Development of polyhydroxybutyrate based blends for compostable packaging

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Development of Polyhydroxybutyrate Based Blends for Compostable Packaging

by

Min Zhang

A doctoral thesis submitted in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy of Loughborough University

Project Supervisor : Dr. N. L. Thomas
Date : 20 September 2010
ABSTRACT

In this research, three polymers have been blended with polyhydroxybutyrate: poly(ethylene glycol), maize starch and polylactic acid. Their morphology, structure, thermal, rheological, mechanical properties and biodegradation behaviour have been studied.

Blends of PHB and PEG, at three different concentrations (2, 5 and 10 wt %) were prepared by solvent-casting. For these blends the glass transition temperature and crystallization temperature decreased with increasing PEG content, while the addition of a low level of PEG (2% and 5%) did not change the thermal stability of the blends.

Blends of PHB with maize starch (72% amylopectin), at different weight ratios of 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50, respectively, were prepared by melt compounding. The physical properties were found to be optimum at a 70/30 ratio. Blends of PHB with two types of maize starch (28% amylose and 70% amylose) were prepared at a ratio of 70/30. The starch granules act as a filler and nucleating agent for PHB. Intermolecular hydrogen bonding was observed in the PHB/starch blends. Hydrogen bonding was found to be stronger between PHB and high amylose content starch. Thus the PHB/70% amylose starch blends showed greater improvement in thermal stability, melt viscosity and mechanical properties compared with the PHB/28% amylose starch blends.

Blends of PHB and PLA at a number of different weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) were prepared by melt compounding. The results indicate that PLA/PHB blends are immiscible but exhibit some molecular interaction. PHB is highly crystallisable and it enhances the recrystallization of PLA and results in an increase in the heat distortion temperature. Adding PLA to PHB improves the mechanical properties of PHB. In fact, blending with PHB is also a viable approach to improve the mechanical properties of PLA because the PLA/PHB 75/25 blend exhibits significantly improved tensile properties compared with pure PLA. This is due to the finely dispersed PHB crystals acting as a filler and nucleating agent in PLA. The biodegradability of the blends, studied by weight change measurement at room temperature, improved with increasing PHB content.
KEYWORDS

Polyhydroxybutyrate, Maize starch, Polylactic acid, Blends, Thermal properties, Mechanical properties, Biodegradability.
ACKNOWLEDGEMENTS

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Last but not least, my dear parents and close friends who have always been on hand to offer their support.
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<tr>
<td>PHA</td>
<td>Polyhydroxyalkanoate</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>PHB</td>
<td>Polyhydroxybutyrate</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PHBV</td>
<td>Poly(hydroxybutyrate-co-hydroxyvalerate)</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactone</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl acetate)</td>
</tr>
<tr>
<td>TPS</td>
<td>Thermoplastic starch</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide angle X-ray diffraction</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>PBS</td>
<td>Poly(butylenes succinate)</td>
</tr>
<tr>
<td>PGA</td>
<td>Poly(glycolic acid)</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>GPA</td>
<td>Gigapascal</td>
</tr>
<tr>
<td>MPA</td>
<td>Megapascal</td>
</tr>
<tr>
<td>J/m</td>
<td>Joule per meter</td>
</tr>
</tbody>
</table>
%  Percentage
PLLA  Poly-L-lactic acid
PDLA  Poly-D-lactic acid
$\Delta H$  Enthalpy
$E$  Young's modulus
$M_w$  Weight average molecular weight
$J/g$  Joule per gram
$Kg/mol$  Kilogram per mole
XRD  X-ray diffraction
cm  Centimetre
$M_n$  Number average molecular weight
$M_v$  Volume average molecular weight
wt  weight
CAB  Cellulose acetate butyrate
CAP  Cellulose acetate propionate
$E'$  Storage modulus
$E''$  Loss modulus
NMR  Nuclear Magnetic Resonance
POM  Polyoxymethylene (poly(methylene oxide), PMO)
PEO  Poly(ethylene oxide)
PGMA  Poly(glycidyl methacrylate)
MMT  Montmorillonite
OMMT  Organically modified montmorillonite
TGA  Thermogravimetric analysis
EDAX  Energy dispersive X-ray analysis
MFI  Melt flow index
mL  Milliliters
mm  Millimeter
ATR  Attenuated total reflectance
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Fig. 5.20 Plot of log (shear viscosity) vs. log (shear rate) from capillary rheometry for PHB and PHB/starch blends.

Fig. 6.1 Polarizing optical micrographs of the spherulites of PHB in (a) pure PHB, (b) 25% PLA, (c) 50% PLA, (d) 75% PLA and (e) pure PLA after cooling.

Fig. 6.2 SEM micrographs of the fracture surface of (a) pure PHB, (b) 25% PLA, (c) 50% PLA, (d) 75% PLA and (e) pure PLA.

Fig. 6.3 FTIR spectra of quenched samples of PLA, PHB and PHB/PLA blends.

Fig. 6.4 WAXD profiles of quenched samples of PLA, PHB and PHB/PLA blends.

Fig. 6.5 DSC curves of PLA, PHB and PHB/PLA blends obtained from (a) the 1st heating run, (b) cooling run, and (c) 2nd heating run.

Fig. 6.6 DMA curves for PLA and PHB/PLA blends.

Fig. 6.7 Mechanical properties: (a) tensile stress and (b) elongation at break of PLA and PHB/PLA blends as a function of PLA content.

Fig. 6.8 Plot of impact strength as a function of PLA content for PLA and PHB/PLA blends.

Fig. 6.9 Weight change of PHB, PLA and PHB/PLA blends buried in soil as a function of time.

Fig. 6.10 SEM micrographs of the fracture surface of biodegraded PHB/PLA blends: (a) 75% PLA, (b) 50% PLA, (c) 25% PLA, t = 50 weeks.

Fig. 6.11 Polarized light optical micrographs of (a) quenched 75% blend, (b) annealed 75% blend, (c) quenched pure PLA and (d) annealed PLA samples.
Fig.6.12  SEM micrographs of the fracture surface of (a) quenched 75% PLA blend, and (b) annealed 75% PLA blend.

Fig.6.13  FTIR spectra of the quenched and annealed samples of PLA and 75% PLA blend

Fig.6.14  WAXD profiles of the quenched and annealed samples of PLA and 75% PLA blend

Fig.6.15  DMTA curves for quenched and annealed samples of 75% PLA blends

Fig.6.16  Polarized light optical micrographs of spherulites of PHB in PLA/PHB/HYLON VII blends: (a) 50/50/0, (b) 50/40/10 and (c) 50/35/15

Fig.6.17  SEM micrographs of the fracture surface of PLA/PHB/HYLON VII blends: (a) and (a') 50/50/0, (b) and (B') 50/40/10 and (c) and (c') 50/35/15

Fig.6.18  DSC curves of PLA/PHB/HYLON VII blends obtained from (a) the 1st heating run, (b) cooling run, and (c) 2nd heating run

Fig.6.19  DMA curves for PLA/PHB/HYLON VII blends

Fig.6.20  Mechanical properties: (a) tensile stress and (b) elongation at break of PLA/PHB/HYLON VII blends.

Fig.6.21  Plot of impact strength for PLA/PHB/HYLON VII blends.
CHAPTER 1  INTRODUCTION

1.1 Introduction

During the past decade, the environmental impact of plastic waste has been of global concern. Most plastic waste is incinerated or buried, but incineration may generate toxic air pollution (if not properly controlled) and landfill sites are limited. Also, petroleum resources are finite. Thus it becomes important to find polymers that are bio-based and biodegradable to substitute for conventional polymers, especially in short term packaging and disposable applications.

Bio-based polymers are polymers that are generated from renewable natural sources. They are often biodegradable. Biodegradable polymers are polymers that can be assimilated by micro-organisms, and thus introduced into the natural cycle [1]. Biodegradable polymers can be classified into two groups: polymers coming from natural resources, such as starch, cellulose, polylactic acid and polyhydroxyalkanoates; and polymers synthesized from petroleum, such as polyesteramide and poly (vinyl alcohol). However, biodegradable polymers are not suitable for all applications, due to their poor durability and expensive manufacturing and composting process. Absorbable medical implantations, compostable bags for biowaste, compostable food packaging containers and agricultural mulch films are the major uses of biodegradable polymers [2].

Polyhydroxyalkanoates (PHAs) are a family of polyesters produced by bacterial fermentation with the potential to replace conventional polymers. They were first identified by the French microbiologist Maurice Lemoigne in 1925 [3, 4]. High molecular weight polyhydroxyalkanoates are synthesized and stored in the cell cytoplasm as water insoluble inclusions by various microorganisms [4-6]. Generally, PHA plastics are semicrystalline
thermoplastics with the following generic structure [7, 8] (Fig.1.1).

![Fig.1.1 Structure of polyhydroxyalkanoates (PHA)](image)

R can be hydrogen or hydrocarbon chains of up to around C13 in length, and x can range from 1 to 3 or more. Varying x and R provides a broad range of physical and mechanical properties, such as hydrophobicity, glass transition temperature ($T_g$), melting point ($T_m$), and level of crystallinity which can range from around 70% to very low, giving excellent stiffness or elasticity as needed.

When R is a methyl group and x=1, the polymer is Polyhydroxybutyrate (PHB), which is the basic homopolymer in the PHA natural plastics family. PHB is made by a controlled bacterial fermentation and it can completely degrade to CO$_2$ and H$_2$O when attacked by various enzymes. PHB is a semi-crystalline material with a high melting temperature and a high degree of crystallinity. Its mechanical properties are comparable to those of isotactic polypropylene. However, PHB has a relatively high glass transition temperature which is near room temperature, and thus it is stiff and brittle at ambient temperature [4, 9]. At room temperature, the longer it is stored the more brittle it becomes, resulting from secondary crystallization at room temperature. It is 100% biodegradable but not soluble in water, and has the potential to be used in biodegradable packaging since its barrier properties are as good as PVC and PET. PHB is perfectly isotactic and does not include any chain branching and therefore it flows easily during processing.
However, PHB has three main drawbacks:

1. The fermentation and extraction process is inefficient and expensive;
2. It has poor formability and mechanical properties. It is purer than the commercial polymers, i.e. it has a lower nucleation density, and thus it forms large spherulites with cracks and splits, which have a negative influence on the mechanical properties [10];
3. Its thermal decomposition temperature, 210°C, is just above melting temperature, 175°C, therefore leaving a narrow temperature window for processing. The degradation of PHB in a temperature range of 180°C to 200°C is due to the random chain scission, as shown in Fig. 1.2, causing a gradual decrease in molecular weight. The basic problem with PHB is that at its melting point its chain scission rate is too fast [8, 10-15].

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{CH} \quad \text{CH} \quad \text{CH}_2 \quad \text{O} \\
\text{O} & \quad \text{OH} \\
\end{align*}
\]

Fig. 1.2 A scheme of chain scission process in thermal degradation of PHB [12]

Several attempts have been made to improve the thermal and mechanical properties of PHB, such as addition of nucleating agents, which can reduce the size of the spherulitic crystals, to improve the mechanical properties. Another approach was to produce new copolymers, such as poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) [16], although such product is very expensive and
the crystallization requires longer time, which leads to a longer cycle time for
injection moulding. However, the most economical and commonly used
method is to blend PHB with other polymers or additives. Examples are starch
[17, 18], cellulose and cellulose derivative [19, 20], polylactic acid (PLA) [21,
22], polycaprolactone (PCL) [23, 24], poly(vinyl acetate) (PVAc) [25, 26],
plasticizers [27, 28] and clay filler [29, 30] etc.

![Structures of amylose and amylopectin](image)

**Fig.1.3** (a) Structure of amylose and (b) structure of amylopectin

Starch is considered as an attractive biopolymer due to its low cost, low density,
non-abrasive nature, and biodegradability. Starch is composed of a linear
polymer (amylose) and a branched polymer (amylopectin) (Fig.1.3). The
degree of starch crystallinity is affected by the amylose content which depends
on the starch source [1, 31]. However, native starch generally exists in a
granular state due to its inherent hydrogen bonding between molecules, and
this makes the dispersion of starch into a polymer matrix at a fine scale difficult.

Thermoplastic starch (TPS) is obtained by mixing starch powder, water, and/or
plasticizers, such as polyols, mono-, di- or oligosaccharides, fatty acids, lipids
and derivatives, through a ‘gelatinization’ process [32]. By definition,
gelatinization is a transition process that occurs in the presences of water and
heat, during which the intermolecular bonds between starch molecules break
down, and the starch paste is obtained.
Polylactic acid (PLA), \([-\text{CH(CH}_3\text{)}\text{COO}]_n\), is one of the most widely used and well studied biopolymers. It is synthesized from lactic acid monomer which is obtained from the fermentation of renewable resources, such as corn, etc [33]. PLA is relatively thermally stable up to 240-250°C. The crystallisable content can be controlled by the ratio of ‘l’ and ‘d’ isomers of lactic acid (Fig.1.4) used in its synthesis [34,35]. The PLA used in the current study was poly(d,l-lactic acid), which is amorphous with a glass transition temperature of around 60°C. It is a highly transparent and rigid material with thermal and mechanical properties comparable to poly(ethylene terephthalate) (PET) [35,36]. PLA can be fully biodegraded to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) at temperatures of 60°C or above. The first stage of degradation is via a non-enzymatic hydrolysis to water-soluble low molecular weight polymers and oligomers, and the second stage is biological degradation by a variety of microorganisms. However, as a potentially biodegradable packaging polymer, two disadvantages of PLA are required to be solved: its low heat distortion temperature (softening above 60°C) and also its inability to biodegrade at ambient temperature, i.e. it is not ‘home compostable’.

1.2 Aims of Project

Blending of polymers is an effective alternative way to develop new materials with desired properties. The current study focuses on biodegradable PHB based blends with better thermal and mechanical properties. The objectives of
Chapter 1

Introduction

The project are:

- To improve the processability and impact resistance of PHB by adding plasticizers, fillers, such as starch, and/or other polymers, such as PLA;
- To improve the thermal stability of PHB by either lowering melting temperature or heightening the thermal decomposition temperature, i.e. avoid or retard the chain scission degradation;
- To lower the cost by adding either organic or inorganic fillers.

1.3 Publications

Much of the work presented in Chapter 5 and 6 of this thesis has already been published or accepted for publication. Details are given as follows:


Abstract

This study examines the properties of polyhydroxybutyrate (PHB) when blended with two types of maize starch, Starch 1 (containing 70% amylose) and Starch 2 (containing 72% amylopectin). The PHB/starch blends were prepared at a ratio of 70/30 by weight and characterized in terms of their morphology, structure, thermal and rheological properties by means of optical microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), wide angle X-ray diffraction (WAXD), dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), capillary rheometry and tensile test. The addition of starch showed a decrease in the size of the PHB spherulites, however, the starch granules only act as
filler and nucleating agent for PHB. FTIR and WAXD results showed that the intermolecular hydrogen bonding in the PHB/starch blends related to bonding between the carbonyl groups in PHB and the hydroxyl groups in starch. Hydrogen bonding was found to be stronger between PHB and Starch 1 than between PHB and Starch 2 by DMTA analysis. This explains why the PHB/Starch 1 blends showed greater improvement in thermal stability, melt viscosity and mechanical properties compared with the PHB/Starch 2 blends.

M. Zhang and N. L. Thomas, Blending Polylactic Acid (PLA) with Polyhydroxybutyrate (PHB): the Effect on Thermal, Mechanical and Biodegradation Properties, Advances in Polymer Technology, 2010 (in press)

Abstract

Blends of Polylactic acid (PLA) and Polyhydroxybutyrate (PHB) at a number of different PLA/PHB weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) have been prepared by melt compounding. The morphology, thermal properties, mechanical properties and biodegradation behaviour of these blends have been investigated. The results indicate that PLA/PHB blends are immiscible but exhibit some molecular interaction. PHB is highly crystallisable and it enhances the recrystallization characteristics of PLA and resulting in an increase in the heat distortion temperature. Adding PLA to PHB improves the mechanical properties of PHB. In fact, blending with PHB is also a viable approach to improve the mechanical properties of PLA because the PLA/PHB 75/25 blend exhibits significantly improved tensile properties compared with pure PLA. This is due to the finely dispersed PHB crystals acting as a filler and nucleating agent in PLA. The biodegradability of the blends, studied by weight change measurement at room temperature, improved with increasing PHB content.
CHAPTER 2  LITERATURE REVIEW

2.1 Introduction

This chapter reviews the published literature on PHB and PHB based blends and composites, in order to offer an overview on this area of research and point out the way forward for the current project.

2.2 Biodegradable Aliphatic Polyesters

Several aliphatic polyesters having properties comparable to conventional plastics have been developed and used as biodegradable plastics, such as polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polylactic acid (PLA), poly(glycolic acid) (PGA), polycaprolactone (PCL), poly(butylenes succinate) (PBS), and so on. Table 2.1 lists the basic physical properties of the commonly studied biodegradable polyesters.

Table 2.1  Thermal and mechanical properties of commonly studied biodegradable polyesters (the test samples were fabricated by moulding) [37]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (g/cm³)</th>
<th>Temperature (°C)</th>
<th>Appearance</th>
<th>Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Impact strength* (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>melting</td>
<td>Glass transition</td>
<td></td>
<td>tensile</td>
<td>blending</td>
</tr>
<tr>
<td>PLA</td>
<td>1.27</td>
<td>175-180</td>
<td>58</td>
<td>Transparent</td>
<td>59</td>
<td>73</td>
</tr>
<tr>
<td>PGA</td>
<td>-</td>
<td>227-230</td>
<td>37-42</td>
<td>Milky</td>
<td>Samples difficult to fabricate</td>
<td></td>
</tr>
<tr>
<td>PBS</td>
<td>1.26</td>
<td>113-115</td>
<td>-38</td>
<td>Milky</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>PCL</td>
<td>1.14</td>
<td>57-60</td>
<td>-60</td>
<td>Milky</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>PHBV</td>
<td>1.23</td>
<td>154(177)</td>
<td>2</td>
<td>Milky</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>

*Notched Izod
**Requires refinement
Most of these polyesters are biodegradable polymers derived from the chemical synthesis of crude oil, except PLA, which can be synthesized either from petroleum or genetically modified corns [33, 35], and PHAs, which are synthesized from microorganisms or plants [5, 6]. Regarding the biodegradation mechanism, aliphatic polyesters can be classified into two groups. The first group mainly starts to degrade with enzyme-catalyzed hydrolysis reaction, e.g. PHB, PHBV and PBS. The other group is mainly degraded by a non-enzymatic hydrolysis reaction, e.g. PLA and PGA [33, 38-41].

2.2.1 Polyhydroxyalkanoates (PHAs) and Polyhydroxybutyrate (PHB)

Fig. 2.1 Transmission electron micrograph showing sectioned microbial cells containing discrete granules of PHB [38]

High molecular weight PHAs are synthesized by various microorganisms and stored as water insoluble carbon and energy storage compounds in the cell
cytoplasm [5, 6, 9, 42]. The transmission electron micrograph in Fig.2.1 shows a thin section of microbial cells containing discrete granules of polyhydroxybutyrate (PHB). Over 300 different bacteria have been reported to accumulate various PHAs [43], and more than 100 different monomers have been found with different R and x values (Fig.2.2). The different chemical structures of PHAs result in a wide range of physical properties, from stiff and brittle plastics to soft elastomers. The major problem of PHAs for commercial applications is the high cost of bacterial fermentation, making PHA polymers 5-10 times more expensive than petroleum based polymers. And thus synthesis of PHA in plants was carried out to lower the cost [6].

![Structure of polyhydroxyalkanoates (PHA) and x, R values for typical PHA polymers](image)

<table>
<thead>
<tr>
<th>x</th>
<th>R</th>
<th>polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>methyl group</td>
<td>Polyhydroxybutyrate</td>
</tr>
<tr>
<td>1</td>
<td>ethyl group</td>
<td>Polyhydroxyvalerate</td>
</tr>
<tr>
<td>1</td>
<td>propyl group</td>
<td>Polyhydroxyhexanoate</td>
</tr>
<tr>
<td>1</td>
<td>pentyl group</td>
<td>Polyhydroxyoctanoate</td>
</tr>
<tr>
<td>1</td>
<td>nonyl group</td>
<td>Polyhydroxydodecanoate</td>
</tr>
<tr>
<td>2</td>
<td>hydrogen</td>
<td>Poly (4-hydroxybutyrate)</td>
</tr>
<tr>
<td>3</td>
<td>hydrogen</td>
<td>Poly (5-hydroxyvalerate)</td>
</tr>
</tbody>
</table>

**Fig.2.2** Structure of polyhydroxyalkanoates (PHA) and x, R values for typical PHA polymers [38]

PHB, which is the base homopolymer in PHA family, is highly crystalline with a melting temperature of about 180°C and a glass transition temperature of about 5°C [44]. Several researchers reported that double melting peaks of PHB were observed in differential scanning calorimetry (DSC) analysis (Fig.
2.3) [45-48]. The lower temperature peak corresponds to the melting of the 'as-formed' PHB crystals, while the higher temperature peak corresponds to the melting of the PHB crystals formed from the recrystallization during the DSC heating process. The relative areas of the two peaks were affected by the heating rate: the faster the heating rate, the larger the lower temperature peak area, as shown in Fig. 2.3.

![DSC melting peaks as a function of heating rate for PHB](image)

**Fig.2.3** DSC melting peaks as a function of heating rate for PHB at heating rate of: (a) 20°C min$^{-1}$, (b) 10°C min$^{-1}$, (c) 5°C min$^{-1}$ [48]

The combination of high crystallinity and low nucleation density of PHB results in large spherulites with cracks and splits, and thus makes the PHB products very brittle [44, 49]. Thus copolymers based on hydroxybutyrate monomer and other PHA monomers have been investigated. To date, the most widely studied PHB based copolymer is a copolymer of HB and hydroxyvalerate (HV), PHBV, which was marketed under the trade name “Biopol” by ICI Zeneca in UK (now is Metabolix in US). However, the fermentation process for producing copolymers of PHB is expensive.
It can be seen from Table 2.2 [5, 38], that the PHBV copolymer has much improved mechanical properties compared with PHB, and the copolymer becomes tougher and more flexible as the content of HV increases. The effect of HV content on Young's modulus and the notched Izod impact strength is represented in Fig. 2.4 [50]. The decrease in stiffness and increase in toughness of the copolymer is due to the addition of HV units which reduces the force between PHB chains resulting in the reduction in crystallinity, glass transition temperature and melting point. In practice, the bacteria are able to produce a range of thermoplastic polymers, including hard and brittle polymers with PS-like feel at low HV content, polymers having a good balance of stiffness and toughness like PP at middle HV content, and soft and tough polymers with PE-like feel at high HV content.

Table 2.2 Comparison of PHB with copolymers of PHB and common plastics in thermal and mechanical properties [38]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting temp. (°C)</th>
<th>Young's modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation to break (%)</th>
<th>Notched Izod impact strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(3HB)</td>
<td>179</td>
<td>3.5</td>
<td>40</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>P(3HB-co-3HV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 mol% 3HV</td>
<td>170</td>
<td>2.9</td>
<td>38</td>
<td>—</td>
<td>60</td>
</tr>
<tr>
<td>9 mol% 3HV</td>
<td>162</td>
<td>1.9</td>
<td>37</td>
<td>—</td>
<td>95</td>
</tr>
<tr>
<td>14 mol% 3HV</td>
<td>150</td>
<td>1.5</td>
<td>35</td>
<td>—</td>
<td>120</td>
</tr>
<tr>
<td>20 mol% 3HV</td>
<td>145</td>
<td>1.2</td>
<td>32</td>
<td>—</td>
<td>200</td>
</tr>
<tr>
<td>25 mol% 3HV</td>
<td>137</td>
<td>0.7</td>
<td>30</td>
<td>—</td>
<td>400</td>
</tr>
<tr>
<td>P(3HB-co-4HB)a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 mol% 4HB</td>
<td>166</td>
<td>—</td>
<td>28</td>
<td>45</td>
<td>—</td>
</tr>
<tr>
<td>10 mol% 4HB</td>
<td>159</td>
<td>—</td>
<td>24</td>
<td>242</td>
<td>—</td>
</tr>
<tr>
<td>16 mol% 4HB</td>
<td>—</td>
<td>—</td>
<td>26</td>
<td>444</td>
<td>—</td>
</tr>
<tr>
<td>64 mol% 4HB</td>
<td>50</td>
<td>30</td>
<td>17</td>
<td>591</td>
<td>—</td>
</tr>
<tr>
<td>90 mol% 4HB</td>
<td>50</td>
<td>100</td>
<td>65</td>
<td>1080</td>
<td>—</td>
</tr>
<tr>
<td>P(4HB)b</td>
<td>53</td>
<td>149</td>
<td>104</td>
<td>1000</td>
<td>—</td>
</tr>
<tr>
<td>P(3HHx-co-3HO)g</td>
<td>61</td>
<td>—</td>
<td>10</td>
<td>300</td>
<td>—</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>170</td>
<td>1.7</td>
<td>34.5</td>
<td>400</td>
<td>45</td>
</tr>
<tr>
<td>Polyethylene-terephthalate</td>
<td>262</td>
<td>2.2</td>
<td>56</td>
<td>7300</td>
<td>3400</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>110</td>
<td>3.1</td>
<td>50</td>
<td>—</td>
<td>21</td>
</tr>
</tbody>
</table>
The thermal instability of PHB in the melt is one of the major drawbacks to commercial use of PHB. The chain scission process occurs in the thermal degradation of PHB according to a β-hydrogen elimination reaction as shown in Fig.1.2 [10-15]. This type of degradation results in a gradual decrease in molecular weight. The basic problem with PHB is that the onset temperature of chain scission degradation is about 180°C, which is slightly higher than its melting temperature. In principle, the degradation might be avoided or limited either by reducing the melting temperature to lower the processing temperature, or by introducing some chemical groups to re-polymerize the thermally degraded polymer [51]. Thus, the development of PHBV copolymer using a bacterial fermentation method is one of the approaches to resolve the thermal instability of PHB. Another drawback of both PHB and PHBV copolymers is that they undergo a physical ageing process on storage at room temperature [52, 53]. The physical ageing, attributed to the development of
secondary crystallization and a progressive decrease of the amorphous content, causes an increase in yield stress and modulus and a decrease in elongation at break and fracture toughness. Due to the low crystallization rate, the interlamellar secondary crystallization of PHB occurs to form thin, small crystallites in the amorphous region during storage at room temperature. The presence of the small crystallites reduces the mobility of the chain segments thus embrittling the plastic. Effect of storage at room temperature on the tensile stress and strain of 8% HV copolymer is shown in Fig. 2.5. The secondary crystallization of the copolymer can be reduced by crystallizing the copolymer at high temperature, which leads to rejection of the HV units into the amorphous regions [53].

![Graph](image.png)

**Fig. 2.5** Effect of storage at room temperature on the tensile stress and strain of the 8% HV copolymer [53]

The main advantage of PHAs over other types of biodegradable polymers is that they can be completely degraded by microorganisms under aerobic and anaerobic conditions, such as soil, activated sludge and sea water [5, 48, 54-55]. The end products of PHA degradation in aerobic conditions are CO₂ and water, while in the anaerobic conditions is methane. It has been found that
the rate of biodegradation of PHA materials depends on many factors, including both those related to the environment (temperature, moisture level, pH and nutrient supply) and those related to the PHAs themselves (composition, crystallinity, additives and surface area) [5, 30]. The life cycle of PHAs is illustrated in Fig. 2.6 [38].

**Fig. 2.6** The life cycle of PHAs [38]

PHA polymers have been widely used in medical applications, such as drug delivery and surgical swabs, due to it being biocompatible and biodegradable. Commercial grades of PHA are Biopol PHBV, being developed by Metabolix, and Nodax PHA copolymer, marketed by Procter & Gamble (now licensed to Meridian). The products of PHBV under trade name of Biopol have been commercially used on the market. In 1990, the German hair-care company, Wella, marketed a shampoo bottle (SANARA) made from Biopol, but production was stopped due to the high cost.
2.2.2 Polylactic acid (PLA)

PLA is a biodegradable thermoplastic synthesized either by ring opening polymerization through lactide or by direction condensation polymerization from the lactic acid monomer (Fig. 2.7). Lactic acid can be obtained by carbohydrate fermentation based on corn starch or sugarcane, or by chemical synthesis of non-renewable resources [33].

Fig. 2.7 Polymerization and polycondensation scheme of PLA [56]

Compared with ring opening polymerization, direct condensation polymerization is the method with easier manufacturing steps and lower cost. However, the resultant PLA polymer has low molecular weight. Thus, the ring opening polymerization of PLA is the primary method to obtain the high molecular weight product [56].

Due to the stereoisometric nature of lactic acid, several distinct forms of polylactic acid exist: poly-L-lactic acid (PLLA), the product resulting from
polymerization of L-lactide; poly-D-lactic acid (PDLA), the product resulting from polymerization of D-lactide; and poly-DL-lactic acid (PDLLA), the product resulting from polymerization of a racemic mixture L- and D-lactides (Fig.2.7) [33, 35-36, 56].

Both physical properties and biodegradability of PLA are associated with the purity of the lactic acid stereocopolymers. The homopolymers PLA resulting from polymerization of pure L- or D-lactide and high L- or D-lactide copolymers have very regular structures to form a crystalline phase. For example, PLLA is a hard, transparent and crystalline polymer having a crystallinity of 37%, a melting temperature of about 170-180°C and a glass transition temperature of 50-60°C [57]. PLA polymers may be either amorphous or semicrystalline at room temperature, depending on the L- to D-lactic acid ratio. PLA polymers containing more than 93% of L-lactic acid are semicrystalline, while PLA with 50-93% L-lactic acid is amorphous [58, 59]. These PLA polymers can be processed like most thermoplastic polymers with extrusion, injection moulding, blow moulding, or fiber spinning processes into various products. Due to its very low crystallization rate, the thermal treatment history of PLLA strongly affects its physical properties since the longer physical aging time decreases the ratio of amorphous phase, and thus increases the crystallinity.

The effects of annealing treatment on the thermal properties, morphologies and mechanical properties of PLLA films have been investigated by Tsuji et al [60]. Solvent casted PLLA films were treated at three different annealing conditions in the temperature range of 100°C to 160°C: A, direct annealing of the ‘as-casted’ film; B, melting and annealing; and C, melting, quenching and annealing. In the case of condition A, the annealed films showed similar morphology to that of the unannealed films. The crystallinity and melting temperature increased with increasing annealing temperature, but were slightly affected by annealing time. Young’s modulus and tensile strength of
PLLA samples increased with increasing crystallinity, however, elongation at break decreased with increasing crystallinity.

![Micrographs of PLLA films prepared by melting and annealing at different temperatures, (t = 600min): (A) 100°C; (B) 120°C; (C) 140°C; (D) 160°C [60]](image)

In the case of condition B, the radius of the spherulites increased with annealing temperature and time, as shown in Fig. 2.8 and 2.9. The crystallinity and melting temperature increased with increasing annealing temperature and time in condition B. Young's modulus increased with increasing crystallinity, and tensile strength showed similar behaviour to Young's modulus, but decreased when large spherulites were formed. Same as in condition A, elongation at break decreases with increasing crystallinity.
Fig. 2.9 Micrographs of PLLA films prepared by melting and annealing at different times, \( T = 140^\circ C \): (A) 5min; (B) 10min; (C) 30min; (D) 60min [60]

In annealing condition C, the morphology slightly depended on the annealing temperature and time, however, the radius of the spherulites formed was much smaller compared with that of samples prepared by condition B, as shown in Fig. 2.10. In addition, the nucleation density of the PLLA samples prepared by condition C, was higher, and this is due to the nucleation occurring during the quenching or heating process after quenching. The effects of crystallinity on the thermal and mechanical properties were similar to that of the samples prepared by condition B, while the elongation at break did not show clear dependence on annealing temperature and time.
Fig.2.10 Micrographs of PLLA films prepared by melting, quenching and annealing at different times, (T = 140°C): (A) 3min; (B) 5min; (C) 10min [60]

Tensile strength and elongation at break of the PLLA films as a function of annealing temperature at different annealing conditions have been studied [60]. As shown in Fig.2.11, film A is directly annealed from the 'as-casted' film; film B is melted and then annealed; and film C is melted, quenched and annealed. Tensile strength of film A did not change with annealing temperature, while tensile strength of films B and C decreased with increasing annealing temperature. At the annealing temperature range between 100 to 140°C, film B showed the highest tensile strength value compared with the other two films. However, at the annealing temperature of 160°C, film B showed the lowest tensile strength value. Elongation at break of films A and B decreased with increasing annealing temperature, while that of film C did not show dependence on annealing temperature. Film A showed the highest elongation at break value at the annealing temperature range between 100 to 120°C, and finally at the annealing temperature of 160°C, the three films reached the same value.
The effect of molecular weight and crystallinity on polylactic acid properties has been studied in the past decades. Perego et al. [61] studied the mechanical properties of samples of amorphous PLA, and two semi-crystalline PLLA samples, ‘as-prepared’ (with less than 15% crystallinity) and annealed (45–70% crystallinity). They found that the semi-crystalline PLLA samples (both ‘as-prepared’ and annealed) showed higher values of tensile strength at break and notched Izod impact strength, as listed in Table 2.3. Furthermore, the annealed semi-crystalline PLLA samples showed higher tensile strength at break and notched Izod impact strength values compared with the ‘as-prepared’ PLLA samples, although the elongation at break values were slightly lower. Additionally, they reported that the properties of amorphous PLA and PLLA samples with low crystallinity (i.e. ‘as-prepared’ PLLA) did not vary with the molecular weight. However, the mechanical properties of annealed PLLA samples increased with increasing molecular weight, and the crystallinity
levels in annealed PLLA samples decreased with increasing molecular weight.

**Table 2.3** Mechanical properties of amorphous PLA and semi-crystalline PLLA samples (unannealed and annealed) at various molecular weights [61]

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔH (J g⁻¹)</th>
<th>Mᵥ (kg mol⁻¹)</th>
<th>σᵥ (MPa)</th>
<th>εᵥ (%)</th>
<th>E (GPa)</th>
<th>Notched Izod I.S. (J m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>47.5</td>
<td>40</td>
<td>7.5</td>
<td>3.65</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>—</td>
<td>75</td>
<td>44</td>
<td>4.8</td>
<td>4.05</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>114</td>
<td>44</td>
<td>5.4</td>
<td>3.90</td>
<td>18</td>
</tr>
<tr>
<td>PLLA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>23</td>
<td>59</td>
<td>1.5</td>
<td>3.55</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>31</td>
<td>55</td>
<td>5.5</td>
<td>3.55</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>58</td>
<td>58</td>
<td>5.0</td>
<td>3.75</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>66</td>
<td>59</td>
<td>7.0</td>
<td>3.75</td>
<td>26</td>
</tr>
<tr>
<td>Annealed PLLA①</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>65</td>
<td>20</td>
<td>47</td>
<td>1.3</td>
<td>4.10</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>59</td>
<td>30</td>
<td>54</td>
<td>3.3</td>
<td>4.10</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>48</td>
<td>47</td>
<td>59</td>
<td>3.5</td>
<td>4.05</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>66</td>
<td>66</td>
<td>4.0</td>
<td>4.15</td>
<td>66</td>
</tr>
</tbody>
</table>

①Annealed at 105°C for 90 min under nitrogen atmosphere.

PLA products can be degraded and subsequently biodegraded into CO₂ and water. PLA degrades primarily by hydrolysis, after several months’ exposure to moisture. PLA degradation occurs in two steps: first, random non-enzymatic chain scission of the ester groups lead to a reduction in molecular weight, and second, low molecular weight PLA can diffuse out of the bulk polymer and be used by microorganisms [33, 40-41]. The hydrolytic degradation of PLA is strongly temperature dependant, and it is found that PLA is fully biodegradable when composted at temperatures of 60°C or above. The life cycle of PLA polymers is illustrated in Fig.2.12 [62]
The manufacture of PLA was pioneered by Carothers in 1932 [63] and further developed by Dupont and Ethicon [64]. It was first widely used in medical applications and currently used in packaging as an alternative to PET, such as films, containers and short term bottles. However, recently many researchers argue that the wide usage of PLA in packaging may result in some problems: firstly, the genetically modified corn, which is the resource for lactic acid, may result in environmental problems, and secondly, PLA products, which have similar appearance to PET products, make either recycling or composting processes difficult [65]. Because a small amount of PLA can contaminate recycling of conventional plastics, and PET is difficult to be cleaned out of the compost facilities.
2.3 PHB Based Blends/Composites

2.3.1 PHB/Thermoplastic Starch Blends

Starch is a natural occurring polymer obtained from renewable sources. As described in chapter 1, it is composed of a linear polymer (amylose) and a branched polymer (amylopectin) (Fig.1.3). Some efforts have been made to produce PHB/starch blends with improved mechanical properties. Up to now, blends of PHB were prepared either by a conventional solvent casting method usually from chloroform solution, or by hot processing methods, such as injection moulding and compression moulding, after melt mixing [17-18, 66].

The thermal and mechanical properties of solvent-casted films of PHB and starch/thermoplastic starch (TPS) were studied by Godbole, Gote, etc [17]. TPS was obtained by mixing starch powder, water and glycerol in the certain composition. The researchers observed that the blends in a PHB: TPS ratio of 0.7: 0.3 showed best properties with reduced cost compared with the other blends. As shown in Table 2.4, the tensile strength and extension at break of the blend with the ratio of 0.7: 0.3 PHB: TPS was a maximum, i.e. 31.45 MPa and 11.70%, respectively, compared with other blends and pure PHB.

**Table 2.4 Mechanical properties of PHB and starch films in different ratios** [17]

<table>
<thead>
<tr>
<th>Sample ratio PHB:starch (wt/wt)</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (MPa)</th>
<th>Extension to break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:0.0</td>
<td>18.29</td>
<td>1708</td>
<td>3.32</td>
</tr>
<tr>
<td>0.9:0.1</td>
<td>17.20</td>
<td>1716</td>
<td>9.8</td>
</tr>
<tr>
<td>0.8:0.2</td>
<td>19.7</td>
<td>1085</td>
<td>6.0</td>
</tr>
<tr>
<td>0.7:0.3</td>
<td>19.23</td>
<td>949</td>
<td>9.4</td>
</tr>
<tr>
<td>0.6:0.4</td>
<td>7.7</td>
<td>856</td>
<td>8.5</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>10.06</td>
<td>694</td>
<td>5.27</td>
</tr>
<tr>
<td>0.4:0.6</td>
<td>5.24</td>
<td>686</td>
<td>3.45</td>
</tr>
<tr>
<td>0.3:0.7</td>
<td>4.99</td>
<td>578</td>
<td>4.3</td>
</tr>
<tr>
<td>PHB:(TS) 0.5:0.5</td>
<td>11.13</td>
<td>1689</td>
<td>2.65</td>
</tr>
<tr>
<td>PHB:(TS) 0.7:0.3</td>
<td>31.45</td>
<td>3334</td>
<td>11.70</td>
</tr>
</tbody>
</table>
The thermal properties of different combinations of PHB: starch/TPS are represented in Table 2.5. The melting temperature for all the films ranged between 165 and 168°C, i.e. the addition of starch or TPS did not shift the melting temperature, indicating there is no interaction between these blended polymers. Apart from this, the thermal decomposition temperature of films with starch was in the range of 200 to 223°C, whereas the thermal decomposition temperature of films with TPS was increased by 30°C (260°C). Generally, the films with TPS containing glycerol showed improved properties compared with the films with native starch granules, because the TPS is easily deformed and distributed in the blending process and it can be reprocessed at elevated temperatures retaining its flexibility.

Table 2.5 Thermal properties of PHB and starch films in different ratios [17]

<table>
<thead>
<tr>
<th>PHB:starch ratio (wt/wt)</th>
<th>Melting point (°C)</th>
<th>Thermal stability (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:0.0</td>
<td>168.1</td>
<td>223.3</td>
</tr>
<tr>
<td>0.9:0.1</td>
<td>165.9</td>
<td>203.20</td>
</tr>
<tr>
<td>0.8:0.2</td>
<td>166.9</td>
<td>207.33</td>
</tr>
<tr>
<td>0.7:0.3</td>
<td>167.0</td>
<td>217.0</td>
</tr>
<tr>
<td>0.6:0.4</td>
<td>165.8</td>
<td>217.0</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>167.9</td>
<td>219.7</td>
</tr>
<tr>
<td>0.4:0.6</td>
<td>167.1</td>
<td>200.5</td>
</tr>
<tr>
<td>0.3:0.7</td>
<td>165.9</td>
<td>220.1</td>
</tr>
<tr>
<td>PHB:(TS)</td>
<td>165.4</td>
<td>259.9</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHB:(TS)</td>
<td>165.5</td>
<td>260.3</td>
</tr>
<tr>
<td>0.7:0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lai et al. [67] studied the mechanical properties and biodegradability of solvent-casted films with TPS as a matrix reinforced by PHB (1, 3, 5, 7 wt%). They reported that the mechanical properties, i.e. tensile strength and tear strength, of films increased with PHB content, whereas the values of water absorption and weight loss decreased with increasing PHB content because
PHB is hydrophobic and more stable than starch in the short term, as shown in Fig. 2.13.

**Fig 2.13** (a) Water absorption and (b) weight loss, of TPS/PHB films with different PHB content and glycerol content [67]
In addition, the mechanical properties, water absorption and weight loss of TPS blended with PHB films were also affected by the glycerol content, as shown in Fig. 2.13 and 2.14. For TPS blended with PHB with 25% glycerol, tensile strength significantly increased with increasing PHB content, whereas for the blends with 33% glycerol, tensile strength marginally increased with PHB content. These results indicated that the native starch required a suitable glycerol content to achieve the best compatibility with PHB. The values of water absorption and weight loss increased with increasing glycerol content. This is attributed to the higher gelatinization degree, resulting from the higher glycerol content, causing the disruption of hydrogen bonding between crystalline galleries, and thus resulting in a more open structure for water to diffuse into.

![Fig 2.14 Tensile strength of TPS/PHB films with different PHB content and glycerol content [67]](image)

Compression moulded PHB/starch blends with starch content varied between 0 and 50% were studied by Thiré et al [66], using X-ray diffraction, tensile
testing, thermal analysis, contact angle measurements, and scanning electron microscopy (SEM). As shown in Fig 2.15, they observed that higher starch contents led to poorer mechanical properties, and this might be explained by the lack of interfacial adhesion between starch and PHB, which can also be seen from SEM images (Fig.2.16). However, the blends with starch content up to 30 wt% showed much better mechanical properties than the blends with higher starch content. Also, they reported that the addition of starch decreased the degree of crystallinity without affecting the PHB crystalline lattice: the results from X-ray diffraction studies showed the same peak positions with different intensities.

![Mechanical properties of compression-moulded PHB/starch blends](image)

**Fig.2.15** Mechanical properties of compression-moulded PHB/starch blends: (a) Young’s modulus, (b) tensile strength, (c) elongation at break [66]
Fig. 2.16  SEM micrographs of PHB/starch blends’ fractured surfaces with varied starch contents (wt %): (a) 0, (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50 [66]

2.3.2 PHB/PLA Blends

As already discussed, PLLA is a well studied biodegradable and biocompatible crystalline polymer. It shows thermal and mechanical properties comparable to
those of commercial polymers. There have been a number of studies to investigate poly(l-lactic acid) (PLLA)/PHB blends\[21, 22, 45, 68-71]. According to these studies, the miscibility of PLLA/PHB blends depends on the molecular weight of PLLA. PHB is only miscible with low molecular weight PLLA in the melt stage (~200°C), and the crystallization dynamics of PHB in blends are affected by the presence of PLLA [21, 22].

\[2\]

![Fig.2.17](image)

**Fig.2.17** Comparison of carbonyl group stretching band of (a) PHB, high M\textsubscript{w} PLLA and their 50:50 blend, and (b) PHB, low M\textsubscript{w} PLLA and their 50:50 blend [22]

Zhang et al [22] investigated the miscibility and crystallization behaviours of PHB with two types of PLLA having different molecular weights of 150000 and 4300 g mol\textsuperscript{-1}, respectively. Fig.2.17 compares the Infra-red spectra in the carbonyl group stretching vibration of PHB, PLLA and their 50:50 blends at 200°C. They pointed out that the band at 1776cm\textsuperscript{-1} comes from PLLA, which might be associated with the structural defects of PLLA. In the spectrum of the PHB/high M\textsubscript{w} PLLA blend, apart from the band at 1776cm\textsuperscript{-1}, two major carbonyl stretching bands can be observed, while in the spectrum of PHB/low M\textsubscript{w} PLLA blend, there is only one vibration band (as marked). These results indicated that PHB is immiscible with the high M\textsubscript{w} PLLA, but miscible with the
low Mw PLLA.

Blümm et al. [21] studied the crystallization and melting of the miscible PHB/PLLA blends, i.e. PHB blended with low molecular weight PLA (Mn = 1759). They reported that two types of spherulites were formed on rapidly cooling the sample from the melt to 100°C and holding for several minutes, corresponding to the crystallization of PHB and PLLA respectively. The radial growth rate of PHB spherulites decreased with increasing PLLA content (Fig.2.18). This is due to the addition of PLLA diluting the melt and retarding the crystallization growth rate of PHB.

![Fig.2.18 Radial growth rate of PHB spherulites in PHB/PLLA (Mn = 1759) blends (crystallization temperature = 100°C) [21]](image)

Ohkoshi et al. [70] studied the miscibility and solid-state structure of PLLA blended with atactic-PHB with different molecular weights (Mw = 9400, 21000 and 140000 g mol$^{-1}$). They reported that the blends of PLLA and atactic-PHB with Mw = 9400 showed a single glass transition temperature, and the value decreased with increasing atactic-PHB content. In contrast, the blends of PLLA
with atactic-PHB with Mw = 140000 showed two glass transition temperatures. These results also indicated that PLLA is only miscible with low molecular weight atactic-PHB.

![Polarized light micrographs of cast films of PHB/PLLA blends: (A) PHB/PLLA = 80/20, (B) PHB/PLLA = 60/40, (C) PHB/PLLA = 40/60, (D) PHB/PLLA = 20/80](image)

**Fig.2.19** Polarized light micrographs of cast films of PHB/PLLA blends: (A) PHB/PLLA = 80/20, (B) PHB/PLLA = 60/40, (C) PHB/PLLA = 40/60, (D) PHB/PLLA = 20/80 [45]

Furukawa et al. [45] analyzed the structure, dispersibility and crystallinity of PHB/PLLA blends with a PLLA content of 20, 40, 60 and 80 wt%, and found that the blend properties are heavily dependant on concentration. Different PHB/PLLA blends were prepared by solvent-casting from chloroform solutions. Fig.2.19 shows the optical micrographs of PHB/PLLA blends under polarized
light. The micrographs of PHB/PLLA 80/20, 60/40 and 40/60 blends show large spherulite structures the same as pure PHB, while the micrograph of PHB/PLLA 20/80 blend shows a tiny spherulite structure. These results indicated that all PHB/PLLA blends are immiscible and for the PHB/PLLA 20/80 blend, PHB formed as a very small spherulite structure. DSC was used to study the crystallization and melting behaviour of the PHB/PLLA blends. Fig.2.20 shows the DSC curves of PHB, PLLA and their blends during the cooling and heating processes. During the cooling process (Fig.2.20 (A)), the crystallization peak of PHB can be observed, while no discernible crystallization peak of PLLA can be observed. The crystallization peaks of PHB were observed for PHB/PLLA 80/20, 60/40 blends, a broad crystallization peak was observed for the 40/60 blend, and the corresponding peak was not observed for the 20/80 blend. This indicated that PHB in the 40/60 blend crystallized very slowly and in 20/80 blend did not crystallize much during the cooling process. During the heating process, besides the pure PLLA, the recrystallization peak of PLLA can only be observed in PHB/PLLA 20/80 blend, and the lowering of the recrystallization temperature for the blend compared with that of pure PLLA indicated that the PHB formed finely dispersed crystals acting as nucleating agent for PLLA.
Fig. 2.20 DSC curves during the cooling and heating processes of PHB, PLLA and PHB/PLLA blends: (A) cooling process, (B) heating process [45]

In addition, the solvent-cast films of PHB/poly(d, l-lactic acid) (PLA) blends have also been investigated in terms of their miscibility, crystallization, morphology and mechanical properties by Zhang et al. [72]. They found that PHB/PLA blends are immiscible and exhibit different thermal properties over the composition range, as listed in Tables 2.6 and 2.7. It was found that the blends exhibit two glass transition temperatures corresponding to the glass transitions of PHB and PLA, and the melting temperature and crystallinity of PHB remained constant over the whole composition range. The morphologies of PHB and PHB/PLA blends crystallized at 90°C were studied, and it was
found that the rate of growth of PHB spherulites decreased with increasing PLA content. For the PHB/PLA 20/80 blend, no discernible crystal structure was observed. Mechanical properties of cast films of PHB/PLA blends were studied, and it was found that the addition of amorphous PLA reduced the Young's modulus and stress at break, and increased the elongation at break.

Table 2.8 lists the tensile properties of PHB and the PHB/PLA 60/40 blend. Another blend sample of PHB/PLA 40/60 prepared by melt blending was studied as well. They found that the sample prepared at high temperature showed a lower melting temperature of PHB component and lower glass transition temperature of PLA component. This indicated the melt blended sample exhibited better miscibility. This was possibly due to the transesterification between PHB and PLA chains which occurs at about 190°C, and thus a small amount of PHB/PLA copolymers, which can act as a compatibilizer to improve the miscibility of PHB and PLA, were produced.

Table 2.6 Glass transition temperatures of pure PHB, pure PLA and PHB/PLA blends [72]

<table>
<thead>
<tr>
<th>PHB/PLA composition (w/w)</th>
<th>( T_{g(PHB)} ) (°C)</th>
<th>( T_{g(PLA)} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Midpoint</td>
<td>Onset</td>
</tr>
<tr>
<td>100/0</td>
<td>1.76</td>
<td>9.6</td>
</tr>
<tr>
<td>80/20</td>
<td>4.45</td>
<td>11.0</td>
</tr>
<tr>
<td>60/40</td>
<td>0.28</td>
<td>10.3</td>
</tr>
<tr>
<td>40/60</td>
<td>4.86</td>
<td>10.6</td>
</tr>
<tr>
<td>20/80</td>
<td>3.27</td>
<td>10.4</td>
</tr>
<tr>
<td>0/100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Data obtained from the DSC cooling run at a scan rate of 10°C/min
Table 2.7 Melting points and crystallinity of pure PHB and PHB in the blends from the DSC heating run [72]

<table>
<thead>
<tr>
<th>PHB/PLA composition (w/w)</th>
<th>$T_m$ $^\circ$C</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$X_{c(blend)}^*$ (%)</th>
<th>$X_{c(PHB)}^{**}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>175.1</td>
<td>82.2</td>
<td>56.3</td>
<td>56.3</td>
</tr>
<tr>
<td>80/20</td>
<td>175.4</td>
<td>64.2</td>
<td>43.9</td>
<td>54.9</td>
</tr>
<tr>
<td>60/40</td>
<td>175.0</td>
<td>47.6</td>
<td>32.6</td>
<td>54.3</td>
</tr>
<tr>
<td>40/60</td>
<td>174.6</td>
<td>31.6</td>
<td>21.6</td>
<td>54.1</td>
</tr>
<tr>
<td>20/80</td>
<td>174.7</td>
<td>16.5</td>
<td>11.0</td>
<td>55.0</td>
</tr>
</tbody>
</table>

* The crystallinity of the blends, $X_{c(blend)} = (\Delta H_f/\Delta H_f^0) \times 100$

** The crystallinity of the PHB phase, $X_{c(PHB)} = C_{r(\text{blend})}/w_{\text{PHB}}$

Table 2.8 Mechanical tensile properties of PHB and PHB/PLA 60/40 blend [72]

<table>
<thead>
<tr>
<th>PHB/PLA composition (w/w)</th>
<th>Modulus (kg mm$^2$)</th>
<th>Stress at break (kg mm$^2$)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>366</td>
<td>8.7</td>
<td>3.7</td>
</tr>
<tr>
<td>60/40</td>
<td>274</td>
<td>6.5</td>
<td>27.7</td>
</tr>
</tbody>
</table>

2.3.3 PHB/Cellulose Derivatives Blends

PHB based materials with better mechanical properties and less cost can be prepared by compounding with natural fibers, such as cellulose fibers or cellulose derivatives. Cellulose is a linear polymer of (β-1,4)-D-glucopyranose units in crystalline forms [73]. Cellulose derivatives, such as cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP), have been often mixed with PHB to study the miscibility, morphology, crystallization kinetics and mechanical properties [19-20, 74].
Two PHB/CAB blend systems, differing in the molecular weight of CAB (for CAB1 $M_n=61\times10^3$ and for CAB2 $M_n=71.6\times10^3$), have been studied by Pizzoli et al [19]. The results obtained by differential scanning calorimetry (DSC), as shown in Fig. 2.21, indicate that the dependence on composition of the glass transition temperature of the blends is different according to the composition range: $T_g$ decreases with increasing PHB content form 0 to 50 wt %, whereas
the blend $T_g$ only slightly depends on composition at higher PHB content. Moreover, the melting temperature and crystallization temperature are determined both by type of CAB and composition of blends. For example, when PHB amounts were less than 60 wt %, no crystalline phase develops above $T_g$ in PHB/CAB2 blends, while in PHB/CAB1 blends it is the cellulosic component undergoing crystallization, as clearly indicated by the inversion of dependence on composition of $T_m$.

![Graph showing radial growth rate (G) as a function of $T_c$ for PHB, PHB/CAB1 blends, and PHB/CAB2 blends.](image)

**Fig.2.22** Radial growth rate (G) as a function of $T_c$ for (○) PHB, (●) PHB/CAB1 blends and (△) PHB/CAB2 blends. Number on curves: CAB content [19]
Fig. 2.22 shows the spherulite radial growth rate $G$ as a function of $T_c$ for PHB/CAB1 and PHB/CAB2 blends with different composition, together with $G$ vs. $T_c$ curve for pure PHB for comparison. It is seen that $G$ increases with $T_c$ up to a maximum value, which remains almost unchanged for all blends, and then decreases, following the same trend in pure polymers. Furthermore, the radial growth rate $G$ is seen to decrease gradually with increasing CAB content in both systems, which is mainly associated with the dilution effect produced by the presence of the cellulosic component. Buchanan [75], El-Shafee [76] also found similar results.

![Graph](image)

**Fig. 2.23** Radius of spherulite during isothermal crystallization at 120°C for pure PHB and PHB/cellulose derivative blends as a function of time [20]

Structure and mechanical properties for binary PHB/cellulose derivative blends have been studied by Yamaguchi et al [20] using dynamic mechanical analysis (DMA) and tensile testing. Four types of cellulose derivatives used in their study are as follows: CAP46 ($M_n=77\times10^3$) is cellulose acetate propionate (CAP) with 46% of propionyl, CAB52 ($M_n=20\times10^3$) is CAB with 52% of butyryl,
CAB38 ($M_n=25\times10^3$) is CAB with 38% of butyryl and CAB37 ($M_n=77\times10^3$) is CAB with 37% of butyryl. It is found that the addition of cellulose derivative results in a great decrease in spherulite growth rate, as shown in Fig. 2.23. It is also seen from the figure that the blends of PHB and the cellulose derivative with high molecular weight (CAP46 and CAB 37) show a greater decrease in spherulite growth rate compared with the other ones. This may be due to their higher viscosity, which results in a reduction of the molecular diffusion of PHB chains during crystallization. As a result of this, the blends of PHB and high molecular weight cellulose derivative have more amorphous chains of PHB fraction than pure PHB and the other two systems.

As plotted in Fig. 2.24, the curves of storage modulus $E'$ for PHB/CAP46 blend and PHB/CAB37 blend are quite different from that of pure PHB, PHB/CAB38 blend and PHB/CAB52 blend: the level of $E'$ for PHB/CAP46 and PHB/CAB37 decreases dramatically at around room temperature, i.e. β relaxation temperature due to glass transition, and then increases with temperature after reaching a minimum value at about 40°C. The increase in $E'$ may be attributed to the re-crystallization of PHB during the measurement, indicating the original specimens produced by compression moulding have low crystallinity. Moreover, as demonstrated in the $E''$ curves, the β relaxation temperatures for PHB/CAP46 and PHB/CAB37 are located at lower temperature than that of the pure PHB, although these cellulose derivatives have high glass transition temperature. This may be explained by the improved mobility of amorphous PHB chains by the reduction of crystallinity. However, the β relaxation temperatures for PHB/CAB38 and PHB/CAB52 are located at almost the same temperature as that of pure PHB.
Fig. 2.24 Temperature dependence of (a) storage modulus $E'$ and (b) loss modulus $E''$ at 10Hz for pure PHB and PHB/cellulose derivative blends [20]
Fig. 2.25 Stress-strain curves at 23°C for (a) PHB and PHB/CAB52 (80/20) and (b) PHB/CAB52 (80/20) and PHB/CAP46 (80/20) [20]

Although the cellulose derivatives are quite brittle materials, the blends of PHB and cellulose derivatives show better deformability than the pure PHB, as illustrated in Fig. 2.25. Furthermore, there is a significant difference in tensile
properties between PHB/CAP46 blend and PHB/CAB52 blend, differing in the molecular weight of the cellulose derivative. It is obvious that the blends of cellulose derivative with high molecular weight (PHB/CAP46) possess better deformability due to the low degree of crystallinity and the consequently improved mobility of the amorphous PHB chains.

2.3.4 PHB Blends with Other Polymer

2.3.4.1 PHB/Polycaprolactone (PCL) Blends

Polycaprolactone is a synthetic semicrystalline linear aliphatic polyester which is biocompatible and biodegradable. It is ductile and has a significantly lower melting point than PHB at about 60°C [77]. Blends of PCL and PHB have attracted much attention due to their inherent biodegradability and biocompatibility, although they are immiscible on the molecular scale as proven by Kumagai et al [78] and Chiellini et al [79], using thermogravimetric analysis and optical microscopy (Fig. 2.26 and 2.27).

![Thermogravimetric analysis (TGA) traces of PHB-PCL blends](image)

**Fig. 2.26** Thermogravimetric analysis (TGA) traces of PHB-PCL blends [79]
The thermal behaviour of PHB/PCL and PHB/modified PCL blends were studied by D. Lovera et al [24], using DSC. The molecular weights for the PCL and modified PCL were 120,000, 2,000 and 600, respectively. They found that the addition of either PCL or modified PCL made the PHB crystallization more difficult, exhibiting a strong reduction in the crystallization temperature and crystallization enthalpy. The thermal transition temperatures of the PHB phase did not exhibit significant variation on addition of PCL, while these temperatures shifted to lower values with increasing content of modified PCL, as shown in Fig. 2.28. The reduction of thermal transition temperatures of the PHB phase was due to the partial miscibility between PHB and modified PCL. It was found that the lower the molecular weight of PCL, the higher the magnitude of the reduction.
In general, PCL acts as a polymeric plasticizer in PHB/PCL blends to moderate the mechanical properties, as shown in Fig. 2.29 [79]. From dynamic-mechanical measurements, it has been found that for a PCL content of 60% and above, the PCL phase forms a continuous matrix, with PHB spherulites embedded in it. The mechanical behaviour of the blends is then dominated by the ductile PCL matrix. On the other hand, for compositions with less than 60% of PCL, the PHB phase becomes continuous. However the inclusion of soft PCL does not catastrophically lower the rigidity of the sample. Similar results were obtained by D. Lovera et al [24] through tensile property measurements.

**Fig. 2.28** Effect of PCL content and molecular weight on PHB (a) melting temperature and (b) glass transition temperature [24]
Fig. 2.29 Mechanical properties of PHB-PCL blends: (a) Young's modulus, (b) Yield strength [79]
2.3.4.2 PHB/Poly (vinyl acetate) (PVAc) and PHB/Poly (vinyl alcohol) (PVA) Blends

PHB/PVAc or PVA blends were extensively studied. The PVAc and its derivatives by hydrolysis, such as the PVA, are miscible with PHB in the melt. Greco et al [25] studied the PHB/PVAc blends prepared by film casting, and they reported that the PHB/PVAc blends are characterized by only one $T_g$, which is between that of the PHB and PVAc and depends on their composition. Apart from this, at a given temperature, the growth rate of PHB spherulites decreased with increasing PVAc content and a significant decrease on the equilibrium melting temperature of PHB was found. This indicated that PHB spherulites grow in equilibrium with a single-phase melt.

Fig. 2.30 DSC curves for PHB/PVAc blends with different PVAc content [26]

Similar results were found by El-Hadi et al [26] and Ghaffar [49], although in their study PHB was not only blended with PVAc but also with other additives such as plasticizer, lubricant and nucleation agent. The DSC results indicating the composition dependence of thermal transition temperatures are illustrated.
in Fig. 2.30 [26]. The optical micrographs of PHB spherulites and PHB/PVAc spherulites are shown in Fig. 2.31. PHB formed large spherulites with cracks (Fig. 2.31 (A) and (B)), while the PHB/PVAc blends had small spherulites due to PVAc acting as nucleation sites in the blends. Further, the size of PHB spherulites decreased with the increasing PVAc content, as shown in Fig. 2.31 (C) and (D).

Fig. 2.31 Polarized optical micrographs of (a) spherulites of PHB obtained by isothermal crystallization at 100°C, (b) spherulites of PHB obtained by isothermal crystallization at 80°C, (c) spherulites of PHB/PVAc (82/4) blend isothermally crystallized at 80°C, and (d) spherulites of PHB/PVAc (80/8) blend isothermally crystallized at 80°C [49].

The physical properties and rheological properties of the blends were also investigated [26, 49]. Fig. 2.32 shows the stress-strain curves of pure PHB and
PHB/PVAc (74/20) blend, indicating the great increase in the elongation at break due to the decreasing crystallinity of the blend caused by the addition of PVAc. Apart from this, the addition of PVAc weakens the secondary crystallization of PHB at room temperature, and thus the blends show stable physical properties during storage at room temperature. Fig. 2.33 shows the thermal stability of PHB and PHB/PVAc (82/4) blend: at the beginning the viscosity of the blend is lower than that of PHB due to the addition of lubricant and plasticizer, however, the blend is more stable than PHB.

![Stress-Strain curves at room temperature for pure PHB and PHB/PVAc (74/20) blend](image)

**Fig. 2.32** Stress-Strain curves at room temperature for pure PHB and PHB/PVAc (74/20) blend [49]
The thermal behaviour and miscibility of PHB/PVA blend films was studied by Yoshie et al [80]. The DSC results indicated that the melting temperature, $T_m$, of the PHB phase decreased with increasing PVA content, whereas $T_m$ of the PVA phase remained almost unchanged. The crystallinity of the PHB in the blends decreased with increasing PVA content (Fig. 2.34), indicating that the addition of PVA affected the thermal behaviour of the PHB. Moreover, miscibility in the amorphous phase of the blends was analyzed by density measurement and solid-state $^{13}$C NMR. Experimental results indicated that the increase of PVA content enhanced miscibility between PHB and PVA.

Fig. 2.33 Viscosity versus time for pure PHB and PHB/PVAc (82/4) blend [26]
Fig. 2.34 Phase crystallinity of PHB for PHB/PVA (●) and PHB/PVA/glycerine (▲) [80]

2.3.4.3 PHB/ Polyoxymethylene (POM, poly(methylene oxide), PMO) and PHB/ Poly(ethylene oxide) (PEO) Blends

POM, -[CH₂-O]ₙ-, is a semi-crystalline polymer having a similar melting point as PHB, about 180°C. Blends of PHB/POM, prepared by melt mixing and subsequent compression moulding, have been studied by Avella et al [81]. Miscibility, crystallization behaviour, thermal behaviour, morphological and mechanical properties of the blends were investigated.
Fig. 2.35 Loss factor of PHB/POM blends as a function of the temperature [81]

The DMA trace showed two peaks corresponding to the $T_g$ of the two components, as shown in Fig. 2.35, which indicated the immiscibility of these two polymers in the amorphous phase. By cooling the PHB/POM blends, it was possible to isothermally crystallize the POM at temperatures $\geq 150^\circ$C, meanwhile the PHB remained in the liquid state. The subsequent crystallization of PHB was obtained by further cooling at temperature below $120^\circ$C. For different compositions, almost spherical particles of the minor phase were dispersed in the major phase and the size-distribution of the particles depended on the crystallization conditions. An example of POM spherulites growing at $151^\circ$C from their own molten phase in the PHB/POM 40/60 (w/w) blend is shown in Fig. 2.36. Moreover, a significant decrease of the melting point of the PHB phase was found in the blends, whereas the $T_m$ of POM remained almost unchanged. This decrease of melting temperature was attributed to the change of lamellar morphology of PHB in the blends due to the previous crystallization of POM. Furthermore, the authors reported that the mechanical properties of the blends did not show clear dependence of the blend composition.
Fig. 2.36 Polarized optical micrograph of POM spherulites growing from PHB/POM (40/60 wt%) at 151°C [10]

PEO, whose repeating unit is $-\text{CH}_2-\text{CH}_2-\text{O}$, is a polyether with a molecular weight above 20,000 g/mol. Different from PHB and POM, PHB and PEO have very different melting points, about 175°C and 60°C, respectively. The blends of PHB and PEO, obtained by slowly solution casting from chloroform, were studied by Kumagai and Doi [82]. They found that the PHB/PEO blends showed a single glass transition temperature $T_g$ in the whole composition range, indicating a complete miscibility of the two components in the amorphous phase. The glass transition temperature was found to depend on the composition. From the DSC curves of PHB/PEO samples, it was found that in presence of PEO, the melting temperature of PHB decreased significantly. As an example, the melting temperature of the blend containing the 20% of PEO was found equal to 163°C, while the pure PHB crystallized under the same conditions, showed a melting point of 194°C. This fact allowed processing of the blends at lower temperature than neat PHB, avoiding the degradation of PHB, which occurs at only few degrees above its melting point.
Fig. 2.37 Enzymatic degradation (erosion) profiles of the films of PHB and PHB PEO 75/25 blend in the aqueous solution of PHB depolymerase at 37°C and pH 7.4 [82]

The enzymatic degradation of the PHB/PEO blends, performed in a 0.1 M phosphate buffer solution by adding an extracellular PHB depolymerase at 37°C and pH 7.4, has also been studied by Kumagai et al [82]. The rate of the PHB degradation of the PHB/PEO film was faster than that of the neat PHB film. The acceleration of enzymatic degradation of PHB in PHB/PEO blends was caused by the enhanced permeability of PHB depolymerase, due to the PEO dissolution.

Choi et al [83] have studied the thermal, morphological and rheological properties of PHB/PEO blends by low shear rate and dynamic flow experiments. PHB and PEO were found to be miscible in the melt state. The PHB/PEO blend containing 20% of PHB showed higher values of shear viscosity and storage viscosity modulus than PHB, i.e. the rheology of this
composition blend is better than that of the pure PHB. In addition, the loss modulus was higher than the storage modulus for all composition, indicating that the energy dissipation caused by the viscosity is larger than the elastic energy storage. The rheological behaviour has been further explained by the morphological feature of PHB/PEO blends by using scanning electron microscopy (SEM). The SEM micrographs showed that pure PHB had many gaps throughout the fracture surface and 20% of PEO filled the gaps of the PHB matrix, as shown in Fig.2.38. This morphology performance of the PHB blend containing 20% of PEO improved the rheological properties.

![Fig.2.38 SEM micrographs of impact fracture surface of (a) PHB and (b) PHB blend containing 20% PEO [83](image)](image)

### 2.3.4.4 PHB/Poly(glycidyl methacrylate) (PGMA) Blends

Park et al [84, 85] found that polyhydroxyalkanoates (PHAs) with epoxide pendant groups have a higher thermal stability because the pendant epoxide groups could be used effectively to re-polymerize the thermally degraded PHB by reacting with the fragmented carboxyl chain ends. Thus PGMA, whose glass transition temperature $T_g$ is around 60°C, was studied as a polymeric thermal stabilizer for PHB by Lee et al [86]. PHB/PGMA blends with the PGMA content up to 30 wt % were prepared by a solution precipitation method. The
thermal decomposition of blends was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperatures of the two components were almost constant, independent of the blend composition, as shown in Fig. 2.39. As shown in Fig. 2.40, the blends contained a two-step degradation process. These results indicated the immiscibility of PHB and PGMA in the range of blend compositions studied. Moreover, as the PGMA content in the blends increased up to 30 wt %, their thermal stability (as measured by the first decomposition temperature) increased gradually, whereas the second decomposition temperature, which might be caused by a thermal crosslinking reaction during the degradation process, remained almost unchanged. It was also found that the residual weights for PHB/PGMA blends at 400°C increased up to 21% with increasing PGMA content, while that for pure PHB was 0% and for pure PGMA was 4% at that temperature.

Fig.2.39 DSC thermograms of PHB/PGMA blends [86]
Another extensively studied method to improve the mechanical and thermal properties of PHB is addition of low molecular weight plasticizers such as polyethylene glycol (PEG), dibutyl sebacate (DBS), dioctyl sebacate (DOS), etc [27]. The plasticizer weakens the intermolecular forces between adjacent polymer chains. Consequently, there is a change in free volume that causes reduction of the glass transition temperature in the system. Furthermore, plasticizers can also affect the processes of crystallization of the semicrystalline polymer.

PHB/low molecular weight PEG (normally PEG 300), obtained from solvent casting from chloroform solution, is the most extensively studied plasticization system. As reported in many papers [27, 28, 87-88], PHB is completely miscible with PEG 300, and both glass transition temperature $T_g$ and crystallinity decrease with the increasing PEG content. However, the addition
of PEG does not change the thermal stability of the blend. Moreover, Rodrigues et al [87] reported that an increase in the PEG content increases the water permeability and solubility due to the hygroscopic character of PEG.

**Table 2.9** DSC results (melting temperature, $T_m$; crystallinity, $n$; glass transition temperature, $T_g$) of melt quenched plasticized PHB systems as a function of plasticizer content [88]

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>PEG-300</th>
<th>Laprol 503</th>
<th>DBS</th>
<th>DOS</th>
<th>Laprol 5003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>16</td>
<td>33</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$T_m$, °C</td>
<td>182.6</td>
<td>174.8</td>
<td>168.8</td>
<td>174.5</td>
<td>172.8</td>
</tr>
<tr>
<td>$X_c$, %</td>
<td>58.3</td>
<td>62.8</td>
<td>69.9</td>
<td>65.8</td>
<td>66.6</td>
</tr>
<tr>
<td>$T_g$, °C</td>
<td>5.4</td>
<td>-74.3</td>
<td>-73.2</td>
<td>-12.6</td>
<td>-59.6</td>
</tr>
</tbody>
</table>

where, PEG stands for polyethylene glycols; Laprol stands for oxypropylated glycerols; DBS stands for dibutylsebacate; DOS stands for dioctylsebacate.

A comparison between various plasticized PHB systems with six different nontoxic low molecular weight plasticizers was reported by Bibers et al [27] and Kalnins etc [88]. Temperature characteristics of plasticized PHB, measured by the DSC method (as listed in Table 2.9), showed that generally plasticization did not affect the ability of PHB to crystallize. The exothermal crystallization temperature, $T_c$, and glass transition temperatures, $T_g$, of PHB were decreased with an increase in the plasticizer content, although the amount differed with different plasticizers. The effect could be explained by a higher mobility of PHB amorphous chains. In addition, the presence of some plasticizers decreased the PHB melting point, $T_m$, by 10-15°C and as a result the processing window could be enlarged. Fig.2.41 shows the physical properties (tensile strength and elongation at break) of plasticized PHB systems. The tensile strength at break of all the studied compositions
decreased with the increasing content of plasticizer. The elongation at break of all the compositions also depended on the plasticizer content: at lower plasticizer content, the elongation at break increased slightly, whereas with a further increase in the content of plasticizer, the elongation at break showed a sharp increase, although various compositions differed in the maximum value. Combined with the DSC results, it was found that the addition of plasticizer does not affect the crystallinity, the change in tensile strength and strain of the PHB/low molecular weight plasticizer blends is mainly due to a considerably weakened intermacromolecular interaction in the amorphous phase of PHB.

![Tensile strength and breaking elongation](image)

**Fig.2.41** (a) Tensile strength $\sigma_b$ and (b) breaking elongation $\varepsilon_b$ of plasticized PHB systems as a function of the plasticizer content: ○-L503, ◇-DOS, □-L5003, △-DBS, ▽-PEG, and 0-PIB (polyisobutylene) [27]

A series of PHB based blends with different additives, such as plasticizers (glycerol, tributyrin etc.), lubricants (glycerol monostearate etc.) and nucleation agents (saccharin), was investigated by Ghaffar [49]. Fig. 2.42 shows the DSC curves for all the compositions. It was found that the addition of plasticizers depressed the glass transition temperature and melting temperature. Furthermore, the glass transition temperature and melting temperature of the blends decreased with increasing plasticizer content from 5.5 to 13.5 wt %.
The author also found that the presence of plasticizer depressed the crystallinity of PHB by 10-20%. However, the crystallinity of the plasticized PHB blends did not show clear dependence with the content of plasticizer.

**Fig. 2.42** DSC curves for PHB/plasticizer blends: (a) melting peaks and (b) glass transition temperature [49]
2.3.6 PHB/Nano-Clay Composites

Polymer/clay nanocomposites have attracted considerable attention due to their remarkable improvement of physical, mechanical and thermal behaviour via nanoscale reinforcement. However, little efforts have been made in PHB/nano-clay composites [89].

![X-ray diffraction curves for various PHB/OMMT nanocomposites with various OMMT content](image)

**Fig. 2.43** The X-ray diffraction curves for various PHB/OMMT nanocomposites with various OMMT content [30]

To enhance the mechanical and thermal properties of PHB incorporation of layered silicates of montmorillonite (MMT) into PHB has been studied by Cheng et al [90], and similar work on PHB/organically modified montmorillonite (OMMT) (Cloisite 25A) has been done by Lim et al [30]. The insertion of PHB into OMMT layers was confirmed by X-ray diffraction patterns, as shown in Fig.2.43. It can been seen that the diffraction peak shifts to a lower 2θ value
with the increase OMMT content, and the intensity of the diffraction peak increased with increased OMMT content. This means that the overall clay platelets dispersed in the polymer matrix could participate in the nano-scale polymer-clay interaction. Fig. 2.44 shows the FT-IR spectra of pure PHB, OMMT, and PHB/OMMT (100/9) nanocomposite. The spectrum of the nanocomposite represents a characteristic absorption of both PHB and OMMT, indicating that two different phases coexist. The change of peak intensity indicates the intercalation of polymer chain in PHB nanocomposite.

![FT-IR spectra of pure PHB, OMMT and PHB/OMMT (100/9) nanocomposite](image)

**Fig.2.44** FT-IR spectra of pure PHB, OMMT and PHB/OMMT (100/9) nanocomposite [30]

The thermal degradability of the PHB/OMMT nanocomposites was studied by thermogravimetric analysis (TGA) [30], as shown in Fig. 2.45. It was found that the addition of OMMT affected the thermal behaviour of nanocomposites: the onset decomposition temperature for PHB/OMMT (100/3) was higher than that
for pure PHB due to the nanoscale dispersed OMMT layers preventing the outward diffusion of the volatile decomposition products. However, the onset decomposition temperature did not increase at higher OMMT content, which may be attributed to the intercalated low molecular weight organic surfactant beginning to degrade about 150°C. On the other hand, this instability may be also caused by insufficient dispersion.

**Fig. 2.45** TGA curves for pure PHB and PHB/OMMT nanocomposites with various OMMT content [30]

In addition the thermal behaviour of PHB/MMT nanocomposites were measured by Cheng etc [90], by using differential scanning calorimetry (DSC), and the data obtained are listed in Table 2.10. They reported PHB/MMT nanocomposites with 1 wt % clay loading showed a great effect on the crystallization behaviour of PHB, which may be explained by the exfoliated morphology with almost complete dispersion of the silicate layers. The
exfoliated nanocomposite exhibited higher crystallization temperature and faster crystallization rate due to the heterogeneous nucleating effect. However, when the content of MMT increased, the thermal behaviour became similar to that of pure PHB, which may be attributed to dispersion: the high clay content could lead to insufficient dispersion. Apart from this, the shape and dimensional orientation of layered silicate can affect the permeability of PHB: the well dispersed and layered structure of clay acted as a barrier in PHB matrix to reduce the permeation.

Table 2.10 The thermal behaviours of PHB/MMT nanocomposites [90]

<table>
<thead>
<tr>
<th>PHB/MMT</th>
<th>PHB</th>
<th>MMT 1%</th>
<th>MMT 5%</th>
<th>MMT 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_m (°C)</td>
<td>174</td>
<td>173</td>
<td>174</td>
<td>172</td>
</tr>
<tr>
<td>X_c (%)</td>
<td>67.1</td>
<td>60.1</td>
<td>66.7</td>
<td>63.4</td>
</tr>
<tr>
<td>T_c (°C)</td>
<td>87</td>
<td>96</td>
<td>87</td>
<td>80</td>
</tr>
</tbody>
</table>

Layered nano-kaolinite has been used to reinforce PHB, where a structural and morphological study was carried out by Gardolinski et al [29]. They also characterized the intercalation process by X-ray diffraction and FT-IR, and similarly their TG/DSC results showed that the addition of nano-kaolinite just slightly affected the decomposition temperature of the nanocomposites. The morphology of pure kaolinite and nano-kaolinite/PHB composite are illustrated in Fig. 2.46. As can be seen, kaolinite shows morphology with well defined hexagonal edges and corner angles. In comparison, the scanning electron micrograph of nano-kaolinite/PHB composite shows significantly different morphology from that of pure kaolinite: the hexagonal morphology of the intercalated kaolinite almost totally collapsed, and there is a severe modification of the crystallite surface, which might be caused by the fact that lateral crystalline expansion during the thermal intercalation causes the kaolinite to break and finally causes crystallite disruption. However, the
morphology of the nanocomposites depends not only on the crystalline expansion but also on many external factors.

Fig. 2.46 SEM images form (a) raw kaolinite and (b) nano-kaolinite/PHB intercalated phase [29]
CHAPTER 3  EXPERIMENTAL METHODS

In order to improve the thermal properties, mechanical properties and processability of polyhydroxybutyrate (PHB), three different materials were blended with PHB: poly(ethylene glycol) (PEG), starch and polylactic acid (PLA). Thus, there are four sections in the experimental work: characterization of PHB, plasticization of PHB by PEG, blends based on PHB and starch, and blends based on PHB and PLA.

3.1 Materials

All raw materials used in this project with their trade name and the supplier for each ingredient are listed in Table 3.1.

Table 3.1 Raw materials used in this project

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Supplier</th>
<th>Trade name</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhydroxybutyrate (PHB)</td>
<td>Biomer</td>
<td>PHB</td>
<td>Melting range: 168-172°C</td>
</tr>
<tr>
<td>Poly(ethylene glycol) (PEG)</td>
<td>Acros</td>
<td>PEG 300</td>
<td>Molecular weight ~ 300</td>
</tr>
<tr>
<td>Maize starch</td>
<td>National Starch &amp; Chemical Co.</td>
<td>ECO-MAIZE</td>
<td>regular maize starch containing 72% amylopectin</td>
</tr>
<tr>
<td>Maize starch</td>
<td>National Starch &amp; Chemical Co.</td>
<td>HYLON VII</td>
<td>native food starch refined from high amylose maize starch containing 70% amylose</td>
</tr>
<tr>
<td>Polylactic acid (PLA)</td>
<td>Hycaill, BV (now Tate &amp; Lyle)</td>
<td>HM1010</td>
<td>Glass transition: 60°C</td>
</tr>
</tbody>
</table>
Pure polyhydroxybutyrate (PHB), in the form of a white powder, was studied in this project. Its weight average molecular weight (Mw) was found to be $283 \times 10^3$, determined by Gel Permeation Chromatography (GPC). A commercially formulated PHB based product, Biomer P226, was kindly supplied by Dr Haenggi, Biomer Company, Germany. A comparison of properties of PHB and Biomer P226 was carried out.

Poly (ethylene glycol) with molecular weight of 300 was selected as a plasticizer to improve the flexibility of PHB. Chloroform, obtained from Acros Organics, was used as the solvent for the solvent-casting method.

Two types of maize starch with different structures were chosen, as listed in Table 3.1. No plasticizer or other additive was used for processing the PHB/starch blends.

Polylactic acid (PLA) used in this project was in the form of semi-transparent pellets. Its weight average molecular weight (Mw) was found to be $224 \times 10^3$ by GPC.

### 3.2 Sample preparation

Plasticized PHB films were obtained by solvent-casting, using poly(ethylene glycol) (PEG) as a plasticizer.

Blends based on PHB and maize starch were prepared by melt compounding, and the effects of different starch contents and different starch types were studied.

Blends of PHB and PLA were prepared by melt compounding at a number of different PHB/PLA concentrations. The effect of the addition of HYLON VII
starch on the properties of PHB/PLA blends was further studied.

### 3.2.1 Solvent-casting

PHB and PEG, with three distinct concentrations (2, 5, 10% by weight), were dissolved in chloroform at 70°C under stirring. Then the solution was cast onto a glass Petri dish and the solvent was evaporated at room temperature over a period of 5 days to obtain a dry film.

### 3.2.2 Melt-compounding

![Haake Polylab Rheomix 600 and roller rotors](image)

**Fig. 3.1** (a) Haake Polylab Rheomix 600, and (b) roller rotors

All raw materials were pre-dried at 60°C for 24hr in a vacuum oven prior to processing. PHB was blended with maize starch and/or PLA by mixing in a Haake Polylab Rheomix 600 (Thermo Electron Corporation Waltham, MA) (Fig. 3.1). For each shot, the total mass was about 60 g. The formulations and compounding conditions are listed in Tables 3.2, 3.3, 3.4 and 3.5.
Table 3.2 Formulations and compounding conditions of PHB/ECO-MAIZE blends

<table>
<thead>
<tr>
<th>PHB (wt %)</th>
<th>ECO-MAIZE (wt %)</th>
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<th>Temperature (°C)</th>
<th>Time (min)</th>
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Table 3.3 Formulations and compounding conditions of PHB/maize starch blends

<table>
<thead>
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<th>ECO-MAIZE (wt %)</th>
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<th>Time (min)</th>
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Table 3.4 Formulations and compounding conditions of PHB/PLA blends

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<th>PLA (wt %)</th>
<th>Rotor speed (rpm)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
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Table 3.5 Formulations and compounding conditions of PHB/PLA/HYLON VII blends

<table>
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<tr>
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<th>PLA (wt %)</th>
<th>HYLON VII (wt %)</th>
<th>Rotor speed (rpm)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
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3.2.3 Granulation of PHB/maize starch blends

Fig. 3.2 (a) Zerma Granulator GSL 180/130, (b) rotating knives in cutting chamber, and (c) granulator screen
Following compounding, the prepared PHB/HYLON VII 70/30 and PHB/ECO-MAIZE 70/30 blends were then granulated for the capillary rheometry study, using a Zerma Granulator GSL 180/130 (Zerma Machinery & Recycling Technology Ltd., China) (Fig. 3.2).

Lumps of PHB/maize starch blends were placed into the granulator, which works by blocking off the material exit chute with a steel screen, and this caused all materials to remain in the cutting chamber until the particle size (~5mm) was achieved, allowing particles to go through the screen. However, the granule size and shape obtained was very irregular. The granulation process was left for approximately 3 minutes, and then the granules were collected.

### 3.2.4 Compression moulding

PHB based blends obtained from the Haake Polylab Rheomix (section 3.2.2) were hot pressed at 180°C to form sheets for optical microscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), mechanical and biodegradation testing. The compression moulding machine used was a 20 Ton Lab pressCO1123/1 from Modular Manchester UK.

The melt compounded PHB/maize starch blends were placed into a mould with a thickness of 3mm, which consisted of two plates with the protection of poly(ethylene terephthalate) (PET) films on both sides. The assembly was put into the press set at 180°C and preheated for 5-8 minutes before pressure was applied. The pressure was then increased to 15 tons and applied for 3 minutes. After the hot press, the mould assembly was moved to another press (approximately 110°C) and 10 tons was applied this time for 15 minutes, and then cooled down to room temperature.
Samples of PHB/PLA blends and PHB/PLA/HYLON VII blends were produced using a similar procedure with two types of mould with thicknesses of 1mm and 3 mm, respectively. However, the sheets obtained were quenched after hot-pressing at 180°C. Sheets of pure PLA and PHB/PLA blend containing 75% PLA were further processed by reheating to 100°C and holding for 5min, i.e. annealing. This temperature was chosen because it is the starting point of the recrystallization of PLA.

3.3 Morphological Analysis

3.3.1 Optical Microscopy

Optical microscopy is the simplest and most commonly used method to examine the microstructures of materials, using visible light and a system of lenses.

A Leica DMLM Microscope (Leica Microsystems Ltd, Germany), equipped with a FP82 hot stage and a FP90 control unit (Mettler-Toledo Ltd, UK) was used to study the crystallization behaviour and spherulitic morphology of pure PHB, Biomer P226 and other PHB based blends. Samples were placed between two glass slides and were heated up to 200°C at 10°C/min, held for 1 minute, and then cooled down naturally to room temperature. The cooled samples were then reheated to 200°C and recooled to room temperature.

3.3.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope images the sample surface by scanning it with a high-energy beam of electrons. Energy dispersive X-ray analysis (EDAX) is a technique used to investigate the elemental composition of a sample, and is commonly found on many scanning electron microscopes.
A scanning electron microscope (SEM), LEO 1530 VP, was used to examine the size and shape of the PHB powders. A tiny sample of PHB powder was coated with gold to make it electrically conductive, preventing charging up and allowing it to be analyzed using this technique. The powders were then examined.

Fracture surfaces of the tensile specimens of Biomer P226 and other PHB based blends were coated with gold and examined using the SEM to investigate the fracture surface morphology. EDAX was used to study the fillers in the Biomer P226 specimen.

3.4 Fourier Transform Infrared (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a method used to identify the sample composition.

FTIR spectra by attenuated total reflectance (ATR) were obtained at room temperature on a FTIR-8400S spectrometer. The scanned wavenumber range was 4000-600 cm\(^{-1}\). All spectra were recorded at a resolution of 4 cm\(^{-1}\), and 64 scans were averaged for each sample.

3.5 Wide Angle X-Ray Diffraction (WAXD)

Wide angle X-ray diffraction (WAXD) is a technique to examine the crystalline structure of materials.

Samples of 60mm × 60mm × 1mm square compressed sheets of Biomer P226 and all PHB based blends were prepared for WAXD study. WAXD traces were recorded for 2θ between 0 and 40° using a Bruker AXS D8 X-ray diffractometer equipped with a copper tube operating at 40 kV and 40 mA producing CuK\(\alpha\)
radiation of 0.154 nm wavelength.

3.6 Differential Scanning Calorimetry (DSC)

The differential scanning calorimeter (DSC) is a technique to measure the thermal transition temperatures and crystallinity of polymers.

The measurements were performed on a DSC 2010 apparatus fitted with sampler and mechanical cooler (TA Instruments Inc, USA). Samples of approximately 10-15 mg in mass were placed in sealed aluminium pans and loaded into the sampler. First, samples obtained from melt-compounding (section 3.2.2) were heated from -25°C to 200°C at 10°C /min and left for 1 minute to measure the melting point of the as-formed sample, and then they were cooled down at 10°C/min to -25°C. Then the samples were reheated to 200°C at 10°C /min so that the melting could be studied.

Due to PHB and PHB/ECO-MAIZE samples possessing high crystallinity, DSC measurements were carried out to study the glass transition by heating the sample from -30°C to 20°C at 5°C /min.

3.7 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is used to measure the change in weight during heating and thus studies the thermal stability and composition of the sample.

Samples of PHB, Biomer P226 and plasticized PHB, of approximately 10 mg in mass, were prepared in the form of powder or thin film. TGA tests were performed in a TGA 2920 (TA Instruments Inc, USA) under nitrogen at a heating rate of 10°C /min from room temperature to 500°C.
3.8 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) is a thermal analysis technique used to measure changes in the viscoelastic response of a material as a function of temperature, time, or deformation frequency.

DMTA measurements of PHB/starch blends were performed using DMA Q800 apparatus (TA Instruments Inc, USA) in the flexure (Dual Cantilever) mode ($L_0 = 35$mm). Rectangular specimens (width $\sim 13$mm, thickness $\sim 3$mm, $L_0 = 35$mm) of PHB/maize starch blends, PHB/PLA blends and PHB/PLA/HYLON VII blends were prepared. The specimens of PHB/maize starch blends were heated from $-50 \degree C$ to $100 \degree C$ at $3 \degree C /$min, while the specimens of PHB/PLA blends were heated from $-50 \degree C$ to $150 \degree C$ at $3\degree C$/min, with a constant frequency of 10 Hz. The storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan \delta$) were recorded.

3.9 Rheological Analysis

3.9.1 Melt Flow Index (MFI)

Melt flow index is commonly used for quantifying melt flow properties. Melt flow index (MFI) is defined as the weight of polymer in grams flowing in 10 minutes through a capillary of specific diameter and length under an applied load [91]. Generally, a higher MFI value indicates lower melt viscosity.
MFI measurements were carried out in a MP600 Extrusion Plastometer (Tinius Olsen Inc, USA) (Fig. 3.3). Samples of approximately 5 g in mass were preheated for 200 seconds at 175 ºC for the PHB powder or at 170 ºC for the Biomer pellet in the barrel. The samples were then extruded through the die (2.096mm × 8.001mm) under a constant load of 2.16 kg.

3.9.2 Capillary Rheometry

Capillary rheometry is the most commonly used technique for measuring rheological properties, such as shear rate, shear stress and shear viscosity.

The shear rheology of the PHB, Biomer P226 and PHB/maize starch blends was studied using a twin bore Rosand RH7 capillary rheometer (Rosand Precision Ltd., UK) with version 6×10 software. One bore of the rheometer was fitted with a long capillary die (L/D ratio = 16) and the other bore was fitted with a short die (L ~ 0). The diameter of both capillary dies was 1 mm. Melt viscosity
was determined at shear rates of 20, 63, 200, 633 and 2000 s\(^{-1}\). The Bagley correction was applied when using two bores for Biomer P226 and PHB/maize starch blends. Due to the melt viscosity of pure PHB being too low, its viscosity was measured with a single bore with the long die (L/D = 16).

### 3.10 Mechanical Testing

#### 3.10.1 Tensile Testing

Tensile testing measures the tensile properties, such as Young’s modulus, tensile stress at break and elongation at break.

Tensile testing on Biomer and PHB/maize starch blends was performed on a LLOYD INSTRON L10000 Tensometer (Lloyd Instruments Ltd, UK). The dumbbell-shape specimens (width ~ 4mm, thickness ~ 3mm, L\(_0\) = 25mm) were extended at a crosshead speed of 5 mm/min. Specimens of PHB/PLA blends (width ~ 4mm, thickness ~ 1mm, L\(_0\) = 25mm) were extended at a crosshead speed of 10 mm/min on a Hounsfield tensile testing machine.

#### 3.10.2 Charpy Impact Testing

The Charpy testing measures impact strength which is defined as the energy absorbed per unit area in breaking a notched specimen.

Charpy impact testing was carried out on a RAY-RAN universal pendulum impact system with a maximum impact energy of 7.502J. The specimen size was 10×55×3.3mm with a V-notch (2mm deep, with 45° angle and 0.25mm radius along the base), and the weight of the hammer and the impact velocity were 1.039kg and 3.8m/s, respectively.
3.11 Biodegradability

Biodegradation was monitored at room temperature by burying the weighed sample sections in 100mL of water and 50g of ‘multi-purpose compost’ (purchased from Wilkinson Hardware Stores Ltd). Five specimens were prepared for PHB, Biomer P226 and PHB/PLA formulations. The weight change, taken as an indication of biodegradability, was calculated as follows:

\[
\text{Weight} \, (\%) = \frac{W_m}{W_0} \times 100\% 
\]

where \( W_0 \) is the original sample weight and \( W_m \) is the measured sample weight after burial in moist compost.
CHAPTER 4 CHARACTERIZATION OF POLYHYDROXYBUTYRATE AND BIOMER P226

4.1 Introduction

In this chapter, the characterization of polyhydroxybutyrate (PHB) was carried out to investigate the inherent properties of PHB. Also a comparison between PHB and the formulated PHB based polymer (Biomer P226) was made. An initial study on adding poly(ethylene glycol) (PEG) into PHB was carried out to find out how plasticizer affects the properties of PHB.

4.2 Results and Discussion

4.2.1 Characterization of PHB and Biomer P226

4.2.1.1 Morphological Properties: Optical Microscopy and SEM Analysis

The melting and crystallization behaviour of PHB powder and Biomer P226 were studied using an optical microscope equipped with a hot stage. It was observed that PHB powder began to melt at about 168°C, and totally melted at about 174°C, where its melt viscosity was very low. During the cooling run, the maximum crystallization rate was located around 100°C, and large spherulites were formed (Fig. 4.1 (a)). During the second heating run, the recrystallization process was observed between room temperature and about 60°C, as shown in Fig. 4.1(c). The melting and crystallization behaviour were further studied by DSC (section 4.2.3).
Fig. 4.1 Polarizing optical micrographs of the spherulites of PHB at (a) 25°C, (b) 45°C and (c) 60°C during the 2\textsuperscript{nd} heating run
Biomer P226 film (1μm) was investigated using the optical microscope equipped with a hot stage. The recrystallization process was observed during the heating run as shown in Fig. 4.2 (a) and (b). At least three kinds of fillers were seen when the PHB matrix had totally melted (Fig. 4.2 (c)). These included large particles which might be an amorphous component, a highly birefringent filler which might be clay or CaCO₃, and some very fine birefringent fillers. During the cooling run, the spherulites appeared at about 110°C, and the spherulitic growth rate for Biomer P226 was higher than PHB powder. In addition, the size of spherulites for Biomer P226 is smaller and more uniform compared with PHB spherulites, as shown in Fig. 4.3.

**Fig. 4.2** Polarizing optical micrographs of the spherulites of PHB in Biomer P226 at (a) 25°C, (b) 110°C, (c) 180°C and (d) cooled down to 60°C
Fig. 4.3 Polarizing optical micrographs of the spherulites of (a) PHB and (b) Biomer P226 when cooled down to 60°C

Fig. 4.4 shows the micrographs of the PHB powder using SEM. The size of the particles, which is about 500nm, was measured, and the shape of the particles can be seen clearly from the micrograph.

Fig. 4.4 Scanning electron micrographs of PHB powder at different magnifications

According to the SEM-EDAX study on the fracture surface of Biomer P226, only one type of inorganic filler, which contains peaks for magnesium and silicon, was found in the Biomer P226 sample (Fig.4.5 (b)). As shown in Fig. 4.5 (a), the filler has a plate-like shape and a size of 5μm. Thus, it is identified
as possibly a type of clay. Due to the lack of identification of any other inorganic component, the fine birefringent filler detected from hot-stage microscopy may be an organic filler, such as starch.

Fig. 4.5 (a) SEM micrograph of Biomer P226, and (b) EDAX result of the filler marked in the micrograph

4.2.1.2 Structure Study: WAXD Analysis

Fig. 4.6 WAXD spectra of PHB powder and Biomer P226
As shown in the WAXD spectra (Fig. 4.6), there are two strong diffraction peaks for PHB located at $2\theta = 13^\circ$ and $2\theta = 17^\circ$, which correspond to the planes (020) and (110) in PHB, respectively [66]. There is no visible peak shift in the Biomer spectrum compared with pure PHB.

Comparing the X-ray patterns for pure PHB and Biomer P226, the peaks possibly corresponding to the clay filler added to Biomer P226 can be ascertained. The diffraction peaks are located at $2\theta = 9^\circ$, $2\theta = 21^\circ$ and $2\theta = 29^\circ$. Theoretically, the most probable chemical structure of the filler can be derived by combining the EDXA results with the X-ray peaks, according to ‘Powder Diffraction File-Inorganic Phase’ (1983). However, it is very difficult to find the right structure.

4.2.1.3 Crystallization and Thermal Properties: DSC and TGA Analysis

Fig. 4.7 shows the DSC curves of samples of pure PHB powder, hot-pressed PHB and Biomer P226 during the whole DSC run.

Fig. 4.7 DSC curves of PHB powder, pressed PHB and Biomer P226 pellet.

As shown in Fig. 4.7 (a), the samples of pure PHB powder, hot-pressed PHB
and Biomer P226 show only one melting peak of the PHB phase during the first DSC heating run. The melting temperature for hot-pressed PHB, 163°C, is much lower than 173°C for PHB powder. This is due to the chain scission degradation [10-15] when PHB is pressed higher than 170°C, which causes the decrease in molecular weight and chain length of PHB. The melting temperature for the PHB phase in Biomer P226, which is 162°C, is much lower than 170°C. Thus Biomer P226 can be processed at lower temperature to avoid or limit the chain scission degradation. The DSC curve for Biomer P226 sample shows another melting peak at 50°C, which may be associated with the melting of a low molecular weight additive.

During the second DSC heating run, the samples of PHB powder and hot-pressed PHB show two separate endothermic peaks (Fig. 4.7 (a)): the one located at lower temperature is associated with the melting of as-formed PHB crystals during cooling, while the higher temperature peak is associated with the melting of the PHB crystals formed from the recrystallization during the heating [45-48]. However, because the recrystallization process occurs gradually during the heating, no visible recrystallization peak can be observed. The shoulder located at 166°C on the melting peak for Biomer P226 is associated with the melting of recrystallized crystals as well. The melting temperatures during second heating run for both PHB powder and hot-pressed PHB shift to lower values compared with first heating run, due to the chain scission degradation. However, the melting temperature during second heating run for Biomer P226 is only slightly lower than the temperature during the first heating run, which might be due to the effect of additives in Biomer P226.

When cooled from the melt, the maximum crystallization temperature (T_c) for hot-pressed PHB was located at a lower temperature than T_c for PHB powder (Fig. 4.7 (b)). This is related to the chain scission degradation. The molecular weight of the hot-pressed PHB is lower than that of PHB powder due to chain
scission during the melt processing, resulting in a lower melt viscosity. The decrease in the molecular weight and viscosity results in slower crystallization kinetics [26]. Thus the hot-pressed PHB needs more time to crystallize, i.e. T<sub>c</sub> is located at lower temperature. The shift of crystallization temperature for pure PHB depends on the amount of melt processing. As shown in the same figure, Biomer P226 exhibits a higher crystallization temperature (T<sub>c</sub>) and sharper crystallization peak compared with the PHB powder, which is due to the addition of nucleation agent/fillers, which accelerate the nucleation and crystallization rate.

Table 4.1 Glass transition temperature, enthalpies and crystallinity of PHB for PHB powder, pressed PHB and Biomer P226 pellet

<table>
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<tr>
<th></th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>ΔH&lt;sub&gt;f1&lt;/sub&gt; (J g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ΔH&lt;sub&gt;c&lt;/sub&gt; (J g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ΔH&lt;sub&gt;f2&lt;/sub&gt; (J g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>X&lt;sub&gt;c&lt;/sub&gt; (%)</th>
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<td>Pressed PHB</td>
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<td>55</td>
<td>50</td>
<td>61</td>
<td>54</td>
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</table>

* value not measured

Glass transition temperature (T<sub>g</sub>), melting enthalpy during first heating run (ΔH<sub>f1</sub>) and second heating run (ΔH<sub>f2</sub>), enthalpy of crystallization (ΔH<sub>c</sub>) and crystallinity of the PHB phase (X<sub>c</sub>) for samples of PHB powder, hot-pressed PHB and Biomer P226 are listed in Table 4.1. It is difficult to observe the glass transition of hot-pressed PHB due to its high crystallinity. Biomer P226 has a glass transition temperature of about 5°C, which is slightly lower than that of PHB powder of about 7°C. The thermodynamic melting enthalpy (ΔH<sub>f0</sub>) of a 100% crystalline PHB sample is 146J g<sup>-1</sup> [71]. The crystallinity of the PHB phase in its blends or composites, X<sub>c</sub>, can be calculated using the following equation:
\[ X_c = \frac{\Delta H_f}{w_{PHB} \cdot \Delta H_{f0}} \times 100\% \]  

(2)

where \( w_{PHB} \) is the weight fraction of PHB, and \( \Delta H_f \) used for this report is the melting enthalpy during first heating run.

According to the TGA results (Fig. 4.8 (a)), the weight fraction of PHB in Biomer P226 is about 70%, and thus the crystallinity of the PHB phase in Biomer P226 is calculated as 54%, which is higher than the value for PHB powder due to the addition of nucleation agent. The crystallinity for hot-pressed PHB has a higher value compared with PHB powder, which may be due to the hot-pressing where the sample is left at 110°C for 15 minutes, as described in section 3.2.4. As listed in Table 4.1, for the samples of PHB powder, hot-pressed PHB and Biomer, the melting enthalpy during the second heating run (\( \Delta H_{f2} \)) shows a higher value than the enthalpy of crystallization (\( \Delta H_c \)), due to the PHB recrystallization process during heating.

![Fig. 4.8](image.png)

**Fig. 4.8** (a) TGA curves, and (b) differential thermogravimetry (DTG) curves of PHB powder and Biomer P226 film

The thermal stability of PHB powder and Biomer P226 is illustrated in Fig. 4.8.
The TGA curve of pure PHB shows a single degradation step with the degradation temperature at 253°C as marked in the differential thermogravimetry curve. The Biomer P226 shows thermal degradation behaviour with four decomposition steps due to its complex chemical composition, and the degradation temperatures have been marked in Fig. 4.8 (b), at 204°C, 275°C, 324°C and 369°C. Thus the formulated product, Biomer P226, has been found to contain five kinds of component as marked in its TGA curve, including 70% PHB, 1.5% clay filler (combined with the SEM and XRD results, section 4.2.1.1 and 4.2.1.2). Although the decomposition temperature of the PHB phase in Biomer P226 shifts to a higher temperature, the initial decomposition temperature of Biomer P226, 204°C, is lower than that for PHB. This might be associated with the addition of starch or thermoplastic starch (combined with optical microscopy and SEM-EDXA results, section 4.2.1.1 and 4.2.1.2). The exact identity of all the components present is not known.

### 4.2.1.4 Mechanical Properties

**Table 4.2** Mechanical properties of PHB and Biomer P226

<table>
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<th>Biomer P226</th>
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<td>Young’s modulus (MPa)</td>
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<tr>
<td>Stress at break (MPa)</td>
<td>18*</td>
<td>13.2±0.7</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>3*</td>
<td>7.2±0.7</td>
</tr>
</tbody>
</table>

* the literature data [17, 66]

The formability of pure PHB is very poor due to its low melt viscosity and brittleness. Thus in the current study, the mechanical data for pure PHB were not obtained. As listed in Table 4.2, the Young’s modulus for Biomer P226 is slightly lower than that of PHB, but still possesses certain stiffness. This might
be due to the lower glass transition temperature of Biomer P226 resulting in a more flexible sample at room temperature compared with pure PHB. The stress at break value for Biomer P226 was measured as 13.2 MPa in the current study. This measured stress value is much lower than the value from the datasheet, which might be due to the processing conditions. The strain at break value increases significantly from 3% for PHB to 7.2% for Biomer P226. However, Biomer P226 is a quite brittle material compared with other polymers used commercially for packaging.

4.2.1.5 Rheological Properties

<table>
<thead>
<tr>
<th></th>
<th>MFI (g/10min)</th>
<th>n</th>
<th>K (Pa·s^n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>22</td>
<td>0.5</td>
<td>325</td>
</tr>
<tr>
<td>Biomer P226</td>
<td>6</td>
<td>0.5</td>
<td>933</td>
</tr>
</tbody>
</table>

The melt flow indexer was used to investigate the rheological properties of pure PHB and Biomer, and the values obtained are listed in Table 4.3. The higher MFI value indicates lower melt viscosity. The MFI value of pure PHB, 22, is much higher than that of Biomer P226, 6, and thus the melt viscosity of PHB is much lower than that of Biomer P226.

MFI represents only a single point of the viscosity curve. Further rheological characterization of pure PHB and Biomer P226 was performed using a capillary rheometer. Measurements are normally made using two dies of different lengths to enable the Bagley correction to be made [92]. However, only the long die was used for testing PHB, due to the melt viscosity of pure PHB being very low. The Bagley corrected values are lower than the
uncorrected values.

![Image](image-url)

**Fig. 4.9** (a) Shear stress vs. shear rate, and (b) log (shear viscosity) vs. log (shear rate) from capillary rheometry for PHB and Biomer P226

As shown in Fig. 4.9 (a), the flow curves obtained for both pure PHB and Biomer P226 represent pseudoplastic behaviour [92]. From the plot of log (shear viscosity) vs. log (shear rate) (Fig.4.9 (b)), the power law index, n, and consistency index, K, were calculated according to the Power Law Equation:

\[
\log \eta = \log K + (n-1) \cdot \log \gamma \\
\]

where, \( \eta \) is shear viscosity, \( \gamma \) is shear rate, \( K \) is consistency index and \( n \) is power law index.

The power law index is a measure of deviation from Newtonian behaviour of the fluid, and the consistency index is the viscosity at the shear rate of \( 1s^{-1} \). As listed in Table 4.3, although the power law index, \( n \), for both PHB and Biomer P226 is 0.5, the consistency index, \( K \), for Biomer P226 is significantly increased from 325 Pa\(\cdot\)s\(^n\) for pure PHB to 933 Pa\(\cdot\)s\(^n\). Apart from this, the \( K \) value for PHB is obtained without the Bagley correction, and thus the corrected \( K \) value should be lower than 325 Pa\(\cdot\)s\(^n\). Thus, at the same shear rate, the
shear viscosity for pure PHB is much lower than that of Biomer P226, which is consistent with the MFI results.

4.2.1.6 Biodegradability

To evaluate the biodegradability of PHB and Biomer P226, the samples were buried about 3cm below the surface of moist compost or immersed in water. However, these results may be affected by environmental conditions, such as temperature. The weight change values were calculated by Equation (1) (section 3.11).

**Fig. 4.10** Weight change of PHB and Biomer P226 buried in (a) soil and (b) water, as a function of time

As shown in Fig.4.10 (a), for both PHB and Biomer P226 the weight change levels show an increment up to 101% and 102%, respectively, at beginning of the soil burial test. This is attributed to the water absorption by the PHB and Biomer P226. As time is increased over 10 weeks, the weight change values decrease rapidly due to the biodegradation. Biomer P226 exhibits a higher biodegradation rate compared with PHB, and this might be due to the addition of an organic component, which could be readily used as a carbon source by
organisms [66], in Biomer P226. Furthermore, signs of patchy degradation and discolouration were observed from both PHB and Biomer P226 samples.

It can be observed that PHB is not soluble in water, and thus its weight change value in water shows an increase during the second week due to the water absorption and then reaches a steady value (Fig.4.10 (b)). No discernible change in appearance can be observed from the PHB samples. In the case of Biomer P226, the weight change value shows an increase during the second week caused by the water absorption, and then decreases rapidly until reaching a steady value, about 94%, after ten weeks. In addition, precipitate can be found in the bottom of the container. The decrease in weight may be due to some water soluble component used in Biomer P226 dissolved in water. However, the PHB matrix is stable in water where the steady value is obtained.
4.2.2 Plasticization of PHB by PEG

4.2.2.1 Crystallization and Thermal Properties: DSC and TGA Analysis

Fig. 4.11 DSC curves of PHB and plasticized PHB (a) first heating run, (b) cooling run, and (c) second heating run 10°C/min, and (d) heating run at 5°C /min.

Fig. 4.11 shows the DSC curves of samples of pure PHB and plasticized PHB with various level of PEG. PHB is completely miscible with PEG 300, thus only one glass transition temperature can be observed (Fig. 4.11 (d)) for the PHB/PEG films. The results show that the glass transition temperature
decreases with increasing content of PEG, due to the plasticizer, PEG, weakening the intermolecular forces between PHB chains, resulting in a change in free volume.

The melting temperature for PHB/PEG films slightly decreases to a lower value with increasing PEG content (Fig. 4.11 (a)). Furthermore, the crystallization peak broadens and shifts to a lower temperature with increasing PEG content (Fig. 4.11 (b)). This is due to the addition of plasticizer leading to a decreased crystallization rate. Consequently, the amorphous phase of PHB is increased and smaller spherulites are formed. This, together with the reduction in $T_g$, results in better flexibility of PHB/PEG samples.

In all cases, the melting temperature during the second heating run shifts to lower temperature compared to the first heating run (Fig. 4.11 (c)), indicating the addition of PEG does not protect PHB from chain scission degradation. For PHB/PEG samples, it is noted that both first heating run and second heating run show two separate endothermic peaks during melting process due to the melting of as-formed PHB crystals and recrystallized crystals formed during heating. As shown in Fig. 4.11 (c), with increasing PEG content, the relative height of the first peak decreases, indicating the improved reorganization of the original crystal due to the lower crystallization rate during the cooling run.

**Table 4.4** Glass transition temperature, enthalpies and phase crystallinity of PHB for pure PHB and plasticized PHB with various level of PEG

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_{l1}$ (J g$^{-1}$)</th>
<th>$\Delta H_{c}$ (J g$^{-1}$)</th>
<th>$\Delta H_{l2}$ (J g$^{-1}$)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>7</td>
<td>71</td>
<td>63</td>
<td>77</td>
<td>50</td>
</tr>
<tr>
<td>PHB 2% PEG</td>
<td>4</td>
<td>70</td>
<td>61</td>
<td>75</td>
<td>49</td>
</tr>
<tr>
<td>PHB 5% PEG</td>
<td>2</td>
<td>69</td>
<td>59</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>PHB 10% PEG</td>
<td>-2</td>
<td>56</td>
<td>49</td>
<td>62</td>
<td>43</td>
</tr>
</tbody>
</table>
Glass transition temperature ($T_g$), melting enthalpy during the first heating run ($\Delta H_{f1}$) and second heating run ($\Delta H_{f2}$), enthalpy of crystallization ($\Delta H_c$) and crystallinity of the PHB phase ($X_c$) for samples of pure PHB and plasticized PHB are listed in Table 4.4. The crystallinity of the PHB phase in plasticized PHB films, $X_c$, can be calculated according to Equation (2) (section 4.4.1.3). Although the addition of PEG at low level, 2% and 5%, decreases the crystallization rate and temperature, it does not affect the crystallinity of the PHB phase. However, increasing the PEG content to 10% causes the crystallinity to decrease from 50 for PHB to 43%. Furthermore, the melting enthalpy for PHB/PEG samples shows a lower value than PHB, indicating that the degree of crystallinity of the plasticized PHB is lower than that of pure PHB and decreases with the increasing PEG content. The increasing melting enthalpy during the second heating run compared with the crystallization enthalpy indicates that recrystallization occurs during the second heating run.

Fig. 4.12 (a) TGA curves and (b) DTG curves of PHB and plasticized PHB with various level of PEG

Fig.4.12 shows the TGA and DTG curves of PHB and plasticized PHB with various contents of PEG: 2%, 5% and 10%. The thermal degradation curves of
pure PHB and plasticized PHB with 2% PEG exhibit a single step degradation with a maximum decomposition temperature at 253°C and 250°C, respectively. However, the TGA curves for plasticized PHB with 5% and 10% PEG show a different pattern from the single step degradation of PHB. As shown in Fig. 4.12, the thermal degradation temperature remains almost constant for PHB/PEG samples containing low content of PEG (2% and 5%), in agreement with other work [28, 87]. However, the degradation temperature, related to the PHB component, dramatically increased from 253°C to 275°C when the PEG level increased to 10%. This might be caused by the possible reaction between PHB and PEG, which retards the degradation of PHB when the PEG concentration reaches a certain amount. However, this disagrees with the results obtained by Parra et al [28], who reported the addition of PEG, up to 40 wt%, did not alter the thermal stability of the PHB/PEG blends.
4.3 Conclusion

From these experimental results, the following conclusions can be drawn:

1. Polyhydroxybutyrate (PHB) is a highly crystalline polymer with a melting temperature of 173°C and an onset decomposition temperature of 230°C, which is only slightly higher than the melting temperature. It exhibits extremely low melt viscosity and poor processability. Its melt viscosity decreases with increasing processing time and temperature. It is stable in water.

2. The PHB based product (Biomer P226) is formulated by using a number of components, including fillers and plasticizers. It shows a lower glass transition temperature, which provides better flexibility at room temperature, and lower melting temperature, which avoids the chain scission degradation at higher temperature. The size of spherulites in Biomer P226 is smaller and more uniform compared with those in pure PHB. The melt viscosity of Biomer P226 is significantly higher than that of pure PHB, resulting in better processability. Furthermore, Biomer P226 exhibits better mechanical properties, especially elongation at break. In addition, Biomer P226 shows an increased biodegradation rate compared with pure PHB.

3. PHB is completely miscible with PEG 300, which acts as a plasticizer in PHB. With increasing PEG content, the plasticized PHB exhibits a lower glass transition temperature, lower melting temperature and lower crystallization temperature. The presence of PEG weakens the intermolecular force between polymer chains and consequently decreases the crystallization rate.
CHAPTER 5  BLENDS BASED ON POLYHYDROXYBUTYRATE AND MAIZE STARCH

5.1 Introduction
This chapter contains two main sections. The first part is a study of the thermal, mechanical and rheological properties of polyhydroxybutyrate (PHB) blended with different contents of maize starch (ECO-MAIZE), which are varied from 0 to 50%. ECO-MAIZE is a regular maize starch containing 72% amylopectin. The second part is a study of the thermal, mechanical and rheological properties of PHB when blended with two different types of maize starch, HYLON VII and ECO-MAIZE, at a fixed ratio of PHB/starch 70/30. HYLON VII is a native food starch refined from high amylose maize containing 70% amylose.

5.2 Results and Discussion
5.2.1 Effect of Maize Starch Content
5.2.1.1 Morphological Properties: Optical Microscopy Analysis

Fig.5.1 shows the micrographs of ECO-MAIZE in water suspension during heating at 10°C/min to 100°C under bright field conditions. The swelling process of ECO-MAIZE in water is observed. As shown in Fig.5.1, when heat is applied to ECO-MAIZE granules suspended in water, the ECO-MAIZE granules absorb water and swell. Starch molecules have many hydroxyl groups which react with the water molecules, attracting and holding them, while the volume of swollen starch granules dramatically increase [32, 93]. Thus the swelling process, i.e. gelatinization, results in the increased viscosity. This process is irreversible.
Fig. 5.1 Bright field micrographs of ECO-MAIZE-water suspension at (a) 25°C, (b) 55°C, (c) 72°C and (d) 90°C
Fig. 5.2 Polarizing optical micrographs of PHB/ECO-MAIZE blend with 10% ECO-MAIZE at (a) 25°C, (b) 200°C, (c) cooled down to 103°C and (d) 45°C

The optical micrographs of PHB/ECO-MAIZE blends, with ECO-MAIZE content of 10%, 30% and 50%, under cross polarized light during heating at 10°C/min to 200°C and cooling down to room temperature are shown in Figs. 5.2 – 5.4. For all PHB/ECO-MAIZE blends investigated, the ECO-MAIZE granules do not swell, indicating that the ECO-MAIZE works as a filler in PHB. However, it was observed that the melt viscosity of PHB/ECO-MAIZE blends increases with increasing ECO-MAIZE content, because the addition of ECO-MAIZE arrests the molecular motion during melting. The ECO-MAIZE acts as a filler to provide a nucleating effect in the PHB/ECO-MAIZE blends.
Fig. 5.3 Polarizing optical micrographs of PHB/ECO-MAIZE blend with 30% ECO-MAIZE at a) 25°C, (b) 200°C, (c) cooled down to 93°C and (d) 35°C
Fig. 5.4 Polarizing optical micrographs of PHB/ECO-MAIZE blend with 50% ECO-MAIZE at a) 25°C, (b) 200°C, (c) cooled down to 98°C and (d) 38°C

Fig.5.5 shows the polarizing optical micrographs of the spherulites of PHB in pure PHB and PHB/ECO-MAIZE blends after crystallization during the cooling process. In general, the presence of ECO-MAIZE significantly reduced the size of PHB spherulites and made them more uniform in size due to the nucleating effect of ECO-MAIZE. Furthermore, the size of PHB spherulites decreased with increasing ECO-MAIZE content. It can be observed that cracks and splits occur during crystallization for both the 10% ECO-MAIZE blend and the 50% ECO-MAIZE blend. In the case of the 10% ECO-MAIZE blend, the presence of cracks may be due to the higher crystallinity resulting in greater shrinkage. In the case of the 50% ECO-MAIZE blend, the volume fraction of the crystalline phase is lower than that of the other blends, and, as indicated in Fig.5.5 (c), a
large amount of ECO-MAIZE was located in the interspherulitic regions resulting in poor mechanical properties.

**Fig. 5.5** Polarizing optical micrographs of the spherulites of PHB in PHB/ECO-MAIZE blends after crystallization, (a) 10% ECO-MAIZE blend, (b) 30% ECO-MAIZE blend, (c) 50% ECO-MAIZE blend, and (d) pure PHB
5.2.1.2 Crystallization and Thermal Properties: DSC Analysis

Fig. 5.6 DSC curves of PHB/ECO-MAIZE blends (a) first heating run, (b) cooling run, and (c) second heating run at 10°C/min

Fig. 5.6 shows the DSC curves of samples of plain PHB and PHB/ECO-MAIZE blends containing the ECO-MAIZE content up to 50 wt %. PHB is not miscible with ECO-MAIZE, and no discernible glass transition of the PHB/ECO-MAIZE blends was observed by DSC. Dynamic mechanical thermal analysis (DMTA), a sensitive technique to study polymer relaxation, was used to study the glass transition of PHB/ECO-MAIZE blends (section 5.2.1.3).
Table 5.1 Thermal transition temperatures, enthalpies and phase crystallinity of PHB in PHB/ECO-MAIZE blends

<table>
<thead>
<tr>
<th>%ECO-MAIZE</th>
<th>$T_{m1}$ (°C)</th>
<th>$\Delta H_{f1}$ (J g$^{-1}$)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J g$^{-1}$)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_{f2}$ (J g$^{-1}$)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>171</td>
<td>79</td>
<td>91.12</td>
<td>65</td>
<td>163</td>
<td>75</td>
<td>51</td>
</tr>
<tr>
<td>10</td>
<td>170</td>
<td>76</td>
<td>92.93</td>
<td>62</td>
<td>165</td>
<td>75</td>
<td>57</td>
</tr>
<tr>
<td>20</td>
<td>170</td>
<td>62</td>
<td>93.25</td>
<td>49</td>
<td>165</td>
<td>61</td>
<td>52</td>
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<tr>
<td>30</td>
<td>171</td>
<td>61</td>
<td>94.24</td>
<td>41</td>
<td>168</td>
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</tr>
<tr>
<td>40</td>
<td>168</td>
<td>50</td>
<td>96.60</td>
<td>42</td>
<td>170</td>
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<td>56</td>
</tr>
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<td>50</td>
<td>171</td>
<td>45</td>
<td>99.38</td>
<td>38</td>
<td>168</td>
<td>44</td>
<td>60</td>
</tr>
</tbody>
</table>

The thermal transition temperatures, melting and crystallization enthalpies and crystallinity of the PHB phase ($X_c$) for samples of pure PHB and PHB/ECO-MAIZE blends under same processing conditions are listed in Table 5.1. The melting temperature of PHB/ECO-MAIZE blends was almost constant, independent of the ECO-MAIZE content during the first heating run. For PHB/ECO-MAIZE blends with ECO-MAIZE content less than 20 wt%, the melting temperature during the second heating run was much lower than the value obtained during first heating run, while the two melting temperatures were only slightly different for the blends containing an ECO-MAIZE content over 30 wt%. This might be due to the possible interaction between PHB and ECO-MAIZE granules inhibiting the formation of the six-membered ring, and thus limiting the chain scission degradation of PHB [10-15]. This improvement in the thermal stability of PHB is further explained in section 5.2.2.3.

The crystallization temperature shows similar values at ECO-MAIZE contents of 10 and 20 wt%, and increases when the ECO-MAIZE content is over 30 wt% (Fig.5.6 (b)), due to the ECO-MAIZE acting as a nucleation agent in the blends increasing the crystallization rate.
The two separate melting peaks, attributed to the melting of as-formed PHB crystals and recrystallized PHB [45-48], during the DSC heating runs were observed. As shown in 5.6 (c), with increasing ECO-MAIZE content, the relative height of the second peak decreases, indicating less recrystallization of PHB during the heating process in these blends due to the higher nucleating agent content during cooling.

The values of phase crystallinity of PHB, $X_c$, listed in Table 5.1 were calculated using the melt enthalpy during second heating run, $\Delta H_{f2}$, according to Equation (2) (section 4.4.1.3). The results show that the presence of maize starch increases the phase crystallinity of PHB. This is due to the nucleating effect of the starch.

5.2.1.3 DMTA Analysis

Fig.5.7 to Fig.5.9 show the DMTA curves for PHB/ECO-MAIZE blends with ECO-MAIZE content up to 50 wt%. In the current study, the DMTA data for pure PHB were not obtained due to its poor formability. As shown in Fig. 5.7, PHB/ECO-MAIZE blends exhibit typical dynamic mechanical properties for semicrystalline polymers. The storage modulus decreases from about 0°C due to the glass transition relaxation of PHB.
**Fig. 5.7** Plot of log (storage modulus (E')) vs. scan temperature for the PHB/ECO-MAIZE blends

**Fig. 5.8** Plot of log (loss modulus (E'')) vs. scan temperature for the PHB/ECO-MAIZE blends
The peaks present in the $E''$ and $\tan \delta$ curves in the range between 0 and 60°C is attributed to the glass transition (Fig. 5.8 and Fig.5.9). The glass transition temperature values obtained from Fig.5.9 are listed in Table 5.2. The glass transition temperature shows an increase at ECO-MAIZE contents of 10 and 20 wt%, and decreases with the increasing ECO-MAIZE content. The increase in $T_g$ is associated with the small amount of starch acting as a filler to reduce the chain mobility of PHB [94]. The decrease in $T_g$ is possibly due to the interaction between PHB and starch hindering the hydrogen bonding between adjacent chains of PHB.
Table 5.2 Glass transition temperatures of the PHB/ECO-MAIZE blends

<table>
<thead>
<tr>
<th>%ECO-MAIZE</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>40</td>
<td>29</td>
</tr>
<tr>
<td>50</td>
<td>27</td>
</tr>
</tbody>
</table>

5.2.1.4 Mechanical Properties

The tensile properties of hot-pressed PHB/ECO-MAIZE blends as a function of ECO-MAIZE content are shown in Fig.5.10, and, as is the case for all PHB/ECO-MAIZE blends investigated in this project, they exhibit brittle fracture during testing, (i.e. the maximum tensile stress is the stress at break). The formability of pure PHB is very poor due to its low melt viscosity and brittleness. Thus in the current study, the mechanical data for pure PHB were not obtained. The addition of ECO-MAIZE starch improves the formability of PHB. The data for pure PHB were obtained from the literature from Godbole et al.’s work [17]. In agreement with their results, generally the physical properties were found to be optimum at a 70/30 PHB/ECO-MAIZE ratio, although the values obtained in the present study were lower than their results. It is well known that the tensile properties greatly depend on many factors, such as the experimental conditions, specimen shape and the materials used.
As shown in Fig. 5.10, the Young’s Modulus greatly decreases on addition of ECO-MAIZE compared with pure PHB, making the material more flexible at room temperature. The values of tensile stress at break of PHB/ECO-MAIZE blends are very low compared with the commercially used polymer and pure PHB, and this result is in agreement with other studies [18, 66]. The reduction in tensile stress is possibly due to the lack of interfacial adhesion between PHB and ECO-MAIZE. The elongation at break for PHB/ECO-MAIZE blends displays a slightly lower value compared with pure PHB (about 3%) except the 70% ECO-MAIZE blend (5%).

Fig. 5.10 Mechanical properties of PHB/ECO-MAIZE blends
These results, indicating the poor mechanical properties of PHB/ECO-MAIZE blends, are probably because hydrophobic PHB is not miscible with hydrophilic starch. Both Godbole [17] and Innocentini-Mei [18] reported that the addition of modified starch (TPS) provided better mechanical properties.

5.2.1.5 Rheological Properties

![Fig. 5.11](a) Torque vs. time plot, and (b) temperature vs. time plot from Haake Polylab Rheometer

During the blending process, the Haake rheometer records the torque and temperature as a function of time. These results can be used to get a rough evaluation of the rheological properties of pure PHB and PHB/ECO-MAIZE blends, although, these results greatly depend on the processing conditions.

Fig. 5.11 (a) shows the measured torque during the blending process of PHB and ECO-MAIZE, and for comparison pure PHB and Biomer P226 were processed under the same conditions. The first few minutes of the graph shows an initial region where the materials were introduced to the machine and this portion of the graph should be largely ignored. After this, the torque
decreases when the materials begin to melt and mix. At the beginning, the ECO-MAIZE exists as agglomerates in melted PHB and then these agglomerates are gradually broken down and dispersed into the melted PHB by continual motion of the rotor. Thus the torque reaches a stable value. The melt viscosity of the sample can be evaluated either according to the steady state torque value or the time needed to reach the steady state. Generally, when the ECO-MAIZE content is over 30 wt%, the steady state torque value of PHB/ECO-MAIZE blends increases with increasing ECO-MAIZE content, and the time needed to reach the steady state exhibits similar behaviour. This fact indicates that the melt viscosity increases with increasing ECO-MAIZE content for the blends containing ECO-MAIZE content over 30 wt%. These results may be because the interaction between ECO-MAIZE and PHB arrests the molecular motion of PHB during melting. However, this effect is less evident when the ECO-MAIZE content is less than 30 wt%. In the case of the blends containing an ECO-MAIZE content over 30 wt%, the steady state torque values are only slightly higher than those of pure PHB. This indicates that the interaction between PHB and ECO-MAIZE starch is weak. The steady state torque value of Biomer P226 is much higher compared with the PHB/ECO-MAIZE blends, and the migration of additives seems not to occur due to the strong chemical interaction between PHB and additives.

Fig. 5.11(b) shows the measured temperature during the blending process as a function of time for the samples of pure PHB, Biomer P226 and PHB/ECO-MAIZE blends. The setting processing temperatures for Biomer P226 and PHB/ECO-MAIZE blends are 165°C and 175°C respectively, as marked in Fig.5.11 (b). It can be observed that the shear heat of the PHB/ECO-MAIZE blends increases with ECO-MAIZE content.
5.2.2 Effect of Different Starch Type

5.2.2.1 Morphological Properties: Optical Microscopy and SEM Analysis

In section 5.2.1, it was found that the optimum additional level of starch into PHB is 30 wt%. Thus the PHB/starch blends with two different types of starch were prepared at a ratio of 70/30 by weight. The two types of starch used were ECO-MAIZE (containing 72% amylopectin) and HYLON VII (containing 70% amylose), as explained in Table 3.1. The major difference between amylopectin and amylose is that amylopectin is branched and amylose is nearly linear, as shown in Fig.1.3.

Fig.5.12 Polarizing optical micrographs of the spherulites of PHB during cooling in (a) pure PHB, (b) PHB/HYLON VII blend and (c) PHB/ECO-MAIZE blend
Fig. 5.12 shows the dark field optical micrographs of the spherulites of PHB in pure PHB and PHB/starch blends after heating to 200°C and cooling at 10°C/min. In general, the presence of starch significantly reduced the size of the PHB spherulites and gave a more uniform size distribution due to the nucleating effect of starch.

![Micrographs](image)

**Fig. 5.13** Scanning electron micrographs of fracture surfaces of (a) pure PHB, (b) PHB/HYLON VII blend and (c) PHB/ECO-MAIZE blend

The SEM micrographs of Fig. 5.13 show that the starch granules do not gelatinize or melt during processing. Hence the starch granules act as a filler for PHB. Poor interfacial interaction between the two materials was also observed in Fig. 5.13. Similar results were obtained by Thiré et al [66].
5.2.2.2 Structure Study: FTIR and WAXD Analysis

Fig. 5.14 shows typical FTIR spectra of PHB, starch and PHB/starch blends. The spectra of HYLON VII starch and ECO-MAIZE starch are very similar. In the spectrum of HYLON VII, the band at 3400 cm\(^{-1}\) is a strong and broad peak, which is related to the hydroxyl vibration. The changes in the peak in width and intensity indicate the intensity of intermolecular and intramolecular hydrogen bonds occurring in starch. In the spectrum of pure PHB, there is a strong and sharp peak at 1724 cm\(^{-1}\), which is attributed to the stretching vibrations of crystalline carbonyl groups; the amorphous carbonyl vibration of PHB at 1750 cm\(^{-1}\) is very weak and cannot clearly be observed in the spectrum. It is found that the FTIR spectra of PHB/starch blends are different from the vibration peaks of the components.

![FTIR spectra of HYLON VII, ECO-MAIZE, PHB, and PHB/starch blends](image)

**Fig. 5.14** FTIR spectra of HYLON VII, ECO-MAIZE, PHB, and PHB/starch blends

As shown in Fig. 5.14, the spectra of PHB/starch blends show an obvious decrease in the intensity of the band of the hydroxyl group at 3400 cm\(^{-1}\) compared with the pure starch. Furthermore, the centre of the band of the
hydroxyl group in PHB/starch blends shifts to higher wavenumber compared with pure starch, and this suggests the formation of intermolecular hydrogen bonds between PHB and starch. There is an obvious broadening of the peaks in the carbonyl region of the blends compared with pure PHB. The peak at 1724 cm\(^{-1}\) has become weak, and the ratio of the peaks at 1750 cm\(^{-1}\) and 1724 cm\(^{-1}\) has increased. The band centered at 1709 cm\(^{-1}\), which is attributed to the vibration of the hydrogen-bonded carbonyl groups [95], increases on addition of starch. These results indicate that intermolecular hydrogen bonding occurs between the two components of the blends, and the hydroxyl groups in the starch chains and the carbonyl groups in the PHB participate in intermolecular interactions. Moreover, the change in the peak shoulder at 1750 cm\(^{-1}\), attributed to the PHB amorphous carbonyl vibration [95, 96], indicates that the intermolecular hydrogen bonding is mainly due to the interactions between PHB and starch in the amorphous phase. These interactions may affect the crystal structure of the components. This is further investigated in the WAXD analysis.

Similar changes in the FTIR spectra of PHB/Chitosan blends were reported in the work of C. Chen et al [96]. Using FTIR and WAXD, they found the existence of hydrogen bonding between PHB and chitosan.
Fig. 5.15 WAXD profiles of HYLON VII, ECO-MAIZE, PHB and PHB/starch blends.

As shown in the WAXD patterns of Fig. 5.15, the diffraction peak for (020) in PHB is located at $2\theta = 13^\circ$ and that for (110) is located at $2\theta = 17^\circ$ [66]. In both PHB/starch blends the (020) and (110) diffraction peaks are lower in intensity compared with those of pure PHB.

| Table 5.3 Ratio of $I_{(020)}/I_{(110)}$ in PHB and PHB/starch blends. |
|---|---|---|---|
| | PHB | PHB/HYLON VII | PHB/ECO-MAIZE |
| $I_{(020)}/I_{(110)}$±0.01 | 1.33 | 1.49 | 1.42 |

The intensity ratio values $I_{(020)}/I_{(110)}$ for PHB and the PHB/starch blends are shown in Table 5.3. It is seen from Table 5.3 that the addition of starch increases the $I_{(020)}/I_{(110)}$ ratio compared with pure PHB. This indicates that the original crystal structure of PHB has been disturbed and this is thought to be
due to the hydrogen bonding between PHB and the starch granules. The change in the $I_{(020)}/I_{(110)}$ ratio is greater for PHB/HYLON VII blend than for the PHB/ECO-MAIZE blend compared with PHB, and this implies that the hydrogen bonding effect is stronger in the PHB/HYLON VII blend than in the PHB/ECO-MAIZE blend. This result is further supported by the DMTA data.

### 5.2.2.3 Crystallization and Thermal Properties: DSC Analysis

![DSC curves of PHB and PHB/starch blends.](image)

**Fig. 5.16** DSC curves of PHB and PHB/starch blends.

Fig. 5.16 shows the DSC curves of PHB and PHB/starch blends heated at a rate of 10°C/min. During first heating run, the melting temperatures of PHB and PHB/starch blends are very similar, about 171°C. However, during the second heating run, the melting temperatures for pure PHB significantly shift to lower temperature, due to chain scission. The melting point of the blend containing ECO-MAIZE starch is not reduced as much as that of pure PHB during the
second heating run — showing less degradation. The blend of PHB and HYLON VII shows virtually no degradation during the second heating run.

Improvement in the thermal stability of PHB is thought to be due to the hydrogen bonding between the hydroxyl groups of starch and the carbonyl groups of PHB. According to the work of N. Grassie et al [11-13], thermal degradation of PHB is due to chain scission via a widely accepted ring ester decomposition mechanism involving a six-membered ring transition state, as shown in Fig.1.2. Hydrogen bonding between starch and PHB may inhibit the formation of the six-membered ring and hence improve the thermal stability of PHB.

5.2.2.4 DMTA Analysis

![Fig. 5.17 Plot of tanδ vs. scan temperature for PHB/starch blends](image)

The tanδ peak obtained from DMTA measurements can be used to assess
interfacial bonding in polymer composites [97, 98]. Fig.5.17 shows the plots of tanδ versus scan temperature for PHB/starch blends. PHB/HYLON VII blend gives a lower peak height compared with PHB/ECO-MAIZE blend. This result indicates that the PHB/HYLON VII blend dissipates less energy than PHB/ECO-MAIZE blend, i.e. the PHB/HYLON VII blend has a stronger interface. Moreover, the PHB/HYLON VII blend shows a narrower tanδ peak than the PHB/ECO-MAIZE blend; this indicates that the PHB/HYLON VII blend has better interfacial bonding as well. This might be due to the fact that the linear structure of HYLON VII makes it easier to form hydrogen bonding between PHB and starch. The proposed mechanism is shown schematically in Fig.5.18.

Fig.5.18 Schematic for proposed mechanism of the formation of the hydrogen bonds in the blends of (a) PHB/amylose and (b) PHB/amylopectin

The tanδ peak temperature (i.e. glass transition temperature) of PHB/HYLON VII blend (35°C) is slightly lower than that of PHB/ECO-MAIZE blend (37°C). This may be due to the stronger intermolecular interaction between PHB and HYLON VII, compared with ECO-MAIZE.
5.2.2.5 Mechanical Properties

![Hot pressed PHB and PHB/starch blends sheets](image)

**Fig. 5.19** The physical appearance of hot pressed PHB and PHB/starch blends sheets.

The formability of pure PHB is very poor due to its low melt viscosity and brittleness. Thus in the current study, the mechanical data for pure PHB were not obtained. The addition of starch improved the formability of PHB, as shown in Fig. 5.19.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Impact strength (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB/HYLON VII</td>
<td>12.52±0.74</td>
<td>3.87±0.49</td>
<td>0.89±0.14</td>
</tr>
<tr>
<td>PHB/ECO-MAIZE</td>
<td>7.33±1.06</td>
<td>2.78±0.47</td>
<td>0.67±0.11</td>
</tr>
</tbody>
</table>

**Table 5.4** Tensile strength, elongation at break and impact strength of PHB/starch blends

It can be seen from Table 5.4 that the mechanical properties of PHB/starch blends are still poor. As shown in Fig. 5.12, the starch granules are acting as a filler in PHB. However, tensile strength, elongation at break and impact strength are greater for PHB/HYLON VII blend compared with...
PHB/ECO-MAIZE blend. Presumably this is due to the better hydrogen bonding between PHB and HYLON VII.

### 5.2.2.6 Rheological Properties

Melt viscosity of pure PHB and PHB/starch blends was measured on a twin bore Rosand RH7 capillary rheometer. It was found that the melt viscosity of pure PHB was very low and the addition of starch made the polymer easier to process.

![Log (shear viscosity) vs. log (shear rate) from capillary rheometry for PHB and PHB/starch blends.](image)

**Fig. 5.20** Plot of log (shear viscosity) vs. log (shear rate) from capillary rheometry for PHB and PHB/starch blends.

Fig. 5.20 shows a plot of log (shear viscosity) vs. log (shear rate) and it is seen that the shear viscosity of PHB/starch blends is much higher than that of pure PHB, and the shear viscosity of PHB/HYLON VII blend was significantly improved compared with that of PHB/ECO-MAIZE blend.
Table 5.5 Power Law Index, n, and consistency coefficient, K, values for PHB and PHB/starch blends

<table>
<thead>
<tr>
<th></th>
<th>Power law index (n)</th>
<th>Consistency coefficient (K) Pa•s^n</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>0.6</td>
<td>132</td>
</tr>
<tr>
<td>PHB/HYLON VII</td>
<td>0.6</td>
<td>1000</td>
</tr>
<tr>
<td>PHB/ECO-MAIZE</td>
<td>0.6</td>
<td>331</td>
</tr>
</tbody>
</table>

The values of power law index, n, and consistency coefficient, K, were calculated according Equation (3) (section 4.2.1.5). As listed in Table 5.5, the values of power law index for PHB/HYLON VII blend, PHB/ECO-MAIZE blend and PHB, are same. This implies that with increasing shear rate, the decrease in shear viscosity of PHB/starch blends is similar to that of PHB. The consistency index for PHB/ECO-MAIZE blend is increased from 132 Pa•s^n for pure PHB to 331 Pa•s^n. However, the K value for PHB/HYLON VII blend, 1000 Pa•s^n is significantly higher than that of pure PHB and PHB/ECO-MAIZE blend. These results are also due to the increasing hydrogen bonding interaction between PHB and starch with high amylose content (i.e. HYLON VII).
5.3 Conclusion

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

1. ECO-MAIZE starch is not compatible with PHB. Blends of PHB with natural starch, ECO-MAIZE, have a lower glass transition temperature and higher crystallization temperature compared with PHB alone. The chain scission degradation of PHB is inhibited when the ECO-MAIZE content reaches 30 wt%. The increasing ECO-MAIZE content results in less recrystallization of PHB in the blends. The size of PHB spherulites decreases with increasing ECO-MAIZE content. The PHB/ECO-MAIZE blends show poor mechanical properties. The blend at the PHB/ECO-MAIZE ratio of 70/30 provides better mechanical properties than other blends. The melt viscosity of PHB/starch blends increases with increasing ECO-MAIZE content when the ECO-MAIZE content is over 30 wt%.

2. Starch particles act as nucleating agents for PHB crystallite formation. Intermolecular hydrogen bonding occurs between PHB and both types of maize starch, HYLON VII and ECO-MAIZE. As indicated from the WAXD results, the addition of starch affects the crystal structure of PHB. Compared with ECO-MAIZE, HYLON VII has stronger intermolecular hydrogen bonding with PHB due to its high amylose content and linear structure. The existence of hydrogen bonding improves the thermal stability, melt viscosity and mechanical properties of PHB/starch blends. Hydrogen bonding between the hydroxyl groups of starch and carbonyl groups of PHB may inhibit chain scission degradation in PHB, and thus improve its thermal stability. The stronger hydrogen bonding effect between PHB and HYLON VII makes PHB/HYLON VII blend more stable than PHB/ECO-MAIZE blend. Furthermore PHB/HYLON VII blend shows higher
melt shear viscosity and better mechanical properties than PHB/ECO-MAIZE blend. However, the mechanical properties of PHB/starch blends are still poor.
CHAPTER 6  BLENDS BASED ON POLYHYDROXYBUTYRATE AND POLYLACTIC ACID

6.1 Introduction

In this chapter, a study on blending polyhydroxybutyrate with different amounts of PLA was carried out. The blends had the following ratios by weight of PHB/PLA: 100/0, 75/25, 50/50, 25/75 and 0/100. These blends were prepared by melt compounding and quenching as described in section 3.2, and their morphology, thermal properties, mechanical properties and biodegradation behaviour have been investigated. In addition, a further annealing process was carried out at 100°C for 5 minutes, as described in section 3.2.4, to investigate the effect of thermal treatment on the morphology and mechanical properties of the blends. The final part of the chapter is a study of thermal and mechanical properties after adding high amylose maize starch (HYLON VII) into PHA/PLA blends. The PLA/PHB/HYLON VII blends were prepared at three different weight ratios (50/50/0, 50/40/10 and 50/35/15), and characterized in terms of their morphology, thermal and mechanical properties.

6.2 Results and Discussion

6.2.1 Effect of PLA content

6.2.1.1 Morphological Properties: Optical Microscopy and SEM Analysis

Fig. 6.1 shows the optical micrographs taken between crossed polars of pure PHB, pure PLA and PHB/PLA blends after heating to 200°C and cooling at 10°C /min. In general, the presence of amorphous PLA significantly reduced the size of the PHB spherulites, especially when the PLA content is over 50%.
Fig. 6.1 Polarizing optical micrographs of the spherulites of PHB in (a) pure PHB, (b) 25% PLA, (c) 50% PLA, (d) 75% PLA and (e) pure PLA after cooling

Fig. 6.1 (b) and Fig. 6.1 (c) show that the crystalline PHB was the continuous phase in the PHB/PLA blends containing 25% and 50% PLA. It is seen that the blend containing 50% PLA gives a more uniform size distribution of the PHB
spherulites compared with the blend containing 25% PLA. However, the optical micrograph of the blend containing 75% PLA is quite different from those of other blends, as shown in Fig. 6.1 (d). It can be observed that the PHB crystalline particles are very small (≤5μm), and are well dispersed in the continuous amorphous PLA phase. Furthermore, the rate of crystallization of PHB becomes very slow under such particle size [69]. A discernible spherulitic structure of PLA is not observed in any of these quenched PHB/PLA blends, and this indicates that PLA exists as an amorphous phase or as tiny spherulites too small to be resolved.

Scanning electron microscopy was used to study the fracture surfaces of PHB/PLA blends after tensile testing. The micrographs are illustrated in Fig. 6.2. It can be seen that pure PHB shows an irregular fracture surface due to its crystalline structure (Fig. 6.2 (a)), while pure PLA shows a typical fracture surface of an amorphous polymer (Fig. 6.2 (e)). It can be seen that all PHB/PLA blends consist of two phases which indicates that PHB/PLA blends are immiscible. Fig. 6.2 (d) shows that PHB particles dispersed as fillers in PLA, which should improve the mechanical properties.
Fig. 6.2 SEM micrographs of the fracture surface of (a) pure PHB, (b) 25% PLA, (c) 50% PLA, (d) 75% PLA and (e) pure PLA.
6.2.1.2 Structure Study: FTIR and XRD Analysis

Fig. 6.3 shows typical FTIR spectra of PHB, PLA and PHB/PLA blends. In the spectrum of PLA, the band at 1745 cm\(^{-1}\) is a strong peak, which is related to the amorphous carbonyl vibration. The crystalline carbonyl vibration of quenched PLA at 1755 cm\(^{-1}\) is very weak and cannot clearly be observed in the spectrum [69, 70]. In the spectrum of pure PHB, there is a strong and sharp peak at 1718 cm\(^{-1}\), which is attributed to the stretching vibrations of crystalline carbonyl groups; the amorphous carbonyl vibration of PHB at 1740 cm\(^{-1}\) is very weak and therefore is not clearly visible in the spectrum [22, 71].

![FTIR spectra of quenched samples of PLA, PHB and PHB/PLA blends](image)

**Fig. 6.3** FTIR spectra of quenched samples of PLA, PHB and PHB/PLA blends

Briefly, it is found that the FTIR spectra of PHB/PLA blends show two major carbonyl stretching bands due to PHB and PLA, respectively, and the intensity ratio of these two bands changes with the composition ratio. The spectra of the blends containing 25% PLA and 50% PLA are very similar to that of PHB, however, the peaks at 1718 cm\(^{-1}\) show a slight shift. This indicates that PHB and PLA are immiscible in these blends and there are no strong molecular
interactions between them.

For the blend containing 75% PLA, the FTIR spectrum is different from the other blends. It is noted that there are two strong bands located at 1722 cm\(^{-1}\) and 1745 cm\(^{-1}\), which are assigned to the crystalline carbonyl stretching of PHB and amorphous carbonyl stretching of PLA, respectively. However, compared with pure PLA, the peak at 1745 cm\(^{-1}\) has become broadened, and the ratio of the shoulder at 1755 cm\(^{-1}\) and the peak at 1745 cm\(^{-1}\) has increased. Furthermore, the carbonyl stretching band at 1722 cm\(^{-1}\) has a different peak position from the crystalline carbonyl band of pure PHB at 1718 cm\(^{-1}\). These results indicate that there is some interaction between PHB and PLA in the blend containing 75% PLA, although PHB and PLA are most likely immiscible. The possible reaction may be the transesterification of PHB and PLA at the melting stage [72].

In principle, the transesterification reaction [99-106] may take place when melt mixing the two polyesters, PHB and PLA. If this were to occur, PHB/PLA ‘block copolymers’ would be produced by the interchange reaction at the interface between PHB and PLA phases, though limited in amount. These polymers would act as an in situ compatibilizer in the blend to improve the miscibility between PHB and PLA. However, the degree of transesterification strongly depends on the blending conditions, such as processing temperature, processing time and composition ratio etc. Furthermore, the possible transesterification reaction can be further proved by the DMTA results in section 6.2.1.4.

Fig. 6.4 shows the wide-angle X-ray diffraction patterns for quenched PLA, PHB and PHB/PLA blend samples. The quenched pure PLA sample shows a typical amorphous broad ‘hump’, while the highly crystalline pure PHB sample shows two strong diffraction peaks located at 2\(\theta\) = 13° and 2\(\theta\) = 17°,
associated with (020) and (110), respectively.

![WAXD Profiles](image)

**Fig. 6.4** WAXD profiles of quenched samples of PLA, PHB and PHB/PLA blends

In general, the patterns of all the PHB/PLA blends are very similar to that of PHB, although for the blend containing 75% PLA, the peak located at 17° is very weak and cannot clearly be observed in the pattern. Furthermore, the presence of amorphous PLA significantly reduces the crystallinity of the quenched PHB/PLA blend samples, and this result is not only due to the reduction in the content of PHB but also due to that the present of PLA reduces the crystallization rate of PHB. For the 75% PLA blend, as shown in Fig. 6.4, the intensity ratio $I_{(020)}/I_{(110)}$ is obviously different from that of pure PHB. This indicates that the original crystal structure of PHB in the blend containing 75% PLA has been disturbed and this is thought to be due to the interaction between PHB and PLA.
6.2.1.3 Crystallization and Thermal Properties: DSC Analysis

The DSC curves of PLA, PHB and PHB/PLA blends with a heating rate of 10°C/min are shown in Fig. 6.5. During first heating run, as shown in Fig. 6.5 (a), pure PLA shows a glass transition temperature at about 55°C and a melting peak at 155°C, as marked. For pure PHB, a sharp melting peak is observed at about 172°C and a discernible glass transition is difficult to observe. For PHB/PLA blends, the glass transition at about 50°C for the PLA component can be observed, and the glass transition temperatures slightly shift with composition. It is difficult to observe the glass transition of the PHB component due to its high crystallinity.

The recrystallization peaks of PLA at about 107°C can be observed in all PHB/PLA blends, indicating the addition of PHB can recrystallize PLA in all compositions. However, the blend containing 75% PLA shows a relatively strong recrystallization peak which is due to the small finely dispersed PHB crystals acting as nucleating agent in PLA. A recrystallization peak of PHB at about 75°C can be observed in the blend containing 25% PLA, and this is thought to be due to the lower crystallization rate of PHB on addition of PLA. For the 25% PLA blend, it shows a sharp melting peak at about 165°C, corresponding to the melting of the PHB component and a shoulder at about 155°C, corresponding to the melting of the PLA component. For the 50% and 75% blends, the DSC curves give three peaks in the melting process: the lowest temperature peak, at around 155°C, corresponds to the melting of the PLA component, the next peak, corresponds to the melting of the ‘as-formed’ PHB crystallites during processing, and the highest temperature peak corresponds to the melting of the PHB crystals formed from the recrystallization during heating [107]. These results also indicate that PLA/PHB blends are immiscible.
During the cooling process at the rate of 10°C/min, as shown in Fig. 6.5 (b), pure PHB has a crystallization peak at about 60°C, while that of PLA cannot be clearly observed. These results indicate that the crystallinity and crystallization rate of PHB is much higher than that of PLA. The crystallization peak of PHB can be observed in the blends containing 50% and 25% PLA, but cannot be observed in the blend containing 75% PLA. This indicates that PHB in the 75% PLA blend does not crystallize much during the cooling process.

During the second heating run, as shown in Fig. 6.5 (c), pure PLA shows a similar trace to

*Fig. 6.5* DSC curves of PLA, PHB and PHB/PLA blends obtained from (a) the 1st heating run, (b) cooling run, and (c) 2nd heating run.
that of the first heating run, while pure PHB shows a significantly lower melting point compared with that of the first heating run, due to chain scission degradation of PHB. In general, in all PHB/PLA blends, the glass transition temperatures for the PLA component are slightly shifted with composition and the recrystallization of PLA appears in all compositions. However, for the blends containing 50% and 75% PLA, the DSC curves appear similar to the first heating run, while for the blend containing 25% PLA, the DSC curve shows a double melting peak corresponding to the melting of the ‘as-formed’ and recrystallized PHB component. Apart from these observations, for the blends containing 50% PLA and 25% PLA, the melting peaks slightly shift to lower temperatures, and for the blends containing 75% PLA, no peak shift can be observed. The improvement in thermal stability of PHB in PHB/PLA blends indicates that there is potential interaction between PHB and PLA though they are immiscible.

6.2.1.4 DMTA analysis

Fig. 6.6 displays the temperature dependence of the dynamic storage modulus, loss modulus and loss factor tanδ of PLA and PHB/PLA blends. As mentioned in section 5.2.1.4, the formability of PHB is too poor to form the DMTA specimen.
As shown in Fig. 6.6 (a), the storage modulus of pure PLA is almost constant at the temperatures below the glass transition temperature (about 60°C), and then pure PLA shows a drop in storage modulus corresponding to the glass transition of the amorphous structure. In general, the PHB/PLA blends show improved storage modulus at temperatures below the glass transition of the PLA component, although these curves show a gradual decrease in storage modulus from around 30°C which is associated with the glass transition of the PHB component. For the PHB/PLA blend containing 75% PLA, the storage modulus shows

![DMA curves for PLA and PHB/PLA blends.](image)

**Fig. 6.6** DMA curves for PLA and PHB/PLA blends.
a dramatic drop at about 55°C due to the glass transition of amorphous PLA, and then shows an increase, indicating the recrystallization of PLA. For the PHB/PLA blend containing 50% PLA, the storage modulus shows less reduction at the glass transition temperature of PLA, and the further improvement in the storage modulus indicates the recrystallization of PLA. For PHB/PLA blend containing 25% PLA, the storage modulus shows a gradual decrease from about 60°C, and it is difficult to observe the recrystallization of PLA. Although it is not possible to avoid the drop in storage modulus due to the glass transition of amorphous PLA, the PHB/PLA blends exhibit better mechanical properties at higher temperature compared with pure PLA due to the recrystallization of PLA.

Fig. 6.6 (b) and Fig. 6.6 (c) show two distinct glass transitions for the PHB/PLA blends. The lower peaks at around 30°C corresponds to the glass transition of the PHB component, and the higher peaks at around 60°C corresponds to the glass transition of the PLA component. However, both glass transition temperatures are slightly affected by the relative compositions. These results suggest that the transesterification interaction exists in the essentially immiscible PHB/PLA blends.

6.2.1.5 Mechanical Properties

The formability of pure PHB is very poor due to its low melt viscosity and brittleness. Thus in the current study, the mechanical data for pure PHB were not obtained. The addition of PLA improved the formability of PHB.
The tensile properties of PLA and PHB/PLA blends as a function of PLA content are shown in Fig. 6.7. All these samples exhibited brittle fracture during testing. It can be observed that for PHB/PLA blends, both tensile stress and elongation at break improve with PLA content. This is thought to be due to the better mechanical properties of PLA and the good interfacial bonding between PHB and PLA. For the blends containing 25% PLA and 50% PLA, the values of both tensile stress and elongation at break are lower than that of pure PLA. This is due to PHB, which possesses very poor mechanical properties, acting as the continuous phase. For the blend containing 75% PLA, it shows better mechanical properties compared with pure PLA. These improvements may be mainly attributed to the tiny, finely dispersed PHB crystals acting as filler to enhance the properties of the PLA matrix, as displayed in Fig.6.1 (d) and Fig.6.2 (d), and the possible interaction between PHB and PLA causing strong interfacial bonding.
Charpy impact testing was carried out to measure the impact strength of PLA and PHB/PLA blends containing 50% PLA and 75% PLA. Due to both PHB and PLA being brittle, the impact specimen of the PHB/PLA blend containing 25% PLA could not be obtained in current study and the impact properties of PHB/PLA blends containing 50% PLA are very poor. For the blend containing 75% PLA, the impact strength value is comparable to that of pure PLA, and this is thought to be due to the possible interaction between PHB and PLA. However, the impact properties of the blending containing 75% PLA are not as outstanding as its tensile properties. This is due to the discontinuous PHB phase being brittle and thus cannot act as an impact modifier.

**Fig. 6.8** Plot of impact strength as a function of PLA content for PLA and PHB/PLA blends
6.2.1.6 Biodegradability

![Graph showing weight change of PHB, PLA, and PHB/PLA blends over time]

**Fig. 6.9** Weight change of PHB, PLA and PHB/PLA blends buried in soil as a function of time

As shown in Fig. 6.9, the weight change values, calculated by Equation (1) (section 3.11), for all samples show an increment in weight at the beginning of the soil burial test. This is attributed to water absorption by PHB and PLA. It can be observed that the water absorption by PHB is greater than that by PLA, and that addition of PHB increased the water absorption. The weight change value of PLA is almost constant after the first three weeks indicating that the PLA samples may not biodegrade at room temperature.

There appears to be an induction time for the biodegradation that can be clearly observed from Fig. 6.9, as marked. As time increases over a period of eight weeks, the weight shows a rapid decrease for pure PHB due to its biodegradation. For the 50% PLA and 25% PLA blends, the induction time
period lasts for about fourteen weeks with greater weight loss for the blend with greater PHB content. For the 75% PLA blend, gradual biodegradation occurred from week 23 and the weight slightly decreased. However, signs of patchy degradation and discolouration were observed from all samples tested except PLA, and the discolouration increased with increasing time and PHB content.

Fig. 6.10 SEM micrographs of the fracture surface of biodegraded PHB/PLA blends: (a) 75% PLA, (b) 50% PLA, (c) 25% PLA, t = 50 weeks.

The SEM micrographs of Fig. 6.10 show the fracture surface of the biodegraded PHB/PLA blends after 50 weeks. It can be seen that the biodegradation occurred in both PHB and PLA phases for all concentrations. This indicates that the addition of PHB improved the biodegradability of PLA at
room temperature. This is thought to be due to the increased water uptake and thus enhanced hydrolysis of PLA. Furthermore, it can be observed that PHB and PLA exhibit different degradation mechanisms: PHB is eroded from the sample surface, whereas degradation of PLA takes place throughout the whole of the sample. PHB is mainly degraded by attacked various enzymes at the surface, while degradation of PLA is mainly started with non-enzymatic hydrolysis, which is strongly temperature dependent.
6.2.2 Effect of Thermal Treatment

6.2.2.1 Morphological Properties: Optical Microscopy and SEM Analysis

Fig. 6.11 Polarized light optical micrographs of (a) quenched 75% blend, (b) annealed 75% blend, (c) quenched pure PLA and (d) annealed PLA samples.

Fig. 6.11 shows the optical micrographs obtained between crossed polars of the quenched and annealed 75% PLA blends and pure PLA. It can be seen that recrystallization of PLA occurs in both annealed pure PLA and the 75% PLA blend. However, the annealed 75% PLA blend shows a stronger recrystallization phenomenon, and this is thought to be due to the tiny PHB crystals acting as a nucleating agent in the PLA matrix.
Chapter 6

Results and Discussion

Fig. 6.12 SEM micrographs of the fracture surface of (a) quenched 75% PLA blend, and (b) annealed 75% PLA blend.

Fig.6.12 shows the SEM micrographs of the fracture surfaces of the quenched and annealed 75% PLA blends. It can be seen that PHB crystals dispersed as fillers in PLA matrix, as marked in Fig.6.12. Moreover, the PLA component in the quenched 75% PLA blend shows a ‘clean’ fracture surface (Fig.6.12 (a)), while the PLA component in the annealed 75% PLA blend shows an irregular fracture surface (Fig.6.12 (b)). This is possibly due to the improved crystallinity of PLA in the annealed sample.

6.2.2.2 Structure Study: FTIR and XRD Analysis

Fig. 6.13 shows the FTIR spectra of the PLA and 75% PLA blend samples after different treatments: quenching and annealing. For pure PLA, the spectrum of the annealed sample shows a peak shoulder at 1755 cm\(^{-1}\) which is attributed to the crystalline carbonyl vibration. This indicates that recrystallization of PLA occurs during the annealing treatment. For the 75% PLA blend, the spectrum of the annealed sample shows an obvious increase in the intensity of the crystalline carbonyl stretching peak of pure PHB at 1722 cm\(^{-1}\), and this suggests that recrystallization of PHB occurs during the annealing treatment.
The ratio of the peaks at 1755 cm\(^{-1}\), assigned to the crystalline carbonyl vibration of PLA, and 1745 cm\(^{-1}\), assigned to the amorphous carbonyl vibration of PLA, has increased. This increase indicates that recrystallization of PLA occurs in the 75% PLA blend.

**Fig. 6.13** FTIR spectra of the quenched and annealed samples of PLA and 75% PLA blend

**Fig.6.14** WAXD profiles of the quenched and annealed samples of PLA and 75% PLA blend
Fig. 6.14 compares the WAXD patterns for samples of the annealed PLA and 75% PLA blend with those of the quenched PLA and 75% PLA blend. The annealed pure PLA sample exhibits a significant diffraction peak at $2\theta = 16.4^\circ$, associated with (020) diffraction [108, 109]. This result indicates that the recrystallization of PLA occurs during the annealing process. For the 75% PLA blend, the annealed sample shows a typical crystalline polymer pattern with two strong peaks at $2\theta = 13^\circ$ and $2\theta = 16.4^\circ$, associated with (020) for PHB and (020) for PLA, respectively. The intensity of the peak at $2\theta = 13^\circ$ is slightly higher than that of the quenched sample, while the peak at $2\theta = 16.4^\circ$ is dramatically increased. These results indicate that the recrystallization of both PLA and PHB occurs during the annealing process, with a significant increase in crystallinity for PLA. Other typical diffraction peaks located at $2\theta = 15^\circ$ and $18.5^\circ$ were also observed. Mihai et al [108] observed these peaks only in the fully crystallized PLA sample. This implies that the presence addition of PHB crystallites significantly improves the crystallinity and crystallization rate of PLA in the 75% PLA blend.
6.2.2.3 DMTA Analysis

Fig.6.15 (a) shows the temperature dependence of the dynamic storage modulus for both quenched and annealed samples of 75% PLA blends. The annealed 75% PLA blend sample shows higher dynamic storage modulus before melting compared with the quenched sample. Furthermore, in contrast with the quenched 75% PLA blend sample, the storage modulus of the annealed sample shows a small and gradual decrease from the glass transition temperature of PLA. These results indicate that the annealed 75% PLA blend sample exhibits better mechanical properties and higher thermal distortion temperature. This is due to the tiny PHB crystals greatly increasing the

Fig.6.15 DMTA curves for quenched and annealed samples of 75% PLA blends
crystallization ability of PLA, and hence the annealing process producing a thermally stable blend.

Fig.6.15 (b) and Fig.6.15 (c) show the temperature dependence of the loss modulus and loss factor tanδ of quenched and annealed 75% PLA blend samples. The glass transition peaks of the PHB component for both the quenched and annealed 75% blends are too weak to identify. The glass transition peak of PLA component for the annealed blend slightly shift too lower temperature compared with the quenched blend. The reason for this decrease in PLA glass transition temperature may be stronger intermolecular bonding between PHB and PLA during the annealing process. Furthermore, as discussed in section 5.2.2.4, the tanδ peak obtained from DMTA measurements can be used to assess interfacial bonding in polymer composites [97, 98]. As shown in Fig.6.15 (c), the annealed 75% PLA blend gives a lower tanδ peak compared with the quenched blend sample, indicating that the annealed 75% PLA blend dissipates less energy and has a lower internal friction. The main reason of this result may be the increased crystallinity and better facial bonding of the annealed 75% PLA blend compared with the quenched blend. Similar DMA results were reported by M. Hrabalova et al [110].
6.2.3 Effect of Adding Maize Starch

6.2.3.1 Morphological Properties: Optical Microscopy and SEM Analysis

High amylose content maize starch, HYLON VII, was adding into PHB/PLA blends at different weight ratios as described in section 3.2.2.

![Fig.6.16 Polarized light optical micrographs of spherulites of PHB in PLA/PHB/HYLON VII blends: (a) 50/50/0, (b) 50/40/10 and (c) 50/35/15](image)

Fig. 6.16 shows the optical micrographs obtained between crossed polars of PLA/PHB/HYLON VII blends after heating to 200°C and cooling at 10°C /min. As discussed in section 6.2.1.1, in PLA/PHB/HYLON VII 50/50/0 blend, PHB and PLA are immiscible, and the crystalline PHB phase acts as a continuous phase (Fig.6.16 (a)). The 50/40/10 blend shows an immiscible polymer blend
with a co-continuous phase structure, and the HYLON VII starch granules are dispersed as a filler (Fig.6.16 (b)). As shown in Fig.6.16 (c), in the 50/35/15 blend the size of the PHB spherulites is significantly decreased and well dispersed in the PLA matrix. This is due to the nucleating effect of starch granules.

The SEM micrographs of fracture surface of PLA/PHB/HYLON VII blend samples after tensile testing are displayed in Fig.6.17. It can be seen that the PLA/PHB/HYLON VII blends (Fig.6.17 (b) and (c)) show more irregular of the fracture surface compared with the PLA/PHB blend (Fig.6.17 (a)). As circled in Fig. 6.17 (a) and (a'), the gaps between PHB and PLA phases are visible, though ‘strings’ can be seen between the two phases. In contrast, the PLA/PHB/HYLON VII blends show ‘intimate contact’ between PHB and PLA phases, as circled in Fig.6.17 (b') and (c'). These results indicate that the addition of HYLON VII starch improves the interfacial adhesion between PHB and PLA, which is possibly caused by a finer dispersion of the PHB phase by adding starch. The wavy fracture surface morphology shown in Fig.6.17 (b') and (c') is possibly due to the improved tensile properties of the PLA/PHB/HYLON VII blends.

Furthermore, as marked in Fig.6.17 (b') and (c'), the gaps between starch granules and polymer blend matrix are visible, and many starch granules were pulled out from the matrix during tensile testing. These results indicate that there are no strong interfacial reaction between HYLON VII and both PHB and PLA.
Fig. 6.17 SEM micrographs of the fracture surface of PLA/PHB/HYLON VII blends: (a) and (a’) 50/50/0, (b) and (b’) 50/40/10 and (c) and (c’) 50/35/15
6.2.3.2 Crystallization and Thermal Properties: DSC Analysis

The DSC curves of PLA/PHB/HYLON VII blends with a heating rate of 10°C/min are shown in Fig. 6.18.

During the first heating run, as shown in Fig. 6.18 (a), a glass transition of about 50°C for the PLA component is observed in all PLA/PHB/HYLON VII blends as marked, and there are minor variations in the glass transition temperatures with composition. As discussed, the glass transition temperature of the PHB component can not be observed due to its high crystallinity and low concentration.

The recrystallization peaks of PLA at about 110°C can be seen in all PLA/PHB/HYLON VII blends, Fig. 6.18 DSC curves of PLA/PHB/HYLON VII blends obtained from (a) the 1st heating run, (b) cooling run, and (c) 2nd heating run.
indicating that the recrystallization of PLA occurs in all compositions. In the 50/40/10 blend, the recrystallization peak is located at a higher temperature (112°C) compared with that of the 50/50/0 blend (109°C). This is due to the crystalline PHB phase and the addition of starch arresting the mobility of PLA polymer chains, and thus the recrystallization of PLA occurs at a higher temperature. In the 50/35/15 blend, the recrystallization peak becomes broadened. This is possibly due to the combination of the nucleating and arresting effects of the PHB crystals and HYLON VII granules. Moreover, the enthalpy of recrystallization of PLA increases with the increasing starch content, indicating that the HYLON VII granules act as a nucleating agent. For all PLA/PHB/HYLON VII blends, the DSC curves show three peaks in the melting process: the lowest temperature peak, at around 155°C, corresponds to the melting of the PLA component; the next peak corresponds to the melting of the ‘as-formed’ PHB crystallites during processing; and the highest temperature peak corresponds to the melting of the recrystallized PHB.

During the cooling process, as shown in Fig.6.18 (b), the crystallization peak of PHB can be observed in all PLA/PHB/HYLON VII blends, and the enthalpy decreased with decreasing PHB content. In the 50/35/15 blend, the crystallization peak of PHB is very weak compared with the other two blends. This may due to the continuous amorphous PLA phase restricting the molecular mobility of PHB chains during crystallization.

During the second heating run, as shown in Fig.6.18 (c), all PLA/PHB/HYLON VII blends show similar curves to those obtained from the first heating run. This indicates that the thermal stability of PHB is improved by adding PLA and starch, as discussed in chapter 4 and 5.
6.2.3.3 DMTA Analysis

Fig.6.19 shows the temperature dependence of the dynamic storage modulus and loss modulus for the PLA/PHB/HYLON VII blends.

As shown in Fig.6.19 (a), the storage modulus of all PLA/PHB/HYLON VII blends gradually decreases from around 30°C which is associated with the glass transition of PHB. The values of storage modulus drop at the glass transition of amorphous PLA, but then increase at about 100°C, indicating the recrystallization of PLA. The reduction in the storage modulus at the $T_g$ of PLA becomes greater with the decreasing concentration of PHB. However, the storage modulus of all compositions reaches similar values at...
temperatures above 100°C.

Fig.6.19 (b) and (c) show two distinct glass transitions for the PLA/PHB/HYLON VII blends from the values of loss modulus and tanδ. The lower peaks at around 30°C correspond to the glass transition of the PHB component, and the higher peaks at around 60°C correspond to the glass transition of the PLA component. These results suggest that there is no strong interaction produced in PLA/PHB/HYLON VII blends by adding HYLON VII.

6.2.3.4 Mechanical Properties

![Mechanical properties: (a) tensile stress and (b) elongation at break of PLA/PHB/HYLON VII blends.](image)

The tensile properties of PLA/PHB/HYLON VII blends are shown in Fig.6.21. All these samples exhibited brittle fracture. It can be seen that for PLA/PHB/HYLON VII blends, both tensile stress at break and elongation at break increase with HYLON VII starch content. These improvements may be mainly attributed to two reasons: the improved interfacial adhesion between PHB and PLA caused by the finer dispersion of PHB phase; and the HYLON VII granules acting as a filler to enhance the properties, as shown in Fig.6.16.
and Fig.6.17.

![Graph showing impact strength vs. PLA-PHB-HYLON VII (wt%)](image)

**Fig. 6.21** Plot of impact strength for PLA/PHB/HYLON VII blends.

Charpy impact testing was carried out to measure the impact strength of PLA/PHB/HYLON VII blends, as shown in Fig.6.21. In general, all PLA/PHB/HYLON VII blends show poor impact properties. However, the addition of starch improves the impact strength. This may be due to the increased crystallinity of PLA and smaller spherulites of PHB caused by adding starch as a nucleating agent.
6.3 Conclusion

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

1. PLA/PHB blends are immiscible but exhibit molecular interaction. PHB is highly crystallisable and it increases the recrystallization of PLA and consequently increases the heat distortion temperature. Adding PLA to PHB improves the mechanical properties of PHB. In fact, blending with PHB is also a viable approach to improve the mechanical properties of PLA because the PLA/PHB 75/25 blend exhibits significantly improved tensile properties compared with pure PLA. This is due to the finely dispersed PHB crystals acting as a filler in PLA. The biodegradability, studied by weight change measurement at room temperature, increased with increasing PHB content due to its higher water absorption.

2. Recrystallization of PLA can be observed during the annealing process, and thus annealing can be used to produce a thermally stable PHB/PLA 25/75 blend. The annealed sample shows improved modulus, thermal distortion temperature and interfacial bonding.

3. Adding HYLON VII starch to PHB/PLA blends produces an irregular fracture surface with a finer dispersion of PHB phase in PLA. Starch acts as a filler and nucleating agent in PHB/PLA blends, and thus improves the recrystallization and thermal distortion temperature of PLA. The addition of HYLON VII starch in PHB/PLA blend improves the mechanical properties, and this may be due to the improved interfacial bonding between PHB and PLA by adding starch granules.
CHAPTER 7 CONCLUSIONS AND FURTHER WORK

7.1 Conclusions

The initial objective of this project was to modify the morphology, thermal and mechanical properties of polyhydroxybutyrate by blending with low molecular weight poly(ethylene glycol), regular maize starch ECO-MAIZE (72% amylopectin), high amylase maize starch HYLON VII (70% amylose) and polylactic acid. The morphology, structure, crystallization behaviour, thermal properties, mechanical properties and biodegradation behaviour of PHB and PHB based blends have been investigated. The findings show that various improvements in PHB properties can be obtained as summarized below:

7.1.1 Characterization of pure PHB

Characterization of pure PHB was carried out. As reported in the literature, it was found that PHB is a highly crystalline, biodegradable polymer with a melting temperature of 173°C. It forms large spherulites with cracks and splits at the spherulite boundaries, and hence it is brittle. It has poor thermal stability due to chain scission, which occurs at a temperature slightly higher than its melting temperature. It exhibits poor processability due to its extremely low melt viscosity. Its melt viscosity decreases with the increasing processing time and temperature.

Plasticized PHB with addition of PEG 300 was prepared by solvent-casting. PEG 300 acts as a plasticizer to weaken the intermolecular force between the PHB polymer chains. The addition of PEG 300 improved the flexibility of PHB by lowering the glass transition temperature, and broadened the processing temperature window by lowering the melting point. The addition of a high level of PEG 300, such as 10%, increased the thermal decomposition temperature.
of plasticized PHB.

### 7.1.2 Modification of PHB by blending with maize starch

As discussed in section 2.3.1, efforts were made to produce PHB/starch blends. It was found that starch granules act as a nucleating agent for PHB crystallite formation to refine the spherulite size. The novelty of this work was the investigation of the interaction between PHB and maize starch and the effect of different types of maize starch.

It is proposed that the mechanism of the modification of PHB by maize starch is the formation of intermolecular hydrogen bonding between PHB and starch. It is known that the CH$_3$ and C=O groups in PHB form a C-H···O=C hydrogen bond that results in the formation of a six-membered ring, and thus the β-hydrogen elimination reaction, i.e. chain scission degradation of PHB, occurs. However, it is easier to form an O-H···O=C hydrogen bond than a C-H···O=C hydrogen bond, and so the addition of starch may give rise to hydrogen bonding between the –OH groups in starch and C=O groups in PHB, thus inhibiting the formation of the six-membered ring and limiting the chain degradation of PHB. In addition, the formation of hydrogen bonding between starch and PHB should improve the mechanical and rheological properties.

The linear structure of HYLON VII starch (70% amylose content) exhibits more hydrogen bonding sites with PHB, and thus PHB has stronger hydrogen bonding with HYLON VII starch compared with ECO-MAIZE starch (72% amyllopectin content). The blend based on PHB and HYLON VII starch showed greater improvement in thermal stability, mechanical properties and melt viscosity compared with the blend based on PHB and ECO-MAIZE starch.
7.1.3 Modification of PHB by blending with PLA

Blending of polymers is an effective and economical way to obtain new materials with desired properties. However, it is well known that mixing of polymers is unfavorable. Normally blending is an endothermic process, i.e. there is a positive contribution to $\Delta H$ (change in enthalpy). Theoretically, there is also a positive contribution to $\Delta S$ (change in entropy) during mixing. However, because of the long chain structure of polymer, the change in entropy is very small. Thus the change in Gibbs free energy ($\Delta G$) is positive, i.e. mixing is unfavourable. In the rare case of specific interactions between the components, the exothermic interactions result in a negative contribution in $\Delta H$, and may result in a miscible polymer blend. However, theoretically, the interactions between components have a negative contribution to $\Delta S$, which may overcome the negative contribution to $\Delta H$, and result in a positive $\Delta G$, i.e. an immiscible blend. Therefore, in the case of specific interactions between the components, the miscibility of polymer blends depends on many factors, such as polymer conformation and chain flexibility.

The blends of the crystalline component PHB and amorphous component PLA are not miscible over the whole composition, although it is proposed in this thesis that a molecular interaction, which is thought to be transesterification, exists between PHB and PLA in all PHB/PLA blends. For the blend with a low concentration of PHB, PHB forms small spherulites that are well dispersed in the amorphous PLA matrix and has a slow crystallization rate and low crystallinity of the PHB phase. Thus, the change in entropy is small. With the transesterification interaction between PHB and PLA, the degree of compatibility between PHB and PLA components is higher in the blend with a low concentration of PHB. The blend with a low concentration of PHB exhibits improved tensile properties compared with pure PHB and PLA.
For the PHB/PLA 75/25 and 50/50 blends, crystalline PHB acts as the continuous phase. The mechanical properties of these blends increase with increasing PLA content.

The addition of highly crystallisable PHB in PLA increases the recrystallization of PLA and consequently increases the heat distortion temperature. During the annealing process, recrystallization of PLA can be observed in both pure PLA and PHB/PLA 25/75 blend. The annealed PHB/PLA 25/75 sample is thermally stable with an improved thermal distortion temperature.

Pure PHB shows rapid biodegradation at room temperature by enzymatic degradation from the surface, while pure PLA mainly degrades with non-enzymatic hydrolysis. The biodegradability of PHB/PLA blends was found to show a combined degradation mechanism, which is started with both enzymatic degradation and hydrolysis.

7.1.4 Modification of PHB by blending with PLA and HYLON VII starch

A study on PLA/PHB/HYLON VII blends was carried out. HYLON VII starch granules act as a filler and nucleating agent resulting in a reduction in PHB spherulite size and a finer dispersion of the PHB phase in the PLA matrix. The improved dispersion of the PHB phase and shear heat with the addition of starch granules may increase the transesterification interaction between PLA and PHB.

The addition of starch granules increases the recrystallization temperature of the PLA component due to the arresting effect of the PHB phase and starch granules.

For the PLA/PHB/HYLON VII blends, the mechanical properties increase with
the content of HYLON VII starch up to 15% by weight.

The biodegradability of PLA/PHB/HYLON VII blends is expected to be improved by adding starch. This is due to the fact that starch is more easily biodegradable, and once it degrades the space left will increase the contact surface for microorganisms and the amount of water absorption, and thus increase the biodegradation rate of PHB and PLA.
7.2 Further Work

The following further work is suggested:

1. Study on the optimum composition of PHB and PLA: it is suggested to have a further study on the PHB/PLA blends between the composition of 50/50 to 25/75 with a 5% increment or less. As described in Chapter 6, the PHB/PLA 25/75 blend showed different structure and improved properties compared with that of the PHB/PLA 50/50 blend. This further study can be used to investigate whether there is a reaction composition of PHB and PLA.

2. Study on optimum composition of PLA/PHB/HYLON VII: based on the results of suggestion 1, it is suggested to investigate the optimum composition of PHB/PLA/HYLON VII with desired properties and relatively low cost.

3. Using inorganic fillers in PHB/PLA blends: it would be interesting to study the structure, thermal and mechanical properties of PHB/PLA blends by adding inorganic fillers, such as CaCO₃, clay, etc.

4. Using soy protein as an additive in PHB/PLA blends: soy protein is a commercially available natural biopolymer. It would be interesting to study the effect of the addition of soy protein on the properties of PHB/PLA blends and whether soy protein can act as a compatibilizer in PHB/PLA blends.
CHAPTER 8  REFERENCES

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