20	5% (GTA – UM (50/50))	6% Nano Clay

4.1 PBS-PCL Blends

Polybutylene succinate (PBS)- Polycaprolactone (PCL) blend films, with 10, 20, 30, and 40 wt% PCL were prepared by hot blending the required quantities of polymer resins, followed by injection molding and hot pressing. The fabrication parameters were optimized, and 0.25mm thick polymer films were produced by hot pressing at 120°C [199], at 1MPa pressure, for 3 min. The polymer blend films were characterized, and the results are presented below:

4.1.1 Appearance/ Photographs:

Digital photographs of the PBS-PCL blend films were taken using a high-resolution camera, shown in Fig. 4.1. All the PBS – PCL films were translucent and were uniform in appearance. The commercial available neat PBS film was translucent as well. The amount of PCL was increased in PBS- PCL blends show that no change in the appearance, as shown in fig 4.1

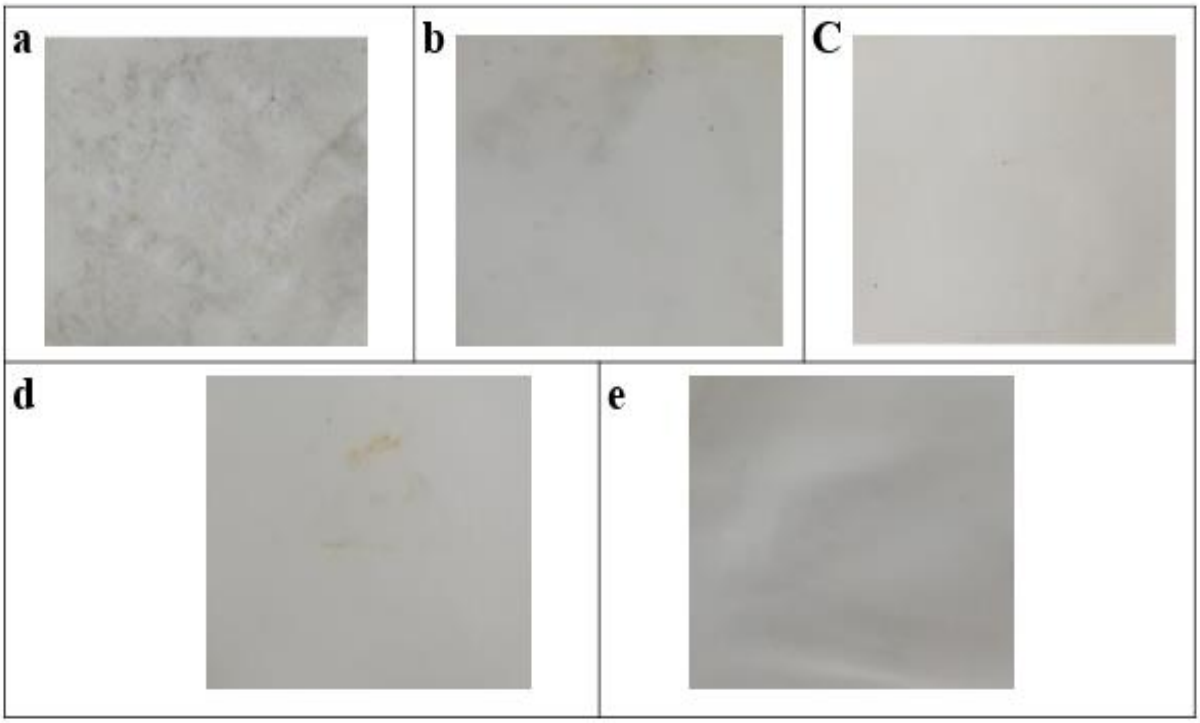


Fig 4. 1 Photograph of PBS/PCL Blends a) PBS 100, b) PBS-PCL10, c) PBS-PCL20, d) PBS-PCL30 e) PBS-PCL40

4.1.2 Mechanical- Tensile properties of PBS-PCL blend films

The PBS-PCL blend film's tensile properties were evaluated by the ASTM D882 method [200] to understand PCL's effect on tensile properties. The results obtained for tensile strength and elongation at break are presented in Table 4.2 and Fig.4.2 (a). The tensile properties of PBS PCL blends based upon the rule of the mixture were shown in fig 4.2 (b) [201].

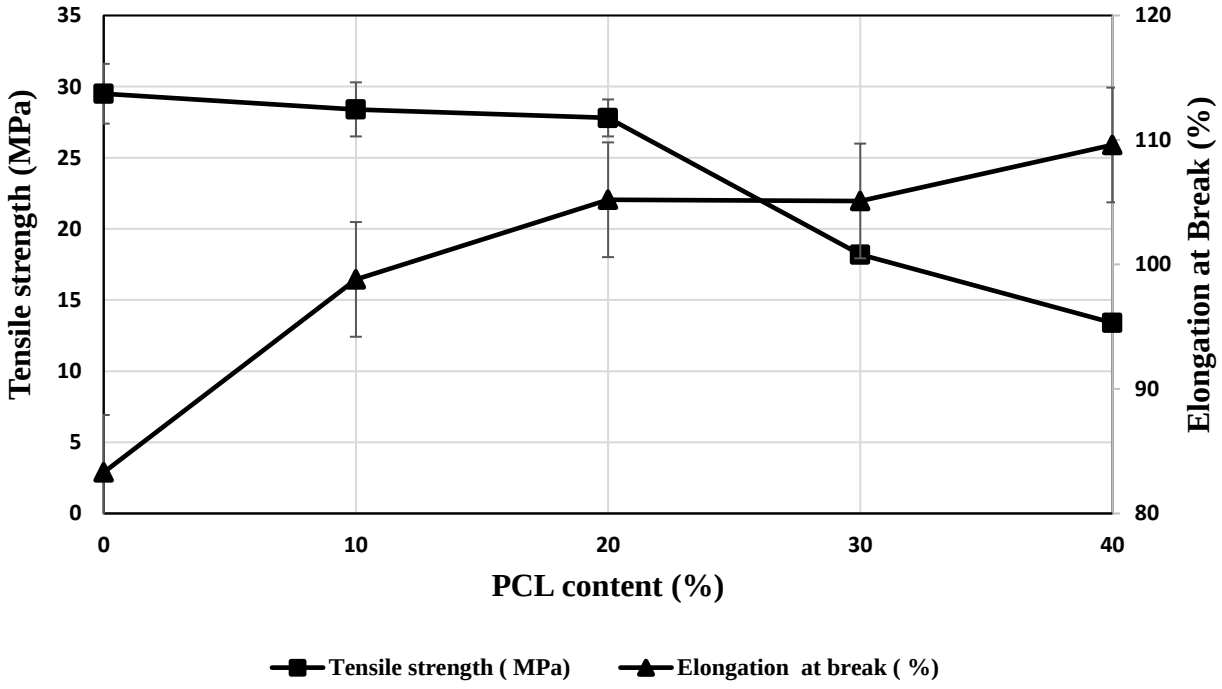
Fig.4.2 (a) indicates that the elongation at break of the PBS-PCL blend continuously increases with the increasing addition of PCL. The increase in elongation was more rapid, up to 20% PCL, and PCL's further additions resulted in a slow increase. The elongation at break obtained for neat PBS was 83.3 %, and it increased to 105.2 % (about 26% increase) for the blend with 20% PCL, and further, it increased only slightly, up to a maximum value of 109.6 % (about 32% increase), for the blend with 40% PCL.

Fig. 4.2 (a) also indicates that the tensile strength of the PBS-PCL blend decreases with the addition of PCL. The decrease in tensile strength, compared to neat PBS, was very marginal for the blends containing up to 20% PCL, and for the blends with higher amounts of PCL, there was a sudden decrease in tensile strength. The tensile strength of neat PBS was 29.5 MPa, and it slightly reduced to 28.4 MPa (4% reduction) with 10 % PCL and then to 27.8 MPa (6% reduction) with 20% PCL. It reduced drastically to 18.2 MPa (38% reduction) and 13.4 MPa (55% reduction), respectively, for the blends with 30 % and 40% PCL.

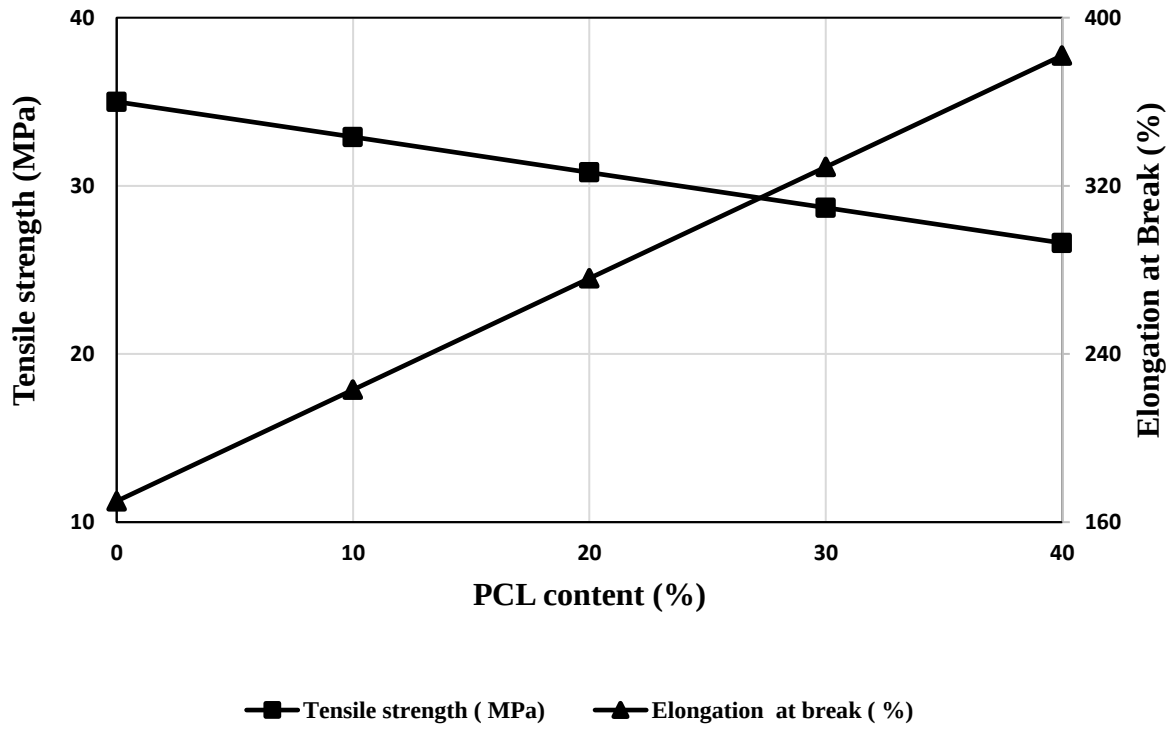
Thus, PBS-PCL blend with 20% PCL was found to have balanced properties with respect to tensile strength and elongation at break. Hence, a blend with 20% PCL was selected for further studies.

Table 4. 2 Tensile properties of PBS-PCL Blends

Film	Tensile strength (MPa)	Elongation at break (%)
PBS	29.5±1.4	83.3±6
PBS-PCL10	28.4±2.1	98.8±5.4
PBS-PCL20	27.8±1.9	105.2±4.9
PBS-PCL30	18.2±1.3	105.1±6.8
PBS-PCL40	13.4±0.6	109.6±7.5



(a)



(b)

Fig 4. 2 (a) Effect of PCL on Tensile strength and Elongation at break of PBS-PCL blends,(b) Tensile properties of PBS-PCL blends, based on the rule of mixtures

The observed increase in elongation at break with PCL is expected due to much higher elongation at break of for neat PCL. Robertson et al. [89] have reported an elongation at break of 500-700%, and Liu and Zhou [117] have reported a value of 586 % for elongation at break for neat PCL. Besides, PCL might have acted as a plasticizer to PBS and effectively increased elongation at break. The use of PCL as a plasticizer for PVC polymer is reported in the literature. [202, 203]. PCL, with its comparatively long polymer chain, was effective in screening the polymeric chains of PBS, reduce interactions between PBS polymer chains, and thus increase PBS polymer chain mobility [92, 204] leading to enhanced ductility for the blend.

The reduction in tensile strength can be attributed to the lower tensile strength of neat PCL compared to PBS [117, 120], low compatibility between PBS and PCL, especially at high concentrations of PCL, as reported by many researchers. [113] [117, 205].

Scanning Electron Microscopy (SEM) studies of the PBS-PCL blend films were taken to understand the phase morphology and find any correlation with mechanical properties. Fig 4.3 a, b, c d, and e represent the SEM images of the cryo-fractured surfaces of neat PBS film and for the blends with 10, 20, 30, and 40% PCL, respectively. The blends' SEM images indicate the presence of spherulites of PCL in the PBS matrix for all the blends, which confirms low compatibility of PBS and PCL and may be contributing to the decrease in tensile strength with blending PBS with PCL.

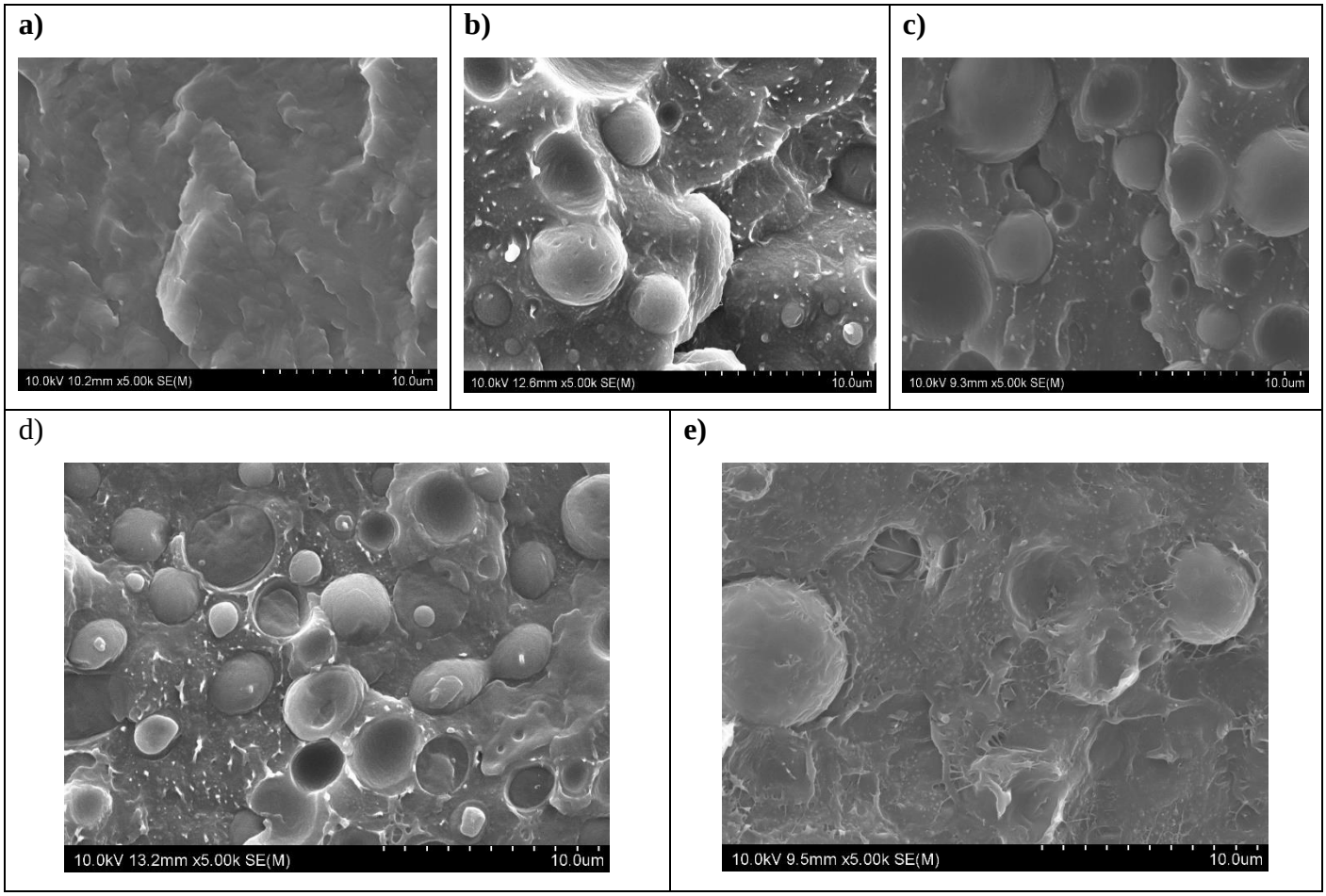


Fig 4. 3 SEM Micrographs (SEM) of PBS-PCL blends a) PBS 100, b) PBS-PCL10, c) PBS-PCL20, d) PBS-PCL30 e) PBS-PCL40

4.1.3 Barrier property- Water vapor transmission rate (WVTR) of PBS-PCL Blend films

The barrier property/ water vapor transmission rates (WVTR) of PBS-PCL Blend films of 0.25mm thickness**,** with 10, 20, 30, and 40 % PCL was measured as per ASTM E96 method [185], at 25˚C, 100% RH, for 30 days, till a steady-state was attained. The films were preconditioned to reduce the time required to attain a steady state. The experimental results on WVTR, after normalization for a film thickness of 25 µm, are presented in Table 4.3 and Fig.4.4

The blend's barrier property was found to improve/ WVTR of the PBS-PCL blend was found to decrease continuously with the addition of PCL at all concentrations. WVTR of the neat PBS film was 452 g m^{-2} $d^{-1,}$ and it decreased sharply to a value of 368 g m^{-2} d^{-1} (~19% reduction) with 10% PCL, and further, it decreased to 324 g m^{-2} d^{-1} (~28% reduction) for a blend with 20% PCL and to a value of 294 g m^{-2} d^{-1} (~ 35% reduction) for a blend with 40% PCL.

Table 4. 3 Water vapor transmission rate (WVTR) of PBS-PCL blend films

Film	**WVTR at 25˚C, 100% RH, for 25µm film g.$m^{-2}d^{-1}$**
PBS	452±15
PBS-PCL10	368±19
PBS-PCL20	324±9
PBS-PCL30	316±12
PBS-PCL40	294±14

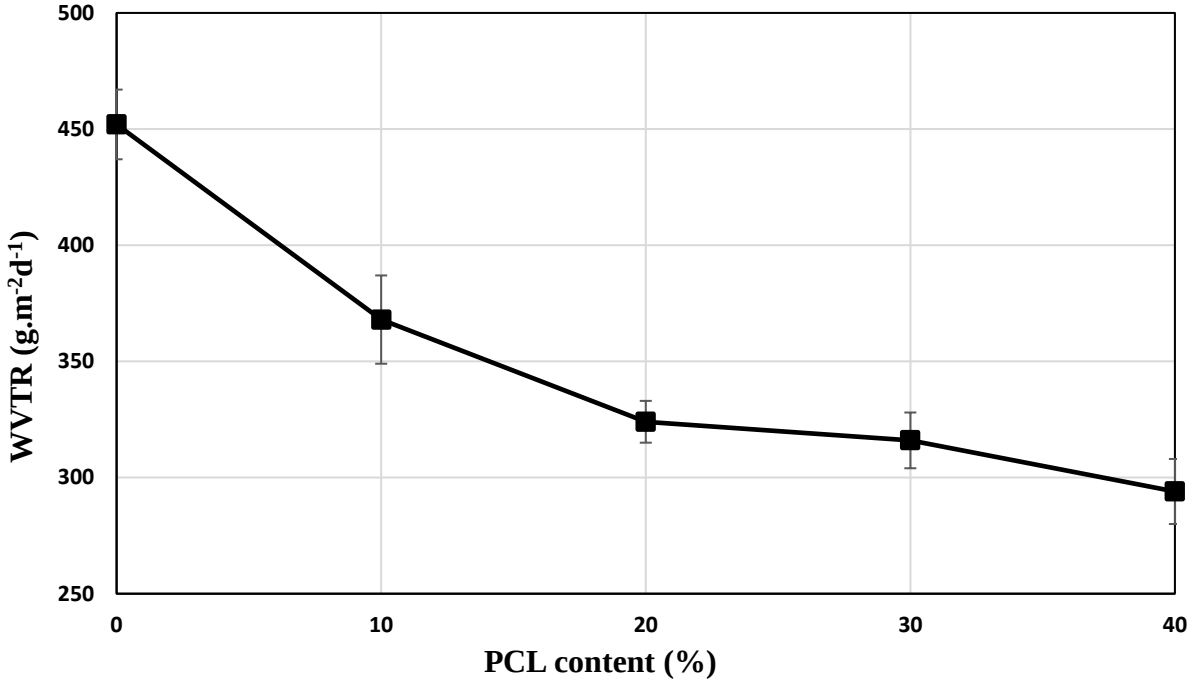


Fig 4. 4 WVTR vs composition curves for PBS-PCL blend films, at 25˚C, 100% RH, 25µm film thickness

The observed improvement in water barrier property/ decrease in WVTR with PCL addition can be explained due to lower WVTR for neat PCL [89]. One of the factors that influence permeability is the amount of free volume in the polymer and its connection. The lower WVTR of PBS-PCL blends may be due to the reduction in free volume with PCL (with a lower WVTR) and reduction in the interconnection between the free volumes/ voids, resulting from the interactions of the polymer chain of PBS and PCL through hydrogen bonding observed by Huang et al., through their FTIR studies [118].

4.1.4 Biodegradation characteristics of PBS-PCL Blend films

Biodegradation studies of PBS and PBS-PCL blends were carried out in compost medium, as per ASTM D5338-15 method [187] and in seawater medium [57], at 25˚C ±5˚C, by measuring the carbon dioxide evolved at frequent intervals, for a period up to 180 days. PBS-PCL30 was skipped for biodegradation tests to reduce the number of experimental samples, as the biodegradation experiment was very labor-intensive. More details are given below:

- **Biodegradation test results for PBS-PCL blends in compost medium:**

Before starting the biodegradation test in compost, important compost parameters, such as total solids, volatile solids, pH, and biological activity of the compost, were checked, and the values obtained are given in Table 4.4. Biological activity of the compost was checked by measuring the CO2 evolved in 10 days and was found to be and 68 mgCO_2/g organic matter/10days (6.8mg CO_2/g organic matter/d), which was well within the requirement of the 50-150 mgCO_2/g of organic matter, for 10 days [187].

Table 4. 4 Properties of the compost

Property	**Standard recommendation# ASTM D5338**	**Actual value**
Dry solids (%)	50-55 (Moisture 45-50%)	50
Volatile solids / organic matter (%)	>30 (Ash < 70%)	54
pH	7.0-8.2	7.5
C/N ratio	10-40	29 *
Compost activity (CO_2 in 10 days) mgCO_2/g of volatile solids	50-150	68

#Ref. ASTM D5338 [187], * Data provided by the supplier

After checking the composting activity, biodegradation studies were conducted in biometer flasks containing test samples (2 grams) with compost, cellulose reference with compost, and vessels with compost alone (blank). The amount of carbon dioxide (CO_2) gas generated from the flasks with blank, positive reference (cellulose) and test samples were measured at various time intervals,

up to 180 days. The cumulative amount of CO_2 generated from the cellulose reference and test samples were calculated by deducting the cumulative amount of CO_2 from the empty vessel. The % biodegradation at various intervals was calculated by dividing the actual CO_2 evolved by the theoretical CO_2 evolved, as per the equation given below:

$$D_t = \frac{\Sigma(CO_2)_T - \Sigma(CO_2)_B}{ThCO_2} * 100\% \quad (4.1)$$

Where

D_t is the % Biodegradation at time t

$\Sigma(CO_2)_T$ is the cumulative amount of carbon dioxide in the vessel containing test material or reference, in grams, from the start to test time t.

$\Sigma(CO_2)_B$ is the cumulative amount of carbon dioxide evolved in the empty vessel, in grams, from the start to test time t.

$ThCO_2$ is the theoretical CO_2 from the test material, calculated from a molecular formula.

The biodegradation test results for PBS-PCL blends, in compost medium at 25˚C, is presented in Table.4.5. The table indicates % biodegradation, and the cumulative amount of CO_2 evolved for the cellulose reference, neat PBS, and PBS-PCL blends at various time intervals. Biodegradation curves, the plot of % biodegradation vs time, were plotted for the neat PBS, PBS-PCL blends, and cellulose reference, with respect to biodegradation compost medium and is presented in Fig.4.5.

Table 4.5 and Fig 4.5, the % biodegradation/ mineralization of cellulose reference in compost medium at 25˚C was 82.3 % after 180 days. Biodegradation of neat PBS in compost was found to be lower compared to cellulose reference and was found to be 26.5% at the end of 180 days. With the addition of PCL, the biodegradation rate was found to increase, though, with the initial addition of 10% PCL, the increase was less. A plateau phase in the biodegradation curve for cellulose at the last stages was not seen in the biodegradation curve for other PBS and PBS blends. The biodegradation rate for the PBS blends was found to be 28.7% (8.3% increase), 32.3% (21.9% increase), and 38.5% (45.3% increase) respectively for the PBS-PCL blends with 10, 20, and 40% PCL, compared to 26.5% biodegradation for neat PBS.

The above-observed mineralization for cellulose is in line with the validity requirements of ASTM D6400 [206] and ISO 17088 standard specifications [49, 207] (minimum 60% biodegradation/ mineralization for homopolymers) for biodegradation in compost media, confirming our test results and the activity of the compost medium.

- **Biodegradation test results for PBS-PCL blends in seawater medium**

Test results for biodegradation of PBS and PBS-PCL blends in the seawater medium are presented in Table 4.6 and Fig 4.6. The above table indicates the cumulative amount of CO_2 evolved and % biodegradation for the cellulose reference, neat PBS, and PBS-PCL blends at various time intervals. The above results indicate that for the cellulose reference, 40.2% biodegradation was achieved in 180 days. This result obtained for the cellulose reference in seawater is in agreement/ comparable to the results obtained by other researchers. [208] [209]. Compared to cellulose reference, the biodegradation test results of neat PBS and PBS blends indicate a lower seawater degradation rate. The biodegradation rate for PBS in seawater was 10.3 % at the end of 180 days. The biodegradation rate was found to increase with PCL addition and was found to increase with increasing PCL content. The % biodegradation for the PBS-PCL blends with 10, 20, and 40% PCL was found to be 11.4% (11% increase), 13.5% (31% increase) and 16.6% (62% increase) respectively, at the end of 180 days.

Thus, the rate of biodegradation of the PBS-PCL blends in compost and seawater was found to follow the order:

Cellulose reference > PBS-PCL 40 > PBS-PCL20 > PBS-PCL10 > PBS.

The observed increase in biodegradability with an increase in PCL concentration for the PBS-PCL blends in compost medium and seawater can be explained due to the higher biodegradability of PCL in compost [118] and in seawater, as reported by many researchers, [210, 211], and PCL improved the mobility of PBS chains. [92]

Table 4. 5 Cumulative amount of CO2 evolved and % biodegradation for PBS-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25˚C.

	Cellulose Reference ($ThCO_2$:3.23g)		**PBS100% ($ThCO_2$:4.03g)**		**PBS-PCL10% ($ThCO_2$: 4.09g)**		**PBS-PCL20% ($ThCO_2$:4.15g)**		**PBS-PCL40% ($ThCO_2$:4.27g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.16	4.9±1.2	0.06	1.5±1.7	0.08	2±1.6	0.10	2.4±1.6	0.10	2.4±1.3
30	0.27	8.4±1.6	0.21	5.2±2.6	0.25	6±2.7	0.30	7.2±1.7	0.31	7.4±1.6
45	0.67	20.7±1.4	0.37	9.2±1.8	0.43	10.5±1.8	0.50	12.1±2.8	0.60	14±2.8
60	0.96	29.7±2.5	0.46	11.4±1.4	0.53	12.9±1.4	0.60	14.5±1.4	0.69	16.2±1.7
75	1.17	36.4±1.6	0.60	15±2.6	0.64	15.6±1.6	0.74	17.9±2.6	0.83	19.4±2.3
90	1.39	43.1±1.4	0.68	16.9±2.7	0.74	18.1±2.8	0.79	19±1.7	0.92	21.6±1.4
105	1.77	54.7±2.5	0.79	19.5±1.9	0.83	20.4±1.9	0.88	21.3±2.6	0.96	22.5±2.8
120	1.94	60.2±1.6	0.85	21.1±2.4	0.90	22.1±2.4	0.96	23.1±1.4	1.11	26±1.9
135	2.31	71.5±2.4	0.89	22.1±1.8	0.96	23.5±1.9	1.03	24.9±2.9	1.19	28±2.4
150	2.45	75.9±1.4	0.93	23.1±1.9	1.06	25.9±2.6	1.14	27.5±2.4	1.28	30±1.3
165	2.64	81.8±1.5	1.05	26±2.8	1.10	26.9±2.8	1.28	30.8±1.6	1.45	34±2.4
180	2.66	82.3±1.6	1.07	26.5±2.7	1.17	28.7±1.7	1.34	32.3±1.3	1.64	38.5±1.6

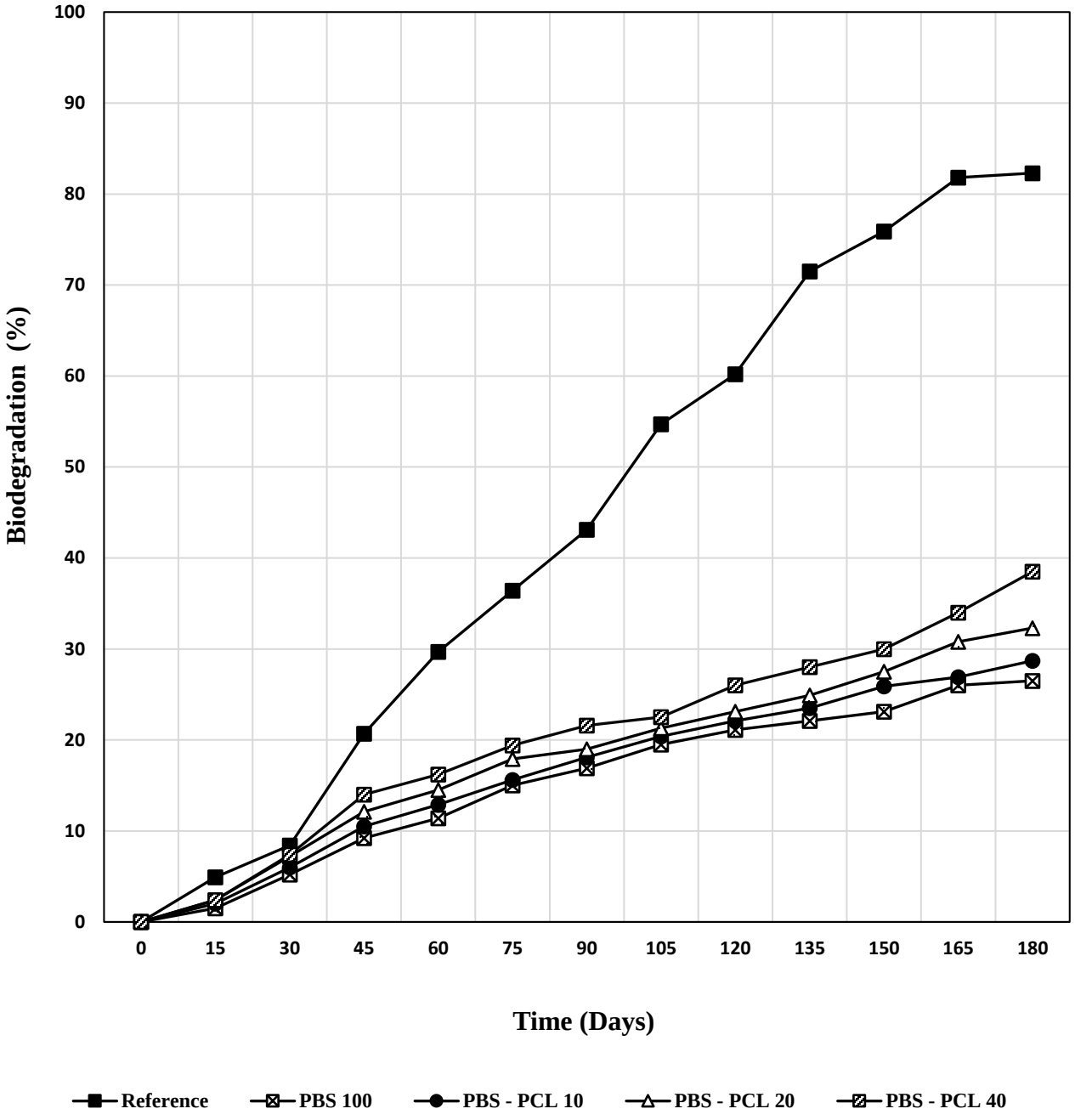


Fig 4. 5 Biodegradation curve of PBS-PCL blends in compost at 25˚C

Table 4. 6 Cumulative amount of CO_2 evolved and % biodegradation for PBS-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25˚C.

	Cellulose Reference ($ThCO_2$:6.45 g)		**PBS100% ($ThCO_2$:8.07g)**		**PBS-PCL10% ($ThCO_2$: 8.18g)**		**PBS-PCL20% ($ThCO_2$: 8.30g)**		**PBS-PCL40% ($ThCO_2$: 8.54g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.04	0.6±1.5	0.00	0	0.00	0	0.03	0.4±2.4	0.06	0.7±1.7
30	0.14	2.1±1.4	0.03	0±1.7	0.07	0.9±2.7	0.11	1.3±2.6	0.16	1.9±2.5
45	0.41	6.4±2.6	0.11	0.4±1.5	0.11	1.4±1.6	0.16	1.9±1.6	0.25	3±2.6
60	0.75	11.6±2.8	0.15	1.4±1.4	0.20	2.4±1.4	0.31	3.7±1.7	0.41	4.8±2.7
75	1.02	15.8±1.7	0.19	1.9±2.6	0.25	3.1±2.4	0.34	4.1±2.7	0.44	5.1±1.7
90	1.44	22.3±2.9	0.30	2.4±2.5	0.29	3.5±2.7	0.43	5.2±2.7	0.45	5.2±2.8
105	1.60	24.8±2.6	0.37	3.7±1.6	0.45	5.5±1.8	0.50	6±2.4	0.61	7.2±2.6
120	1.90	29.4±2	0.46	4.6±2.7	0.49	6±2.9	0.53	6.4±2.6	0.69	8.1±1.7
135	2.11	32.7±1.4	0.51	5.7±1.4	0.56	6.8±1.7	0.74	8.9±1.6	0.86	10.1±2.7
150	2.21	34.3±2.6	0.68	6.3±1.6	0.75	9.1±2.6	0.83	10±2.8	0.92	10.8±2.7
165	2.48	38.5±1.7	0.73	8.4±1.6	0.80	9.8±2.7	0.99	11.9±2.5	1.10	12.9±2.9
180	2.59	40.2±2.9	0.83	9.1±2.4	0.93	11.4±2.6	1.12	13.5±1.7	1.42	16.6±1.7

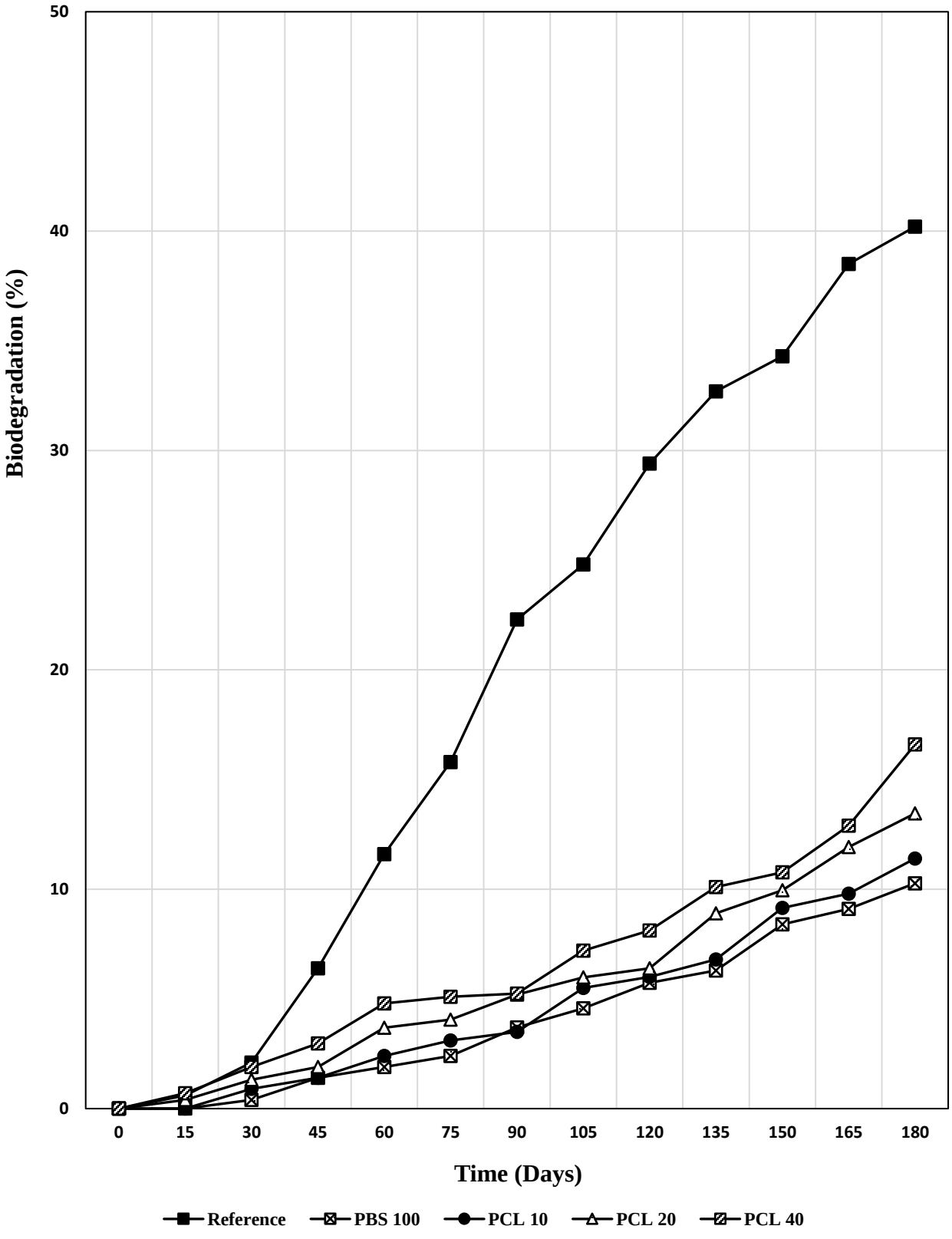


Fig 4. 6 Biodegradation curve of PBS-PCL blends in seawater at 25˚C

4.2 Plasticized PBS-PCL blend films

The effect of various plasticizers on the PBS-PCL blend was investigated to improve the tensile elongation properties further. Blend with 20% PCL, namely PBS-PCL20, was chosen for plasticization since our studies on various blends indicated that the blends 20% PCL provides the best/ balanced properties with respect to tensile strength and elongation at break. However, blends with higher PCL loading was beneficial for higher water vapor barrier properties and higher biodegradability. Three biodegradable plasticizers, namely i) a monomeric plasticizer (P1), Triacetin / Glyceryl Triacetate (GTA), ii) a polymeric plasticizer (P2), Ultramoll IV (UM), an adipic acid polyester, and iii) a mixture of the above two plasticizers, 1:1 ratio by weight (P3), were used for the plasticization study. For plasticization, 5 wt% of plasticizers were used, since phase separation and exudation of plasticizer with high percentages of plasticizer. The plasticized PBS-PCL20 blend films, with plasticizers P1, P2, and P3, of thickness 0.25mm, designated as PBS-PCL20-P1, PBS-PCL20-P2, and PBS-PCL20-P3, were prepared by hot pressing and were characterized by standard methods and the results are presented below:

4.2.1 Appearance/ Photographs of Plasticized PBS-PCL Blends

Digital photographs of the Plasticized PBS-PCL blend films are shown in Fig. 4.7, taken by a high-resolution camera. Apart from the blend PBS-PCL20-P2, with plasticizer P2, all the other plasticized polymeric films were uniform in appearance.

Fig 4. 7 Photographs of Plasticized PBS-PCL Blends a) PBS-PCL20-P1, b) PBS-PCL20-P2, c) PBS-PCL20-P3

4.2.2 Mechanical- Tensile properties of Plasticized PBS-PCL Blend films

The tensile properties of plasticized PBS-PCL20 blend with 5 wt% of various plasticizers are presented in Table 4.7 and Fig.4.8. These results indicate an increase in tensile elongation with all three plasticizers. A higher elongation increase was observed with monomeric plasticizer P1, glyceryl triacetate, least increase with polymeric plasticizer P2, and medium increase with mixed plasticizer P3. The order of elongation at break was ε: P1>P3>P2. The Tensile elongation increased from 105.2% (for un-plasticized PBS-PCL20) to 131.7%, 110.6%, and 128.3 % with plasticizers P1, P2, and P3, respectively, corresponding to an increase of 25%, 5%, and 22% for an un-plasticized blend.

The test results on tensile strength indicate a decrease in tensile strength with plasticization. The decrease in tensile strength was more with monomeric plasticizer P1, glyceryl triacetate, the smallest decrease was observed with mixed plasticizer, P3 and medium decrease in tensile strength were medium with polymeric plasticizer P2. The order of tensile strength was σ: P3>P2>P1. The tensile strength of the plasticized PBS-PCL20, with plasticizers P1, P2, and P3, was found to be 20.2 MPa, 23.4 MPa, and 26.3 MPa, respectively, compared to 27.8 MPa for the un-plasticized blend. The corresponding % decrease in tensile strength (for un-plasticized PBS-PCL20) was found to be approximately 27%, 16%, and 5% for plasticizers P1, P2, and P3, respectively.

Table 4. 7 Tensile properties of Plasticized PBS-PCL Blends

Film	**Tensile strength (MPa)**	**Elongation at break (%)**
PBS-PCL20	27.8±1.9	105.2±4.9
PBS-PCL20-P1	20.2±1.4	131.7±11.2
PBS-PCL20- P2	23.4±1.1	110.6±5.7
PBS-PCL20- P3	26.3±2.9	128.3±2.2

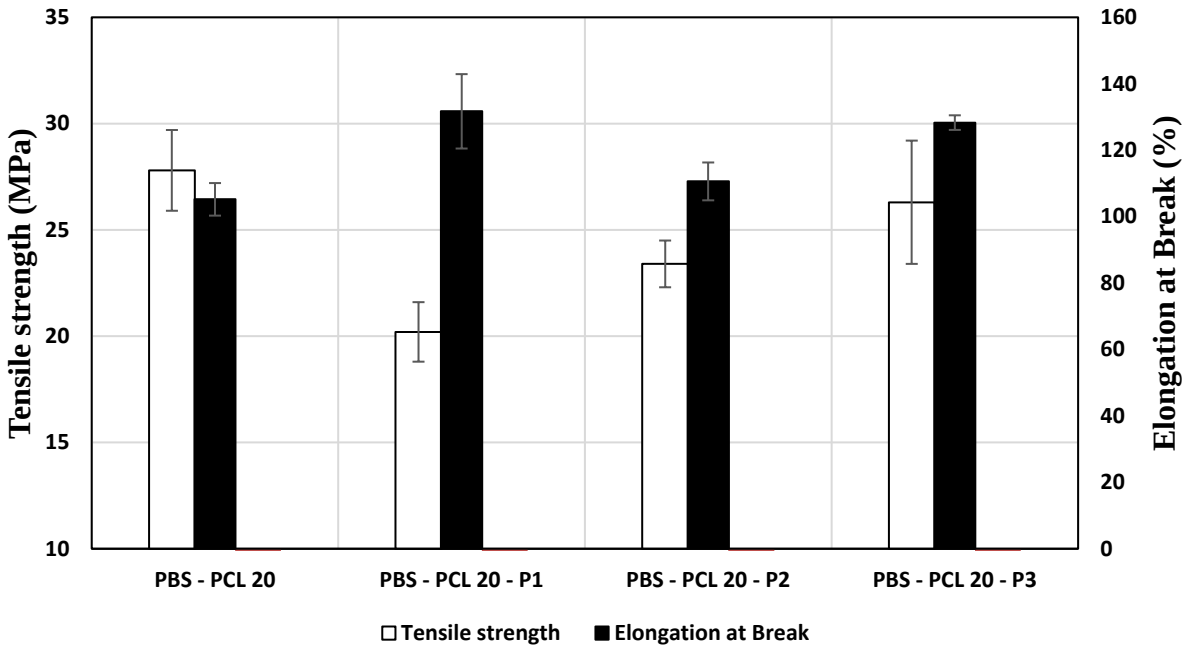


Fig 4. 8 Tensile strength and Elongation at break of Plasticized PBS-PCL Blends

The increased elongation on plasticization can be explained due to an increase in polymer chain mobility, as the plasticizer's introduction increases the free volume/ internal space available inside the polymer. Monomeric plasticizer being small, can penetrate more effectively, deep inside the polymer contributing to higher ductility than bigger polymeric plasticizer.

The decrease in tensile strength with plasticizers' addition is usually expected and has been reported by many researchers since the plasticizer penetrates between the polymer chains, decreases the intermolecular forces, and reduces polymer chain cohesion. [212].

The SEM images of plasticized PBS-PCL20 blends were taken at 5000 magnification and are given below. For comparison, the SEM image of the un-plasticized PBS-PCL20 blend is also shown. The plasticized blends' SEM images indicate a drastic change compared to that for an un-plasticized blend. On plasticization, the spherulites of PCL disappears, improves the mixing of PBS and PCL phases, and supports our explanation for increased ductility for the plasticized blends.

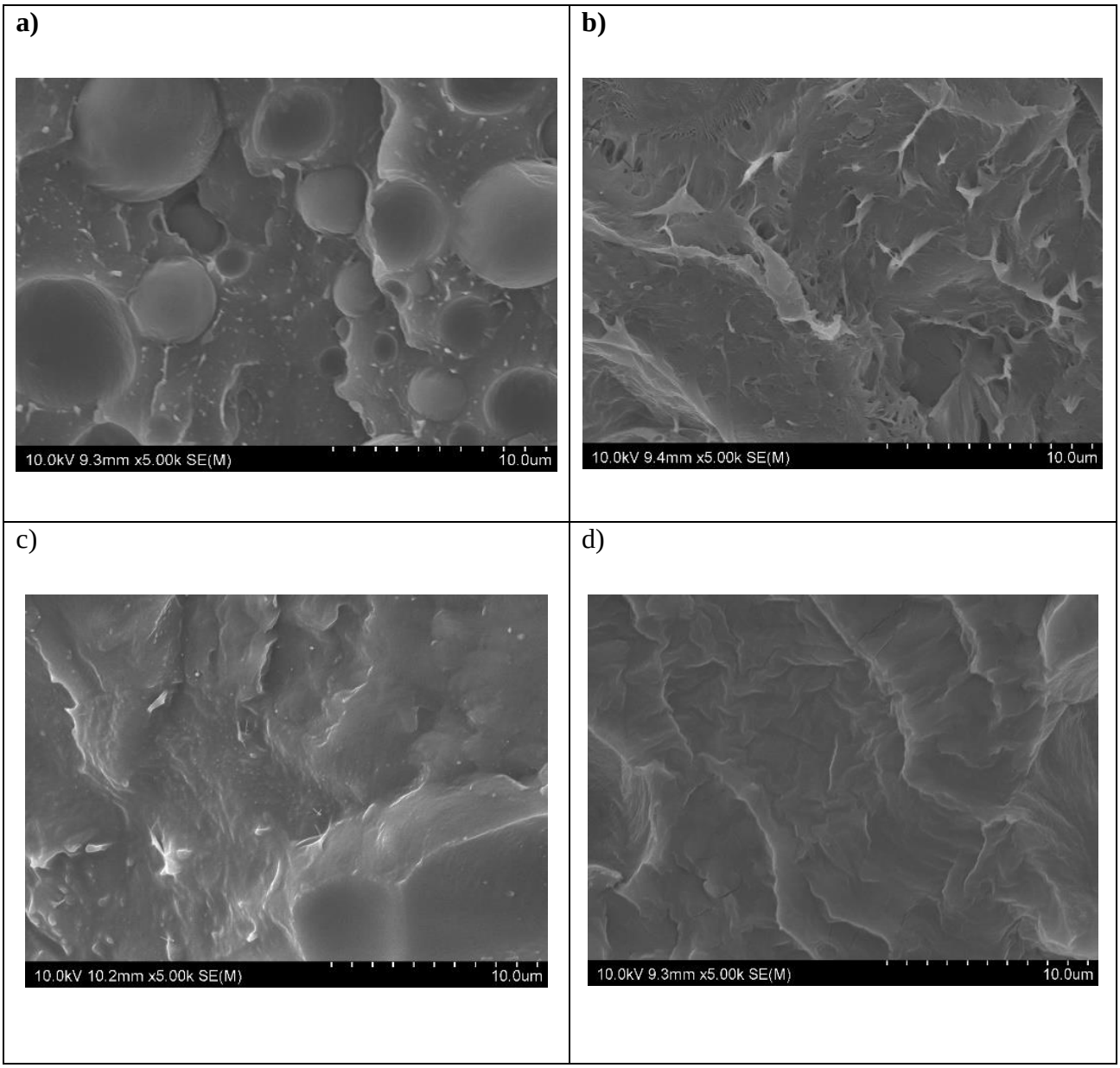


Fig 4. 9 SEM of Plasticized PBS-PCL Blends and un-plasticized PBS-PCL blend

a) PBS-PCL20 blend, b) PBS-PCL20-P1, c) PBS-PCL20- P2, and d) PBS-PCL20-P3

4.2.3 Water vapor transmission rates (WVTR) of Plasticized PBS-PCL Blend films

The water vapor transmission rate (WVTR) of plasticized PBS-PCL20 blend films with various plasticizers was investigated, and the results obtained are presented in table 4.8 and Fig.4.10. The results indicate that the WVTR increases/ barrier property decreases with all three plasticizers. The increase in WVTR / loss in barrier property was maximum with plasticized blend with monomeric plasticizer P1 and least with mixed plasticizer P3. WVTR values for the plasticized blends were thus WVTR: P1>P2>P3. WVTR of the un-plasticized PBS-PCL20 film was 324 g $m^{-2}d^{-1,}$ and it increased to 374 g $m^{-2}d^{-1}$, 345 g $m^{-2}d^{-1,}$ and 338 g $m^{-2}d^{-1}$, with the addition of plasticizers P1, P2, and P3, respectively. This WVTR increment corresponds to an increase in WVTR by 15.4%, 6.5%, and 4.3%, respectively.

An increase in WVTR with the addition of plasticizers is expected, and is due to an increase in free volume, changes in hydrophilicity of the films, and increased solubility of permeating molecules [79, 152].

Table 4. 8 WVTR of Plasticized PBS-PCL blend films, at 25ºC, 100% RH, for 25µm film thickness

Film	**WVTR at 25°C, 100% RH, for 25µm film g.$m^{-2}d^{-1}$**
PBS-PCL20	324±9
PBS-PCL20-P1	374±15
PBS-PCL20-P2	345±11
PBS-PCL20-P3	338±8

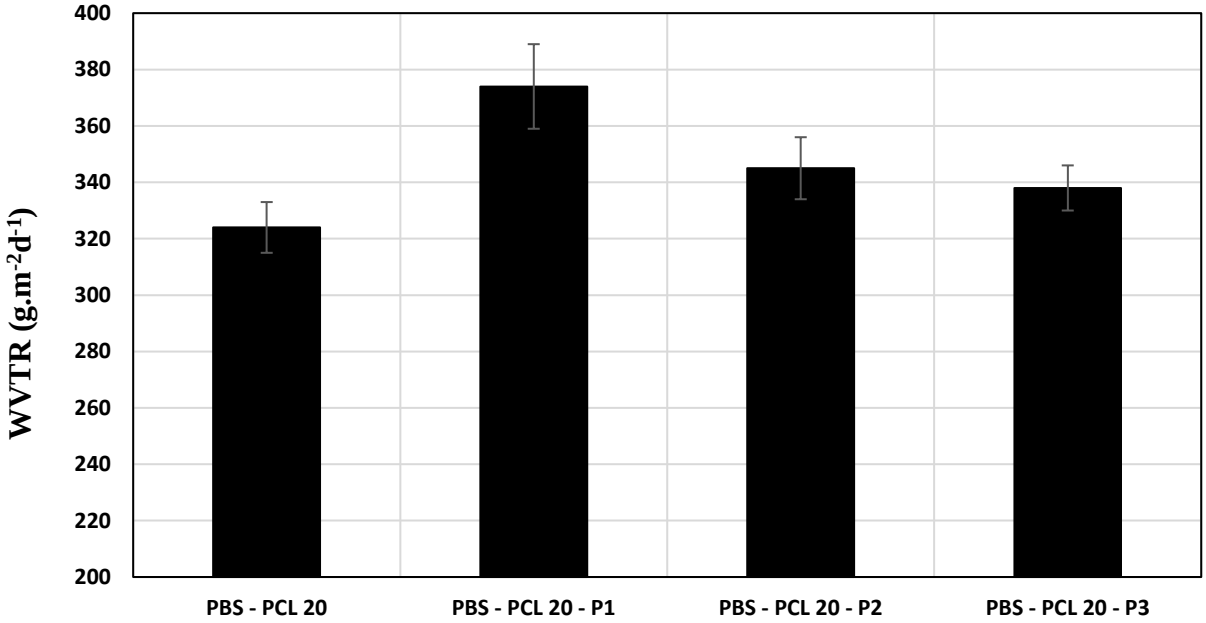


Fig 4. 10 WVTR of Plasticized PBS-PCL blend films, at 25˚C, 100% RH, for 25µm film

4.2.4 Biodegradation characteristics of Plasticized PBS-PCL Blend films

Biodegradation characteristics of plasticized PBS-PCL20 blends, namely PBS-PCL20-P1, PBS-PCL20-P2, and PBS-PCL20-P3, with plasticizers P1, P2, and P3, were evaluated in home compost medium, and seawater medium, for a period up to 180 days, by carbon dioxide evolution method.

- **Biodegradation of Plasticized PBS-PCL blends in compost medium at 25ºC**

Biodegradation test results for the plasticized blends in compost medium are given in Table 4.9 and Fig 4.11. These results indicate an increase in the biodegradation rate for all the plasticized PBS-PCL blends than the un-plasticized PBS-PCL blend film. The % biodegradation obtained for the plasticized films with the plasticizers were 40.5%, 36.8%, and 38.6% for the blends with monomeric plasticizer P1, polymeric plasticizer P2, and mixed plasticizer P3 respectively, in compost medium at the end of 180 days, compared to 32.3% biodegradation for the un-plasticized PBS-PCL blend.

- **Biodegradation of Plasticized PBS-PCL blends in seawater**

Test results on the biodegradation of plasticized blends in seawater are presented in Table 4.10 and Fig 4.12. These results indicate an increase in the biodegradation rate for all the plasticized PBS-PCL blends, compared to the un-plasticized PBS-PCL blend film, as in the case with biodegradation tests in compost medium.

The % biodegradation in seawater for the plasticized blends was found to be lesser compared to compost medium and were 17.3%, 14.5%, and 16.4%, respectively, for the plasticized blends with plasticizer P1, P2, and P3, compared to a biodegradation rate of 13.5% for un-plasticized blend film. These correspond to an increase in biodegradation by 28.8%, 8%, and 22.1%, respectively, for plasticized blends with P1, P2, and P3.

It can be seen that the % biodegradation of the plasticized blends in compost and seawater medium follow the same order, namely:

PBS-PCL20-P1> PBS-PCL20-P3 > PBS-PCL20-P2 > PBS-PCL20

However, the biodegradation rate in seawater was significantly lower than that in the compost medium, as expected due to the lesser population of microbes in seawater than compost. The increase in the biodegradation rate with plasticizer's addition can be explained due to increased hydrophilicity/ wettability with plasticizers' addition. [77]

Table 4. 9 Cumulative amount of CO_2 evolved and % biodegradation for plasticized PBS-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25˚C.

	Cellulose Reference ($ThCO_2$:3.23g)		**PBS-PCL20 ($ThCO_2$:4.15g)**		**PBS-PCL20- P1 ($ThCO_2$:4.12g)**		**PBS-PCL- P2 ($ThCO_2$:4.13g)**		**PBS-PCL- P3 ($ThCO_2$:4.13g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.16	4.9±1.2	0.10	2.4±1.6	0.12	3±1.8	0.11	2.7±1.4	0.12	2.9±2.4
30	0.27	8.4±1.6	0.30	7.2±1.7	0.37	9±1.6	0.33	7.9±1.6	0.36	8.6±1.8
45	0.67	20.7±1.4	0.50	12.1±2.8	0.62	15.2±2.4	0.52	12.6±2.7	0.59	14.2±2.4
60	0.96	29.7±2.5	0.60	14.5±1.4	0.75	18.2±2.7	0.64	15.6±2.4	0.72	17.3±1.9
75	1.17	36.4±1.6	0.74	17.9±2.6	0.87	21.1±1.9	0.76	18.5±1.6	0.85	20.7±2.7
90	1.39	43.1±1.4	0.79	19±1.7	1.05	25.4±2.8	0.85	20.6±1.8	1.00	24.3±1.6
105	1.77	54.7±2.5	0.88	21.3±2.6	1.19	28.9±2.4	0.90	21.8±1.6	1.02	24.7±1.3
120	1.94	60.2±1.6	0.96	23.1±1.4	1.19	29±1.5	1.02	24.8±1.4	1.14	27.6±2.4
135	2.31	71.5±2.4	1.03	24.9±2.9	1.28	31.2±1.7	1.17	28.4±1.8	1.23	29.7±1.2
150	2.45	75.9±1.4	1.14	27.5±2.4	1.50	36.4±1.2	1.29	31.4±1.4	1.36	32.9±1.4
165	2.64	81.8±1.5	1.28	30.8±1.6	1.59	38.6±1.3	1.35	32.7±2.4	1.55	37.6±1.6
180	2.66	82.3±1.6	1.34	32.3±1.3	1.67	40.5±1.4	1.52	36.8±1.9	1.59	38.6±2.7

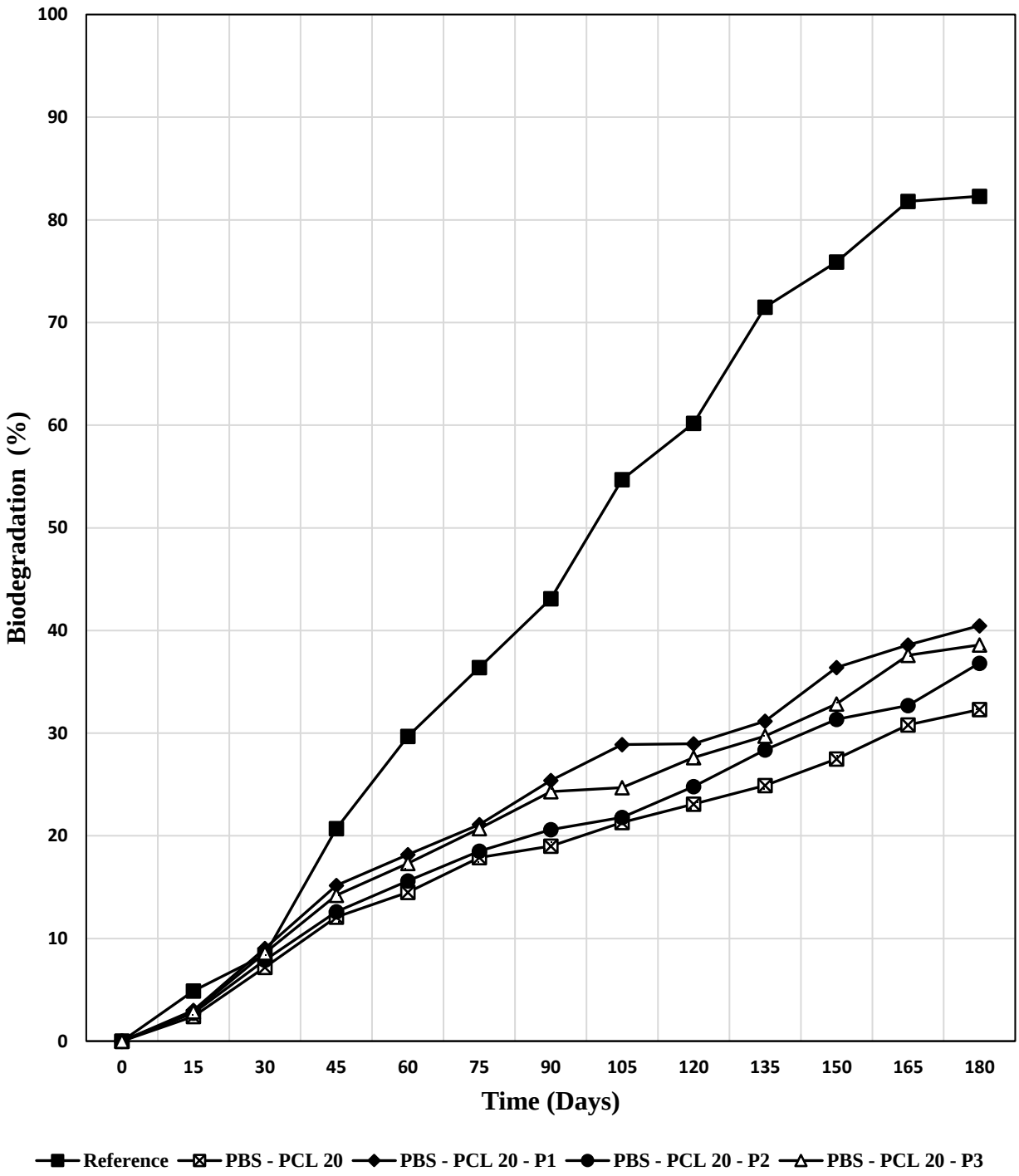


Fig 4. 11 Biodegradation curve of Plasticized PBS-PCL blends, in compost at 25˚C

Table 4. 10 Cumulative amount of CO_2 evolved and % biodegradation for plasticized PBS-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25˚C.

	Cellulose Reference ($ThCO_2$:6.45g)		**PBS-PCL20 ($ThCO_2$:8.30g)**		**PBS-PCL20- P1 ($ThCO_2$:8.25g)**		**PBS-PCL- P2 ($ThCO_2$:8.27g)**		**PBS-PCL- P3 ($ThCO_2$:8.27g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0	0	0	0	0	0
15	0.04	0.6±1.5	0.03	0.4±2.4	0.10	1.2±1.7	0.03	0.3±1.7	0.05	0.6±1.4
30	0.14	2.1±1.4	0.11	1.3±2.6	0.21	2.5±1.6	0.09	1.1±2.4	0.15	1.8±1.8
45	0.41	6.4±2.6	0.16	1.9±1.6	0.40	4.9±1.4	0.21	2.5±1.6	0.33	4±1.5
60	0.75	11.6±2.8	0.31	3.7±1.7	0.50	6±1.2	0.33	3.9±1.4	0.40	4.8±2.4
75	1.02	15.8±1.7	0.34	4.1±2.7	0.53	6.4±2.4	0.40	4.8±2.5	0.52	6.3±2.6
90	1.44	22.3±2.9	0.43	5.2±2.7	0.63	7.7±2.9	0.57	6.9±2.9	0.66	8±2.8
105	1.60	24.8±2.6	0.50	6±2.4	0.75	9.1±2.8	0.59	7.1±2.7	0.68	8.2±1.7
120	1.90	29.4±2	0.53	6.4±2.6	0.80	9.7±1.4	0.68	8.2±1.8	0.78	9.5±1.9
135	2.11	32.7±1.4	0.74	8.9±1.6	0.96	11.7±1.6	0.72	8.7±1.9	0.86	10.5±2.4
150	2.21	34.3±2.6	0.83	10±2.8	1.04	12.6±2.7	0.83	10.1±2.4	1.01	12.2±2.6
165	2.48	38.5±1.7	0.99	11.9±2.5	1.27	15.4±1.4	1.01	12.2±1.6	1.14	13.8±2
180	2.59	40.2±2.9	1.12	13.5±1.7	1.35	17.3±1.6	1.10	14.5±1.8	1.25	16.4±1.4

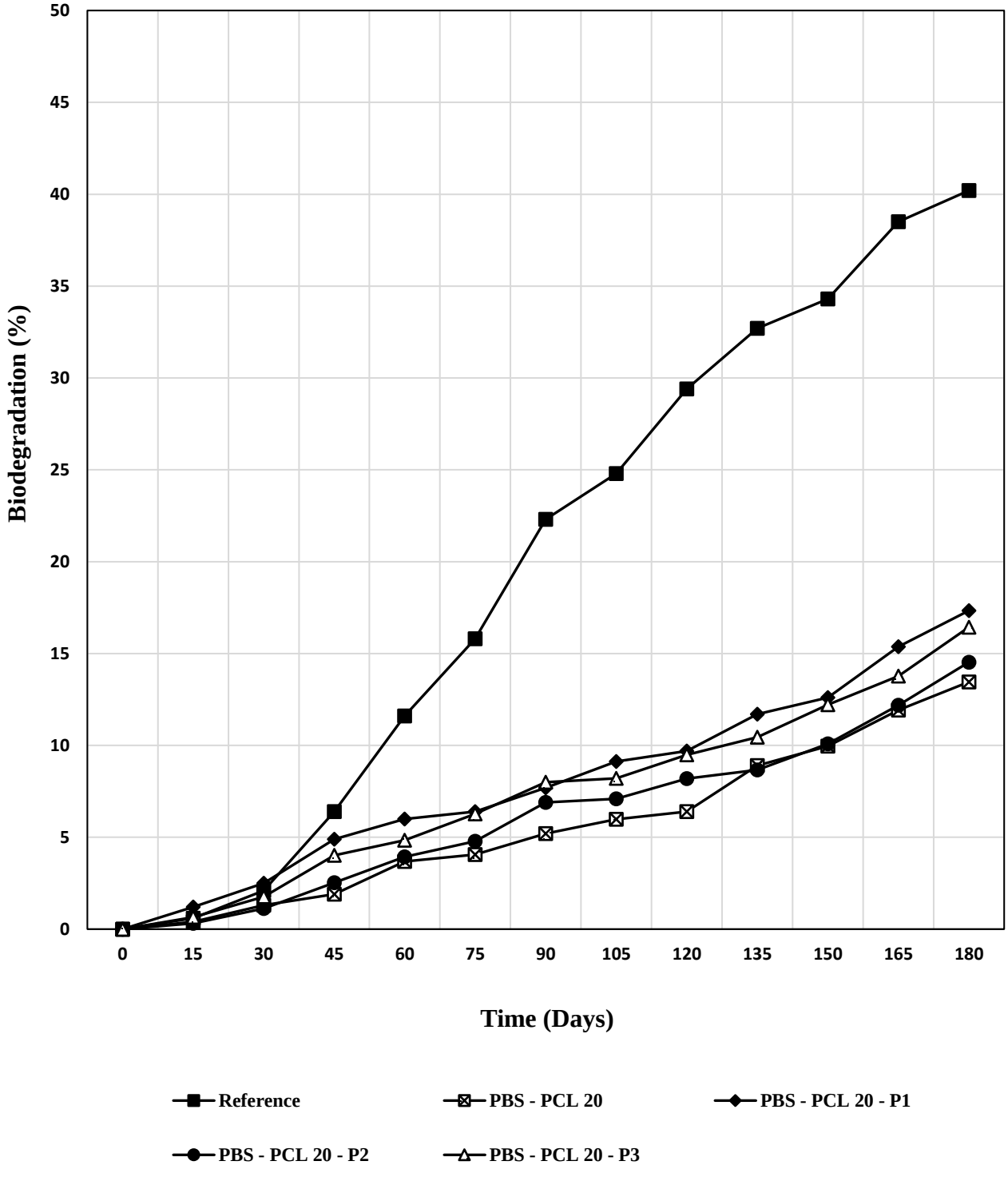


Fig 4. 12 Biodegradation curve of Plasticized PBS-PCL blends in seawater at 25^0C.

4.3 Nanocomposite films based on plasticized PBS-PCL blend

Nanocomposite films based on plasticized PBS-PCL blend were prepared by incorporating nano-cellulose (nCell) and nano clay (nClay), at different loadings (1, 3, and 6 wt%), into the polymer blend PBS-PCL20-P3 and were characterized by standard methods, and the results obtained are given below:

4.3.1 Appearance/ Photographs of Nanocomposite films based on PBS – PCL blend

Photographs of nano cellulose-based polymeric film are shown in Figures 4.13 (a, b, c) and nano clay-based polymeric film portrayed in figure 4.13 (d, e, f). All polymeric films were uniform in appearance, except the polymer film with nCell 6wt%.

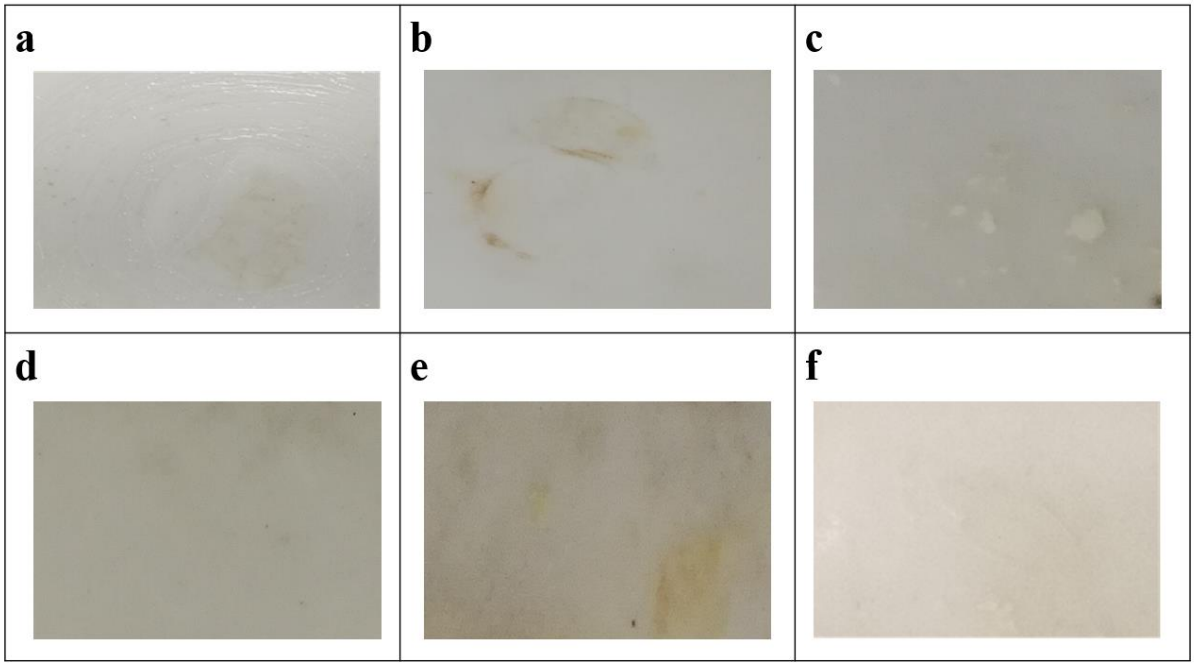


Fig 4. 13 Photographs of Nano composite films based on plasticized PBS-PCL blend a) PBS-PCL20- P3-nCell 1, b) PBS-PCL20- P3-nCell 3, c) PBS -PCL20- P3-nCell 6, d) PBS-PCL20-P3-nClay 1, e) PBS-PCL20- P3-nClay 3, f) PBS-PCL20- P3-nClay 6

4.3.2 Mechanical - Tensile properties of nanocomposite films based on PBS – PCL

The tensile testing of nanocomposites based on plasticized PBS-PCL20, incorporated with different nano-cellulose and nano-clay loadings, was carried out, and the results are presented in Table 4.11. It can be seen from the above results that the tensile properties of nanocomposites are very much dependent on the type and concentration of the nanomaterials.

The variation in tensile strength is presented in Fig. 4.14 for different nano cellulose and nano clay loadings. It indicates a slight increase in tensile strength with the addition of nano cellulose, though the increase was lesser at higher loadings, and maximum tensile strength was obtained at 1 wt% cellulose loading. The tensile strength of nanocomposite with 1, 3, and 6 wt% nano-cellulose was 28.2 MPa, 28MPa, and 27.1 MPa, respectively, compared to a value of 26.3MPa before adding nano cellulose.

A continuous increase in tensile strength with nano clay loading and highest tensile strength was obtained at 6 wt% nano clay loading. The nanocomposite's tensile strength with 1, 3, and 6 wt % nano clay was found to be 31.4 MPa, 36.2 MPa, and 38.1 MPa, respectively.

Fig 4.15 shows the results of tensile elongation of nanomaterials, and it indicates a decrease in tensile elongation by incorporating both the nanomaterials. The elongation at break of the nanocomposites with nano cellulose was found to be 125, 111, and 74%, respectively, for nanocomposites with 1, 3, and 6 wt% nano cellulose. With nano clay, tensile elongation was reduced, and the tensile elongation was found to be ~123, 119, and 115% with 1, 3, and 6 wt% loadings of nano clay. Thus, the decrease elongation at break with increased nanomaterial loading was sharper in nano cellulose than nano clay.

Table 4. 11 Tensile properties of nanocomposite films based on PBS - PCL

Film		Tensile strength (MPa)	Elongation at break (%)
PBS-PCL20- P3		26.3±0.5	128.3±2.2
Nano Cellulose	**PBS-PCL20- P3-nCell 1**	28.2±1.6	125.1±7
	PBS-PCL20- P3-nCell 3	28±2.1	111.4±4.2
	PBS-PCL20- P3-nCell 6	27.1±1.2	74.2±3.1
Nano Clay	**PBS-PCL20- P3-nClay1**	31.4±1.5	122.91±5.1
	PBS-PCL20- P3-nClay3	36.2±2.5	118.6±4.3
	PBS-PCL20- P3-nClay6	38.1±1.9	115.1±1

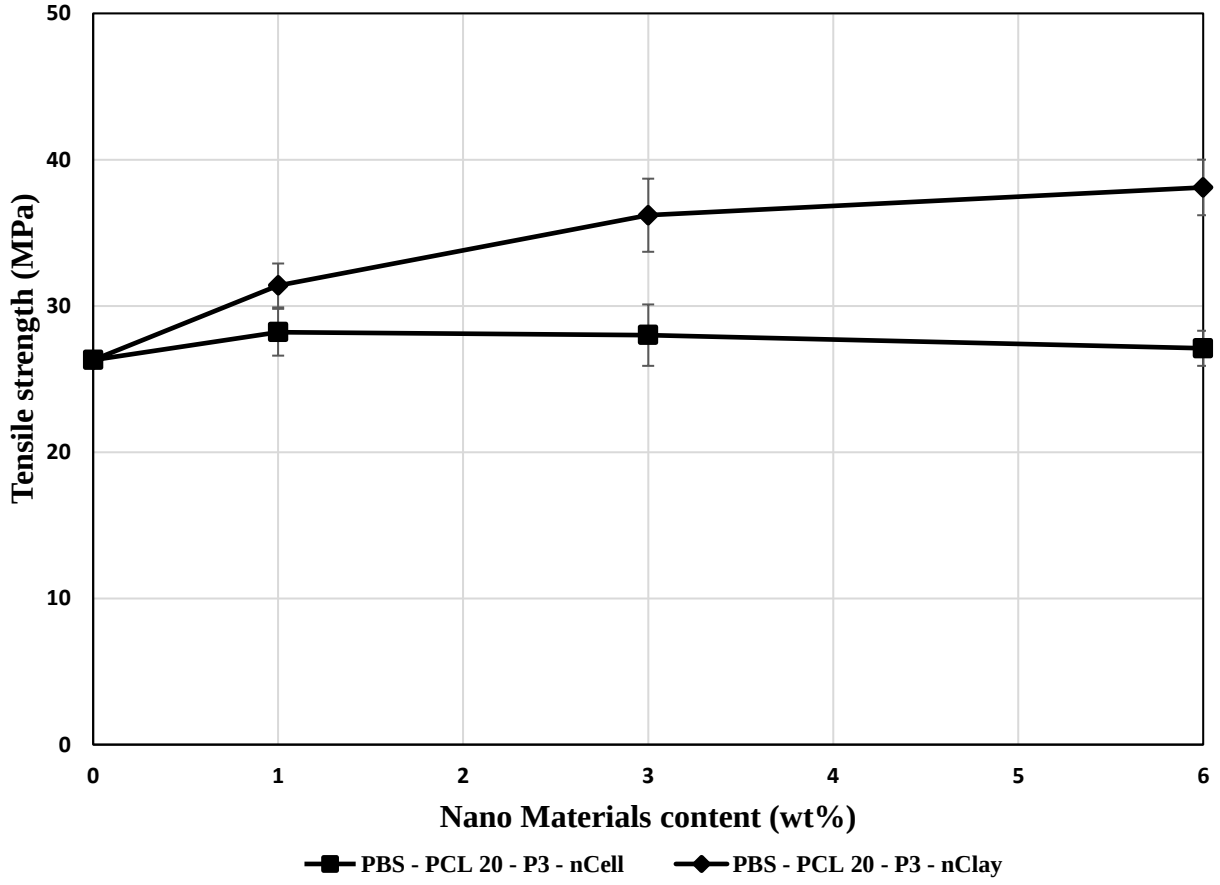


Fig 4. 14 Tensile Strength of nanocomposite films based on PBS - PCL

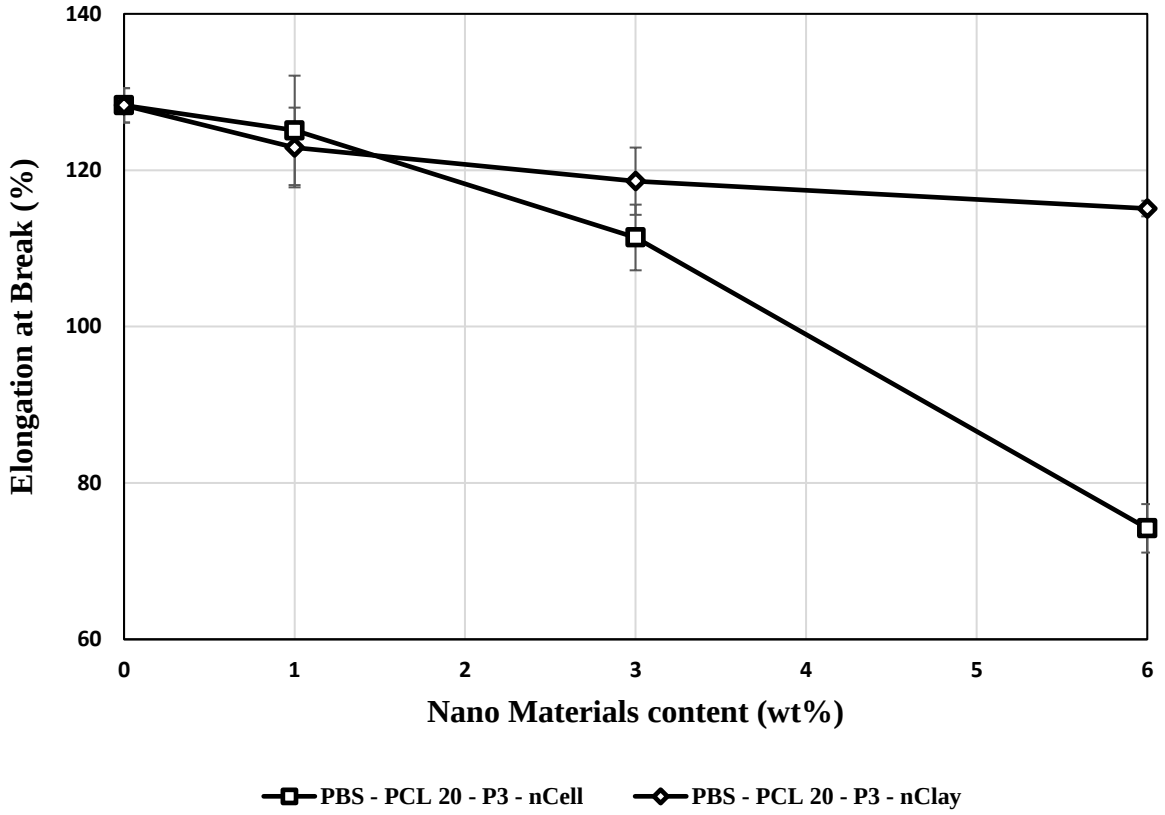


Fig 4. 15 Elongation at break of nanocomposite films based on PBS – PCL

The increasing tensile strength observed with nano clay and nano cellulose may be due to nanoparticles' reinforcing effect. The observed decrease in tensile strength with a high nanomaterials concentration may be due to non-uniform distribution, inter-particle sticking, and nanomaterials' agglomeration at high concentrations. A decrease in tensile elongation with the incorporation of nanomaterials may be due to phase separation due to the agglomeration of nanoparticles.

The SEM images of the nanocomposites of plasticized PBS-PCL20 with nano cellulose and nano clay were taken and are shown below (fig 4.16). This SEM image of the plasticized PBS-PCL20 blend before adding nanomaterials is also is shown for comparison. Changes in phase morphology with nanomaterials and changes with increasing the amount of nanomaterials can be seen, especially SEM of nanocomposite with 6 wt% nano cellulose indicates agglomeration, non-uniform structure, with more voids. These SEM images support our findings on the tensile properties of nanocomposites.

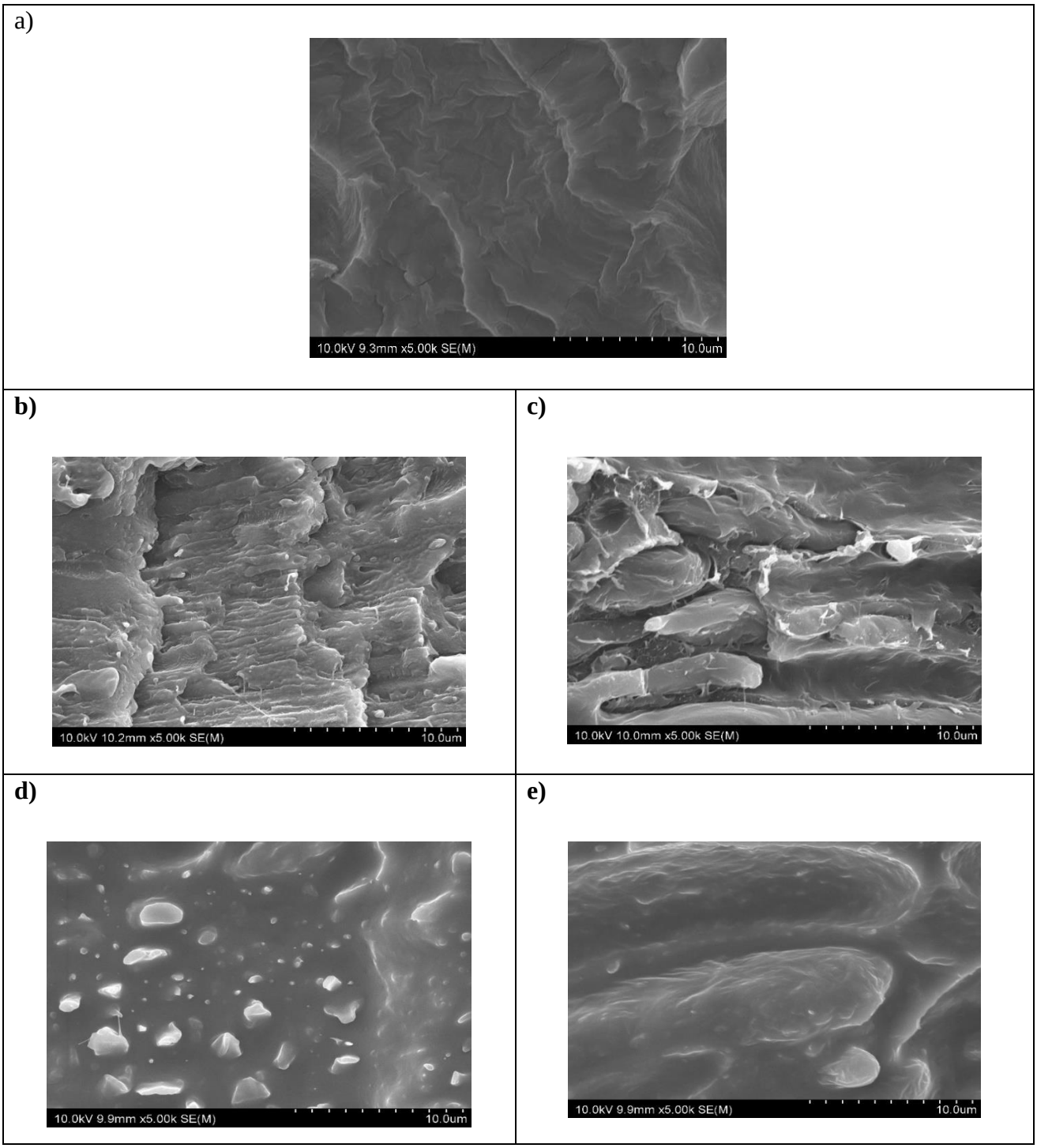


Fig 4. 16 Morphology/ SEM of Nano composite films based on PBS – PCL and plasticized PBS-PCL films without nano composite a)) PBS-PCL20- P3, b) PBS-PCL20- P3-nCell 1, c) PBS - PCL20- P3-nCell 6, d) PBS-PCL20- P3-nClay 1, e) PBS-PCL20- P3-nClay 6

4.3.3 Water vapor transmission rates (WVTR) of Nanocomposite films of PBS-PCL

WVTR tests of nanocomposite films based on PBS-PCL20-P3 blend, with various amounts of nano cellulose and nano clay (1, 3, and 6 wt%) was carried out to understand the comparative effect of nanomaterials and the effect of nanomaterial loading on water vapor barrier properties and the results obtained is presented in Table 4.12 and Fig.4.17

The results obtained indicate a considerable decrease in WVTR (improvement in water barrier property) with nano cellulose and nano clay. WVTR of the blend before the addition of nanomaterial was 338 $g.m^{-2}d^{-1}$, and with 1% loadings of the nano cellulose, it reduced to 184 $g.m^{-2}d^{-1}$, while with the same loading, WVTR of nano-clay based composite reduced only up to 196 $g.m^{-2}d^{-1}$, indicating slightly higher efficiency for nano-cellulose at lower loadings. However, in the case of nano-cellulose, after the drastic decrease in WVTR with 1% loading, the further reduction was not observed, while with nano-clay, a continuous decrease in WVTR up to 6% nano clay was observed. In the case of nano cellulose, best / least WVTR was observed at 1% nano cellulose, while with nano clay, best/ least WVTR was observed at 6% nano clay loading.

Table 4. 12 WVTR of Nano Composites films based on PBS-PCL, at 25˚C, 100% RH, ($g.m^{-2}d^{-1}$) 25µm film thickness

Film		**WVTR at 25˚C, 100% RH, for 25µm film $g.m^{-2}d^{-1}$**
PBS-PCL20- P3		338±8
Nano Cellulose	**PBS-PCL20- P3-nCell1**	184±12
	PBS-PCL20- P3-nCell3	212±9
	PBS-PCL20- P3-nCell6	288±15
Nano Clay	**PBS-PCL20- P3-nClay1**	196±11
	PBS-PCL20- P3-nClay3	168±11
	PBS-PCL20- P3-nClay6	162±10

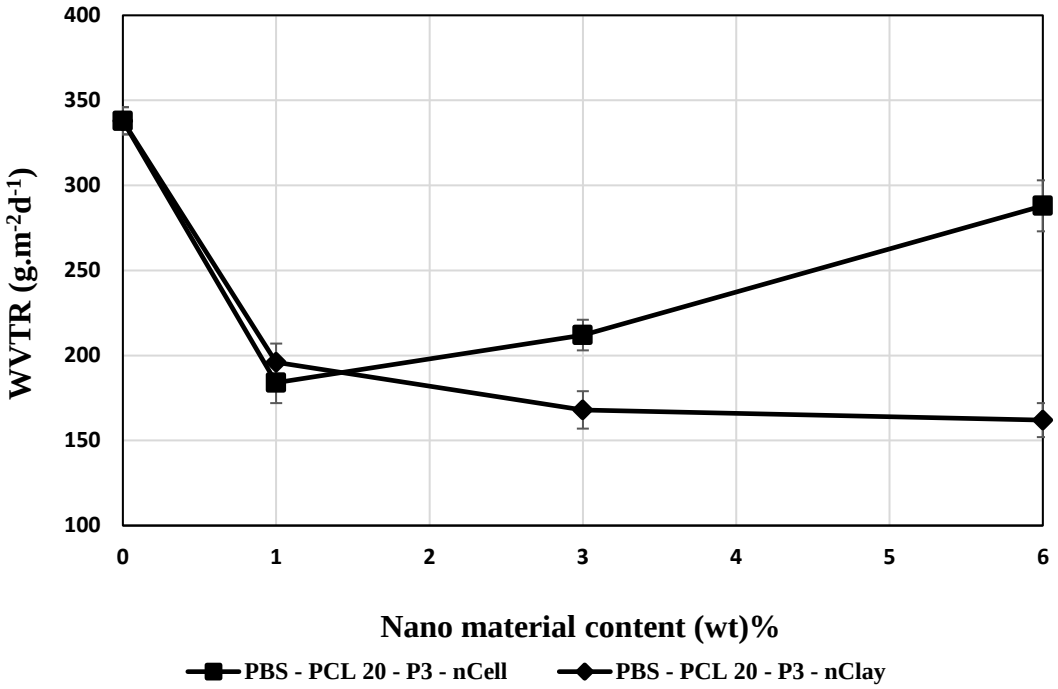


Fig 4. 17 WVTR of Nano Composites films based on PBS-PCL, at 25˚C, 100% RH, 25µm film thickness.

Improvement in barrier property/ reduction of WVTR observed with the addition of nanomaterials is expected and is ascribed to an increase in the flow path/introduction of the torturous path due to the nanomaterials in the polymer matrix. The lesser performance of nano cellulose at higher loadings can be attributed to improper dispersion/ agglomeration of nanoparticles at higher nano cellulose concentrations. The SEM images were taken for the nanocomposites with 6 wt% nano cellulose (Fig 4.16 C) also indicates a more void structure for nanocomposites with 6 wt% nano cellulose. The commercially available nano clay, which we used, is organically modified, and hence its dispersion was comparatively better, and thus it showed improved performance at higher loadings.

The above results obtained for the barrier performance of nanocomposites with nano cellulose is very significant. At low loading of 1 wt%, nano cellulose reduced the WVTR by 46%, compared to a 42% reduction in WVTR with 1 wt% nano clay, indicating higher efficiency for nano cellulose compared to nano clay at low loadings. With more optimization and maybe with better dispersion, it may be possible to get higher efficiency at higher nano cellulose loadings. The use of nano cellulose is advantageous since it is biodegradable and does not contain the organic materials

present in the organically modified nano-clay, commonly used by all researchers to improve barrier properties.

4.3.4 Biodegradation characteristics of Nanocomposites films based on PBS - PCL

Biodegradation studies of the nanocomposites with 1wt % nano cellulose and 6 wt% nano clay were carried out in compost medium at 25˚C and seawater medium at 25˚C, by measurement of CO_2 generated at various intervals, and the results are presented below:

- **Biodegradation in Compost medium, at ambient conditions**

Biodegradation test results of nanocomposite with 1wt % nano cellulose and 6 wt% nano clay in the home compost medium are presented in Table.4.13 and Fig.4.18. These results show an increase in biodegradation rate with nano cellulose and nano clay in the home compost medium. However, the increase in % biodegradation was significantly less and were lesser than that of the reference cellulose sample.

The biodegradation rate of nanocomposites with nano cellulose and nano clay was 41.3% and 39.0%, respectively, after 180 days, in compost medium at 25 ˚C, corresponding to an increase in biodegradability by 7.0% and 1.0% for polymer blend without nanomaterial. Thus, these results indicate slightly higher biodegradation for the nano cellulose-based nanocomposites compared to nano clay-based nanocomposites.

- **Biodegradation of Nanocomposite films in seawater**

The biodegradation results of PBS-based nanocomposites with 1wt % nano cellulose and 6 wt% nano clay, in seawater, at 25˚C, is presented in Table 4.14 and Fig.4.19. The results show a slight improvement in the biodegradation rate with the addition of both the nanomaterials.

The %biodegradation of plasticized film was 16.4% in seawater, and the %biodegradation was increased to 18.4% and 17.6%, for 1wt% nano cellulose and 6 wt% nano clay.

An increase in biodegradation by 12% and 7.1%, for nanocomposites based on nano cellulose and nano clay, respectively, after 180 days biodegradation, showing slightly higher biodegradation with nano cellulose-based nanocomposite compared to nano clay-based nanocomposite, as in the case of biodegradation in compost medium.

The improvement in biodegradability with nanomaterials' addition may be due to the increase in the wetting characteristics/ hydrophilicity with nano cellulose and nano clay [105]**.** Slightly lower biodegradation for the nano clay-based nanocomposites than nano cellulose-based nanocomposites may be due to the higher water vapor barrier properties (lower WVTR) nanocomposites with 6wt% nano clay.

Table 4. 13 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PBS - PCL & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25ºC.

	Cellulose Reference ($ThCO_2$:3.23g)		**PBS - PCL20 - P3 ($ThCO_2$: 4.13g)**		**PBS - PCL20 - P3 -nCell1 ($ThCO_2$: 4.12g)**		**PBS - PCL20 - P3 – nClay6 ($ThCO_2$: 3.89g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0	0	0	0
15	0.16	4.9±1.2	0.12	2.9±2.4	0.1	2.9±2.4	0.2	4.2±1.9
30	0.27	8.4±1.6	0.36	8.6±1.8	0.4	9.6±1.5	0.4	9.7±1.4
45	0.67	20.7±1.4	0.59	14.2±2.4	0.7	16.4±1.6	0.6	16.2±2.6
60	0.96	29.7±2.5	0.72	17.3±1.9	0.8	18.9±1.4	0.8	19.8±2.7
75	1.17	36.4±1.6	0.85	20.7±2.7	0.9	21.8±2.4	1.0	21.3±1.6
90	1.39	43.1±1.4	1.00	24.3±1.6	1.0	24.8±2.6	1.0	24.7±1.4
105	1.77	54.7±2.5	1.02	24.7±1.3	1.1	26.7±2.8	1.2	26.7±2.7
120	1.94	60.2±1.6	1.14	27.6±2.4	1.2	29.3±1.7	1.3	28.7±1.5
135	2.31	71.5±2.4	1.23	29.7±1.2	1.4	33.5±2.6	1.3	32.9±2.4
150	2.45	75.9±1.4	1.36	32.9±1.4	1.5	35.7±3.4	1.5	34.9±2.8
165	2.64	81.8±1.5	1.55	37.6±1.6	1.6	38.6±2.7	1.6	36.6±1.6
180	2.66	82.3±1.6	1.59	38.6±2.7	1.7	41.3±2.4	1.6	39±1.4

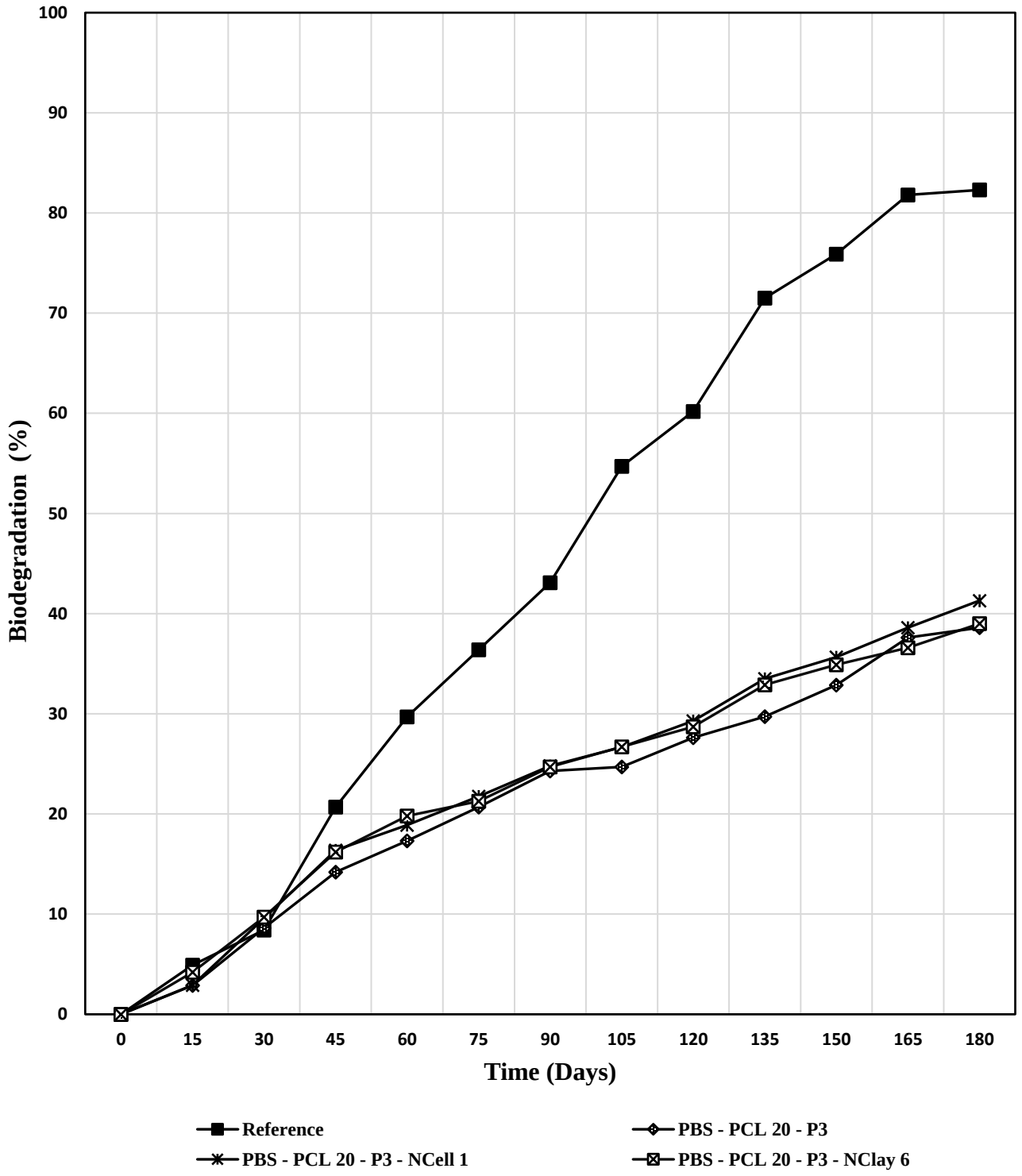


Fig 4. 18 Biodegradation curve of Nanocomposites films based on PBS - PCL, in compost at 25°C.

Table 4. 14 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PBS - PCL & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25ºC.

	Cellulose Reference ($ThCO_2$:6.45g)		**PBS - PCL20 - P3 ($ThCO_2$: 8.27g)**		**PBS - PCL20 - P3 -nCell1 ($ThCO_2$: 8.25g)**		**PBS - PCL20 - P3 – nClay6 ($ThCO_2$: 7.77g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0	0	0.00	0	0.00	0
15	0.04	0.6±1.5	0.05	0.6±1.4	0.07	0.8±1.4	0.04	0.5±1.4
30	0.14	2.1±1.4	0.15	1.8±1.8	0.17	2.1±1.6	0.10	1.3±2.5
45	0.41	6.4±2.6	0.33	4±1.5	0.44	5.3±2.5	0.24	3.1±1.6
60	0.75	11.6±2.8	0.40	4.8±2.4	0.49	5.9±2.4	0.38	4.8±2.7
75	1.02	15.8±1.7	0.52	6.3±2.6	0.62	7.5±2.1	0.48	6.2±2.8
90	1.44	22.3±2.9	0.66	8±2.8	0.71	8.6±1.5	0.54	6.9±1.6
105	1.60	24.8±2.6	0.68	8.2±1.7	0.89	10.8±1.7	0.64	8.2±1.9
120	1.90	29.4±2	0.78	9.5±1.9	0.95	11.5±2.6	0.84	10.8±2.4
135	2.11	32.7±1.4	0.86	10.5±2.4	1.02	12.4±1.6	0.86	11.1±2.8
150	2.21	34.3±2.6	1.01	12.2±2.6	1.20	14.6±2.4	0.92	11.9±2.6
165	2.48	38.5±1.7	1.14	13.8±2	1.42	17.2±1.5	1.12	14.5±2.3
180	2.59	40.2±2.9	1.25	16.4±1.4	1.52	18.4±2.8	1.37	17.6±2.4

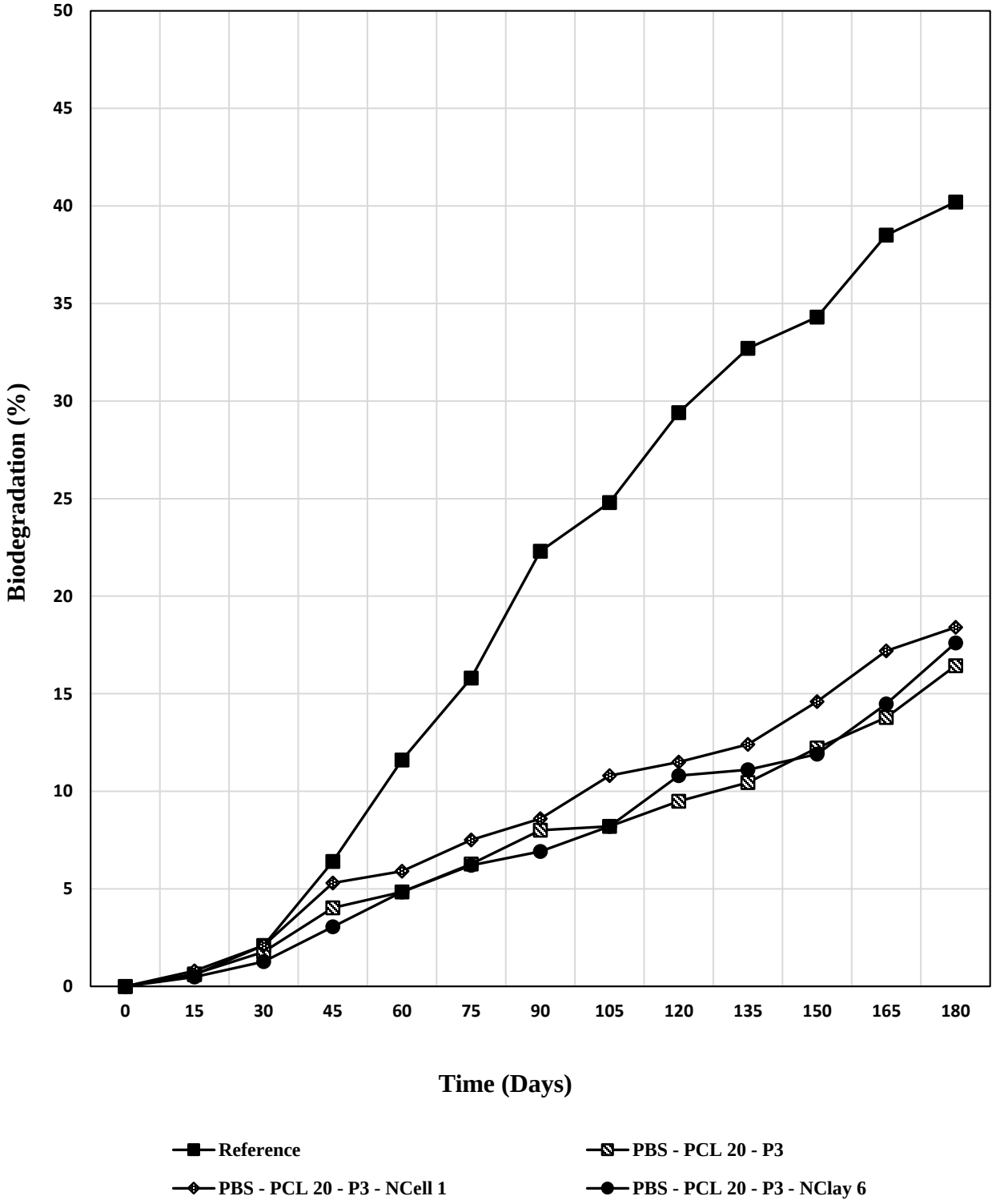


Fig 4. 19 Biodegradation curve of Nano Composites films based on PBS - PCL, in seawater, at 25°C.

4.4 Summary of investigation on PBS

The summary of investigations carried on polybutylene succinate polymer to improve its properties, such as tensile properties, water vapor barrier properties, and biodegradability characteristics, by PCL blending, plasticizing, and incorporating nanomaterials, is given below. Table 4.15 summarizes research results related to tensile properties (elongation at break and tensile strength) and water vapor barrier properties (WVTR). The PBS – PCL blends had a blending effect, not a cumulative effect. In other cases, the cumulative effect of blending and plasticization is mentioned in table 4.16. The summary of biodegradation results in home compost (composting at ambient temperature) and in seawater is presented in Table 4.16.

Table 4. 15 Summary of investigation of tensile and barrier properties on PBS Blends / Composite

Material designation	**Elongation at Break % (% change) ((cumulative))**	**Tensile strength MPa (% Change) ((cumulative))**	**WVTR 25˚C, 100 RH, $gm^{-2}d^{-1}$ (% change) ((cumulative))**
PBS – PCL Blends			
PBS	83.3	29.5	452
PBS-PCL10	98.8 (18.6)	28.4 (-3.7)	368 (-18.6)
PBS-PCL20	105.2 (26.3)	27.8 (-5.8)	324 (-28.3)
PBS-PCL30	105.1 (26.2)	18.2 (-38.3)	316 (-30.1)
PBS-PCL40	109.6 (31.6)	13.4 (-54.6)	294 (-35.0)
Plasticized PBS-PCL Blends			
PBS-PCL20-P1	131.7 (25.2) **((58.1))**	20.2 (-27.3) **((-31.5))**	374 (15.4) **((-17.3))**
PBS-PCL20- P2	110.6 (5.1) **((32.8))**	23.4 (-15.8) **((-20.7))**	345 (6.5) **((-23.7))**
PBS-PCL20- P3	128.3 (22.0) **((54.0))**	26.3 (-5.4) **((-10.8))**	338 (4.3) **((-25.2))**
Nanocomposites of PBS-PCL			
PBS-PCL20- P3 - nCell 1	125.1 (-2.5) **((50.2))**	28.2 (7.2) **((-4.4))**	184 (-45.6) **((-59.3))**
PBS-PCL20- P3 - nCell 3	111.4 (-13.2) **((33.7))**	28 (6.5) **((-5.1))**	212 (-37.3) **((-53.1))**
PBS PCL20- P3 - nCell 6	74.2 (-42.2) **((-10.9))**	27.1 (3.0) **((-8.1))**	288 (-14.8) **((-36.3))**
PBS-PCL20- P3 - nClay 1	122.9 (-4.2) **((47.6))**	31.4 (19.4) **((6.4))**	196 (-42.0) **((-56.6))**

PBS-PCL20- P3 - nCell 3	118.6 (-7.6) **((42.4))**	36.2 (37.6) **((22.7))**	168 (-50.3) **((-62.8))**
PBS-PCL20- P3 - nClay 6	115.1 (-10.3) **((38.2))**	38.1 (44.9) **((29.2))**	162 (-52.1) **((-64.2))**

( ) %change, (( )) %cumulative

Table 4. 16 Summary of investigation of Biodegradation on PBS Blends / Composite

Material designation	**Biodegradation (%) at 25˚C, for 180 days (% change) ((% cumulative))**	
	Compost	**Seawater**
PBS – PCL Blends		
PBS	26.5	10.3
PBS-PCL10	28.7 (8.3)	11.4 (11.0)
PBS-PCL20	32.3 (21.9)	13.5 (31.0)
PBS-PCL40	38.5 (45.3)	16.6 (61.6)
Plasticized PBS-PCL Blends		
PBS-PCL20-P1	40.5 (25.3) **((52.7))**	17.3 (28.8) **((68.3))**
PBS-PCL20- P2	36.8 (14) **((39.0))**	14.5 (8.0) **((41.1))**
PBS-PCL20- P3	38.6 (19.5) **((45.7))**	16.4 (22.1) **((59.6))**
Nanocomposites of PBS-PCL		
PBS-PCL20- P3 - nCell 1	41.3 (7.0) **((55.8))**	18.4 (12) **((78.6))**
PBS-PCL20- P3 - nClay 6	39.0 (1.0) **((47.5))**	17.6 (7.1) **((70.9))**

( ) %change, (( )) %cumulative

The investigation on the effect of blending PBS with PCL demonstrated enhancement of tensile elongation (ε), improvement in water vapor barrier property (decrease in WVTR), and increased in the biodegradation rate (in-home compost and seawater), by with the addition of PCL, though with a slight decrease in tensile strength (σ). It also indicated that PBS blending with 20wt % PCL offer overall balanced enhancement of polymer properties.

Plasticization studies showed a substantial increase in elongation at break and biodegradability, though with a decrease in tensile strength (σ) and water vapor barrier property (increase in WVTR). Among the three plasticizers, monomeric plasticizer P1 was found to offer the highest elongation at break and biodegradability, while the mixed plasticizer P3 was found to provide the highest tensile strength and water vapor barrier property (lowest WVTR). The plasticizer P3 was also found to have a medium elongation at break and medium biodegradability. It was concluded from the plasticization study that mixed plasticizer P3 (1:1 mixture of monomeric plasticizer and polymeric plasticizer) offers the best overall performance enhancement.

Investigation on nanocomposites of PBS demonstrated improved tensile strength, improved water vapor barrier properties (decrease in WVTR), and slightly higher biodegradation rate with the addition of both nanomaterials, though with a decrease in elongation at break. Studies also indicated that overall best performance was obtained with 1wt % nano cellulose and 6% nano clay loading for the nanocomposites.

Compared to neat PBS, the nanocomposites, with nano cellulose (PBS-PCL20- P3 - nCell 1) and nano clay (PBS-PCL20- P3 - nClay 6) was found to have a higher elongation at break, lower WVTR (higher water vapor barrier properties), and higher biodegradation in home compost and seawater medium. The nanocomposite with Nano cellulose had a slight loss in tensile strength, while the nanocomposite with nano clay had high tensile strength.

The present investigation showed that when compared to neat PBS, plasticized blends with 1 wt% nano cellulose and 6 wt% nano clay provides high tensile elongation (50% & 38% higher), high water vapor barrier properties/ lower WVTR (59% & 64% lower WVTR), and biodegradation was high in home compost (56 % & 48% higher), and seawater medium (79% & 71% higher).

the nanocomposite with Nano cellulose had a slight loss in tensile strength (4%). In contrast, the nanocomposite with nano clay had higher tensile strength (29%).

Chapter 5 Experimental Results and discussion PHB-PCL blends/composites

5.0 Introduction

An investigation was carried out to improve/ modify the properties of commercially available Polyhydroxy butyrate (PHB) polymer by preparing polymer blends with Polycaprolactone (PCL) polymer, by plasticization of the PHB-PCL blend, by preparing nanocomposites and characterizing the polymer blend/ nanocomposite films. This chapter presents the outcome of the experimental work carried out on PHB-PCL blends and nanocomposites. The composition and designation of these polymer samples are given below in Table 5.1

Table 5. 1 Composition and designation of PHB-PCL Blends/nanocomposites prepared

Designation	**PHB content (wt%)**	**PCL content (wt%)**	**Plasticizer (wt%) With respect to PHB – PCL Blends**	**Nanomaterial (wt%) With respect to PHB – PCL Blends**
PHB – PCL Blends				
PHB	100	0	0	0
PHB-PCL10	90	10	0	0
PHB-PCL20	80	20	0	0
PHB-PCL30	70	30	0	0
PHB-PCL40	60	40	0	0
Plasticized PHB-PCL Blends				
PHB-PCL20-P1	80	20	5 % Glyceryl Triacetate (GTA/Triacetin)	0
PHB-PCL20-P2	80	20	5% Ultramoll IV (UM)	0
PHB-PCL20-P3	80	20	5% (GTA – UM (50/50))	0

Nanocomposites of PHB-PCL				
PHB-PCL20-P3 -nCell 1	80	20	5% (GTA – UM (50/50))	1 % Nano cellulose
PHB-PCL20-P3 -nCell 3	80	20	5% (GTA – UM (50/50))	3% Nano Cellulose
PHB-PCL20-P3 -nCell 6	80	20	5% (GTA – UM (50/50))	6% Nano Cellulose
PHB-PCL20-P3 -nClay 1	80	20	5% (GTA – UM (50/50))	1% Nano Clay
PHB-PCL20-P3 -nClay 3	80	20	5% (GTA – UM (50/50))	3% Nano Clay
PHB-PCL20-P3 -nClay 6	80	20	5% (GTA – UM (50/50))	6% Nano Clay

5.1 **PHB-PCL Blends**

Polyhydroxy butyrate (PHB) polymer was blended with 10, 20, 30, and 40 wt% of Polycaprolactone (PCL) polymer, and PHB-PCL blend films were prepared by hot blending, injection molding followed by hot pressing at 185˚C [213], at 1MPa pressure, for 3 min. The polymer blend films were characterized, and the results are presented below:

5.1.1 Appearance/ Photographs:

The pure PHB blends are opaque, which was glassy and brittle. Even the commercially available PHB BLENDS are non-transparent. When the amount of PCL addition was increased, the films were better and without cracks, as shown in Fig 5.1.

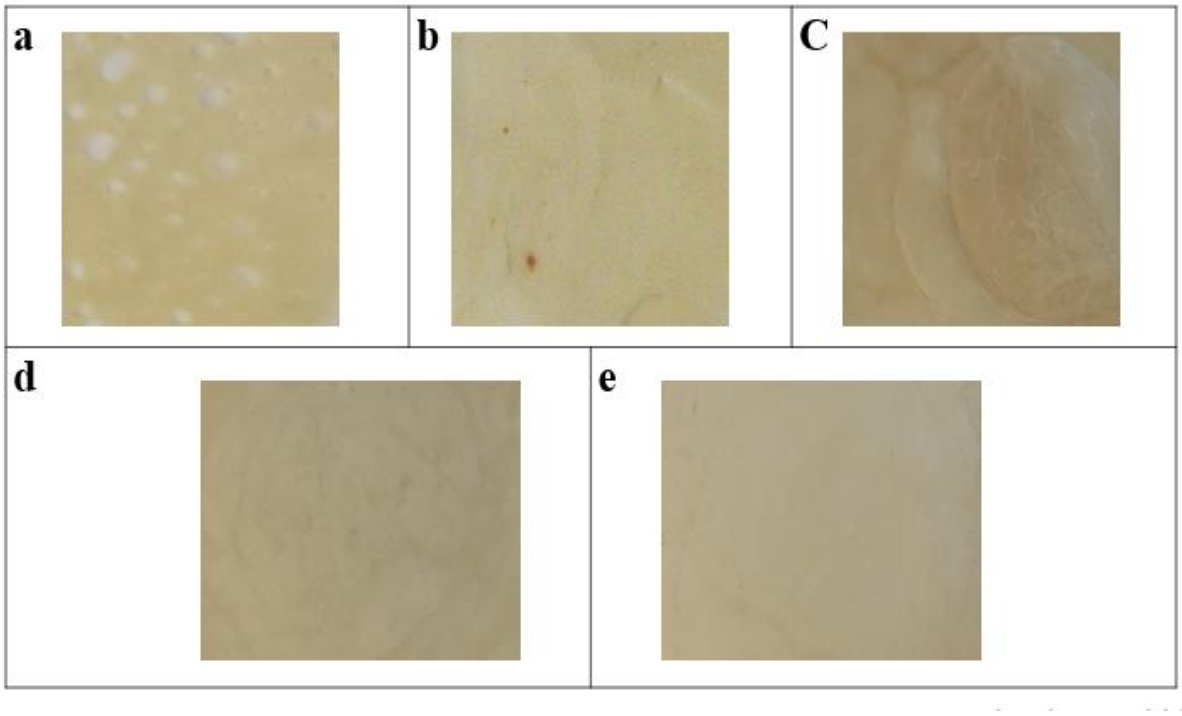


Fig 5. 1Photographs of PHB/PCL Blends a) PHB 100, b) PHB-PCL10, c) PHB-PCL20, d) PHB-PCL30, d) PHB-PCL40

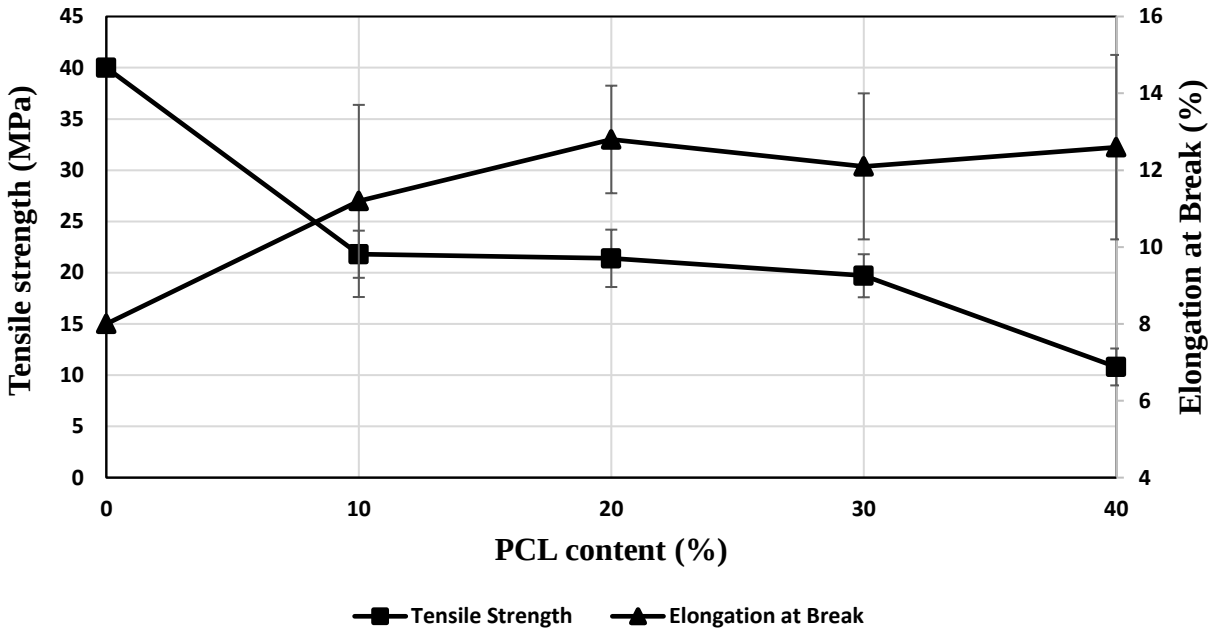
5.1.2 Mechanical- Tensile properties of PHB-PCL blend films

The effect of PCL on tensile strength and elongation at break of PHB was investigated, and the tensile test results for PHB-PCL blend films are presented in Table 5.2 and Fig.5.2 (a).tensile properties of PHB PCL blends based on the rule of mixtures was shown in fig 5.2 b & c [201]. The tensile results obtained for neat PHB were not reproducible, as the neat PHB films were too brittle for tensile testing, and hence we have taken the value reported in the literature [89] for comparison with the values obtained for the blends**.** It is challenging to make good PHB films by hot pressing, and most of the researchers have prepared PHB films by solution casting method [135, 142, 214]. However, we have not attempted to make PHB films by solution casting method since it is environmentally unfriendly, as it involves the use and evaporation of many organic solvents and is not a commercially suitable method.

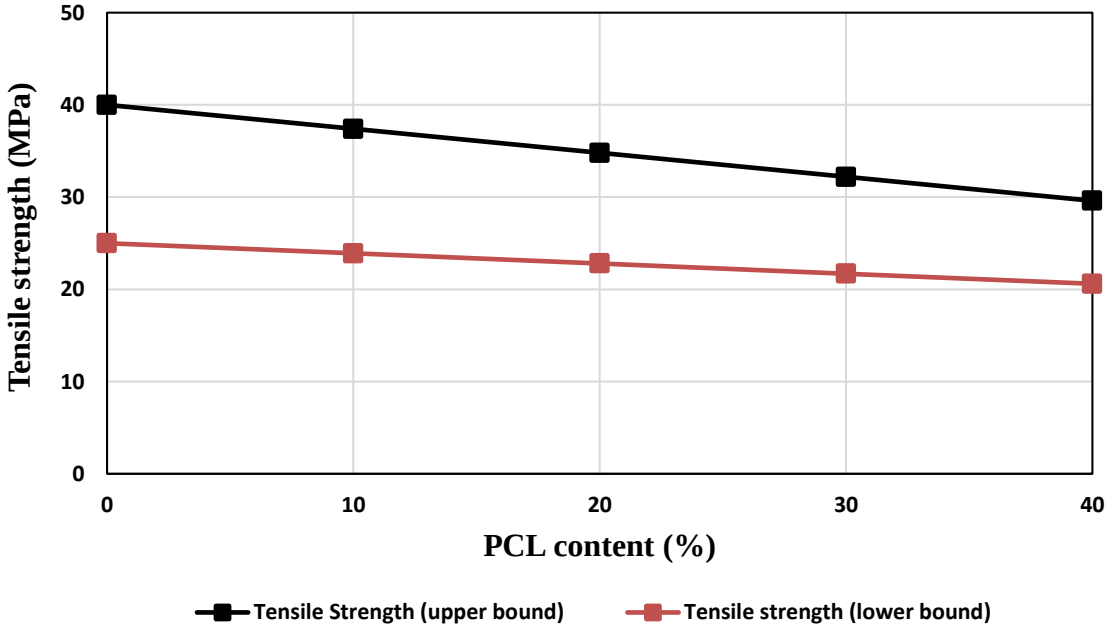
Table 5. 2 Tensile properties of PHB-PCL Blends

Film	Tensile strength (MPa)	Elongation at break (%)
PHB*	40.0	8.0
PHB-PCL10	21.8±2.3	11.2±2.5
PHB-PCL20	21.4±2.8	12.8±1.4
PHB-PCL30	19.7±2.1	12.1±1.9
PHB-PCL40	10.8±1.8	12.6±2.4

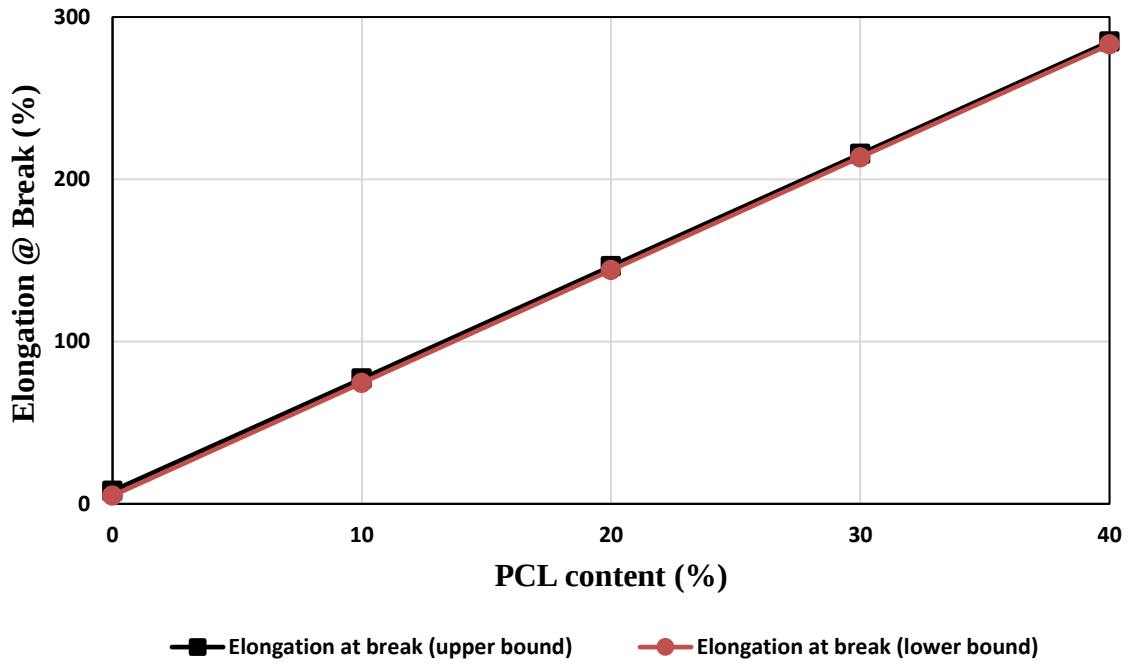
*Adapted from literature Robertson 2016 [89]


Tensile strength (MPa)
Elongation at Break (%)
PCL content (%)
Tensile Strength
Elongation at Break

(a)


Tensile strength (MPa)
PCL content (%)
Tensile Strength (upper bound)
Tensile strength (lower bound)

(b)



(c)

Fig 5. 2(a) Effect of PCL concentration on Tensile strength and Elongation at break for PHB-PCL blends,(b)&(c) Effect of PCL concentration on Tensile strength and Elongation at break for PHB-PCL blends, based on the rule of mixtures.

Results presented in Table 5.2 and Fig 5.2 (a) indicate that the elongation at break increases with PCL and reaches almost an enduring value beyond 20% PCL. The tensile elongation of PHB-PCL blends with 10, 20, 30, and 40% PCL was found to be 11.2, 12.8, 12.1, and 12.6%, respectively, corresponding to an increase in tensile elongation by 40%,60%,51.3%, and 57.5%, when compared to neat PHB.

Fig5.2 (a) indicates that the tensile strength of the PHB-PCL blend decreases with an increasing amount of PCL, significantly beyond 30% PCL. The tensile strength of PHB-PCL blends with 10, 20, 30, and 40% PCL was 21.8, 21.4, 19.7, and 10.8 MPa.

The increase in elongation break with PCL's addition may be due to the very high ductility of PCL and the plasticizing action of PCL, as reported elsewhere, for PVC polymer [203].

This decrease in tensile strength may be due to PCL's low solubility in PHB and poor adhesion between PHB and PCL. Scanning electron microscopy (SEM) images of the neat PHB and PHB-PCL blends were taken and are shown in Fig 5.3. In general, these SEM images indicate a coarse

morphology with sharp interfaces. The SEM images of PHB-PCL with 10 % and 20% indicate the presence of Spherulites of PCL dispersed in the PHB matrix, confirming low miscibility.

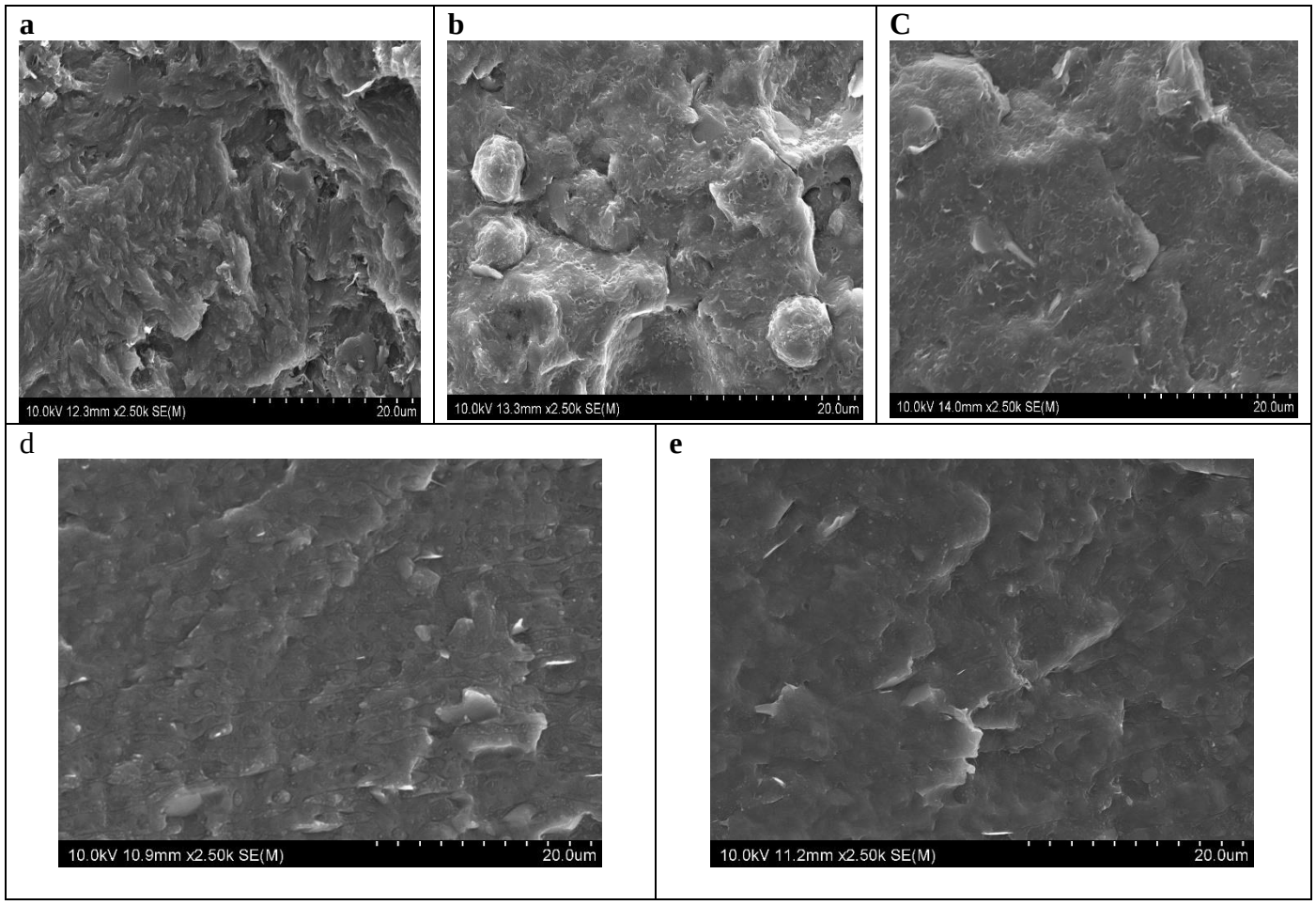


Fig 5. 3 SEM Micrographs of PHB-PCL blends a) PHB 100, b) PHB-PCL10, c) PHB-PCL20, d) PHB-PCL30 e) PHB-PCL40

5.1.3 Barrier property- Water vapor transmission rate (WVTR) of PHB-PCL Blend films

Studies on water vapor transmission rate of PHB-PCL blend films were carried out to understand the effect of blending with PCL and the results obtained, after normalization for a film thickness of 25µm, is shown in Table 5.3 and Fig 5.4

Water vapor barrier property improves/ WVTR decreases with the addition of PCL to PHB. The WVTR was found to decrease sharply from 254 g m^{-2} d^{-1} to a value of 196 g m^{-2} d^{-1} for the PHB-PCL blend with 10% PCL, and there was only a smaller change with further additions of PCL.

WVTR for the PHB-PCL blends with 20, 30, and 40% PCL were 186, 184, and 199g m^{-2} d^{-1} respectively.

The standard deviations of our WVTR values were considerable (varied from 29-52 g m^{-2} d^{-1}), and it may be perhaps due to the presence of micro-cracks in the films. The WVTR values reported in the literature for neat PHB by most researchers are comparatively lower than us' value (254 g m^{-2} d^{-1}). Robertson et al. reported WVTR of 158-217 g m^{-2} d^{-1} at 37˚C, 90% RH (which corresponds to 84.8-116 g m^{-2} d^{-1} at 25˚C, 100% RH). However, Zhang et al. has reported a higher WVTR value of 298.7 g m^{-2} d^{-1} at 25˚C and RH 75%, which corresponds to 398 g m^{-2} d^{-1} at 25˚C, 100% RH. [89, 215].

Table 5. 3 Water vapor transmission rate (WVTR) of PHB-PCL blend films

Film	**WVTR at 25˚C, 100% RH, for 25µm film g.$m^{-2}$$d^{-1}$**
PHB	254±47.2
PHB-PCL10	196±52.7
PHB-PCL20	186±39.1
PHB-PCL30	184±34.5
PHB-PCL40	199±29.7

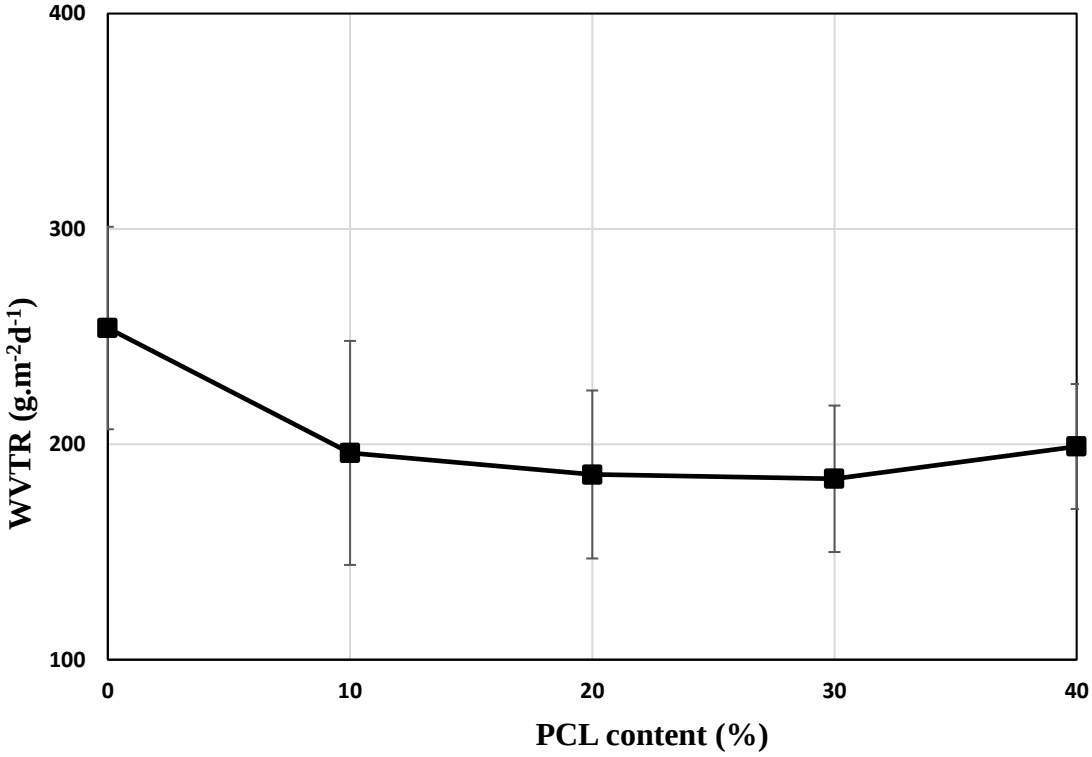


Fig 5. 4 WVTR vs sample composition curves for PHB-PCL blend films, at 25˚C, 100% RH, 25µm film thickness

5.1.4 Biodegradation characteristics of PHB-PCL Blend films

- **Biodegradation in compost medium**

Biodegradation studies of PHB-PCL blends were conducted in compost medium, at 25˚C ±5˚C, by the measurement of CO_2, for 180 days. The studies were carried out in a biometer flask containing a sample mixed with moist compost. The ratio of 1: 6 for the test sample: inoculum weight on a dry basis was maintained. Studies were carried out using cellulose as a reference, and a blank test with compost alone was also done. The cumulative CO_2 evolved from the test sample and the cellulose reference sample, after deducting the blank value, along with the % biodegradation at various time intervals is presented in Table 5.4, and the % biodegradation for the cellulose reference and test samples are graphically represented in Fig 5.5

The above results show a comparatively high biodegradation rate of 66.8% for neat PHB, comparable to 82.3% for cellulose reference, after 180 days in compost, at 25˚C. The %

biodegradation for the PHB-PCL blends, with 10, 20, and 40% PCL content was 65.4%, 71.1%, and 74.4%, respectively, indicating a slight decrease initially and then an increase in biodegradation with the addition of PCL

- **Biodegradation in marine medium**

The biodegradation studies of PBS and PBS-PCL blends were carried out in seawater medium also at 25˚C, and the results are presented in Table 5.4 and Fig 5.5. The above results show that the biodegradation rate for neat PBS in seawater was 36.1%, comparable to the value of 40.2% obtained for the cellulose reference in seawater after 180 days. The % biodegradation for the PHB-PCL blends was 35.2, 38.8, and 39.7% for the blends with 10, 20, and 40% PCL. As in biodegradation in compost, an increase in biodegradation rate was observed for the PHB-PCL blends compared to neat PHB.

A similar increase in biodegradation of PHB with PCL has been reported by few other researchers [138] and has been explained due to decreased crystallinity, phase-segregated morphology for the blends, and morphology with a larger surface area etc., for the PHB-PCL blends.

The high biodegradation rate of PHB, comparable to cellulose reference, is reported by other researchers [149, 216]. However, data on biodegradation of PHB and PHB-PCL blends in compost medium at ambient temperature/home compost conditions is not available in the literature.

Table 5. 4 Cumulative amount of CO_2 evolved and % biodegradation for PHB-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25˚C.

	Cellulose Reference ($ThCO_2$: 3.23g)		**PHB100% ($ThCO_2$:4.03g)**		**PHB-PCL10% ($ThCO_2$: 4.09g)**		**PHB-PCL20% ($ThCO_2$: 4.15g)**		**PHB-PCL40% ($ThCO_2$: 4.27g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.16	4.9±1.2	0.28	6.9±3.5	0.25	6.2±3.6	0.20	4.7±1.2	0.22	5.1±2.9
30	0.27	8.4±1.6	0.55	13.7±4.6	0.55	13.4±3.5	0.47	11.4±1.6	0.49	11.5±3.5
45	0.67	20.7±1.4	0.86	21.4±2.5	0.84	20.5±3.9	0.78	18.7±1.4	0.90	21±3.4
60	0.96	29.7±2.5	1.16	28.7±2.6	1.16	28.4±3.7	1.12	27.1±2.6	1.24	29±2.6
75	1.17	36.4±1.6	1.43	35.4±2.7	1.49	36.4±2.5	1.44	34.7±2.9	1.58	37±2.9
90	1.39	43.1±1.4	1.70	42.1±2.3	1.84	45.1±2.6	1.58	38.1±3.8	1.92	45±3.8
105	1.77	54.7±2.5	2.02	50.1±2.5	2.13	52.1±2.9	1.88	45.2±3.4	2.18	51±3.4
120	1.94	60.2±1.6	2.27	56.4±2.4	2.33	57±3.5	2.08	50.1±3.9	2.57	60.1±4.1
135	2.31	71.5±2.4	2.43	60.4±3.2	2.41	59±3.6	2.30	55.4±2.3	2.67	62.5±4.6
150	2.45	75.9±1.4	2.56	63.4±3.6	2.48	60.6±3.4	2.58	62.2±2.5	2.72	63.7±2.5
165	2.64	81.8±1.5	2.65	65.7±3.9	2.58	63.1±2.5	2.77	66.7±2.4	2.90	67.8±3.5
180	2.66	82.3±1.6	2.69	66.8±2.6	2.67	65.4±2.6	2.95	71.1±3.2	3.18	74.4±3.4

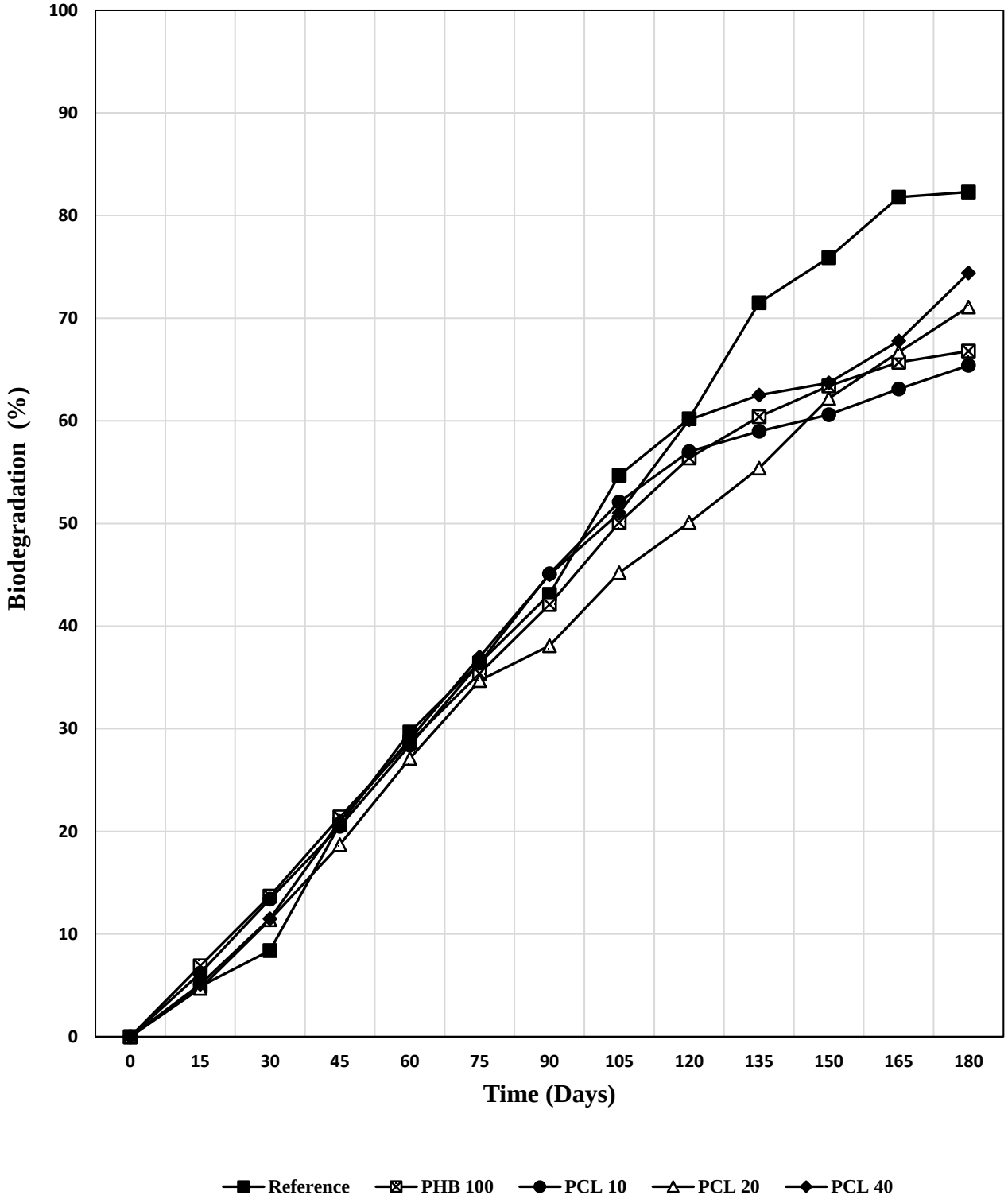


Fig 5. 5 Biodegradation curve of PHB-PCL blends in compost at 25˚C

Table 5. 5 Cumulative amount of CO_2 evolved and % biodegradation for PHB-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25˚C.

	Cellulose Reference (ThCO_2: 6.45g)		**PHB100% (ThCO_2:8.07g)**		**PHB-PCL10% (ThCO_2:8.18 g)**		**PHB-PCL20% (ThCO_2:8.30 g)**		**PHB-PCL40% (ThCO_2:8.54 g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.04	0.6±1.5	0.11	1.4±2.3	0.07	0.8±1.6	0.13	1.6±2.5	0.16	1.9±2.6
30	0.14	2.1±1.4	0.19	2.4±2.6	0.13	1.6±3.5	0.31	3.7±3.6	0.36	4.2±3.5
45	0.41	6.4±2.6	0.28	3.5±2.4	0.23	2.8±3.9	0.57	6.9±2.4	0.61	7.2±2.7
60	0.75	11.6±2.8	0.87	10.8±2.8	0.48	5.9±3.4	0.94	11.3±2.6	1.14	13.4±2.8
75	1.02	15.8±1.7	0.90	11.2±3.6	0.73	8.9±2.5	1.28	15.4±3.5	1.83	21.4±3.6
90	1.44	22.3±2.9	1.27	15.7±3.4	0.90	11±2.8	1.80	21.7±3.1	1.85	21.7±2.4
105	1.60	24.8±2.6	1.78	22.1±3.8	1.63	19.9±2.6	2.01	24.2±2.6	1.97	23.1±3.6
120	1.90	29.4±2	2.21	27.4±2.4	1.82	22.3±2.4	2.16	26±3.5	2.51	29.4±2.5
135	2.11	32.7±1.4	2.13	26.4±2.4	1.99	24.3±2.5	2.65	31.9±3.8	2.68	31.4±3.9
150	2.21	34.3±2.6	2.58	32±3.6	2.57	31.4±2.9	2.78	33.4±1.4	3.13	36.7±4.8
165	2.48	38.5±1.7	2.90	35.9±3.8	2.76	33.7±1.5	3.05	36.7±1.9	3.21	37.5±1.4
180	2.59	40.2±2.9	2.91	36.1±2.4	2.88	35.2±2.5	3.22	38.8±1.4	3.39	39.7±2.5

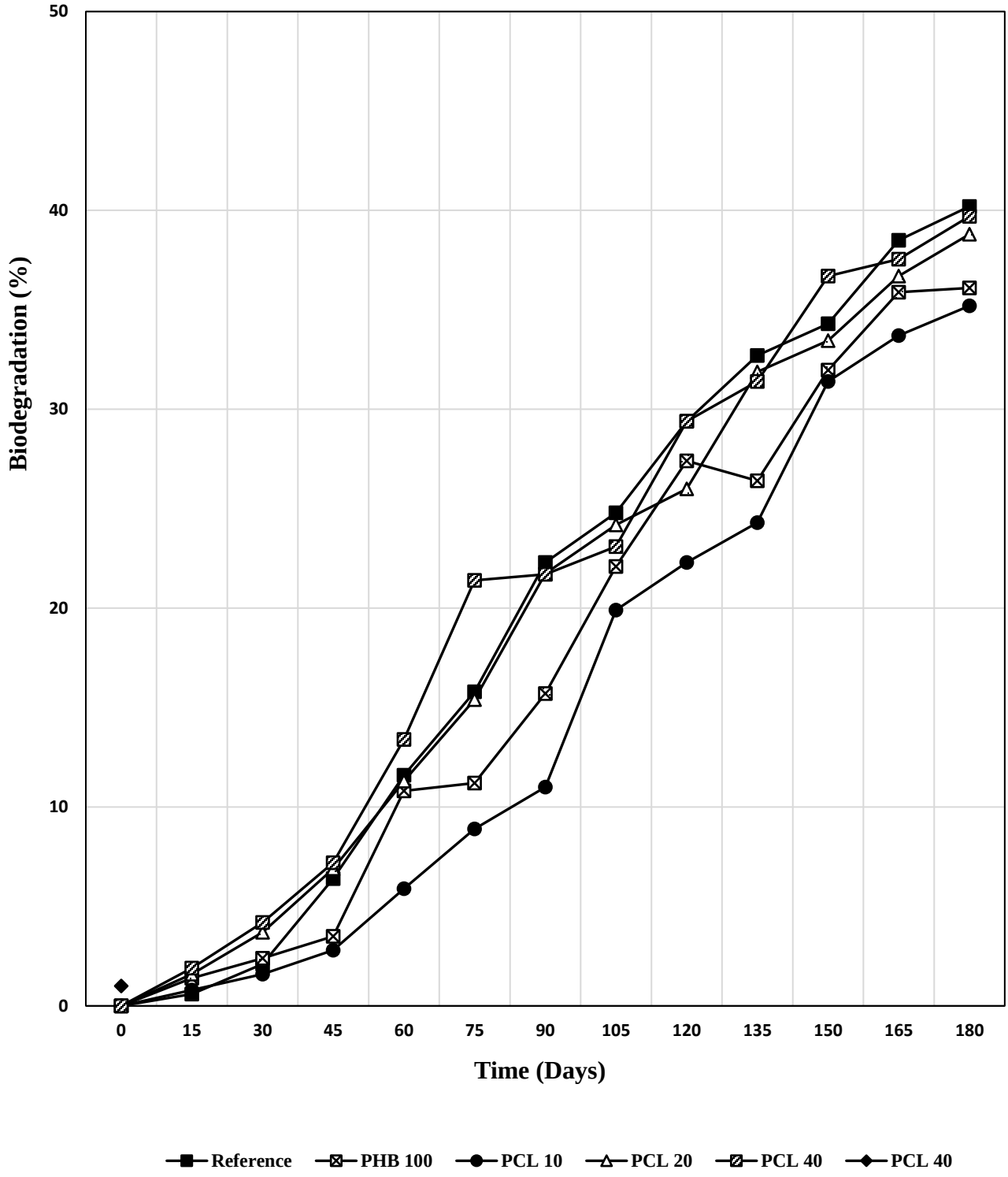


Fig 5. 6 Biodegradation curve of PHB-PCL blends in seawater at 25^0C

5.2 Plasticized PHB-PCL blend films

Studies on the effect of plasticizers on PHB-PCL blends were carried out using a blend with 20% PCL, namely PHB-PCL20, (as this blend was found to give comparatively balanced tensile and WVTR properties) to improve the ductile properties of films further. Plasticization studies were carried out using 5 wt% (concerning the blend) of three biodegradable plasticizers, namely i) a monomeric plasticizer (P1), Glyceryl Triacetate (GTA), ii) a polymeric plasticizer (P2), Ultramoll IV (UM), an adipic acid polyester, and iii) a mixture of the above two plasticizers, 1:1 ratio by weight (P3). Plasticized blend films of PHB-PCL20, with plasticizers P1, P2, and P3, of thickness 0.25mm, were prepared by injection molding followed by hot pressing and were characterized by standard methods and the results are presented below:

5.2.1 Appearance/ Photographs of Plasticized PHB-PCL Blends

The photographs of the plasticized PHB-PCL20 films with plasticizers P1, P2, and P3 is given below (fig. 5.7). These indicate more uniform films after plasticization, compared to films before plasticization.

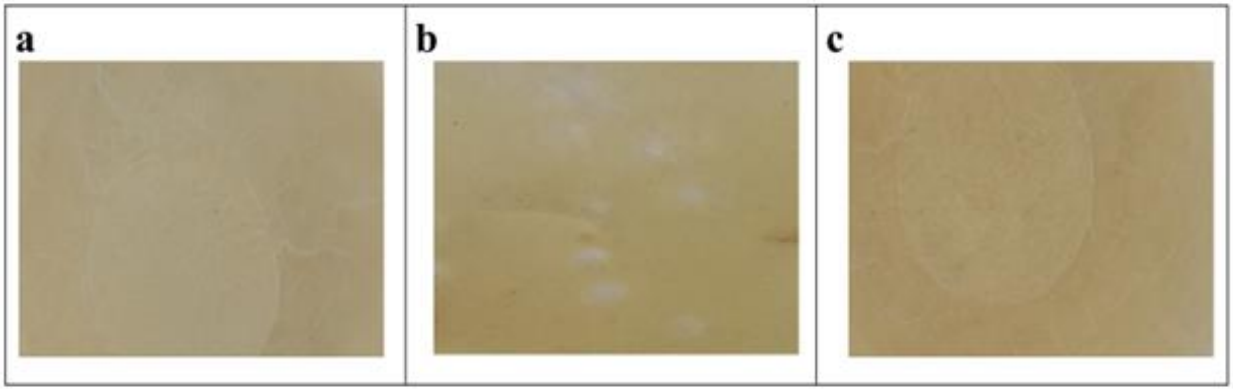


Fig 5. 7 Photographs of Plasticized PHB-PCL Blends a) PHB-PCL20-P1, b) PHB-PCL20-P2, c) PHB-PCL20-P3

5.2.2 Mechanical- Tensile properties of Plasticized PHB-PCL Blends

Studies on tensile properties of plasticized PHB-PCL Blend films were carried out as per ASTM test method ASTM D882 method [200], .and the results obtained are shown in Table 5.6 and Fig 5.8.

The above results show an increase in elongation at break, with all three plasticizers. Monomeric (P1) and mixed plasticizer (P3) were found to have more effective compared to a polymeric plasticizer (P2). The tensile elongation increased to 23.8, 16.3, and 22.6% with plasticizers P1, P2, and P3, from an initial value of 12.8%, which corresponds to an increase of 85.9%. 27.3% and 76.6% respectively for P1, P2, and P3 plasticizers.

The results obtained on tensile strength indicate a decrease in tensile strength with all the three plasticizers. The plasticized blends' tensile strength was 14.2 MPa, 13.4 MPa, and 19.6 MPa for the blends plasticized with plasticizer P1, P2, and P3. The highest tensile strength was observed with mixed plasticizer P3, and the least tensile strength was observed with polymeric plasticizer P2, though the tensile strength of plasticized blends was lesser than that of an un-plasticized blend.

Table 5. 6 Tensile properties of Plasticized PHB-PCL Blends

Film	Tensile strength (MPa)	Elongation at break (%)
PHB-PCL20	21.3±2.8	12.8±1.4
PHB-PCL20-P1	14.2±2.1	23.8±3.2
PHB-PCL20-P2	13.4±1.8	16.3±2.4
PHB-PCL20-P3	19.6±2.5	22.6±2.7

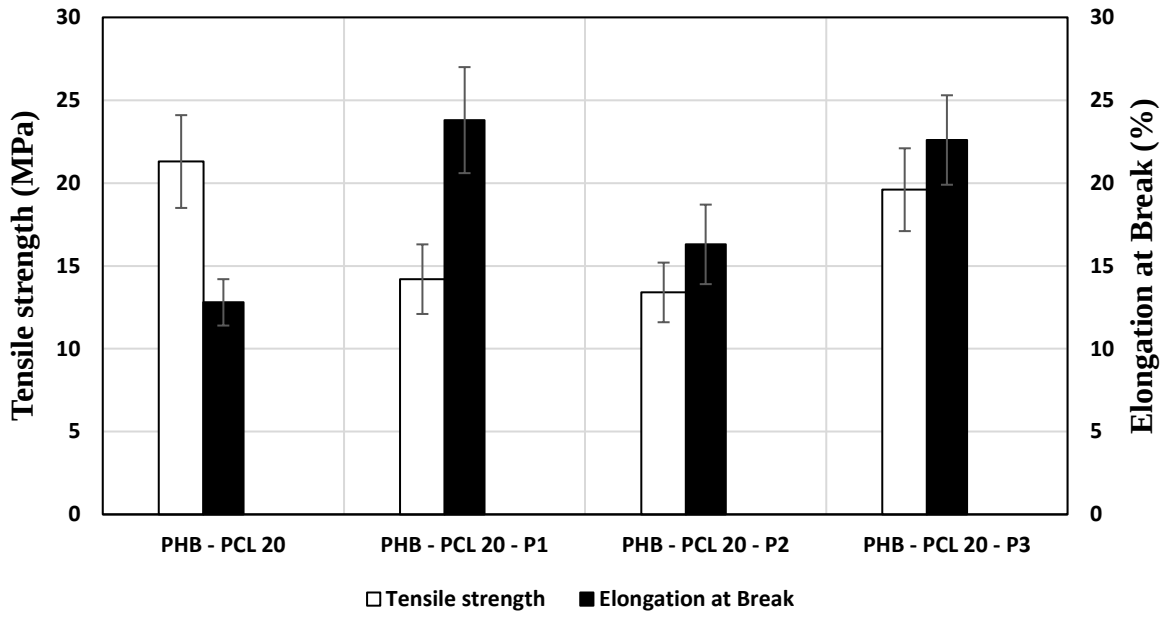


Fig 5. 8 Tensile Strength and Elongation at break of Plasticized PHB-PCL Blends

The improvement in tensile elongation with the plasticizers is attributed to increased polymer chain mobility. The maximum increase in tensile elongation with monomeric plasticizer P1 may be due to its easier penetration into the PHB matrix because of its smaller molecular size. The least increase was observed with polymeric plasticizer, maybe because of its larger molecular size, though it is also expected to produce a good increase in tensile elongation because its solubility parameter is close to that of PHB. [127, 128].

The decrease in tensile strength of plasticized blend compared to neat PHB-PCL blend may be due to the increase in free volume with plasticizer addition and the reduction in intermolecular forces between polymer chains with plasticizers' addition.

SEM images of the plasticized PHB-PCL blends with plasticizers P1, P2, and P3 were given below in Fig. 5.9 b, c, and d. For comparison, an SEM image of an un-plasticized blend is also shown (Fig 5.9a). The SEM image Fig 5.9c of the plasticized blend with polymeric plasticizer P2 indicates very rough, disconnected phases, which supports our observation of least tensile elongation and tensile strength with a polymeric plasticizer.

SEM image for a plasticized blend with monomeric plasticizer P1 and mixed plasticizer P3, shown in Fig 5.9 b and d, indicates a more uniform morphology than that for polymeric plasticizer. These blends were exhibiting higher ductility/ elongation at break compared to that with polymeric plasticizer P2. In the blend with mixed plasticizer P3, a monomeric plasticizer may help the polymeric plasticizer reach deep into the PHB matrix and maybe help achieve better miscibility of the PHB and PCL phases, leading to better performance compared to that with polymeric plasticizer alone.

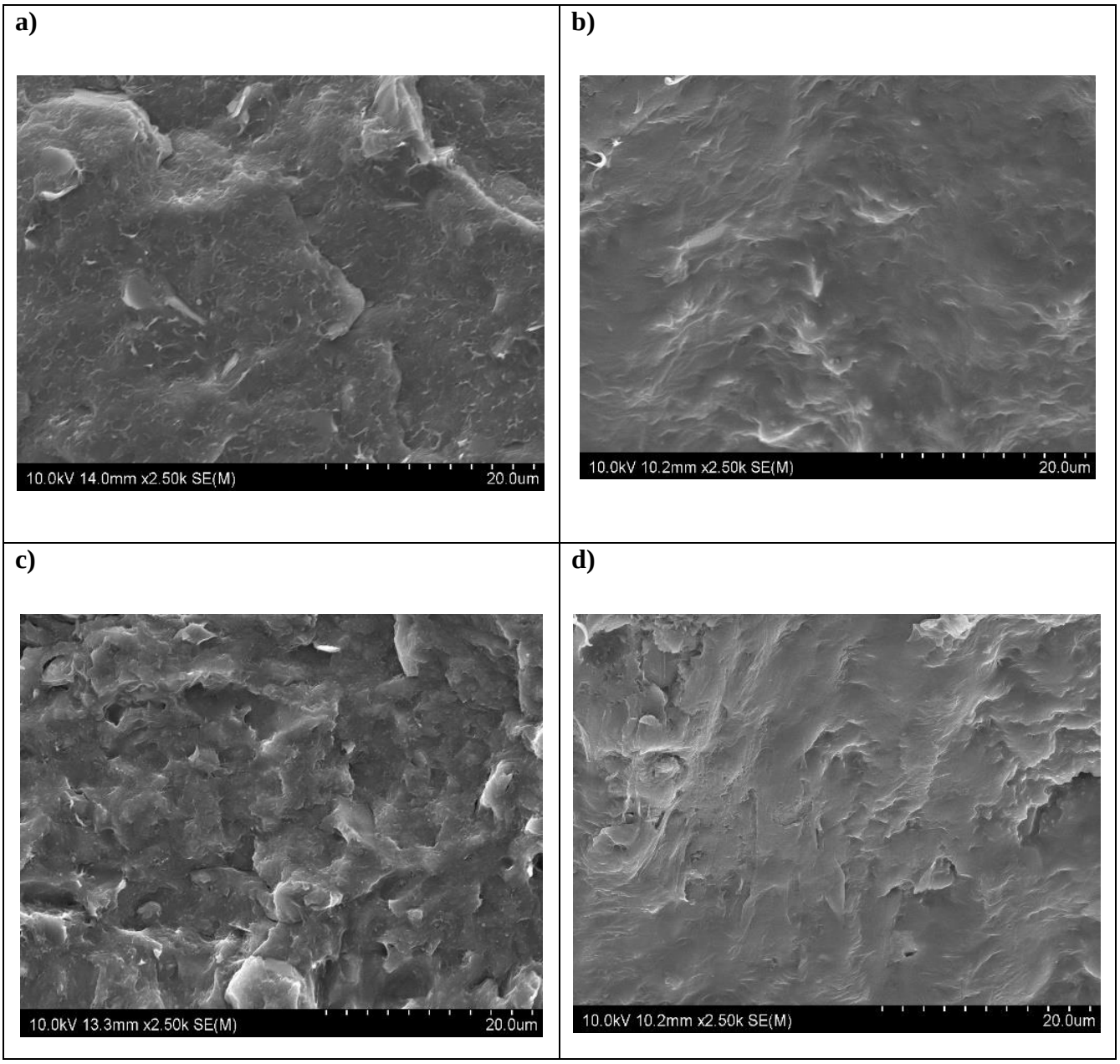


Fig 5. 9 SEM of Plasticized PHB-PCL Blends and un-plasticized PHB-PCL blend a) PHB-PCL20, b) PHB-PCL20-P1, c) PHB-PCL20-P2, d) PHB-PCL20-P3

5.2.3 Water vapor transmission rates (WVTR) of Plasticized PHB-PCL Blend films

The water vapor transmission studies of plasticized PHB-PCL20 films, with plasticizers P1, P2 and P3 were carried out at 25˚C, 100% RH conditions, and the results were obtained after normalizing for 25µm film thickness, is presented in Table 5.7 and Fig 5.10

The WVTR of all the plasticized blends was higher than that of the un-plasticized blend, indicating a decrease in barrier property. Results show that the plasticized blends' WVTR values increased from 186 g m^{-2} d^{-1} (corresponding to unplasticized film) to a 200, 227, and 195 g m^{-2} d^{-1} result of plasticization with plasticizer P1, P2, and P3, respectively. The highest increase in WVTR was observed with polymeric plasticizer P2, and the lease increase/ highest barrier property was observed with mixed plasticizer P3.

The increase in water vapor permeability with the addition of plasticizers may be due to increased hydrophilicity, higher free volume in the polymer matrix [80] with plasticizers, and hence higher solubility of water vapor in the polymer matrix. The introduction of polymeric plasticizer P2 might have created more pores, more free volume, and evidenced from the SEM image 5.9c, leading to higher water vapor permeability.

Table 5. 7 WVTR of Plasticized PHB-PCL blend films, at 25˚C, 100% RH, for 25µm film thickness

Film	**WVTR at 25˚C, 100% RH, for 25µm film g.$m^{-2}$$d^{-1}$**
PHB-PCL20	186±39
PHB-PCL20-P1	200±30
PHB-PCL20-P2	227±44
PHB-PCL20-P3	195±34

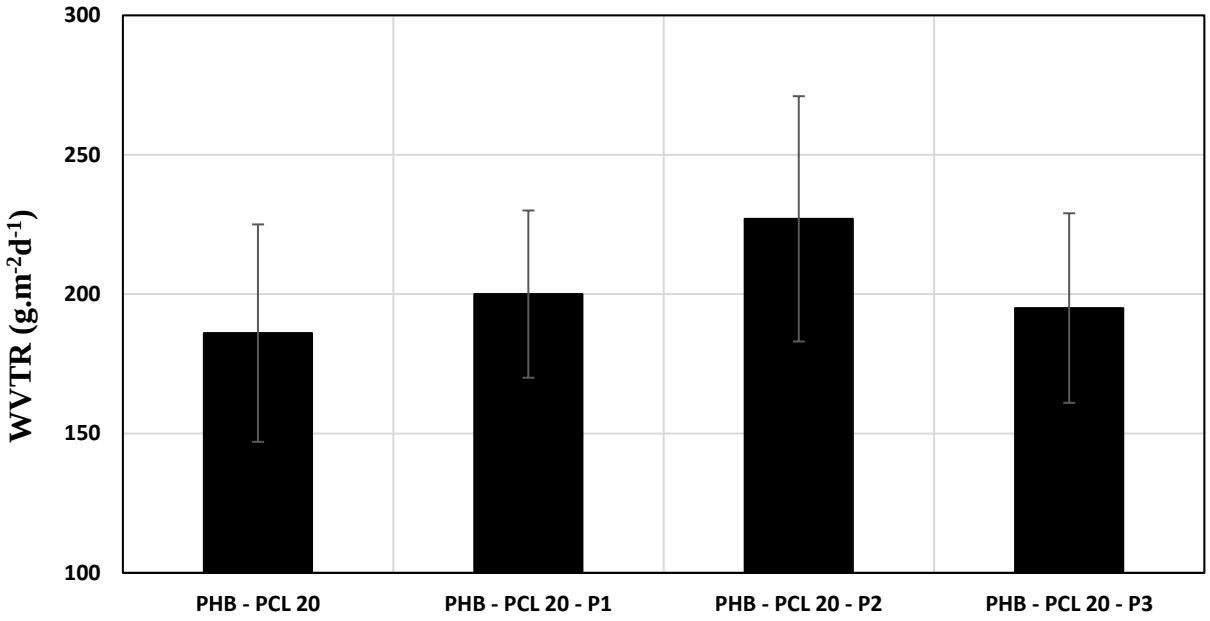


Fig 5. 10 WVTR of Plasticized PHB-PCL blend films, at 25˚C, 100% RH, for 25µm film thickness

5.2.4 Biodegradation characteristics of Plasticized PHB-PCL Blend films

Biodegradation studies of plasticized PHB-PCL20 blends, namely PHB-PCL20-P1, PHB-PCL20-P2, and PHB-PCL20-P3, with plasticizers P1, P2, and P3 were carried out in home compost medium, and in seawater medium, for a period up to 180 days, by carbon dioxide evolution method.

- **Biodegradation in Compost medium, at ambient conditions**

Biodegradation results of plasticized PHB-PCL blends in compost medium, at 25˚C, for 180 days, is presented in Table 5.8 and Fig 5.11

The %biodegradation for the plasticized blend with plasticizer P1, P2, and P3 was 74.7%, 70.1%, and 73.7%, respectively, compared to 71.1% biodegradation for the un-plasticized blend, which corresponds to an increase of 5.1%, -1.4%, and 3.6% respectively.

The biodegradation rate of un-plasticized PHB-PCL blend itself is high, in compost medium, near to that of cellulose reference (82.3% biodegradation), and hence the addition of plasticizer has increased the in-biodegradation rate only to a limited extent.

- **Biodegradation in seawater medium**

The results obtained for the biodegradation of plasticized PHB-PCL blends in seawater medium, at 25°C, for 180 days, is provided in Table 5.9 and Fig 5.12

The biodegradation rate of plasticized PHB-PCL blends was 42.2%, 38.3%, and 39.5%, respectively for the plasticized blends with P1, P2, and P3, compared to 38.8% biodegradation without plasticizer, which corresponds to a change in biodegradability by 8.8 %, -1.3% and 1.8% for P1, P2, and P3.

The biodegradation rate of plasticized PHB-PCL blends with plasticizer P1 (42.2%) was higher than even the cellulose reference, with a % biodegradation of 40.2%, after 180 days, in seawater. A very high biodegradation rate for PHB, comparable to or even higher than that of cellulose reference, is reported in the literature [149].

The increase in biodegradation rate with plasticizers' addition may be due to the increased wettability of plasticizers, which aids microbes and enzymes to penetrate the polymer matrix for biodegradation. It is reported in the literature that plasticizers may act as accelerators for enzymatic degradation of polymer chains [77]

Table 5. 8 Cumulative amount of CO_2 evolved and % biodegradation for Plasticized PHB-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25˚C.

	Cellulose Reference ($ThCO_2$:3.23g)		**PHB-PCL20 ($ThCO_2$:4.15g)**		**PHB-PCL20- P1 ($ThCO_2$:4.12g)**		**PHB-PCL- P2 ($ThCO_2$:4.13g)**		**PHB-PCL- P3 ($ThCO_2$:4.13g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.16	4.9±1.2	0.20	4.7±3.5	0.17	4.2±2.5	0.26	6.2±2.4	0.18	4.3±1.5
30	0.27	8.4±1.6	0.47	11.4±2.6	0.44	10.6±2.3	0.43	10.4±3.6	0.40	9.8±2.6
45	0.67	20.7±1.4	0.78	18.7±3.4	0.78	18.9±3.6	0.79	19.1±2.8	0.69	16.7±3.5
60	0.96	29.7±2.5	1.12	27.1±2.6	1.09	26.4±3.5	1.12	27.1±3.9	0.98	23.7±3.4
75	1.17	36.4±1.6	1.44	34.7±2.4	1.35	32.7±2.5	1.36	32.9±2.4	1.26	30.4±2.6
90	1.39	43.1±1.4	1.58	38.1±3.7	1.69	40.9±2.4	1.59	38.6±3.6	1.56	37.8±2.9
105	1.77	54.7±2.5	1.88	45.2±2.5	2.01	48.7±2.6	1.90	45.9±3.5	1.91	46.2±3.5
120	1.94	60.2±1.6	2.08	50.1±3.5	2.18	53±3.4	2.26	54.7±1.2	2.15	52±2.4
135	2.31	71.5±2.4	2.30	55.4±2.6	2.54	61.7±2.8	2.58	62.4±2.4	2.39	57.8±2.8
150	2.45	75.9±1.4	2.58	62.2±3.9	2.90	70.5±3.8	2.59	62.7±3.5	2.72	65.9±3.5
165	2.64	81.8±1.5	2.77	66.7±3.4	3.00	72.7±2.6	2.85	68.9±3.8	2.95	71.4±3.6
180	2.66	82.3±1.6	2.95	71.1±3.7	3.08	74.7±2.6	2.90	70.1±2.9	3.04	73.7±2.6

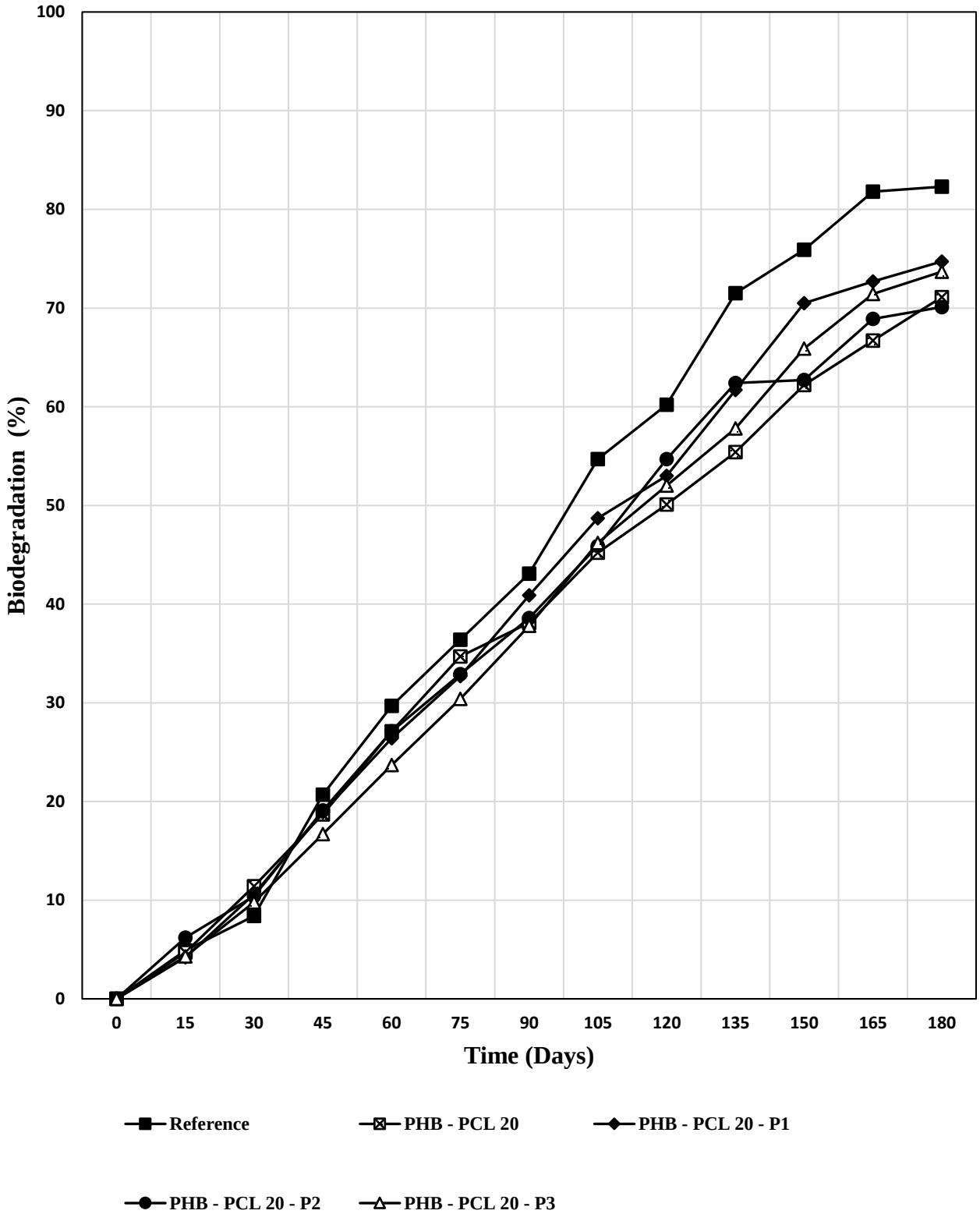


Fig 5. 11 Biodegradation curve of Plasticized PHB-PCL blends, in compost at 25°C

Table 5. 9 Cumulative amount of CO_2 evolved and % biodegradation for Plasticized PHB-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25˚C.

	Cellulose Reference ($ThCO_2$:6.45g)		**PHB-PCL20 ($ThCO_2$:8.30g)**		**PHB-PCL20- P1 ($ThCO_2$:8.25g)**		**PHB-PCL- P2 ($ThCO_2$:8.27g)**		**PHB-PCL- P3 ($ThCO_2$:8.27g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.04	0.6±1.5	0.13	1.6±2.5	0.12	1.5±2.6	0.07	0.8±3.5	0.04	0.5±3.5
30	0.14	2.1±1.4	0.31	3.7±3.6	0.26	3.2±3.5	0.14	1.7±2.9	0.09	1.1±2.6
45	0.41	6.4±2.6	0.57	6.9±2.4	0.69	8.4±3.4	0.53	6.4±2.7	0.38	4.6±2.9
60	0.75	11.6±2.8	0.94	11.3±2.6	1.21	14.7±2.5	0.95	11.4±3.6	0.83	10±3.4
75	1.02	15.8±1.7	1.28	15.4±3.5	1.54	18.7±3.6	1.41	17±3.5	1.22	14.7±2.8
90	1.44	22.3±2.9	1.80	21.7±3.1	1.96	23.7±3.8	1.57	19±2.4	1.36	16.5±3.7
105	1.60	24.8±2.6	2.01	24.2±2.6	2.04	24.7±2.4	1.91	23.1±2.9	1.81	21.9±2.6
120	1.90	29.4±2	2.16	26±3.5	2.34	28.4±3.9	2.08	25.2±3.5	2.04	24.6±3.4
135	2.11	32.7±1.4	2.65	31.9±3.8	2.45	29.7±2.7	2.37	28.7±2.6	2.34	28.3±2.7
150	2.21	34.3±2.6	2.78	33.4±1.4	3.00	36.4±3.6	2.81	34±3.4	2.65	32.1±2.9
165	2.48	38.5±1.7	3.05	36.7±1.9	3.26	39.5±2.4	3.15	38.1±2.8	3.18	38.4±3.5
180	2.59	40.2±2.9	3.22	38.8±1.4	3.48	42.2±3.8	3.17	38.3±2.7	3.27	39.5±2.6

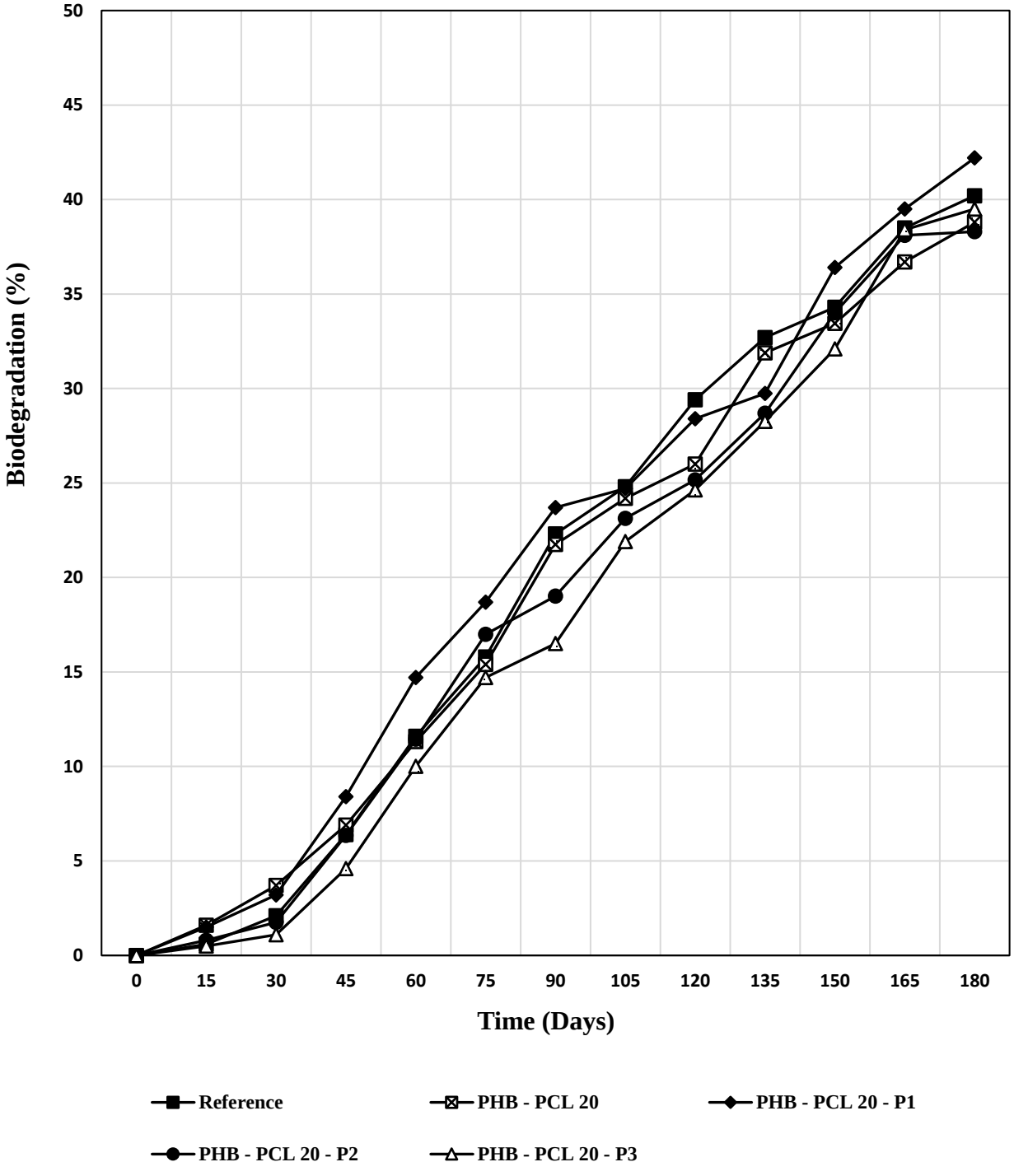


Fig 5. 12 Biodegradation curve of Plasticized PHB-PCL blends in seawater at 25^0C.

5.3 Nanocomposite films based on PHB-PCL blend

Nanocomposites of plasticized PHB-PCL20 blend films were prepared using nano cellulose (nCell) and nano clay (nClay), with different loadings of 1, 3, and 6 wt% with respect to the PHB-PCL20 blend, by injection molding followed by hot pressing and characterized for mechanical, water vapor permeation and biodegradability and the results obtained are presented below:

5.3.1 Appearance/ Photographs of Nanocomposite films based on PHB – PCL

The photographs of nanocomposites of the PHB-PCL20-P3 polymer blend, incorporated with 1, 3, and 6 wt% Nano cellulose and nano clay are given below. All the nanocomposite films based on nano clay were uniform, while the films with 1% nano cellulose alone, was found to be uniform in appearance.

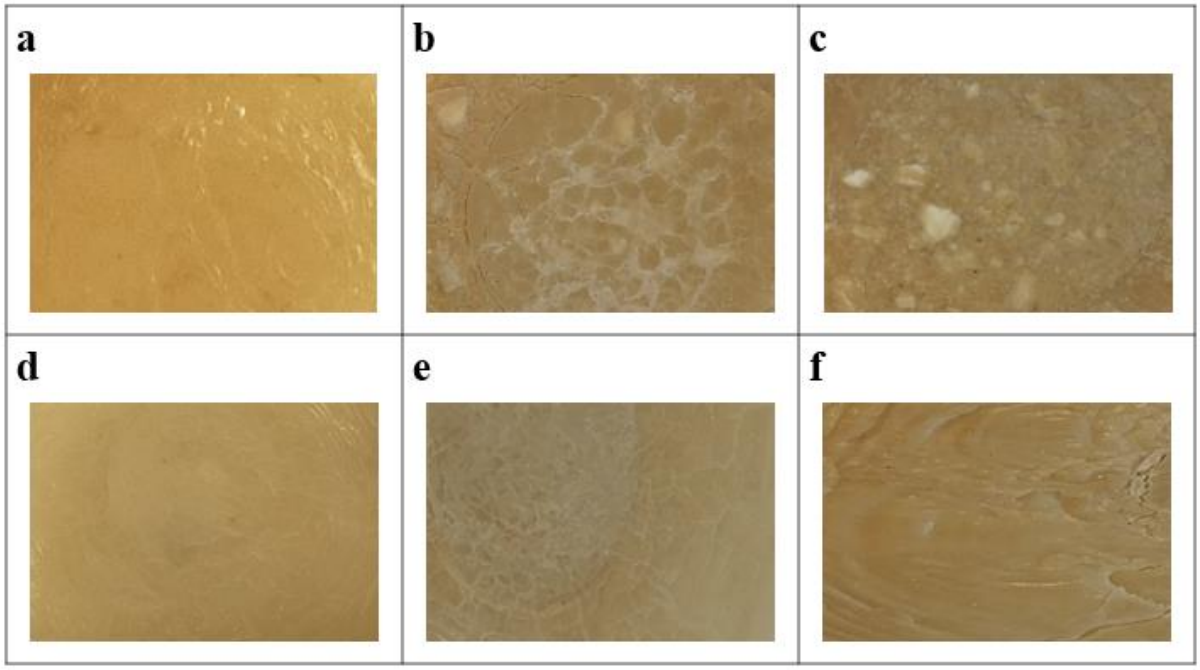


Fig 5. 13 Photographs of Nano composite films based on PHB - PCL a) PHB-PCL20- P3-nCell 1, b) PHB-PCL20- P3-nCell 3, c) PHB -PCL20- P3-nCell 6, d) PHB-PCL20- P3-nClay 1, e) PHB-PCL20- P3-nClay 3, f) PHB-PCL20- P3-nClay 6

5.3.2 Tensile properties of Nanocomposite films based on PHB – PCL

Nanocomposites of plasticized PHB-PCL20 blend, with different loadings of nano- cellulose and nano clay loadings, were prepared, mainly for improving barrier properties. However, the effect of these nanomaterials on tensile properties was evaluated, and the test results are presented in Table 5.10 and Fig 5.14 & 5.15

Nano-composite based on nano-cellulose exhibited a slight increase in tensile strength, from 19.6MPa for the blend without nano-materials to 23.8 MPa, 21.3 MPa, and 20.8 MPa for films with 1%, 3%, and 6 wt% nano-cellulose respectively, the increase was more with 1%, compared to that with higher loadings. Maximum tensile strength was obtained at 1 wt% cellulose loading. In the case of nano clay-based nanocomposites, the addition of nano clay resulted in a continuous increase of tensile strength from 19.6 MPa to 21.4, 22.8, and 23.4 MPa, respectively with 1, 3, and 6% nano-clay. The highest tensile strength was obtained at 6 wt% nano clay loading.

Regarding elongation at break of nano-composites, nano-cellulose and nano-clay addition resulted in a decrease in elongation at break, with both the nanomaterials, the initial addition of 1% of the nano-materials, resulted in a very slight decrease in elongation at break only, the values were very near to that of blend without nanomaterials. More decrease in elongation at break was observed with nano cellulose compared to nano clay at higher loadings. The tensile elongation of the PHB-PCL20- P3 blend before adding nanomaterial was 22.6%, and with the addition of 1, 3, and 6 wt% nano cellulose, the elongation at break reduced to 21.4, 17.3, and 13,1%, respectively. The elongation at break with 1, 3, and 6 wt% nano clay was 21.8, 20.3, and 19.7%, respectively.

Table 5. 10 Tensile properties of nanocomposite films based on PHB – PCL

Film		Tensile strength (MPa)	Elongation at break (%)
PHB-PCL20- P3		19.6±2.5	22.6±2.7
Nano Cellulose	**PHB-PCL20- P3-nCell 1**	23.8±2.2	21.4±2.8
	PHB-PCL20- P3-nCell 3	21.3±2.8	17.3±2.4
	PHB-PCL20- P3-nCell 6	20.8±2.9	13.1±1.9
Nano Clay	**PHB-PCL20- P3-nClay1**	21.4±2.4	21.8±3.7
	PHB-PCL20- P3-nClay3	22.8±1.9	20.3±3.1
	PHB-PCL20- P3-nClay6	23.4±2.7	19.7±3.4

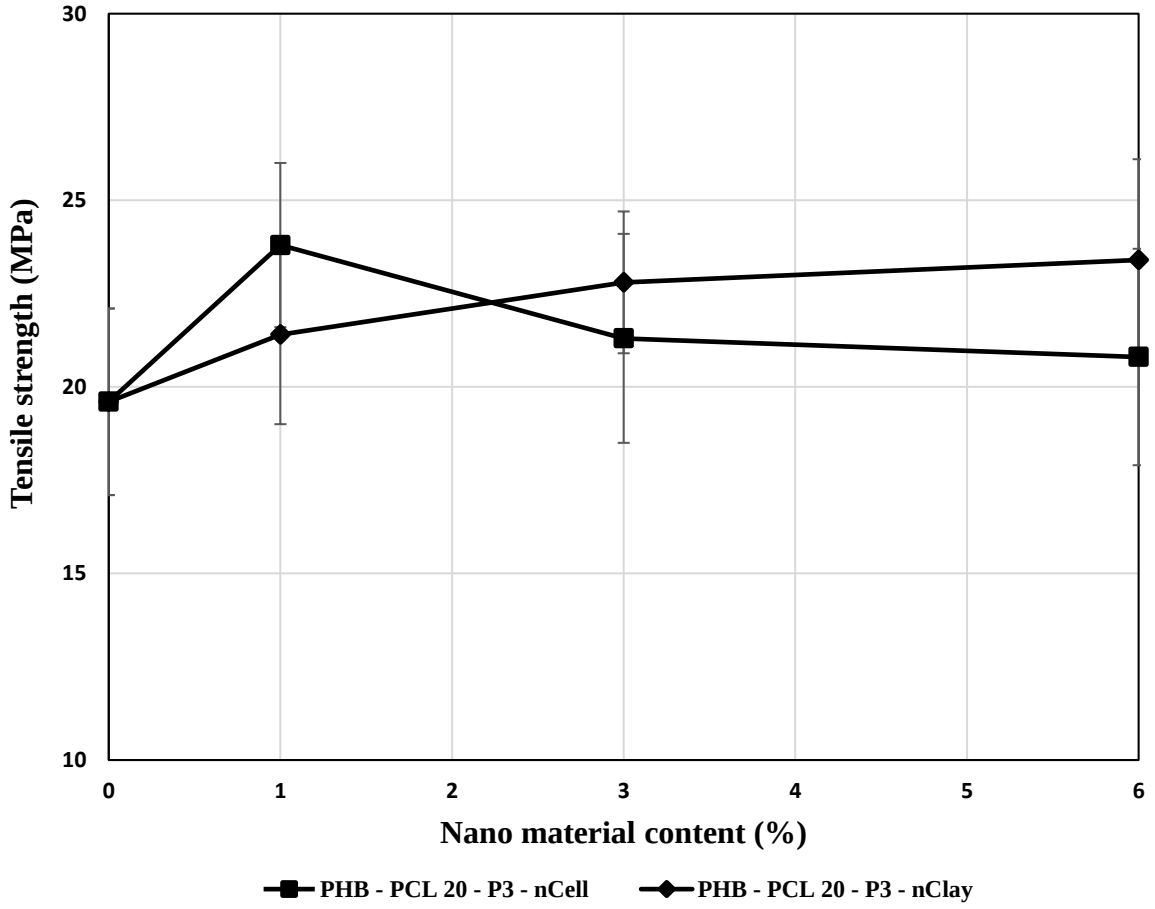


Fig 5. 14 Tensile Strength of nanocomposite films based on PHB – PCL

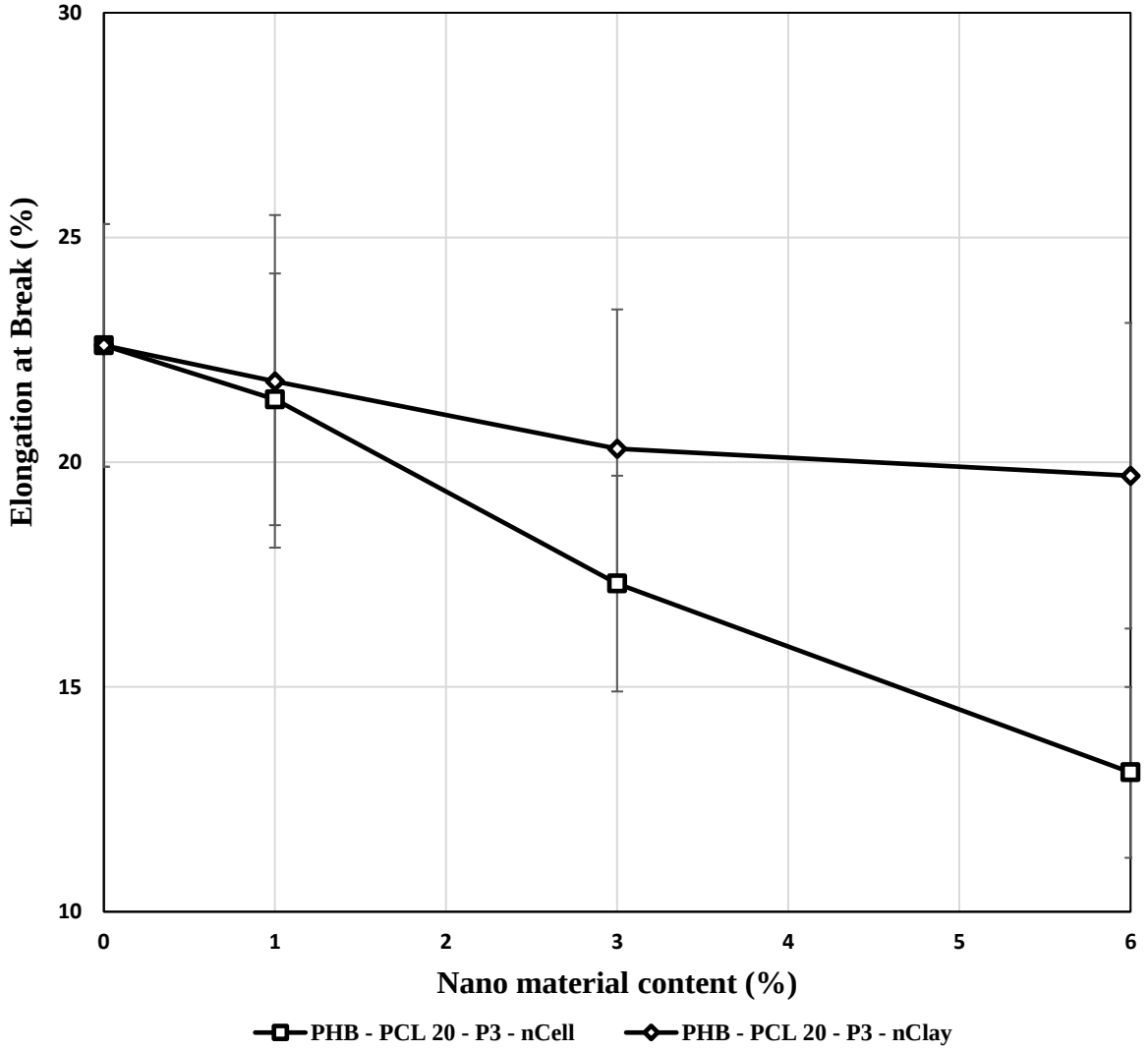


Fig 5. 15 Elongation at break of nanocomposite films based on PHB - PCL

The slight increase in tensile strength with nanomaterials' addition may be due to reinforcement of the polymer chains with nanomaterial particles. A decrease in tensile elongation with the addition of nanomaterials may be due to decreased polymer chain mobility due to nanomaterials' presence, and a more considerable decrease at higher concentrations may be due to the non-uniform distribution of nanoparticles.

SEM images of the nanocomposites with 1 and 6 wt% of nano cellulose and nano clay are shown below in Fig 5.16. For comparison, the SEM image (a) of the blend PHB-PCL20- P3 before

nanomaterial addition is also shown. Though difficult to interpret, the SEM images of nano cellulose with 6 wt% show non-uniform distribution with more phase separation correlating with the observed lesser ductility.

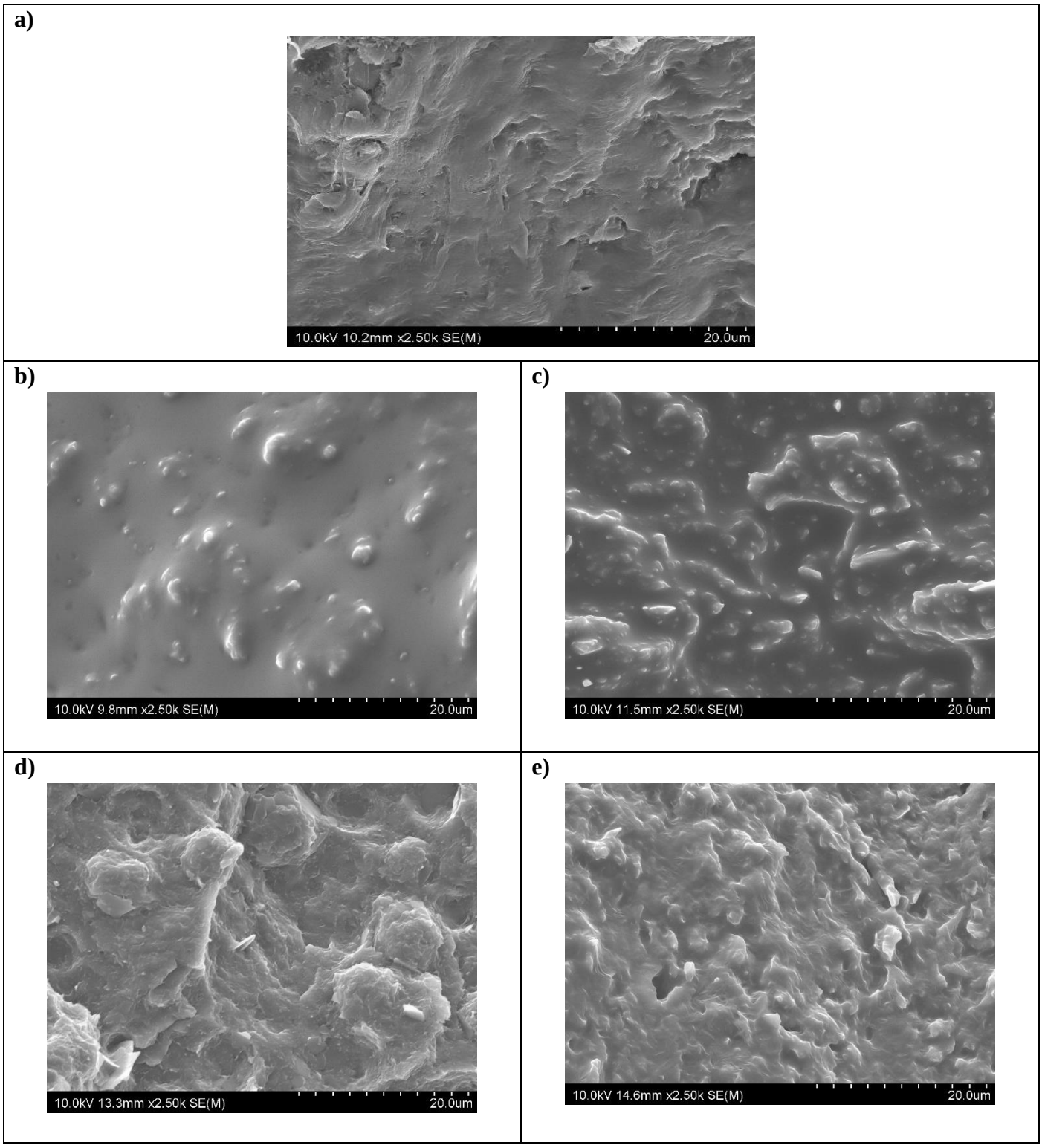


Fig 5. 16 Morphology/ SEM of Nano composite films based on PHB - PCL and plasticized PHB-PCL films without nano composite a) PHB-PCL20- P3, b) PHB-PCL20- P3-nCell 1, c) PHB - PCL20- P3-nCell 6, d) PHB-PCL20- P3 -nClay 1, e) PHB-PCL20- P3 -nClay 6

5.3.3 **Water vapor transmission rates (WVTR) of Nano-composite films of PHB-**PCL

Nano-composites of PHB-PCL were prepared, mainly to improve the water barrier properties, and WVTR tests were carried out to understand the effect of nanomaterials and the results obtained with 1, 3, and 6 wt% of nano-cellulose and nano-clay is presented in Table 5.11and Fig 5.17

The results on WVTR indicate a considerable decrease in WVTR / improvement of barrier property with both the nanomaterials.

In the case of nano-cellulose based PHB-PCL nanocomposites, WVTR decreased from a value of 195 g m^{-2} d^{-1} (WVTR of the plasticized PHB-PCL, without nano-material) to 138 g m^{-2} d^{-1} with 1% nano cellulose and then slightly increased to 148 and 174 g m^{-2} d^{-1} respectively with 3 and 6 wt% loadings of nano cellulose. The least WVTR/ maximum barrier property was observed with 1 wt% nano cellulose.

In the case of nano-clay based nanocomposites, the WVTR values decreased from an initial value of 195 g m^{-2} d^{-1} respectively to 152, 115, and 108 g m^{-2} d^{-1}, with 1 % and 3% and 6 wt% nano clay. Thus, the lowest value of WVTR / highest barrier property was obtained with 6 wt % clay.

Table 5. 11 WVTR of Nano Composites films based on PHB-PCL, at 25˚C, 100% RH, (g.$m^{-2}d^{-1}$) 25µm film thickness

Film		**WVTR at 25˚C, 100% RH, for 25µm film g.$m^{-2}d^{-1}$**
PHB-PCL20- P3		195±34
Nano Cellulose	**PHB-PCL20- P3-nCell1**	138±22
	PHB-PCL20- P3-nCell3	148±28
	PHB-PCL20- P3-nCell6	174±31
Nano Clay	**PHB-PCL20- P3-nClay1**	152±25
	PHB-PCL20- P3-nClay3	115±26
	PHB-PCL20- P3-nClay6	108±35

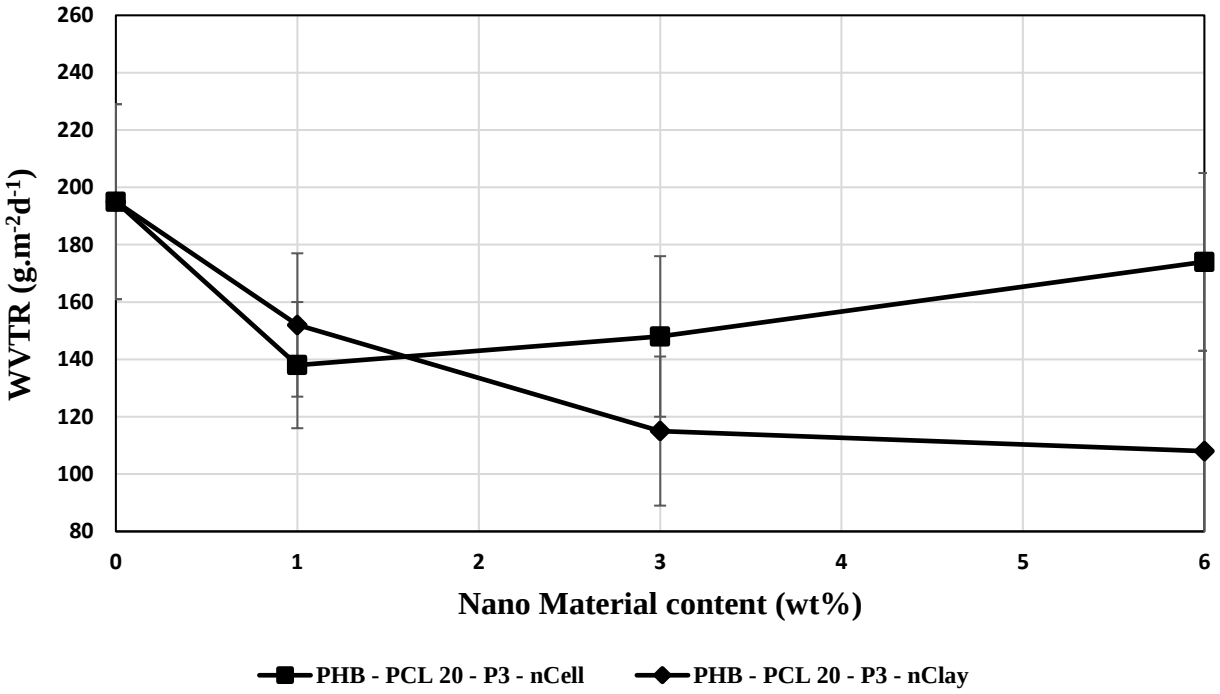


Fig 5. 17 WVTR of Nano Composites films based on PHB-PCL, at 25˚C, 100% RH, 25µm film thickness.

Comparison of the WVTR of nano cellulose and nano clay indicates that, though the lowest WVTR was obtained with nano-clay (with 6 wt% loadings), the value of WVTR obtained with a lower dose (1%) of nano-material was lower in the case of nano-cellulose, or in other words, nano-clay was able to provide a better water barrier property compared to nano-cellulose at a lower dose of nano-material.

The higher barrier property/ lower WVTR obtained with nanocomposites is due to the creation of more torturous pathways. In the case of nano cellulose, though excellent barrier property was obtained, the decrease in barrier property observed at higher concentrations may be due to agglomeration of nano cellulose and microchannels' creation.

5.3.4 Biodegradation characteristics of Nanocomposites films based on PHB - PCL

Biodegradation studies of nanocomposites based on PHB-PCL were carried out in compost medium and seawater medium, for 180 days, at 25˚C, by measurement of CO_2 evolved and the results obtained are given below:

- **Biodegradation in Compost medium, at ambient conditions**

The biodegradation test results of PHB-PCL nanocomposites with 1 of nano cellulose and 6 wt% of nano clay in home compost, is presented in Table 5.12 and Fig 5.18. The test results indicate a slight increase in the biodegradation rate with both the nanomaterials.

The biodegradation rate increased from 73.7% for the blend without nanomaterials to 75.6% and 74.3%, respectively, with 1% of nano cellulose and 6% of nano clay, which corresponds to 2.6% and 0.8% improvements for 1% of nano cellulose and 6% of nano clay. The biodegradation rate of nanocomposite with nano cellulose (1 wt%) was higher than nanocomposite with nano clay (6 wt%).

- **Biodegradation of Nanocomposites films in seawater**

The results obtained for the biodegradation of nanocomposites in seawater are indicated in table 5.13 and Fig 5.19. Compared to the blend without nanomaterials, the results obtained show a slight increase or almost the same biodegradation of nanocomposites in seawater. The biodegradation rate of the blend PHB-PCL20- P3, before the addition of nanomaterials, was 39.5%, and there was almost no change with nano cellulose addition (it increased to 39.8%), and with nano clay addition, the biodegradation slightly increased to 40.1%.

Thus, in the compost medium and seawater medium, only a minimal increase or no increase in biodegradation rate was observed in the case of PHB based nanocomposites, which may be due to the action of two opposing factors, increased surface area due to the nanocomposites may be promoting faster biodegradation, while increased barrier properties (lower WVTR) of nanocomposites may be retarding the biodegradation. As a result, there was a small increase or no increase in biodegradation for PHB based nanocomposites.

Table 5. 12 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PHB - PCL & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25˚C.

	Cellulose Reference ($ThCO_2$: 3.23g)		**PHB - PCL20 - P3 ($ThCO_2$: 4.13g)**		**PHB - PCL20 - P3 -nCell1 ($ThCO_2$: 4.12g)**		**PHB - PCL20 - P3 – nClay6 ($ThCO_2$: 3.89g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.16	4.9±1.2	0.18	4.3±1.5	0.21	5.1±1.6	0.26	6.8±2.6
30	0.27	8.4±1.6	0.40	9.8±2.6	0.47	11.3±3.9	0.44	11.4±2.4
45	0.67	20.7±1.4	0.69	16.7±3.5	0.79	19.2±2.6	0.77	19.7±3.6
60	0.96	29.7±2.5	0.98	23.7±3.4	1.09	26.5±2.4	1.07	27.6±2.8
75	1.17	36.4±1.6	1.26	30.4±2.6	1.43	34.7±3.5	1.35	34.8±3.7
90	1.39	43.1±1.4	1.56	37.8±2.9	1.64	39.8±3.9	1.60	41.1±2.5
105	1.77	54.7±2.5	1.91	46.2±3.5	1.88	45.7±2.8	1.89	48.7±2.6
120	1.94	60.2±1.6	2.15	52±2.4	2.17	52.7±1.5	2.11	54.2±2.4
135	2.31	71.5±2.4	2.39	57.8±2.8	2.50	60.7±3.4	2.39	61.4±3.1
150	2.45	75.9±1.4	2.72	65.9±3.5	2.78	67.4±2.8	2.55	65.7±3.9
165	2.64	81.8±1.5	2.95	71.4±3.6	2.97	72±1.9	2.74	70.4±2.5
180	2.66	82.3±1.6	3.04	73.7±2.6	3.11	75.6±3.7	2.89	74.3±1.6

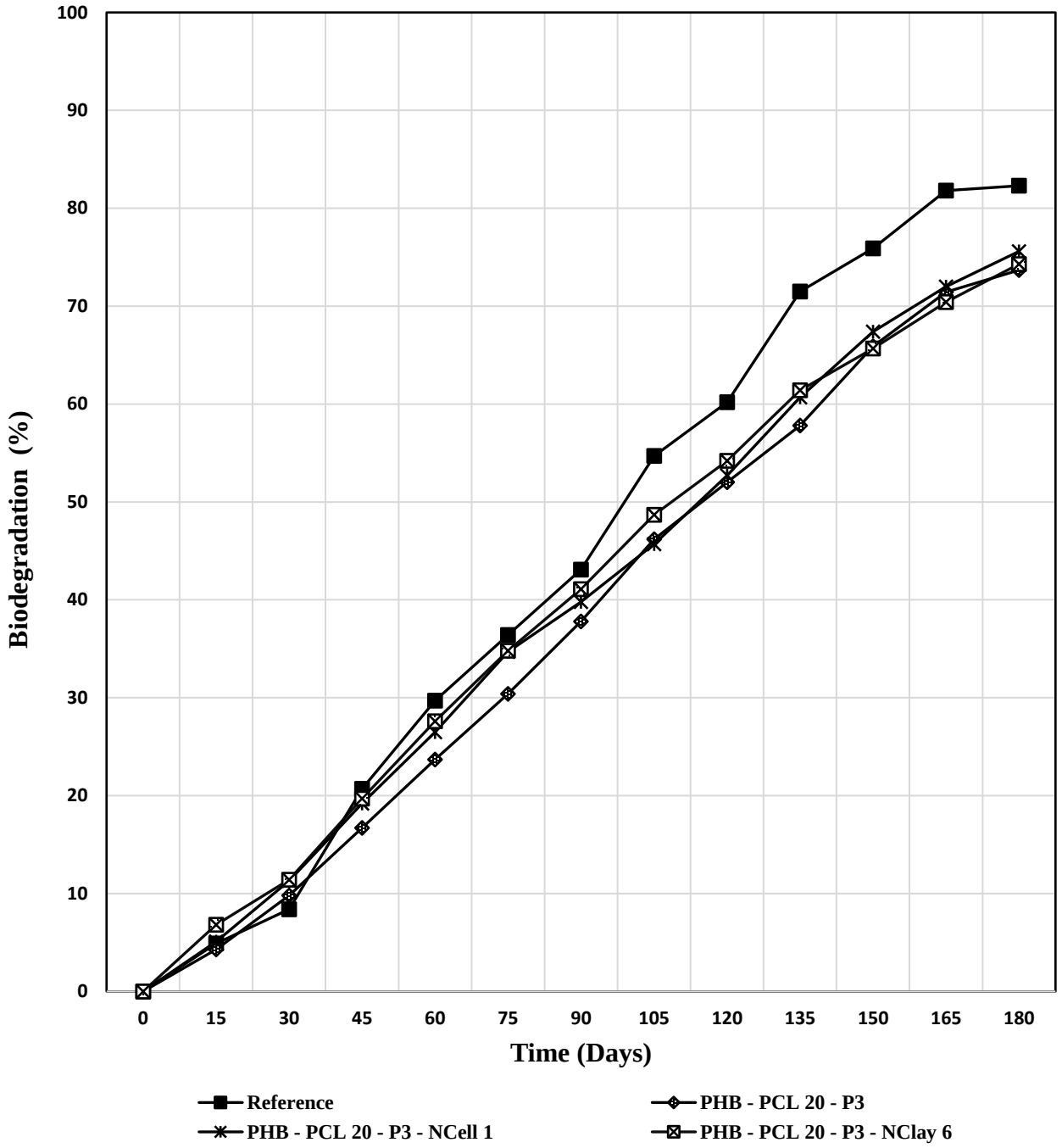


Fig 5. 18 Biodegradation curve of Nanocomposites films based on PHB - PCL, in compost at 25°C.

Table 5. 13 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PHB - PCL & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25˚C.

	Cellulose Reference ($ThCO_2$: 6.45g)		**PHB - PCL20 - P3 ($ThCO_2$: 8.27g)**		**PHB - PCL20 - P3 -nCell1 ($ThCO_2$: 8.25g)**		**PHB - PCL20 - P3 – nClay6 ($ThCO_2$: 7.77g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0.00	0	0.00	0	0.00	0	0.00	0
15	0.04	0.6±1.5	0.04	0.5±3.5	0.08	1±2.5	0.09	1.2±2.5
30	0.14	2.1±1.4	0.09	1.1±2.6	0.21	2.6±3.6	0.37	4.7±3.6
45	0.41	6.4±2.6	0.38	4.6±2.9	0.57	6.9±2.4	0.57	7.4±3.4
60	0.75	11.6±2.8	0.83	10±3.4	1.05	12.7±3.8	1.06	13.7±2.6
75	1.02	15.8±1.7	1.22	14.7±2.8	1.36	16.5±3.9	1.47	18.9±2.1
90	1.44	22.3±2.9	1.36	16.5±3.7	1.62	19.6±2.6	1.60	20.6±2.8
105	1.60	24.8±2.6	1.81	21.9±2.6	1.97	23.9±2.7	2.07	26.7±3.6
120	1.90	29.4±2	2.04	24.6±3.4	2.18	26.4±2.6	2.15	27.6±3.4
135	2.11	32.7±1.4	2.34	28.3±2.7	2.41	29.3±3.4	2.26	29.1±3.9
150	2.21	34.3±2.6	2.65	32.1±2.9	2.67	32.3±3.1	2.55	32.8±2.5
165	2.48	38.5±1.7	3.18	38.4±3.5	3.04	36.9±2.9	2.87	36.9±2.1
180	2.59	40.2±2.9	3.27	39.5±2.6	3.28	39.8±3.8	3.12	40.1±2.9

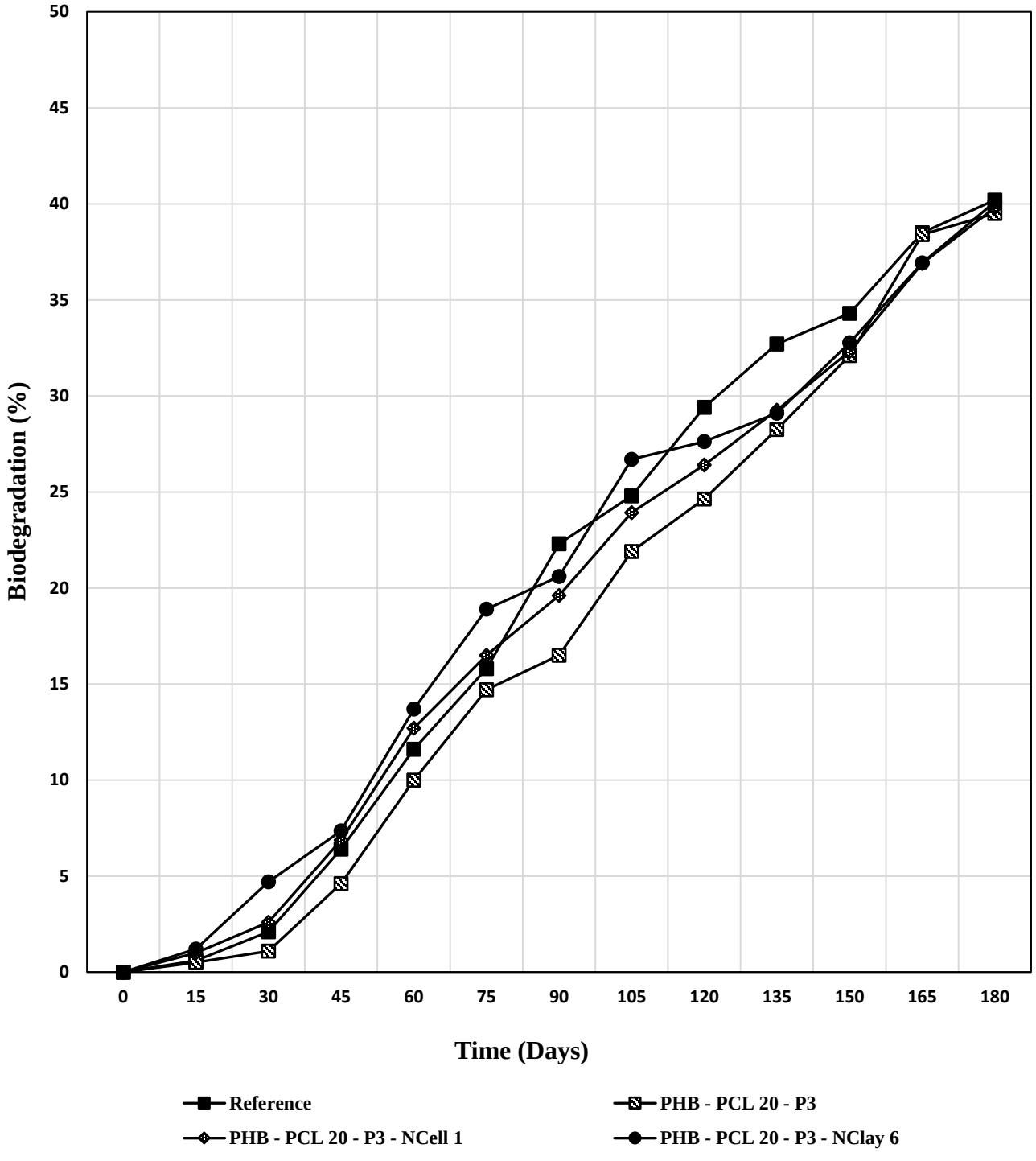


Fig 5. 19 Biodegradation curve of Nano Composites films based on PHB - PCL, in seawater, at 25˚C.

5.4 Summary of investigation on PHB

The summary of the present investigations related to polybutylene succinate polymer, for further improving its properties, with respect to tensile properties, water vapor permeability, and biodegradation characteristics, by blending, plasticization, and fabrication of nanocomposites is given below. Table 5.14 summarizes results on investigations related to tensile properties (elongation at break and tensile strength) and water vapor transmission rate (WVTR). The summary of biodegradation results in home compost (composting at ambient temperature) and in seawater is presented in Table 5.15.

Table 5. 14 Summary of investigation of tensile test and barrier properties on PHB Blends / Composite

Material designation	Elongation at Break % (% change) ((cumulative))	Tensile strength MPa (% Change) ((cumulative))	WVTR 25˚C, 100 RH, $gm^{-2}d^{-1}$ (% change) ((cumulative))
PHB – PCL Blends			
PHB	8	40	254
PHB-PCL10	11.2 (40.0)	21.8 (-45.5)	196 (-22.8)
PHB-PCL20	12.8 (68.0)	21.4 (-46.5)	186 (-26.8)
PHB-PCL30	12.1 (51.3)	19.7 (-50.8)	184 (-27.6)
PHB-PCL40	12.6 (57.5)	10.8 (-73.0)	199 (-21.7)
Plasticized PHB-PCL Blends			
PHB-PCL20-P1	23.8 (85.9) **((197.5))**	14.2 (-33.3) **((-64.5))**	200 (7.5) **((-21.3))**
PHB-PCL20-P2	16.3 (27.3) **((103.8))**	13.4 (-37.1) **((-66.5)**	227 (22.0) **((-10.6))**
PHB-PCL20-P3	22.6 (76.6) **((182.5))**	19.6 (-8.0) **((-51))**	195 (4.8) **((-23.2))**
Nanocomposites of PHB-PCL			
PHB-PCL20-P3 - nCell 1	21.4 (-5.3) **((167.5))**	23.8 (21.4) **((-40.5))**	138 (-29.2) **((-45.7))**
PHB-PCL20-P3 - nCell 3	17.3 (-23.5) **((116.3))**	21.3 (8.7) **((-46.8))**	148 (-24.1) **((-41.7))**
PHB -PCL20-P3 - nCell 6	13.1 (-42.0) **((63.8))**	20.8 (6.1) **((-48.0))**	174 (-10.8) **((-31.5))**
PHB-PCL20-P3 - nClay 1	21.8 (-3.5) **((172.5))**	21.4 (9.2) **((-46.5))**	152 (-22.1) **((-40.2))**
PHB-PCL20-P3 - nClay 3	20.3 (-10.2)	22.8 (16.3)	115 (-41.0)

	((153.8))	**((-43.0))**	**((-54.7))**
PHB-PCL20-P3 - nClay 6	19.7 (-12.8) **((146.3))**	23.4 (19.4) **((-41.5))**	108 (-44.6) **((-57.5))**

( ) %change, (( )) %cumulative

Table 5. 15 Summary of investigation of Biodegradation on PHB Blends / Composite

Material designation	**Biodegradation (%) at 25˚C, for 180 days % change (% cumulative)**	
	Compost	**Seawater**
PHB – PCL Blends		
PHB	66.8	36.1
PHB-PCL10	65.4 (-2.1)	35.2 (-2.5)
PHB-PCL20	71.1 (6.4)	38.8 (7.5)
PHB-PCL40	74.4 (11.4)	39.7 (10.0)
Plasticized PHB-PCL Blends		
PHB-PCL20-P1	74.7 (5.1) **((11.9))**	42.2 (8.8) **((16.9))**
PHB-PCL20- P2	70.1 (-1.4) **((4.9))**	38.3 (-1.3) **((6.1))**
PHB-PCL20- P3	73.7 (3.6) **((10.3))**	39.5 (1.8) **((9.4))**
Nanocomposites of PHB-PCL		
PHB-PCL20- P3 - nCell 1	75.6 (2.6) **((13.2))**	39.8 (0.8) **((10.2))**
PHB-PCL20- P3 - nClay 6	74.3 (0.8) **((11.2))**	40.1 (1.5) **((11.1))**

( ) %change, (( )) %cumulative

The studies on the effect of blending PHB polymer with PCL polymer resulted in enhancement of tensile elongation (ε), improvement in water vapor barrier property (decrease in WVTR), and a very slight increase in the biodegradation rate (in-home compost and seawater), by with the addition of PCL, though with a slight decrease in tensile strength (σ). The studies also indicated comparatively better/ balanced properties for the PHB-PCL blends with 20-30 wt % PCL.

Studies with plasticizers showed a substantial increase in elongation at break, a slight increase in biodegradation, though with a decrease in tensile strength (σ) and water vapor barrier property (increase in WVTR). Among the three plasticizers, monomeric plasticizer P1 was found to offer the highest elongation at break and biodegradability, while the mixed plasticizer P3 was found to provide the highest tensile strength and water vapor barrier property (lowest WVTR). Plasticized blend with polymeric plasticizer P2 was found to have maximum WVTR (lowest barrier property). The plasticizer P3 was also found to have a medium elongation at break and medium biodegradability. The Plasticization study indicated that the mixed plasticizer P3 (1:1 mixture of monomeric plasticizer and polymeric plasticizer) offers the best overall performance enhancement.

Studies carried out on nanocomposites of PHB demonstrated improved tensile strength, improved water vapor barrier properties (decrease in WVTR), and slightly higher biodegradation rate with nanomaterials, though with a decrease in elongation at break. Studies also indicated that overall best performance was obtained with 1wt % nano cellulose and 6% nano clay loading for the nanocomposites.

The present investigation showed that compared to neat PHB, the nanocomposites, with nano cellulose (PHB-PCL20- P3 - nCell 1) and nano clay (PHB-PCL20- P3 - nClay 6) provides higher elongation at break (168% & 146% higher), higher water vapor barrier properties/ lower WVTR (46% & 58% lower WVTR), and higher biodegradation in home compost (13 % & 11% higher) and seawater medium (10% & 11% higher), though the nanocomposite had a slight loss in tensile strength (41% & 42% lower) compared to neat PHB.

Chapter 6 Experimental Results and discussion PLA-PCL blends/composites

6.0 Introduction

This chapter provides the results and discussion on the investigation carried out on biodegradable Polylactic acid (PLA) polymer by various means, such as by blending with a Polycaprolactone (PCL) polymer, by plasticization with plasticizers, and by the fabrication of polymer nanocomposites, to improve/modify properties of PLA. The composition and designation of these polymer samples are given below in Table 6.1

Table 6. 1 Composition and designation of PLA-PCL Blends/nanocomposites prepared

Designation	**PLA content (wt%)**	**PCL content (wt%)**	**Plasticizer (wt%) With respect to PLA – PCL Blends**	**Nanomaterial (wt%) With respect to PLA – PCL Blends**
PLA – PCL Blends				
PLA	100	0	0	0
PLA-PCL10	90	10	0	0
PLA-PCL20	80	20	0	0
PLA-PCL30	70	30	0	0
PLA-PCL40	60	40	0	0
Plasticized PLA-PCL Blends				
PLA-PCL20-P1	80	20	5 % Glyceryl Triacetate (GTA/Triacetin)	0
PLA-PCL20-P2	80	20	5% Ultramoll IV (UM)	0
PLA-PCL20-P3	80	20	5% (GTA – UM (50/50))	0

Nanocomposites of PLA-PCL				
PLA-PCL20-P3-nCell 1	80	20	5% (GTA – UM (50/50))	1 % Nano cellulose
PLA-PCL20-P3-nCell 3	80	20	5% (GTA – UM (50/50))	3% Nano Cellulose
PLA -PCL20-P3-nCell 6	80	20	5% (GTA – UM (50/50))	6% Nano Cellulose
PLA-PCL20-P3-nClay 1	80	20	5% (GTA – UM (50/50))	1% Nano Clay
PLA-PCL20-P3-nClay 3	80	20	5% (GTA – UM (50/50))	3% Nano Clay
PLA-PCL20-P3-nClay 6	80	20	5% (GTA – UM (50/50))	6% Nano Clay

6.1 PLA-PCL Blends

Commercially available polylactic acid (PLA) polymer was blended with 10, 20, 30, and 40 wt% of polycaprolactone (PCL) by hot blending, and PLA-PCL blend films of thickness 0.25mm were prepared by injection molding followed by hot pressing at 180˚C [217], 1MPa pressure for 3 min. These blend films were characterized by tensile testing, water vapor permeation studies, and biodegradation studies in compost and marine media, and the results obtained are given below:

6.1.1 Appearance/ Photographs:

The polymer film of neat PLA without PCL was transparent, similar to the commercially available neat PLA film. When increasing the amount of PCL in PLA - PCL blends, the blends had lower transparency. The photographs of neat PLA film and PLA-PCL blend films are indicated in Fig.6.1. These photographs indicate that all the films are uniform in appearance.

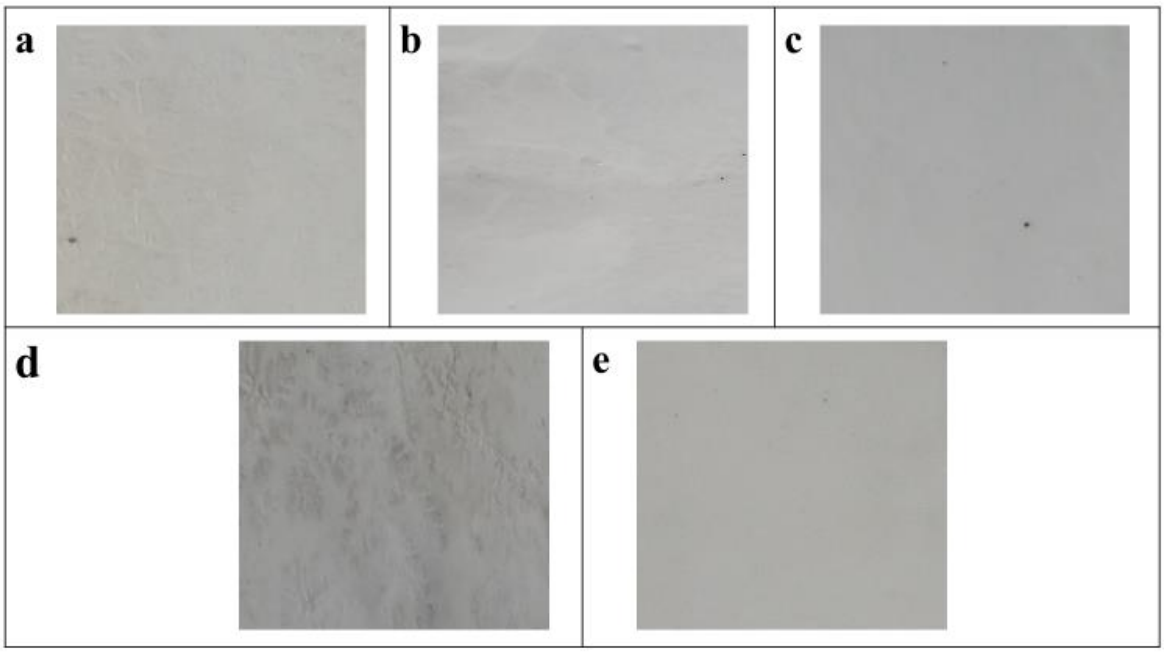


Fig 6. 1 Photographs of PLA/PCL Blends a) PLA 100, b) PLA-PCL10, c) PLA-PCL20, d) PLA-PCL30 e) PLA-PCL40

6.1.2 Mechanical- Tensile properties of PLA-PCL blend films

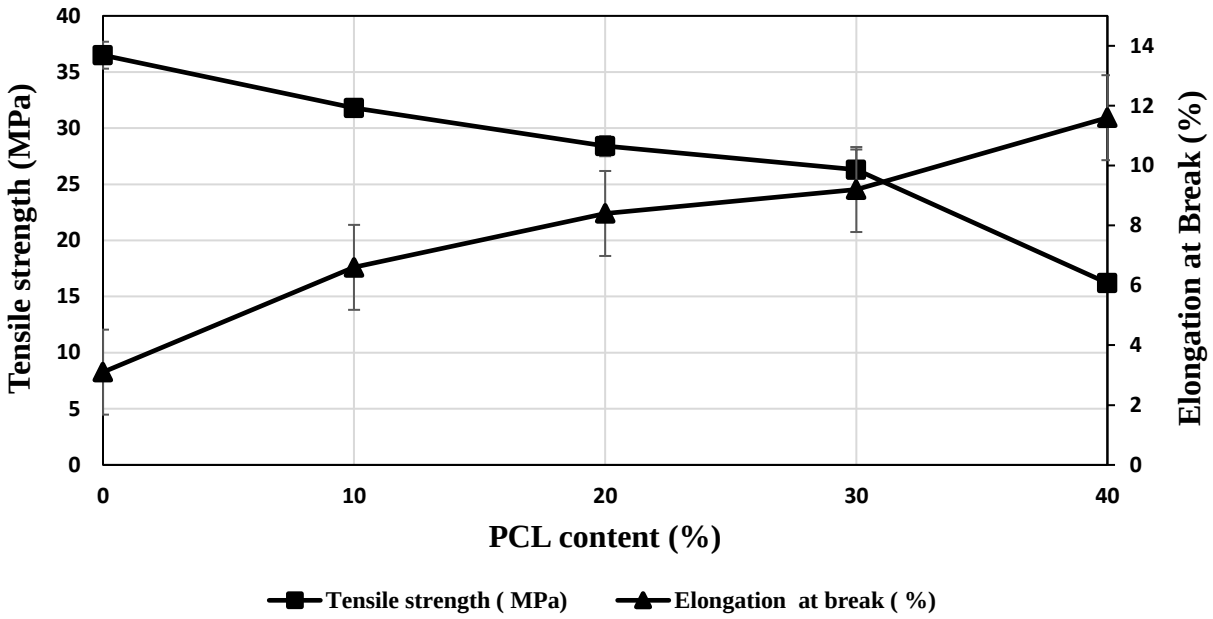
The effect of PCL on the tensile properties of PLA was investigated, and the results for tensile strength and elongation at break for PLA-PCL blends are shown in Table 6.2 and Fig 6.2 (a), respectively. Tensile properties of PLA- PCL blends, based on the rule of mixtures, were shown in fig 6.2 b & c [201].

The tensile strength of pure PLA was found to be 36.5 MPa, and with the addition of PCL, tensile strength was found to decrease gradually up to about 30% PCL and then decreases sharply with 40% PCL. The tensile strength of PLA-PCL blends with 10, 20, 30, and 40% PCL was 31.8, 28.4, 26.3, and 16.2 MPa.

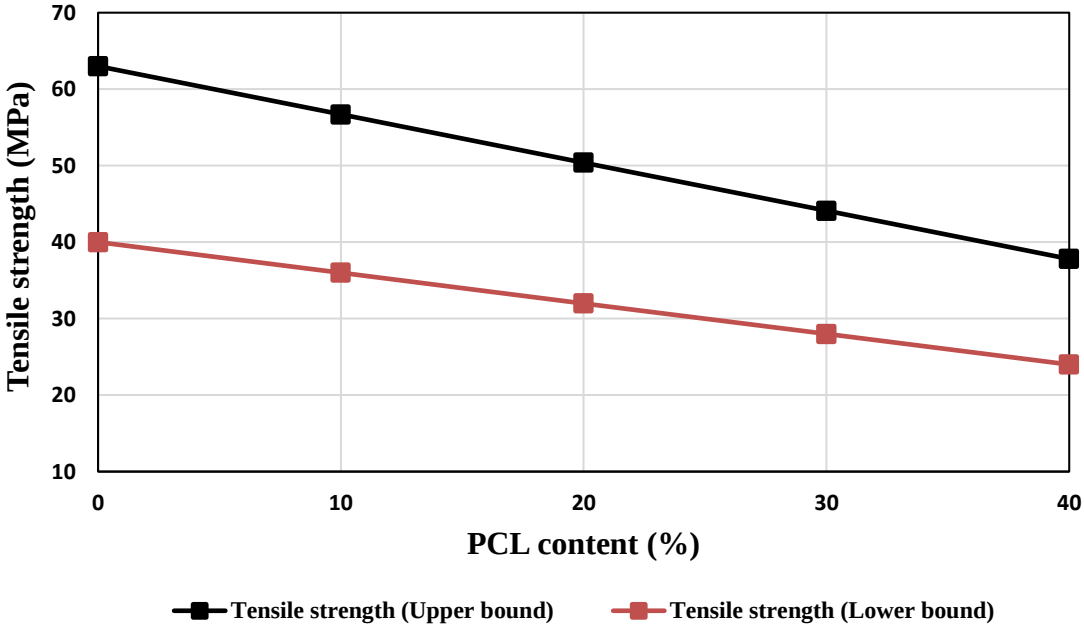
The elongation at break of PLA was continuously increasing with PCL's addition for all the blends studied, up to 40% PCL. Elongation at break of neat PLA and PLA-PCL blends with 10, 20, 30, and 40% PCL were found to be 3.1, 6.6, 8.4. 9.2 and 11.6%, respectively.

Table 6. 2 Tensile properties of PLA-PCL Blends

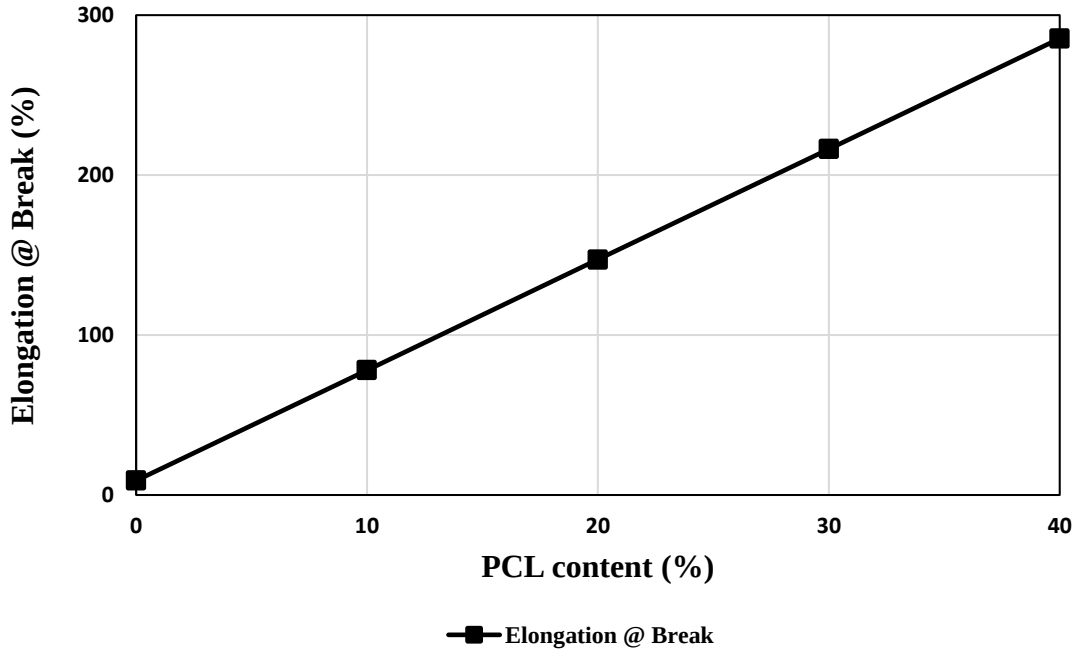
Film	Tensile strength (MPa)	Elongation at break (%)
PLA	36.5±1.4	3.1±0.9
PLA-PCL10	31.8±1.2	6.6±1.5
PLA-PCL20	28.4±0.6	8.4±0.8
PLA-PCL30	26.3±0.9	9.2±0.6
PLA-PCL40	16.2±1.8	11.6±0.7


Tensile strength (MPa)
Elongation at Break (%)
PCL content (%)
Tensile strength (MPa)
Elongation at break (%)

(a)


Tensile strength (MPa)
PCL content (%)
Tensile strength (Upper bound)
Tensile strength (Lower bound)

(b)



(c)

Fig 6. 2 (a) Effect of PCL concentration on Tensile strength and Elongation at break for PLA-PCL blends, (b)&(c) Effect of PCL concentration on Tensile strength and Elongation at break for PLA-PCL blends, based on the rule of mixtures

A similar increase in tensile elongation and a decrease in tensile strength, with increasing PCL's concentration, has been reported in the literature [171] and is expected due to very high tensile elongation and low tensile strength of PCL, compared to PLA.

PLA-PCL blends with 10, 20, and 30% PCL were having balanced properties with respect to tensile strength and elongation at break, and a blend with 20% PCL was chosen for further investigations.

Scanning electron microscopy (SEM) examination of the PLA-PCL blend films and neat PLA film was carried out to understand any correlation between observed properties and morphology. The SEM images obtained are given below in Fig a, b, c, d, and e for the neat PLA and the blends with 10, 20, 30, and 40% PCL, respectively. The SEM images for the blends were found to be entirely different from that for neat PLA. The SEM images of the PLA-PCL blend indicate the low miscibility/ immiscible nature of PLA and PCL. The images indicate spherules of PCL in the PLA matrix, and an increase in the size of PCL spherules is seen in blends with higher PCL. The immiscible nature of the blend with poor adhesion between PLA and PCL may be responsible for decreasing tensile strength compared to neat PLA.

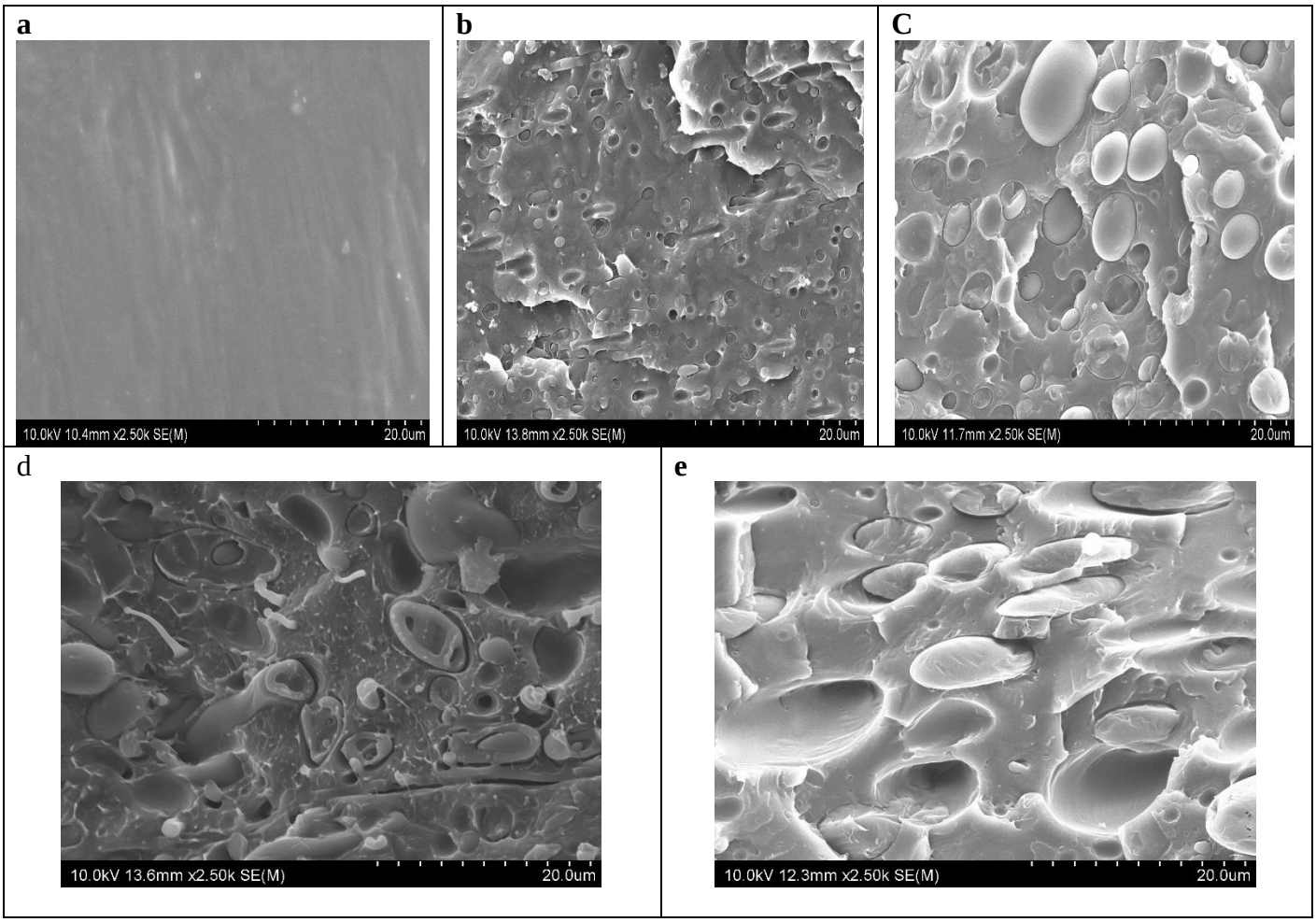


Fig 6. 3 SEM Micrographs of PLA-PCL blends a) PLA 100, b) PLA-PCL10, c) PLA-PCL20, d) PLA-PCL30, e) PLA-PCL40

6.1.3 Barrier property- Water vapor transmission rate (WVTR) of PLA-PCL Blend films

Studies on barrier properties/water vapor transmission rate (WVTR) of neat PLA and PLA-PCL films was carried out, and the results obtained, after normalization for a film thickness of 25µm is given in Table 6.3 and Fig 6.4

The above results show a sharp decrease in WVTR with 10% PCL, followed by a slight decrease with 20, 30, and 40% PCL. The WVTR value observed for neat PLA and PLA-PCL blends with 10, 20, 30, and 40% PCL was 244, 188, 170, 164, and 160 g m^{-2} d^{-1}.

Table 6. 3 Water vapor transmission rate (WVTR) of PLA-PCL blend films

Film	**WVTR at 25°C, 100% RH, for 25µm film $g.m^{-2}d^{-1}$**
PLA	244±2.1
PLA-PCL10	188±3.4
PLA-PCL20	170±4.1
PLA-PCL30	164±1.9
PLA-PCL40	160±2.6

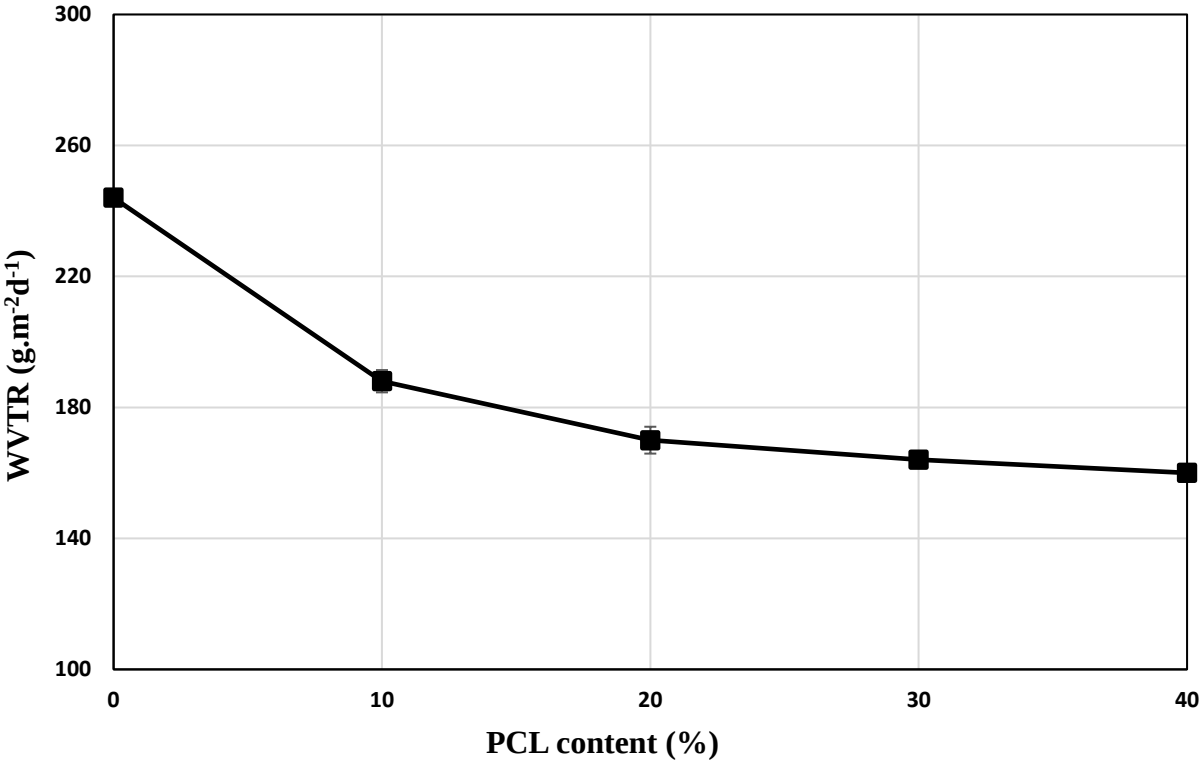


Fig 6. 4 WVTR vs sample composition curves for PLA-PCL blend films, at 25^0C, 100% RH, 25µm film thickness

The reduction in the WVTR / improved barrier property of PLA with the addition of PCL may be due to an increase in the gas diffusion path length for the water vapor molecule, due to the PCL spherulites dispersed in the PLA matrix, and due to increased crystallinity with the blending of PLA with PCL [218]. A similar decrease in WVTR with the addition of PCL has been reported by [177].

6.1.4 Biodegradation characteristics of PLA-PCL Blend films

Biodegradation studies of PLA-PCL blends were carried out in compost medium and seawater medium, for 180 days, at 25°C, and the results are described below.

- **Biodegradation of PLA-PCL Blend films in home compost media (at 25ºC)**

Biodegradation studies of PLA and PLA-PCL blends were conducted in compost medium, at 25 ±5˚C, by monitoring the amount of CO_2 evolved at various intervals. The studies were carried out in moist compost with a moisture content of 50-55%, containing a small amount of river sand, for air permeability, and the experiments were carried out in duplicate, using cellulose as a positive reference and a ratio of 1: 6 test sample: inoculum weight ratio on a dry matter basis was maintained. The cumulative amount of CO_2 evolved from the blank, reference sample, neat PLA sample, and PLA-PCL blends with 10, 20, and 40% PCL was measured at various time intervals, and the corresponding % biodegradation at various time intervals was calculated using equation 3.12, and the results are presented in Table 6.4 and Fig 6.5

The % biodegradation for the neat PLA in compost (at 25˚C) was very low, was 10.4% after 180 days compared to a biodegradation rate of 82.3% for cellulose reference, under similar conditions. An increase in the biodegradation rate with the addition of PCL was observed. The % biodegradation for the PLA-PCL blends with 10, 20 and 40% PCL were 12.8, 12.6, and 19.3% respectively, corresponding to an increase of 23.1, 21.2 and 85.6%, compared to that with neat PLA.

- **Biodegradation of PLA-PCL Blend films in seawater**

Biodegradation test results of PLA-PCL blends in seawater, at 25˚C, is provided in table 6.5 and Fig 6.6

The results obtained for neat PLA indicate a low biodegradation rate of 3.6% in compost at 25˚C, after 180 days, compared to a value of 40.2% biodegradation obtained for cellulose reference after 180 days. An increase in biodegradation rate with PCL blending was observed, and the biodegradation rate obtained for the PLA-PCL blends with 10, 20, and 40% PCL were found to be 3.9, 4.2, and 8.4 %.

Most of the biodegradation studies of PLA in compost medium reported in the literature are carried out at industrial composting conditions, at 58-60˚C. Few studies are reported on the biodegradation

studies of PLA and PLA blends at ambient/home composting conditions and under marine conditions. Itavarra et al. [146] have reported low biodegradation/ mineralization of about 10% after 210 days, for PLA at 25-37˚C, while very high mineralization of 90% at about 55˚C. It is once again proven that though PLA is considered highly biodegradable, it is not biodegradable under ambient temperature/ home-composting conditions. PLA requires an elevated temperature of 55-60˚C, for high biodegradation, for the initial hydrolysis step of biodegradation [219]. Also, it is reported that PLA-degrading microorganisms in the natural environment are significantly less than other degraders of biodegradable polyesters, such as PHB, PCL. [220].

Table 6. 4 Cumulative amount of CO_2 evolved and % biodegradation for PLA-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25°C.

	Cellulose Reference (ThCO_2: 3.23g)		**PLA100% (ThCO_2:3.67g)**		**PLA-PCL10% (ThCO_2: 3.76g)**		**PLA-PCL20% (ThCO_2: 3.86g)**		**PLA-PCL40% (ThCO_2: 4.05g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0	0	0	0	0	0	0	0	0	0
15	0.16	4.9±1.2	0.00	0	0.00	0	0.00	0	0.00	0
30	0.27	8.4±1.6	0.04	1±1.5	0.05	1.4±2.4	0.04	1±2.4	0.06	1.5±1.6
45	0.67	20.7±1.4	0.06	1.7±1.9	0.08	2.2±1.6	0.06	1.6±1.5	0.10	2.4±2.4
60	0.96	29.7±2.5	0.11	2.9±1.7	0.12	3.3±1.5	0.12	3.2±2.6	0.12	3±1.6
75	1.17	36.4±1.6	0.13	3.6±2.6	0.14	3.6±2.4	0.15	3.8±2.4	0.20	4.9±2.4
90	1.39	43.1±1.4	0.17	4.7±2.4	0.18	4.8±2.8	0.17	4.3±1.7	0.27	6.7±1.58
105	1.77	54.7±2.5	0.20	5.4±1.5	0.23	6±2.3	0.20	5.1±2.8	0.34	8.4±2.7
120	1.94	60.2±1.6	0.23	6.3±1.6	0.26	6.8±1.5	0.25	6.4±1.9	0.35	8.6±1.8
135	2.31	71.5±2.4	0.26	7.1±2.4	0.30	7.9±2.4	0.27	7±2.4	0.38	9.3±2.9
150	2.45	75.9±1.4	0.28	7.7±2.4	0.36	9.7±1.4	0.32	8.2±1.6	0.48	11.8±2.7
165	2.64	81.8±1.5	0.31	8.5±1.6	0.44	11.8±2.4	0.34	8.8±2.4	0.55	13.7±1.8
180	2.66	82.3±1.6	0.38	10.4±2.4	0.48	12.8±2.8	0.49	12.6±1.6	0.78	19.3±1.4

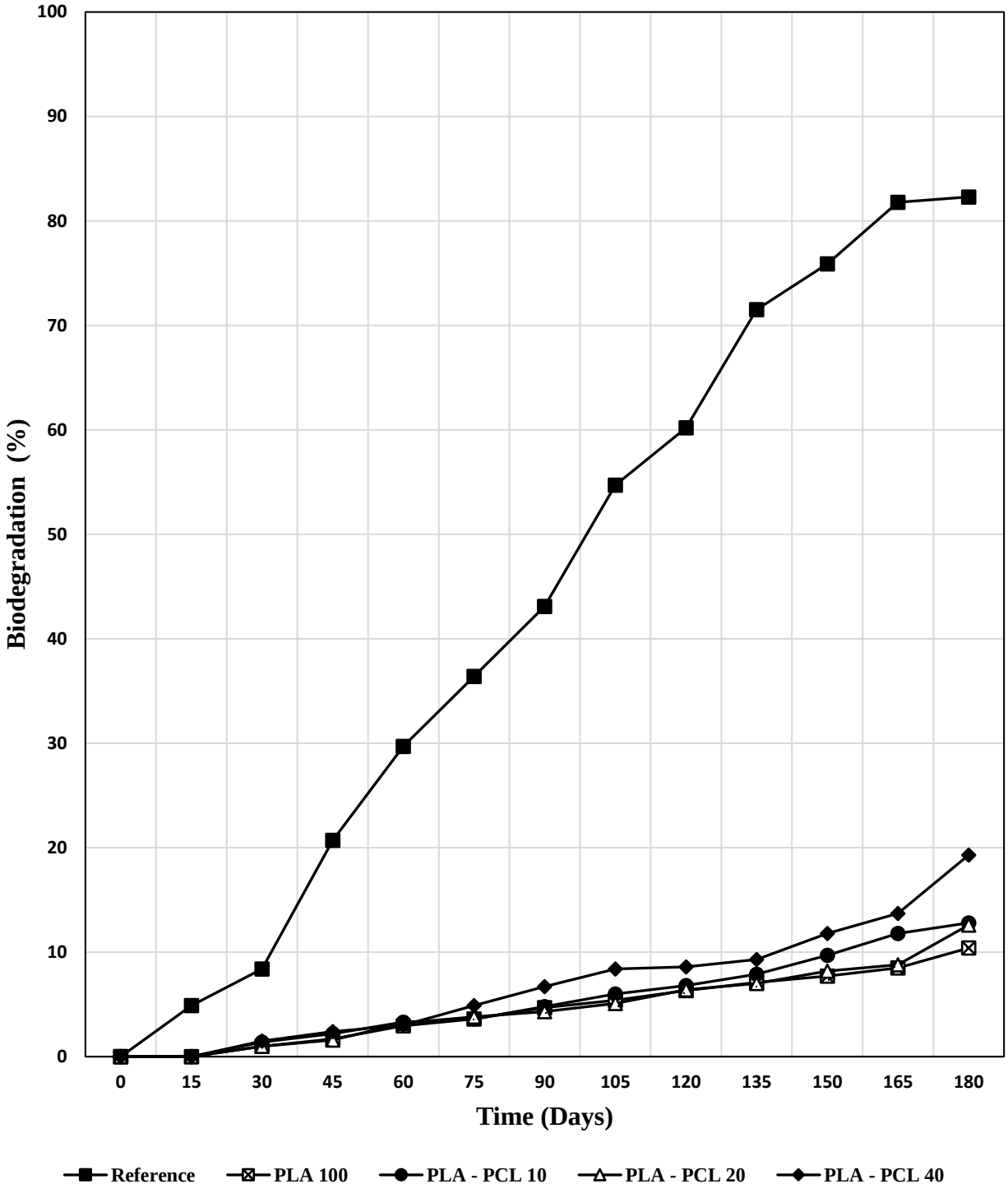


Fig 6. 5 Biodegradation curve of PLA-PCL blends in compost at 25^0C

Table 6. 5 Cumulative amount of CO_2 evolved and % biodegradation for PLA-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25^0C.

	Cellulose Reference (ThCO₂: 6.45g)		**PLA100% (ThCO₂: 7.33g)**		**PLA-PCL10% (ThCO₂: 7.52g)**		**PLA-PCL20% (ThCO₂: 7.71g)**		**PLA-PCL40% (ThCO₂: 8.10g)**	
Time Days	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**
0	0	0	0	0	0	0	0	0	0	0
15	0.04	0.6±1.5	0.00	0	0.00	0±1.6	0.00	0	0.01	0.1±0.7
30	0.14	2.1±1.4	0.00	0	0.02	0.2±1.5	0.01	0.2±1.4	0.02	0.2±1.6
45	0.41	6.4±2.6	0.01	0.2±2.8	0.05	0.6±1.8	0.05	0.7±1.9	0.06	0.8±1.4
60	0.75	11.6±2.8	0.04	0.5±3.1	0.06	0.8±2.7	0.09	1.2±2.7	0.11	1.4±2.8
75	1.02	15.8±1.7	0.06	0.8±3.3	0.12	1.5±1.6	0.10	1.3±2.4	0.18	2.2±2.9
90	1.44	22.3±2.9	0.10	1.4±3.6	0.17	2.2±2.4	0.17	2.3±1.6	0.28	3.4±1.7
105	1.60	24.8±2.6	0.12	1.7±2.4	0.19	2.4±2.3	0.21	2.8±1.8	0.34	4.2±1.4
120	1.90	29.4±2	0.18	2.4±2.9	0.22	2.9±1.5	0.23	3.1±2.7	0.40	4.9±2.8
135	2.11	32.7±1.4	0.21	2.9±3.5	0.27	3.5±2.4	0.25	3.3±1.8	0.46	5.7±1.6
150	2.21	34.3±2.6	0.22	3±3.3	0.28	3.6±1.6	0.27	3.6±1.4	0.56	6.9±2.4
165	2.48	38.5±1.7	0.25	3.4±3.7	0.29	3.7±2.8	0.29	3.8±2.5	0.61	7.5±1.5
180	2.59	40.2±2.9	0.26	3.6±2.7	0.30	3.9±1.7	0.32	4.2±2.1	0.68	8.4±2.7

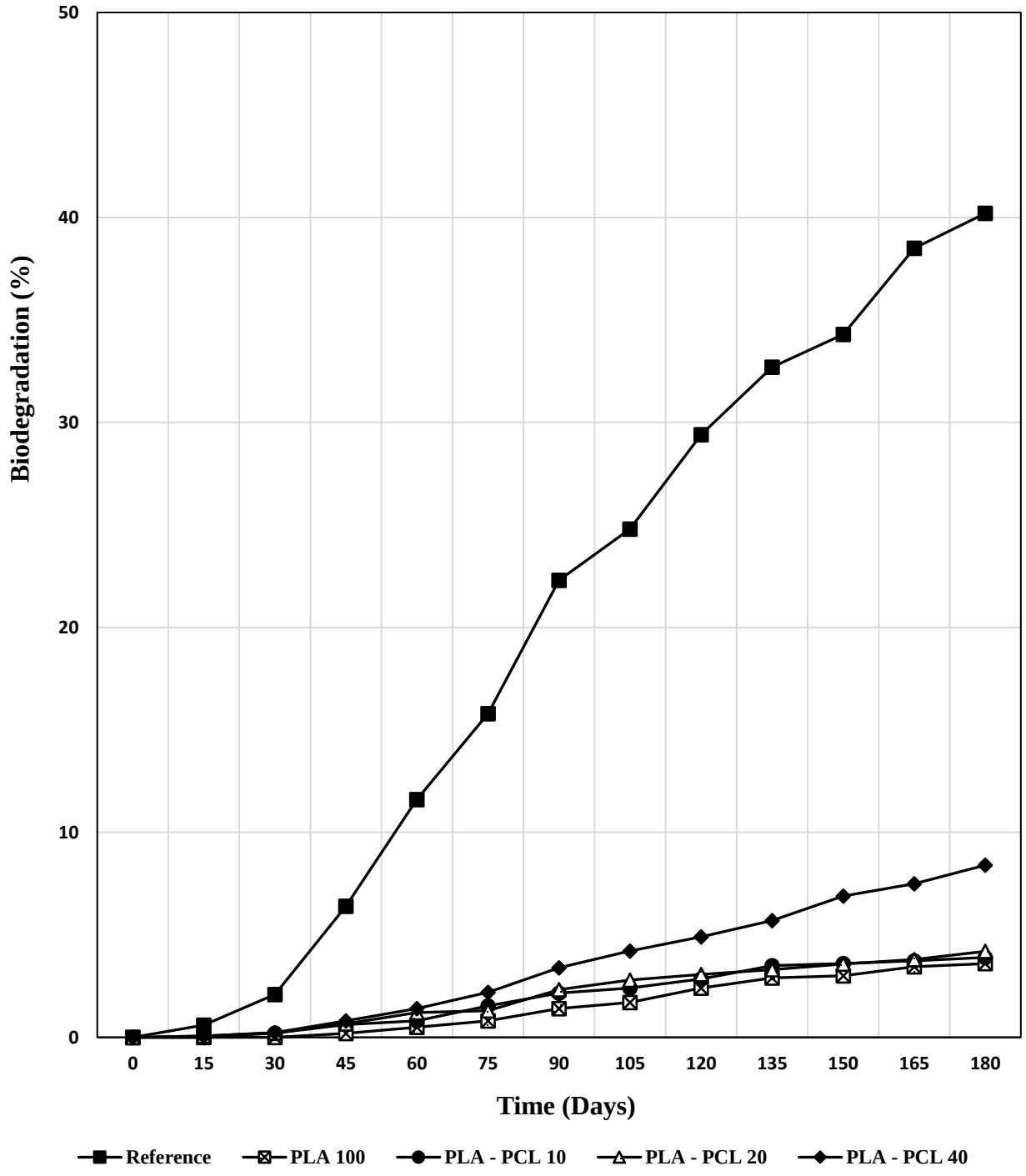


Fig 6. 6 Biodegradation curve of PLA-PCL blends in seawater at 25^0C

6.2 Plasticized PLA-PCL blend films

The effect of plasticizers on the PLA-PCL20 blend, with 20 wt% PCL, was investigated to improve the mechanical properties of PLA further. Plasticization was carried out using three biodegradable plasticizers; namely, i) a monomeric plasticizer (P1), Glyceryl Triacetate (GTA), ii) a polymeric plasticizer (P2), Ultramoll IV (UM), an adipic acid polyester, and iii) a mixture of the above two plasticizers, 1:1 ratio by weight (P3). The amount of plasticizer used was 5 wt%, with respect to the PLA-PCL20 blend. Plasticized blend films with a thickness of 0.25mm, were prepared by injection molding followed by hot pressing and were characterized by standard methods, and the results are given below:

6.2.1 Appearance/ Photographs of Plasticized PLA-PCL Blends

Photographs of plasticized PLA-PCL20, plasticized with plasticizers P1, P2, and P3, are given below, which indicate crack-free and uniform films with all three plasticizers.

Fig 6. 7 Photographs of Plasticized PLA-PCL Blends a) PLA-PCL20-P1, b) PLA-PCL20-P2, c) PLA-PCL20-P3

6.2.2 Mechanical- Tensile properties of Plasticized PLA-PCL Blends

The effect of plasticizers on tensile properties of PLA-PCL was investigated, and the results obtained for the plasticized PLA-PCL20 blend with plasticizers P1, P2 and P3 are presented in Table 6.6 and Fig 6.8

The above test results for plasticized PLA-PCL blend films indicate a substantial increase in elongation at break with all plasticizers. The maximum increase was observed with monomeric plasticizer P1, and the minimum increase was observed with polymeric plasticizer P2, and an intermediate increase was observed with mixed plasticizer P3. The tensile elongation values observed were 21.2%, 14.8%, and 20.1%, respectively, for the blends plasticized with plasticizers P1, P2, and P3, respectively, compared to a value 8.4% for the un-plasticized PLA-PCL20 blend. The above increase corresponds to an increase in elongation at break by 152.4%, 76.2%, and 139.3%, for plasticizers P1, P2, and P3, compared to un-plasticized blend.

The tensile strength of plasticized PLA-PCL blends presented in Fig 6.8 indicates decreased tensile strength with plasticizers' addition. For the un-plasticized PLA-PCL20 blend film, the tensile strength was 28.4MPa, and for the plasticized blend films with plasticizers P1, P2, and P3, the observed tensile strength was 18.2, 20.5, and 22.2 MPa, respectively. Maximum tensile strength was observed with plasticizer P3, and the least tensile strength was observed with plasticizer P1.

Table 6. 6 Tensile properties of Plasticized PLA-PCL Blends

Film	**Tensile strength (MPa)**	**Elongation at break (%)**
PLA-PCL20	28.4±0.6	8.4±0.8
PLA-PCL20-P1	18.2±1.1	21.2±1.3
PLA-PCL20-P2	20.5±1.6	14.8±0.6
PLA-PCL20-P3	22.2±0.7	20.1±1.4

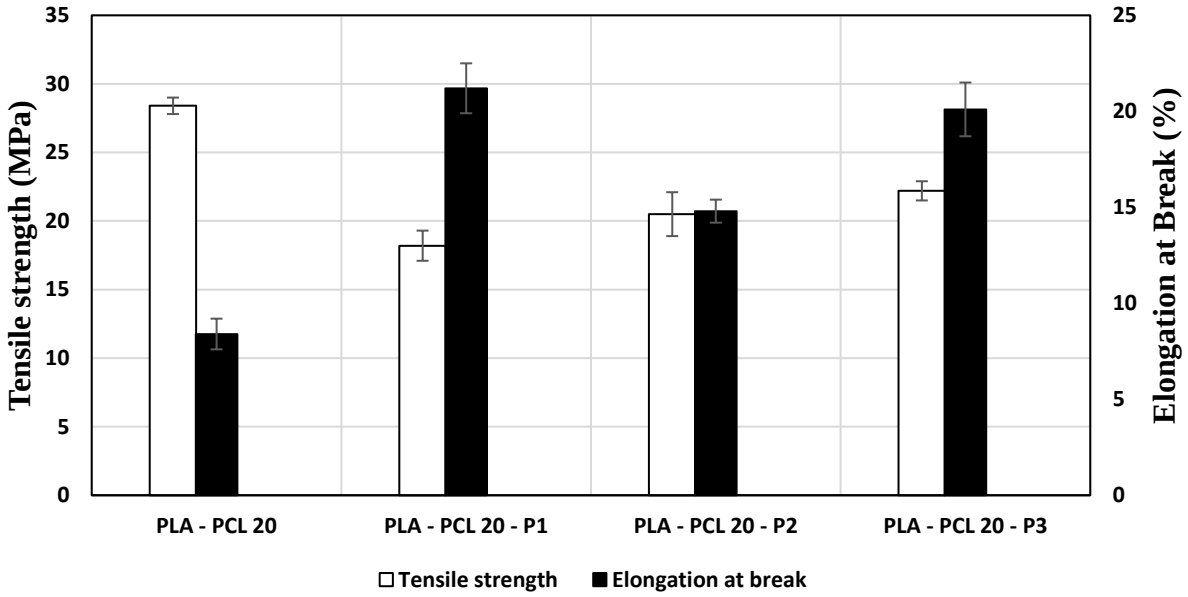


Fig 6. 8 Tensile Strength and Elongation at break of Plasticized PLA-PCL Blends

The increase in elongation at break/ ductility with the addition of plasticizers is well known, and due to the polymer chain mobility increase. Increased polymer chain mobility with plasticizers maybe because plasticizers increase the free space in the polymer matrix, decreasing the intermolecular forces between the polymer chains, and may sometimes substitute with hydrogen bonds between plasticizer and polymer molecules, depending on the polymer and the plasticizer type. [221]

Higher elongation at break observed with a monomeric plasticizer (P1) and lowest elongation with a polymeric plasticizer (P2) may be due to the smaller molecular size of plasticizer P1, glyceryl triacetate, and larger molecular size of plasticizer P2, Ultramoll, adipic acid polyester. It is reported that, in general, plasticizer molecules with smaller molar mass are more effective plasticizers as they can facilitate easy interaction between plasticizer–polymer molecular chains [150, 221, 222]

The decrease in PLA's tensile strength with the addition of plasticizers is reported by other researchers [212]. It may be due to the penetration of plasticizer between the polymer chains and

the disruption of polymer-polymer chain interactions, reducing intermolecular force, which causes polymer chain cohesion.

SEM images of the plasticized PLA-PCL20 blends were taken to understand the morphology changes with the addition of plasticizers. Fig 6.9 a, b, c, and d indicate SEM images of the un-plasticized blend, plasticized blend with plasticizers P1, P2, and P3, respectively. Comparison of the SEM images of the plasticized with that of the plasticized blend indicates drastic changes in the PCL spherulite shape. Spherical PCL domains can be seen as elongated in the SEM of the blends. Maximum elongated domains can be seen in the SEM image for the plasticized blend with monomeric plasticizer P1, which might have caused maximum plasticity, maximum tensile elongation.

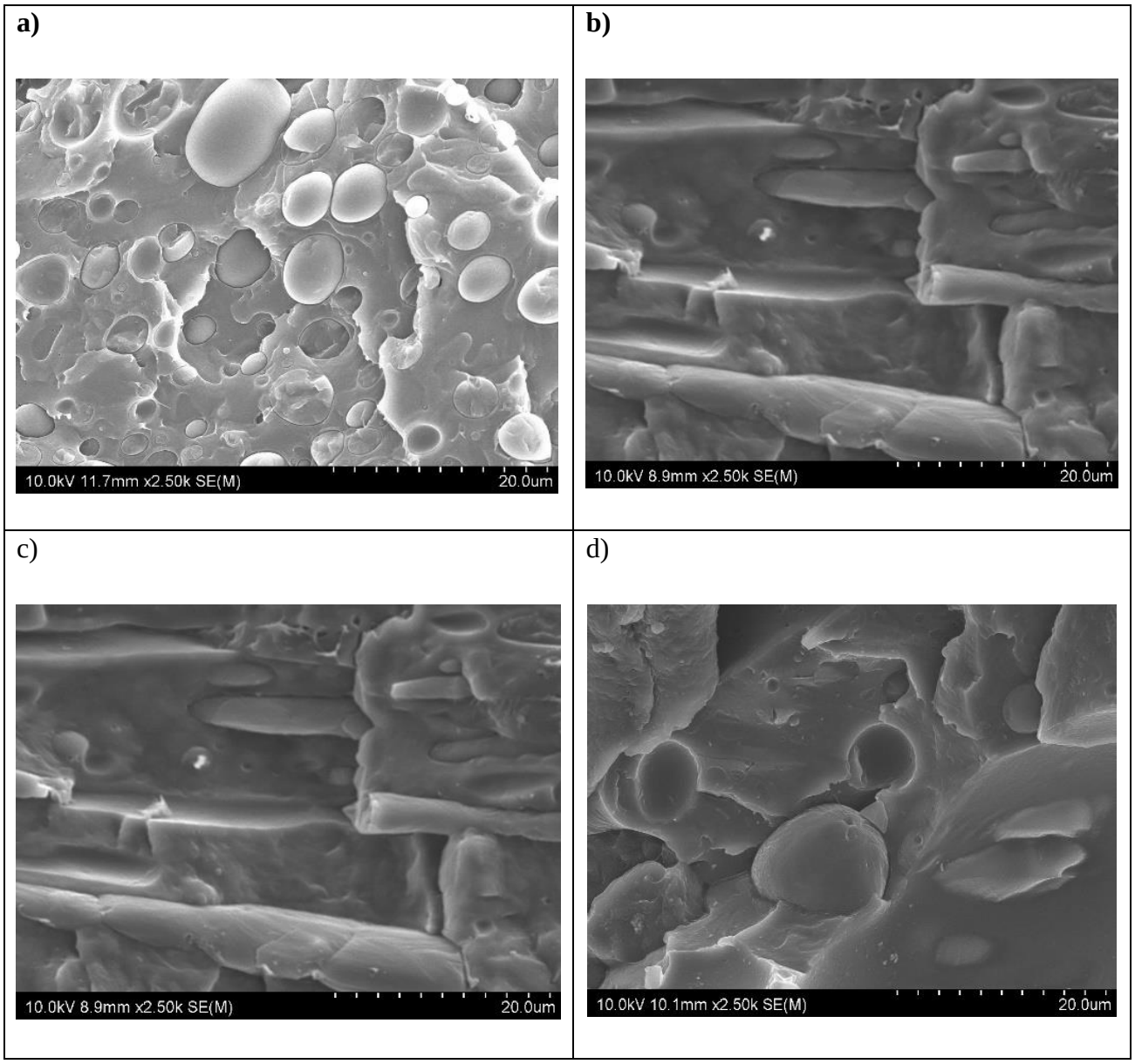


Fig 6. 9 SEM of Plasticized PLA-PCL Blends a) PLA-PCL20, b) PLA-PCL20-P1, c) PLA-PCL20- P2, d) PLA-PCL20-P3

6.2.3 Water vapor transmission rates (WVTR) of Plasticized PLA-PCL Blend films

Plasticization of PLA-PCL20 blend was carried out for improving ductility/ elongation at break, but it may alter the barrier/ WVTR characteristics. Hence studies were carried out on WVTR of plasticized blends, and the results obtained are presented in Table 6.7 and Fig 6.10

The results obtained show a slight increase in WVTR/ reduction in barrier property due to plasticization. The WVTR of the plasticized blends with P1, P2, and P3 were found to be 197, 183, and 180 g m^{-2} d^{-1} respectively, compared to 170 g m^{-2} d^{-1} for an un-plasticized blend.

Table 6. 7 WVTR of Plasticized PLA-PCL blend films, at 25^0C, 100% RH, for 25µm film thickness

Film	**WVTR at 25°C, 100% RH, for 25µm film g.m^{-2}d^{-1}**
PLA-PCL20	170±4.1
PLA-PCL20-P1	197±5.4
PLA-PCL20-P2	183±3.8
PLA-PCL20-P3	180±4.8

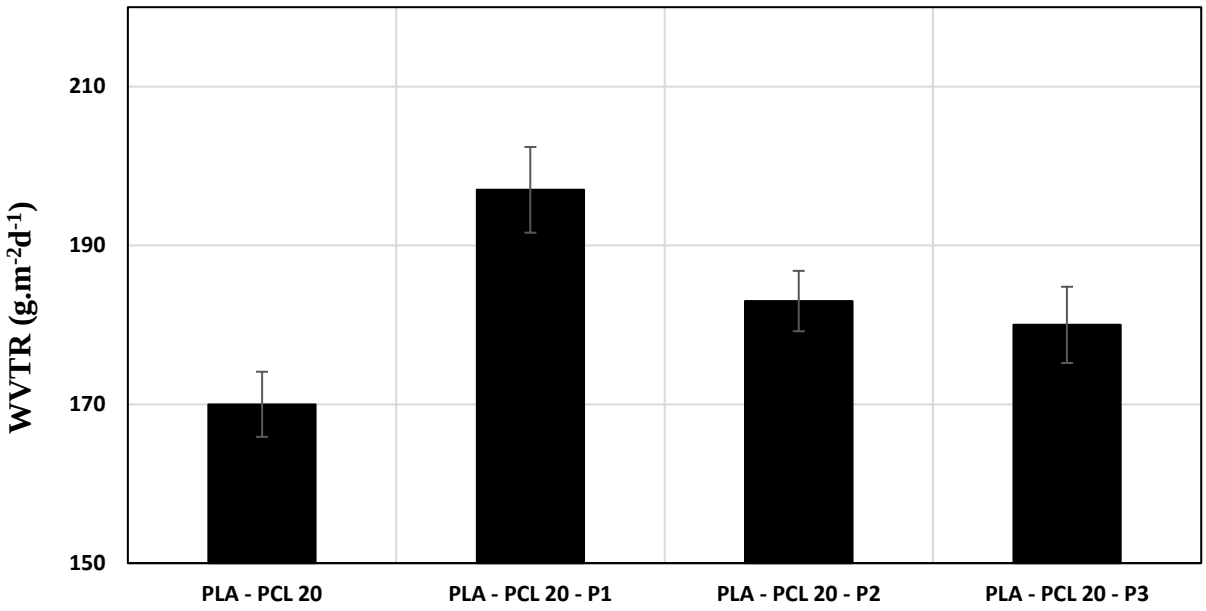


Fig 6. 10 WVTR of Plasticized PLA-PCL blend films, at 25^0C, 100% RH, for 25µm film thickness

A similar increase in the WVTR with a plasticizer ATBC is reported in the literature [152]. Gas transport is strongly associated with free volume, and the increased water vapor transport (WVTR) with the addition of plasticizer is due to an increase in free volume in a polymer matrix [223].

6.2.4 Biodegradation characteristics of Plasticized PLA-PCL Blend films

Biodegradation studies of the plasticized PLA-PCL blends were carried out in compost medium and seawater medium, for 180 days, at 25˚C, by measurement of CO_2 evolved at various time intervals.

- **Biodegradation in Compost medium, at ambient conditions**

The biodegradation test results for the plasticized PLA-PCL20 films in compost medium at 25˚C is given in Table 6.8 and Fig 6.11. The results show an increase in the biodegradation rate with the addition of all three plasticizers. The biodegradation rate of the un-plasticized PLA-PCL20 film was 12.6%, and after plasticization, it increased to 18.6%, 16.9 %, and 17.5% with plasticizer P1, P2, and P3, respectively. It corresponds to an increase of 47.6, 34.1, and 38.9%, respectively.

- **Biodegradation in seawater medium**

The biodegradation test results for the plasticized PLA-PCL blends in seawater medium is presented in Table 6. 9 and Fig 6.12

It can be seen from the results that the rate of biodegradation in seawater has increased with plasticization. The biodegradation rate of un-plasticized PLA-PCL20 film was 4.2%, increased to 6.1%, 4.9%, and 5.5% on plasticization with P1, P2, and P3, respectively, which corresponds to an increase by 56.4%, 25.6%, and 41%, respectively.

A higher biodegradation rate was observed with all plasticizers in compost and in seawater medium. Maximum biodegradation rate was obtained with monomeric plasticizer P1 and minimum with polymeric plasticizer P2.

An increase in biodegradation by adding plasticization is reported in the literature [81, 83]. Higher biodegradation rate obtained with monomeric plasticizer may be due to its low molecular weight, higher plasticizing efficiency [224] and hence increased free volume in the polymer matrix, and lower water barrier property upon plasticization, which facilitate more easy penetration of water molecules, bacteria, and enzymes for biodegradation.

Table 6. 8 Cumulative amount of CO_2 evolved and % biodegradation for plasticized PLA-PCL blends & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25^0C.

	Cellulose Reference (ThCO₂:3.23g)		**PHB-PCL20 (ThCO₂:3.86g)**		**PHB-PCL20- P1 (ThCO₂:3.84g)**		**PHB-PCL- P2 (ThCO₂:3.85g)**		**PHB-PCL- P3 (ThCO₂:3.86g)**	
Time Days	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**
0	0	0	0	0	0	0	0	0	0	0
15	0.16	4.9±1.2	0.00	0	0	0	0	0	0	0
30	0.27	8.4±1.6	0.04	1±2.4	0.12	3.1±2.4	0.08	2.1±1.4	0.09	2.4±2.4
45	0.67	20.7±1.4	0.06	1.6±1.5	0.22	5.6±1.6	0.09	2.3±2.5	0.13	3.4±1.6
60	0.96	29.7±2.5	0.12	3.2±2.6	0.25	6.4±2.9	0.18	4.7±1.7	0.21	5.4±2.8
75	1.17	36.4±1.6	0.15	3.8±2.4	0.35	9.2±2.7	0.19	4.9±2.8	0.25	6.4±1.9
90	1.39	43.1±1.4	0.17	4.3±1.7	0.40	10.4±1.8	0.23	5.9±1.9	0.37	9.7±2.4
105	1.77	54.7±2.5	0.20	5.1±2.8	0.48	12.4±1.9	0.32	8.4±2.4	0.44	11.4±1.6
120	1.94	60.2±1.6	0.25	6.4±1.9	0.49	12.7±2.4	0.41	10.7±1.6	0.46	12±2.4
135	2.31	71.5±2.4	0.27	7±2.4	0.56	14.5±2.1	0.43	11.2±2.5	0.51	13.1±2.8
150	2.45	75.9±1.4	0.32	8.2±1.6	0.62	16.1±1.9	0.45	11.8±1.4	0.56	14.5±1.7
165	2.64	81.8±1.5	0.34	8.8±2.4	0.64	16.7±1.6	0.52	13.4±1.6	0.58	15.1±2.6
180	2.66	82.3±1.6	0.49	12.6±1.6	0.71	18.6±1.7	0.65	16.9±2.7	0.68	17.5±2.4

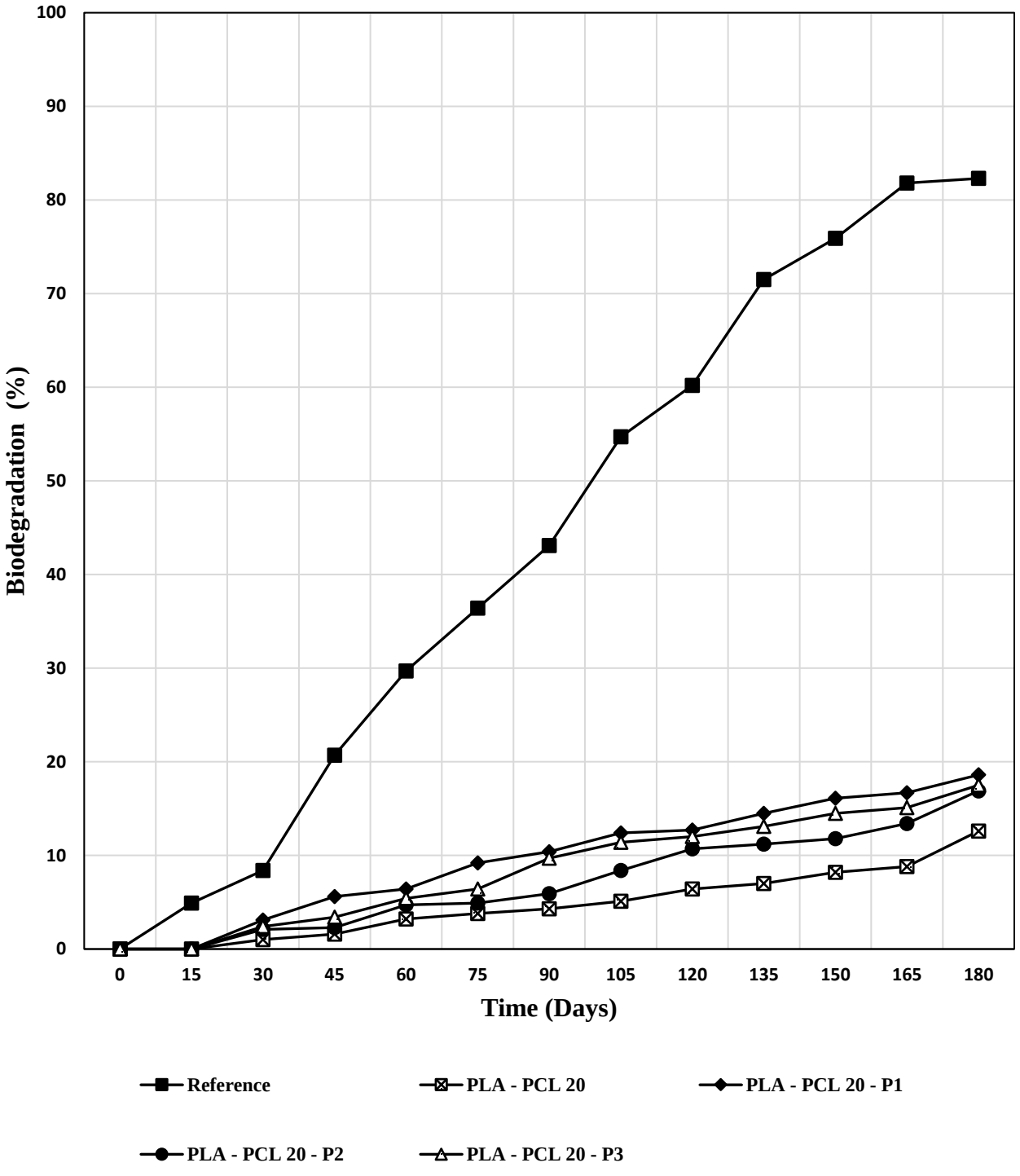


Fig 6. 11 Biodegradation curve of Plasticized PLA-PCL blends, in compost at 25^0C

Table 6. 9 Cumulative amount of CO_2 evolved and % biodegradation for plasticized PLA-PCL blends & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25^0C.

	Cellulose Reference (ThCO₂:6.45g)		**PHB-PCL20 (ThCO₂:7.71g)**		**PHB-PCL20- P1 (ThCO₂:7.69g)**		**PHB-PCL- P2 (ThCO₂:7.71g)**		**PHB-PCL- P3 (ThCO₂:7.71)**	
Time Days	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**	**ΣCO₂ (g)**	**%D**
0	0	0	0	0	0	0	0	0	0	0
15	0.04	0.6±1.5	0.00	0	0.00	0	0.00	0	0.00	0
30	0.14	2.1±1.4	0.01	0.2±1.4	0.05	0.7±2.4	0.02	0.2±1.4	0.03	0.4±2.4
45	0.41	6.4±2.6	0.05	0.7±1.9	0.14	1.8±1.8	0.06	0.8±1.9	0.08	1.1±1.6
60	0.75	11.6±2.8	0.09	1.2±2.7	0.16	2.1±2.7	0.11	1.4±1.4	0.18	2.3±2.8
75	1.02	15.8±1.7	0.10	1.3±2.4	0.23	3±1.6	0.19	2.4±2.6	0.26	3.4±1.4
90	1.44	22.3±2.9	0.17	2.3±1.6	0.28	3.7±2.4	0.20	2.6±2.4	0.28	3.6±2.9
105	1.60	24.8±2.6	0.21	2.8±1.8	0.31	4±1.6	0.26	3.4±1.8	0.32	4.1±1.4
120	1.90	29.4±2	0.23	3.1±2.7	0.33	4.3±1.5	0.28	3.6±2.7	0.34	4.4±1.7
135	2.11	32.7±1.4	0.25	3.3±1.8	0.38	4.9±2.4	0.29	3.8±1.6	0.35	4.6±1.2
150	2.21	34.3±2.6	0.27	3.6±1.4	0.39	5.1±2.7	0.31	4±1.4	0.37	4.8±2.4
165	2.48	38.5±1.7	0.29	3.8±2.5	0.45	5.9±1.9	0.35	4.6±2.8	0.41	5.3±2.6
180	2.59	40.2±2.9	0.32	4.2±2.1	0.47	6.1±2.4	0.38	4.9±2.7	0.42	5.5±2.7

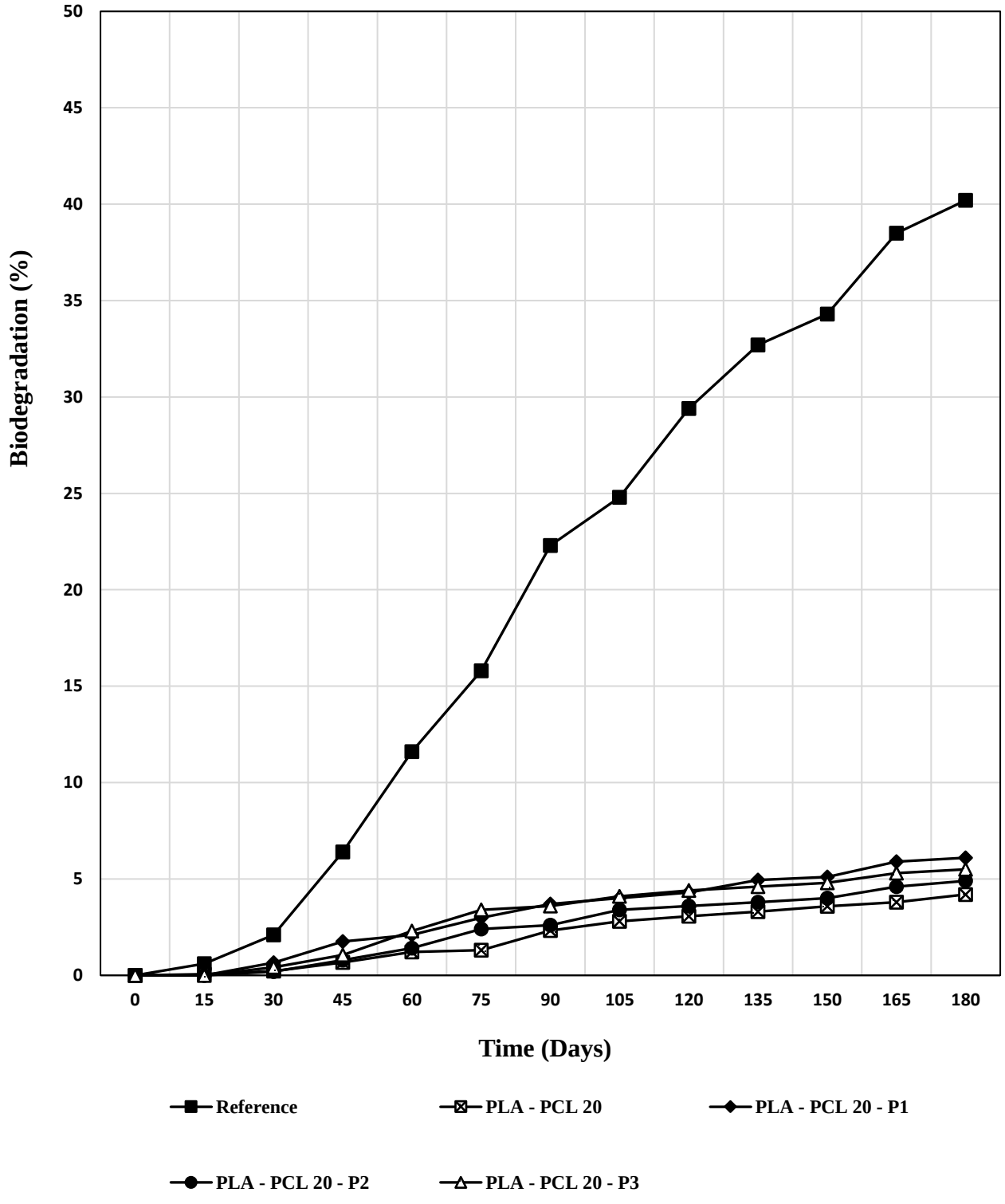


Fig 6. 12 Biodegradation curve of Plasticized PLA-PCL blends, in seawater at 25^0C.

6.3 Nanocomposite films based on PLA-PCL blend

Nanocomposite films based on plasticized PLA-PCL20 blend were prepared using 1, 3, and 6 wt% of Nano cellulose (nCell) and Nano clay (nClay) by melt blending the nanomaterials with the plasticized blend, followed by injection molding and hot pressing to 0.25mm thickness films.

6.3.1 Appearance/ Photographs of Nanocomposite films based on PLA - PCL

The photographs of the nanocomposite films of plasticized PLA-PCL20 blend with 1, 3, and 6 wt % nano cellulose and nano clay are shown below. Nanocomposite films with 1 wt% nano cellulose and all the nano clay-based films and were uniform in appearance. The films with 3 and 6 wt % nano cellulose were slightly non-uniform in appearance.

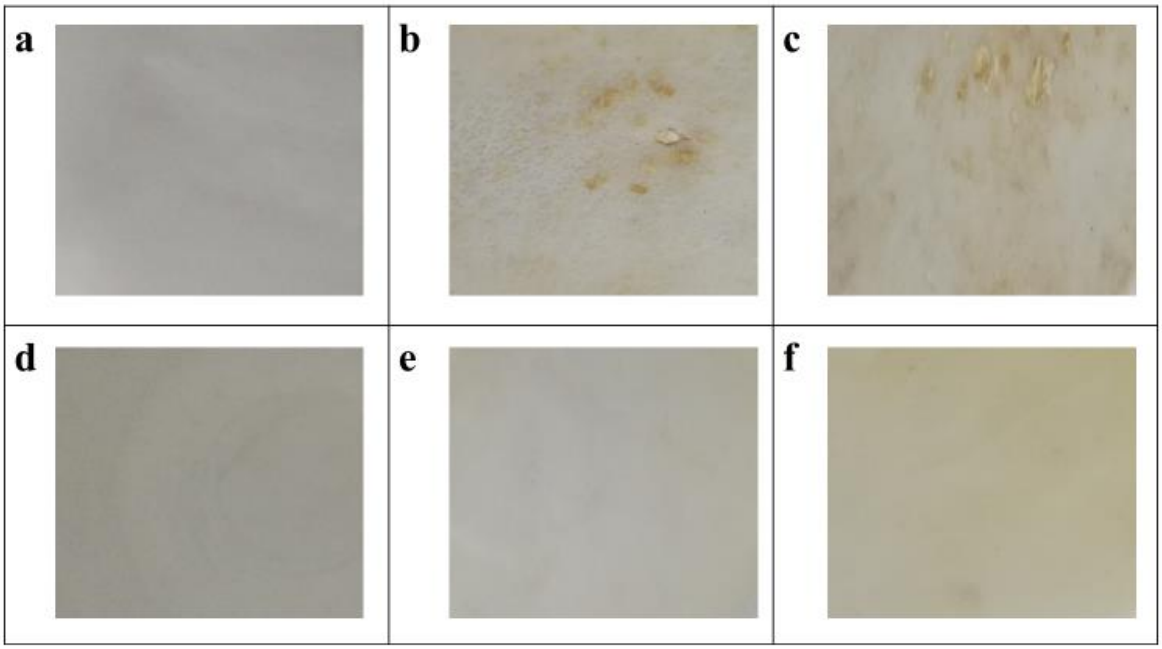


Fig 6. 13 Photographs of Nano composite films based on PLA - PCL a) PLA-PCL20- P3-nCell 1, b) PLA-PCL20- P3-nCell 3, c) PLA -PCL20- P3-nCell 6, d) PLA-PCL20- P3-nClay 1, e) PLA-PCL20- P3-nClay 3, f) PLA-PCL20- P3-nClay 6

6.3.2 Tensile properties of Nanocomposite films based on PLA – PCL

Studies were carried out on the tensile properties of polymer nanocomposites based on plasticized PLA-PCL 20 with nano cellulose, and nano clay and the results obtained are shown in Table 6.10 and Fig 6.14 and 6.15.

With both the nanomaterials, a continuous decrease of elongation at break with increasing amounts of nano-materials was observed. In nano-cellulose, the drop in tensile elongation with a nanomaterial concentration was steeper compared to nano-clay.

The observed elongation at break of nanocomposites based on 1, 3 & 6 % nano-cellulose were 18.4%, 14.2 %, and 6.3% respectively. For nano-clay based nano-composites the elongation at break was 19.9%, 18.7% and 17.8% respectively for 1, 3 & 6% loading of nano-clay.

Regarding the effect of nanomaterials on tensile strength, the effects were different. With nano-cellulose, a smaller decrease in tensile strength was observed. The tensile strength was 22.2 MPa for material without any nano-material, and for the nano-composites with 1, 3, and 6% nano-cellulose, the observed values of tensile strength were 20.9, 20.5, and 18.8 MPa, respectively.

In the case of nano-clay based composite, there was a slight increase in tensile strength with the addition of nano clay. The tensile strength value observed for 1, 3 & 6% nano-clay-based nanocomposites was 24.1, 28.2, and 28.8 MPa, respectively.

Table 6. 10 Tensile properties of nanocomposite films based on PLA – PCL

Film		Tensile strength (MPa)	Elongation at break (%)
PLA-PCL20- P3		22.2±0.7	20.1±1.4
Nano Cellulose	**PLA-PCL20- P3-nCell 1**	20.9±1.8	18.4±1.6
	PLA-PCL20- P3-nCell 3	20.5±1.4	14.2±0.7
	PLA-PCL20- P3-nCell 6	18.8±2.4	6.3±1.8
Nano Clay	**PLA-PCL20- P3-nClay1**	24.1±0.9	19.9±1.3
	PLA-PCL20- P3-nClay3	28.2±1.9	18.7±0.8
	PLA-PCL20- P3-nClay6	28.8±1.7	17.8±1.1

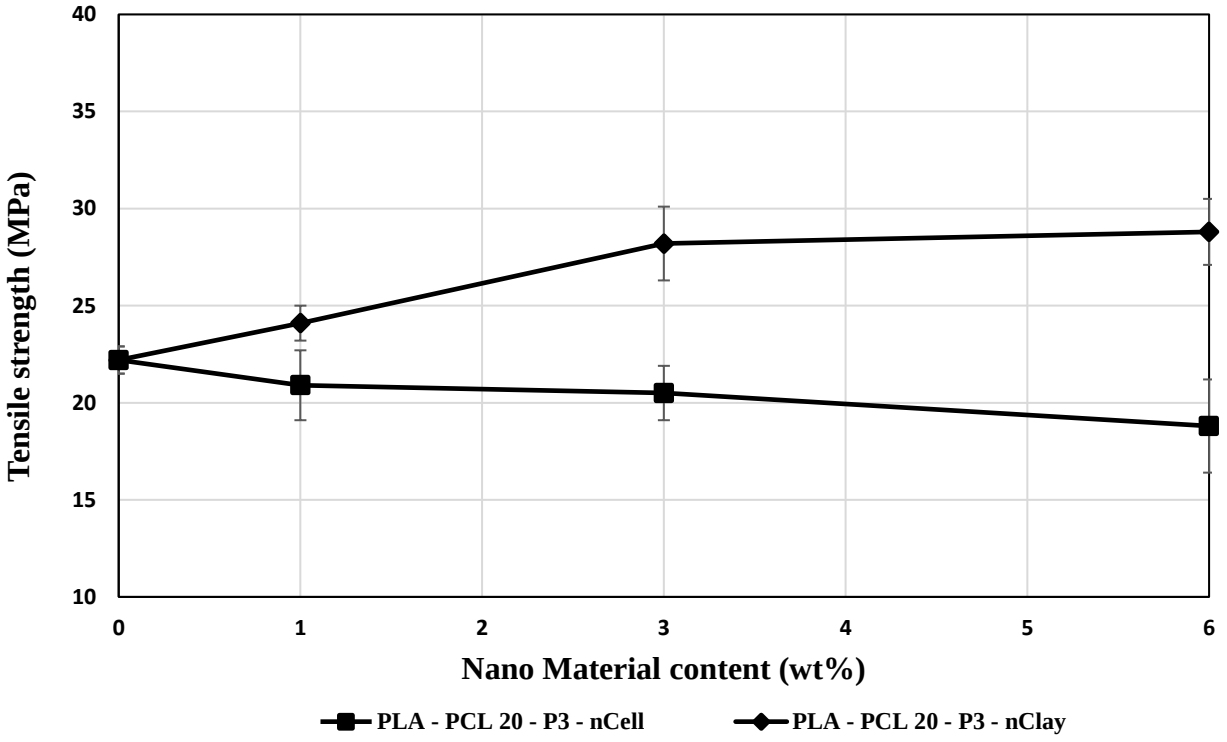


Fig 6. 14 Tensile Strength of nanocomposite films based on PLA - PCL

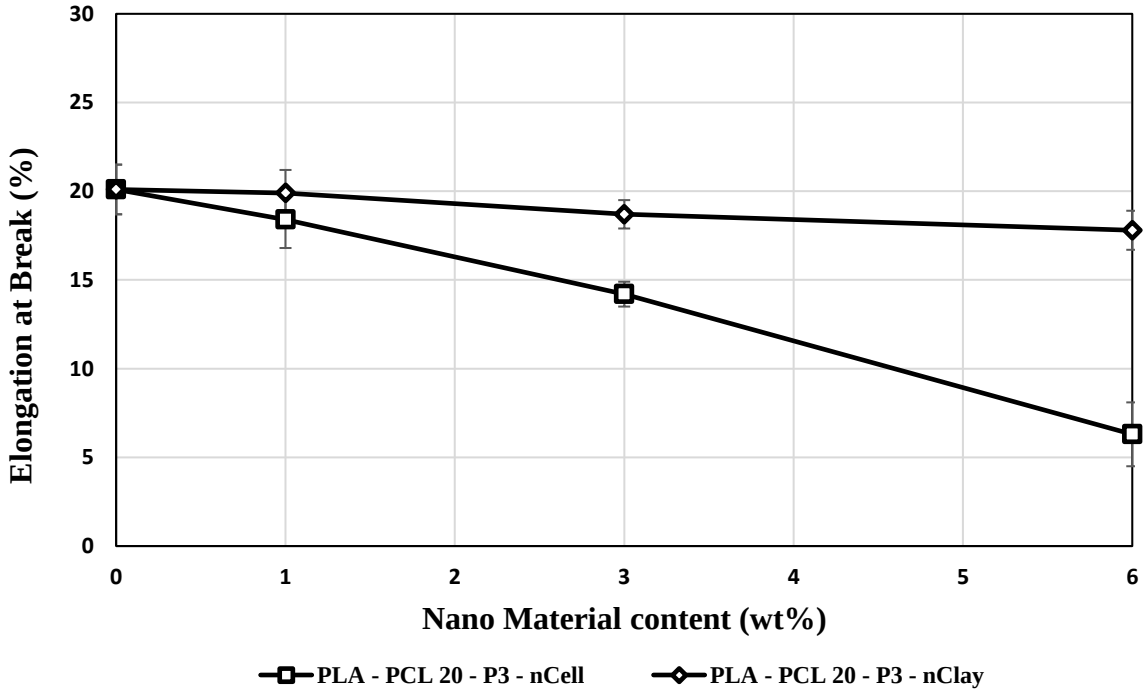
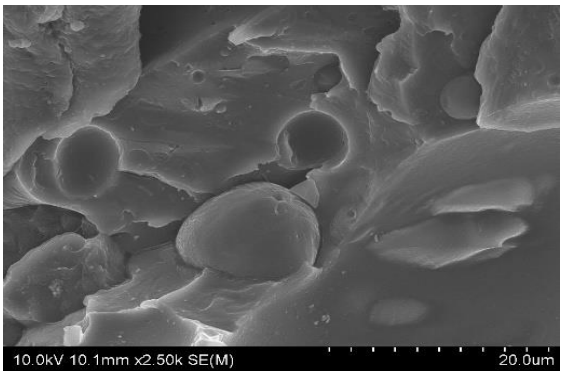


Fig 6. 15 Elongation at break of nanocomposite films based on PLA – PCL

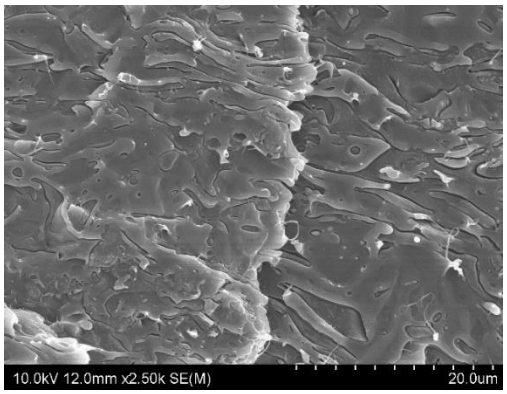
Few researchers have reported an increase in the tensile strength and a decrease in elongation at break with nanomaterials. [133, 161]. A slight increase in the tensile strength observed by us with the addition of nano-clay may be due to clay nanoparticles' reinforcement effect. However, an increase was not observed with nano cellulose, perhaps due to its weaker integration with the polymer chains, compared to nano clay, since the surface of nano cellulose was not organically modified, unlike the organically modified nano clay used. A decrease in the elongation at break observed with nanomaterials' addition may be due to the higher interaction between the nanomaterial, because of high surface area available with nanomaterial, and the restricted mobility of the polymer chains.

Scanning electron microscopy studies of the polymer nanocomposites were carried out to understand the phase morphology and distribution of nanoparticles, and the SEM images are shown in Fig 6.16 a - e. The image (Fig 6.16a) shows the SEM images of plasticized PLA-PCL20 blend without nanomaterial, and images Fig 6.16 b and c show the images for 1 and 6 wt% nano cellulose, and SEM image d and e show the images for 1 and 6 wt% nano clay respectively. Comparing the SEM images of nanocomposites with that of blend without nanomaterials (image a) indicates a drastic change in morphology. The spherulites of PCL seen in the image ‘a’ (blend without nanomaterial) can be seen elongated in other images for the nanocomposites because of the strong interaction between the nanomaterial and polymer chains and might have improved the tensile strength of nano clay-based nanocomposites, which might have reduced the mobility of the polymer chains and reduced ductility.

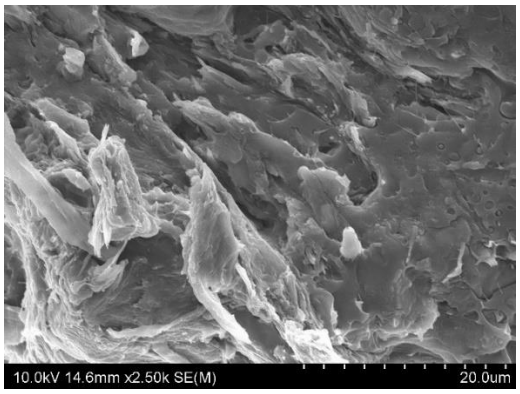
a)



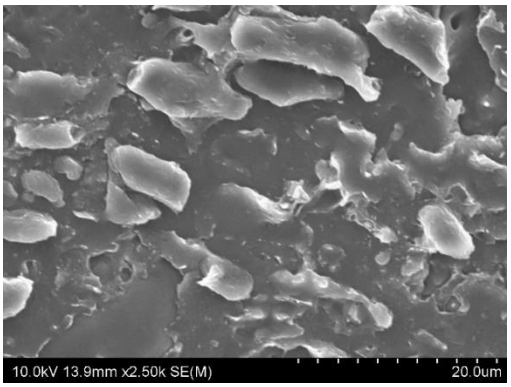
b)



c)



d)



e)

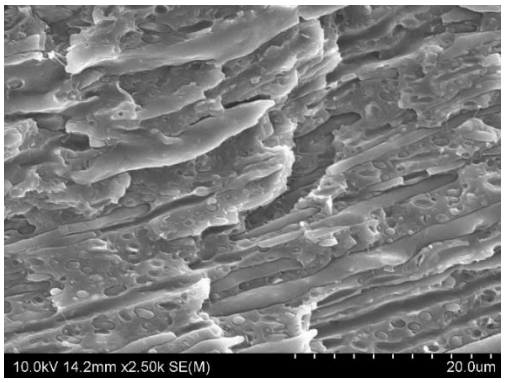


Fig 6. 16 Morphology/ SEM of Nano composite films based on PLA - PCL a) PLA-PCL20- P3, b) PLA-PCL20- P3-nCell 1, c) PLA -PCL20- P3-nCell 6, d) PLA-PCL20- P3-nClay 1, e) PLA-PCL20- P3-nClay 6

6.3.3 Water vapor transmission rates (WVTR) of Nano-composite films based on PLA-PCL

An investigation was carried out on barrier properties/ water vapor transmission rates of nano-composite films based on plasticized PLA-PCL, with 1, 3 & 6% nano-cellulose and nano-clay, and the WVTR test results are given in Table 6.11 and Fig 6.17

It was observed that incorporation of both the nanomaterials resulted in lowering WVTR/ improvement of barrier property. The WVTR of plasticized PLA-PCL20 was 180 g m^{-2} $d^{-1,}$ and the addition of 1% nano-cellulose resulted in a decrease in WVTR to a value of 126 g m^{-2} $d^{-1,}$ and then there was no further reduction with further addition of Nano cellulose. The addition of 3% and 6% nano-cellulose increased WVTR to 137 and 168 gm^{-2} d^{-1}. The lowest WVTR value obtained with nano-cellulose was 126 g m^{-2} d^{-1} for the nanocomposite with a 1% nano-cellulose loading.

In the case of nanocomposites based on nano-clay, the WVTR values observed were 137, 102, and 94 g m^{-2} d^{-1} for nano-composites with 1, 3, and 6% nano-clay, respectively. The lowest WVTR obtained with nano-clay was 94 g m^{-2} d^{-1} for the nanocomposite with a 6% nano-clay loading.

Comparison of effects of low loadings of nano-cellulose and nano-clay indicates that nano-cellulose is equally or / slightly more effective compared to nano clay at 1wt% loading. WVTR of 1% nano-cellulose based nano-composite of PLA-PCL20 was 126 g m^{-2} d^{-1}, while WVTR of 1% nano-clay based nano-composite was 137 g m^{-2} d^{-1}. At higher loadings, nano clay was more effective in lowering the WVTR.

Table 6. 11 WVTR of Nano Composites films based on PLA-PCL, at 25ºC, 100% RH, ($g.m^{-2}d^{-1}$) 25µm film thickness

Film		Water vapor transmission rate (WVTR) at 25°C, 100% RH, $g.m^{-2}d^{-1}$, for 25µm film
PLA-PCL20- P3		180±4.8
Nano Cellulose	PLA-PCL20- P3-nCell1	126±3.7
	PLA-PCL20- P3-nCell3	137±2.6
	PLA-PCL20- P3-nCell6	168±2.4
Nano Clay	PLA-PCL20- P3-nClay1	137±2.4
	PLA-PCL20- P3-nClay3	102±3.4
	PLA-PCL20- P3-nClay6	94±2.8

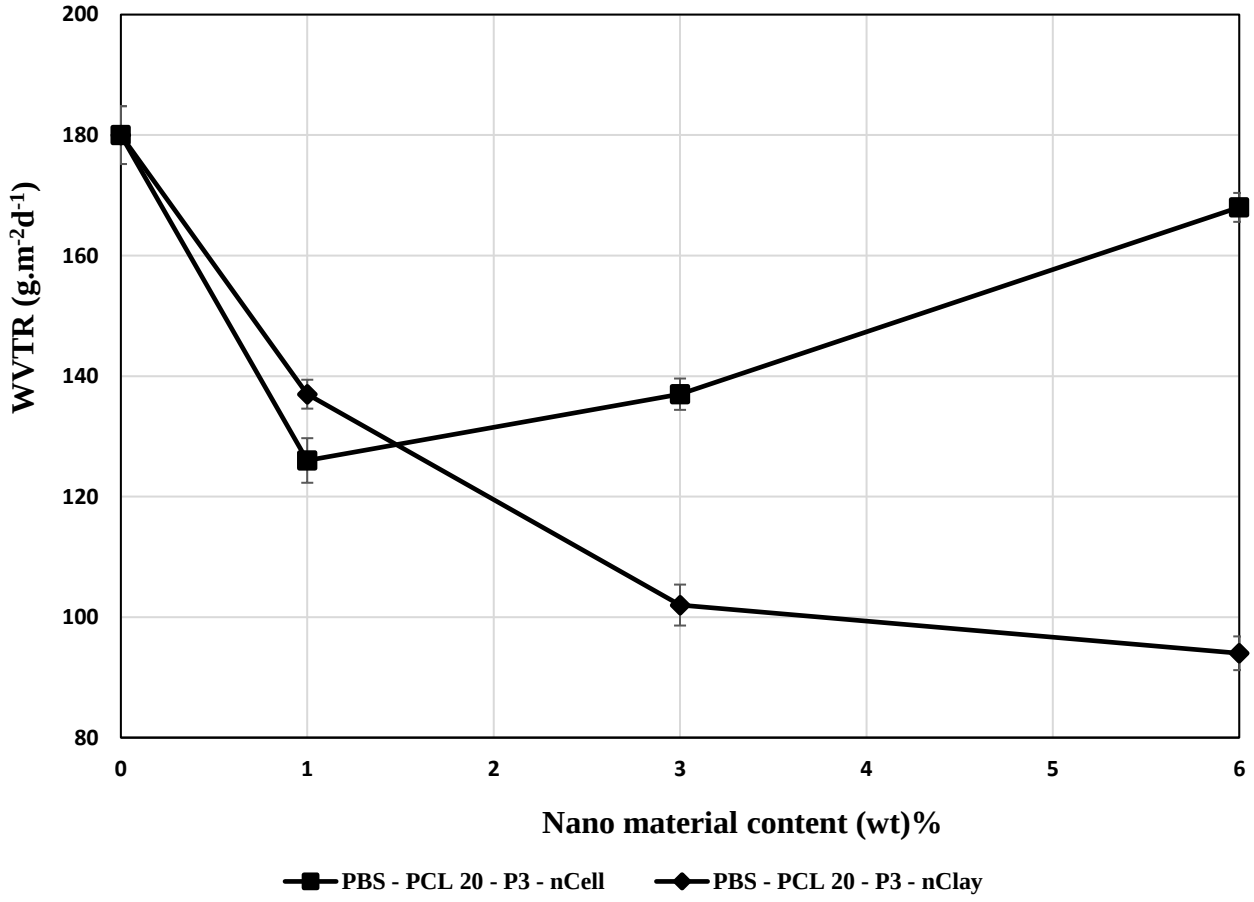


Fig 6. 17 WVTR of Nano Composites films based on PLA-PCL, at 25ºC, 100% RH, 25µm film thickness.

A decrease in the WVTR/ improvement in barrier property with nanomaterials such as nano clay is reported [163]; however, not much success is reported with nano cellulose, though it has more advantages /such as biodegradability. The decrease in WVTR with nanomaterials' addition is due to the changes in the gas diffusion pathways for the penetrant molecules, due to the formation of more torturous and more prolonged pathways by the addition of nanomaterials. [82].

6.3.4 Biodegradation characteristics of Nanocomposites films based on PLA - PCL

Biodegradation studies of polymer nanocomposites based on PLA-PCL blend with 1wt% nano cellulose and 6 wt% nano clay were carried out in compost medium and in seawater medium, for 180 days, at 25°C and the results are presented below:

- **Biodegradation of nanocomposites in compost medium, at 25°C**

The test results about the biodegradation of nanocomposites based on PLA-PCL blend in compost medium, at 25°C, are presented in table 6.12 and Fig 6.18. The test results show an increase in biodegradation rate with the addition of both nano cellulose and nano clay, compared to plasticized PLA-PCL20-P3 blend, without nanomaterials.

The biodegradation rate of nano cellulose and nano clay-based nanocomposites were 20.1% and 18.6%, respectively, compared to 17.5% for the blend without nanomaterial, which shows an improvement in biodegradability by 14.9% and 6.3 respectively with the addition of nano cellulose and nano clay. The biodegradation rate of nanocomposite with nano cellulose (1 wt%) was higher than of nanocomposite with nano clay (6 wt%).

- **Biodegradation of nanocomposites in seawater medium at 25°C**

The biodegradation test results of nanocomposites of PLA-PCL blend in seawater at 25°C is shown in Table 6.13 and Fig 6.19. The biodegradation test results indicate a low biodegradation rate for the nano cellulose-based and nano clay-based PLA nanocomposites, compared to reference cellulose (40.2% biodegradation) at ambient conditions.

The biodegradation rate for the nanocomposites with nano cellulose and nano clay was found to be 6.9% and 5.8%, respectively, compared to 5.5% biodegradation for the PLA-PCL20-P3 blend without nanomaterial. The increase though very small, corresponds to an increase in biodegradation by 25.5% and 5.5%, respectively, for the nanocomposites with nano cellulose and nano clay.

The above-observed increase in biodegradation with the addition of nanomaterials, especially with nano cellulose, may be due to increased wettability due to the presence of many free hydroxyl groups on its surface, which accelerates attachment of bacteria and enzymes on the nanocomposites and thereby facilitating biodegradation.

Comparatively lower increase in biodegradability was observed for the nano clay-based nanocomposite than the nano cellulose-based nanocomposite, which may be due to the higher water barrier property of 6wt % nano clay. Few of the investigators have observed increased biodegradation of PLA with nano clay [19, 166], while few other researchers have observed decreased biodegradation of PLA with nano clay [165, 167].

Table 6. 12 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PLA - PCL & reference sample (2 grams), at various time intervals, during biodegradation in compost, at 25^0C.

	Cellulose Reference ($ThCO_2$:3.23 g)		**PHB - PCL20 - P3 ($ThCO_2$:3.86 g)**		**PHB - PCL20 - P3 -nCell1 ($ThCO_2$: 3.85g)**		**PHB - PCL20 - P3 – nClay6 ($ThCO_2$: 3.62g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0	0	0	0	0	0	0	0
15	0.16	4.9±1.2	0	0	0	0	0	0
30	0.27	8.4±1.6	0.09	2.4±2.4	0.12	3.2±1.6	0.08	2.3±2.4
45	0.67	20.7±1.4	0.13	3.4±1.6	0.22	5.7±2.7	0.12	3.2±1.6
60	0.96	29.7±2.5	0.21	5.4±2.8	0.24	6.2±1.9	0.21	5.7±2.8
75	1.17	36.4±1.6	0.25	6.4±1.9	0.37	9.5±2.8	0.25	6.8±2.3
90	1.39	43.1±1.4	0.37	9.7±2.4	0.38	9.9±1.6	0.29	8.1±1.4
105	1.77	54.7±2.5	0.44	11.4±1.6	0.45	11.7±2.4	0.39	10.7±1.8
120	1.94	60.2±1.6	0.46	12±2.4	0.49	12.6±1.5	0.42	11.5±1.7
135	2.31	71.5±2.4	0.51	13.1±2.8	0.52	13.6±2.3	0.46	12.8±2.6
150	2.45	75.9±1.4	0.56	14.5±1.7	0.62	16±1.2	0.59	16.3±2.4
165	2.64	81.8±1.5	0.58	15.1±2.6	0.69	17.9±1.6	0.62	17±1.9
180	2.66	82.3±1.6	0.68	17.5±2.4	0.77	20.1±2.4	0.67	18.6±1.8

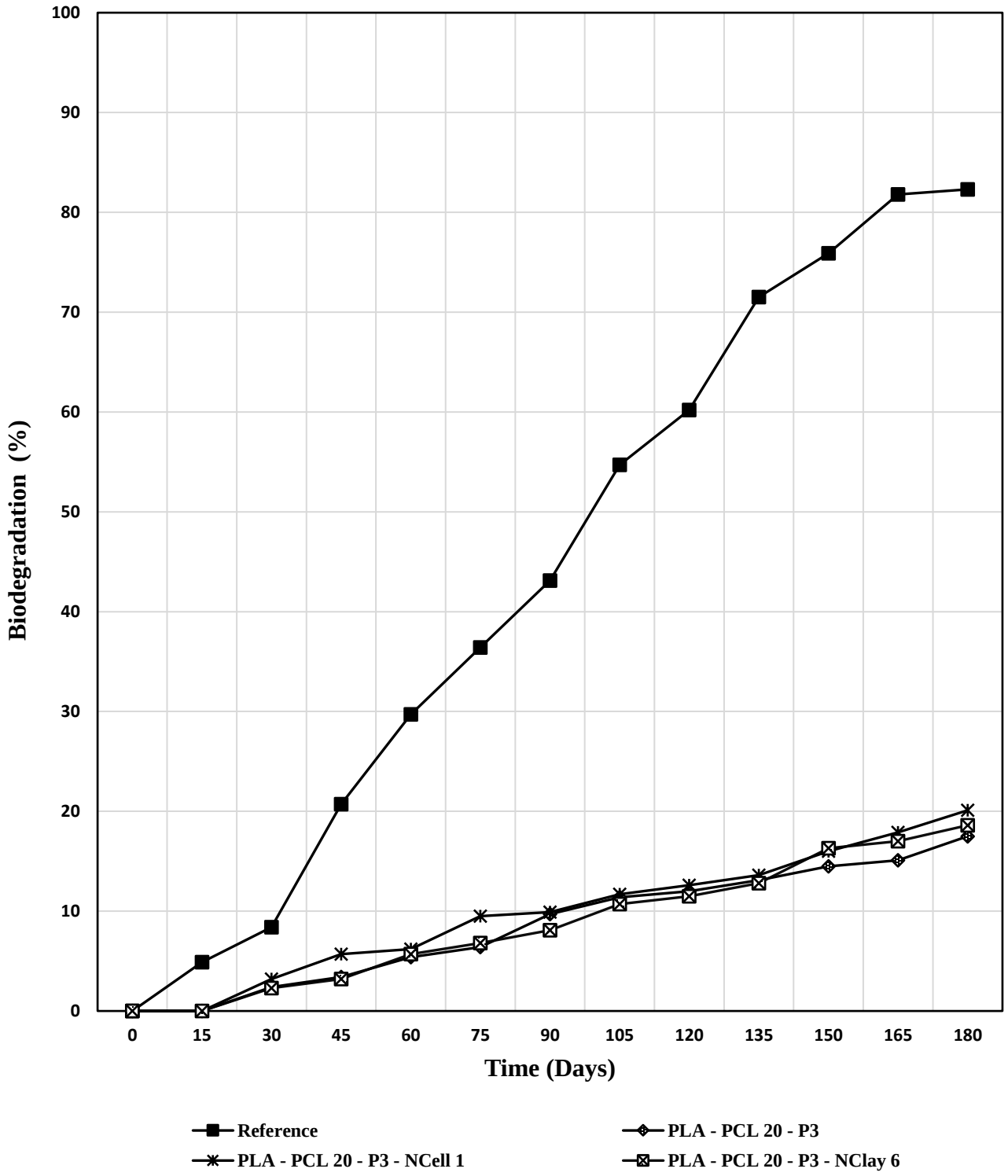


Fig 6. 18 Biodegradation curve of Nano composites films based on PLA - PCL, in compost at 25^0C.

Table 6. 13 Cumulative amount of CO_2 evolved and % biodegradation for Nanocomposites films based on PLA - PCL & reference sample (4 grams), at various time intervals, during biodegradation in Seawater, at 25^0C.

	Cellulose Reference ($ThCO_2$: 6.45g)		**PHB - PCL20 - P3 ($ThCO_2$: 7.71g)**		**PHB - PCL20 - P3 -nCell1 ($ThCO_2$:7.70 g)**		**PHB - PCL20 - P3 – nClay6 ($ThCO_2$:7.25 g)**	
Time Days	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**	**ΣCO_2 (g)**	**%D**
0	0	0	0	0	0	0	0	0
15	0.04	0.6±1.5	0.00	0	0.00	0	0.00	0
30	0.14	2.1±1.4	0.03	0.4±2.4	0.09	1.1±2.5	0.06	0.9±1.7
45	0.41	6.4±2.6	0.08	1.1±1.6	0.16	2±1.6	0.11	1.5±1.6
60	0.75	11.6±2.8	0.18	2.3±2.8	0.23	2.9±3.1	0.16	2.2±2.4
75	1.02	15.8±1.7	0.26	3.4±1.4	0.32	4.2±1.7	0.20	2.8±1.8
90	1.44	22.3±2.9	0.28	3.6±2.9	0.35	4.5±2.4	0.24	3.3±1.4
105	1.60	24.8±2.6	0.32	4.1±1.4	0.36	4.7±1.4	0.28	3.9±2.5
120	1.90	29.4±2	0.34	4.4±1.7	0.39	5±2.8	0.31	4.3±2.4
135	2.11	32.7±1.4	0.35	4.6±1.2	0.49	6.3±1.7	0.36	5±1.4
150	2.21	34.3±2.6	0.37	4.8±2.4	0.51	6.6±2.4	0.39	5.4±1.5
165	2.48	38.5±1.7	0.41	5.3±2.6	0.52	6.8±1.6	0.41	5.6±1.6
180	2.59	40.2±2.9	0.42	5.5±2.7	0.53	6.9±2.9	0.42	5.8±1.7

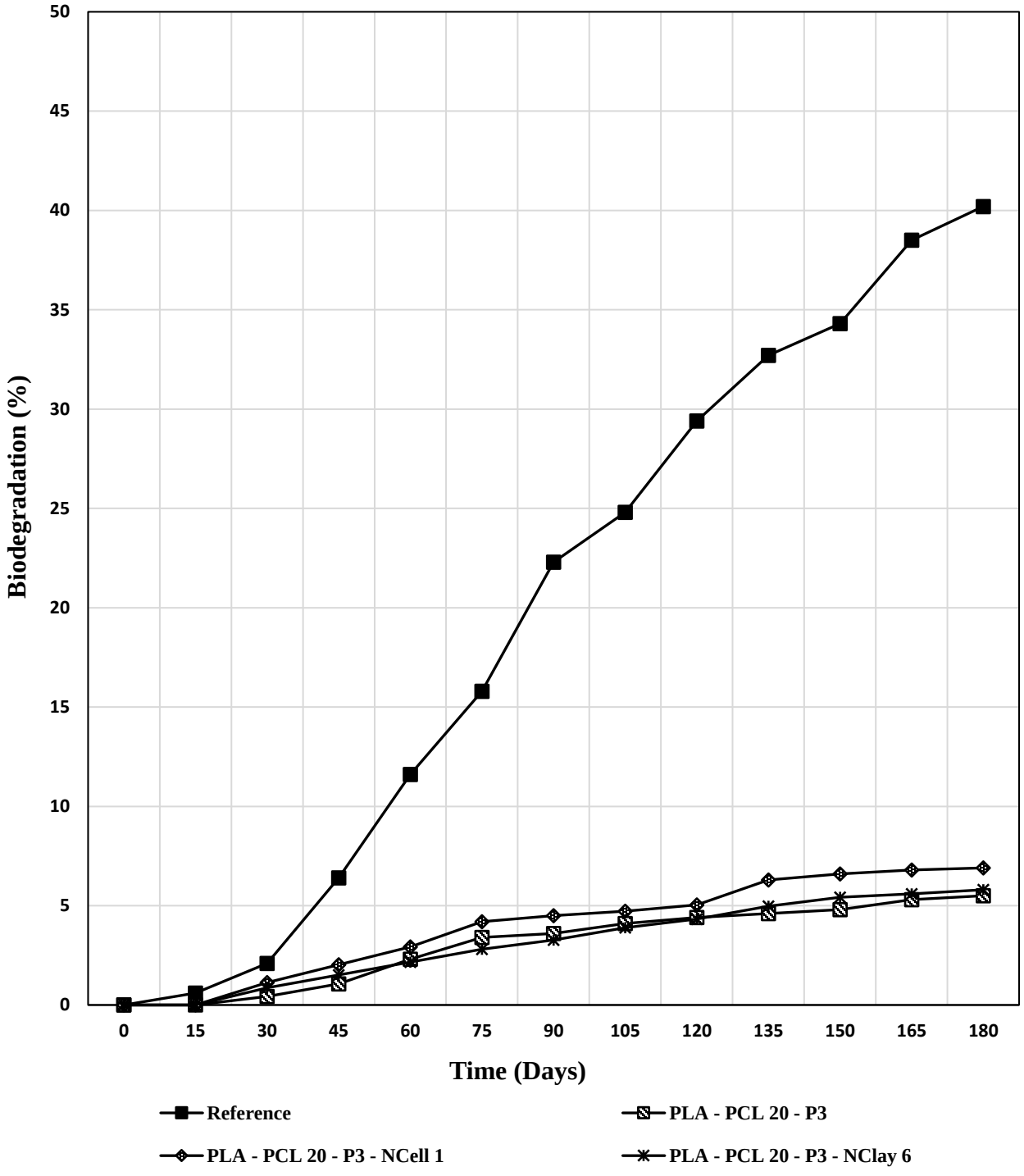


Fig 6. 19 Biodegradation curve of Nano Composites films based on PLA - PCL, in seawater, at 25^0C.

6.4 Summary of investigation on PLA

The summary of the research findings related to the investigations on polylactic acid (PLA) polymer, for improving the polymer properties, with respect to tensile properties, barrier properties/ water vapor transmission rate (WVTR), and biodegradability characteristics, by blending, plasticization, and by incorporating nanomaterials, is given below in Table 6.14 and Table 6.15.

Table 6. 14 Summary of investigation of tensile test and barrier properties on PLA Blends / Composite

Material designation	**Elongation at Break %** **(% change)** **((cumulative))**	**Tensile strength MPa** **(% Change)** **((cumulative))**	**WVTR 25˚C, 100 RH, $gm^{-2}d^{-1}$** **(% change)** **((cumulative))**
PLA – PCL Blends			
PLA	3.1	36.5	244
PLA-PCL10	6.6 (112.9)	31.8 (-12.9)	188 (-23.0)
PLA-PCL20	8.4 (171.0)	28.4 (-22.2)	170 (-30.3)
PLA-PCL30	9.2 (196.8)	26.3 (-27.9)	164 (-32.8)
PLA-PCL40	11.6 (274.2)	16.2 (-55.6)	160 (-34.4)
Plasticized PLA-PCL Blends			
PLA-PCL20-P1	21.2 (152.4) **((583.9))**	18.2 (-35.9) **((-50.1))**	197 (15.9) **((-19.3))**
PLA-PCL20- P2	14.8 (76.2) **((377.4))**	20.5 (-27.8) **((-43.8))**	183 (7.6) **((-25.0))**
PLA-PCL20- P3	20.1 (139.3) **((548.4))**	22.2 (-21.8) **((-39.2))**	180 (5.9) **((-26.2))**
Nanocomposites of PLA-PCL			
PLA-PCL20- P3 - nCell 1	18.4 (-8.5) **((493.5))**	20.9 (-5.9) **((-42.7))**	126 (-30.0) **((-48.4))**
PLA-PCL20- P3 - nCell 3	14.2 (-29.4) **((358.1))**	20.5 (-7.7) **((-43.8))**	137 (-23.9) **((-43.9))**
PLA -PCL20- P3 - nCell 6	6.3 (-68.7) **((103.2))**	18.8 (-15.3) **((-48.5))**	168 (-6.7) **((-31.1))**
PLA-PCL20- P3 - nClay 1	19.9 (-1.0) **((541.9))**	24.1 (8.6) **((-34.0))**	137 (-23.9) **((-43.9))**
PLA-PCL20- P3 - nClay 3	18.7 (-7.0) **((503.2))**	28.2 (27.0) **(-22.7)**	102 (-43.3) **((-58.2))**

PLA-PCL20- P3 - nClay 6	17.8 (-33.8) **((474.2))**	28.8 (29.7) **((-21.1))**	94 (-47.8) **((-61.5))**

( ) %change, (( )) %cumulative

Table 6. 15 Summary of investigation of Biodegradation on PLA Blends / Composite

Material designation	**Biodegradation (%) at 25˚C, for 180 days % change (% cumulative)**	
	Compost	**Seawater**
PLA – PCL Blends		
PLA	10.4	3.6
PLA-PCL10	12.8 (23.1)	3.9 (8.4)
PLA-PCL20	12.6 (21.2)	4.2 (16.6)
PLA-PCL40	19.3 (85.6)	8.4 (133.5)
Plasticized PLA-PCL Blends		
PLA-PCL20-P1	18.6 (47.6) **((78.8))**	6.1 (56.4) **((69.4))**
PLA-PCL20- P2	16.9 (34.1) **((62.5))**	4.9 (25.6) **((36.1))**
PLA-PCL20- P3	17.5 (38.9) **((68.3))**	5.5 (41.0) **((52.8))**
Nanocomposites of PLA-PCL		
PLA-PCL20- P3 - nCell 1	20.1 (14.9) **((93.3))**	6.9 (25.5) **((91.7))**
PLA-PCL20- P3 - nClay 6	18.6 (6.3) **((78.8))**	5.8 (5.5) **((61.1))**

( ) %change, (( )) %cumulative

The studies on the effect of blending PLA with PCL demonstrated improvement in tensile elongation (ε), improvement in water vapor barrier property (decrease in WVTR), and increased

in the biodegradation rate (in-home compost and seawater), with the addition of PCL, though with a decrease in tensile strength (σ). It studies indicated that PLA blending with 20% (10-30 %) PCL offers overall improved properties.

Investigations on plasticization of PLA-PCL20 blends showed an enhancement in the elongation at break and biodegradability with plasticizers' addition, though with a decrease in tensile strength (σ) and water vapor barrier property (increase in WVTR). Studies with three plasticizers P1, P2, and P3, showed that monomeric plasticizer P1 was found to offer the highest elongation at break and biodegradability while the mixed plasticizer P3 was found to provide the highest tensile strength and water vapor barrier property (lowest WVTR). The mixed plasticizer P3 was also found to have a medium elongation at break and medium biodegradability. Hence it was concluded that mixed plasticizer P3 offers the overall best performance.

Investigation of PLA nanocomposites demonstrated improved tensile strength and improved water vapor barrier properties (decrease in WVTR), and slightly higher biodegradation rate with both nanomaterials, a decrease in elongation at break. Studies on nanocomposites showed the overall best performance was obtained for nanocomposites with 1wt % nano cellulose and 6% nano clay. Compared to neat PLA, the nanocomposites, with nano cellulose (PLA-PCL20- P3 - nCell 1) and nano clay (PLA-PCL20- P3 - nClay 6) was found to have a higher elongation at break, lower WVTR (higher water vapor barrier properties), and slightly higher biodegradation in home compost and seawater medium.

The present study portrayed that, compared to neat PLA, plasticized PLA – PCL blends with nano cellulose (PLA-PCL 20- P3 - nCell 1) and nano clay (PLA-PCL 20–P3 – nClay 6) had higher elongation at break (494% & 474% higher), higher water vapor barrier properties/ lower WVTR (48% & 62% lower WVTR), and higher biodegradation in home compost (93 % & 79% higher) and seawater medium (92% & 61% higher), however, the plasticized PLA – PCL blends with low loading nano cellulose had more loss in tensile strength than high loading nano clay, which was 43% and 21% respectively, compared to neat PLA.

Chapter 7 summary of the research findings, conclusions, and recommendations

This chapter presents a summary of the research findings, conclusions, and recommendations for future investigations regarding biodegradable polymers for packaging applications:

7.0 Summary

During the current project, three commercially available, biodegradable aliphatic polyesters, namely, Polybutylene succinate (PBS), Polyhydroxybutyrate (PHB), and Polylactic acid (PLA), were chosen for investigation. To improve the properties of PBS, PHB, and PLA polymers, such as tensile properties, barrier properties (for water vapor), and biodegradability, research work was carried out by:

- Blending with Polycaprolactone (PCL) polymer (10, 20, 30, and 40 wt% PCL)
- Plasticization with three plasticizers (5 wt% GTA-a monomeric plasticizer, Ultramoll IV- a polymeric plasticizer, and 1:1 mixture of GTA+Ultramoll IV)
- Fabrication of nanocomposites, using nano cellulose and nano-clay (1, 3, and 6 wt%)

The summary of these investigations are given below:

7.1 Effect of blending PBS, PHB & PLA with PCL

Polybutylene succinate (PBS), Polyhydroxybutyrate (PHB), and Polylactic acid (PLA) polymers were blended with Polycaprolactone (PCL) polymer (10, 20, 30, and 40 wt%), and PBS-PCL, PHB-PCL, and PLA-PCL blend films of thickness 0.25mm were prepared by injection molding, followed by hot pressing. The polymer blends films were characterized for mechanical/ tensile properties, water vapor barrier properties, and biodegradability characteristics, and the summary of the results related to the effect of blending with PCL is given below:

7.1.1 Tensile testing of the PBS-PCL, PHB-PCL, and PLA-PCL blend films:

The tensile testing of the PBS-PCL, PHB-PCL, and PLA-PCL blend films was carried out as per ASTM D882-18 [200] method.

Tensile testing of PBS, PHB, and PLA and blends with PCL indicated an increase in the elongation at break (ε) for the blend films with an increasing PCL amount.

The tensile strength (σ) of PBS-PCL, PHB-PCL, and PLA-PCL was found to decrease with the addition of PCL, and the decrease was comparatively less up to 20% PCL**.**

The elongation at break for neat PBS, neat PHB*, and neat PLA was 83.3%, 8.0%, and 3.1%, respectively, and on blending with 20wt% PCL, the elongation at break increased by 26.3%, 68%, and 171% respectively.

The tensile strength of neat PBS, neat PHB* and neat PLA was 29.5 MPa, 40.0 MPa, and 36.5 MPa, respectively, and on blending with 20wt% PCL, the tensile strength decreased by 5.8%, 46.5%, and 22.2%, respectively.

(*In the case of neat PHB, tensile tests could not be determined, as it was too fragile, and hence ε and σ values for neat PHB, are taken from the literature [89] (Reobertson 2016), for comparison purpose).

7.1.2 Water vapor transmission rate (WVTR) studies of the PBS-PCL, PHB-PCL, and PLA-PCL blend films:

The barrier property of the PBS-PCL, PHB-PCL, and PLA-PCL blend films was evaluated by WVTR tests, as per ASTM E96-16 test method [185].

The WVTR results indicated a significant decrease in WVTR (improvement in water vapor barrier property) on blending PBS, PHB, and PCL with PCL. The WVTR of neat PBS, neat PHB and neat PLA was 452 $g.m^{-2}d^{-1}$, 254 $g.m^{-2}d^{-1,}$ 244 g.m-2d-1, respectively, and blending with 20wt% PCL, the WVTR decreased by (barrier property improved by) 28.3%, 26.8%, and 30.3% respectively.

7.1.3 Biodegradability studies of PBS-PCL, PHB-PCL, and PLA-PCL blend films:

Biodegradation studies of PBS-PCL, PHB-PCL and PLA-PCL blend films and neat polymer films were carried out in home compost conditions (at ambient temperature), as per ASTM 5338-15 method [187] and in seawater medium, as per ASTM D6691-17, [57] by measuring the carbon dioxide evolved during biodegradation, at $25^{o}C$, for a period up to 180 days.

The % biodegradation of the neat polymers was 26.5% for PBS, 66.8% for PHB, and 10.4% for PLA, in the compost medium (ambient/ home compost), at $25^{\circ}C$, after 180 days of biodegradation.

Under the same conditions, the % biodegradation of cellulose reference standard was 82.3% in compost medium after 180 days, which is in line with the validity requirements of ASTM D6400 and ISO 17088 standard specifications (minimum 60% biodegradation/ mineralization for homopolymers). [49, 206, 207].

In the seawater medium, biodegradation of neat polymers was found to be lesser than compost medium, and the % biodegradation was found to be 10.3% for PBS, 36.1% for PHB, and 3.6% for PLA, after 180 days of biodegradation at 25^{o}C. The % biodegradation of cellulose reference in the seawater medium was 40.2%, after 180 days, comparable to the results obtained by other researchers. [208] [209], establishing the validity of our experimental results.

The biodegradation studies of PBS-PCL, PHB-PCL, and PLA-PCL blend films indicated an increase in the biodegradation rate on blending with PCL, in compost medium as well as in seawater medium, though the blends with low PCL (10%PCL) had a biodegradation rate almost equal or less than the neat PHB and PLA polymer.

For the PBS, PHB and PLA blends with 20% PCL, % biodegradation observed was respectively 32.3%, 71.1% and 12.6% (corresponding to an increase of 21.9, 6.4 and 21.2 %), in compost medium and 13.5%, 38.8% and 4.2% biodegradation (corresponding to an increase of 31%, 7.5%, and 16.6% increase) in seawater medium.

The observed % biodegradation of all the blends with PCL is summarised in following Table 7.1 & 7.2

Table 7. 1 Biodegradation of PCL Blend films, Compost Medium

Biodegradation of PBS-PCL, PHB-PCL, and PLA-PCL blend films Compost medium, 25^{o}C, Biodegradation % after 180days. Cellulose reference: Biodegradation 82.3%				
PBS-PCL	PBS-PCL40 >	PBS-PCL20 >	PBS-PCL10 >	PBS
	38.5%	32.3%	28.7%	26.5%
PHB-PCL	PHB-PCL40>	PHB-PCL20>	PHB>	PHB-PCL10
	74.4%	71.1%	66.8%	65.4%
PLA-PCL	PLA-PCL 40>	PLA-PCL 20 =	PLA-PCL 10>	PLA
	19.3%	12.6%	12.8%	10.4%

Table 7. 2 Biodegradation of PCL Blend films, Seawater medium

Biodegradation of PBS-PCL, PHB-PCL, and PLA-PCL blend films Seawater medium, 25ºC, Biodegradation % after 180days. Cellulose reference: Biodegradation 40.2%				
PBS-PCL	PBS-PCL40 > 16.6%	PBS-PCL20 > 13.5%	PBS-PCL10 > 11.4%	PBS 10.3%
PHB-PCL	PHB-PCL40> 39.7%	PHB-PCL20> 38.8%	PHB> 36.1%	PHB-PCL10 35.2%
PLA-PCL	PLA-PCL40> 8.4%	PLA-PCL20> 4.2%	PLA-PCL10> 3.9%	PLA 3.6%

For further studies, polymer blends with 20% PCL were chosen, as it was found to give an overall good performance.

7.2 Effect of plasticizers:

Plasticized blend films of polymer blends containing 20 wt% PCL, namely PBS-PCL20, PHB-PCL20, and PLA-PCL20 were prepared by plasticizing the polymer blends with three plasticizers, i) Glyceryl triacetate (GTA), a monomeric plasticizer (P1), ii) Ultramoll IV, a polymeric plasticizer based on an adipic acid polyester (P2) and iii) a mixture of the above two plasticizers, 1:1 ratio by weight (P3), all with 5 wt % of plasticizer. The plasticized blend films were characterized, and the results are summarized below:

7.2.1 Tensile testing of plasticized PBS-PCL20, PHB-PCL20, and PLA-PCL20 blend films

The plasticized blend films' tensile testing indicated an increase in elongation at break and decreased tensile strength with all the plasticizers, for all polymers.

The effect of plasticizers on % elongation was found to follow the order ε: P1>P3>P2.
The highest increase in elongation at break was observed with a monomeric plasticizer (P1), medium increase with a mixed plasticizer (P3), and least increase with a polymeric plasticizer (P2).

The % increase in elongation at break obtained with mixed plasticizer P3 was 22%, 76.6%, and 139.3%, respectively, for PBS-PCL, PHB-PCL, and PLA-PCL-based plasticized films, compared to un-plasticized blend.

Tensile strength decreased with all the plasticizers, and the least decreasing effect / highest tensile strength was observed for the mixed plasticizer (P3). The plasticized blend's tensile strength was found to follow the order σ: P3>P2>P1 for the blends of PBS and PLA, and the order was σ: P3>P1>P2 for PHB based blend films.

The % decrease in tensile strength observed with mixed plasticizer P3 was 5.5%, 7.9%, and 21.8%, respectively, for PBS-PCL, PHB-PCL, and PLA-PCL-based plasticized films, compared to un-plasticized blend.

7.2.2 WVTR studies of plasticized PBS-PCL20, PHB-PCL20, and PLA-PCL20 blend films:

The studies on WVTR tests of plasticized PBS-PCL, PHB-PCL, and PLA-PCL blend films indicated a slight increase in WVTR (decrease in barrier property) with the addition of all plasticizers. Least WVTR (highest barrier property) was observed with mixed plasticizer P3 for all three plasticized blend films. WVTR of the plasticized blend was found to follow the order WVTR: P1>P2>P3 for PBS and PLA blends and P2>P1>P3 for PHB blends.

7.2.3 Biodegradation studies of plasticized PBS-PCL20, PHB-PCL20, PLA-PCL20 blend films:

Biodegradation studies of plasticized blend films indicated, in general, an increase in the biodegradation rate with plasticization, in compost medium as well as in seawater medium, except PHB blend with plasticizer P2.

The maximum increase in biodegradation was observed with monomeric plasticizer P1, while the plasticizer P2 had a minimum increase or no increase (with PHB based blend), and the mixed plasticizer P3 showed a medium increase. The order of biodegradation with plasticizers was found to be P1>P3>P2.

The % biodegradation with mixed plasticizer P3 was 38.6%, 73.7%, and 17.5% in ambient compost conditions and 16.4%, 39.5%, and 5.5% in seawater medium for PBS-PCL, PHB-PCL, and PLA-PCL based plasticized films, respectively.

The % increase in biodegradation with mixed plasticizer P3 was 19.5%, 3.6%, and 38.9% in compost medium and 22.1%, 1.8%, and 41.0% in seawater medium for PBS-PCL, PHB-PCL, and PLA-PCL based plasticized films, respectively, compared to un-plasticized blend.

The % biodegradation obtained for the plasticized blends of PBS-PCL20, PHB-PCL20, and PLA-PCL20 blend films, with the three plasticizers, P1, P2, and P3, in compost medium and seawater medium are summarized in Table 7.3 and 7.4.

Table 7. 3 Biodegradation of Plasticized Blend films, Compost Medium

Biodegradation of plasticized PBS-PCL, PHB-PCL & PLA-PCL blend films Compost medium, 25^{o}C, Biodegradation % after 180days. Cellulose reference: Biodegradation 82.3%				
Plasticized PBS-PCL	P1> 40.5%	P3> 38.6%	P2> 36.8%	NIL 32.3%
Plasticized PHB-PCL	P1> 74.7%	P3> 73.7%	NIL > 71.1%	P2 70.1%
Plasticized PLA-PCL	P1> 18.6%	P3> 17.5%	P2> 16.9%	NIL 12.6%

Table 7. 4 Biodegradation of Plasticized Blend films, Seawater Medium

Biodegradation of plasticized PBS-PCL, PHB-PCL & PLA-PCL blend films Seawater medium, 25ºC, Biodegradation % after 180days. Cellulose reference: Biodegradation 40.2%				
Plasticized	P1>	P3>	P2>	NIL
PBS-PCL	17.3%	16.4%	14.5%	13.5%
Plasticized	P1>	P3>	NIL=	P2
PHB-PCL	42.2%	39.5%	38.8%	38.3%
Plasticized	P1>	P3>	P2>	NIL
PLA-PCL	6.1%	5.5%	4.9%	3.9%

The plasticized blends using mixed plasticizer P3 was found to have the overall best performance. Hence, for further improvement, especially barrier property, plasticized blends using mixed plasticizer P3 was chosen and was modified by incorporating nanomaterials/ by fabrication of polymer nanocomposites.

7.3 Effect of Nanomaterials:

Polymer nanocomposite films based on PBS, PHB, and PLA were prepared by incorporating nano-cellulose and nano-clay (1, 3, and 6 wt%) into plasticized blends, namely PBS-PCL20-P3, PHB-PCL20-P3, and PLA-PCL20-P3 blends. These nanocomposite films were characterized, and the summary of the results are as follows:

7.3.1 Tensile testing of nanocomposite films:

Tensile testing of nanocomposites indicated a decrease in elongation at break with increasing nanomaterial content with nano-cellulose and nano clay. The quantum of decrease in elongation at break with concentration was more pronounced with nano cellulose than nano clay, especially at high concentrations.

The tensile strength of nanocomposites was very much dependent on the polymer blend and nanomaterial content/loading.

Tensile strength of nano clay-based nanocomposites showed an increase in the tensile strength with increasing concentration of nano clay for all blends, and nanocomposite 6wt % nano clay showed maximum tensile strength for all polymers.

Tensile strength of nano cellulose-based nanocomposites of PBS and PHB showed an increase with nano cellulose (and a decreasing trend beyond 1% nano cellulose), while a decrease in tensile strength was observed for PLA based nanocomposites with nano cellulose. Maximum tensile strength was observed with 1 wt% nano cellulose for all polymers.

7.3.2 WVTR studies of nanocomposite films:

Studies on the WVTR property of nanocomposites of PBS, PHB, and PLA indicated a considerable decrease in WVTR (improvement in barrier property) with all the polymer nanocomposites incorporated with nano cellulose and nano clay.

In the case of nano clay-based nanocomposites, a continuous decrease in WVTR (improvement in barrier property) with increasing nano clay loading was observed, and the lowest WVTR (best barrier property) was obtained with 6% nano clay loading.

In the case of nano cellulose-based nanocomposites, the lowest WVTR (best barrier property) was obtained with 1 wt% nano cellulose loading. At higher loadings of nano cellulose, an increasing trend in WVTR was observed.

The lowest WVTR obtained with nano clay (with 6wt% nano clay) was 162 $gm^{-2}d^{-1}$, 108 $gm^{-2}d^{-1}$, and 94 $gm^{-2}d^{-1}$, respectively for PBS, PHB, and PLA based nano clay nanocomposites, which corresponds to a decrease of WVTR by 52.1%, 44.6%, and 47.8% respectively, compared to plasticized blend without nanomaterial.

The lowest WVTR obtained with 1% nano cellulose was 184 $gm^{-2}d^{-1}$,138 $gm^{-2}d^{-1}$ and 126 $gm^{-2}d^{-1}$ respectively for PBS, PHB, and PLA based nano cellulose nanocomposites, which corresponds to a decrease of WVTR by 45.6%, 29.2%, and 30% respectively, for PBS, PHB and PLA based film. Nanocomposites with 1% nano cellulose and 6% nano clay were the overall best performance.

7.3.3 Biodegradation studies of nanocomposites:

Biodegradation studies of nanocomposites of PBS, PHB, and PLA, incorporated with 1wt % nano cellulose and 6 wt% nano clay, were carried out in the home compost medium and seawater

medium. These studies indicated an increase in biodegradation rate with nanomaterials, in-home compost medium, and seawater medium. However, the increase was significantly less, especially with PHB based nanocomposites. The biodegradation for the nano cellulose-based nanocomposites was slightly higher than the nano clay-based nanocomposites, except in the case of PHB nanocomposites.

The biodegradation rate of nano cellulose-based nanocomposites of PBS, PHB, and PLA, in-home compost media, increased to 41.3, 75.6, and 20.1%, respectively, from 38.6, 73.7, and 17.7% for the blend without nanomaterials. In the seawater media, the biodegradation rate of three polymers such as PBS, PHB, and PLA based nanocomposites with nano cellulose changed to 18.4, 39.8, and 6.9% respectively, from 16.4, 39.5, and 5.5%, respectively for the blend without nanomaterials.

In-home compost media, the biodegradation rate for nano clay-based nanocomposites of PBS, PHB, and PLA, increased to 39.0, 74.3, and 18.6%, respectively 38.6 73.7 and 17.7% for the blend without nanomaterials. In the seawater media, the biodegradation rate of three polymers such as PBS, PHB, and PLA based nanocomposites with nano clay increased to 17.6, 40.1, and 5.8%, respectively, from 16.4, 39.5, and 5.5%, respectively for the blend without nanomaterials, after 180 days of biodegradation.

The % biodegradation of nanocomposite films based on PBS-PCL20-P3, PHB-PCL20-P3, and PLA-PCL20-P3 blends, with nano cellulose and nano clay, in-home compost, and seawater medium at 25˚C, are shown in table 7.5 and 7.6

A comparison of the biodegradability between polymer blends/composite and commercially available polymer in compost/soil medium and the marine medium was shown in table 7.7 and 7.8

Table 7. 5 Biodegradation of Nanocomposite films, Compost Medium

Biodegradation of Nanocomposite films based on PBS, PHB, and PLA **Compost medium, 25ºC, Biodegradation % after 180days.** **Cellulose reference: Biodegradation 82.3%**					
PBS based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	41.3%		39%		38.6%
PHB based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	75.6%		74.3%		73.7%
PLA based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	20.1%		18.6%		17.5%

Table 7. 6 Biodegradation of Nanocomposite films, Seawater Medium

Biodegradation of Nanocomposite films based on PBS, PHB, and PLA **Seawater medium, 25ºC, Biodegradation % after 180days.** **Cellulose reference: Biodegradation 40.2%**					
PBS based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	18.4%		17.6%		16.4%
PHB based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	39.8%		40.1%		39.5%
PLA based	n-cellulose	>	n-clay	>	without nanomaterials
Nanocomposite	6.9%		5.8%		5.5%

Table 7. 7 A comparison of the biodegradability between polymer blends/composite and commercially available polymer in compost/ soil medium was shown below.

Year	Author	Blend composition	% Biodegradation at various intervals (days)								
			Medium	Temp	Days							
					30	45	60	90	120	180	270	365
2001	Hoshino[225]	PCL	Soil (Land)	23.9C TO 28.3C Rain: 880 to 1943mm	-	-	-	17.3	-	29.7	45	53.7
		PBS			-	-	-	4.2	-	11.3	23.5	34.2
		PLA			-	-	-	0	-	5.6	11	10.6
2005	Zhao[226]	PBS Powder	Compost	58±2°C	45	56	66	71.9	-	-	-	-
		PBS Film			22	40	52.5	60.7	-	-	-	-
		PBS Granule			2	7.5	12	14.1	-	-	-	-
2013	Calabia[99]	neat PBS		58°C	33.75	-	56	64	-	-	-	-
2009	Funabashi[54]	PLA Powder from Pellet (125-250µm)			60	90	96	-	-	-	-	-
		PLA Powder from 25µm film			51	74	77	-	-	-	-	-
		PLA Film (25µm,1*1cm)			84	102	102	-	-	-	-	-
		PLA Film (25µm,5*5cm)			58	84	90	-	-	-	-	-
Polymer blends/ nanocomposite												
		PBS – PCL 20-P3-nCell 1	Compost	25°C	9.6	16.4	18.9	24.8	29.3	41.3	-	-
		PBS – PCL 20 – P3 – nClay 6			9.7	16.2	19.8	24.7	28.7	39	-	-

		PHB – PCL 20-P3-nCell 1			11.3	19.2	26.5	39.8	52.7	75.6	-	-
		PHB – PCL 20 – P3 – nClay 6			11.4	19.7	27.6	41.1	54.2	74.3	-	-
		PLA – PCL 20-P3-nCell 1			3.2	5.7	6.2	9.9	12.6	20.1	-	-
		PLA – PCL 20 – P3 – nClay 6			2.3	3.2	5.7	8.1	11.5	18.6	-	-

Table 7. 8 A comparison of the biodegradability between polymer blends/composite and commercially available polymer in marine medium was shown below.

Year	Author	Blend composition	% Biodegradation at various intervals (days)										
			Medium	Temp	Days								
					15	30	45	60	90	120	150	180	270	365
2011	Heimowska [210]	**PCL**	Marine	25°C	10	20	100	-	-	-	-	-	-	-
2012	Tosin [198]	**MasterBi** Is made with a partially bio-based copolyester (renewable monomers made starting from vegetable oils).		11 to 26 °C	5	10	15	22	35	48	60	62	-	-
2015	Alvarez [197]	**Ecovio** is manufactured by polylactic acid (PLA) and Ecoflex®		30°C	2	5	10	-	-	-	-	-	-	-
2016	Tosin[227]	**PHB**		25°C	15	30	50	70	87	90	91	94	-	-

2018	Greeni Report[149]	PLA			0	1	1	2	2	3	4	4	-	-
		PHA 2200			1	4	10	14	18	25	33	38	-	-
		PHA 4100		30°C	1	10	20	22	27	35	41	47	-	-
Polymer blends/ nanocomposite														
		PBS – PCL 20-P3-nCell 1	Marine	25°C	0.8	2.1	5.3	5.9	8.6	11.5	14.6	18.4	-	-
		PBS – PCL 20 – P3 – nClay 6			0.5	1.3	3.1	4.8	6.9	10.8	11.9	17.6	-	-
		PHB – PCL 20-P3-nCell 1			1.0	2.6	6.9	12.7	19.6	26.4	32.3	39.8	-	-
		PHB – PCL 20 – P3 – nClay 6			1.2	4.7	7.4	13.7	20.6	27.6	32.8	40.1	-	-
		PLA – PCL 20-P3-nCell 1			0.0	1.1	2.0	2.9	4.5	5.0	6.6	6.9	-	-
		PLA – PCL 20 – P3 – nClay 6			0	0.9	1.5	2.2	3.3	4.3	5.4	5.8	-	-

7.4 Conclusion / Significant research contributions

The project's main objective was “development and characterization of biodegradable polymer films for flexible packaging application, with high-performance characteristics.”

Towards the above objective, research was carried out on improving the properties of commercially available biodegradable polymers, such as Polybutylene succinate (PBS), Polyhydroxybutyrate (PHB), and Polylactic acid (PLA) based polymers by blending with Polycaprolactone (PCL) polymer, by plasticization of the polymer blends with biodegradable plasticizers (monomeric, polymeric and mixed plasticizers), and by fabricating polymer nanocomposites incorporated with nano cellulose and nano clay.

Following are the conclusions and significant research contributions that emerged from the present investigation:

- Successfully fabricated polymer blend films, plasticized blend films, and polymer nanocomposite films based on PBS, PHB and PLA, by optimizing the fabrication parameters, by injection molding followed by hot pressing, and characterized these polymer films.
- The experimental setup was made to evaluate polymer films by standard ASTM test methods, including an experimental setup for water vapor transmission rate (WVTR) measurements and biodegradation rate measurements by the carbon dioxide evolution method.
- Blending studies of PBS, PHB, and PLA polymer with various amounts of PCL polymer resulted in the development of blend films with superior performance characteristics, such as higher ductility, higher biodegradability, and higher water vapor barrier properties. However, it resulted in a reduction in tensile strength. Polymer blends with 10%-20% PCL were found to give optimum /balanced properties without much tensile strength reduction.

  Polymer blends fabricated with 20% PCL were found to have improved properties, such as 26%, 68%, and 171% higher elongation at break; 28%, 27%, and 30% improved water vapor barrier properties (lesser WVTR);, 22%, 6%, and 21% higher biodegradation rate in home compost media, 31%, 8%, and 17% higher biodegradation rate in seawater media (after 180 days), respectively for the blends PBS-PCL20, PHB-PCL20 and PLA-PCL20, compared to PBS, PHB, and PLA. However, there was a decrease in tensile strength for all the blends compared to neat polymers.

- Plasticization studies of PBS-PCL20, PHB-PCL20, and PLA-PCL20 blends (with 20% PCL) with monomeric plasticizer (P1/GTA), polymeric plasticizer (P2/ ultrasmall), and mixed plasticizer (P3/ 1:1 mix of GTA: Ultramoll), resulted in the development of plasticized blend films with enhanced performance characteristics, such as higher tensile elongation, and higher biodegradability, though with a decrease in water vapor barrier property and tensile strength. Plasticization with a mixed plasticizer (P3) consisting of a 1:1 mix of monomeric and polymeric plasticizer, which gave more balanced properties.

  Plasticized polymer blends with 5wt% mixed plasticizer P3, was found to have improved properties (cumulative effect of blending and plasticization), such as 54%, 183%, and 584% higher elongation at break; 25%, 23%, and 26% improved water vapor barrier properties (lesser WVTR); 46%, 10%, and 68% higher biodegradation rate in home compost media; 60%, 9%, and 53% higher biodegradation rate in seawater media (after 180 days), respectively for the blends PBS-PCL20-P3, PHB-PCL20-P3, and PLA-PCL20-P3, compared to PBS, PHB, and PLA. However, there was a decrease in tensile strength for all the blends compared to neat polymers.

- Studies on polymer nanocomposites, prepared by incorporating nano cellulose and nano clay (1, 3, and 6 wt%) into plasticized blends, namely PBS-PCL20-P3, PHB-PCL20-P3, and PLA-PCL20-P3 blends, resulted in the development of nanocomposites with superior performance characteristics, with substantially higher water vapor barrier properties (lower WVTR) and slightly higher biodegradation properties. The addition of nanomaterials also increased the tensile strength (except in PLA), though it slightly lowered ductility. Though there was a decrease in elongation at break with nanomaterials' addition to the plasticized blends, there was a cumulative improvement for neat polymers.
- The present study indicated that the overall best performance was obtained with PBS/PHB/PLA nanocomposites with 1wt% nano cellulose and 6% nano clay loading. The nanocomposites with 1% nano cellulose had slightly higher elongation at break and biodegradability, while the nanocomposites with 6 wt% nano clay had slightly higher tensile strength, water vapor barrier properties. Thus PBS/PHB/PLA nanocomposites with 1% nano cellulose or 6% nano clay may be used depending on the application requirement.

Compared to neat PBS, PHB, and PLA, the nanocomposites with nano cellulose (1 wt%), namely PBS-PCL20-P3-nCell1, PHB-PCL20-P3- nCell1, and PLA- PCL20-P3-nCell1was found to have improved properties, such as improvement in elongation at break by 50%, 168% and 494%; improved water vapor barrier properties (lesser WVTR) by 59%, 46% and 48%; higher biodegradation rate in home compost media by 56%, 13%, and 93%; and higher biodegradation rate in seawater media (after 180 days) by 79%, 10%, and 92% respectively.

- The nanocomposites with nano clay (6 wt%), namely PBS-PCL20-P3-nClay6, PHB-PCL20-P3- nClay6, and PLA-PCL20-P3- nClay6 was found to have improved properties, such as higher elongation at break by 38%, 146%, and 474%; higher water vapor barrier properties (lesser WVTR) by 64%, 58% and 62%; higher biodegradation rate in home compost media by 48%, 11%, and 79%; and higher biodegradation rate in seawater media (after 180 days) by 71%, 11%, and 61% respectively, compared to neat PBS, PHB, and PLA

- Thus, the present investigation demonstrated the overall performance improvement of PBS, PHB, and PLA polymers through blending, plasticization, and nanomaterials. Also, the present research outcome suggests PBS, PHB, and PLA nanocomposites of compositions PBS-PCL20-P3- nCell1/nClay6, PHB-PCL20-P3- nCell1/nClay6 and PLA-PCL20-P3- nCell1/nClay6, with high-performance characteristics, for flexible packaging applications, maybe after minor improvements.

- In addition to the above research contributions, the present investigation has generated valuable data on the biodegradation of PBS, PHB, and PLA neat polymers, their blends with PCL, plasticized blends, and polymer nanocomposites, under ambient temperature/ home composting conditions and under marine environment. These biodegradation data are not available in the open literature and will be of great help for future researchers for further advancement of biodegradable polymers.

7.5 Future research directions/ recommendations for future works

Further research work on biodegradable polymers for packaging application is recommended, covering the following aspects:

- In the present work, investigation on blending with PCL was limited up to 40% PCL content. It is recommended to investigate the properties of PBS, PHB, and PLA blends with higher amounts of PCL. Such blends are expected to have different morphology with PCL as the primary phase, with PBS, PHB, PLA dispersed in the PCL matrix, and is expected to have much higher tensile elongation and biodegradation properties.
- It is recommended to carry out more investigations with other polymeric and mixed plasticizers, using a lesser percentage of monomeric plasticizers, as the migration of plasticizer to surface/loss of plasticizer is one of the problems with a monomeric plasticizer. However, monomeric plasticizers usually have higher plasticization efficiency.
- During our studies on nanocomposites with nano cellulose, a decrease in water barrier properties at high loadings of nano cellulose was observed (though it showed very high water barrier properties at low loadings, even better than nano clay). Future investigations may consider using surface modified nano cellulose to improve the dispersion / reduce the agglomeration for improved performance with nano cellulose.
- Most of the current test methods for biodegradation/ screening of polymers for biodegradation are cumbersome and destructive. It is recommended to develop electrochemical impedance spectroscopy (EIS) technique, a non-destructive and easy technique, for biodegradation testing/ for detecting the early stages of degradation of polymers. Only a few studies have been reported on the use of the EIS method for biodegradation testing [228, 229], despite its advantages.
- During the present research, polymer films' barrier/ permeation properties for water vapor (WVTR) only were studied due to time limitations, even though oxygen and carbon dioxide barrier /permeability characteristics are also essential for packaging films. Hence, future investigations may consider the evaluation of these parameters also. Future investigations may also consider evaluating other properties, such as tear strength and thermal properties of the polymer nanocomposite films developed during this research project.

Chapter 8 References

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