Studies on Reactive Blends of
Poly (hydroxybutyrate-co-valerate) and Poly (butylene succinate) Bioplastics

by

Praphulla

A Thesis
presented to
The University of Guelph

In partial fulfillment of requirements
for the degree of
Master of Applied Science
in
Engineering

Guelph, Ontario, Canada

© Praphulla, December, 2012
ABSTRACT

STUDIES ON REACTIVE BLENDS OF POLY (HYDROXYBUTYRATE-CO-VALERATE) AND POLY (BUTYLENE SUCCINATE) BIOPLASTICS

Praphulla            Advisor: Dr. Amar Mohanty
University of Guelph, 2012     Co-Advisor: Dr. Manju Misra

Various commodity plastics used today are based on fossil fuels. Most of these plastics are non-biodegradable and will persist in the environment over a long time. The bioplastics from renewable resources have the potential to support a greener economy. The two of such renewably resourced bioplastics are poly (hydroxyl butyrate-co-valerate), PHBV and poly (butylene succinate), PBS. We have used petro-based PBS in our study, but renewable resource based PBS is expected to be available on a commercial scale in a very near future. These two bioplastics are both biodegradable. These two bioplastics are both biodegradable. In our study we have used PBS from petroleum resource but PHBV is a brittle bioplastic with a high modulus value and a low elongation at break while PBS is a low modulus bioplastic with a high elongation at break. Complementary properties can be obtained by blending PHBV and PBS. The direct melt blends showed poor mechanical properties due to limited interaction between PHBV and PBS phases.

This research focuses on increasing the interaction between PHBV and PBS blends by using compatibilizers. The compatibilizers used in this thesis were dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA. Use of an in situ compatibilization method was done for the melt mixing of PHBV and PBS yielding blends with improved characteristics. The investigations were performed at three different ratios of PHBV and PBS blends. The increase in the compatibility between the two phases was demonstrated through various thermal, thermo-mechanical, rheological and morphological means. The increase in elongation at break was used as a primary marker for compatibilization. The optimization of DCP and TMPTA was carried out,
which showed the enhanced interaction between PHBV and PBS phases, with the successful stress transfer from PHBV phase to the PBS phase resulting in increase in elongation at break. Inward shifts in tan delta peak on addition of DCP and TMPTA to the blends also showed increase in compatibility between the two phases. The interfacial adhesion between a brittle and ductile polymer, PHBV and PBS respectively was increased by using DCP and TMPTA. This opened gateways to various novel applications of PHBV and PBS blends via in situ reactive extrusion process.
Acknowledgements

I dedicate this thesis to my mother, Vandna Tiwary and my father, Pramod Tiwary, without their tremendous support and encouragement, nothing would have been possible. I also dedicate my thesis to my brother, Prateek Tiwary and sister, Kavya Tiwary who have supported me on my various adventurous undertakings. This thesis is also dedicated to my mentor Dr. Chandan Guria for his valuable inputs throughout my short but fruitful research career.

I wish to express my sincere gratitude to my advisor Dr. Amar K. Mohanty and co-advisor Dr. Manjusri Misra for providing me the opportunity to pursue graduate studies with them. They inspired me through their assistance, support, and guidance for which I shall be ever grateful.

I would like to acknowledge my advisory committee, Dr. Misra, Dr. Mohanty, and Dr. Stefano Gregori, for their suggestions during the study and their time and efforts in reviewing this thesis. Finally, I would like to thank the Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA) for their financial support via New directions research program (SR9235). We would also like to thank Canadian Foundation for Innovation (CFI) and Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA) for their equipment supports.
# Table of contents

Acknowledgements ................................................................................................................... iv

List of tables ............................................................................................................................ viii

List of figures ........................................................................................................................... ix

List of abbreviations and defined terms .................................................................................... xi

Chapter 1. Introduction ........................................................................................................... 1
  1.1 Classifications of bioplastics ............................................................................................. 3
  1.2 Biodegradable polymer market scenario .......................................................................... 11
  1.3 Bio-based biodegradable polymer market ....................................................................... 12
  1.4 Current issues with biopolymers ..................................................................................... 14

Chapter 2. Literature review ................................................................................................ 18
  2.1 Poly (hydroxybutyrate-co-valerate) ................................................................................ 18
  2.2 Poly (butylene succinate) ............................................................................................... 23
  2.3 Polymer blends ................................................................................................................ 25
     2.3.1 Compatibilization method ......................................................................................... 27
     2.3.2 Literature survey on melt blending of polymers ....................................................... 30
  2.4 Improving compatibility between PHBV and PBS .......................................................... 33
     2.4.1 Use of peroxide .......................................................................................................... 33
     2.4.2 Use of TMPTA with peroxide .................................................................................... 35
  2.5 Need for alternative research direction .......................................................................... 36
  2.6 Mathematical models ...................................................................................................... 37

Chapter 3. Purpose and hypothesis ....................................................................................... 39

Chapter 4. Significance ......................................................................................................... 42

Chapter 5. Objectives .............................................................................................................. 43
Chapter 9. Conclusions

References
List of tables

Table 1: Values of ‘x’ and ‘y’ for aliphatic polyester
Table 2: Values of ‘n’ and ‘R’ that are possible in a PHA structure
Table 3: Physical properties of PHA copolymers
Table 4: Various thermal properties of PBSA
Table 5: Effect of DCP dosage on PHBV / PBS (70:30 w/w) blend
Table 6: Concentration of DCP and TMPTA in 70:30 (w/w %) of blend
Table 7: Various formulations used in analysis and corresponding mechanical properties
(elongation at break values and notched Izod impact values are highlighted in bold, optimized
formulation is highlighted with red color)
Table 8: Elongation at break values (%) for 70:30 of PHBV and PBS blend at various dosage levels
of DCP and TMPTA.
Table 9: Zero Shear viscosity obtained via extrapolation through Carreau-Yasuda model (A: PHBV
neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F:
0.150% DCP and 1% TMPTA)
Table 10: Values of modulus and strength of PHBV and PBS blends (A: PHBV neat, B: PBS neat,
PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1%
TMPTA)
Table 11: Enthalpy and percentage crystallinity values of neat and reactive blends (A: PHBV neat,
B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F:
0.150% DCP and 1% TMPTA)
List of figures

**Figure 1**: Classification of bioplastics based on feedstock

**Figure 2**: Structure of polylactic acid, PLA

**Figure 3**: Structure of poly (ε-caprolactone), PCL

**Figure 4**: General structure of aliphatic copolyesters

**Figure 5**: Structure of poly (butylene adipate-co-teraphthalate), PBAT

**Figure 6**: Structure of polyesteramides, PEA

**Figure 7**: Structure of poly (vinyl alcohol), PVOH

**Figure 8**: Structure of poly (trimethylene teraphthalate), PTT

**Figure 9**: Bio-based plastics and the concept of the carbon neutrality

**Figure 10**: Bioplastic production

**Figure 11**: Structure of PHAs, ‘R’ - side chain length and ‘n’ - main chain length

**Figure 12**: Melting point comparison of PHA with other commonly used plastics

**Figure 13**: T<sub>g</sub> of various plastics vs. PHA

**Figure 14**: A typical structure of poly (butylene succinate), PBS

**Figure 15**: Effect of compatibilizer on particle size distribution of dispersed phase polymer

**Figure 16**: A typical reaction mechanism of PHBV and PBS in presence of DCP

**Figure 17**: A typical Structure of TMPTA, with reactive sites encircled

**Figure 18**: Contour plot of elongation at break (%) of 70:30 (PHBV: PBS) vs. DCP and TMPTA dosage (%) levels

**Figure 19**: Extruder force values for neat and reactive blends (A: PHBV neat, B: PBS neat, C: PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 20**: Complex Viscosity for neat and reactive blends of PHBV and PBS, the solid line shows corresponding Carreau-Yasuda fit. (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E: PHBV:PBS=30:70, F:PHBV:PBS=70:30*, G: PHBV:PBS=50:50*, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 21**: Complex modulus for reactive and neat blends of PHBV and PBS, palierre correlations are given by solid line. (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E: PHBV:PBS=30:70, F:PHBV:PBS=70:30*, G: PHBV:PBS=50:50*, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 22**: Tensile modulus and tensile strength of reactive and neat blends of PHBV and PBS (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E:PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 23**: Flexural modulus and flexural strength of reactive and neat blends of PHBV and PBS (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E:PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 24**: Stress vs Strain graph of reactive and neat blend (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)
**Figure 25:** Composition dependent compatibility of PHBV/PBS blend: A comparison of elongation at break determined experimentally for neat and reactive blends with rule of mixture value.

**Figure 26:** Notched Izod impact strength of neat and reactive blends of PHBV and PBS (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 27:** DMA tan delta peaks for neat and reactive blends of PHBV and PBS (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 28:** SEM micrographs of impact fractured surface of reactive and neat blends (Ratio PHBV:PBS)

**Figure 29:** Derivative weight loss curve for reactive and neat PHBV/PBS blend (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 30:** DSC melting graph of reactive and neat blends (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 31:** DSC crystallization graph of reactive and neat blends (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*)(* – reactive blends with 0.150% DCP and 1% TMPTA)

**Figure 32:** Polarized optical pictures of blends (A:PHBV:PBS=70:30, B:PHBV:PBS=70:30*, C:PHBV:PBS=50:50, D: PHBV:PBS=50:50*, E: PHBV:PBS=30:70, F: PHBV:PBS=30:70*)(* – reactive blends with 0.150% DCP and 1% TMPTA)

x
List of abbreviations and defined terms

1. DCP: Dicumyl peroxide
2. TMPTA: Trimethylolpropane triacrylate
3. PHBV: Poly(hydroxybutyrate-co-valerate)
4. PHB: Polyhydroxybutyrate
5. PHAs: Polyhydroxyalkanoates
6. PBS: Poly (butylene succinate)
7. USA: United States of America
8. PLA: Poly(lactic acid)
9. PLLA: Poly (L-lactide)
10. PDLA: Poly (D-lactide)
11. PDLLA: Poly (D,L-lactide)
12. LDPE: Low density polyethylene
13. PE: Polyethylene
14. PP: Polypropylene
15. PC: Polycarbonate
16. PS: Polystyrene
17. TPP: Triphenyl phosphite
18. DSC: Differential Scanning Calorimetry
19. DMA: Dynamic Mechanical Analysis
20. TGA: Thermogravimetric Analysis
21. POM: Polarized Optical Microscopy
22. SEM: Scanning Electron Microscopy
23. mDSC: Modulated Differential Scanning Calorimetry
24. PBAT: Poly (butylene adipate-co-terapthalate)
25. PTAT: Poly(tetramethylene adipate-co-terephthalate)
26. PCL: Poly (Ɛ-caprolactone)
27. PEA: Polyesteramide
28. PVOH: Polyvinyl alcohol
29. T_g: Glass transition temperature
30. ROM: Rule of mixture
31. x,y: Main chain length in a polymer
32. MFI: Melt flow index
33. EPR: Ethylene-propylene rubber
34. TPV: Thermoplastic vulcanates
35. PET – Poly(ethylene teraphthalate)
36. EPDM- Ethylene-propylene-diene monomer
Chapter 1. Introduction

Polymeric materials are used in a vast array of products. They exist in various applications from the automotive to various packaging products. Even though application requirements vary widely, polymeric materials can be synthesized to meet these varied conditions. Also, polymers form a critical aspect of our life. They are highly desirable material due to their durability and resistance to rotting and rusting. However, these unique properties make them persist in the environment for a long time. Due to their inertness and resistance to breakdown, several polymeric materials remain in the environment for a long time, penetrating the animal food chain and creating certain environmental concerns related to the waste disposal.

Recycling is the process of converting used materials into new articles [1]. It is usually accomplished via melting of the polymers followed by remolding into certain finished articles. Recycling can mean recycling of the industrial scrap or post-consumer plastic [1]. Thermoplastics are a class of polymer which can be repeatedly melted and formed into articles while thermosets on the other hand cannot be reprocessed again once formed into an article [2]. Thus the process of recycling is more prevalent in thermoplastics than the thermosets. Another way to dispose plastics at the end of life is by either landfilling or incineration. Landfilling is declining due to the rising cost as well as issues with the ground water pollution. Incineration on the other hand is not a totally environmentally friendly option due to the greenhouse gas generation that is related to global warming [1].

Degradation is defined as a change in the chemical structure of a plastic under certain environmental conditions [3]. Biodegradation is defined as the usage of microorganisms which are present in the selected disposal environment to completely breakdown and disintegrate plastic
Biodegradation is an end of life option where the plastic materials are disposed in a certain environment. The disposal environment plays an important role in the degradation of plastics and helps to judge the time required for the degradation to complete. Some of the disposal methods prevalent in industry are: biodegradation under composting conditions, under soil conditions, under anaerobic conditions and under marine conditions [4].

An answer to some of the disposal problems faced by plastics presently can be the use of plastics that degrade after the end of life cycle. The bio-based plastics are made from natural resources that are renewable such as agricultural feedstock. Some of these bio-based plastics are biodegradable. Therefore, the use of plastics that are both renewable resource based and biodegradable can solve some of the plastic waste disposal problem. Renewable resources that based on plants are a strategic alternative to meet the growing need for development of certain sustainable materials [5,6]. Polymers based on natural resources are emerging as an alternative to petroleum based polymers owing to the depletion of global oil reserves, the subsequent increase in fossil-fuel based resin prices and to have reduced carbon footprint. Also, the exponential growth of polymeric materials in everyday life has led to the accumulation of huge amounts of non-degradable waste materials across our planet. The fossil fuel based polymers are a key part of country’s economy. As such, it is likely beneficial for a long term scenario, to switch from the fossil fuel based economy to a renewable resource based economy. Biodegradable and bio-based polymeric materials can be a solution to these problems, yet they are not used on a large scale due to issues relating to cost and property limitations.
1.1 Classification of bioplastics

The bioplastics are broadly classified based on the raw material source. The bioplastics are classified into three major types as:

A. Renewable resource based bioplastic,
B. Petroleum based biodegradable bioplastic,
C. Plastic from mixed sources (renewable and petroleum).

The classification as depicted in the figure 1 is based on current state of scientific literature. It is expected that some of the polymers may change from one classification to another on the basis of the raw material source.

Figure 1: Classification of bioplastics based on feedstock (redrawn aft. ref. [7])
1.1.1. Renewable resource based plastics

Renewable resource based plastics have either their origin from plant or biological resources. Few examples of this class of bioplastics are discussed as follows:

1.1.1.1 Poly (lactic acid), PLA

A typical structure of PLA is shown in figure 2. Poly (lactic acid), PLA is manufactured from biomass such as corn and sugar beets [8]. PLA is a linear and aliphatic polyester and is produced by condensation reaction of lactic acid or by catalytic ring opening of the lactide group [9,10]. PLA is a rigid and stiff thermoplastic biopolymer. The stereochemistry of the polymer backbone dictates the final property. Incorporation of D-lactic acid in the PLA backbone increases the flexibility of resultant polymer [9,10].

![Figure 2: Structure of poly (lactic acid), PLA](image)

PLA has high melting point ($T_m$) range of 130 - 230°C depending on the structure [11]. PLLA has a $T_m$ of 180°C. Incorporation of L-, D- and meso lactide monomers into natural PLA affects the stereochemistry and crystallization [9]. Using such monomer incorporation, branching, molecular weight distribution, and isomer contents, it is possible to make a wide variety of PLA resins for specific applications.
1.1.1.2 Starch

Starch is an inexpensive and annually renewable material derived from plants. Starch can be isolated from plants such as corn, wheat, potato, cassava, pea, etc. Amylose and amylopectin form an integral part of starch. Amylose is a linear portion of starch while the amylopectin is the branched portion of the starch [12]. In the field of polymers, unplasticized or un-gelatinized starch is used as filler. Starch can be used as plastic material by destructurization and plasticization [13]. This is accomplished by using water or a non-volatile plasticizer. Such destructurized starch is termed as “plasticized starch” [14]. Starch exhibits gelatinization which involves breaking of hydrogen bonds by heat in the presence of water. At the elevated temperatures, the three hydrogen bonds of starch break down allowing the water to enter. This disturbs the granular organization of starch molecules and makes new H-bonds between amylose and amylopectin forming a gel-like structure [12].

1.1.1.3 Cellulosics

Cellulosics are the most abundant renewable-resource based materials. Cellulosics are semi-crystalline in nature and are used primarily for reinforcements in polymer composites. Cellulose can be converted to thermoplastic polymer by modification via acetylation [15]. This modified cellulose is called cellulose ester. The cellulose ester includes cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB) [15]. The cellulosic plastics are used in a variety of plastic applications such as toothbrush handles and screwdriver handles.

1.1.2 Petroleum based biodegradable polymers

These polymeric materials do not occur in the nature and are synthesized by means of chemical reactions called polymerization [2]. Polymerization is performed on the monomers that
are derived from the fossil fuels. Most of the commercial polymers belong to the category of synthetic polymers. Synthetic polymers can be reclassified based upon their thermal behavior, monomer sequence, types of monomers, type of reaction, type of process, nature of application and type of structure [2,7,16].

1.1.2.1 Aliphatic polyesters

The condensation of diols (1,2 ethanediol, 1,3-propanediol, or 1,4-butanediol) and carboxylic acids (adipic, sebacic, or succinic acid) give aliphatic polyesters. In this type of the reaction both the monomers have a linear or a branched aliphatic structure. Poly (Ɛ-caprolactone), PCL (Figure 3) and poly(butylene succinate-co-butylene adipate), PBSA (Figure 4) belong to this class of polyester [17].

![Figure 3: Structure of Poly (Ɛ-caprolactone), PCL](image)

![Figure 4: General structure of aliphatic copolyesters](image)

The values of ‘x’ and ‘y’ in the structure shown in the Figure 4 can be varied to give aliphatic polyesters of various structure and properties. The table 1 shows various types of polyesters that are possible with the variation of ‘x’ and ‘y’.
### Table 1: Values of ‘x’ and ‘y’ for aliphatic polyester as shown in Figure 4 above

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Name of the aliphatic polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>Poly (ethylene succinate)</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Poly (butylene succinate)</td>
</tr>
<tr>
<td>4</td>
<td>2,4</td>
<td>Poly (butylene succinate-co-butylene adipate)</td>
</tr>
</tbody>
</table>

1.1.2.2 Aliphatic-aromatic co-polyesters

Aromatic co-polyesters are often based on terephthalic acid. The condensation reaction of aliphatic and aromatic monomers gives aliphatic-aromatic class of polyesters. Poly (butylene adipate-co-teraphthalate), PBAT (Figure 5) is an example of aliphatic-aromatic polyesters which is produced by condensation reaction of 1,4-butanediol with terephthalic acid and adipic acid [18].

![Figure 5: Structure of poly (butylene adipate-co-teraphthalate), PBAT](image)

1.1.2.3 Polyesteramides

Polyesteramides, PEAs (figure 6) are synthesized by the co-polycondensation of polyamide (PA 6 or PA 6-6) monomers and adipic acid [19]. This polymer is highly polar but it has extremely low water vapour barrier. Though PEAs are biodegradable, researchers have reported negative eco-
toxicological impacts on the material of the compost [20]. This was attributed to the high amount of NH$_3$ released during laboratory scale composting of poly (esteramides) [20].

![Figure 6: Structure of polyesteramides, PEAs](image)

### 1.1.2.4 Poly(vinyl alcohol)

Poly(vinyl alcohol), PVOH (Figure 7) is synthesized in an alcohol medium by the reaction of poly(vinyl acetate) with sodium hydroxide [21]. PVOH has been reported to be biodegradable by the researchers [22]. PVOH is water soluble and has excellent barrier to odour, flavours, oil and fat.

![Figure 7: Structure of Poly (vinyl alcohol), PVOH](image)

### 1.1.3 Polymers from mixed sources (renewable and petroleum)

#### 1.1.3.1 Polyesters

Poly (trimethylene terephthalate), PTT (figure 8) is a condensation polyester of 1,3-propane diol and terephthalic acid. The monomer 1,3-propanediol can be renewable resource based while
the monomer, terephthalic acid can be based on fossil fuel. The sourcing of monomers from renewable resources increases the bio based content of PTT. The renewable resource content of PTT is 37% by weight [23]. This polyester has many desirable properties like heat resistance, strength, stiffness, and toughness. It also has low melt temperatures, and faster cycle time with excellent dimensional stability and chemical resistance [23].

![Figure 8: Structure of poly (trimethylene terephthalate), PTT](image)

1.1.3.2 Thermosets

Thermosets are class of polymers that once hardened and set into shape cannot be reshaped via heating [2]. This happens due to crosslink reaction during the formation of thermoset. Few examples of thermosets are unsaturated polyester resins, epoxy resins, and urethane resins. Bio-based thermoset is a terminology for a thermoset in which certain portion is produced from renewable resources. Polyester resins are made of a glycol and an unsaturated acid. An unsaturated polyester resin being blended with derivatized vegetable oil has been used as a matrix material for composite for application in the housing structures [24]. Polyurethanes (PU) are a class of thermosets that are made by the reaction of an isocynate and a polyol. The isocyanate component is always derived from the petroleum resources but the polyol component has a potential to be derived from bioresources [25]. Bio-based epoxy is another class of thermoset that is gaining popularity in the recent times [26]. Epoxidized vegetable oil on blending with petro-based epoxy resin can result in bio-based epoxy resin.
1.1.3.3 Biodegradable blends

The biodegradable blends are mixtures of at least two biodegradable polymers. The biodegradable polymers like PLA, PHBV, PBS, etc have already been discussed in this thesis. Since the constituents are biodegradable, it is expected that the blends will be biodegradable [27]. Similarly, mixtures of polymers which have at least one of the blending polymers from renewable source are known as bio-based polymers. The literatures on bio-based and biodegradable polymers have been dealt in this thesis at a later stage.
1.2 Biodegradable polymer market scenario

The biodegradable biopolymer market has a competition with the petroleum based biodegradable biopolymer and non-biodegradable biopolymer [28]. Many biodegradable biopolymers like PLA, PHBV, cellulosics and starch polymer have been previously discussed in this thesis. PBAT, PTAT etc. belong to petroleum based biodegradable biopolymer. Bio-polyethylene and bio-based epoxy are two examples of such non-biodegradable biopolymer. The advantages of using bio-based biodegradable polymers are evident from the following figure 9.

*Figure 9: Bio-based plastics and the concept of the carbon neutrality*

The use of bio-based biodegradable polymer supports the concept of carbon neutrality as is evident from the Figure 9 [29]. The monomers are derived from the plants which are polymerized in to polymers. These bio-based polymers are then converted into the products of daily use [29].
Upon fulfillment of the lifecycle of the article, these materials are then degraded in a suitable disposal conditions (compost etc.) where they are decomposed by the bacteria and the carbon is returned back to nature where this whole cycle is repeated again [29].

Such a cycle is self-sustainable and is required for the growth of a renewable economy. The depleting resources for fossil fuel and increase in greenhouse gas emission coupled with global rise in temperatures are some of the factors that have directed research and development in the area of bio-based polymers.

1.3 Bio-based biodegradable polymer market [28]

The global bioplastic production capacity was estimated to reach 766,000 metric tons (MT) by 2009 and 1.5 million MT by 2011 (Figure 10). It is clear from the figure 10 that the production of petroleum based biodegradable plastics has not shown much increase from 2007 – 2011. On the other hand the production of bio-based biodegradable and bio-based non-biodegradable polymer have extensively grown from 2007 to 2009 to 2011.
This trend shows a growing shift of biopolymer market towards bio-based degradable or non-degradable varieties. The 2nd European bio-plastics conference also forecasted significant growth for the bio-based biodegradable polymer share of about 60% increase [28]. Such increases in production have to be satiated by appropriate generation of demand. The market demand for biopolymers is dependent on the factors such as price competitiveness, the potential growth of “fit-for-use” applications, laws and regulations, and the optimization of commercial composting processes [28].

**Figure 10: Bioplastic production (redrawn aft. ref. [28])**
1.4. Current issues with biopolymers

Some of the current issues that are related to biopolymers are:

1.4.1 Cost,
1.4.2 Raw material availability,
1.4.3 Application development,
1.4.4 Aging and durability, and
1.4.5 End-of-life Issues

1.4.1 Cost

Cost is an important criterion for the biopolymer development. According to the European Bioplastic Association, the current biopolymer prices are 80% lower compared to 10 years ago [28]. However, this decrease in price is still not significant enough when compared to many fossil fuel based polymers [30]. Various companies such as Dupont, Novamont, and Metabolix are making joint ventures with the agricultural companies to produce monomers to overcome the cost and the procurement of monomers [30,31]. Another way to decrease the cost is to scale up to a higher production volume.

1.4.2 Raw material availability

Most of the current biopolymers have their raw material sourced from plants. Some of the by-products of biofuel industry are used in synthesis of biopolymers. Therefore, the availability of raw materials for biopolymers is closely linked to the biofuel production. For example, to replace a 10% of the fossil fuels used for transportation, USA would need to use 43% of its total agricultural land and the EU, 38% [30,31]. As biomass is available in very large quantities, using biomass as a
renewable raw material source could solve the problem for both biofuels and biopolymers. Many countries have set biofuel consumption targets. Unfortunately, the technologies that make full use of these materials have not yet been fully developed [30,31].

1.4.3 Application development

The mechanical and thermo-mechanical performance of some biopolymers are inferior when compared to certain fossil fuel based polymers. This demands research and development initiatives that will allow the tailoring of biopolymers for specific applications. The blending of biopolymers is a major research area presently, as a blend of two or more polymers can produce a polymer with optimum properties of the individual polymers. Another developing area is natural fibre reinforced composites (biocomposites), for which the bioadditives and the biofillers also need to be developed. Developing biocomposites would be essential, because bioplastics alone are a mediocre structural material. As with the fossil fuel based polymers, adding fibre reinforcement can improve its structural and thermal properties. The similar concept is being researched on biopolymers. Natural fibres have been extensively used in moulded parts [28,30,31]. This research has focussed on improving wettability, and adhesion through suitable surface modification, and to overcome problems such as high batch-to-batch variability, fibre thermo-degradation, and yellowing during compounding and processing [28,30,31].

To further develop market potential, research is being done in the areas like the processability of biopolymers, specifically with respect to its sensitivity to moisture and temperature, optimization of processing lines, and finishing processes such as coating, painting, metallizing, laser marking, mechanical assembly, etc [28].
1.4.4 Aging and durability

The performance of polymeric materials for outdoor applications depends on their weatherability and service lifetime. Weathering of the polymers and the composites are strongly related to the aging methods, degradation, and stabilization phenomena [30]. All these aspects of the weathering phenomena are key settings for the durability analysis and lifetime prediction of the polymers. Limited studies exist on indoor and outdoor ageing, and durability properties of biopolymers. This prevents usage of biopolymers in the production of durable goods or structural applications [30].

1.4.5 End-of-life issues

End-of-life issues deal with disposal of biopolymers. Disposal of biopolymers can be done either via recycling or complete breakdown in composting conditions. Recycling is a process of using the polymers used in the products back again using appropriate techniques. Recycling involves collecting various articles from household and industrial facilities and sorting the articles on basis of the polymer type [4]. These sorted articles are then cut into small pieces so that they can be processed in extruders easily. After passing through extruders the strands are cut and pelletized. These pelletized polymers are then bagged and shipped to the convertors who melt it again and form articles. The low volume of biopolymers and the lack of infrastructure to accommodate bioplastics are few of major challenges of recycling biopolymers [28,30].

Composting on the other hand involves disposal of biopolymers in industrial composting plants. Composting is defined as the process of biodegradation under aerobic conditions [4]. Composting
of usually takes place in an industrial composting plants. In the industrial composting facilities, controlled conditions (e.g. temperature, humidity, aeration) are maintained for the bacteria to act on the polymer. At the end of usage life cycle, bioplastics can be diverted to the composting waste stream. The chain structures of compostable polymers are used by microbes, like bacteria or fungi with their enzymes, to digest as a source of nutrition. The resulting end products are water, carbon dioxide (CO₂), and biomass. For a biopolymer to be certified as compostable it has to fulfill requirements of certain standards (ISO-14855, EN – 13432 or ASTM D 6400) [4]. Such an effort for certification has already been made in European countries and some North American cities [28,30,31].

In the previous sections of the thesis we have discussed various biopolymers, their categorization based on feedstock and issues related to them. Since, this thesis deals with two biopolymers blends from two important bioplastics – polyhydroxyalkanoates and poly (butylene succinate), an in depth literature survey was done on structure and property of these two biopolymers in coming sections.
Chapter 2. Literature Review

2.1. Polyhydroxyalkanoates, PHAs

2.1.1. History

PHAs belong to a class of biodegradable polymers which are derived from bacteria. PHAs are therefore known as bacterial polyesters [32]. A typical structure of PHA is shown in Figure 11.

![Figure 11: Structure of PHAs, various combinations of “R”, side chain length and “n”, main chain length are shown in table 2](image)

Table 2: Values of n, main chain length and R, side chain length that are possible in a PHA structure [32]

<table>
<thead>
<tr>
<th>n</th>
<th>R</th>
<th>Type of PHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogen</td>
<td>Poly-3-hydroxypropionate</td>
</tr>
<tr>
<td></td>
<td>Methyl</td>
<td>Poly-3-hydroxybutyrate</td>
</tr>
<tr>
<td></td>
<td>Ethyl</td>
<td>Poly-3-hydroxyvalerate</td>
</tr>
<tr>
<td></td>
<td>Propyl</td>
<td>Poly-3-hydroxyhexanoate</td>
</tr>
<tr>
<td></td>
<td>Pentyl</td>
<td>Poly-3-hydroxyoctanoate</td>
</tr>
<tr>
<td></td>
<td>Nonyl</td>
<td>Poly-3-hydroxydodecanoate</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>
William and Martin [32] highlighted the choice of using various types of functional groups in place of ‘n’ and ‘R’ depending upon requirement (Table 2). All the major types of PHA were discovered in the past 20 years. One of the first PHA, poly-3-hydroxybutyrate (PHB) was discovered in 1925 by a French scientist Lemoigne is the only exception to this case, being discovered earlier than the rest [28].

The commercial grades of PHAs were first launched by a British company, Imperial Chemical industries (ICI), named as poly-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) under the trade name of Biopol®. The major application remained in biomedical applications as price was high (20 USD/lb. in 2008) to be applicable to commodity polymer sector [28]. ICI transferred its PHA division to Zeneca in 1993. By 1995 Zeneca further sold it to Monsanto. Monsanto took the production of PHA forward through transgenic approaches [28]. In 2001, Metabolix further acquired PHA division from Monsanto and currently PHAs are produced under Mirel® trade name.

2.1.2. Extraction of PHAs

PHAs are accumulated in certain microorganism as carbon and energy storage materials. Polyhydroxyalkanoates are produced when certain microorganisms are subjected to a growth conditions with limited nutrient. Some recumbent forms of the microorganisms are designed to produce PHA on a mixed feed. As supply of the limiting nutrient is restored, stored PHA is degraded. This degradation is carried out by intracellular depolymerases. The resultant is metabolized as carbon and energy source. The accumulation of PHAs in the cells varies depending upon the species of bacteria [32,33].
2.1.3 Polyhydroxyalkanoate properties

Melting point of a polymer is the upper ceiling temperature of the polymer up to which a certain polymer can be used safely without melting the article. We see from the above Figure 12 that PHAs have the right melting point to replace most of the plastics. PHBV has a range of melting point between 110°C to 170°C [33], depending upon the type of main chain “R” and side chain “n”. This shows that for a certain application, specific type of PHAs can be designed to suit the application requirement. The most important application can be ‘retort’ capability. Retort application requires polymer to be heated up under pressure to sterilize the products. Polypropylene, PP is the most suitable polymer for the retort applications due to its high melting point. Poly (hydroxybutyrate), PHB which has similar melting point as PP can be a promising candidate for ‘retort’ applications [33].

**Figure 12**: Melting temperature comparison of PHA with other commonly used plastics (redrawn aft. ref. [33])
The glass transition temperature, \(T_g\) is the temperature below which the segmental motion of polymer chains are hindered [2]. Below the \(T_g\), a polymer behaves as a glassy substance making it brittle and break like a glass while above the \(T_g\), the behaviour of polymer is less brittle. In the various applications, \(T_g\) signifies the lowest threshold of operating temperature for a product. If we compare PHAs with various plastics (Figure 13), PHA range competes with PP homopolymer which has \(T_g\) of 9 °C [33]. The proximity of \(T_g\) for PHAs near 0°C pose a problem for applications that require freezing, as below \(T_g\) PHAs will act like a glassy material breaking easily. This puts a limitation on sub-zero applications for PHAs.

One of the focus polymers of this dissertation is poly (hydroxybutyrate-co-valerate), PHBV and so this section will concentrate on various properties of PHBV.

![Figure 13: \(T_g\) of various plastics vs. PHA (redrawn aft. ref. [33])](image-url)
Incorporation of hydroxyvalerate unit in PHA improves the physical properties like notched Izod impact strength (Table 3). Random polymers of PHB with other hydroxyalkanoate units have different chain lengths. It has been noted that of PHAs with higher valerate content exhibit high impact strength. Literature has shown that by increasing the valerate content in a typical PHA a maximum Izod impact of 400 J/m was attainable with 25% valerate. The properties of PHAs with various valerate content have been shown in Table 3 [34,35]. However, increasing the valerate unit in a PHA is a costly technique and has been reported to increase the cost of copolymers due to time and cost involved with genetic modification of PHA producing bacteria [36].

**Table 3: Physical Properties of PHA copolymers** [34, 35]

<table>
<thead>
<tr>
<th>Valerate Content (%)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Notched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>179</td>
<td>40</td>
<td>3.5</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>170</td>
<td>38</td>
<td>2.9</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>162</td>
<td>37</td>
<td>1.9</td>
<td>95</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>150</td>
<td>35</td>
<td>1.5</td>
<td>120</td>
</tr>
<tr>
<td>20</td>
<td>-1</td>
<td>145</td>
<td>32</td>
<td>1.2</td>
<td>200</td>
</tr>
<tr>
<td>25</td>
<td>-6</td>
<td>137</td>
<td>30</td>
<td>0.7</td>
<td>400</td>
</tr>
</tbody>
</table>

Low valerate content PHBV as such cannot be used in many commodity sector applications due to its brittleness, low notched Izod impact strength and low elongation at break values (~ 5-10%)[33]. The PHAs with comparatively higher valerate content are costly. Therefore, a cheaper alternative has to be explored. One of the alternatives for modifying the properties of PHAs is blending with a polymer which has complimentary properties such as high elongation and Izod impact strength. Polymer blending is considered to be an economical approach to modify the properties of the constituent polymers.
2.2. Poly (butylene succinate)

A general structure of aliphatic copolyester was discussed in section 1.1.2.1. This general structure can be modified with the choice of repeating units in main chain with \(x = 2\) and \(y = 4\). This gives a typical structure of PBS (Figure 14). PBS is a highly crystalline polyester. The tensile yield strength of injection molded specimen has been reported to be in range of 30–35 MPa [37-39]. PBS has high elongation at break (%) with very low modulus values (~ 450 MPa) [37-39]. The lack of appropriate stiffness-toughness value makes PBS unsuitable for many applications. Various properties of PBS can be tailored by random copolymerization with various chemical reagents in presence of the suitable catalysts [40]. Titanium compounds display the highest catalytic activity for polyester polycondensation reactions [41].

![Figure 14: A typical structure of poly (butylene succinate), PBS](image)

Bio-based monomers have come into light with the recent developments in the fermentation technology. One of the top twelve bio-based chemicals that are produced from sugars and have potential market value is succinic acid (SA) [40]. Succinic acid is used as a monomer for the production of poly(butylene succinate), PBS. Reduction of succinic acid, SA further gives 1,4-butanediol (BDO). BDO is another monomer that is used in synthesis of PBS. Thus PBS can be fully bio-based. It has been reported that Polyolefins can be substituted by PBS in some applications [40].
Recently, copolymer, poly (butylene succinate-co-adipate), PBSA has been developed which has better thermal stability. This copolymer has briefly been discussed earlier (in section 1.1.2.1 of this thesis). Copolymerization with adipic acid gives a particularly useful copolymer: poly (butylene succinate-co-adipate), PBSA. PBSA has unique properties which depend on the amount of adipic acid monomer in the chain. Table 4 shows various thermal properties of PBS and its copolymers. The melting point, $T_m$ and the glass transition temperature, $T_g$ of PBSA is closely related to the copolymer content. PBSA with 20% adipic acid has shown a decrease in melting point (Table 4). PBS under trade name “Bionolle” was first commercially manufactured by Showa High polymer, Japan [42]. Bionolle is aliphatic polyester and its process ability is similar to the conventional resins like polyethylene. It is one of the most suitable materials for processing into films which can be used to make agricultural films, shopping bags, compost bags, and so on. Some of the companies in production of PBS are Xinfu pharmaceutical, Hexing, and Jinf tape, China.

**Table 4: Various thermal properties of PBSA [40]**

<table>
<thead>
<tr>
<th>PBS/PBSA - x</th>
<th>$T_m$ ($°C$)</th>
<th>$T_g$ ($°C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS / PBSA - 0</td>
<td>112</td>
<td>-18</td>
</tr>
<tr>
<td>PBSA – 5</td>
<td>108</td>
<td>-21</td>
</tr>
<tr>
<td>PBSA – 10</td>
<td>103</td>
<td>-23</td>
</tr>
<tr>
<td>PBSA – 15</td>
<td>99</td>
<td>-27</td>
</tr>
<tr>
<td>PBSA – 20</td>
<td>92</td>
<td>-34</td>
</tr>
</tbody>
</table>

* – degree of crystallinity calculated from DSC considering melting enthalpy of completely crystalline material as 110.3 J/g, PBSA – x: where x is amount of adipic acid (%)
2.3. Polymer blends

Polymer blending is a concept that involves mixing two or more polymers to get desired or some optimized properties [43,44]. Polymer blends have been used even before synthetic polymers became available [45]. Natural polymers like resins, natural rubber, cellulose etc. were combined to produce coating and adhesive materials [45]. The commercial product nitrocellulose first manufactured in mid 1800s contained shellac to improve the coating thickness [45]. One of the first examples can be the commercial application of phenolic thermosetting polymers in 1900s, which was a blend with natural rubber [46]. This was one of the first application of interpenetrating network. As time progressed, with growing expertise in research and development, and know-how on polymer blending led to the development of various types of commercial polymer blends. One of the commercial blends, developed in 1940, was of poly (vinyl chloride), PVC and butadiene-acrylonitrile rubber, NBR co-polymer elastomer which is still available today [47,48].

The age of polymer blends truly took off after 1940, with introduction of poly(2,4-dimethyl-1,4-phenylene oxide), PPO and polystyrene, PS blends by General Electric under trade name of Noryl. This blend was significant as both the polymers were miscible and the properties of blends were intermediate, dependant on weighted average of constituents [45].

The miscibility of polymer blends is an important criterion for development of certain properties. The mechanical properties like modulus and elongation are found to follow additive rule with miscible blends [45]. In certain cases, immiscible polymer blends have exhibited to have higher impact strength than constituent polymers [45]. Such phenomenon has also been reported in literature due to formation of core-shell morphology. The co-continuous blends have been shown to exhibit superior mechanical properties [49]. The morphologies of polymer blends are dependent on the processing conditions and thermal history [49]. Compatibilizers are added to increase interfacial
adhesion between polymers and to prevent molten polymer material from coalescing [50-53]. The
graft copolymers formed via reactive blending in presence of the compatibilizers have been
reported to migrate at the interface of two polymers (Figure 15). This is exhibited by a decrease in
the particle size of dispersed phase in the blend (Figure 15) [50-53].

![Diagram showing compatibilizer effect on particle size distribution](image)

**Figure 15:** Effect of compatibilizer on particle size distribution of dispersed phase polymer

One approach of compatibilization is the ‘two-step’ process. In the first step, the functionalization
of polymers is achieved though addition of suitable reagents. In the second step, the functionalized
polymers are blended in the extruder [45,49]. This blending leads to generation of graft reactions
between the functionalized groups. This results into an in situ formation of graft copolymers.

Another process for compatibilization of the polymers is the ‘one-step’ process. In one step process,
the low molecular weight reagents are added to the molten blends. This leads to in situ formation of
graft copolymers during extrusion. The one-step process is preferred in industry due to economics
involved and the ease of scale up from the laboratory [49,54]. We have discussed on various
compatibilization methods in next section of this thesis.
2.3.1. Compatibilization methods

Compatibilization of polymer blends can be achieved through following ways [45]:

2.3.1.1. Ternary polymer addition (nonreactive),

2.3.1.2. Interpenetrating polymer networks (IPNs),

2.3.1.3. Block copolymer addition / partial co-polymerization, or

2.3.1.4. In situ reactive extrusion.

2.3.1.1. Ternary polymer addition (nonreactive)

In this compatibilization method, a third polymer (ternary polymer) is added in the binary polymer mixture that has to be compatibilized. The third polymer disperses at the interface of two immiscible polymers. There is absence of chemical reaction between polymer species. The addition of ternary polymer component to a binary blend of immiscible polymer has been applied to improve dispersion and to improve properties [55].

The choice of ternary polymer is done such that it has a good interfacial adhesion to both components and also has the interfacial tension values that will allow the concentration at interface of binary mixture [55]. The ternary polymer acts as a “surfactant” and stabilizes the interfacial area, allowing smaller particle size of dispersed phase, and improves stress transfer across phases [55]. One example of such a blend system is blend of poly (butylene teraphthalate), PBT and polycarbonate, PC. Addition of poly (hydroxyether of bisphenol A), PHE has been shown to improve the miscibility of PBT/PC blends [45,56]. Similar observation has been made in literature where ethylene propylene rubber has been added to blend of high density polyethylene, HDPE and polypropylene, PP blend in improving the impact properties of the blends [55].
2.3.1.2. **Interpenetrating network (IPNs)**

This method involves simultaneous or sequential polymerization to form polymer networks [57]. The blends that are created with this approach are termed as interpenetrating polymer networks (IPNs). IPNs work on hypothesis that interlocking rings of polymers (catenane structures) would lead to compatibilization of polymer. The concept involves single phase behaviour of monomer-monomer or monomer-polymer mixtures with appropriate crosslinking agents. The monomers used in the IPNs have unsaturation or reactive groups in the structure. This unsaturation or reactive groups react with other reactive groups in presence of crosslinking agents to form a cage-like structure. The various types of IPNs are sequential IPNs, and simultaneous IPNs. Thermosets are the major class of polymer that utilize the concept of IPNs for compatibilization. In thermoplastics, EPDM and PP have been compatibilized by using the concept of IPNs [58, 59].

2.3.1.3. **Partial co-polymerization / block copolymer addition**

Partial co-polymerization method is used to compatibilize two immiscible polymer system by addition of chemical species that have structurally two parts: one that is miscible with polymer A and other part which is miscible with polymer B [55,60]. When the two polymer systems are mixed, the copolymer acts as a binding agent. Polystyrene, PS and polypropylene, PP blends have been reported to be compatibilized by addition of styrene-butadiene-styrene, SBS block copolymer system [61]. Similar concept of compatibilization via addition of copolymer has been used in compatibilization of PS and HDPE blends by addition of PS-PE block copolymer [61,62]. In this system, improvement in interfacial
adhesion was observed with addition of PS-PE block copolymer. For such cases, the compatibility between the polymers has been found to be dependent on processing conditions, the length and sequence of copolymer distribution. Generally the block copolymer systems are costly to produce separately and involve one more addition to the extrusion system. Therefore, this process is suitable only for the specialty polymer systems where the economics of manufacturing and addition of block copolymer can be extracted profitably [55].

2.3.1.4. **In situ reactive extrusion**

Industrially, in situ reactive extrusion process is the most prevalent means of mixing two or more polymers. It involves processing two or more polymers simultaneously. This leads to generation of reactive sites which interact with the other polymer chains and localize themselves at interphase of the two polymers. Such localization at interface gives improvement in mechanical properties and decreases particle size of the dispersed phase. A polymer blend system that is inert during processing, peroxides are added which enhance free radical production mechanism [2,63].

Reactive extrusion is a practical method of compatibilization in terms of economics and ease of scale up from a laboratory setup. The reactive extrusion can lead to formation of graft copolymers. The in situ reactive extrusion requires careful control of the chemical reaction. Some of the commercial examples of in situ compatibilized blends are ethylene-propylene rubber toughened polyamides (Super-tough Nylon) and poly (2,6-dimethyle-1,4-phenyl oxide and Nylon 6,6 blends (Noryl GTX) [55]. This method of reactive compatibilization was also applied to compatibilize an extreme case of incompatible
polymer blends. Polyolefins are hydrophobic polymer and poly(vinyl alcohol), PVOH is a hydrophilic polymer [55]. The incompatibility between PVOH and polyolefin was remedied by the addition of peroxides. This led to formation of a graft copolymer consisting of both the phases, located on phase boundary which stabilizes the blend [55]. This stabilization of blends prevented the coalescence in the blend system. This lead to generation of a finer morphology and greatly improved adhesion between the hydrophilic and hydrophobic phases [55].

Single pass reactive extrusion process is preferred in an in situ reactive extrusion process. In this process, the components are either added into the extruder at various zones or fed simultaneously. The extruders generally employed are twin screw with co or counter rotating screws providing shear and mixing during melt extrusion. PP and PET have been compatibilized through use of glycidyl methacrylate and maleic anhydride [64]. Similar process was employed to compatibilize PP and PVOH blend where increase in elongation values was observed with the addition of dicumyl peroxide (DCP) and maleic anhydride [65,66].

### 2.3.2 Literature survey on in situ melt blending of polymers

Melt mixing is the most favourable thermoplastic processing method as it combined the ease of processability with the scalability. The melt mixing was chosen to blend the biopolymers, PHBV and PBS.

Polyester and polystyrene were in situ compatibilized in a literature [67]. The compatibilization was characterized by the measurement of shift in the glass transition temperature, $T_g$ [67]. The chemical species used in the reaction cannot be replicated in case of biopolymers as
they are polyesters. Polystyrene which was a non-reactive polymer was made reactive by the use of a chain transfer agent. In this paper, the authors enhanced interaction between the two phases of PP and PS in presence of a chain transfer agent [67]. In such conditions, the mechanical property was poor due to prolonged exposure of polymer under the chosen reaction conditions. This was attributed to the degradation of the polymer species [67].

In another paper, authors have used dicumyl peroxide, DCP with multifunctional monomer to improve the compatibilization between PP and PS [68]. The concept was novel as the concentrations of free radicals were controlled by DCP while the grafting reactions were controlled by a multifunctional monomer. They also compared various multifunctional monomers but they failed to highlight any mechanical property [68]. Also, the effect of processing conditions on compatibilization would have given a closer insight towards the mechanism of reactions.

In another study, authors have used reactive agent for compatibilization between two polymer species and the mechanical properties of the blends have been thoroughly investigated [69]. The reactive group investigated was styrene maleic anhydride. The reaction between PP and PE was impossible as they both were non-reactive. The peroxides were used to generate reactive sites in this work. Maleic anhydride grafted onto the back bone generating interaction between the two polymers. Grafting of amino methacrylate further improved the compatibility between the two polymer phases. The FTIR was used to detect the generation of graft species. The increase in elongation values and impact values were considered closely related to increase in compatibility.

In another literature, the authors have applied in situ blending process using ultrasonic aided extrusion [70]. The process involved mixing PP and EPDM by subjecting to the ultrasonic waves. The generation of the free radical was controlled by ultrasonic generator frequency and distance
from the extrudate. The large energy input due to the use of ultrasonic generator has been related to increase in the input price for a large scale production.

Wang et al. [71] have used a novel method of compatibilization by the use of reaction species that promote transesterification reaction. They used triphenyl phosphite to enhance the transesterification reaction. The drawback of the above reaction mechanism was the long reaction time given for chemical species to react. The long reaction time enhanced the transesterification reaction but degraded the polymer system to an extent that measurement of mechanical properties was not possible. The use of more eco-friendly and effective compatibilizer can further develop more sustainable blend system.

Tatsushima et al. [72] used solvent casting method to determine the miscibility of the two biopolymers, poly (butylene succinate) and cellulose acetate blends. Chloroform was used as a solvent. Authors have concluded that the two polymer systems were miscible and formed a single phase.

In another paper, the two biopolyesters (PLA and PBS) were mixed in an extruder [73]. The interaction between the blends was detected by various thermal analyses methods [73]. In polymer blends, the occurrence of single glass transition temperature has been linked to enhanced miscibility of the phases. The crystalline behaviour was thoroughly studied and analysed for miscibility.

In another paper, authors [74] have discussed an in situ reaction of PP with EPDM. They have observed an increase in izod impact strength. In this in situ reaction, triallyl-cyanurate was used as compatibilizing agent while peroxide was used to generate free radical sites. The concept of thermoplastics vulcanite, TPVs was illustrated in the literature. The increase in tensile strength, modulus, and hardness was related to the increased thermoplastic hard component in the blend. Dicumyl peroxide (DCP) was found to be the most efficient out of the four peroxides investigated.
The paper on poly (trimethylene terapthalate), PTT discusses effect of core shell morphology on the impact values for PTT [52]. In this paper, Wang et al. [52] used multifunctional monomer along with a peroxide to generate core shell morphology. Drastic increase in Izod impact values supported the formation of core shell morphology. The major drawback could be the degradation of polymers due to the addition of DCP. Also, the Increase in Izod values cannot be attributed to formation of core shell morphology only. The changes in molecular weight and molecular weight distribution with formation of comonomers could also lead to increased Izod values.

From the above literature we saw that the use of peroxide was a possible way forward in compatibilization of PHBV and PBS. The peroxide was expected to generate reactive sites as demonstrated by literature. The important parameters to consider were peroxide dosage and half-life of the chosen peroxide. Furthermore, the addition of multifunctional monomer was said to enhance the interaction between the polymer constituents. The use of multifunctional monomer could be a step forward after peroxide optimization. Peroxide addition coupled with multifunctional monomer addition has been proven to provide drastic increase in properties of polymer blends. The core shell morphology development can be a possible morphology resulting from this modification.

2.4. Improving compatibility between PHBV and PBS

2.4.1. Use of peroxide [75]

Ma et al. [75] have discussed the usage of DCP to compatibilize PHBV and PBS (70/30) blend with high un-notched Izod impact strength. This was achieved via use of a compatibilizer (DCP) in the reactive extrusion process. This reactive extrusion process had the capability to enhance the interaction between PHBV and PBS phases. Also, the notch sensitivity of the compatibilized
material made the use of this material unsuitable for various real life applications. The free radical generated on one polymer chain would attack other chain leading to formation of polymer with grafting. This methodology is pictorially represented in Figure 16.

![Figure 16: A typical reaction mechanism of PHBV and PBS in presence of DCP (redrawn aft. ref. [75])](image)

Increase in mechanical property was observed with the above compatibilization technique but notch Izod impact of blend still remained low. This low notch Izod impact strength limited the application of PHBV and PBS blends in many applications. Moreover, in this literature, the compatibilization was done at only one composition of blend (70:30, w/w) which further limited the complete understanding of compatibilization, morphology, and rheology of the blends at other ratios of PHBV and PBS blends.

Peroxides work by hydrogen abstraction mechanism generating a free radical at the reactive site at the polymer chain (Figure 16). These chains have tendency to combine with other the polymer chains to form copolymers. The copolymers that are formed in reactive extrusion process have a surface energy value in between the constituent polymers. Therefore, graft polymers are localized at interface of the two polymer blends [49]. This tendency of graft polymers to localize at interface prevents coagulation of molten polymer resulting in smaller particle size distribution.
2.4.2. Use of trimethylolpropane triacrylate, TMPTA along with peroxides

TMPTA has been extensively used in photo-initiated reactions. The structure of TMPTA is shown in Figure 17 [76]. The multi-reactive sites of TMPTA make them ideal for grafting reactions. In photo initiated reactions, the double bond reactive sites of TMPTA open up via some energy source. One TMPTA molecule attacks the adjacent TMPTA molecule. This leads to formation of cross-linked structure. We have used high temperature as an energy source in our melt blending process to open up these double bond sites.

![Structure of TMPTA](image)

**Figure 17**: A typical Structure of TMPTA, with reactive sites encircled [76]

Peroxides have been used in extrusion to generate free radical sites via in situ reaction. The use of multifunctional monomer further attacks those free radical sites to generate graft copolymers. The same concept has been used extensively in various studies which have been dealt in the literature survey previously.
2.5. Need for alternative research direction – PBS and PHBV compatibilization

Polymer blending is a concept to utilize properties of blended polymers. In this study, PHBV had a high flexural modulus but had a low elongation at break values. On the other hand, PBS had a high elongation value but low modulus value.

A natural rationale would be to utilize the blend of PHBV and PBS to get a balance of stiffness and modulus. Literature [37] has shown that the blends of PHBV and PBS are partially miscible. This was predicted based on thermal properties of the blends. At a low ratio of PBS in the blend, the miscibility of PHBV and PBS was high while increasing the content of PBS in the blend resulted in poor mechanical properties. The poor mechanical property was attributed to immiscibility and phase separation at the high ratio of PBS in the blend. Compatibilization was the method to improve the adhesion between PHBV and PBS phases. A reactive extrusion process, due to its ease of scale up to industrial process and economic feasibility, has attracted attention in recent years. Reactive extrusion of PHBV and PBS has been studied by Ma et al. [75]. They used 70:30 (w/w) blend of PHBV and PBS using DCP as a compatibilizer. Increase in interfacial adhesion and increase in elongation at break values suggested compatibilization between PHBV and PBS phase. It was reported that there was no change in the notch Izod impact strength with the addition of DCP and TMPTA.

Moreover, Ma et al. [75] have used DCP to compatibilize only one ratio of PHBV/PBS blend (70:30, w/w). Thus, there exists a gap in knowledge on various blend ratios of PHBV and PBS, and also on compatibilization methods. This gap in knowledge if addressed can lead to
the development of new compatibilized blends of PHBV and PBS which can be used in various applications.

The novelty of this thesis lies in the fact that the compatibilizers dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA have been used for the first time in our knowledge to compatibilize PHBV and PBS blend system. Also, we have investigated the possibilities of compatibilization with DCP and TMPTA at other ratios of PHBV and PBS (50:50 and 30:70 of PHBV: PBS).

2.6. Mathematical Models

2.6.1. Palierne Model

The linear viscoelastic responses of the neat and reactive blends were modeled through use of Palierne model. Palierne model was applied to the relaxation spectra of the blend which was expressed as a blending rule applied to the relaxation spectra of base polymers [77]. The properties of blends are dependent on viscoelastic properties of phases, mixing conditions and compositions [77,78]. A generalized form of morphology is the emulsion like morphology. In emulsion type morphology, one polymer formed a continuous phase while other formed a spherical dispersed phase [77]. The linear viscoelastic response of immiscible blends have been successfully modelled through Palierne model [68,77]. Palierne model expresses the complex modulus of immiscible blends as [77]:

\[
G^*(\omega) = G^*m (\omega) \frac{1+3\phi H(\omega)}{1-2\phi H(\omega)}
\]

(1)

with \(H(\omega) = \frac{4\left(\frac{\omega^2}{R}\right)[2G_m^*+5G_d^*]+[G_m^*-G_d^*][16G_m^*+19G_d^*]}{40\left(\frac{\omega^2}{R}\right)[G_m^*+G_d^*]+[2G_m^*+3G_d^*][16G_m^*+19G_d^*]}\)

(2)
where $G_{d*}$ and $G_{m*}$ are complex moduli of the dispersed phase and matrix respectively, $\alpha$, the interfacial tension, $\varphi$, the volume fraction of disperse phase, $\omega$ is the studied frequency and $R$ is the particle radius. Literature has shown that the palierne model was applicable for the polydispersity of a droplet size distribution less than 2.3 [79].

2.6.2. Carreau-Yasuda Model

The melt viscosity data obtained through Rheometer was modelled through Carreau-Yasuda model. This model has been extensively used to extrapolate the melt viscosity to get zero shear viscosity by the equation [80]

$$\mu = \mu_\infty + (\mu_0 - \mu_\infty)(1 + (K|\gamma|)^n)^{\frac{n-1}{a}}$$

(3)

where $\gamma$ is shear rate, $\mu_0$ is the viscosity at zero shear rate, $\mu_\infty$ is the viscosity at infinite shear rate, $a$, and $K$ are constant parameter and $n$ is a dimensionless constant [80].

2.6.3. Rule of Mixture, ROM

The rule of mixture is an empirical mathematical expression which gives specific property of polymer blends in terms of the constituents. The mechanical properties of polymer blends can be modeled based on the composition of constituents [45]. We have used ROM to theoretically predict the elongation at break of the blends. The formula used in such case was [45]:

$$\varepsilon = \varepsilon_a \chi_a + \varepsilon_b \chi_b$$

(4)

where $\varepsilon$ is the theoretical elongation of blend with $\varepsilon_a$ and $\varepsilon_b$ as the elongation of polymer ‘a’ and ‘b’ respectively, $\chi_a$ and $\chi_b$ are the weight fraction of the component ‘a’ and ‘b’ respectively.
Chapter 3. Purpose and hypothesis

The purpose of the study is to increase the interaction between two immiscible bioplastic blends by the addition of compatibilizers. The bioplastics are at the forefront in the development of a renewable and sustainable economy. The two chosen bioplastics of this thesis are poly (hydroxyl butyrate-co-valerate), PHBV and poly (butylene succinate), PBS. These two bioplastics are both biodegradable. We have used petro-based PBS in our study, but renewable resource based PBS is expected to be available on a commercial scale in a very near future. PHBV is a brittle bioplastic with a high modulus value and a low elongation at break; PBS, on the other hand, is a low modulus bioplastic with a high elongation at break. Complementary properties can be obtained by mixing PHBV and PBS.

The literature shows that PHBV and PBS are immiscible bioplastics [75]. Due to this immiscibility, the direct melt blends have poor mechanical properties. Compatibilizers can solve the immiscibility problem by reacting with the constituents to produce a compatibilization reaction that can yield graft copolymers. This graft copolymer increases the compatibility between the two immiscible polymers. The results are called as compatibilized or reactive blends. It has also been shown that compatibilized blends possess complimentary properties [44,51,68,75,81]. Applications for the compatibilized blends are shown to exist in many more areas than for neat blends.

This research focuses on increasing the interaction between PHBV and PBS blends by using compatibilizers. The compatibilizers used in this thesis were dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA. Use has been made of both peroxides and TMPTA to increase the interaction between polymer blends [76, 82-85]. In such compatibilized polymer blends, peroxides acted as a free radical generator, leading to the formation of reactive sites and
trimethylolpropane triacrylate acted as a grafting agent [76,82-85]. The two species have been shown to increase the interaction between immiscible polymer blends.

The hypothesis of the compatibilization of PHBV and PBS blends is based on the formation of graft copolymers. Literature has shown that this graft copolymer (PHBV-g-PBS) will localize at the interface of PHBV and PBS [75]. The localization of graft polymer at the interface will prevent coalescence of dispersed phase. This can be detected by surface morphology of the blends with scanning electron microscopy, SEM.

The compatibilization of PHBV and PBS blends by dicumyl peroxide, DCP and trimethylol propane triacrylate, TMPTA is expected to influence the melt processing of PHBV and PBS in a twin screw extruder leading to the formation of graft copolymers at interface. Such interaction can help to compatibilize the PHBV/PBS polymer system. The two factors forming the hypothesis in this study are:

1. DCP will attack the polymer chains generating free radicals.
2. TMPTA will attack on the free radical sites generated by DCP forming a graft copolymer system.

The inward shift of glass transition temperature ($T_g$) is a sign of increased compatibility between the polymer blends [37,44,75,86]. This shift in $T_g$ is validated by various thermal methods such as differential scanning calorimetry and thermo-mechanical methods such as dynamic mechanical analysis. For a case in which, one polymer has to be a brittle polymer while the other has to be a highly ductile polymer, which is true for PHBV and PBS. The compatibilization of two polymers can be quantified via measurement of the changes in elongation at break values [75]. Increase in elongation at yield values will be expected upon compatibilization of brittle PHBV and ductile PBS.
It has been shown that formation of graft copolymers can also result in increases in the extruder force values while in situ processing [51]. Such increase in force value has been attributed to the resistance offered by graft copolymer when flowing past each other. Therefore, it is expected that in situ compatibilization of PHBV and PBS will result in an increased extruder force value.
Chapter 4. Significance

Various commodity polymers used today are based on fossil fuels. Because these polymers are non-biodegradable and will persist in the environment over a long time, the development of biopolymers from renewable resources are crucial to support a green economy. Poly(hydroxybutyrate-co-valerate), PHBV and poly (butylene succinate), PBS are the two biopolymers that can be renewably resourced as well as can be used for feasible biodegradable products. The standalone applications of PHBV and PBS provide several limitations, but the suitable compatibilized blends can offer much more superior properties.

The direct melt blends of PHBV and PBS have shown poor mechanical properties due to limited miscibility. This research focuses on blending PHBV and PBS in the presence of compatibilizers, dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA to increase the interactions. Use of an in situ compatibilization method was done for the melt mixing of PHBV and PBS yielding blends with improved characteristics. Ease of scale up to an industrial process was provided by using an in situ compatibilization method. The novelty of this work lies in the fact that it is the first time in situ compatibilization of PHBV and PBS bioplastics has been studied extensively in presence of DCP and TMPTA. The effect of DCP and TMPTA on the various mechanical, thermal, rheological, morphological, and thermo-mechanical properties have been extensively analyzed. This work also studies the reactive blends of PHBV and PBS blends with varying compositions (30:70, 50:50 and 70:30 wt %).
Chapter 5. Objectives

The literature has shown that PHBV and PBS are immiscible bioplastics [75]. Due to this immiscibility, the direct melt blends have shown poor mechanical properties like elongation at break, notch Izod impact strength, modulus, and strength values. Compatibilizers can solve the immiscibility problem by reacting with the constituents to produce a compatibilization reaction that yields graft copolymers. This graft copolymer can increase the compatibility between the two immiscible polymers. Complementary properties can be obtained by mixing PHBV and PBS. This research focuses on increasing the interaction between PHBV and PBS blends by using compatibilizers, dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA. Literature has shown that for a blend of brittle and ductile polymer, increase in elongation at break value can be associated with compatibilization and increased interaction between polymer phases [75]. Use of an in situ compatibilization method was done for the melt mixing of PHBV and PBS yielding blends with improved characteristics. Ease of scale up to an industrial process was provided by using an in situ compatibilization method. The objective was divided into two parts. The first part of the objective dealt with the various concentrations of DCP and TMPTA that are required to compatibilize 70:30 of PHBV: PBS blends. In the second part of the objective, the possibility of increasing interactions between 50:50 and 30:70 of PHBV:PBS blends were also investigated.

5.1 Objective-I

The main objective of thesis work is to improve the compatibility of the blend system having higher content of brittle and high modulus bioplastic i.e poly (hydroxybutyrate-co-valerate), PHBV with lower quantity of flexible bioplastic i.e poly (butylene succinate), PBS. Again the rationality in choosing 70:30 (w/w) blend system of PHBV and PBS is based on the previous literature study
where 70:30 can provide optimized elongation at break, modulus, and strength value [75]. In this portion of the objective, our idea is to use a dual compatibilizing system (in this case DCP and TMPTA) to study their optimum effects in achieving the best compatibilization possible.

In this section of the thesis, the investigation of the various mechanical properties of 70:30 (w/w) PHBV and PBS blends are done. The concentrations of DCP and TMPTA that were required for the compatibilization of PHBV and PBS (70:30, w/w) blend were optimized. Combination of the brittle polymer, PHBV and the ductile one, PBS can be monitored by using an increased elongation at break as a marker for increase in an affinity between PHBV and PBS phases. Addition of DCP and TMPTA in PHBV and PBS blends is expected to lead favorable interaction. This favorable interaction is also quantified via various mechanical, thermal, rheological, thermo-mechanical, and morphological means.

5.2 Objective-II

The previous available literature studied the 70:30 (w/w) of PHBV and PBS blend system [75]. In this part of the thesis, we have furthered the current available knowledge on PHBV and PBS blends. The objective of this part of the thesis is to improve the compatibility of blend system with 50:50 and 30:70 (w/w) of PHBV and PBS. We have investigated the compatibilization between PHBV and PBS phases by using a dual compatibilizer system (DCP and TMPTA). The optimized concentration of DCP and TMPTA obtained in the study-I was used in 50:50 and 30:70 of PHBV:PBS blends to further study their performances. Such a study is expected to give a variation in mechanical, thermal, rheological, thermo-mechanical, and morphological properties. Other variables such as processing conditions and concentration of DCP and TMPTA will be kept constant.
Chapter 6. Materials and sample preparation

6.1. Materials

Poly (hydroxybutyrate-co-valerate), PHBV (grade – Y1010, 3% valerate content, powder, melt flow index, MFI measured - 11g/10 min @ 2.16kg, 190°C) was obtained from Tianin Biologic while poly (butylene succinate), PBS was obtained from Xinfu Pharmaceuticals (Injection Grade pellets, MFI measured - 19.13 g/10 min @2.16 kg, 190°C). Dicumyl peroxide, DCP (99% purity) and trimethylolpropane triacrylate, TMPTA (99% purity) was purchased from Sigma Aldrich and used as received.

6.2. In situ processing

Before processing, PHBV and PBS pellets were dried in an oven (80°C for 12 hr.) to remove excess moisture. The reactive and neat blends were prepared using a micro-extruder (DSM Research, Netherlands) with a barrel volume of 15 cc. The micro-extruder was equipped with co-rotating twin-screws with a length of 150 mm and L/D ratio of 18. The processing temperature was 175°C and the screw speed of the micro-extruder was fixed at 100 rpm for all the formulations. The force values obtained from DSM micro-extruder were recorded. The total amount of material fed into the micro-extruder was kept constant at 8 g so that the comparison between force values at different formulations could be made. After the fixed processing time of 2.5 min (including feed time of 30 sec.) in the micro-extruder, the molten mix was transferred to a preheated micro-injection molding machine. Injection moulding was done with an injection temperature of 180°C, injection pressure of 4 bars for 6 seconds, and holding and packing pressures of 6 bars for 10 seconds each. The mold temperature was maintained at 50°C for fast crystallization of the molded samples. All the samples were tested after 72 hours of conditioning at 25°C and at relative humidity of 50% according to ASTM standard.
Literature has shown that for a blend of brittle and ductile polymer, increase in elongation at break value can be associated with compatibilization and increased interaction between polymer phases [75]. Elongation at break can be modelled on a simple rule of mixture method where the property is assumed to be additive, based on the ratio of the components in the blend [45]. Eight formulations were made with varying the concentration of DCP and TMPTA. The elongation at break values were measured for each of the formulation. Statistical bias was ruled out by testing multiple samples of each experimental condition. The standard deviation was kept low by testing 6 samples of each formulation and measured after conditioning time of 72 hours. Bias was also controlled by keeping all the external factors such as humidity and temperature constant throughout the tests.
Chapter 7. Methods

As discussed earlier; for 70:30 (w/w) blend system of PHBV and PBS, the concentrations of DCP and TMPTA were optimized. The other blend systems (50:50 and 30:70 (w/w)) were studied by taking the concentration of DCP and TMPTA that we optimized for 70:30 of PHBV and PBS blend. One limitation of such selection of additive contents for 50:50 and 30:70 system is that such specific formulation may not be optimized. However the concept here is to investigate the reactive blends of 50:50 and 30:70 under the experimental conditions used. This research involves determination of optimum amount of dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA that is required to compatibilize 70:30 of PHBV and PBS blend. The goal is to understand various mechanical, thermal, thermo-mechanical, rheological, and morphological properties that are affected by addition of compatibilizers.

The experimental plan will be aimed at addressing questions such as:

1) What is the optimized amount of DCP and TMPTA for a blend ratio (70:30,w/w)?

2) What are the physical and mechanical properties that are affected by addition of DCP and TMPTA?

3) Is the optimized amount of DCP and TMPTA from 70:30 of PHBV:PBS successful in increasing the interactions at other ratios of PHBV and PBS blends (50:50 and 30:70 , w/w)?

All the tests were carried out multiple times to remove statistical bias.

7.1. Melt Rheology

The rheological measurements were carried out on Modular Control Rheometer 302 (Anton Paar) using 25 mm diameter parallel plates. The gap between the parallel plates was set at 1 mm. All rheological measurements were performed at a fixed temperature of 180°C. To avoid moisture absorption, polymers and their blends were vacuum dried at 80 °C for at least 4 hr. and kept in a
desiccator prior to measurements. The dynamic strain sweep tests were first made to determine the linear viscoelastic region. The strain limit of the linear regime was found to be around 0.1% for all the samples. Then, dynamic frequency sweep tests were carried out from 500 to 0.1 rad/s. The experiments were repeated three times to minimize blending shear history and degradation effects. The best of three curves were used for further analysis.

7.2 Mechanical testing

Tensile and flexural tests were performed in an Instron Universal Testing Machine Model 3382 according to ASTM D790 and D638, respectively. Six samples of each formulation were tested to minimize standard deviation. ASTM D 790 specifies that the speed of testing should be such that the sample should break within ½ to 5 min of starting the test. As the elongation at break was used as one of the markers for compatibilization, the speed of testing was chosen so that the elongation values could be quantified clearly. To this objective, tensile testing was conducted using a crosshead movement rate of 5 mm / min which was found to give sufficient elongation for the brittle PHBV. Flexural tests were performed at 1.408 mm/ min. Notched Izod impact strength of the blends were measured according to ASTM D256 using Testing Machines Inc. (TMI 43-02) impact tester. Again, six samples of notched Izod impact, for each formulation, were tested.

7.3 Differential scanning calorimetry (DSC)

DSC tests were performed in a DSC Q 200 from TA instruments equipped with Nitrogen cooling system. Nitrogen flow rate was maintained at 50 mL/min throughout experiments. Conventional DSC tests were done to characterize melting point and crystallization. Best of the three curves were taken for comparison and analysis. The heating rate was kept at 10°C/min while cooling rate was kept at 5°C/min for conventional DSC. Conventional DSC was used to
characterize miscibility in crystalline phase via shift in melting point ($T_m$). Three runs of each formulation were done to ascertain the repeatability of tests.

Percentage crystallinity of PHBV and PBS was calculated by using the following formula:

$$\% \text{ Cystallinity } (\% X_c) = \frac{\Delta H_f}{\Delta H_{f100} \times W_f} \times 100$$  \hspace{1cm} (5)

where, $\Delta H_f$ is the fusion enthalpy and $W_f$ is the weight fractions of the PBS or PHBV. $\Delta H_{f100}$ is the fusion enthalpy for 100% crystalline polymer. $X_c$ is percentage crystallinity of the system. In the analysis, the enthalpy of fusion of 100% crystalline PBS was considered to be 200 J/g [37] while the enthalpy of fusion of PHBV (3% valerate content) was considered to be 146 J/g [87].

7.4 Thermogravimetric analysis (TGA)

TGA was done to study the thermal degradation behavior of the blends in a TA instruments Q 500 equipped with nitrogen cooling system at 10°C/ min of heating rate. The TGA temperature scan was done from room temperature to 600°C. The experiments were performed multiple times to ascertain the repeatability of the results.

7.5 Dynamic mechanical analysis (DMA)

In DMA, the temperature was ramped at 2°C/min while frequency was kept at 1Hz with amplitude of 0.5. DMA runs were performed from -50 to 100°C to see the peak shift and broadening of tan delta peaks for reactive blends and neat blends. The best of three DMA curves were taken for analysis.

7.6 Polarized optical microscopy (POM)

Polarized optical microscopy (POM) was done to study the crystallization phenomena with a Nikon Eclipse LV100 equipped with hot stage setup from Linkan, UK with controlled cooling and heating rates. Thin films of the samples were made by heating the sample between two transparent glass slides. All the samples were heated to 200°C to melt all the crystals and were
cooled at 50°C/min to a hold temperature of 130°C. Hold Temperature of 130°C was chosen as it was above the crystallization temperature of PBS but below crystallization temperature of PHBV. This hold temperature would give effect of DCP and TMPTA on PHBV crystals. The formation of crystals were studied through cross polarizers. Multiple images were taken from a sample to avoid localization effects.

7.7 Scanning electron microscopy (SEM)

A scanning electron microscope, HITACHI S-570, Japan, was utilized to examine the fracture surfaces of the samples. The samples were prepared by freezing into liquid nitrogen. The samples were prepared by sputtering gold particles in order to increase electron conductivity on the surface of the sample, preventing heat accumulation. Furthermore, due to the sensitivity of PHBV and PBS to heat, the electron beam was shot at an intensity of 10 kV to reduce the deformation on the sample surface.

7.8 Sohxlet Extraction

Literature has shown that PHBV and PBS are soluble in chloroform at 60°C [75]. Both the reactive and neat blends were extracted via soxhlet extractor in boiling chloroform for 48 hrs. The amount of material obtained for neat blends were negligible showing complete solubility of PHBV and PBS in boiling chloroform. The crosslinked phase was found to be insoluble in chloroform at 60°C. After extraction the materials obtained on the filter paper were dried in a vacuum oven for 8 hr. to remove the residual chloroform. The amount of material before and after soxhlet extraction was weighed and % gel content was determined by use of equation:

\[
\% \text{ Gel content} = \frac{(M_i - M_f)}{M_i} \tag{9}
\]

where \(M_i\) and \(M_f\) are initial and final amount of material left on filter paper respectively.
Chapter 8. Results and discussion

The section 8.1 of this thesis deals with the optimization of dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA concentration in 70:30 (w/w) of PHBV and PBS blend. The optimization was done based on certain markers that indicate increased interaction between PHBV and PBS. Literature studies [45,75] have shown that a prominent marker for the compatibilization of a brittle polymer, PHBV and a ductile polymer, PBS can be the elongation at break value. So, the elongation at break value was used in this section to quantify for increased interaction between PHBV and PBS. Literature studies [43,45,50,68,75,88] have also shown that secondary markers for compatibilization are shift in glass transition temperature (\(T_g\)) and decrease in particle size of the dispersed phase.

Also, this thesis is further expanded in section 8.2 where the effects of DCP and TMPTA on other ratios of PHBV/ PBS blend (50:50, 30:70, w/w) were studied. The concentration of compatibilizers, DCP and TMPTA, used in this section for analysis was taken from the optimized ratio used in section 8.1. In the section 8.2, we have thoroughly dealt with the effect of DCP and TMPTA on the ratios chosen (50:50 and 30:70 of PHBV and PBS blends) by focusing on mechanical, thermal, rheological, morphological, and thermo-mechanical properties.

8.1 Optimization of DCP and TMPTA content for 70:30 (w/w) of PHBV:PBS

We used dicumyl peroxide, DCP in our preliminary work to increase the compatibility between PHBV and PBS blend system. Different dosage levels of DCP were used in PHBV/ PBS blend (70:30). Various mechanical properties that were obtained via preliminary tests are shown in table 5.
We observed that the change in the concentration of DCP in the blend of PHBV/ PBS (70:30 w/w, %) had an effect on the elongation at break values. All the other mechanical properties like flexural modulus, tensile modulus, and notched Izod impact strength remained the same as the blends without DCP. The elongation at break value was found to be highest for 0.1% DCP within the experimental condition used. Based on mechanical properties of the blend, elongation at break values have been used in literature [75] as an indicator for compatibilization for PHBV and PBS blends system. The elongation at break value obtained by us was low when compared to the rule of mixture (ROM) value. This value is also low when we compare with the literature value of 200% obtained by Ma et al. [75]. This can be due to difference in grades of PHBV and PBS used by Ma et al. than us. Ma et al. [75] have used PHBV with a hydroxyvalerate content of 12.7%. We have used PHBV with a valerate content of 3%. This difference in valerate content can be attributed to the inefficiency of DCP to compatibilize our PHBV/ PBS blend system.
Therefore, we used dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA together to compatibilize 70:30 of PHBV/PBS blend. Due to the large amount of data points originating due to thermo mechanical, thermal, rheological, and morphological studies, only mechanical properties of the various formulations are discussed in this section. Thermal, thermo mechanical, rheological, and morphological studies have been dealt in section 8.2 of the thesis. The amount of DCP was increased in the increments of 0.025 % while amount of TMPTA was increased from 0 to 1 to 2% to study the effect of change in DCP and TMPTA dosage on the elongation at break values and notch Izod impact values. The aim was to increase elongation at break with low standard deviation. The chance occurrences of such increases were negated by processing multiple times with a certain ratio. The following table 6 highlights the various formulations that were used in this section of the thesis:
Table 6: Concentration of DCP and TMPTA in 70:30 (w/w %) of blend

<table>
<thead>
<tr>
<th>Formulation (70:30, w/w)</th>
<th>Concentration of DCP (%)</th>
<th>Concentration of TMPTA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0 D0 (Control)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T0 D0.125</td>
<td>0.125</td>
<td>0</td>
</tr>
<tr>
<td>T1 D0.125</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>T2 D0.125</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>T1 D0.150</td>
<td>0.150</td>
<td>1</td>
</tr>
<tr>
<td>T2 D0.150</td>
<td>0.150</td>
<td>2</td>
</tr>
<tr>
<td>T1 D0.175</td>
<td>0.175</td>
<td>1</td>
</tr>
<tr>
<td>T1 D0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

The various formulations along with the mechanical properties are mentioned in the table 7. We observed that PHBV had high values of modulus and strength (flexural modulus of 3.02 ± 0.091 GPa, flexural strength of 73.40 ± 0.24 MPa, and tensile modulus of 2.6 ± 0.53 GPa). PBS on the other hand exhibited low modulus and strength values (flexural modulus of 0.661 ± 0.0826 GPa, flexural strength of 31.22 ± 0.40 MPa, and tensile modulus of 0.460 ± 0.01 GPa). It was also observed that PHBV and PBS exhibited similar tensile strength values (PHBV: 37 ± 0.46 MPa, PBS: 39.9 ± 0.5 MPa). The elongation at break for PHBV was found to be 3.02 ± 0.091 % while for PBS the value was found to be 273 ± 1.73 %. As mentioned previously in the thesis, the interaction between the blend of PHBV and PBS (70:30) can be quantified by increase in elongation at break value. Out of the 8 formulations studied for optimization of DCP and TMPTA (table 7), it is clear...
from the elongation at break values of T0 D0.125 and T1 D0 that the presence of DCP and TMPTA together in the in situ reaction has a role in increasing the elongation at break values (figure 19). This agrees with our literature survey where DCP acted as free radical generator while TMPTA acted as grafting agent [85]. The formulation, T1 D0.125 showed a marked increase in elongation at break value (51± 8.2 %) over control value of 17± 2.2 %. A decrease in notch Izod impact strength of T1 D0.125 from control value of 27 J/m to 15 J/m was observed. This decrease in notch Izod impact strength can be due to the increased sensitivity of the blend to sudden load. Such notch sensitivity has been observed in literature [75]. The contour graph in figure 18 shows the elongation at break values obtained at various dosage levels of DCP and TMPTA. In our experiment we observed that elongation at break values of various formulations were dependent on both DCP and TMPTA dosage level. All the other mechanical properties like tensile strength, flexural strength, tensile modulus, and tensile strength were found to remain same irrespective of the DCP and TMPTA dosage.
Table 7: Various formulations used in analysis and corresponding mechanical properties (elongation at break values and notched Izod impact values are highlighted in bold, optimized formulation is highlighted with red color)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Description of formulation</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at Break (%)</th>
<th>Flexural Modulus (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Notched Izod Impact (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>PHBV</td>
<td>37 ± 0.46</td>
<td>2.6 ± 0.53</td>
<td>5.2 ± 0.97</td>
<td>3.02 ± 0.091</td>
<td>73.40 ± 0.24</td>
<td>29.4 ± 2</td>
</tr>
<tr>
<td>-</td>
<td>PBS</td>
<td>39.9 ± 0.5</td>
<td>0.460 ± 0.01</td>
<td>273 ± 1.73</td>
<td>0.661 ± 0.0826</td>
<td>31.22 ± 0.40</td>
<td>35.03 ± 3</td>
</tr>
<tr>
<td>T0 D 0 (Control)</td>
<td>PHBV PBS (70:30)</td>
<td>34.3 ± 0.28</td>
<td>1.47 ± 0.018</td>
<td>17.5 ± 2.08</td>
<td>1.786 ± 0.051</td>
<td>52.98 ± 0.096</td>
<td>27.5 ± 1.5</td>
</tr>
<tr>
<td>T0 D0.125</td>
<td>PHBV PBS (70:30) + 0.125 % DCP</td>
<td>34.4 ± 0.42</td>
<td>1.62 ± 0.021</td>
<td>18.7 ± 1.8</td>
<td>1.53 ± 0.018</td>
<td>50.5 ± 0.18</td>
<td>28.06 ± 1.3</td>
</tr>
<tr>
<td>T1 D0.125</td>
<td>PHBV PBS (70:30) + 0.125 % DCP + 1% TMPTA</td>
<td>34.9 ± 0.28</td>
<td>1.6 ± 0.004</td>
<td>51 ± 8.2</td>
<td>1.853 ± 0.017</td>
<td>55.26 ± 0.61</td>
<td>15.6 ± 2.9</td>
</tr>
<tr>
<td>T2 D0.125</td>
<td>PHBV PBS (70:30) + 0.125 % DCP + 2% TMPTA</td>
<td>35 ± 0.41</td>
<td>1.56 ± 0.017</td>
<td>37.2 ± 2.75</td>
<td>1.77 ± 0.014</td>
<td>53.29 ± 0.501</td>
<td>16.6 ± 2.2</td>
</tr>
<tr>
<td>T1 D0.150</td>
<td>PHBV PBS (70:30) + 0.150 % DCP + 1% TMPTA</td>
<td>35 ± 0.37</td>
<td>1.57 ± 0.014</td>
<td>44.8 ± 2.79</td>
<td>1.48 ± 0.004</td>
<td>46.9 ± 0.04</td>
<td>27.7 ± 1</td>
</tr>
<tr>
<td>T2 D0.150</td>
<td>PHBV PBS (70:30) + 0.150 % DCP + 2% TMPTA</td>
<td>29 ± 5.17</td>
<td>1.58 ± 0.047</td>
<td>9.83 ± 10.77</td>
<td>1.404 ± 0.078</td>
<td>43.42 ± 0.02</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>T1 D0.175</td>
<td>PHBV PBS (70:30) + 0.175 % DCP + 1% TMPTA</td>
<td>28.1 ± 2.4</td>
<td>1.540 ± 0.028</td>
<td>4.29 ± 1.26</td>
<td>1.411 ± 0.052</td>
<td>45.01 ± 1.493</td>
<td>26.65 ± 1.2</td>
</tr>
<tr>
<td>T1 D 0</td>
<td>PHBV PBS (70:30) + 1% TMPTA</td>
<td>36.0 ± 0.35</td>
<td>1.61 ± 0.008</td>
<td>12.6 ± 1.51</td>
<td>1.78 ± 0.063</td>
<td>52.01 ± 0.086</td>
<td>24.02 ± 2</td>
</tr>
</tbody>
</table>
Figure 18: Contour plot of elongation at break (%) of 70:30 (PHBV: PBS, w/w, %) vs. DCP and TMPTA dosage (%) levels

Table 8: Elongation at break values (%) for 70:30 of PHBV and PBS blend at various dosage levels of DCP and TMPTA

<table>
<thead>
<tr>
<th>Elongation at Break (%)</th>
<th>DCP (%)</th>
<th>TMPTA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5 ± 2.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18.7 ± 1.8</td>
<td>0.125</td>
<td>0</td>
</tr>
<tr>
<td>51 ± 8.2</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>37.2 ± 2.75</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>44.8 ± 2.79</td>
<td>0.15</td>
<td>1</td>
</tr>
<tr>
<td>9.83 ± 10.77</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>4.29 ± 1.26</td>
<td>0.175</td>
<td>1</td>
</tr>
<tr>
<td>12.6 ± 1.51</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
We further modified T1 D0.125 by tweaking the amount of DCP and TMPTA in the blend of PHBV and PBS keeping the target of low standard deviation value for the elongation at break. From the table, we can see that T1 D0.150 gave the elongation of 44.8 ± 2.79% with notched Izod impact strength of 27 J/m. Thus, the formulation T1 D0.150 was considered to be optimized ratio of DCP and TMPTA for 70:30 of PHBV and PBS.

In this section we saw that the 0.150% of DCP and 1% of TMPTA was able to compatibilize the 70:30 blend of PHBV and PBS. In the section 8.2 section we have thoroughly dealt with the effect of DCP and TMPTA on all the ratios of PHBV and PBS blends by focussing of mechanical, thermal, rheological, morphological, and thermo-mechanical properties.

**8.2 Effect of DCP and TMPTA on various ratios of PHBV/PBS**

We have seen from the previous section that the optimized ratio of DCP and TMPTA for 70:30 (w/w) of PHBV and PBS was 1% of TMPTA and 0.150% of DCP. This formulation gave elongation value with low standard deviation values. In this section, this optimized amount of TMPTA and DCP was investigated for possibilities of compatibilization at 50:50 and 30:70 of PHBV and PBS. From this point on the “reactive blend” refers to PHBV: PBS blends with 0.150% DCP and 1% TMPTA while “neat blend” refers to PHBV: PBS blends with the absence of DCP and TMPTA.

**8.2.1 Extruder force**

The force from extruder was used to infer the melt viscosity of the blends [45, 89]. Neat PHBV was found to have higher melt viscosity than PBS. The micro compounder force value was found to
increase for the entire reactive blends. The increase in extruder force values for reactive blend over neat blend was found to be 1,800 N for 70:30, 3,300 N for 50:50, and 4,600 N for 30:70 of PHBV:PBS blends (figure 19).

![Extruder force values for neat and reactive blends](image)

**Figure 19:** Extruder force values for neat and reactive blends  (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30* , E:PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

From the force values it was observed that the viscosity of reactive 30:70 of PHBV: PBS blend was highest suggesting greater degree of reaction taking place than at other studied compositions. The 50:50 reactive blend of PHBV: PBS also showed higher viscosity compared to neat blend. Increase in extruder force or torque values has been extensively related to grafting reactions in literature [89]. In this literature crosslinking reaction has been related to increase the extruder
torque. This was due to the greater resistance of reactive blend to the mixing in extruder [89]. Similarly, in our study we observed largest amount of force for 30:70 of PHBV: PBS reactive blend. The force value decreases for 50:50 and 70:30 of PHBV: PBS reactive blend. Thus, it can be said that this increase in force value suggested an occurrence of crosslinking reaction occurred in the presence of DCP and TMPTA with maximum amount of reaction for the 30:70 reactive blend of PHBV and PBS. A direct methodology for the determination of melt viscosity is rheology which we have thoroughly discussed in the next section of the thesis.

8.2.2. Viscoelastic properties of blends

The complex viscosities of the blends are shown in figure 20. Firstly, we concentrated on the complex viscosities of neat blends. The neat PHBV showed a high viscosity value compared to the neat PBS at all the frequency ranges. Generally, for an immiscible polymer blend, straight blending of polymers should show the viscosity of blend obeying linear mixing rule [43,77]. Similar observations were made in our study with 70:30, 50:50 and 30:70 of PHBV: PBS neat blends. Such positive deviations can be related to elasticity of dispersed phase [77]. In the literature, authors [77] have studied the viscoelasticity of ethylene/vinyl acetate copolymer and metallocene-catalysed polyethylene (mPEs) blends. They have also observed increases in the complex viscosity, showing a pronounced positive deviation. This has been attributed to the elasticity of the dispersed phase. The differences in complex viscosity of the neat blends were also pronounced at lower frequencies.
Figure 20: Complex viscosity for reactive and neat blends of PHBV and PBS, the solid line shows corresponding Carreau-Yasuda fit. (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E: PHBV:PBS=30:70, F:PHBV:PBS=70:30*, G: PHBV:PBS=50:50*, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

We have discussed the complex viscosity of neat blends. An inflection occurred at lower frequencies for all the neat blends. This inflection was found to be more pronounced with the increase in the ratio of PBS in the blends. The result resembled yield stress like curves. These types of curves are typically observed for the viscosity vs. shear rate curves of the structured liquids [90]. The rheological response of the structured fluids exhibit complex flow behavior due to the multiphase structure [90]. Again, such a characteristic response has been attributed to the elasticity of the dispersed phase in the blends. Since the measurements were done within linear viscoelastic range, the appearance of yield stress like curve cannot be related to inter-particle linkages. Therefore, yield stresses like behavior appearing in neat blends were associated with the presence
of an interface [90]. It can be said that in the neat blends the interface is more developed for the blends with high PBS ratio. One of the reasons for such a response can be due to low viscosity of PBS which enables the chains to interact with high viscosity PHBV chains. Since the main objective of this thesis was to study the reactive blends of PHBV and PBS, we have not investigated this phenomenon further as extensive literature can be found on the topic of immiscible polymer and emulsion morphology [79,91,92].

The reactive blends showed high complex viscosity values in the low frequency regions. This can be related to formation of gels which increase the complex viscosity of blends. At low frequency, highest increase in complex viscosity was found to be for 30:70 of PHBV: PBS reactive blend followed by 50:50 and then 70:30 of PHBV: PBS reactive blends. Literature studies have shown that the increase in complex viscosity can be related to the formation of gels in the blend system [68,91]. Since, the maximum amount of increase in complex viscosity was found to be for 30:70 of PHBV: PBS reactive blend, therefore it can be said that the maximum amount of gels were formed with 30:70 of PHBV:PBS reactive blends. This observation was also supported by the sohxlet extraction data where the amount of gels for the 30:70 reactive blends of PHBV and PBS was found to be 11%. Similarly, the amount of gels found for 50:50 and 70:30 of PHBV: PBS reactive blends were found to be 2% and 0.5% respectively which agree with our rheology data. Formation of gel in an in situ reactive system can be due to formation of grafting reactions [68,91].

Carreau-Yasuda model [80] was found to closely conform to experimental data for both reactive and neat blends (shown by solid line in figure 20). The zero shear viscosity was found according to the model by the extrapolation methods. The table 9 shows the various values of zero shear viscosity calculated for the neat and reactive blends.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Zero Shear Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1,687</td>
</tr>
<tr>
<td>B</td>
<td>191</td>
</tr>
<tr>
<td>C</td>
<td>1,304</td>
</tr>
<tr>
<td>D</td>
<td>1,89,570</td>
</tr>
<tr>
<td>E</td>
<td>1,747</td>
</tr>
<tr>
<td>F</td>
<td>2,03,790</td>
</tr>
<tr>
<td>G</td>
<td>463</td>
</tr>
<tr>
<td>H</td>
<td>3,88,790</td>
</tr>
</tbody>
</table>

From the table 9, we can see that the zero shear viscosity was found to increase with addition of dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA. The zero shear viscosities for neat PHBV and neat PBS were found to be 1,687 and 191 Pa.s respectively. Compatibilization was observed to increase the zero shear viscosity of all the blends considerably. The zero shear viscosity of 70:30 of PHBV: PBS reactive blend was found to be 189,570 Pa.s while the neat value was found to be 1,304 Pa.s. The increase in zero shear viscosity was also observed for 50:50 of PHBV: PBS reactive blends from 1,747 Pa. s to 203,790 Pa.s from neat to reactive blend. Similarly, the zero shear viscosity for 30:70 of PHBV: PBS reactive blend was found to be 388,790 Pa.s from the
neat value of 463 Pa.s. Thus we observed that the highest increase in the zero shear viscosity was observed for 30:70 of PHBV: PBS reactive blend. This suggested that the maximum amount of reaction occurred for 30:70 of PHBV: PBS blend in presence of DCP and TMPTA. As already mentioned, the amount of gel obtained for 30:70 of PHBV: PBS reactive blend was greater than 50:50 and 70:30 of PHBV and PBS reactive blends. Again, the highest increase in zero shear viscosity is also supported by highest amount of gels in 30:70 of PHBV: PBS reactive blends.

Figure 21: Complex modulus, $G'$ for reactive and neat blends of PHBV and PBS, palierne correlations are given by solid line. (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=50:50, E: PHBV:PBS=30:70, F:PHBV:PBS=70:30*, G: PHBV:PBS=50:50*, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

Storage modulus values for all the neat blends at high frequency were found to show high degree of elasticity (figure 21). The neat blends do not show much difference of storage modulus at
high frequency. At low frequency, the differences between the storage modulus of various ratios of neat blends were evident. A typical yield like curve was obtained suggesting interface phenomena. Paleirne model was applied to all the neat blends. The close match between the experimental and model values suggests generation of emulsion like morphology at all the neat blend ratio. Such a response of neat blend has been observed in literature for immiscible blends [91-94].

It was worthwhile to note that upon reactive extrusion, the yield stress like phenomena was not observed with storage modulus and all the reactive blends showed higher level of storage modulus values throughout low frequency range, below 100 rad/s (figure 21). At the high frequencies all the reactive blends showed similar values of storage modulus. At low frequencies, we observed higher values of storage modulus for 30:70 reactive blends followed by 50:50 and 70:30 reactive blends of PHBV: PBS. Increase in storage modulus of reactive blends can be due to graft polymer formation at interface with PHBV/PBS which increases the elastic response of the material. The amount of graft polymer formed after compatibilization can be said to be maximum for 30:70 blend. This also agrees with our data from sohxlet extraction. It was also noted that Paleirne model failed to predict the storage modulus of the reactive blends at low frequency. Though it is expected that the emulsion morphology was still prevalent in the reactive blends, the reactive extrusion increases the elastic response of PBS microspheres, leading to misfit of reactive data with Palierne model.

Complex viscosity and storage modulus values can be used to comment on process ability of PHBV/ PBS blends [95]. Neat blends showed low viscosities at frequencies below 100 rad/s when compared to reactive blends making the blends difficult to process in the processes requiring high melt strength. All the reactive blends showed an increase in melt complex viscosity with decrease in frequency which can be related to superior melt strength properties compared to neat
blends. In the literature authors have used peroxide to modify the melt processing of PP and PE blends [95]. They have observed an increase in melt viscosity with decrease in frequency.

**8.2.3 Mechanical properties**

The parameters like tensile strength, elongation at break, tensile modulus, flexural strength and flexural modulus can be measured from tensile and flexural tests. PHBV was found to have high tensile and flexural modulus of 2,600 MPa and 3,000 MPa respectively. On the other hand the elongation at break value was found to be 5.3%. PBS was found to exhibit a low tensile and flexural modulus of 450 MPa and 550 MPa respectively but high elongation at break value of 273%.

![Tensile modulus and tensile strength of reactive and neat blends of PHBV and PBS](image)

**Figure 22:** Tensile modulus and tensile strength of reactive and neat blends of PHBV and PBS (A: PHBV neat, B: PBS neat, C:PHBV:PBS=70:30, D:PHBV:PBS=70:30*, E:PHBV:PBS=50:50, F:...
PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*) (* – reactive blends with 0.150% DCP and 1% TMPTA)

Firstly, we discussed the tensile strength and tensile modulus of the neat and reactive blends (figure 22). It was observed that the tensile strength and tensile modulus values for 70:30, 50:50, and 30:70 of PHBV: PBS remained the same upon reactive extrusion. The reactive blend of 30:70 of PHBV: PBS showed an increase in the tensile strength to 42 MPa from neat value of 35 MPa. Also, the stress whitening was observed for all reactive blends suggesting a change over from the brittle (no stress whitening) to ductile failure mechanism (stress whitening). Stress whitening could also be related to the stress induced crystallization of the polymer which increased the tensile strength values. Similar observations have been made in the literature [96,97]. Fukahori et al. [96] have proposed a model based on partially crosslinked phase and continuous uncrosslinked phase. The same concept was applied to our polymer system. PHBV and PBS crosslinking in presence of DCP and TMPTA was proposed to be most obvious reason for stress induced whitening and also increase in ultimate tensile strength value for 30:70 of reactive PHBV and PBS (Figure 24).

The flexural modulus and flexural strength of neat and reactive are shown in figure 23. Compatibilization has little effect on flexural modulus and flexural strength values for all the blend compositions. There is net decrease in flexural modulus and flexural strength values upon compatibilization (figure 23) but the decrease was within the standard deviation values (table 10). Also, minor decrease modulus and strength values at the expense of increases in elongation values have been reported in literature [98].
Figure 23: Flexural modulus and flexural strength of reactive and neat blends of PHBV and PBS


<table>
<thead>
<tr>
<th>Formulation</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>37.9 ± 0.04</td>
<td>2600 ± 53</td>
<td>72.3 ± 0.4</td>
<td>3024 ± 91</td>
</tr>
<tr>
<td>B</td>
<td>39.9 ± 0.5</td>
<td>460 ± 10</td>
<td>31.2 ± 0.4</td>
<td>661 ± 82</td>
</tr>
<tr>
<td>C</td>
<td>34.3 ± 0.28</td>
<td>1509 ± 18</td>
<td>52.9 ± 1</td>
<td>1606 ± 51</td>
</tr>
<tr>
<td>D</td>
<td>35 ± 0.38</td>
<td>1450 ± 14</td>
<td>45 ± 2</td>
<td>1480 ± 45</td>
</tr>
<tr>
<td>E</td>
<td>34.5 ± 0.68</td>
<td>1100 ± 14</td>
<td>46.6 ± 0.8</td>
<td>1232 ± 29</td>
</tr>
<tr>
<td>F</td>
<td>34.9 ± 0.86</td>
<td>1090 ± 27</td>
<td>38.1 ± 1.5</td>
<td>1150 ± 28</td>
</tr>
<tr>
<td>G</td>
<td>35 ± 0.38</td>
<td>889 ± 16</td>
<td>34.6 ± 2.5</td>
<td>880 ± 26</td>
</tr>
<tr>
<td>H</td>
<td>35.2 ± 0.39</td>
<td>809 ± 10</td>
<td>30.9 ± 1.4</td>
<td>840 ± 53</td>
</tr>
</tbody>
</table>

It has already been mentioned that for the compatibilization between a brittle and a ductile polymer an increase in the elongation at break value can be taken as a marker for the increased compatibility between the constituent polymers. Elongation at break values were observed to increase for all the blends with DCP and TMPTA (figure 24). The comparison of experimental elongation at break was done with a theoretical additive rule. The additive model used in this thesis
was the rule of mixture where the theoretical elongation at break of the reactive blend was assumed to be the sum of the elongation of each component of blend.

Figure 25 (next page) depicts comparison between the elongation of reactive and neat blends, and the ROM value for elongation. The elongation at break value for 70:30 of PHBV: PBS blend was found to be 44% while the theoretical value predicted through rule of mixture (ROM) was 80%. For 50:50 reactive blend of PHBV and PBS, elongation increase on compatibilization was observed to be 187% from the neat value of 37% (ROM value: 138%). Similar observations were made for 30:70 of PHBV: PBS reactive blend where an increase in the elongation at break to 195% was observed (ROM value: 190%). The neat blend of 30:70 of PHBV: PBS showed an elongation at break value of 18%. Such an increase in elongation values can be due to increased interactions between the PHBV and PBS phase. It was also expected that the grafting reaction between PHBV and PBS will enable stress to be transferred across phases as can be seen from stress vs. strain graph in Figure 24.
Figure 25: Composition dependent compatibility of PHBV/PBS blend: A comparison of elongation at break determined experimentally for neat and reactive blends with rule of mixture value.

It was also observed that reactive 30:70, 50:50, and 30:70 blends of PHBV: PBS showed composition variable compatibility as shown in figure 25 [45]. Similar increase in elongation was observed with reactive extrusion of poly (vinyl-alcohol), PVOH and ethylene propylene rubber, EPR [66]. In this patent, the authors have used peroxide to generate free radical sites on polymer chains. Maleic anhydride was then used to increase compatibility between PVOH and EPR blends. In this patent, authors have reported an increase in elongation at break values upon compatibilization. In another literature, authors have used glycidyl methacrylate to compatibilize ethylene propylene rubber along with poly (butylene terephthalate) via reactive extrusion [100]. They have also reported an increase in the elongation at break value due to successful stress transfer across the phases. Thus, our result of increases in elongation at break values upon addition of DCP.
and TMPTA were in line with the existing literature. Also, minor decrease modulus and strength values at the expense of increases in elongation values have been reported in literature [98].

The toughness of blend could be inferred from the stress vs. strain curve [75,101,102]. The area under the curve stress vs. strain curve is known as toughness [75,101,102]. The area under the curve was calculated for each formulation. PHBV was found to have a toughness of 1.36 J/m³ while PBS was found to have a toughness value of 89 J/m³. Direct melt blending of PHBV and PBS lead to a decrease in toughness values. An increase in the toughness value was observed with the addition of DCP and TMPTA. The toughness value for the 70:30 of PHBV: PBS blend was 5.7 J/m³ which was increased to 13.67 J/m³ (ROM value: 27.65 J/m³) with compatibilization. Similarly for the 50:50 of PHBV: PBS blend a toughness value of 5.35 J/m³ was found to increase with the compatibilization to 60 J/m³ (ROM value: 45 J/m³). For 30:70 of PHBV: PBS, the toughness value was 5.36 J/m³ which increased to 71 J/m³ (ROM value: 62 J/m³) upon addition of compatibilizers. An increase in toughness values upon compatibilization were obvious as the area under the stress vs. strain increased. This increase in area was due to increase in elongation at break value on addition of DCP and TMPTA.

Notched Izod impact strength is one of the critical parameters for real life applications [39,98,103]. PHBV and PBS had notched Izod impact strength of 27 J/m and 35 J/m respectively (figure 26).

An increase in the notch izod impact values for the 30:70 of PHBV: PBS blend from 27 J/m to 57 J/m was observed (figure 26). A similar increase in the notch izod impact strength was also observed for reactive 50:50 blend of PHBV and PBS from 13.3 J/m to 26 J/m (figure 26). It is worthwhile to note here that the notched Izod impact strength of 30:70 reactive blend was found to be higher than notched Izod impact values for individual components of the blend (figure 26). This increase in notch Izod values can be attributed to formation of cross-linked structure [104]. In this literature the effect of crosslinking on nylon and rubber blend have been studied in presence of
maleic anhydride and dicumyl peroxide. Authors have found a significant increase in notch Izod impact strength. Also, in another literature the development of specialized morphology has also been attributed to the increased notched Izod impact strength [103].

### 8.2.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis, DMA is a thermo-mechanical way to analyze the phase behaviour in the polymer and its blend. The glass transition temperature can be detected by DMA mechanical loss (tan δ) curves. The peak of tan δ curve was assigned to the glass transition temperature. The glass transition temperature is a unique thermal property of a polymer. An immiscible or neat blend generally show glass transition temperature corresponding to the constituent polymer. In a polymer blend system, an increased compatibility of the blend can be detected by inward shift in the glass transition temperature of the constituent polymer [2]. In this thesis, we have used dynamic mechanical analysis to observe shifts in the glass transition temperature (Tg) of the neat and reactive blends. Neat PHBV had tan δ peak at 21°C. This peak was assigned as glass transition temperature of PHBV. Neat PBS had tan δ peak at -19°C which was assigned to Tg of PBS (figure 27).

All the neat blends show tan δ peak corresponding to PHBV and PBS phase at the same temperature as neat PHBV and PBS, suggesting limited miscibility of the blends. Furthermore, 70:30 of PHBV:PBS reactive blend showed similar tan delta curve as the neat blend. Also, for this blend, the tan δ peaks for PHBV and PBS were found corresponding to neat PHBV and PBS. Thus there was limited miscibility between PHBV and PBS phase at 70:30 of PHBV: PBS reactive blends (figure 27). For 50:50 neat blend of PHBV: PBS, two tan δ peaks corresponding to neat PHBV and neat PBS phase were detected. The 50:50 reactive blend of PHBV: PBS showed an inward shift in the tan δ peaks. In this blend, PHBV tan δ peak was observed to be at 18°C and PBS
A tan δ peak was observed to be at -10°C (figure 27). Thus we observed that in 50:50 reactive blend of PHBV and PBS, there was a shift of tan δ peaks corresponding to PHBV and PBS phases towards each other. This shift has been related in literature to the improved miscibility in the blend system [2,45]. Similarly, for 30:70 of PHBV: PBS neat blend, we observed two tan δ peaks corresponding to neat PHBV and neat PBS. This suggested limited miscibility of PHBV and PBS phase. A particular observation was done for 30:70 reactive blend. In this blend, a single broad tan δ peak was obtained. A single broad peak in a polymer blend has been shown to occur in the literature due to enhanced miscibility of the components. It also showed the development of micro-heterogeneous morphology in the 30:70 of PHBV: PBS reactive blends. Micro-heterogeneous morphology consists of large number of phases that exist in varying compositions [45]. Similar development of micro-heterogeneous morphology has been reported in literature where poly (ethylene oxide), PEO and poly(methyl methacrylate), PMMA blends have shown single broad tan δ peaks [105]. In this paper, the authors have attributed the development of micro-heterogeneous morphology as a reason for single broad tan δ [105]. The morphology of the blends were investigated via SEM impact fracture surface in the next section of the thesis.

8.2.5 Scanning electron microscopy (SEM)

The fracture surfaces of the neat and reactive blends are shown in figure 28. The properties of polymer blends are affected by their morphology. Neat 70:30 blend of PHBV and PBS had rough surface with pit marks all over the surface. Such irregular surface can be attributed to incompatibility between the PHBV and PBS phases. Reactive 70:30 blends of PHBV: PBS had smoother morphology than the neat blend. This smooth surface was observed due to successful stress transfer across phases. Neat 50:50 blend of PHBV: PBS showed a drastic change in surface
roughness with pits and holes clearly visible. Reactive blends of 50:50 PHBV: PBS showed a surface without any signs of pit or holes. Similar observation was made in our study for 30:70 neat blend of PHBV and PBS. The surface had signs of pull out showing little or no interaction between PHBV and PBS phases. Reactive blends of 30:70 blends had a smooth surface, again indicating that the compatibility between PHBV and PBS phases were increased via addition of DCP and TMPTA. We have already discussed the change over from brittle failure mechanism to ductile failure mechanism on addition of compatibilizers in the section 8.2.4 of this thesis. In this section we observed that all the neat blends exhibited low elongation at break suggesting brittle failure. All the reactive blends showed increase in elongation at break as compared to their respective neat blends.
Thus, we observed that the neat blends of PHBV and PBS showed rough surface morphology while the reactive blends showed a smooth surface morphology. Similar observation was made by Wang et al. [106]. They have studied in situ compatibilized blends of poly (L-lactic
acid), PLLA and poly (butylene succinate), PBS by use of dicumyl peroxide, DCP. Wang et al. have observed that the morphology of impact fractured surface was related to brittle and ductile failure of the blends [106]. The successful stress transfer across phases has been related to interaction between phases. Brittle failure mechanism is observed when the stress transfer across phases is poor. This poor interaction has been related to rough surface [106]. On the other hand, ductile failure could be observed when the interaction between phases are improved. In such cases, smoother surface could be observed with absence of pits and holes. It has been shown that compatibilization had a marked effect on the morphology of the blends [106]. Thus, our observation of occurrence of smooth morphology with addition of compatibilizers is in line with current literature.

8.2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of blends. The thermal stability of the neat and reactive blends were evaluated with respect to the neat PHBV and neat PBS. It can be observed from the figure 29 that PHBV had a maximum degradation peak at 267°C while PBS had a maximum degradation peak at 392°C (figure 29). All the neat and reactive blends exhibited two derivative weight loss peaks corresponding to the PHBV and PBS phases. The derivative weight loss peaks of the PBS phase in all the neat blends were observed to remain around 392°C. There was an upward shift, towards PBS, in derivative weight loss curves for PHBV phase in all the neat blends. This meant that thermal stability of PHBV was enhanced by addition of PBS. Our observation is consistent with other literature [37]. Zhu et al. [37] have extensively studied the miscibility of PHBV and PBS blends through thermal means. They have also observed that the addition of PBS in PHBV led to an increase in the thermal stability of the PHBV phase.

It was also observed that compatibilization was further increasing the thermal stability of blends. The reactive blends showed typical two stage thermal behavior. The maximum derivative weight peak of the PHBV phase was observed to shift upward for 70:30 of PHBV: PBS reactive blend to 275°C. Similar observations were made for PHBV phase in 50:50 of PHBV: PBS and 30:70 of PHBV:PBS reactive blends where the maximum derivative peak was observed to be at 282°C and 289°C respectively (figure 29). The maximum derivative peak of PBS phase for the 70:30 of PHBV: PBS and 50:50 reactive blends of PHBV and PBS were found to remain at the same temperature (389°C). There was a peculiar observation for 30:70 of PHBV: PBS reactive blend where peak broadening was observed for PBS phase showing increased interaction between
PHBV and PBS phases. Such peak shifts have been associated with the chemical reaction occurring between phases of polymer blend [110,111]. Chuai et al. [111] have studied the thermal stability of polystyrene, PS and poly (methyl methacrylate) blends through TGA. They have used PS-b-PMMA diblock copolymer as a compatibilizer. They have observed that with the addition of the compatibilizer, the thermal stability of PS was enhanced. Similar results has been reported in another literature where Jana and Nando [110] have studied the compatibilization of low density poly ethylene, LDPE and poly (dimethyl siloxane), PDMS. They have used ethylene-methyl acrylate as a compatibilizer. They have also reported increase in thermal stability of their blends with addition of compatibilizer.

8.2.7 Differential scanning calorimetry (DSC)

DSC was used to study crystalline phase interaction of PHBV and PBS blends with addition of DCP and TMPTA. Neat PHBV exhibited single melting point peak at 172°C (figure 30). Neat PBS exhibited double melting point peaks at 107°C and 114°C. The two melting point peaks of PBS have been reported in literature due to the formation of two types of crystals, α and β-crystals [112]. β crystals have higher melting temperature than α crystals of PBS [112]. Therefore, PBS melting point peak of 114°C was assigned to β crystals while the melting point peak of 107°C was assigned to α crystal. Upon the compatibilization, for 70:30 of PHBV:PBS blend the shift in melting point peak for PHBV was minor but two melting peaks of PBS was converted into a single melting peak (figure 30).

Similar observations were made for PBS melting peaks of 50:50 and 30:70 of PHBV: PBS reactive blends. The broad melting peak of PBS for reactive blends was found to be in middle of the peaks assigned for α and β-crystals. Joining of the two melting peaks of PBS into one broad peak upon compatibilization can be attributed to the formation of crystal structures which are similar in size. There were also shifts in melting points of PHBV for 50:50 and 30:70 of PHBV: PBS reactive blends. It was also noted that there was a minor shift in PHBV melting point in 70:30 reactive blend suggesting decreased interaction between the crystalline phase of PHBV and PBS. In the reactive blends, the shift in melting point peak of PHBV towards PBS points to increased
interaction between crystalline phase of PHBV and PBS. Similar observation has been made in literature for PHBV and PCL blends [113]. In this work, Gassner and Owen [113] have studied the miscibility of PHBV and PCL blends by differential scanning calorimetry. They have reported shifts in melting point of the blends due to solubilization of one component into the other. The solubilization was observed by authors due to an increase in the interaction between PHBV and PCL blends. Thus, the shifts in melting point of PHBV and PBS can be related to increased interaction of the components upon addition of DCP and TMPTA.

**Figure 31:** DSC crystallization graph of reactive and neat blends (A: PHBV neat, B: PBS neat, C: PHBV:PBS=70:30, D: PHBV:PBS=70:30*, E: PHBV:PBS=50:50, F: PHBV:PBS=50:50*, G: PHBV:PBS=30:70, H: PHBV:PBS=30:70*)(* – reactive blends with 0.150% DCP and 1% TMPTA)
DSC crystallization curves are obtained in a controlled cooling of the polymer samples. It was observed that the neat PHBV showed a crystallization peak at 127°C while the neat PBS showed a crystallization peak at 93°C (figure 31). The shift of the crystallization temperature in the polymer blends can be used to judge interaction between phases [114]. In this literature Zheng et al. [114] have used phenolphthalein poly (ether ether sulfone) and poly (ethylene oxide). The miscibility of the two polymers were analyzed by DSC crystallization study. The shifts in crystallization peaks can be related to entrapment of polymer chains of one polymer by the other [115]. This process of entrapment is known as co-crystallization [115]. In the literature [115], co-crystallization was observed for PHBV (with 8% valerate content) and PHBP (with 11 % propionate content). Similar results were obtained for our neat and reactive blends. The co-crystallization was observed for all the compositions of neat PHBV and PBS blends (figure 31). The co-crystallization phenomenon was enhanced upon compatibilization. The 70:30 of PHBV: PBS reactive blend showed minor change in crystallization peak with PHBV phase at 126°C and PBS phase at 94°C. For the 50:50 of PHBV:PBS reactive blend, the crystallization peaks for the PHBV and PBS phases were found to be at 124°C and at 96°C respectively. Similarly, for 30:70 of PHBV: PBS reactive blend, the crystallization peak for the PHBV phase was found to be at 117°C and for the PBS phase at 97°C. Thus, we observed that the shift in crystallization peak was pronounced at higher ratio of PBS in the reactive blends. Literature has already shown that such shifts in crystallization peak can be attributed to enhanced interaction between phases. Such enhanced interaction was manifested in an increase in co-crystallization phenomena.

Also, it can be said, from the shifts in crystallization peak of PBS towards PHBV that PHBV was acting as nucleating agent for PBS phase after compatibilization. Similar observation has been made in literature where PHBV acted as nucleating agent for PHBV and PBS blend [75].
The table 11 (next page) shows the value of percentage crystallinity obtained from enthalpy of fusion of the components in the neat and reactive blends. We observed that the percentage crystallinity values of PHBV phase remains the same for all the compositions of neat and reactive blends. But, there was increase in percentage crystallinity values for PBS phase. From table 11, we also see that 10% increase in the percentage crystallinity was observed for 30:70 of PHBV: PBS reactive blend over neat blend. Similarly, for 50:50 of PHBV: PBS reactive blend, an increase of 5% over neat value was observed. For 70:30 of PHBV and PBS the increase in percentage crystallinity was observed to be 2%. Such increases in crystallinity values show that PHBV is enhancing the crystallization of PBS phase after compatibilization.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$H_{mPHBV}$ (J/g)</th>
<th>$H_{mPBS}$ (J/g)</th>
<th>$X_{PHBV}$ (%)</th>
<th>$X_{PBS}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>104.4</td>
<td>-</td>
<td>71.5</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>68</td>
<td>17.1</td>
<td>66.5</td>
<td>28.5</td>
</tr>
<tr>
<td>D</td>
<td>66.5</td>
<td>18.5</td>
<td>65.06</td>
<td>30.9</td>
</tr>
<tr>
<td>E</td>
<td>47.4</td>
<td>32.4</td>
<td>64.9</td>
<td>32.4</td>
</tr>
<tr>
<td>F</td>
<td>46.34</td>
<td>37.1</td>
<td>63.4</td>
<td>37.1</td>
</tr>
<tr>
<td>G</td>
<td>24.6</td>
<td>44.6</td>
<td>56.1</td>
<td>31.9</td>
</tr>
<tr>
<td>H</td>
<td>26.3</td>
<td>57.6</td>
<td>60</td>
<td>41.1</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>63.8</td>
<td>-</td>
<td>31.9</td>
</tr>
</tbody>
</table>

8.2.8 Polarized optical microscopy (POM)

Polarized optical microscopy was used to investigate the effect of compatibilization on crystal size of PHBV at 130°C, which was above the crystallization and melting temperature of PBS (figure 32).
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>E</td>
<td>F</td>
</tr>
</tbody>
</table>

All samples are recorded at the same magnification
Figure 32: Polarized optical pictures of blends  (A:PHBV:PBS=70:30, B:PHBV:PBS=70:30*, C:PHBV:PBS=50:50, D: PHBV:PBS=50:50*, E: PHBV:PBS=30:70, F: PHBV:PBS=30:70*)(* – reactive blends with 0.150% DCP and 1% TMPTA)

Large crystal size of PHBV in neat blends (70:30 and 50:50 of PHBV: PBS) was evident (figure 32). PHBV crystals in these blends have typical maltese cross structure. This structure has been extensively studied in literature [87]. In this literature the authors have studied the effect of poly (propylene carbonate) on crystallization of PHBV crystals. The PHBV crystals were observed to have a typical maltese cross structure. Similar results have been observed in our work. The neat 30:70 blend of PHBV: PBS showed a deviation from crystal development of neat 70:30 and 50:50 of PHBV: PBS blends. In this blend small irregular formed circles predominate the morphology. This can be due to larger amount of PBS molecules hindering crystal formation of PHBV. It was observed that the maltese cross structure of crystals at 70:30 and 50:50 of PHBV: PBS neat blends were converted into square like concentric structures upon compatibilization. PHBV crystals were observed to be uniformly distributed in these blends. There was also change in crystal development pattern for 30:70 of PHBV and PBS blend. The irregular circular morphology was converted to non-banded spherulites. It has been said in literature that there is always competition between phase separation and crystallization [116]. Upon compatibilization, there was an increase in interfacial adhesion between PHBV and PBS. This increase in interfacial adhesion was expected to enhance crystallization of components. Such a phase acted as a thermodynamic bridge between PHBV and PBS forming uniform and equally distributed crystals as compared to neat blends [116]. We have made similar observations.
Chapter 9. Conclusions

This thesis is the first comprehensive report that uses dicumyl peroxide, DCP and trimethylol propane triacrylate, TMPTA to study the reactive blends of poly (hydroxybutyrate-co-valerate), PHBV and poly (butylene succinate), PBS. The mechanical, thermal, thermo-mechanical, rheological, and morphological analysis were done at three different ratios of PHBV and PBS blends. This research has shown that DCP and TMPTA can be successfully used as compatibilizers for various ratios of PHBV and PBS blends.

Implications of study- I

It was observed that PHBV and PBS direct melt blends yielded poor mechanical properties. The two biopolymers showed limited or poor miscibility. The miscibility could be enhanced by the addition of DCP and TMPTA under the experimental conditions used. It was observed that this addition had an effect on elongation at break of 70:30 of PHBV and PBS blend. Using the increase in percentage elongation at break as a marker for compatibilization of 70:30 of PHBV and PBS blend, eight different formulations containing various ratios of DCP and TMPTA were applied in the 70:30 blend. The 70:30 neat blend of PHBV and PBS had an elongation at break value of 17.5% (standard deviation: 2%). All eight of the other formulations showed significant changes in the elongation at break values. One of the formulations with 0.125 % of DCP and 1% of TMPTA showed an elongation at break value of 51.7%. The standard deviation value at break was observed to be comparatively high (8%). The formulation was modified further to decrease the standard deviation values.

The formulation with 0.150 % of DCP and 1% of TMPTA had an elongation at break value of 44 % with standard deviation of 2%. The notch Izod impact strength for this formulation was observed to be 27 J/m. Therefore, the formulation with 0.150 % of DCP and 1% of TMPTA was
considered as an optimized formulation for 70:30 of PHBV and PBS blend. It was also observed that DCP and TMPTA were both played in combination to increase the elongation at break values. The increment in elongation at break value over neat blend suggested a successful stress transfer from the PHBV phase to the PBS phase.

**Implications of study - II (8.2)**

In this study, dicumyl peroxide, DCP and trimethylolpropane triacrylate, TMPTA were used to compatibilize both 50:50 and 30:70 blends of PHBV and PBS. The concentrations of DCP and TMPTA used in this section were 0.150% of DCP and 1% of TMPTA. It was observed that the elongation at break for the 50:50 reactive blend of PHBV and PBS was 195%, while the elongation at break of the neat was observed to be 30%. Similarly, the elongation at break for the 30:70 reactive blend of PHBV and PBS was observed to be 198% (neat elongation at break value being 15%). Thus, 0.150% of DCP and 1% of TMPTA was successful in compatibilizing 50:50 and 30:70 of PHBV and PBS blends. A composition variable compatibility with an increase of the PBS ratio in the blends was also observed.

The addition of DCP and TMPTA had a significant effect on thermal, thermo-mechanical, rheological, and morphological properties (crystallinity, glass transition temperature, complex viscosity, and impact fracture surfaces). Increased interaction in the crystalline phase was observed in relation to the DSC melting point shift. The increase in the thermal stability of PHBV was observed from TGA and the crystal growth for PHBV was seen to be hindered with increase in PBS ratio. More uniform crystal growth occurred upon compatibilization suggesting a co-crystallization mechanism for PHBV and PBS. The SEM pictures of impact fractured surface showed a change over from brittle to ductile failure mechanism.
Overall implications

The hypothesis that the addition of DCP and TMPTA in the blends of PHBV and PBS will lead to increased compatibility between the phases has been shown to be correct. The increase in elongation at break for all the reactive blends was considered for the better behaviour of PHBV and PBS blends. This increase in the compatibility between the two phases was demonstrated through various thermal, thermo-mechanical, rheological, and morphological means. The increase in elongation at break was used as a primary marker for compatibilization. The optimization of DCP and TMPTA carried out showed the enhanced interaction between PHBV and PBS phases, with the successful stress transfer of the stress from PHBV phase to the PBS phase resulting in increase in elongation at break. Inward shifts in tan delta peak on addition of DCP and TMPTA to the blends showed increase in compatibility between the two phases, as well as an increase in melt viscosity upon the addition of DCP and TMPTA. Also, the SEM picture of impact fracture surface showed smooth morphology with compatibilizers. A method to increase the interaction between a brittle and ductile polymer, PHBV and PBS respectively opens gateways to various novel applications of PHBV and PBS blends via in situ reactive extrusion process.
References


96. Fukahori Y. Mechanism of the self-reinforcement of cross-linked NR generated through the strain-induced crystallization. Polymer 2010; 51(7):1621-1631.


