FABRICATION AND MODIFICATION OF COMPRESSION MOLDING POLY(HYDROXYBUTYRATE-CO-VALERATE) THIN SHEET

By

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ABSTRACT

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Poly(hydroxybutyrate-co-valerate), PHBV, is a brittle biodegradable polymer. This study focuses on the modification of PHBV for flexible applications. Blending with nanoparticle titanium dioxide (TiO_2) 1% by weight did not result in toughening. Blending with poly(butylene adipate-co-terephthalate) (PBAT or Ecoflex) at various ratios of PHBV/Ecoflex (80/20, 70/30, and 50/50 by weight) for flexibility with and without nanoparticle TiO_2 also was not promising. Grafting with 2-Hydroxyethyl methacrylate (2HEMA) at ratios of PHBV/2HEMA of 90/10 and 70/30 by weight was also unsuccessful in increasing flexibility. Crosslinking PHBV in the presence of 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (L101) resulted in significantly greater elongation at break and slightly higher tensile strength. The crosslinked PHBV had lower crystallinity than PHBV since the crosslinked network impeded crystalline formation, creating voids for favorable paths for gases resulting in higher permeation. The amount of L101 in the crosslinking reaction was investigated at 0.5, 1, 2, 3, and 4 % by weight. The neat PHBV and crosslinked PHBV sheets were not significantly different in tensile strength. The maximum elongation at break was obtained at L101 content of 2 % by weight where it was twice that of neat PHBV. Thermal analysis showed that crystallinity of the crosslinked PHBVs were lower than neat PHBV. Also, the permeability to gases increased with an increase in L101 content.

To my parents, brother, sisters, and friends

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TABLE OF CONTENTS

LIST OF TABLES……..…viii

LIST OF FIGURES……...x

KEY TO SYMBOLS AND ABBREVIATIONS……..…..…...xiii

1. INTRODUCTION
- **1.1 Introduction and motivation**……..…1
- **1.2 Goal and objectives**……..……..2
- **1.3 Research plan**……..3
  - 1.3.1 Selection of modification methods for improving poly(hydroxybutyrate-co-valerate) properties……3
  - 1.3.2 Selection of the optimum amount of an initiator in order to gain maximum elongation at break……3

2. LITERATURE REVIEW
- **2.1 Introduction**……4
- **2.2 Biodegradable polymers**……6
  - 2.2.1 Petroleum based biodegradable polymers……7
    - 2.2.1.1 Aliphatic polyesters……7
    - 2.2.1.2 Aliphatic-aromatic copolymers……..……..…9
  - 2.2.2 Bio-based polymers……10
    - 2.2.2.1 Starch……10
    - 2.2.2.2 Cellulose……12
    - 2.2.2.3 Soy based bioplastic……...12
    - 2.2.2.4 Zein bioplastic…..……...13
    - 2.2.2.5 Polylactic acid……14
    - 2.2.2.6 Polyhydroxyalkanoates……..16
- **2.3 Biodegradable polymer modification for flexibility**……..17
  - 2.3.1 Polymer blends..……17
    - 2.3.1.1 Characterization of polymer blends……...……..20
  - 2.3.2 Polymer grafting……21
  - 2.3.3 Crosslinking polymers……..……..23
- **2.4 Poly(hydroxybutyrate-*co*-valerate)** ……25
  - 2.4.1 Poly(hydroxybutyrate-*co*-valerate) structure and properties……..27
  - 2.4.2 Enhancement of poly(hydroxybutyrate-co-valerate) properties…….28
    - 2.4.2.1 Poly(hydroxybutyrate-co-valerate) blends……28
    - 2.4.2.2 Poly(hydroxybutyrate-co-valerate) grafting and crosslinking……...30
- **2.5 Biodegradation of poly(hydroxybutyrate-co-valerate)** ……31
  - 2.5.1 Biodegradation mechanism……32
  - 2.5.2 Biodegradation evaluation……..34
  - 2.5.3 Biodegradation of poly(hydroxybutyrate-co-valerate)……...35

3. MATERIALS AND METHODS

3.1 Materials……...37
3.1.1 Polyhydroxybutyrate-co-valerate……37
3.1.2 Poly(butylene adipate-co-terephthalate)……37
3.1.3 Triethyl citrate……37
3.1.4 Titanium dioxide……38
3.1.5 2-Hydroxyethyl methacrylate……38
3.1.6 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane……...38
3.2 Equipment……39
3.2.1 Processing equipment……39
3.2.2 Compression molding……40
3.2.3 Mechanical properties……41
3.2.4 Thermal properties……41
3.2.5 Permeability test equipment……42
3.2.6 Statistical analysis……...42
3.3 Poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate -co-valerate) sheet fabrication……42
3.4 Investigation of the properties of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate) sheet……44

4. SELECTION OF MODIFICATION METHOD FOR IMPROVING POLYHYDROXYBUTYRATE-CO-VALERATE PROPERTIES FOR COMPRESSION MOLDING THIN SHEET

4.1 Introduction……..45
4.2 Fabrication of modified polyhydroxybutyrate-co-valerate……..45
4.2.1 Fabrication of poly(hydroxybutyrate-co-valerate) blend with titanium dioxide……45
4.2.2 Fabrication of poly(hydroxybutyrate-co-valerate)/poly(butylene adipate-co-terephthalate) blend……...47
4.2.3 Fabrication of poly(hydroxybutyrate-co-valerate)/poly(butylene adipate-co-terephthalate)/titanium dioxide blend……48
4.2.4 Fabrication of poly(hydroxybutyrate-co-valerate)/triethyl citrate blend……..48
4.2.5 Fabrication of poly(hydroxybutyrate-co-valerate) grafted with 2-hydroxyethyl methacrylate ……49
4.2.6 Fabrication of crosslinked poly(hydroxybutyrate-co-valerate)……50
4.3 Results and discussion……51
4.3.1 Visual characteristics of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate)……..51
4.3.2 Mechanical properties of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate)……56
4.3.3 Thermal properties of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate)……64
4.3.4 Permeation properties of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate)……85
4.3.4.1 Water vapor permeability……88
4.3.4.2 Oxygen and carbon dioxide permeability……98

4.4 Conclusion……...101

5. INFLUENCE OF THE AMOUNT OF INITIATOR ON THE DEGREE OF PHBV CROSSLINKING AND ITS PROPERTIES
5.1 Introduction……102
5.2 Fabrication of crosslinked polyhydroxybutyrate-co-valerate with different amounts of initiator……103
5.3 Results and discussion……106
5.3.1 Visual characteristics of the crosslinked poly(hydroxybutyrate-co-valerate)s.…….....……..……106
5.3.2 Mechanical properties of crosslinked poly(hydroxybutyrate-co-valerate)s……..……..….108
5.3.3 Thermal properties of crosslinked poly(hydroxybutyrate-co-valerate).…….……113
5.3.4 Permeation properties of crosslinked poly(hydroxybutyrate-co-valerate).…….....119
5.4 Conclusion……...124

6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK
6.1 Summary and conclusions ……125
6.1.1 Selection of modification method for improving polyhydroxybutyrate-co-valerate properties for compression molding thin sheet……...125
6.1.2 Influence of the amount of initiator on the degree of polyhydroxybutyrate-co-valerate crosslinking and its properties..……...127
6.2 Problems and recommendations for future work……...……128

APPENDICES……...…….129
Appendix A- Mechanical properties of neat PHBV and modified PHBV material sheets……..…...…130
Appendix B- Thermal properties of neat PHBV and modified PHBV material sheets……..……...132
Appendix C- Permeation properties of neat PHBV and modified PHBV material sheets……..……...136

REFERENCES……..…….……138

LIST OF TABLES

Table 4.1 Visual characteristics of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate) in different forms in the experiment……..…..55

Table 4.2 Mechanical properties of all compositions of modified poly(hydroxybutyrate-co-valerate) material sheets…….……..…..…60

Table 4.3 Thermal properties of all compositions of modified poly(hydroxybutyrate-co-valerate)…….……..…..67

Table 4.4 Permeation properties of all compositions of modified poly(hydroxybutyrate-co-valerate)……..…….……...…90

Table 5.1 Visual characteristics of PHBV and crosslinked poly(hydroxybutyrate-co-valerate) with L101 of 0.5, 1, 2, 3, and 4 %wt.……...107

Table 5.2 Mechanical properties of crosslinked poly(hydroxybutyrate-co-valerate) at various initiator contents compared to neat poly(hydroxybutyrate-co-valerate)..110

Table 5.3 Thermal properties of crosslinked poly(hydroxybutyrate-co-valerate) at various initiator contents compared to neat poly(hydroxybutyrate-co-valerate)..116

Table 5.4 Permeability properties of crosslinked poly(hydroxybutyrate-co-valerate) at various initiator contents compared to neat poly(hydroxybutyrate-co-valerate)..120

Table A-1 Tensile strength of all compositions of modified PHBV material sheets…….130

Table A-2 Elongation at break of all compositions of modified PHBV material sheets…...130

Table A-3 Tensile strength of crosslinked PHBV at various initiator contents compared to neat PHBV……....131

Table A-4 Elongation at break of crosslinked PHBV at various initiator contents compared to neat PHBV……131

Table B-1 Crystallization temperature of all compositions of modified PHBV material Sheets……...…….132

Table B-2 The first melting temperature of all compositions of modified PHBV material Sheets……....132

Table B-3 The second melting temperature of all compositions of modified PHBV material sheets……...133

Table B-4 Heat of fusion of all compositions of modified PHBV material sheets……....133

Table B-5 Crystallization temperature of crosslinked PHBV at various initiator contents compared to neat PHBV……..…….134

Table B-6 The first melting temperature of crosslinked PHBV at various initiator contents compared to neat PHBV……..…..134

Table B-7 The second melting temperature of crosslinked PHBV at various initiator contents compared to neat PHBV……135

Table B-8 Heat of fusion of crosslinked PHBV at various initiator contents compared to neat PHBV……....135

Table C-1 Water vapor permeation of all compositions of modified PHBV material sheets……....136

Table C-2 Oxygen permeation of all compositions of modified PHBV material sheets…...136

Table C-3 Carbon dioxide permeation of all compositions of modified PHBV material sheets……137

Table C-4 Water vapor permeation of crosslinked PHBV at various initiator contents compared to neat PHBV…….……..137

Table C-5 Carbon dioxide permeation of crosslinked PHBV at various initiator contents compared to neat PHBV……..…….137

LIST OF FIGURES

Figure 2.1 Number of landfills in the United States from 1988 to 2009……...…...5

Figure 2.2 Poly(butylene succinate) molecular structure……..…7

Figure 2.3 Polycaprolactone molecular structure……..…...…8

Figure 2.4 Polyglycolide molecular structure……..…….8

Figure 2.5 Poly(butylene adipate-co-terephthalate) molecular structure……..……9

Figure 2.6 Amylose molecular structure…….11

Figure 2.7 Amylopectin molecular structure……..11

Figure 2.8 Cellulose molecular structure…….....12

Figure 2.9 Molecular structure of D-lactide, L-lactide, and Meso-lactide…….…...….14

Figure 2.10 Molecular structure of poly(lactic acid)……...…….…15

Figure 2.11 Molecular structure of PHAs……..……...……16

Figure 2.12 Polymer blend phase diagram……...…19

Figure 2.13 Graft copolymer diagram……..……21

Figure 2.14 Molecular crosslinking……...……...…24

Figure 2.15 Molecular structure of PHBV……..…….26

Figure 2.16 Biodegradation mechanism of polymers……..33

Figure 3.1 Co-rotating mini twin screw extruder……...39

Figure 3.2 Compression molding machine…….…40

Figure 4.1 Poly(hydroxybutyrate-co-valerate) neat resins……...……..…52

Figure 4.2 Brittleness of PHBV/TiO_2 sheet and crosslinked PHBV sheet…….54

Figure 4.3 Tensile strength of PHBV material sheets……62

Figure 4.4 Elongation at break of PHBV material sheets……...63

Figure 4.5 Two melting temperatures (T_m) of neat PHBV…….65

Figure 4.6 Crystallization temperature (T_c) of neat PHBV……66

Figure 4.7 Thermal decomposition profile of neat PHBV……..68

Figure 4.8 Endothermic and exothermic profiles of neat PHBV and PHBV/ TiO_2 1%wt.....70

Figure 4.9 Thermal decomposition profiles of PHBV and PHBV/TiO_2 1%wt……..…71

Figure 4.10 Endothermic and exothermic profiles of neat PHBV and PHBV/Ecoflex blends……....73

Figure 4.11 Thermal decomposition profiles of neat PHBV and PHBV/Ecoflex blends...…..74

Figure 4.12 Endothermic and exothermic profiles of neat PHBV and PHBV/Ecoflex/TiO_2 blends……....75

Figure 4.13 Thermal decomposition profiles of neat PHBV and PHBV/Ecoflex/TiO_2 blends……....76

Figure 4.14 Endothermic and exothermic profiles of neat PHBV and PHBV/TEC blends.....78

Figure 4.15 Thermal decomposition profiles of neat PHBV and PHBV/TEC blends……..…79

Figure 4.16 Endothermic and exothermic profiles of neat PHBV and PHBV-g-2HEMAs….81

Figure 4.17 Thermal decomposition profiles of neat PHBV and PHBV-g-2HEMAs……....82

Figure 4.18 Endothermic and exothermic profiles of neat PHBV and crosslinked PHBV…..83

Figure 4.19 Thermal decomposition profiles of neat PHBV and crosslinked PHBV……..84

Figure 4.20 Water vapor permeation of PHBV material sheets……..…….92

Figure 4.21 Oxygen permeation of PHBV material sheets……..……....93

Figure 4.22 Carbon dioxide permeation of PHBV material sheets……..……...94

Figure 5.1 Shearing force profile of the molten PHBV crosslinked with a presence of L101 vs. time in the mini twin screw extruder indicating the maximum force of molten polymer reached the highest at reaction time of 1 min.…….104

Figure 5.2 PHBV neat resin and crosslinked PHBV with L101 of 0.5, 1, 2, 3, and 4 %wt..105

Figure 5.3 Tensile strength of neat PHBV and crosslinked PHBV sheets……...111

Figure 5.4 Elongation at break of neat PHBV and crosslinked PHBV sheets……..112

Figure 5.5 Endothermic and exothermic profiles of neat PHBV and crosslinked PHBVs with L101 at 0.5, 1, 2, 3 and 4 %wt……117

Figure 5.6 Thermal decomposition profiles of neat PHBV and crosslinked PHBVs with L101 at 0.5, 1, 2, 3 and 4 %wt.……..….118

Figure 5.7 Water vapor permeation of neat PHBV and crosslinked PHBV sheets……..121

Figure 5.8 Carbon dioxide permeation of neat PHBV and crosslinked PHBV sheets…….122

KEY TO SYMBOLS AND ABBREVIATIONS

Φ_1, Φ_2	=	Volume fraction of polymer 1 and 2, respectively
χ_{12}	=	Flory-Huggins interaction parameter between polymer 1 and 2
A	=	Cross-sectional area
ATRP	=	Atom transfer radical polymerization
CO_2TR	=	Carbon dioxide transmission rate
D	=	Diffusion coefficient
DSC	=	Differential scanning calorimetry
E_p	=	Activation energy
EPA	=	Environmental Protection Agency
F	=	Flow rate
HB	=	Hydroxybutyrate
2HEMA	=	2-Hydroxyethyl methacrylate
ΔH_m	=	Melting enthalpy or heat of fusion
ΔH_m^0	=	Melting enthalpy or heat of fusion of 100% crystalline polymer
HV	=	Hydroxyvalerate
L101	=	Luperox 101, Lupersol 101, or 2,5-bis(tert-butylperoxy) -2,5-dimethylhexane
MSW	=	Municipal solid waste
O_2TR	=	Oxygen transmission rate
P3/4HB	=	Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)
PBAT	=	Poly(butylene adipate-co-terephthalate)
PHA	=	Polyhydroxyalkanoate

PHB	=	Polyhydroxybutyrate
PHBV	=	Poly(hydroxybutyrate-co-valerate)
PHV	=	Polyhydroxyvalerate
PLA	=	Polylactic acid
psi	=	Pounds per square inch
q	=	Quantity of permeant passing through a polymer
R	=	Gas constant
t	=	Travelling time of a permeant passing through a polymer
T	=	Temperature in Kelvin
T_c	=	Crystallization temperature
TEC	=	Triethyl citrate
T_g	=	Glass transition temperature
TGA	=	Thermogravimetric analysis
TiO_2	=	Titanium dioxide
T_m	=	Melting temperature
w_1, w_2	=	Weight fraction of polymer 1 and 2, respectively
wt	=	Weight
WVP	=	Water vapor permeability
WVTR	=	Water vapor transmission rate

1. INTRODUCTION

1.1 Introduction and motivation

Polymers have been used increasingly these days since they have many superior properties over other materials. Plastics of today are mostly products from the petrochemical industry. Over the past century, natural resources including petroleum, oil and natural gas have been enormously used in every activity. Awareness has been raised concerning the depletion of natural resources. Petroleum is one of the greatest concerns. In addition, petrochemical processes for polymer production, especially refinery processes, involve combustion reactions and releases of combustion by-products, which are toxic substances, and other greenhouse gases. These substances have been released to the atmosphere contributing to pollution problems in our ecosystem [1]. Moreover, plastics from everyday life have been accumulating leading to massive waste, which needs waste management measures. All of these burdens have led to research and development of innovative materials.

Biodegradable polymers are alternative materials for this solution, which have been developed and implemented in many areas, especially in packaging applications. Poly(hydroxybutyrate-*co*-valerate), PHBV, is a biodegradable polymer which is formed in bacterial cells as an energy reservoir. With an absence of amino acid producing substances in the media substrate, PHBV is created in the cells. However, PHBV possesses high brittleness, tackiness and lack of elongation [2, 3]. To overcome these drawbacks, there are various plausible modification methods that have been used. These include adding plasticizers to the polymer for improving

flexibility [4, 5]. Nanoparticle inclusions such as titanium dioxide can be applied in order to toughen polymeric materials [6, 7]. Blending with other polymers can improve ductility of the material [8]. Grafting a polymer can enhance mechanical properties [9] and crosslinking can improve ductility and elongation of polymers [10, 11].

1.2 Goal and objectives

The goal of this study focuses on the improvement of PHBV properties so it can be effectively used for flexible applications as well as maintaining its biodegradability. To achieve this goal, crosslinking with the help of an initiator was used to enhance PHBVs mechanical properties.

The objectives of the study were to:

1. Select modification methods for improving PHBV properties
2. Select the optimum amount of an initiator in order to gain maximum elongation at break.

1.3 Research plan

1.3.1 Selection of modification methods for improving poly(hydroxybutyrate-co-valerate) properties

A number of modification methods were selected in efforts to improve PHBV properties. First, PHBV was fabricated by adding TiO_2 to toughen PHBV. Second, PHBV was blended with Ecoflex in order to gain flexibility. Third, PHBV was blended with Ecoflex and added TiO_2 in order to impart both toughening and flexibility to PHBV. Fourth, PHBV was blended with triethyl citrate (TEC) as a plasticizer to improve flexibility. Fifth, 2-hydroxyethyl methacrylate (2HEMA) was grafted onto PHBV in order to diminish PHBV brittleness. Finally, PHBV was crosslinked in the presence of an initiator (2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane, L101). Visual observation, mechanical properties, thermal properties, and permeability were examined.

1.3.2 Selection of the optimum amount of an initiator in order to gain maximum elongation at break

From the results of the experiments discussed above, crosslinking was chosen as the preferred modification method for improving PHBV properties. In this section, investigation of the optimum amount of L101 was performed in order to obtain maximum elongation at break. L101 was evaluated at 0.5, 1, 2, 3, and 4 %wt. Visual observation, and evaluation of mechanical, thermal and permeability properties were used.

2. LITERATURE REVIEW

2.1 Introduction

Plastics, as we know, have a tremendous impact on today's life. They are constituents of many household products around us since they were first commercially introduced in the 1930's. Since then they have become increasingly used. However, plastics are obtained from petroleum resources which may become short in the near future. In addition, a lot of concerns about environmental issues have been cited regarding plastics, especially plastic packaging, after it has been used and becomes trash needing to be disposed. A significant increase in oil prices is another impetus to the change of using biobased polymers instead of their conventional counterparts. According to the US Environmental Protection Agency (US EPA or EPA for short), municipal solid waste (MSW) increased from 88.1 million tons in 1960 to 253.7 million tons in 2005 but dropped a little to 250.4 million tons in 2010 and increased to 250.9 million tons in 2012 [12]. MSW has been handled by processes such as recycling, landfilling, and incineration. The recycling rate has continuously increased from 6.4% in 1960 to 34.5 % in 2012 [12]. Landfilling is also one of the ways to manage the increasing garbage, especially plastics packaging. According to the 2009 EPA report, the number of landfills decreased from 7,924 in 1988 to 1,908 in 2009 as indicated in Figure 2.1 but the landfill sizes increased [13].

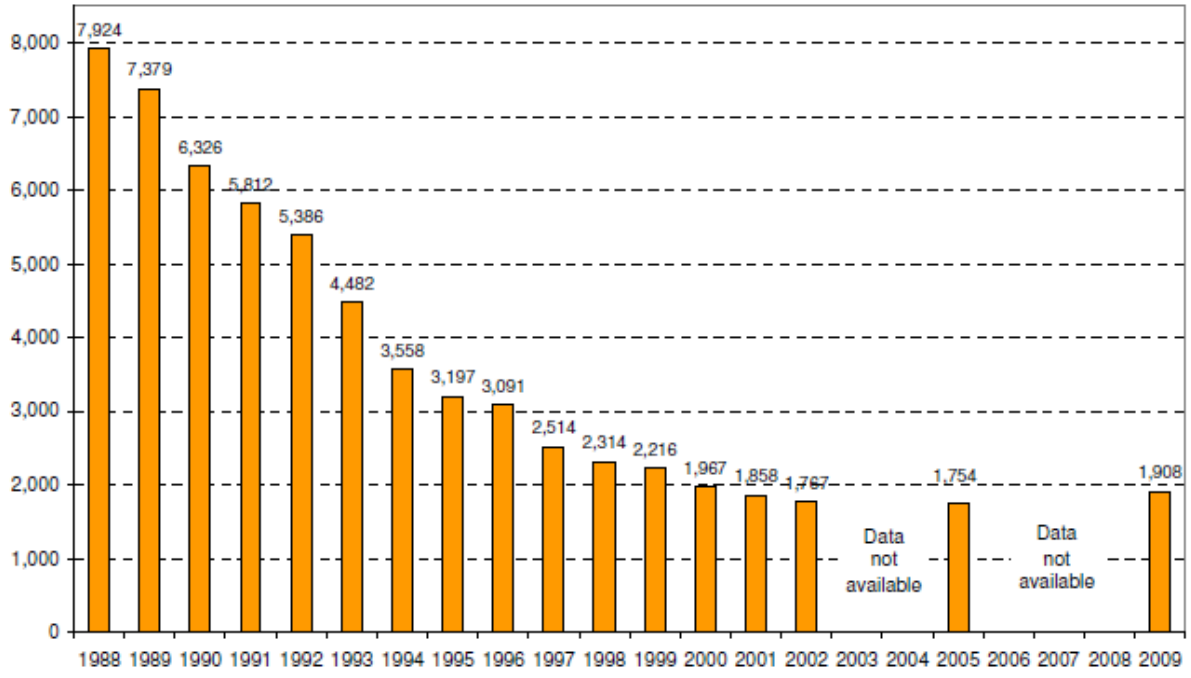


Figure 2.1 Number of Landfills in the United States from 1988 to 2009 [13]

The quantity of MSW discarded to landfill has increased from 82.5 million tons in 1960 to 131.9 million tons in 2009. However, there are many problems in recycling and landfill. In recycling, energy is used (but generally less than in production of new products) during the process which can release greenhouse gases, resulting in environmental problems such as global warming, extreme climate changes and so on [14, 15]. In landfilling, in addition, some of the degradable wastes remain in place, as there is not enough moisture and oxygen for microorganisms to totally degrade such massive waste. This leads to a slow degradation process. Moreover, leachate, a liquid produced by waste, is another problem in landfills. It can contaminate the water reservoirs nearby. Methane gas, a greenhouse gas, from the waste is also a problem and it needs to be monitored and carefully collected out of the sites; otherwise it will release to the atmosphere and cause global warming [16]. In addition to those processes

mentioned above, petroleum based polymers used in household products cannot be easily degraded. Therefore, a potential solution to these problems is to find a new plastic material which can naturally degrade and leave no residue in the environment. The material in the question is biodegradable plastic.

2.2 Biodegradable polymers

Biodegradable plastics are defined as "a degradable plastic in which the degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi, and algae and results finally in production of carbon dioxide and water" according to ASTM D6400-04 [17]. Biodegradable polymers can be classified into two categories depending on their original sources – petroleum based polymers obtained from petroleum products; and bio-based polymers obtained from natural resources. Examples of biodegradable petroleum based polymers are polycaprolactone, polybutylene succinate terephthalate, and polyvinyl alcohol. For bio-based polymers, polysaccharides, proteins, lipids, polyesters obtained from microorganisms such as polyhydroxyalkanoates (PHAs) and polyesters from polymerization of natural monomers such as polylactic acid (PLA) are examples [18].

2.2.1 Petroleum based biodegradable polymers

Several petroleum based biodegradable polymers can be found in today's products. Despite being synthetic polymers, they can be naturally degraded in certain environments.

2.2.1.1 Aliphatic polyesters

Most petroleum-based biodegradable polymers are aliphatic polyesters. Many different monomers can be used to produce these polyesters. They are obtained mostly from ring opening polymerization processes [19, 20].

Poly(butylene succinate), PBS, a crystalline thermoplastic, is produced by condensation polymerization of glycols like ethylene with aliphatic dicarboxylic acids like succinic acid or adipic acid [21]. PBS is produced under the trade name Bionolle® by Showa HighPolymer, Japan and the name Enpol® by Ire Chemical, Korea [22]. The properties are similar to polyethylene and polypropylene in elongation and tensile strength. Moreover, PBS has better processability than PLA. This results in suitability for packaging applications [23].

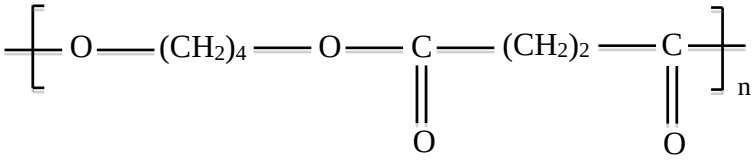


Figure 2.2 Poly(butylene succinate) molecular structure

Polycaprolactone, PCL, a semi-crystalline polymer, is produced by ring opening polymerization of ε-caprolactone with the help of tin acetate as a catalyst [24]. It is sold under the trade name CAPA® from Solvay, Belgium; Celgreen® from Daicel, Japan; and Tone® from Union Carbide, USA [9].

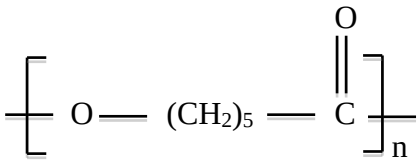


Figure 2.3 Polycaprolactone molecular structure

Polyglycolide, PGA, a crystalline linear polyester, is obtained by ring opening polymerization of cyclic lactone. It has high mechanical properties. However, it has some drawbacks in instability in solvents and high degradation rate [25, 26].

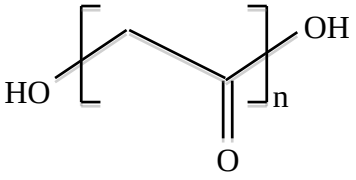


Figure 2.4 Polyglycolide molecular structure

Poly(trimethylene carbonate), PTMC, a flexible polymer, is produced by ring opening polymerization of trimethylene carbonate using diethylzinc as a catalyst. The resulting polymer has poor mechanical properties [27].

2.2.1.2 Aliphatic-aromatic copolymers

Many aliphatic petroleum based biodegradable polymers have been used in several applications. However, there are some drawbacks. These aliphatic polymers tend to have low mechanical properties but high degradation rates, whereas aromatic biodegradable polymers have low degradation rates. In order to trade off the properties of both, aliphatic-aromatic copolyesters have been prepared by copolymerization of aliphatic and aromatic monomers.

Poly(butylene adipate-co-terephthalate), PBAT, is prepared by polycondensation of 1,4-butanedial, and an adipic acid and terephthalic acid mixture. Ecoflex® is its trade name from BASF, Germany; Origo-Bi® from Novamont, Italy; and Easter Bio® from Eastman Chemical, USA. It has high mechanical properties when it contains more than 35 mol % terephthalic acid; however, with more than 55 mol % terephthalic acid, its biodegradability is decreased dramatically [28, 29].

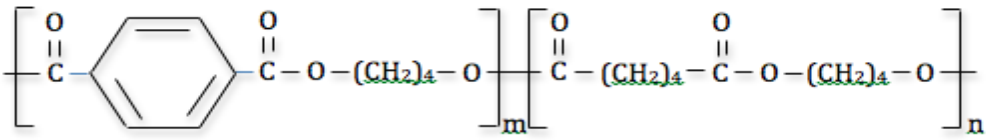


Figure 2.5 Poly(butylene adipate-co-terephthalate) molecular structure

Biomax®, DuPont, USA, has produced this polymer by modification of poly(ethylene terephthalate) with diethylene glycol and dimethylglutarate monomers. By adding the monomers, it leads to weak bonds in the Biomax structure, which are vulnerable to hydrolysis. The degradation process of Biomax is that it first degrades by hydrolysis and then biodegrades by action of microorganisms [30].

2.2.2 Bio-based polymers

Bio-based polymers derive from renewable resources such as starch, corn and microorganisms. They are mostly used as disposable goods especially catering items such as food trays, bowls and kitchen utensils, etc.

2.2.2.1 Starch

Starch, a renewable resource material, is obtained from plants. It is a cheap and available material consisting of chains of two types of starch, amylose and amylopectin, in different ratios from 18-33 % amylose and 72-81 % amylopectin. This results in different types and properties of starch. Amylose is a linear chain of D-glucose joined by α-1, 4 linkages in the main chains with molecular weight of 2,000 – 150,000. Amylopectin is a branched chain of D-glucose with the branches joined by α-1, 6 linkages and α-1, 4 linked backbone. Amylopectin has molecular weight of 65 – 500 million [31, 32, 33]. Amylose in starch ranges from 17% in cassava to 27% in maize. Figure 2.6 and 2.7 show the molecular structures of amylose and amylopectin.

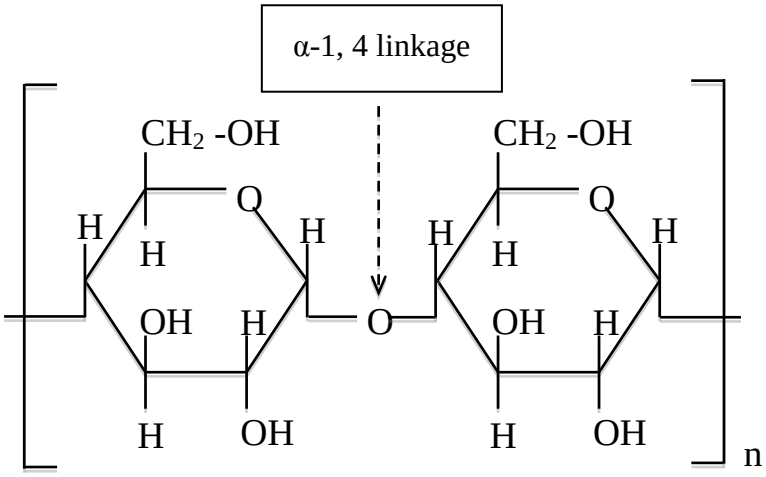


Figure 2.6 Amylose molecular structure

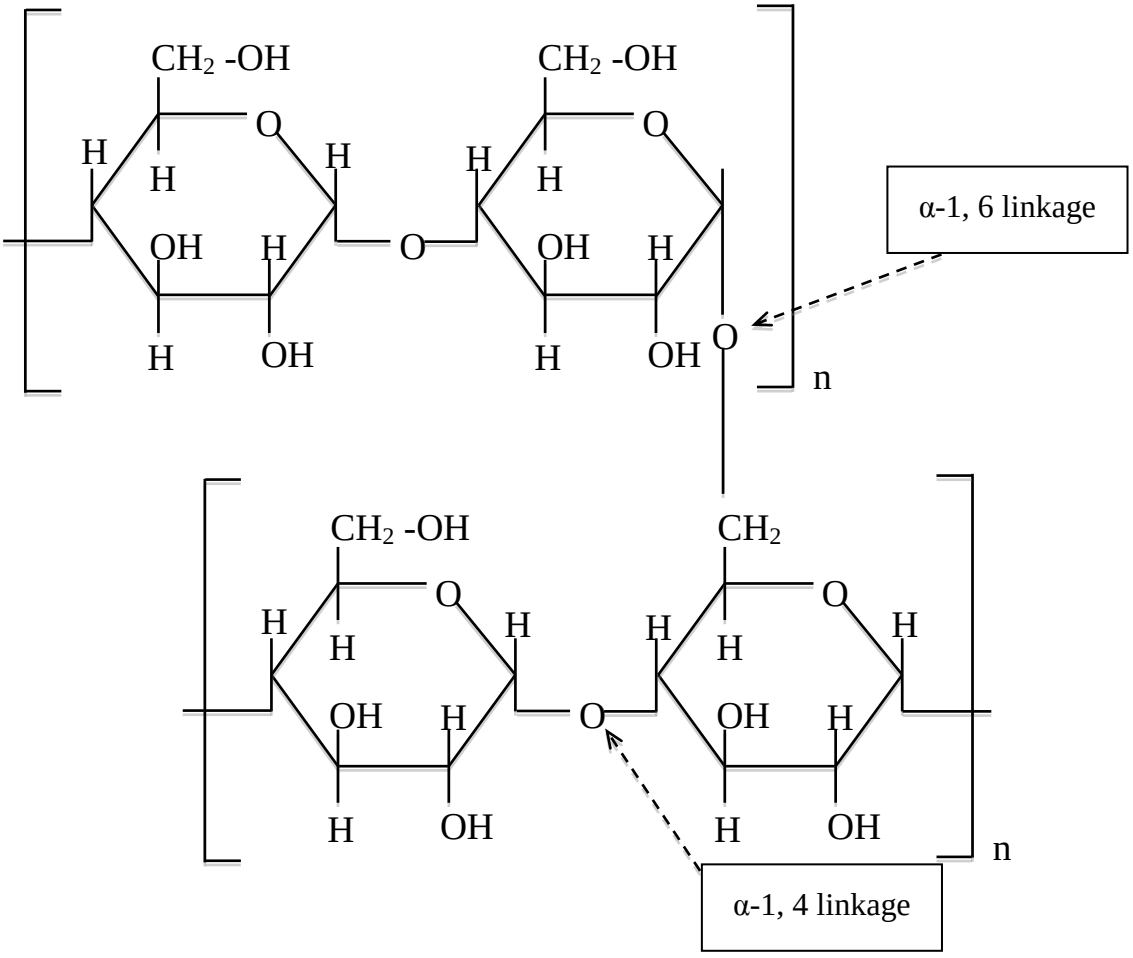


Figure 2.7 Amylopectin molecular structure

2.2.2.2 Cellulose

Cellulose is a renewable resource that consists of long linear chain molecules of β-1,4 linked D-glucose as shown in Fig. 2.8. It is obtained from plant and microorganism cell walls. Unlike starch, it cannot be dissolved in water. Generally, it is used as a reinforcement material in polymer applications [34, 35]. Moreover, cellulose is a main constituent in the paper industry.

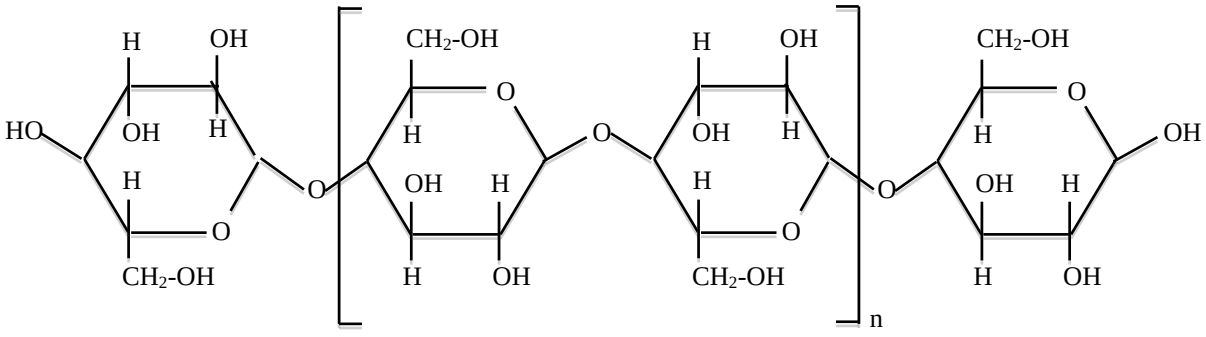


Figure 2.8 Cellulose molecular structure

2.2.2.3 Soy based bioplastic

Soybean is an inexpensive and versatile resource for fabrication of plastics. It consists of 18-20% oil, 40-45% protein, 25-30% carbohydrate and 3% other constituents. Soybean has mostly been used for production of soybean oil, and the remaining material after oil production is used as livestock feed. For polymers, soybean, with amino acids and other side chains as its structure, is fabricated as edible and nonedible film by adding plasticizers for flexibility and crosslinking agents such as glutaraldehyde, formaldehyde, gossypol and lactic acid for water resistance and mechanical strength [36, 37]. Felix et al. blended soy protein and albumin in

several different ratios in the presence of 40%wt. glycerol. They found that, at 50/50% wt., the soy protein and albumin blend reached the highest stress when compared to other ratios of the blends [37]. Zhou et al. studied a blend of guanidine hydrochloride modified plasticized soy meal (mPSM) with polybutylene adipate-co-terephthalate (PBAT) compared to a blend of plasticized soy meal (PSM) with PBAT at the same ratio of 60% wt. PBAT. The PSM/PBAT blend had lower tensile strength and elongation at break than the mPSM/PBAT blend [38].

2.2.2.4 Zein bioplastic

Zein is a protein from corn (maize). It is soluble in alcohol solution and used in the production of coatings, binders, adhesives and biomaterials including food packages [39, 40]. Du et al. reported on blends of zein and polyurethane at different ratios. With an increase of polyurethane weight in the blends, tensile strength decreased whereas elongation increased [40]. Zein is also used for fabrication of composite materials. Zein/montmorillonite (MMT) nanocomposite films were produced by two different approaches, solvent casting and blown extrusion at 0, 1, 3, 5, and 10%wt MMT. The resulting tensile strength of the blends increased with an increase of MMT and reached maximum values at 5%wt MMT for the solvent casting method and 1%wt MMT for the blown extrusion method. Adding MMT in the blends beyond those values decreased tensile strength. Water vapor permeability of the blends was decreased with an increase of MMT [41].

2.2.2.5 Polylactic acid

Polylactic acid, PLA, is a biodegradable aliphatic polyester. It is mostly derived by catalytic ring-opening polymerization of lactide monomers. The molecular structure of PLA is composed of L-lactide, D-lactide, and Meso or L,D-lactide as shown in Figure [42].

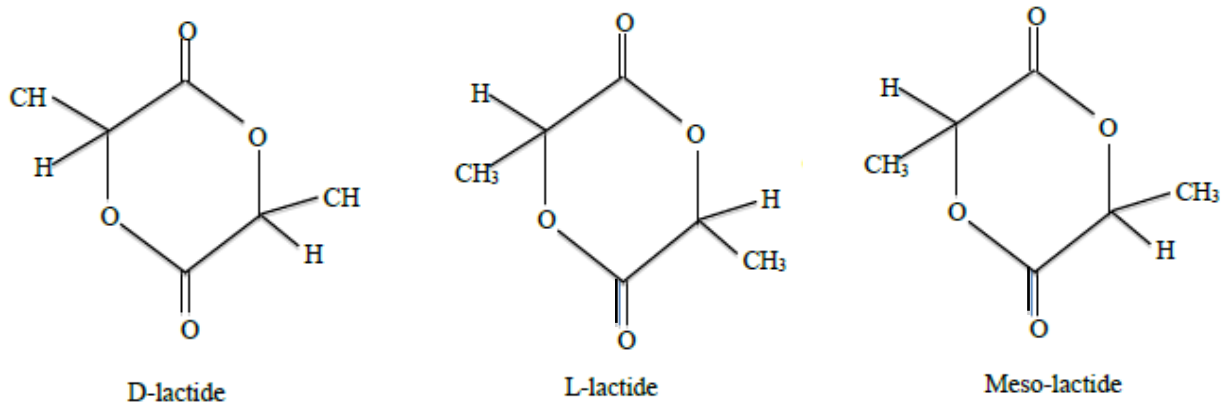


Figure 2.9 Molecular structure of D-lactide, L-lactide, and Meso-lactide

The production of PLA is done by first depolymerization of low molecular weight PLA under low pressure in order to obtain three different lactides. Then all lactides undergo catalytic ring-opening polymerization to produce high molecular weight PLA. With various contents of L-lactide and D-lactide, special types of PLA for different applications are obtained. PLLA, poly-L-lactide, contains a high amount of L-lactide. PDLA, poly-D-lactide, on the other hand, has a high amount of D-lactides. Both are considered to be semicrystalline homopolymers. PDLLA, poly-DL-lactide, is a copolymer of D-lactide and L-lactide. At low D-lactide content in predominantly PLLA, it is semicrystalline; as D-lactide content increases, it becomes amorphous [42, 43].

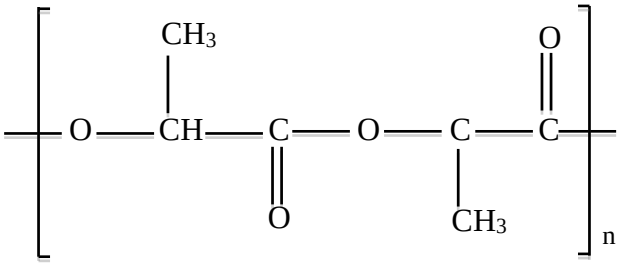
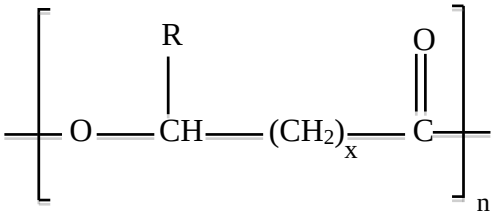


Figure 2.10 Molecular structure of poly(lactic acid)

PLA has glass transition temperature (T_g) and melting temperature (T_m) ranging from 50-80 °C and 130-180 °C, respectively [44]. It has both high tensile strength and Young's modulus whereas its elongation is low. PLA has better barrier for water vapor, oxygen, and carbon dioxide than polystyrene (PS) and starch based polymers [45, 46]. PLA is mostly used in packaging applications, especially in food packages, but its usage is limited in flexible applications due to its lack of flexibility. Many efforts have been made to improve the properties of PLA for suitable applications. PLA was blended with poly(trimethylene carbonate) and talc; the resulting elongation was increased compared to neat PLA even if tensile strength was lower [47]. PLA/PCL (polycaprolactone)/EPO (epoxidized palm oil) blends were studied by Jaffar et al. who found that PLA/PCL (80/20 %wt) with an increase of EPO content increased elongation and reached maximum elongation at EPO 10%wt [48].

2.2.2.6 Polyhydroxyalkanoates

Polyhydroxyalkanoates, PHAs, are linear biodegradable polyesters which are found in bacterial cells. The production of PHAs is based on a fermentation process with control of the carbon substrate and then isolation of PHA from bacteria cells. The most common type of PHA is polyhydroxybutyrate, PHB. Another type of PHA often seen is polyhydroxyvalerate, PHV. The molecular structures of PHB and PHV are shown in Fig. 2.11 [49].



R = CH_3 is PHB

R = CH_2CH_3 is PHV

Figure 2.11 Molecular structure of PHAs

PHAs have a high potential to be used as renewable polymers due to their biodegradability and stiffness for rigid packaging applications. However, brittleness is a serious drawback, so the use of PHAs in flexible applications is limited. Alternatively, the copolymer of PHB and PHV, poly(hydroxybutyrate-*co*-valerate), PHBV, was fabricated in order to improve flexibility but its properties have not yet been accepted by the flexibles industry [18, 49].

2.3 Biodegradable polymer modification for flexibility

2.3.1 Polymer blends

Polymer materials in use today have some limits to their potential use in certain applications. Instead of development of brand new materials, blending is one of the ways to gain some desired properties. It is an inexpensive and easy process. Blending is also useful for optimizing some properties between two or more polymers for specific uses.

Moreover, polymer blends are basically developed for solving polymer application issues, especially for biodegradable polymers, which have many drawbacks largely in polymer processing and application. PHBV has low melt strength, high stiffness, and a low crystallization rate that needs some time to solidify. This, in turn, results in tackiness which is not desirable for processing. A polymer blend is a physical mixture of more than one type of polymer and the resultant polymer is called a polymer alloy. It can be either miscible, immiscible, or partially immiscible. The majority of blends are immiscible due to a weak interface between the two components. The thermodynamic equation of polymer miscibility between two compositions is shown in the following formula [50, 51].

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

where ΔG_{mix} = the free energy of mixing (Gibbs free energy)

ΔH_{mix} = the enthalpy of mixing

ΔS_{mix} = the entropy of mixing

Miscibility occurs when ΔG_{mix} is less than zero. Otherwise, immiscibility will be observed. Moreover, the polymer mixing also needs to follow the equation below in order to avoid phase separation [50].

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial \varphi_i^2}\right)_{T,P} > 0$$

where φ = volume fraction of polymer i in the polymer mixture

The critical point of the spinodal (the boundary of single phase and separated phases) appears as shown in Figure 2.12. The lower critical solution temperature (LCST) is the temperature below which all compositions of a polymer mixture are miscible. The upper critical solution temperature (UCST) is the temperature above which all compositions of a polymer mixture are miscible.

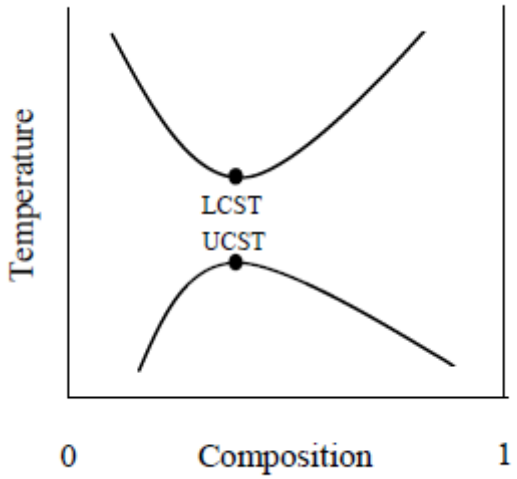


Figure 2.12 Polymer blend phase diagram, adapted from [50]

For binary polymer blends, the free energy can be calculated using the Flory-Huggins model [50].

$$\Delta G_{mix} = kTV\left[\frac{j_1}{V_1}\ln j_1 + \frac{j_2}{V_2}\ln j_2\right] + j_1 j_2 c_{12} kTV / n_r$$

where ΔG_{mix} = the free energy of mixing (Gibbs free energy)

V = total volume

R = gas constant

ϕ_1, ϕ_2 = volume fraction of component 1 and 2

V_1, V_2 = molecular volume of component 1 and 2

ν_r = molecular volume of a specific segment

k = Boltzmann's constant

χ_{12} = Flory-Huggins interaction parameter

2.3.1.1 Characterization of polymer blends

A miscible blend appears to be a single phase, which basically exhibits a single glass transition temperature (T_g). The T_g of the blend has a value between that of each polymer. For partially miscible and immiscible blends, there will be two T_gs which belong to each of the polymers. In miscible blends, T_g can be estimated from the weight fraction of the components in the blend [52].

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

where w_1 = weight fraction of component 1

w_2 = weight fraction of component 2

Blending can be done in mixers and extruders. With shearing force in the equipment, polymer structures break into droplets and mix together, leading to a dispersed phase of one polymer into the continuous phase of another [53]. This behavior of the blend is immiscible. Miscibility of the blends is dependent upon molecular structure, interfacial interaction including polarity, solubility and rheological behaviors of the polymer constituents. Poor blending gives unstable immiscible blends, in which the interfacial force between the two polymers is compromised, resulting in poor mechanical properties. Strong interface interaction between the two polymers gives small droplets dispersed evenly into the continuous phase leading to enhanced properties. This blend is considered as a compatible blend [54, 55, 56]. However, most polymer blends are incompatible, and have weak interfaces in the blend structure resulting in poor properties. Adding of compatibilizer is an answer to this situation. It is added to the blends during the blending process in order to reduce interfacial tension, improve dispersion

and enhance stabilization of the blends [57]. A typical compatibilizer structure is a block copolymer which is miscible in both polymers, or one side of its structure is miscible in one polymer and the other side is miscible in another polymer [57]. The resulting blend is compatible and results in property enhancement. Another method to create a compatible blend is reactive compatibilization. This process involves adding functional groups into the blends during blending in the presence of a catalyst. It creates end group reactions, chain cleavage, bond formation and crosslinking, resulting in interfacial interactions in the blends [55, 57, 58].

2.3.2 Polymer grafting

Polymer grafting is a polymer modification method involving adding monomers onto other polymer chains (backbone) at different spots of the main chain in order to enhance characteristic properties of the backbone and obtain desired properties for suitable applications such as thermal and mechanical resistance. The backbone polymer can be a homopolymer or a copolymer and the monomers as a side chain can be one or more different types. The monomers are bonded covalently onto the polymer main chains and the resulting polymers (copolymers) are branched polymer chains as shown in Figure 2.13 [59, 60, 61, 62].

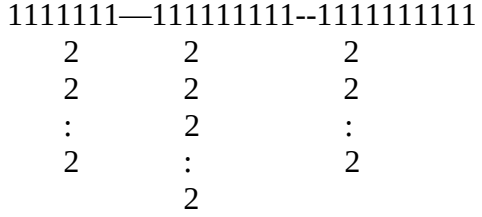


Figure 2.13 Graft copolymer diagram, adapted from [59]

Functional groups in the main chain are essential in the grafting process. They are effective sites for monomer side chains to be covalently bonded onto the backbone. There are two different types of grafting process, grafting from and grafting to. Grafting from is a process in which active sites at functional groups are initiated and then they are polymerized onto the backbone which is previously not initiated. Grafting to is a process in which active spots of both the backbone and monomers are initiated and then polymerization occurs on the reactive sites [60, 63].

Grafting processes can be carried out by different methods. The principle of grafting is to create active sites at functional groups or free radicals on the backbone chain initiating the grafting reaction. There are several grafting processes. Chemical grafting is the process of adding chemicals as initiators to create active spots in the backbone. In radiation grafting, active sites are initiated and controlled by radiation. Enzymatic grafting is another technique with mild environment requirements. Enzymes are used to initiate active sites. In the plasma initiated grafting process, surface grafting is initiated by plasma exposure. The reaction steps of all grafting methods are electron-induced excitation, ionization and dissociation [63].

Polymer grafting normally has an advantage over polymer blending. In the grafting process, two components are covalently bonded, while in blending, two polymers are mixed physically creating a weak interface between them [59, 60].

In a grafted polymer, the T_g is found as the T_g of each polymer constituent in the blend or graft polymer, corresponding to the T_g of each homopolymer. Crystallinity of the grafted polymer

normally consists of crystallinity of each homopolymer in the polymer. If each homopolymer is crystalline, the resulting grafted polymer will have two melting temperatures (T_ms) [64].

Suchao-in et al. reported compatibility of starch grafted poly(butylene succinate) was improved and mechanical properties increased when compared to neat poly(butylene succinate) [65]. Vlcek et al. stated grafting methyl methacrylate onto cellulose diacetate using the atom transfer radical polymerization (ATRP) method, is a modern process to create free radicals. Grafted materials with several lengths and densities can be obtained [66]. Grafting of epoxy onto grapheme oxide in various ratios was reported to significantly increase tensile strength compared to neat epoxy with inherent brittle behavior [67].

2.3.3 Crosslinking polymers

Crosslinking is another polymer modification method in which polymer chains are covalently bonded within molecular chains (intramolecular crosslinking) or between chains (intermolecular crosslinking) in multiple dimensions, as shown in Fig. 2.14. It is an irreversible reaction and resulting polymer properties are dependent upon the degree of crosslinking. At a low degree of crosslinking, crystalline polymers have lower crystallinity because the crosslinked portions in the structure interfere with chain orientation. This results in a polymer with lower melting temperature, soft and elastic characteristics. Crosslinking reduces the free volume due to the change in molecular alignment, resulting in a higher T_g [60].

(a) (b)

Figure 2.14 Molecular crosslinking, adapted from [60]

(a) Intramolecular crosslinking (b) Intermolecular crosslinking

In crosslinked polymers, polymer chains are restricted and cannot easily move with respect to one another. However, crosslinking gives elasticity to amorphous structures. The properties of crosslinked polymer are enhanced depending on the degree of crosslinking. The crosslinked material has good resistance to light, heat, and chemicals and good mechanical strength [60].

Crosslinking processes are similar to those of grafting. In chemical processes, a conventional method is redox reactions. Free radicals are created and reaction occurs. This method is simple and it can be performed at room temperature and in aqueous solution. Another chemical method is living radical formation. Chain growth occurs in the presence of monomers and the chain can continue to grow as long as the monomers are supplied. The constantly growing chains are not hindered by chain termination since the process is controlled by allowing a higher initiation rate than the propagation rate or by eliminating chain termination. In the enzymatic method, enzymes are used to initiate the reaction sites and the crosslinking reaction occurs. This method is mostly used in the grafting process. A polycondensation reaction is a

crosslinking process with an elimination of two reaction sites (functional groups). When two functional groups are eliminated the reaction occurs, simultaneously producing byproducts [60, 63].

Moreover, the use of interpenetrating polymer networks (IPN) is another way for crosslinking. IPN performs by combining two polymer networks and crosslinking one polymer in the presence of another. It differs from chemical crosslinking in that no induced covalent bonds are involved between the two polymers. Elastomer crosslinking is the crosslinking process that is used in elastomers. Elastomers inherently deform under load, resulting in limitations on their use in many applications. The best known elastomer crosslinking is vulcanization. It is a chemical process in which long chain molecules are crosslinked into a 3-dimensional network. The polymer first appears to be thermoplastic and then becomes elastic or hard, depending on the degree of crosslinking. The resulting polymer has mechanical strength, elasticity, rigidity, and durability in deformation under different conditions [60]. The radiation technique is a crosslinking process that uses radiation to induce free radicals in the polymer chain. The reaction occurs at free radical sites [60, 63].

2.4 Poly(hydroxybutyrate-*co*-valerate)

Poly(hydroxybutyrate-*co*-valerate), PHBV for short, is a copolymer in the family of polyhydroxyalkanoates (PHAs). It is a biodegradable aliphatic copolyester produced and stored in bacterial cells as an energy source [2, 18, 68]. Its structure is shown in Fig. 2.15.

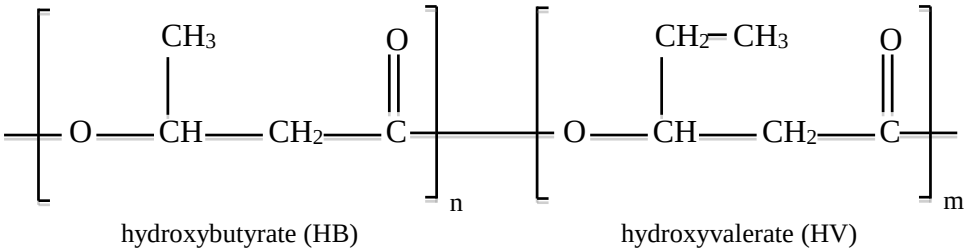


Figure 2.15 Molecular structure of PHBV

The properties are dependent upon the ratio of the length of PHB and PHV chains. The most common form of PHA is poly(3-hydroxybutyrate) (PHB) which has a methyl group as a side group and x as 1 (see Fig 2.11). Another form of PHA is polyhydroxyvalerate (PHV) with an ethyl group as a side group and x as 1. PHB has high crystallinity and excellent mechanical properties, similar to polypropylene (PP) [3, 69]. However it has disadvantages of high brittleness and low elongation. An alternative to overcome the drawbacks is its copolymer, PHBV. PHBV has higher toughness and lower melting point than PHB [3].

PHBV is a copolymer of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV) and is a thermoplastic hydrophilic aliphatic biodegradable polymer in the family of polyhydroxyalkanoates (PHAs). PHBV is produced in order to improve the properties of PHB which is the most common form of PHAs [2, 18]

PHBV is produced by fermentation of bacteria in the presence of a carbon source with a lack of one of the elements that is essential to amino acid production along with adding propionic acid. This results in production of PHBV in the bacteria cells. With the control of ratios of

ingredients in the media, PHBV with various ratios of PHB and PHV can be obtained (see Fig. 2.15) [2].

PHBV's price is high due to the costly production when compared to petroleum-based resins. Biopol, the PHBV trade name, was approximately US$ 4-8 per kg as reported in 1998 compared to petroleum resins such as polypropylene at US$ 0.6-0.9 per kg [70]. Therefore, its price was a barrier to its application. However, there have been efforts to develop bacteria strains and improve the production process to be able to reduce the cost of PHBV, for example, *Alcaligenes eutrophus* produced by ZENECA Bio Product, UK, *Alcaligenes latus* manufactured by Biotechnologische Forschungs Gesellschaft, Austria and so on [71].

2.4.1 Poly(hydroxybutyrate-co-valerate) structure and properties

The properties of PHBV vary depending on the quantity of hydroxyvalerate (HV) in the structure. HV makes PHBV more flexible than PHB, which is more stiff and brittle and inappropriate for many applications, even if its properties are similar to polypropylene [3, 72]. In addition to the flexibility derived by copolymerization, PHBV possesses a lower T_g, T_m, percent crystallinity, tensile strength and flexural modulus, but greater elongation and impact strength than PHB. The lower T_m is beneficial for thermal processing. This is because the low processing temperature reduces thermal degradation of the plastic [2, 18]. Luzier reported that PHBV with 20 % HV which was produced by ICI had significantly reduced percent crystallinity, from 80 % (with 0 % HV) to 35 %, resulting in a reduction of T_m from 177 °C to 130 °C, and of tensile strength from 40 MPa to 20 MPa [2]. Chen and Wu stated similarly that

T_m and tensile strength were reduced with an increase in the quantity of HV [73]. However, PHBV, even though its properties are a little better than PHB, still possesses brittleness, low elongation at break, high crystallinity, and tackiness for several minutes until it solidifies [74, 75, 76, 77]. These characteristics of PHBV mean it is still not suitable to be used in flexible applications.

2.4.2 Enhancement of poly(hydroxybutyrate-co-valerate) properties

2.4.2.1 Poly(hydroxybutyrate-co-valerate) blends

PHBV blending is one of the practical ways to overcome its drawbacks for commercial applications. Wang et al. studied a blend film of PHBV and poly(3-hydroxybutyrate-co-4-hydroxybutyrate (P3/4HB) prepared by a solvent-casting method. The blend was miscible as evidenced by the single T_g observed. It has a helical structure like neat PHBV as measured by FTIR. The elongation at break increased when P3/4HB increased. This means the more P3/4HB in the blend, the greater the amount of ductility observed [78]. A PHBV/PHB blend was studied by Sombatmankhong et al. It was useful for bone scaffolds at 50/50 w/w which indicated maximum alkaline phosphatase (ALP) activity [79]. There was also a study of PHBV/poly(3-hydroxybutyrate-co-3-hydroxypropionate (PHBP). The blend at 1/1 was produced by a solvent-casting method in chloroform and crystallization was analyzed by FTIR. Yoshie at al. found that, at lower spherulite growth rates, both components can have more phase separation. HV units of PHBV were included in the PHB lattice of PHBP, while HP units hardly penetrated the PHBV lattice [80].

Park at al. also investigated PHBV blends with poly(butadiene-co-acrylonitrile) (NBR). A single T_g was observed and shifted with composition of the blend. This means the blend was miscible, corresponding to the fact that NBR suppressed PHBV crystallization. In addition, tensile strength was lower while elongation at break was greater with a higher amount of NBR [81]. Crystallization of PHBV blends with poly(dicyclohexylitaconate) was also studied. The blend was immiscible as shown by FTIR [82]. Another study by Li et al. examined melt blending of PHBV and poly(propylene carbonate) (PPC) at 30:70 w/w. FTIR and SEM study showed that the blend was immiscible with PPC as the continuous phase and PHBV as the dispersed phase [83]. Differential scanning calorimetry (DSC) was applied in analysis of blends of PHBV/poly(ethylene succinate) (PES) prepared by chloroform. The blends were immiscible as observed by having two T_gs. The crystallization process was not changed in the blend and tensile strengths of the specimens decreased while elongation increased with higher amounts of PES [84]. In a degradation study of PHBV blends, Imam et al. observed PHBV/cornstarch blends in natural compost for more than 125 days. They found that weight loss of 50% wt of the cornstarch blend was highest followed by 30% wt of cornstarch and then neat PHBV. Starch in the blend expedited PHBV degradation [85]. Furthermore, degradation of a PHBV and polypropylene (PP) blend film at 4:1 prepared by pressing in a hot plate was investigated by Goncalves et al. The film was buried in soil for 120 days. The degradation occurred at the polymer interfaces of the blend and amorphous portion of PP by microbial activity. This resulted in a change in the morphology of the blend structure. For neat PHBV, it was totally degraded through the action of microorganisms within 30 days [86].

2.4.2.2 Poly(hydroxybutyrate-co-valerate) grafting and crosslinking

Lao et al. reported 2-hydroxyethyl methacrylate, 2HEMA, was grafted onto the surface of PHBV film in the presence of an initiator, benzophenone (BP) or H_2O_2. Fourier transform infrared spectroscopy (FTIR) showed the resulting PHBV was successfully grafted. The grafting process was easy and fast [87]. In addition, PHBV grafted with 2HEMA also was investigated by Wang et al. HEMA was grafted on PHBV in the presence of Lupersol 101 as an initiator in an extruder, in a reactive extrusion process. The existence of grafting was confirmed by nuclear magnetic resonance spectroscopy (NMR). The resulting material was still rigid, brittle and tacky and took a long time to solidify [88]. Wang et al. stated that PHBV grafted with poly(N-vinylpyrrolidone) (PVP) had a higher Young's modulus while its elongation was decreased. Hydrophilicity of the grafted PHBV was increased as measured by water contact angle [89]. Another study of PHBV grafting involved photografting of polyacrylamide. The grafted material was found to have a lower degree of crystallinity than PHBV since grafting hindered the crystallization process. This could be observed by a decrease in endothermic enthalpy or heat of fusion [90]. Gamma irradiation was also used for grafting acrylic acid onto a PHBV surface. The degree of grafting obtained was dependent upon the acrylic acid concentration and radiation dose. The functionalized material was suitable for biomolecules to be attached for tissue engineering [91].

Crosslinking is another modification method for improving serious drawbacks of PHBV properties, especially a lack of flexibility and low elongation. Fei et al. studied blending of 4,4-dihydroxydiphenylpropane (BPA) in PHBV and *p-tert*-butylphenol (TBP) in PHBV. FTIR

revealed that there was a strong H-bond between the blend components, and DSC showed that crystallization of PHBV was decreased by BPA and TBP [92]. Furthermore, PHBV itself was crosslinked with the help of dicumyl peroxide as an initiator. NMR, which was used for indication of the reaction location of the crosslinking, indicated that the reaction position was tertiary carbons in PHBV. Crystallinity and crystallization temperature (T_c) and T_m decreased with a greater amount of initiator. Additionally, compression molded films from the modified PHBV had greater elongation when compared to neat PHBV [93].

2.5 Biodegradation of poly(hydroxybutyrate-co-valerate)

Plastic, as we know, is durable and persistent and does not easily degrade in normal environments. This problem is recognized and waste disposal is becoming a concern in many countries. Plastic is one of the major solid wastes, which are created every year and must be managed properly. As mentioned earlier in this chapter, recycling, landfilling and incineration are used to manage solid wastes [12, 94]. However, one of the alternative ways to manage this problem is to use biodegradable polymers. This is becoming attractive to many researchers. Biodegradable plastics are vulnerable to microbial degradation resulting in reducing waste volume for landfilling. They are considered as environmental friendly materials. They have a potential use in agricultural areas. For example, biodegradable mulch film has been used to control sunlight and insects for perishable products. It can degrade and leave no residue [94].

Biodegradation is the process of microbial attack in order to break down plastic materials (see biodegradable plastic definition in section 2.2). The process occurs in a damp environment.

This means, without the presence of water, microorganisms are unable to consume polymer molecules. The biodegradation steps are that microorganisms release enzymes to depolymerize plastic materials until the material becomes water-soluble intermediates. The molecules in the intermediates need to be sufficiently tiny so they can be transported into the microorganism cells and leave water and carbon dioxide as by products. This process only occurs on the polymer surface since enzymes cannot penetrate deep into the polymer matrix. There are many processes before biodegradation takes place. These processes are able to facilitate biodegradation: chemical hydrolysis, thermal degradation and chain scission and oxidation processes. These reduce the size of the polymer chains so that enzymatic degradation is expedited [94, 95].

Furthermore, the biodegradation process not only depends upon the processes as mentioned earlier, but also on other parameters such as temperature, humidity, pH, salinity, oxygen and nutrient supply. This means these parameters can affect a number of microorganisms and activity of different types of microorganisms resulting in different biodegradation rates. The difference in plastic type and structure also influences biodegradation. Homopolymers and copolymers biodegrade differently. In the same polymer, biodegradation results differ in the crystalline and amorphous portions [94, 95].

2.5.1 Biodegradation mechanism

Polymer biodegradation consists of two main steps, the primary step and the biodegradation step. The primary step (depolymerization) is considered as a pretreatment. The goal is to

reduce the size of molecular chains of plastics in order for microorganisms to bring them into their cells. Either photodegradation, thermal degradation, chemical hydrolysis or oxidative chain scission is involved. The second step is biodegradation (mineralization) [94, 95]. Biodegradation can occur in two different atmospheres, aerobic and anaerobic. Aerobic conditions require oxygen for microorganisms to consume to undergo reaction. An anaerobic environment, on the other hand, is biodegradation without oxygen. This step involves transportation of tiny polymer fragments into cells, assimilation by the microorganisms and mineralization. The process produces many byproducts such as water, minerals, carbon dioxide, methane (from anaerobic environments), hydrogen, nitrogen, and new biomass [95].

Chemical hydrolysis and oxidation mostly occur in the depolymerization step. The following reaction shows hydrolysis of polyester in the presence of acid as a catalyst [94, 95].

$$RCOOR' + H_2O \longleftrightarrow RCOOH + R'OH$$

The reaction produces acid (RCOOH), which can expedite the reaction. Enzymes, additionally, can be used as catalysts in biological hydrolysis [94, 95, 96].

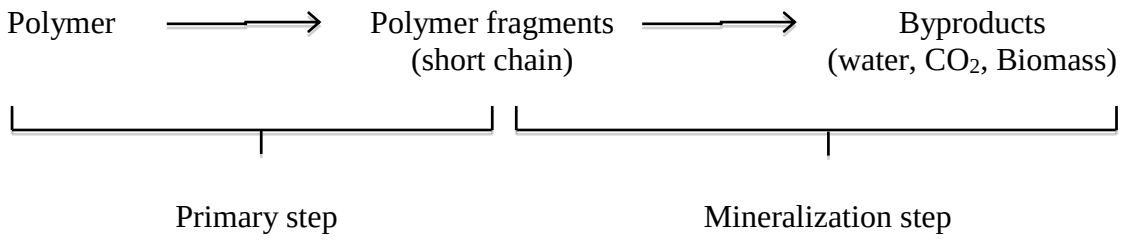


Figure 2.16 Biodegradation mechanism of polymers

2.5.2 Biodegradation evaluation

Biodegradation assessment can be performed in many ways: weight loss, consumed oxygen (BOD), dissolved organic carbon (DOC) and released carbon dioxide. Moreover, infrared (IR), ultraviolet (UV), nuclear magnetic resonance (NMR), electron microscope and mechanical resistance can be used in determining the biodegradation [95].

In aerobic environments, microorganisms use oxygen to oxidize polymers (carbon source) and create end products of biomass, carbon dioxide and water. The following is the respiratory reaction in microorganism cells [95].

$$C_{polymer} + O_2 \longrightarrow CO_2 + H_2O + C_{residue} + C_{biomanss} + \text{salts}$$

In an anaerobic environment, with an absence of oxygen, the reaction evolves methane as shown below [95].

$$C_{polymer} \longrightarrow CO_2 + CH_4 + H_2O + C_{residue} + C_{biomanss} + \text{salts}$$

Carbon dioxide evolution in the mineralization step is evaluated for biodegradation. It is used in the percent biodegradation calculation as shown in the following equation [96].

$$\% \text{ Biodegradability} = \frac{(CO_2)_T - (CO_2)_B}{ThCO_2} \times 100$$

where $(CO_2)_T$ = cumulative amount of carbon dioxide evolved in reactor containing polymer, g

$(CO_2)_B$ = cumulative amount of carbon dioxide evolved in blank reactor, g

$ThCO_2$ = theoretical amount of carbon dioxide created by the polymer, which can be calculated in the equation below

$$ThCO_2 = M_{TOT} \times C_{TOT} \times \frac{44}{12}$$

where M_{TOT} = total dry solids in grams

C_{TOT} = the proportion of total organic carbon in total dry solids in the plastic sample in grams

44 = molecular mass of CO_2

12 = atom mass of C

2.5.3 Biodegradation of poly(hydroxybutyrate-co-valerate)

PHBV is a biodegradable polymer and is susceptible to microbial degradation. There is much research focusing on PHBV biodegradability. Sang et al. conducted a biodegradability test of PHBV in soil. The result showed that fungal biomass increased with respect to time of exposure indicating degradation of PHBV. Scanning electron microscopy (SEM) also showed

the increase of fungal cells [97]. Similarly, SEM proved that PHBV cracked and degraded on its surface [98]. Biodegradation of PHBV also was determined in pilot scale compared to lab scale. PHBV completely degraded in a pilot scale facility. Both biodegradability test results were not different and the percent of biodegradability was 81% [99]. Additionally, PHBV can be completely biodegraded in soil in 30 days [86, 100].

Also, anaerobic conditions were evaluated for PHBV biodegradability. Abou-Zeid et al. studied biodegradability of PHBV and PHB in two anaerobic sludges at 37 °C and the evolution of methane was detected along with weight loss. PHBV gave lower biodegradation than PHB which is in contrast to the result in aerobic conditions [101].

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Polyhydroxybutyrate-co-valerate

Polyhydroxybutyrate-co-valerate, PHBV, in pelletized form, was manufactured by Monsanto, UK. It was donated to Michigan State University.

3.1.2 Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate), PBAT, was supplied in pelletized form by BASF (Florham Park, N.J., USA) under the trade name Ecoflex® F (BX7011).

3.1.3 Triethyl citrate

Triethyl citrate, 99% was supplied by Sigma-Aldrich. It is a transparent liquid. It has been used as a plasticizer in plastic fabrication.

3.1.4 Titanium dioxide

Titanium dioxide, TiO_2, was purchased from Nanostructured & Amorphous Materials Inc., NM, USA. It is in the form of nano-particles in powder rutile form with a size of 10 × 40 nanometers and 98% purity.

3.1.5 2-Hydroxyethyl methacrylate

2-Hydroxyethyl methacrylate, 2HEMA, was supplied by Sigma-Aldrich. It is in liquid form with 97% purity and the boiling point of 67 °C. It was used for grafting onto PHBV.

3.1.6 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane

2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane, L101, is an initiator for polymer reactions. It is a clear liquid product of Arkema Inc., under the trade name of Luperox 101 and was purchased from Sigma-Aldrich. It has a density of 0.877 g/cm^3 at 25 °C, boiling point of 55-57 °C at 7 mmHg and flash point of 65 °C.

3.2 Equipment

3.2.1 Processing equipment

Melt modified extrudates were produced using a co-rotating mini twin screw extruder, DSM Micro 15 compounder, The Netherlands, with 150 mm screw length, 18:1 length to diameter (L/D) ratio, and 15 cc. capacity. The extrudates were introduced to an injection molding machine in order to shape them into disks except for the crosslinked PHBV materials, which were immediately collected from the DSM and cut into pellets, since the reaction time was important to the degree of crosslinking. Figure 3.1 shows the twin screw extruder.

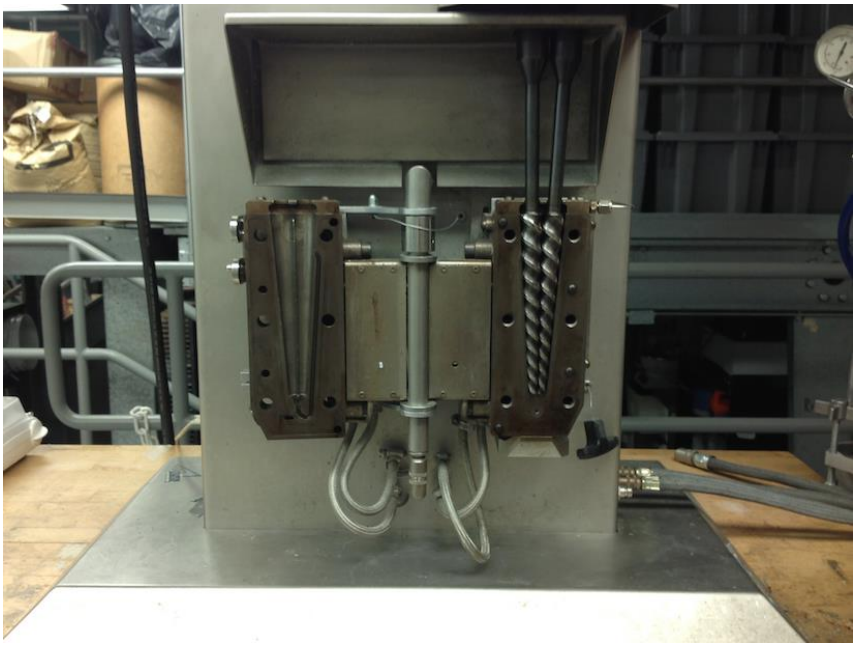


Figure 3.1 Co-rotating mini twin screw extruder

3.2.2 Compression molding

A compression molding machine (M CARVER, Carver Laboratory Press, Menomonee Falls, Wisconsin, USA) was used to transform disk and pellet extrudates into thin sheet. All compositions of modified PHBV and neat PHBV were put in a thin aluminum frame with inner size of 180×180 mm^2 and thickness of 0.25 mm. and compressed at 165 °C and 20,000 psi for 5 minutes. All the materials were cooled with a cooling unit, attached to the compression molding machine for 15 min. The cooling unit used tap water to cool the compression molded material. The compression molding machine is shown in Figure 3.2

Figure 3.2 Compression molding machine

3.2.3 Mechanical properties

Mechanical properties of all PHBV sheets were measured using an Instron Tensile Tester 5565 (Instron, Inc., Norwood, MA, USA), according to ASTM D882-12 [102]. The sheets were conditioned at 23°C, 50% RH for more than 48 hours in accordance with ASTM D618-13 [103]. Then, the sheets were cut into 1 in. wide by 7 in. long samples. The tests were carried out with a grip separation rate of 0.5 in./min, and initial grip separation of 5 in.

3.2.4 Thermal properties

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) of all PHBV materials were obtained using a TGA 2950 (TA Instruments, New Castle, DE, USA) in order to measure weight change as a function of temperature. 10 to 30 mg of the material was heated from 30 °C to 700 °C, at a heating rate of 10 °C/min., under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) of all PHBV materials was performed using a model Q-100 DSC (TA Instruments, New Castle, DE), in accordance with ASTM D3418-03 [104]. DSC indicates the crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m), and melting enthalpy or heat of fusion (ΔH_m). The materials weighing between 5 and 10 mg were put in a non-hermetic aluminum pan. The temperature interval was between -50 and 180 °C, at a heating rate of 10 °C/min.

3.2.5 Permeability test equipment

Mocon Permatran-W 3/33, Mocon Oxtran 2/21, and Permatran-C 4/41 are water vapor, oxygen, and carbon dioxide permeability test equipment for polymer films. In this study, the permeability test conditions were 23°C, 50% relative humidity (RH) for oxygen and carbon dioxide permeability, following ASTM D3985-05, and 23°C, 100% RH for water vapor permeability, following ASTM F1249-05 [105, 106].

3.2.6 Statistical analysis

Analysis of variance (ANOVA) and Tukey tests were performed in order to determine significant differences at the 95% confidence level ($p \leq 0.05$).

3.3 Poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate) sheet fabrication

PHBV neat resins were compression molded into sheets as described in section 3.2.2.

All modified PHBV sheets were produced in a co-rotating mini twin-screw extruder, DSM Micro 15 compounder, Netherlands. The raw materials were placed in the extruder. The production proceeded until the maximum shearing force was reached. The maximum shearing force indicated mixing at which the force from the extruder overcame the viscosity of the melt polymer and designated the residence time in this study. The residence time (reaction time)

was important since PHBV has inherent thermal degradation when exposed to high temperature. The resulting extrudates were transferred through a preheated cylinder at 155 °C to an injection molding machine set at 155 °C, to form into disks. The disks were compression molded as described in section 3.2.2. The extrusion conditions for each type of modified PHBV were as follows:

- For PHBV/TiO_2 blends: PHBV resins and TiO_2 1% by weight were mixed in the extruder at 165 °C for 1 min.
- For PHBV/Ecoflex blends: PHBV and Ecoflex resins were mixed in the extruder at 165 °C for 2 min.
- For PHBV/Ecoflex blend/TiO_2 blends: PHBV, Ecoflex and TiO_2 were mixed in the extruder at 165 °C for 2 min.
- For PHBV/Triethyl citrate: PHBV and triethyl citrate were mixed in the extruder at 165 °C for 30 seconds.
- For PHBV grafted with 2HEMA materials: PHBV, 2HEMA and L101, as an initiator for the grafting reaction, were mixed in the extruder at 165 °C for 1 min.
- For crosslinked PHBV: PHBV and L101 were mixed in the extruder at 165 °C for 1 min.

3.4 Investigation of the properties of poly(hydroxybutyrate-co-valerate) and modified poly(hydroxybutyrate-co-valerate) sheet

The properties of PHBV and modified PHBV sheets were determined as follows.

Visual appearance: PHBV and all modified PHBV were examined for visual characteristics of color and texture.

Mechanical properties: tensile strength and elongation at break were investigated by the Tensile Tester in order to obtain the material resistance under load.

Thermal properties: TGA and DSC were performed in order to determine the thermal behavior of the materials. The obtained TGA profile indicates thermal degradation characteristics (weight change) of the materials from 23 °C – 600 °C. DSC showed thermal profiles, both endothermic and exothermic behaviors, from which transition properties, T_c, T_m, ΔH_c, and ΔH_m can be determined. The tests were performed in the temperature range of -30 °C to 180 °C.

Permeability properties: WVTR, O_2TR, and CO_2TR indicate the ability of the polymer materials to allow water vapor, oxygen and carbon dioxide, respectively, to penetrate through the materials. All the samples were masked with aluminum foil in order to reduce the area to 3.14 in^2 since each of the modified PHBV sheets was produced in small quantity by the mini screw extruder.

4. SELECTION OF MODIFICATION METHOD FOR IMPROVING POLYHYDROXYBUTYRATE-CO-VALERATE PROPERTIES FOR COMPRESSION MOLDING THIN SHEET

4.1 Introduction

In this study, PHBV was modified and fabricated in order to improve its drawbacks of high crystallinity resulting in brittleness and low elongation. This prevents it from being used in packaging applications where flexibility is important. To overcome this problem, PHBV was modified in different ways.

4.2 Fabrication of modified polyhydroxybutyrate-co-valerate

4.2.1 Fabrication of polyhydroxybutyrate-co-valerate blend with titanium dioxide

Titanium dioxide, TiO_2, in nanoparticle form was chosen in order to gain more toughening of PHBV. TiO_2 has been known as a filler for polymers that contributes to reinforcement of the polymers. The size of the particles has an important effect on mechanical properties. Large particles give mechanical strength to polymers but toughness decreases. Nanoparticles enhance modulus and toughness. Additionally, the particles have high surface area leading to more interfacial force between the particles and the polymers. However, they tend to agglomerate, so the shearing force during processing has to be high enough to overcome this behavior [107].

Neat PHBV resin was dried in a vacuum oven at 80 °C for 4 hours and cooled down in a desiccator at room temperature. PHBV resins and TiO_2 were introduced to a co-rotating mini twin screw extruder (DSM Micro 15 compounder, Netherlands). The extruder was set at 165 °C for all three temperature zones and a screw speed of 150 rpm. At the beginning of the blending process, PHBV was soft like rubber and tacky. The force increased steeply and reached a maximum, at which point the blend was well mixed. Further processing beyond the maximum shearing force degraded the PHBV since it is susceptible to thermal degradation so the point of maximum shear force was chosen as the processing time (a residence time of 1 min.). The PHBV/TiO_2 was transferred by a pre-heated cylinder set at 155 °C into the injection molding machine where the disk mold was attached and set at 40 °C. The PHBV/TiO_2 disk obtained was cooled at room temperature. Afterward, the PHBV/TiO_2 disk was placed in an aluminum frame of 180×180 mm^2 and thickness of 0.25 mm. Then it was compressed into a sheet in a compression molding machine at 165 °C and 20,000 psi for 5 min. The sheet was cooled by a cooling unit attached to the compression molding machine (M CARVER, Carver Laboratory Press, Menomonee Falls, Wisconsin, USA) for 15 min. The cooling unit used cold tap water.

4.2.2 Fabrication of polyhydroxybutyrate-co-valerate/poly(butylene adipate-co-terephthalate) blend

Ecoflex is a trade name for poly(butylene adipate-co-terephthalate), PBAT, which is a petroleum-based biodegradable polymer, first commercialized by BASF, Germany [8, 108]. It is an aliphatic-aromatic copolyester consisting of 1,4-butanediol acid, adipic acid, and terephthalic acid monomers [108, 109, 110]. The molecular structure of PBAT is shown in Figure 2.5

It is a soft material, which has low tensile strength, high elasticity, fracture durability, water and oil resistance and full biodegradability within a few weeks with the aid of enzymes [108, 110, 111]. In addition, it possesses high hydrophilicity and high gas permeability [108, 111]. PBAT is suitable for film extrusion and has been used in polymer blends for flexibility [8, 112, 113]. It has a low T_g which makes it suitable to be a toughening agent in polymer blends [113, 114, 115].

Ecoflex neat resin and PHBV neat resin were dried at 80 °C for 4 hours in a vacuum oven and cooled at room temperature in a desiccator. Both Ecoflex and PHBV neat resins in different ratios were simultaneous placed into the co-rotating mini twin screw extruder. The extruder was set at 165 °C for all three temperature zones and a screw speed of 150 rpm. The residence time was 2 min., at which time the maximum shearing force was reached. Thereafter, the process of transforming from the extrudate into the blended sheet was identical to that of the PHBV/TiO_2 blend.

4.2.3 Fabrication of polyhydroxybutyrate-co-valerate/poly(butylene adipate-co-terephthalate) /titanium dioxide blend

Both Ecoflex and TiO_2 can be effective in toughening polymer materials. In this experiment, blends of PHBV/Ecoflex/TiO_2 were developed for evaluation of the effect of both simultaneously.

PHBV and Ecoflex resins were vacuum dried at 80 °C for 4 hours and cooled in a desiccator at room temperature. All materials including TiO_2 were placed in the mini screw extruder which was set at 165 °C for all three temperature zones with a screw speed of 150 rpm. The residence time for the process was 2 min. at which time the maximum shearing force was reached. Thereafter, the process of transforming from the extrudate into the blended sheet was identical to that of the PHBV/TiO_2 blend.

4.2.4 Fabrication of polyhydroxybutyrate-co-valerate/triethyl citrate blend

Triethyl citrate (TEC) is used as a plasticizer. Plasticizers are lubricating materials that facilitate processability and give flexibility and elongation to polymers. Triethyl citrate has been used in many industries such as polymers and personal care and cosmetics [116, 117].

PHBV resin was vacuum dried at 80 °C for 4 hours and cooled at room temperature in a desiccator. PHBV was introduced to the extruder together with triethyl citrate. The extruder temperature in the three temperature zones was 165 °C and the screw speed was 150 rpm. The

reaction proceeded for 30 seconds at which time the maximum shearing force was reached. The transformation process from the extrudate to sheet was identical to the PHBV/TiO_2 blend.

4.2.5 Fabrication of polyhydroxybutyrate-co-valerate grafted with 2-hydroxyethyl methacrylate

2-Hydroxyethyl methacrylate (2HEMA) is a monomer used in many studies as a grafting monomer [118, 119, 120]. Grafting is a process that attaches monomers onto the polymer backbone, creating a branched structure in the polymer. Grafting improves elongation of the polymers [59, 60].

In this experiment, neat PHBV resin was dried in a vacuum oven at 80 °C for 4 hours and cooled in a desiccator at room temperature. 2HEMA and PHBV were placed into the mini twin screw extruder together with 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (L101) as an initiator. L101 is a peroxide used as a crosslinking agent with a molecular formula of $C_{16}H_{34}O_4$ and molecular weight of 290.44 g/mol. It is a colorless liquid with a boiling point of 55-57 °C at 7 mmHg and flash point of 65 °C [121]. The extruder was set at 165 °C for all three temperature zones with a screw speed of 150 rpm. The reaction time for the grafting process was 1 min. at which time the maximum shearing force was reached. The subsequent process, which transformed the extrudate to the grafted PHBV sheet, was similar to the PHBV/TiO_2 blend.

4.2.6 Fabrication of crosslinked polyhydroxybutyrate-co-valerate

Neat PHBV resin was dried at 80 °C for 4 hours in a vacuum oven and then cooled at room temperature in a desiccator. PHBV was introduced into the mini twin screw extruder together with L101 as an initiator (crosslinker). The extruder was set at 165 °C for all three temperature zones. The residence time (reaction time) was 1 min., selected on the basis of the maximum shearing force. The resulting extrudate was removed from the extruder in a strand form with low viscosity and tackiness. The extrudate was placed on aluminum trays at room temperature in order to cool and solidify. Afterwards, the extrudate was cut into pellets. The resulting crosslinked pellets were placed in a 180×180 mm^2 aluminum frame with a thickness of 0.25 mm. and then compressed between aluminum plates at 165 °C, 20000 psi for 5 min. to form compression molded sheet, as described previously.

4.3 Results and discussion

4.3.1 Visual characteristics of PHBV and modified PHBV

PHBV resin is yellow, rigid and soft under compression [122]. It possesses high crystallinity and poor thermal stability, which is a serious concern during processing [123]. Its slow crystallization rate and low melt strength are crucial properties that hinder the ability to process PHBV in cast and blown film applications. When PHBV is exposed to high temperature in the extrusion process, the melt is sticky, similar to a heated starch solution. It can stick to any surface to which it is exposed. PHBV melt possesses elastomeric behavior so its strands can be stretched. It also exhibits slow solidification, as was observed by Wang and Schertz [77]. After cooling down, it becomes rigid and does not adhere to surfaces. In order to obtain a desirable film, a super cooling system needs to be promptly connected to the die [124]. However, PHBV and all modified PHBVs in this study were sticky and could not be directly formed into sheet due to the unavailability of a super cooling unit. The PHBV sheet was flexible but brittle when folded. The PHBV resin is shown in Figure 4.1. Table 4.1 indicates visual characteristics of PHBV and modified PHBVs in different forms.

Figure 4.1 Poly(hydroxybutyrate-co-valerate) neat resins

The PHBV/TiO_2 1%wt. extrudate had low melt strength, elastomeric behavior and stuck to surfaces such as the die. This led to an inability to instantly form polymer sheets. It was necessary to form a disk-like shape in the injection molder before compression into film. After cooling down, the material became rigid but soft, similar to a hard rubber as indicated in Table 4.1. The PHBV/TiO_2 1%wt. sheet was yellow in color and showed brittleness (cracks) all over the sheet when it was bent slightly as shown in Figure 4.2 (a).

The PHBV/Ecoflex blends (PHBV/Ecoflex: 80/20, 70/30, and 50/50 %wt) possessed low melt strength, stickiness and were elastomeric. However, with an increase in Ecoflex content, the extrudates appeared to have a bit more melt strength. All PHBV/Ecoflex blends could not be formed into sheets directly from the extrudate since they stuck to the die surface. They needed to be previously formed into a disk-like shape in the injection molder. When cooled, the

PHBV/Ecoflex blends were yellow, rigid but soft, similar to a hard rubber. The PHBV/Ecoflex blend sheets were flexible but brittle if folded as shown in Table 4.1.

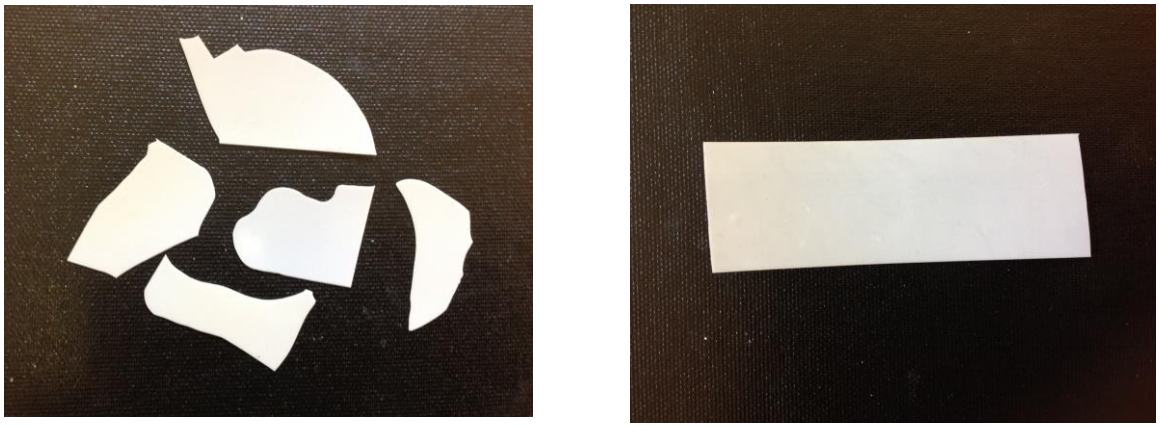
The PHBV/Ecoflex/TiO_2 blends (PHBV/Ecoflex/TiO_2: 79/20/1, 69/30/1, and 49.5/49.5/1 %wt.) had low melt strength, elastomeric texture, and stickiness. When the Ecoflex content increased, the blended extrudates showed higher melt strength. Yet, the extrudates of the blends could not be formed directly into sheets due to stickiness in the die. A disk-like shape was necessary to be formed in the injection molder. The blends were rigid but soft like a hard rubber. The compressed PHBV/Ecoflex/TiO_2 sheets, when cooled, were yellow, flexible but brittle when bent for PHBV/Ecoflex/TiO_2 79/20/1 and 69/30/1 wt., and brittle when folded for PHBV/Ecoflex/TiO_2 49.5/49.5/1 wt.

The PHBV/TEC (80/20 %wt.) blend had low melt strength, elastomeric characteristics and stickiness. This led to an inability to immediately form a PHBV/TEC sheet. Therefore, a disk-like shaped PHBV/TEC was produced in the injection molding machine. The blend was yellow in color, rigid but soft, similar to hard rubber when cooled. However, an oily liquid was observed on the surface of the PHBV/TEC blend due to the migration of the plasticizer. Next, it was compressed into sheet. The PHBV/TEC blend sheet was brittle when folded.

Grafted PHBVs with 2HEMA (PHBV/2HEMA: 90/10 and 70/30 %wt.) had low melt strength, stickiness and elastomeric behavior. Like other modified PHBV as stated previously, they could not be formed as sheet directly from the extrudates because the blended extrudates were sticky to surfaces like the die. It was necessary to form a disk-like shape in the injection

molder. The grafted PHBVs with 2HEMA were yellow, rigid but soft like hard rubber, when cooled. The grafted sheets were brittle when folded.

Crosslinked PHBV formed using L101 2%wt. possessed low melt strength, elastomeric behavior and stickiness. The extrudate was discharged from the extruder so rapidly that the preheated cylinder could not immediately collect the extrudate for injection molding. Instead, the extrudate was collected as strands. When cooled, it was cut into pellets. The material was yellow, rigid but soft like a hard rubber. The crosslinked PHBV sheet, as shown in Figure 4.2 (b), was more flexible than PHBV but still was brittle when it was folded.



a b

Figure 4.2 Brittleness of PHBV/TiO_2 sheet (a) and crosslinked PHBV sheet (b)

Table 4.1 Visual characteristics of PHBV and modified PHBVs in different forms in the experiment.

Material	Extrudate	Disk form	Sheet form
Neat PHBV	-	-	Yellow, flexible but brittle when folded
Blend of PHBV/TiO_2 nanoparticle 1% wt.	Low melt strength, Sticky when heated, Rigid when cooled	Rigid but soft like hard rubber	Yellow, brittle on the sheet when slightly bent
Blend of PHBV/Ecoflex : 80/20 %wt			Yellow, flexible but brittle when folded
Blend of PHBV/Ecoflex : 70/30 %wt			Yellow, flexible but brittle when folded
Blend of PHBV/Ecoflex : 50/50 %wt			Yellow, flexible but brittle when folded
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt			Yellow, flexible but brittle when bent
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt			Yellow, flexible but brittle when bent
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt			Yellow, flexible but brittle when folded
Blend of PHBV/Triethyl citrate : 80/20 %wt		Rigid but soft like hard rubber, Oily liquid migration to the material surface	Yellow, flexible but brittle when folded
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)		Rigid but soft like hard rubber	Yellow, flexible but brittle when folded
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)			Yellow, flexible but brittle when folded
Crosslinked PHBV (L101 2%wt) rxn time 1 min			Yellow, flexible but brittle when folded

4.3.2 Mechanical properties of PHBV and modified of PHBV

The most important property for polymer sheet and film is flexibility, which can be indicated by elongation. The selection of modification methods for the research was based on improving elongation. Basically, neat PHBV is brittle (low elongation); tacky, which is a problem in film processing for both cast and blown film; and has low melt strength. PHBV has mechanical properties similar to those of polypropylene [123]. As a first attempt, TiO_2 nanoparticles were chosen as a toughening agent for neat PHBV. According to Carballeira et al., TiO_2 contributed to toughness of epoxy resin [107]. Also TiO_2 increased the modulus of elasticity [125]. In this study, the PHBV/TiO_2 sheet had cracks all over the sheet. The tensile strength of the modified PHBV was less than of neat PHBV, as was elongation. However, the difference in tensile strength was not statistically significant as opposed to the elongation. The lower elongation at break in PHBV/TiO_2 occurred since TiO_2 probably aggregated and interfered with the PHBV structure. According to Zhu et al., PLA with the incorporation of TiO_2 had lower elongation at break due to aggregation of TiO_2 in the PLA matrix [126]. This material is not suitable for sheet/film applications. Mechanical properties, tensile strength and elongation at break for all modified PHBVs are shown in Table 4.2, Figure 4.3 and Figure 4.4.

In the second attempt, poly(butylene adipate-co-terephthalate), PBAT or Ecoflex, was used as a blend with PHBV. PBAT has been used in blending with other polymers for flexibility [113]. Eslami et al. reported that ductility of PLA/PBAT blends increased with the presence of PBAT, which consequently contributed to higher strain at break [127]. The resulting PHBV/Ecoflex blends in all compositions appeared to have significantly lower elongation at break than neat

PHBV, as indicated in Table 4.2 and Figure 4.4. According to Shahlari et al., elongation of PLA/PBAT blends improves when the content of PBAT is more than that of PLA. In that case PLA/PBAT 20/80 resulted in high elongation and PLA was present as the dispersed phase and PBAT was the continuous phase in the blend [113]. In this experiment, then, lower elongation of the blends than neat PHBV was attributed to less PBAT in the blend than PHBV. In this research, the main focus is PHBV. Therefore, PBAT content that was more than half of the material was not of interest.

In the third attempt, PBAT and TiO_2 were blended with PHBV. In this experiment, it was expected that both PBAT and TiO_2 might contribute to flexibility of the blends. However, the polymer blends in all ratios of PHBV and PBAT at TiO_2 1%wt. possessed significantly lower tensile strength and elongation than neat PHBV. This is because the PBAT ratio in the blends was less than PHBV and TiO_2 may aggregate in the blends as stated in the discussion of the PHBV/TiO_2 blend and PHBV/PBAT blends. Tensile strength and elongation are shown in Table 4.2, Figure 4.3 and Figure 4.4.

In the fourth attempt, triethyl citrate (TEC) was added to PHBV in order to increase flexibility and elongation of PHBV and also promote processability. Zhang and Sun proved that acetyl triethyl citrate, a plasticizer, improved elongation of a PLA/starch/maleic anhydride blend [128]. However, the PHBV/TEC blends showed lower elongation and tensile strength than PHBV, in accordance with the result that was reported by Yang et al. [129]. Epoxidized soybean oil (ESO) and TEC were used as plasticizer of ethyl cellulose (EC) film. It was found that as the content of TEC and ESO increased, elongation at break of the films decreased when

compared to EC without plasticizer [129]. Table 4.2, Figure 4.3 and Figure 4.4 show the tensile strength and elongation at break of the TEC-plasticized PHBV. TEC did not provide flexibility of the PHBV/TEC blend.

In the fifth attempt, 2HEMA and PHBV were introduced into the reactor along with L101 as an initiator for grafting. A grafting process can be used to improving elongation through creation of a graft polymer. According to Wang et al., elongation of the graft copolymer of poly(caprolactone monoacrylate) and cellulose diacetate was found to be higher with an increase of degree of grafting [130]. Additionally, elongation of ethyl methacrylate grafted onto acacia gum improved when compared to that of acacia gum [131]. In contrast, in this experiment, the elongation of 2HEMA grafted onto PHBV in two different ratios, PHBV/2HEMA 70/30 and 90/10, were significantly less than PHBV itself, as were the tensile strengths. Similarly, Wang and Schertz reported that PHBV-g-2HEMA they obtained was brittle and rigid [77]. Table 4.2, Figure 4.3 and Figure 4.4 show the mechanical properties of PHBV-g-2HEMA. This experiment did not produce grafted PHBV that was suitable for use in applications that require flexibility.

The final attempt was based on observation of the melting behavior of PHBV. The flow behavior of neat PHBV in the liquid state was similar to that of uncured natural rubber. In order to cure the rubber from a liquid to an elastic material, vulcanization is used. Vulcanization is a crosslinking process and has been widely used in the rubber industry. Crosslinking is a process in which the molecular chains of a polymer are covalently bonded within and/or between other polymer molecular chains, resulting in a network matrix in multiple directions. The crosslinked

polymer possesses greater elongation than the un-crosslinked. In this experiment, neat PHBV and L101 2%wt. as an initiator for the reaction were introduced into the mini twin screw extruder. The crosslinking reaction (chemical reaction) took place for 1 min. The resulting crosslinked PHBV exhibited twice the elongation at break as the neat PHBV and the tensile strength was also a little higher. However, the apparent increase in tensile strength of the crosslinked PHBV was not statistically significant. Table 4.2 and Figures 4.3 and 4.4 illustrate the mechanical properties of the crosslinked PHBV. The results of this experiment agreed with the findings about crosslinked PHBV reported by Fei et al. [93], who found that PHBV crosslinked with dicumyl peroxide as initiator had higher elongation than neat PHBV. Therefore, the crosslinked PHBV with L101 as initiator obtained in this study was selected to potentially use in flexible applications.

Table 4.2 Mechanical properties of all compositions of modified PHBV material sheets

Material	Tensile strength (MPa)	Elongation at break (%)
Neat PHBV	19.84 ± 0.54^{a}	15.04 ± 0.59^{b}
Blend of PHBV/TiO_2 nanoparticle 1%wt	18.64 ± 0.55^{a}	$10.60 \pm 0.50^{c,d}$
Blend of PHBV/Ecoflex : 80/20 %wt	$9.64 \pm 1.34^{c,d}$	$5.43 \pm 1.27^{e,f,g,h}$
Blend of PHBV/Ecoflex : 70/30 %wt	$8.58 \pm 0.89^{d,e}$	$8.37 \pm 1.74^{c,d,e}$
Blend of PHBV/Ecoflex : 50/50 %wt	4.16 ± 0.45^{f}	$4.47 \pm 0.12^{f,g,h}$
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	12.54 ± 1.02^{b}	$3.57 \pm 0.65^{g,h}$
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	$11.30 \pm 1.20^{b,c}$	$3.83 \pm 1.29^{g,h}$
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	$6.31 \pm 0.56^{e,f}$	$6.47 \pm 1.07^{e,f,g}$

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).

Table 4.2 (Cont'd)

Material	Tensile strength (MPa)	Elongation at break (%)
Blend of PHBV/Triethyl citrate : 80/20 %wt	4.82 ± 1.19^{f}	2.57 ± 0.31^{h}
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	$10.91 \pm 0.16^{b,c,d}$	$7.51 \pm 0.02^{d,e,f}$
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	12.54 ± 0.21^{b}	11.40 ± 1.51^{c}
Crosslinked PHBV (L101 2%wt) rxn time 1 min	20.45 ± 0.66^{a}	37.20 ± 2.25^{a}

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time in the extruder of crosslinked PHBV was 1 min.

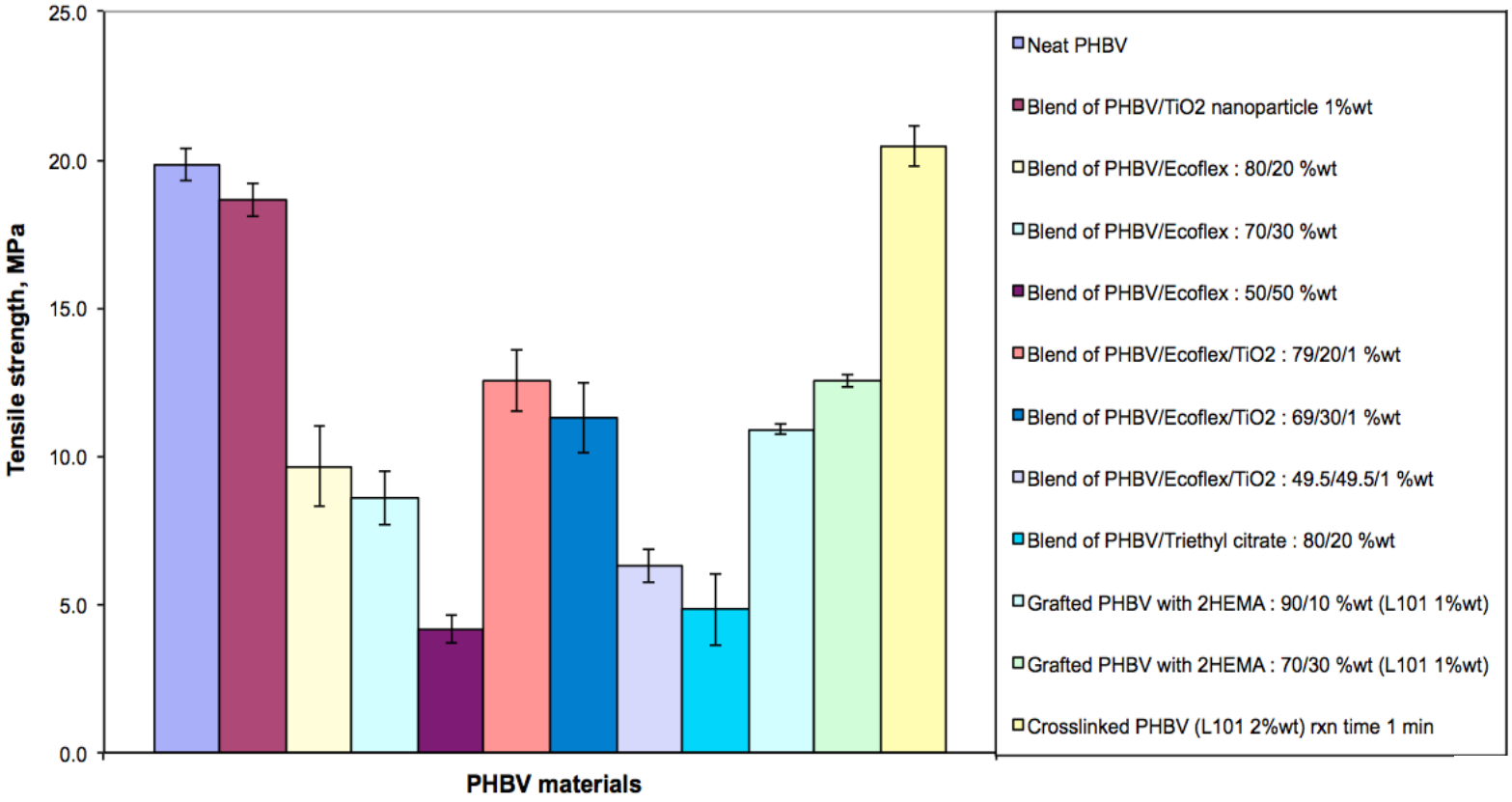


Figure 4.3 Tensile strength of PHBV material sheets

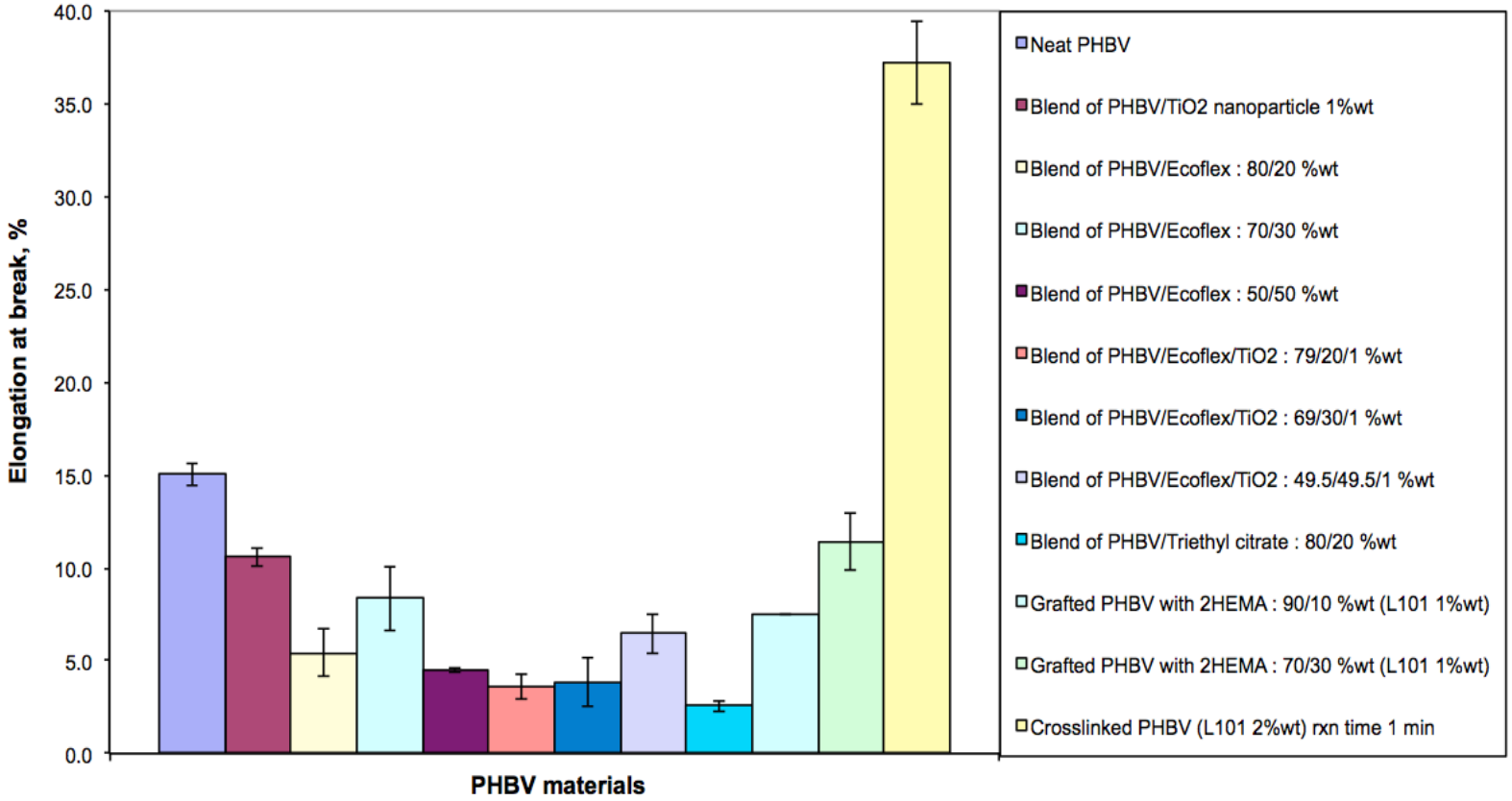


Figure 4.4 Elongation at break of PHBV material sheets

4.3.3 Thermal properties of PHBV and modified PHBV

Differential scanning calorimetry (DSC) was used in the study of thermal properties of PHBV and the modified PHBV materials. Neat PHBV shows two relatively high melting temperatures (T_m). The lower melting temperature corresponds to less perfect crystals which melt at a lower temperature. Then, PHBV recrystallizes with a more perfect structure and subsequently melts at a higher temperature [132, 133, 134, 135]. Moreover, the amount of hydroxyvalerate in HPBV influences the T_m of PHBV. With a higher HV portion in PHBV molecular chains, the T_m of PHBV decreases [136]. In Figure 4.5, the DSC indicates two T_ms at 149.31±0.67 and 156.82±0.56 °C. The glass transition temperature (T_g) of PHBV was not observed in this research. However, Ferreira et al. reported that the T_g of neat PHBV was around 0 °C and could not easily be noticed. This is due to the fact that PHBV crystallizes rapidly and there is little amorphous matrix present. These characteristics result in less mobility of the polymer for characterization of T_g [137]. The peak crystallization temperature (T_c) of PHBV was 107.71±0.40 °C as indicated in Figure 4.6. T_c is the temperature at which maximum crystal formation occurs. The heat of fusion (ΔH_m) indicates the heat required for melting crystallites of polymer. ΔH_m of PHBV was 65.31±0.33 J/g. The crystallinity of PHBV can be obtained by using equation 4.1 [138]. The thermal properties of PHBV are indicated in Table 4.3

$$\%Crystallinity = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad (4.1)$$

where ΔH_m is the enthalpy of melting of PHBV (J/g)

ΔH_m^0 is the enthalpy of melting of 100% crystallinity PHBV (perfect crystalline PHBV) that is 109 J/g [139]

w is the weight fraction of PHBV in the material.

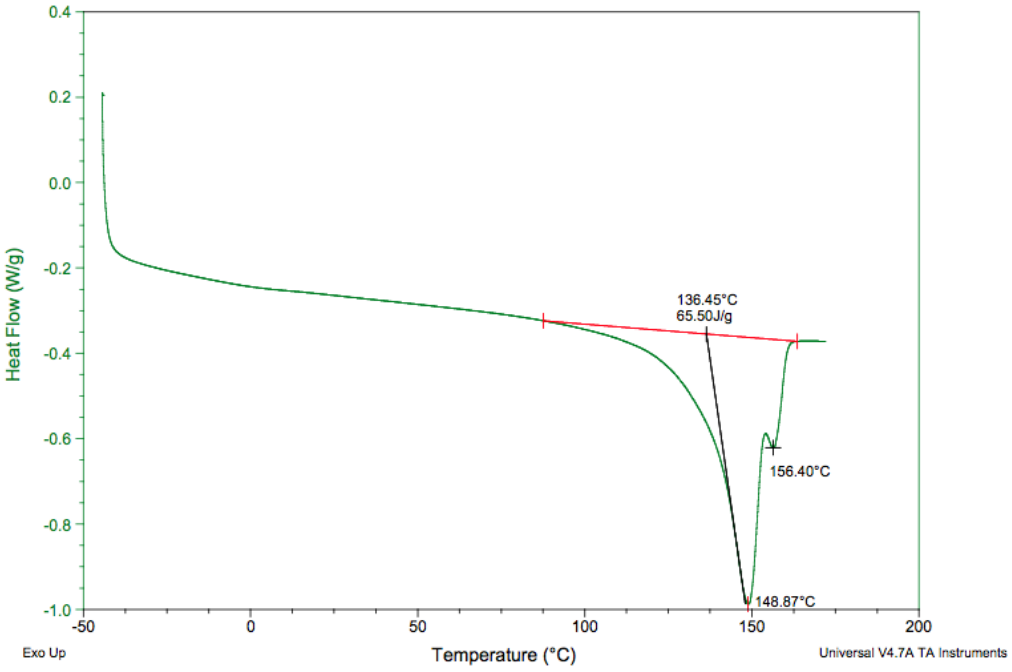


Figure 4.5 Two melting temperatures (T_m) of neat PHBV

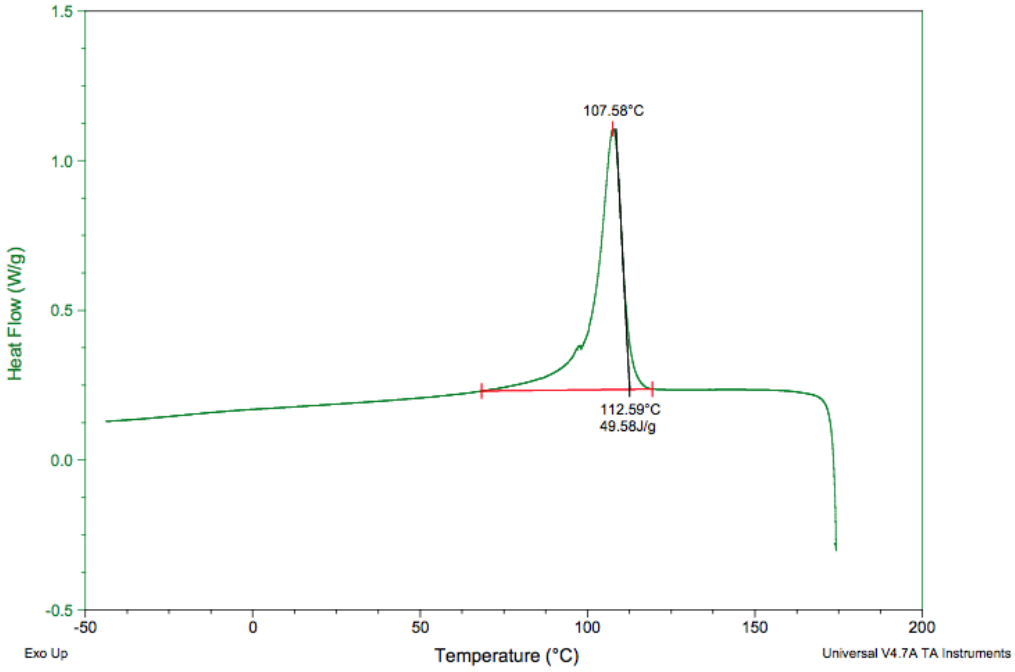


Figure 4.6 Crystallization temperature (T_c) of neat PHBV

Table 4.3 Thermal properties of all compositions of modified PHBV

Material	**T_c (°C)**	**T_m (°C)**		**Heat of fusion, ΔH_m (J/g)**	**PHBV Crystallinity (%)**
Neat PHBV	107.71±0.40[a]	149.31±0.67[b]	156.82±0.56[b,c]	65.31±0.33[a]	59.92±0.30[a]
Blend of PHBV/TiO_2 nanoparticle 1%wt	109.88±0.27[a]	153.20±0.27[a]	159.77±0.22[a]	59.49±0.22[b]	55.13±0.20[b,c]
Blend of PHBV/Ecoflex : 80/20 %wt	70.24±1.05[e]	142.96±0.53[e]	156.64±0.58[c]	50.77±0.17[c,d]	58.22±0.19[a,b]
Blend of PHBV/Ecoflex : 70/30 %wt	68.77±1.14[e]	143.70±1.23[d,e]	156.81±0.66[b,c]	46.12±0.85[e,f]	60.44±1.11[a]
Blend of PHBV/Ecoflex : 50/50 %wt	75.83±0.20[d]	143.34±0.36[e]	156.45±0.29[c]	31.73±0.18[i]	58.23±0.33[a,b]
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	84.68±0.49[c]	145.83±0.20[c,d]	157.73±0.12[b,c]	49.02±0.24[d,e]	56.93±0.28[a,b,c]
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	81.57±0.49[c]	146.01±0.14[c,d]	157.88±0.20[b,c]	43.95±0.38[f,g]	58.43±0.51[a,b]
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	82.46±1.17[c]	146.59±0.33[c]	158.39±0.28[a,b]	31.85±0.14[i]	59.03±0.26[a]
Blend of PHBV/Triethyl citrate : 80/20 %wt	70.39±5.37[e]	130.98±0.88[g]	146.51±0.38[e]	40.54±2.92[h]	46.49±3.35[d]
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	105.00±0.18[a,b]	149.62±0.23[b]	158.01±0.44[b,c]	53.07±1.35[c]	54.10±1.37[c]
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	101.04±2.10[b]	146.46±1.84[c]	156.33±1.22[c]	40.88±1.31[g,h]	53.58±1.71[c]
Crosslinked PHBV (L101 2%wt)	100.00±1.24[b]	140.16±0.81[f]	148.89±0.98[d]	51.42±0.32[c,d]	47.17±0.29[d]

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time in the extruder of crosslinked PHBV was 1 min.

Thermal decomposition of PHBV can be investigated using thermogravimetric analysis (TGA). As can be seen in Figure 4.7, the TGA thermogram of PHBV is steep which indicates a narrow decomposition temperature range. PHBV exhibited onset and maximum temperatures (at which the decomposition rate was maximum), of around 300 °C and 330 °C, respectively. The ending of decomposition was around 340 °C.

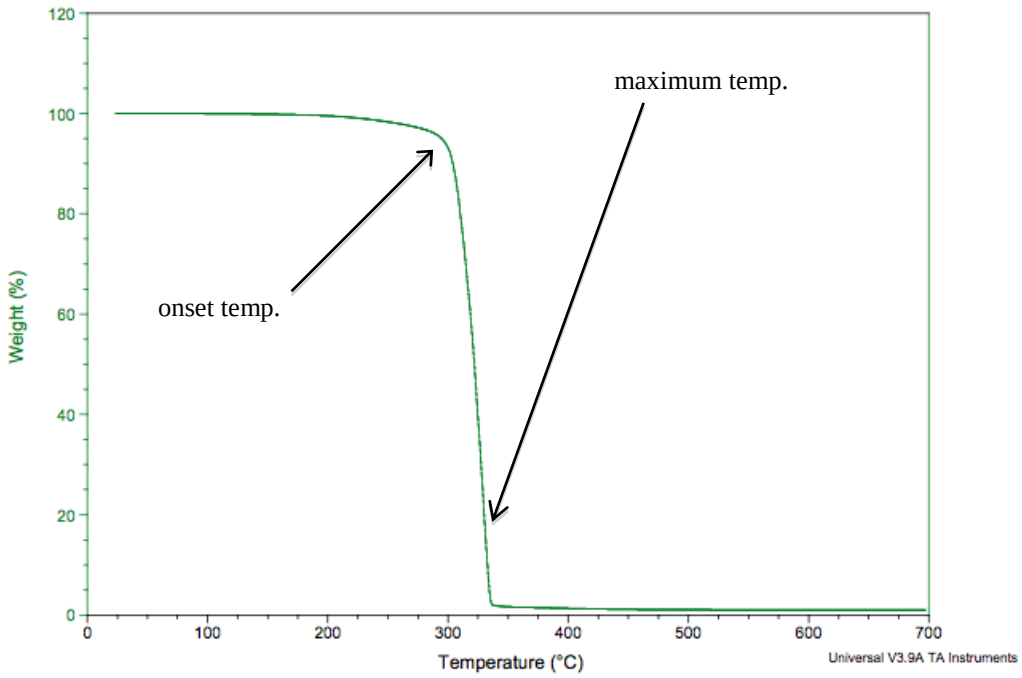
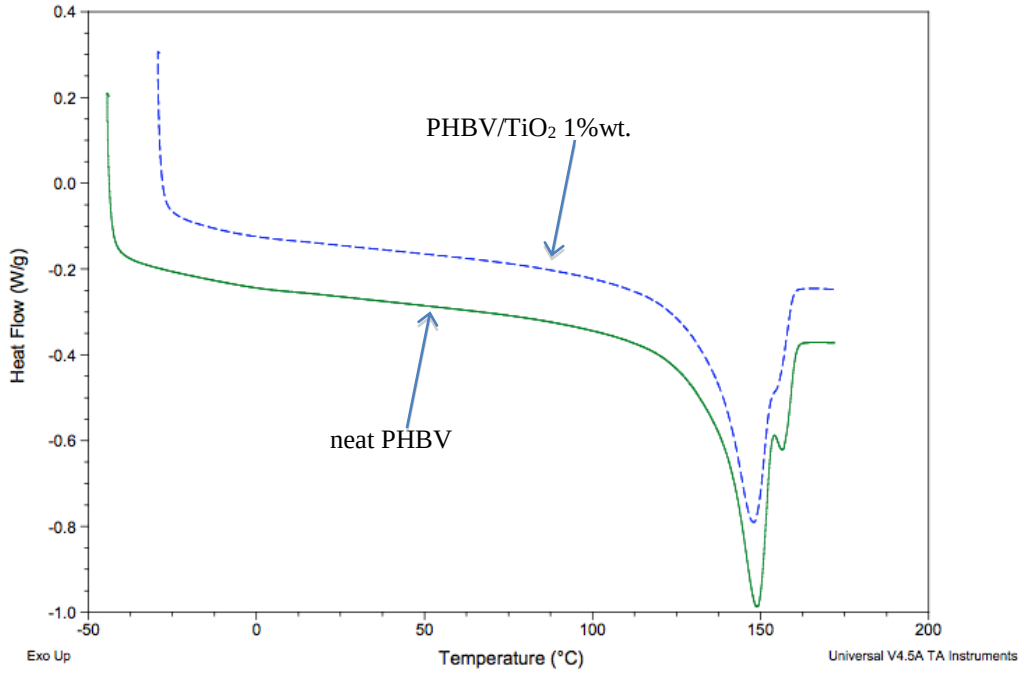


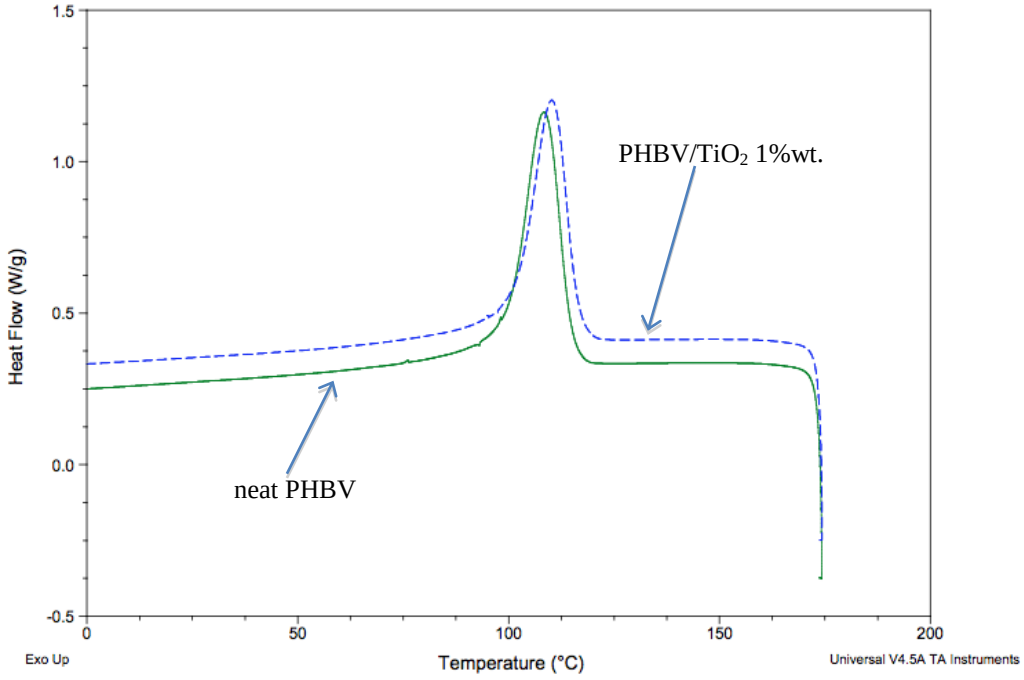
Figure 4.7 Thermal decomposition profile of neat PHBV

The presence of other substances in the PHBV matrix is crucial to thermal properties of the materials. In the first trial, the PHBV/TiO_2 material had two melting temperature peaks (153.20±0.27 °C and 159.77±0.22 °C) similar to those in the heating profile of neat PHBV as shown in Table 4.3. and Figure 4.8 (a). Since TiO_2 is an inorganic compound which has a much higher melting temperature, around 1855 °C [140], the melting points in the thermal cycle involved PHBV. As stated previously, PHBV has two melting points which involved

primary formed crystallites melting at the lower temperature and the recrystallized matrix formed during heat exposure in the DSC melting at the higher temperature [132, 133, 134, 135]. However, in this study, the two melting temperatures of PHBV/TiO_2 shifted slightly to higher temperatures when compared to those of PHBV. This result corresponded to the result from Buzarovka et al., which reported the T_ms of PHBV/TiO_2 blends slightly shifted to higher temperatures, although the T_ms were not dependent upon the TiO_2 quantity [135]. The crystallization temperature (T_c) of the PHBV/TiO_2 blend (109.88±0.27 °C) in this study was not statistically different when compared to PHBV and its cooling cycle behavior in DSC was similar to that of neat PHBV as can be seen in Figure 4.8 (b). According to Buzarovka et al., although the PHBV/TiO_2 blend had slightly higher T_c with an increase in TiO_2 content, there was no robust evidence that TiO_2 showed a nucleating effect on the polymer [135]. Thus, in this study, PHBV/TiO_2 with no significant difference in T_c indicated that TiO_2 probably did not have a significant nucleating effect to facilitate the crystallinity of the PHBV/TiO_2 blend [135]. The heat of fusion of the PHBV/TiO_2 (59.49±0.22 J/g) was slightly lower than that of PHBV. This indicated a slightly lower percent crystallinity in the blend than in PHBV. For thermal decomposition of PHBV/TiO_2, Buzarovka et al. stated that with an increase of TiO_2 in the blend, the decomposition temperature slightly shifted to a higher value [135]. In this study, in contrast, thermal decomposition of PHBV/TiO_2 and PHBV was essentially identical, as can be seen in Figure 4.9. This might be because the TiO_2 content in the PHBV/TiO_2 was so small that it did not influence the thermal behavior of the PHBV.



(a)



(b)

Figure 4.8 Endothermic (a) and exothermic (b) profiles of neat PHBV and PHBV/TiO_2 1%wt.

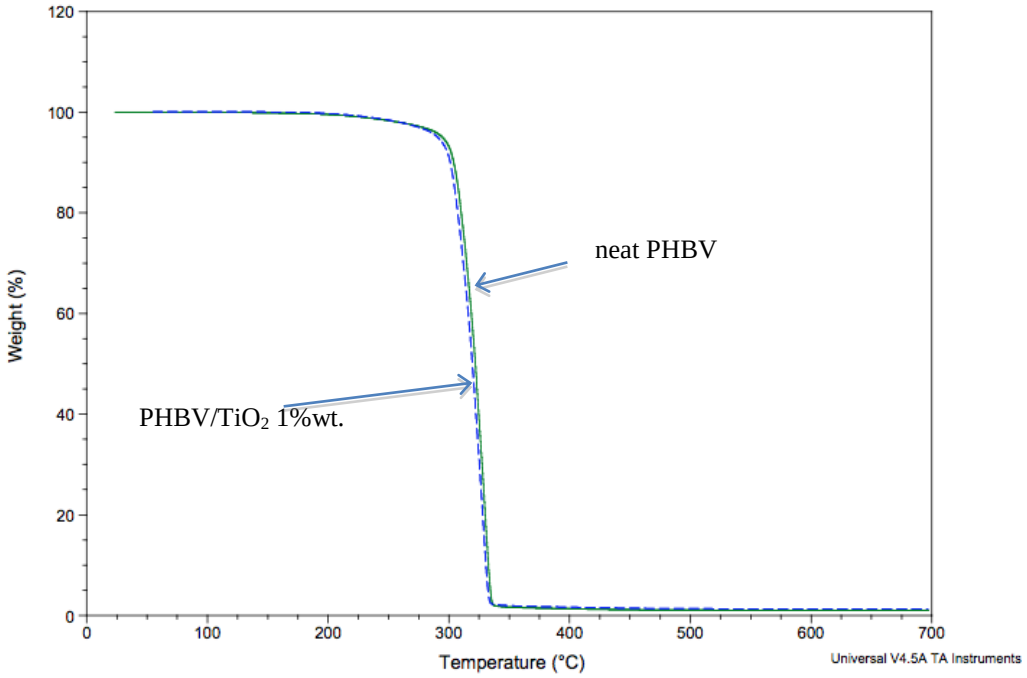


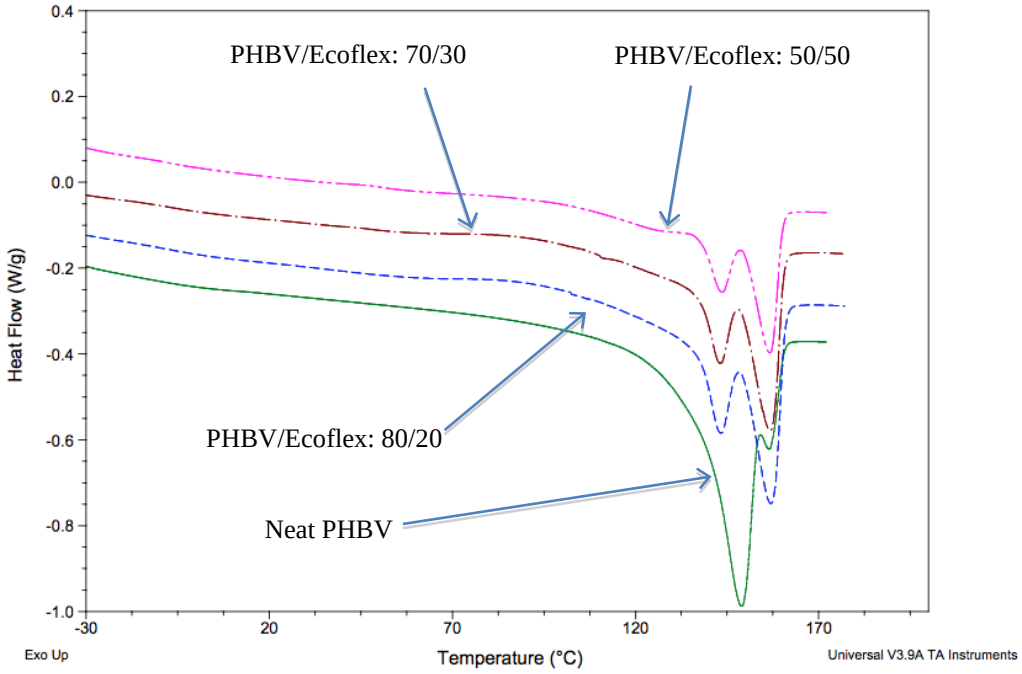
Figure 4.9 Thermal decomposition profiles of PHBV and PHBV/TiO_2 1%wt.

Ecoflex blended with PHBV changed the thermal transition characteristics of the blend. Figure 4.10 shows the heating cycle (a) and cooling cycle (b) profiles of PHBV and PHBV/Ecoflex blends. Table 4.3 shows the thermal properties of PHBV/Ecoflex at different ratios of Ecoflex. The T_ms of the PHBV/Ecoflex blends were 142.96±0.53 °C and 156.64±0.58 °C for 80/20 %wt., 143.70±1.23 °C and 156.81±0.66 °C for 70/30 %wt., and 143.34±0.36 °C and 156.45±0.29 °C for 50/50 %wt. The T_ms of the three compositions of PHBV/Ecoflex blends were not significantly different from each other. However, they were lower than those of the neat PHBV sheet. These results corresponded to the behavior of PHBV/Joncryl blends reported by Duangphet et al [141]. The crystallization rate can be indirectly indicated by the T_m; the lower T_m indicates reduced crystallization [141]. In this study, the heat of fusion values of the blends (50.77±0.17 J/g for 80/20, 46.12±0.85 J/g for 70/30, and 31.73±0.18 J/g for

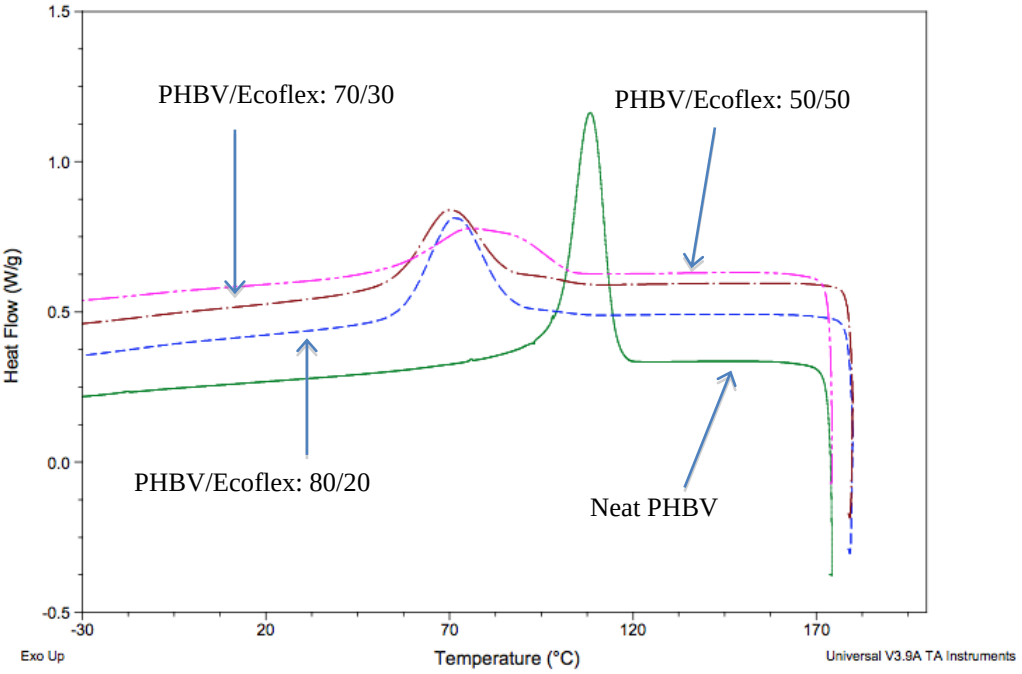
50/50) were lower than the neat PHBV's due to the lesser amount of PHBV in the blends than the neat PHBV. However, the crystallinities of the PHBV/Ecoflex blends were not significantly different from each other and from the neat PHBV, as shown in Table 4.3.

All T_cs of the blends (70.24±1.05 °C for 80/20, 68.77±1.14 °C for 70/30, and 75.83±0.20 °C for 50/50) were considerably lower than the T_c of neat PHBV. The T_c of the 80/20 and 70/30 PHBV/Ecoflex blends were not statistically different from each other whereas the T_c of the 50/50 PHBV/Ecoflex blend was higher than those of the 80/20 and 70/30 blends. This result differed from the study of PHBV/PLLA blends by Ferreira et al. who found no T_c variation of PHBV and PLLA in the blend compared to pure PHBV and pure PLLA. This was because PHBV and PLLA showed a phase separation in which each of them segregated from the blend to form pure domains [137].

Thermal decomposition curves for PHBV and PHBV/Ecoflex blends are shown in Figure 4.11. TGA indicates that PHBV thermally degraded at a lower temperature than PHBV/Ecoflex 50/50. The blends between PHBV and Ecoflex have two thermal degradation steps, which corresponded to the PHBV and Ecoflex components. PHBV in the blends was degraded first, at a lower temperature than that at which neat PHBV degraded, and later Ecoflex degraded at a higher temperature. This thermal behavior of the blend is similar to the polyhydroxyalkanoate (PHA)/epoxidized broccoli oil blend prepared by Audic et al. PHA first degraded and then EBO degraded at a higher temperature. The thermal profile exhibited two different degradation steps [142].



(a)



(b)

Figure 4.10 Endothermic (a) and exothermic (b) profiles of neat PHBV and PHBV/Ecoflex blends

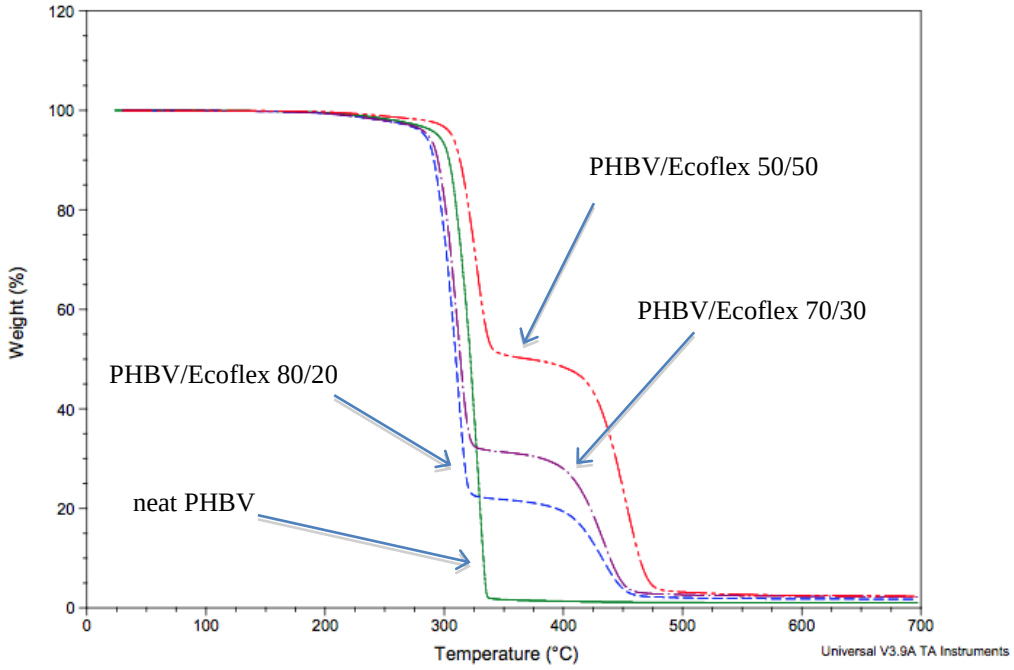
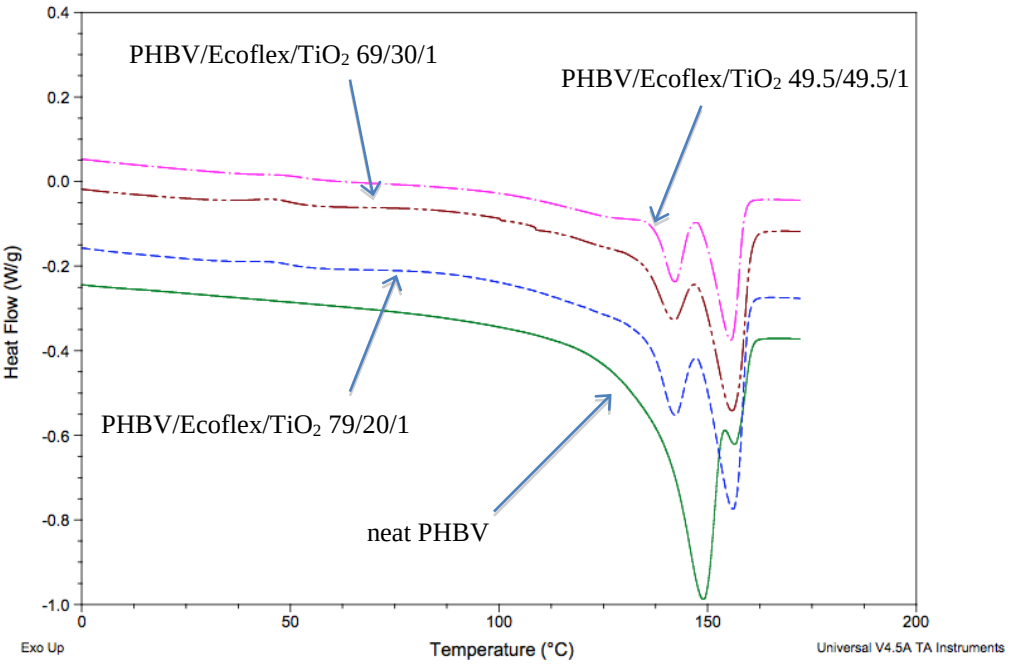


Figure 4.11 Thermal decomposition profiles of neat PHBV and PHBV/Ecoflex blends

In the blend of PHBV/Ecoflex/TiO_2 in the third trial, the thermal transition characteristics of all ratios of the blends were different from those of the neat PHBV but not different from each other, as illustrated in Figure 4.12 and Table 4.3. The presence of TiO_2 in the blends did not have an important effect on T_ms, heat of fusion, or crystallinity of PHBV in the blends when compared to PHBV/Ecoflex blends even though all T_cs of the PHBV/Ecoflex/TiO_2 blends were slightly higher than those of the PHBV/Ecoflex blends. The thermal decomposition characteristics of the blends were also similar to those of PHBV/Ecoflex blends as shown in Figure 4.13. Table 4.3 indicates thermal properties of the blends. Figure 4.12 shows heating cycle and cooling cycle profiles of PHBV and PHBV/Ecoflex/TiO_2 blends.



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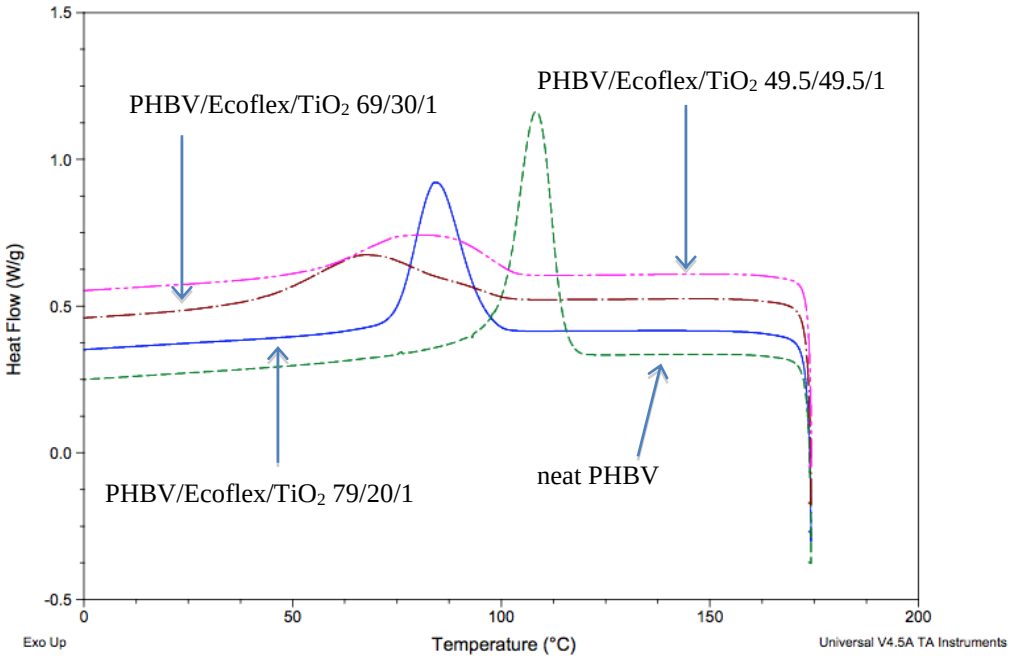
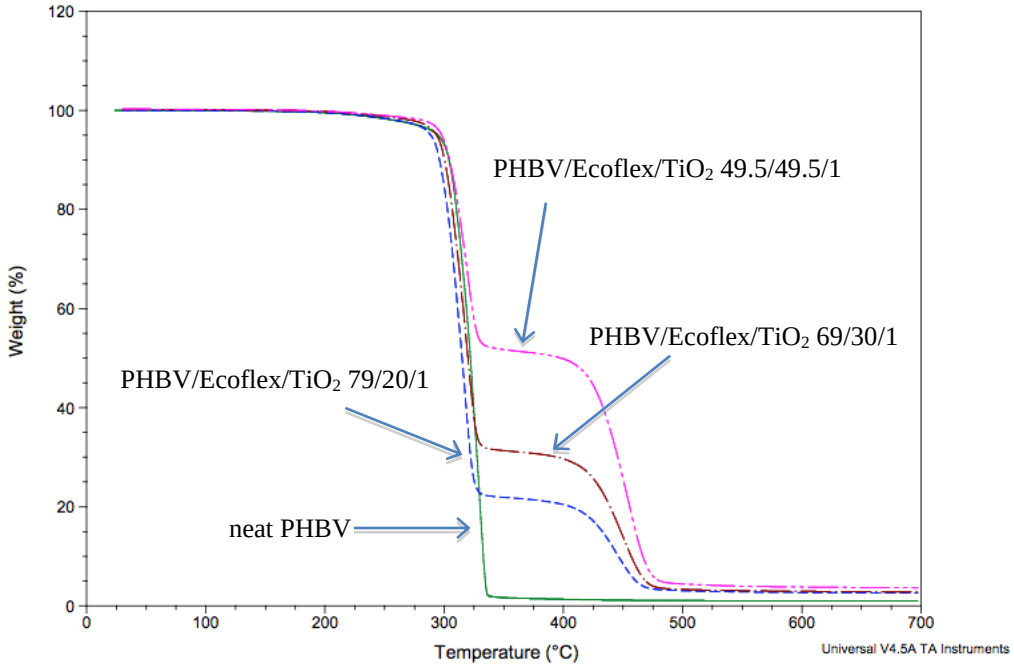


(b)

Figure 4.12 Endothermic (a) and exothermic (b) profiles of neat PHBV and PHBV/Ecoflex/TiO2 blends

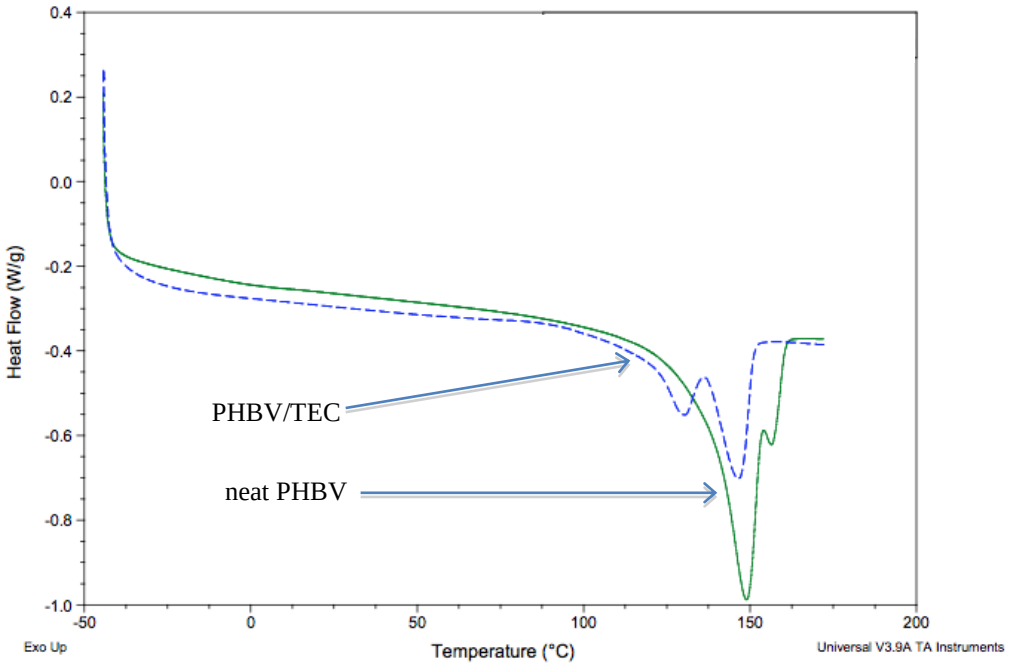


(b)

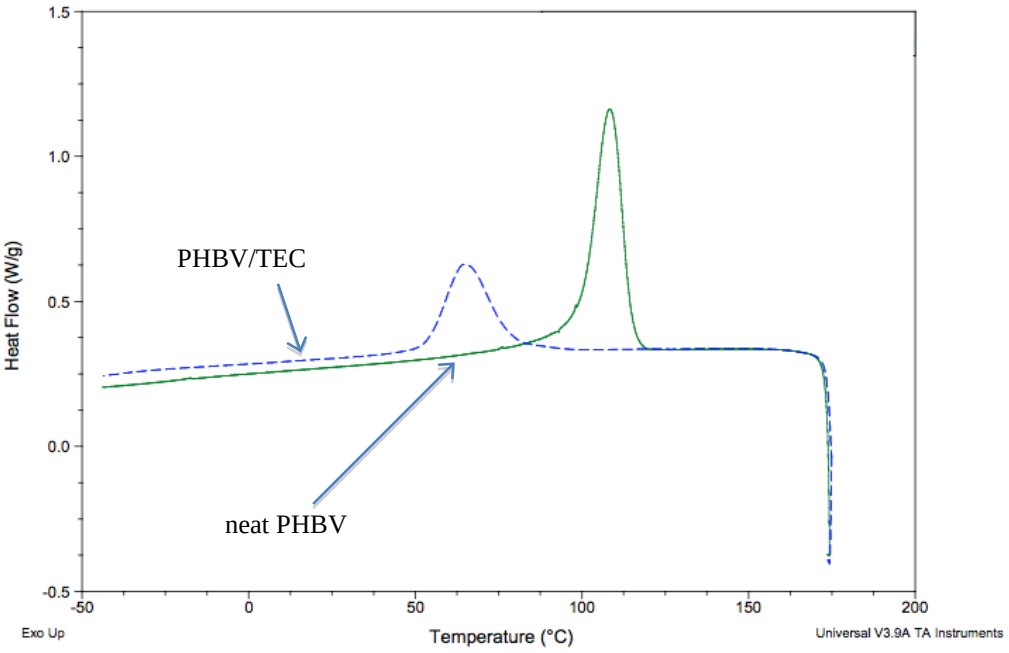
Figure 4.13 Thermal decomposition profiles of neat PHBV and PHBV/Ecoflex/TiO_2 blends

As discussed, Triethyl citrate is a plasticizer that is widely used to impart flexibility. Table 4.3 shows the thermal transition properties of the blends. The blend of PHBV/TEC in the fourth trial was found to have different thermal behavior than neat PHBV. The heat flows in the endothermic and exothermic cycle are illustrated in Figure 4.14. The two T_m points of PHBV/TEC (130.98±0.88 °C and 146.51±0.38 °C) were lower than those of neat PHBV, as was the heat of fusion. This result is in accordance with the decrease of T_m of a PLA/starch/methylenediphenyl diisocyanate blend with TEC as a plasticizer found by Ke et al [143]. The T_m of a PHBV blend with 20% wt. of different plasticizers such as dibutyl phthalate (DBP) and TEC prepared by Choi et al. [144] also decreased. The T_m is an indicator of the lamella thickness of the crystallites in the polymers and the plasticizer in the blend contributes

to reduction in the thickness [144]. With the inclusion of TEC in the PHBV/TEC blend, then, the T_m of the blend and heat of fusion of the blend appeared to be lower when compared to those of neat PHBV. This indicates lower crystallinity of the PHBV in the blend. The T_c also shifted to a lower temperature in the blend, which corresponds to the result obtained in a PLA/starch/maleic anhydride blend with TEC as a plasticizer and a PLA/starch blend with acetyl triethyl citrate (AC) and TEC added as plasticizers [128, 145]. Heat of fusion (ΔH_m) of the PHBV/TEC blend (40.54±2.92 J/g) was lower than the neat PHBV. The result agreed with the decrease in ΔH_m of polyvinyl alcohol (PVA)/glycerin blend. With an increase of glycerin (plasticizer) content in the blend, ΔH_m of the PVA/glycerin blend decreased [146]. Figure 4.15 indicates the thermal decomposition profile of the blend. The thermal decomposition temperature of the PHBV/TEC blend was lower than that of neat PHBV due to the presence of TEC in the blend. The PHBV/TEC blend started to slightly degrade at a low temperature, around 150 °C, and reached maximum weight loss at a temperature of about 300 °C. TEC shifted the decomposition temperature of the blend to a lower point. Thus, TEC contributed to decreased thermal stability of the blend compared to neat PHBV.



(a)



(b)

Figure 4.14 Endothermic (a) and exothermic (b) profiles of neat PHBV and PHBV/TEC blends

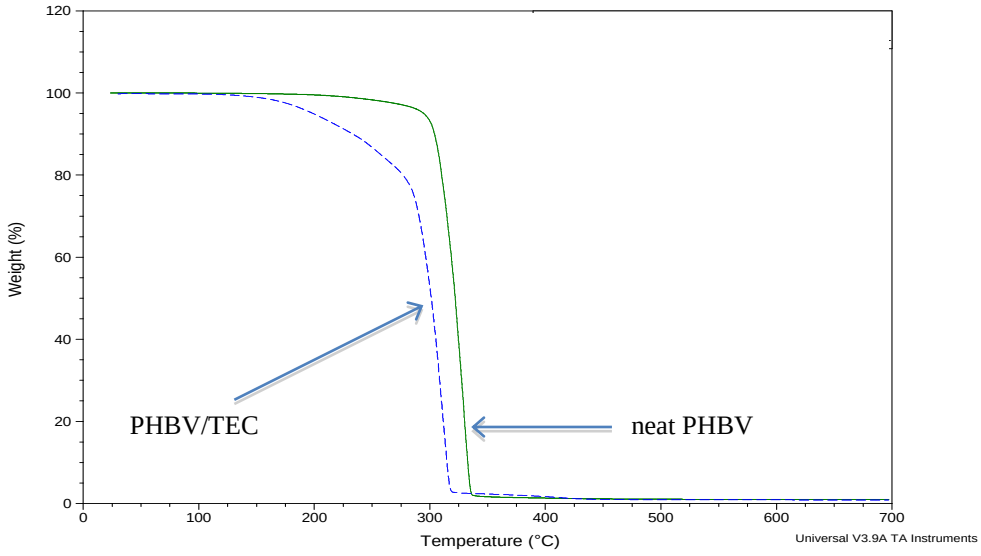
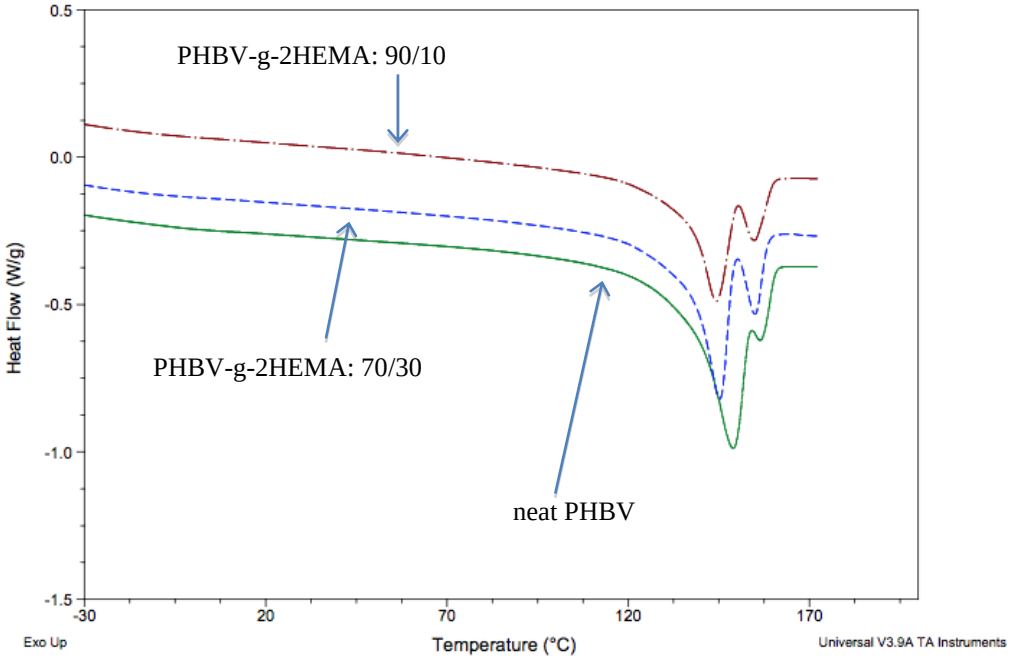


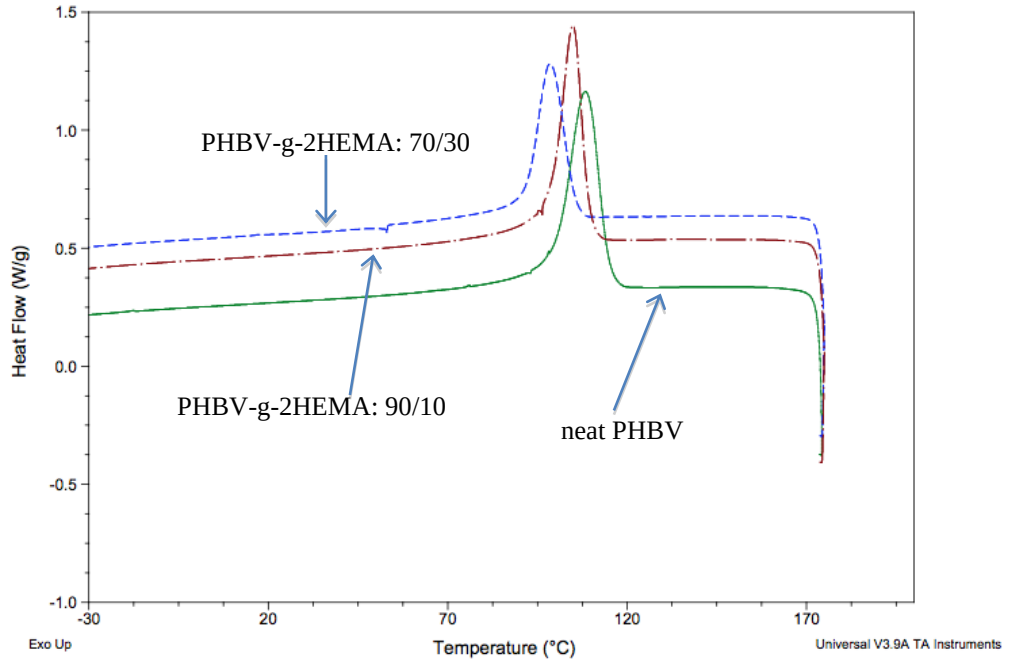
Figure 4.15 Thermal decomposition profiles of neat PHBV and PHBV/TEC blend

PHBV grafted with 2HEMA in the fifth trial exhibited two T_ms (149.62±0.23 °C and 158.01±0.44 °C for PHBV/2HEMA 90/10, 146.46±1.84 °C and 156.33±1.22 °C for 70/30) in the endothermic profile. The T_ms of PHBV-g-2HEMA 70/30 shifted to lower temperatures than neat PHBV whereas the T_ms of PHBV-g-2HEMA 90/10 were not significantly different from the T_ms of neat PHBV, as can be seen in Figure 4.16 (a) and Table 4.3. The exothermic profile is also illustrated in Figure 4.16 (b). In the grafting process, 2HEMA was joined onto the PHBV main chain, resulting in a branched molecular structure in the PHBV-g-2HEMA. The heat of fusion and crystallinity of PHBV in the grafted polymers were also decreased when compared to the neat PHBV. With a higher content of 2HEMA, all thermal transition temperatures decreased. These indicated that 2HEMA grafting introduced in the polymers impeded crystalline formation in the materials [147].

Figure 4.17 shows thermal decomposition profiles of PHBV and two different compositions of PHBV-g-2HEMA. There were two steps of decomposition in the grafted materials. The grafted polymers started to degrade at a lower temperature than PHBV due to 2HEMA in the polymers. According to Demirelli et al., the decomposition product of poly(2HEMA) consists of carbon monoxide, water, ethylene dimethacrylate, ethylene glycol, 3-methyl-5-hydroxy δ-valerolactone, 1,2-diizopropenyloxyethane, 1,3-dioxolane, anhydride rings, and other substances. The poly(2HEMA) decomposition was composed of two main steps: depolymerization to monomers and decomposition of esters, which were side chains. The first step occurred at lower temperature and was considered as the main reaction and the second step was at higher temperature [148]. In this study, PHBV-g-2HEMAs began to degrade at a lower temperature of around 150 °C, and reached the maximum weight loss at 320 °C. The second step occurred at a temperature about 325 °C which might be a decomposition of esters and carbon in the backbone structure [118]. The presence of 2HEMA in the grafted PHBV lowered the decomposition temperature of the materials. This indicated that 2HEMA decreased the thermal stability of the grafted PHBV compared to the neat PHBV.



(a)



(b)

Figure 4.16 Endothermic (a) and exothermic (b) profiles of neat PHBV and PHBV-g-2HEMAs

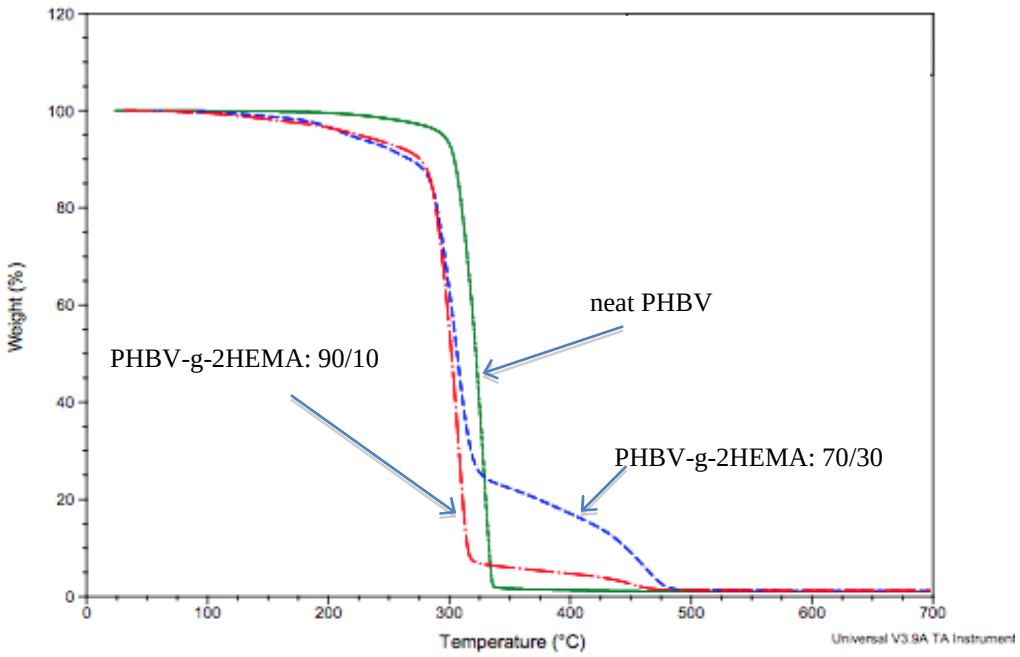
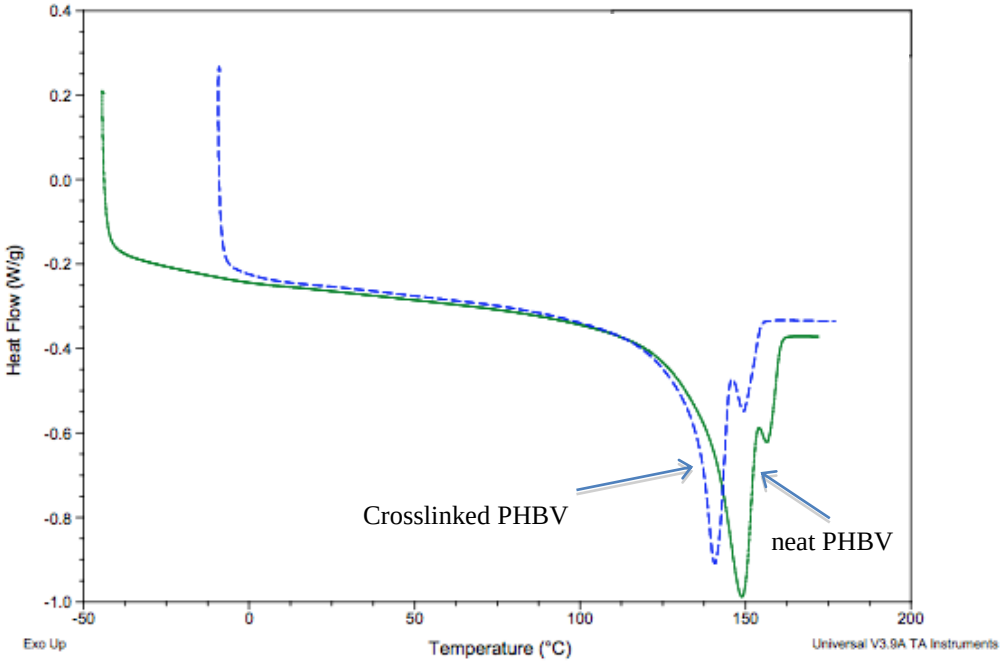
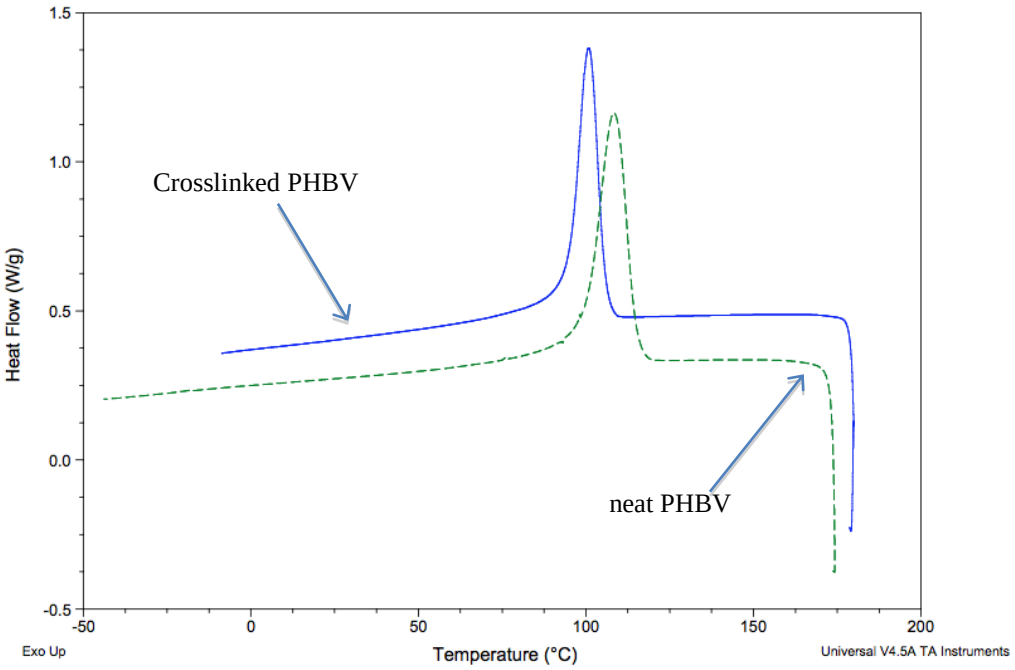


Figure 4.17 Thermal decomposition profiles of neat PHBV and PHBV-g-2HEMAs

Crosslinking is another modification method for improving polymer properties. Table 4.3 shows the thermal properties of the crosslinked PHBV. As can be seen in the endothermic and exothermic curves in Figure 4.18 (a) and 4.18 (b), the melting temperature (T_m) of the crosslinked PHBV has two T_ms (140.16±0.81 °C and 148.89±0.98 °C) that are lower than those of neat PHBV. The heat of fusion of the crosslinked PHBV was also lower than neat PHBV as can be seen in Table 4.3. This indicated lower crystallinity in the structure. Since the crosslinking process caused PHBV molecular chains to be covalently bonded and become a three-dimensional network, this restricted molecular movement. This network created free volume and interfered with crystallite formation in the material. The result corresponded to the crosslinked PHBV using dicumyl peroxide as an initiator prepared by Fei et al [93]. Also, when crystallinity in the crosslinked structure was hindered, irregular crystalline structures were formed starting at lower temperatures than for PHBV [149].



(a)



(b)

Figure 4.18 Endothermic (a) and exothermic (b) profiles of neat PHBV and crosslinked PHBV

The thermal stability of crosslinked PHBV was investigated using TGA. Figure 4.19 shows the decomposition thermogram of crosslinked PHBV. The thermal decomposition profile of the crosslinked PHBV exhibits one-step weight loss, similar to neat PHBV. The onset and maximum temperature of the crosslinked PHBV were slightly less than neat PHBV. This indicated that crosslinking did not provide thermal stability to the crosslinked PHBV.

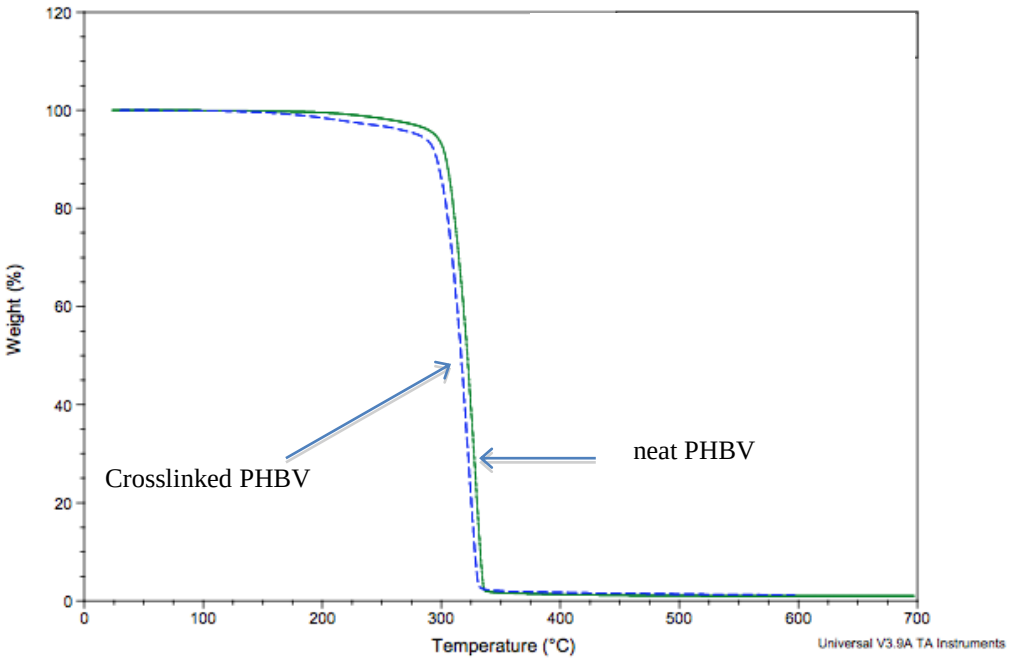


Figure 4.19 Thermal degradation profiles of neat PHBV and crosslinked PHBV

4.3.4 Permeation properties of PHBV and modified PHBV

Permeability is an important property for identifying materials that are suitable as good barriers to atmospheric constituents, especially for packaging films. The substances used in barrier testing were water vapor, oxygen, and carbon dioxide. The ability of permeated substances, especially volatiles, to penetrate through a polymer is specific, depending on interactions between the polymer and the penetrant. The diffusion coefficient is an indicating parameter for this specific barrier behavior. It is the penetrant flux within a polymer matrix as a function of the penetrant concentration gradient. The diffusion equation proposed by Fick, Fick's first law, is shown in equation 4.2 for one dimensional mass transfer [59].

$$F = - D\frac{\partial c}{\partial x} \qquad (4.2)$$

where F = flow rate

D = diffusion coefficient which is specific for each substance; D is temperature dependent

c = the concentration of the diffusing substance in the polymer matrix

x = the distance of diffusant travel within the polymer

The diffusion is not the only characteristic involved in permeation of the penetrant through the polymeric materials; solubility is another factor contributing to the permeation characteristics. Solubility is the ability of the polymer to absorb the permeable substances, which can be described by Henry's law for low concentrations of permeants.

The permeation coefficient is a parameter describing permeability. It can be defined as a function of the diffusion and solubility coefficients based on Fick's first law in equation 4.2. This equation is valid for a low concentration of permeant where D and S are independent of concentration and steady state conditions [59, 150].

$$F = D\frac{c_2 - c_1}{L} = DS\frac{p_2 - p_1}{L} \tag{4.3}$$

where p = the partial pressure of the volatile substance, at low concentration (Henry's law is valid in this case)

L = thickness of the polymer

$$F = \frac{q}{At} = DS\frac{p_2 - p_1}{L} = P\frac{\Delta p}{L} \tag{4.4}$$

where P = permeation coefficient

q = the amount of permeant passing through the polymer

A = cross-sectional area through which the permeant travels

t = time

Δp = partial pressure difference for the permeant between the two sides of the material

In addition, permeability properties of polymeric materials can be affected by various factors. The chemical structure of the polymeric material influences the permeation of volatiles. Polar molecules such as water vapor can be absorbed by polar polymers. The molecular arrangement of polymers also impacts diffusion and absorption of volatiles through the material. Polymer materials with low crystallinity have more amorphous areas where molecules are able to move with respect to one another, creating free volume. This permits a permeant to go through the matrix. Temperature is also a factor affecting permeability. It affects both the solubility and the diffusivity of the permeant through the polymer. This can be described by the Arrhenius equation [59].

$$P = DS = P_0 e^{-E_p/RT}$$

where P_0 = permeability coefficient or pre-exponential factor which is specific for a polymer-permeant system

E_p = activation energy

R = gas constant = 8.314 joules per mole

T = temperature in Kelvin

At higher temperature, permeation of permeants in a polymer matrix exponentially increases.

4.3.4.1 Water vapor permeability

The water vapor transmission rate (WVTR) is defined as the quantity of water vapor that penetrates through a unit area of a material in a unit time. Water vapor permeability (WVP) can be obtained by using equation at 4.2 [59].

$$WVP = \frac{WVTR}{\Delta p} \times L \tag{4.5}$$

where $WVTR = \frac{q}{At}$ in equation 4.4

WVP = P in equation 4.4

Δp = water vapor partial pressure difference between the two sides of the material film

L = film thickness

WVTR can be measured using a water vapor permeation instrument in accordance with ASTM F1249. Table 4.4 indicates water vapor, oxygen, and carbon dioxide permeability. PHBV has a semicrystalline structure with water insolubility and high crystallinity of 59.92±0.30 %. The water vapor permeability coefficient of PHBV is $1.74\times10^{-6}\pm0.9\times10^{-7}$ kg.m/m^2.s.Pa. PHBV has a lower WVTR than PLA and polycaprolactone at various temperatures of 6, 25 and 49 °C [150]. This is because PHBV possesses high crystallinity, which decreases water vapor permeability. Crystallites in PHBV are areas in which the molecules are orderly arranged and tightly packed. This packed crystalline structure is the most thermodynamically stable stage.

The ordered pattern of the crystalline array impedes the water vapor path, resulting in a lower cross-sectional area for water vapor to pass through the material [151, 152]. The diffusion of water into PHBV is dependent upon its amorphous area where molecular mobility occurs. The glass transition temperature is a point where polymeric materials change from a glassy to a rubbery form. Water molecules interact with polar molecular groups of the material and plasticize the polymer by altering the glassy to rubbery stage. In other words, amorphous segments allow water vapor to pass through the PHBV matrix [153].

Table 4.4 Permeation properties of all compositions of modified PHBV

Material	**Water vapor permeation, kg.m/m^2.s.Pa**	**Oxygen permeation, kg.m/m^2.s.Pa**	**Carbon dioxide permeation, kg.m/m^2.s.Pa**
Neat PHBV	$1.74\times10^{-6}\pm0.9\times10^{-7}$[d]	$2.26\times10^{-18}\pm3.4\times10^{-19}$[d,e]	$2.06\times10^{-17}\pm8.5\times10^{-18}$[c]
Blend of PHBV/TiO_2 nanoparticle 1%wt	$1.70\times10^{-6}\pm1.8\times10^{-7}$[d]	$2.60\times10^{-18}\pm1.0\times10^{-19}$[d]	$2.91\times10^{-17}\pm1.3\times10^{-18}$[c]
Blend of PHBV/Ecoflex : 50/50 %wt	$5.53\times10^{-6}\pm2.4\times10^{-7}$[b]	$6.68\times10^{-18}\pm5.3\times10^{-19}$[a]	$7.23\times10^{-17}\pm1.17\times10^{-17}$[a]
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	$4.43\times10^{-6}\pm3.8\times10^{-7}$[b,c]	$5.22\times10^{-18}\pm4.9\times10^{-19}$[c]	-
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	$5.41\times10^{-6}\pm2.1\times10^{-7}$[b,c]	$5.38\times10^{-18}\pm5.2\times10^{-19}$[b,c]	-
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	$5.56\times10^{-6}\pm2.0\times10^{-7}$[b]	$6.30\times10^{-18}\pm0.6\times10^{-19}$[a,b]	$7.95\times10^{-17}\pm9.3\times10^{-18}$[a]

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
Permeability of the PHBV/TEC blend could not be measured since TEC leached out to the polymer surface.

Table 4.4 (Cont'd)

Material	Water vapor permeation, kg.m/m^2.s.Pa	Oxygen permeation, kg.m/m^2.s.Pa	Carbon dioxide permeation, kg.m/m^2.s.Pa
Grafted PHBV with 2HEMA : 90/20 %wt (L101 0.1%wt)	$2.11\times10^{-6}\pm2.6\times10^{-7}$[d]	$1.40\times10^{-18}\pm4.0\times10^{-19}$[e]	$3.06\times10^{-17}\pm0.1\times10^{-18}$[c]
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	$4.13\times10^{-6}\pm8.0\times10^{-7}$[c]	$2.88\times10^{-18}\pm2.3\times10^{-19}$[d]	$5.13\times10^{-17}\pm0.3\times10^{-18}$[b]
Crosslinked PHBV (L101 2%wt)	$8.18\times10^{-6}\pm9.8\times10^{-7}$[a]	-	$2.39\times10^{-17}\pm3.6\times10^{-18}$[c]

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time in the extruder of crosslinked PHBV was 1 min.

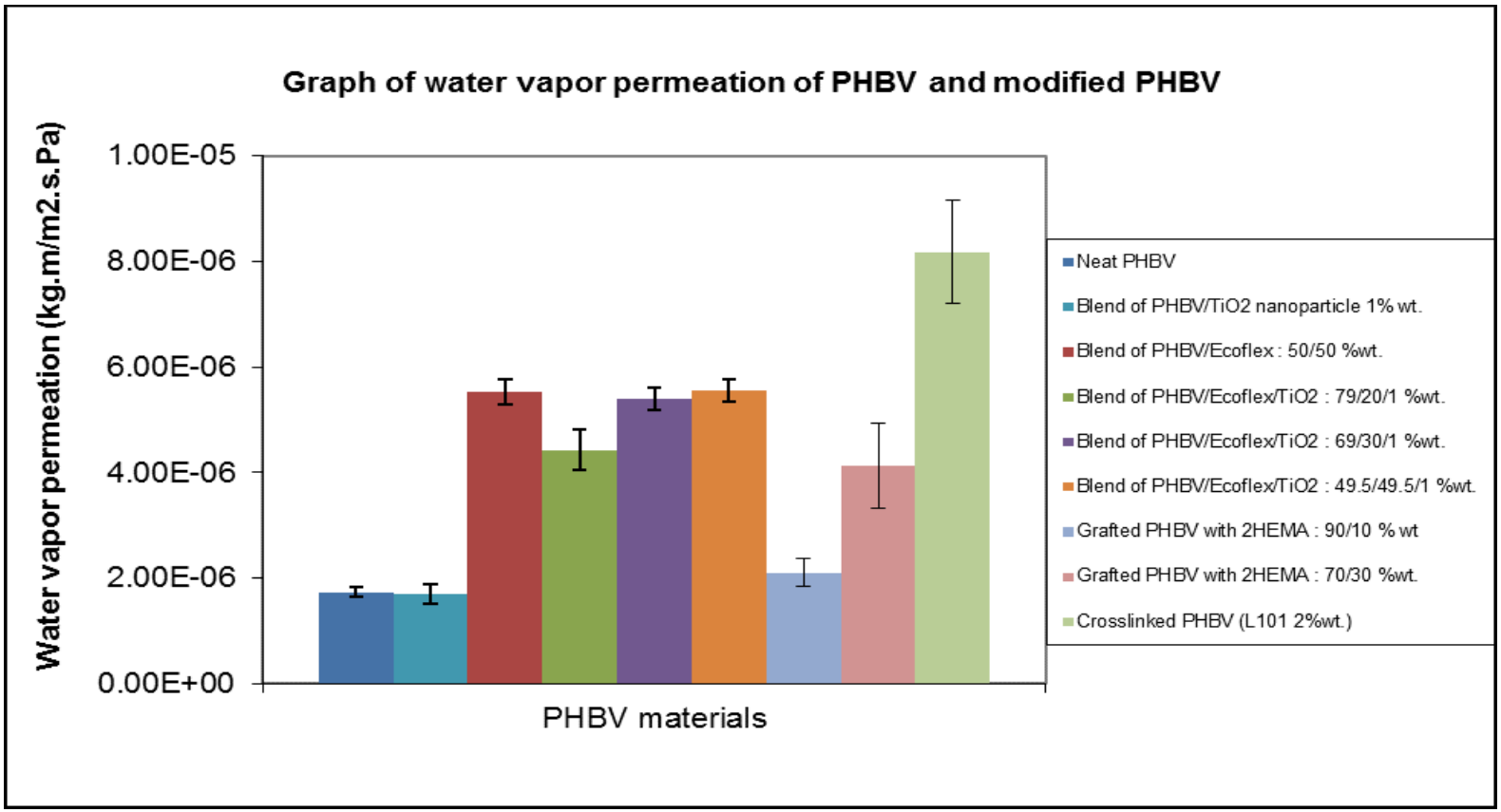


Figure 4.20 Water vapor permeation of PHBV material sheets

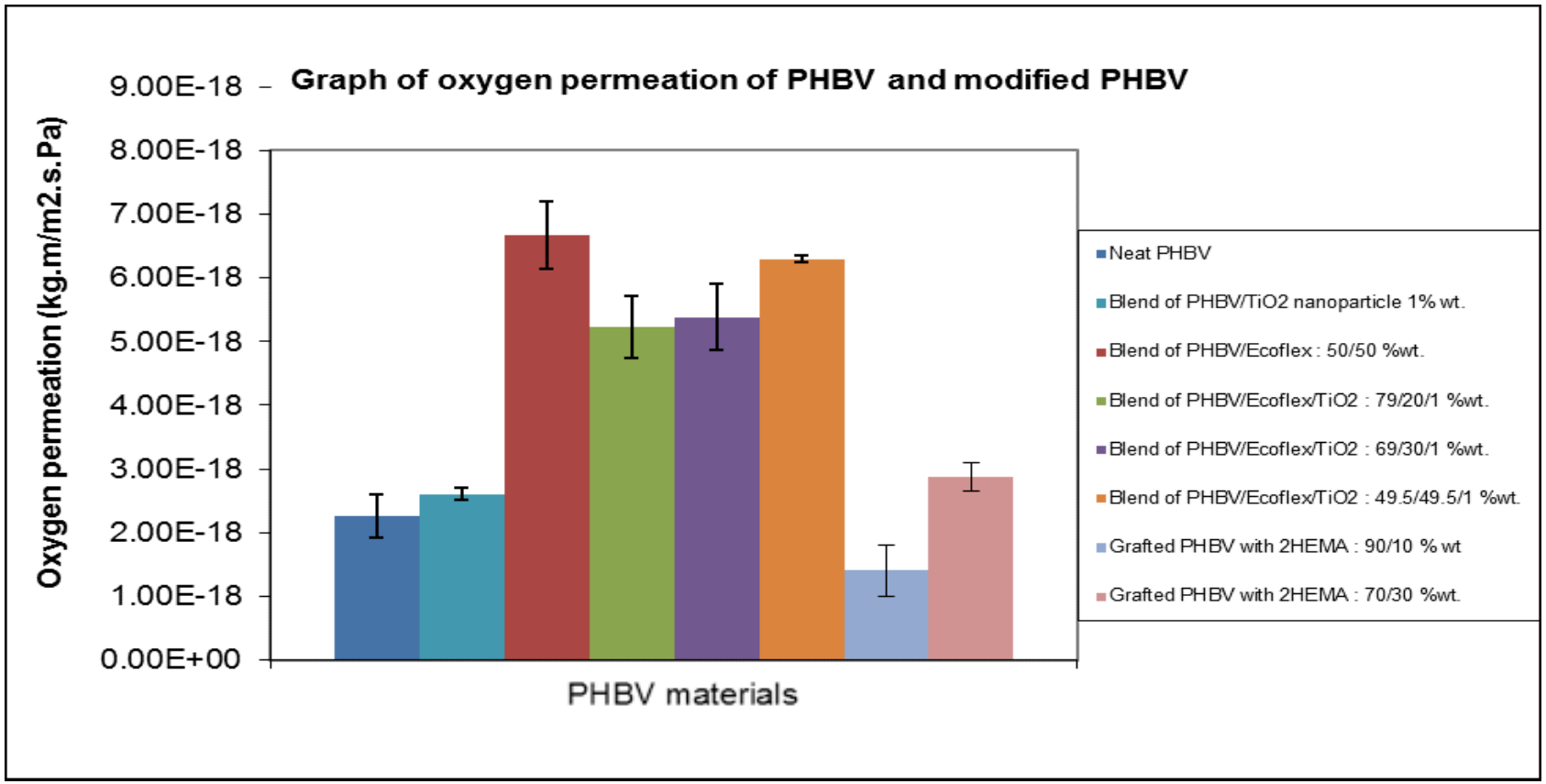


Figure 4.21 Oxygen permeation of PHBV material sheets

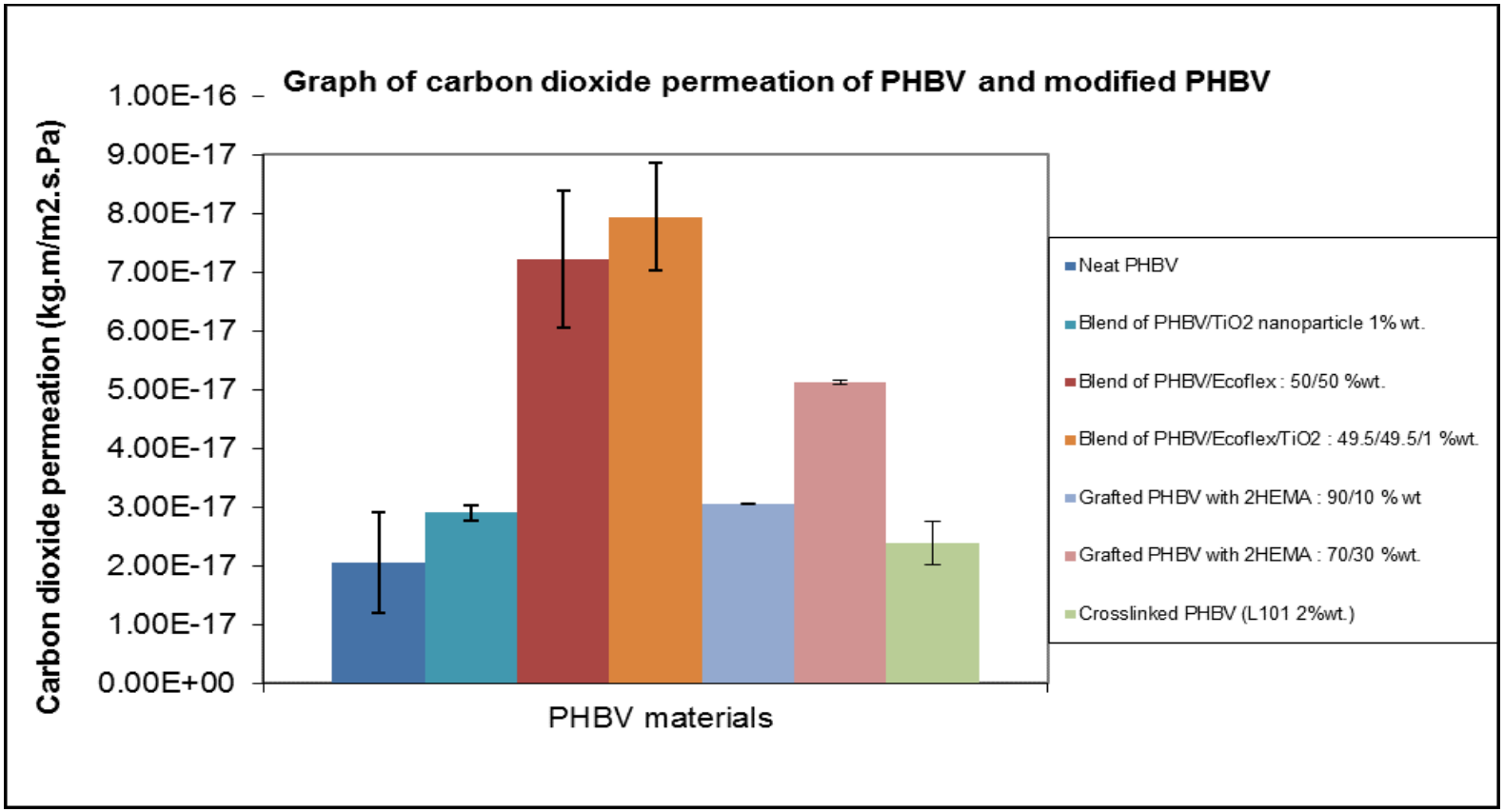


Figure 4.22 Carbon dioxide permeation of PHBV material sheets

Incorporation of other substances has an impact on WVP. PHBV with TiO_2 in this study had WVP insignificantly lower than the neat PHBV. WVP of PHBV/TiO_2 was $1.70\times10^{-6}\pm1.8\times10^{-7}$ kg.m/m^2.s.Pa. This result corresponded with PHBV/fiber blends prepared by Sanchez-Garcia et al. Fiber inclusion in PHBV slightly decreased WVP at a low fiber content of 1% wt. With higher content of fiber, WVP increased due to agglomeration of the fiber. This behavior caused a lack of polymer homogeneity and cohesion in the matrix and created pathways (voids) for permeation [152]. In addition, according to Rhim et al., nanoclay added to PLA improved water vapor barrier when compared to PLA [154]. The PHBV/TiO_2 blend had a better barrier to water vapor than the neat PHBV. This was attributed to the tortuous path created by TiO_2 resulting in low WVP.

Blending with other polymeric material also modified WVP. The inclusion of Ecoflex in the PHBV/Ecoflex blend worsened the water vapor barrier. The WVP of PHBV/Ecoflex 50/50 %wt. of this study was $5.53\times10^{-6}\pm2.4\times10^{-7}$ kg.m/m^2.s.Pa whereas WVP for PHBV/Ecoflex 70/30 and 80/20 could not be measured since the amount of water vapor detected was so large it was beyond the measuring range of the machine. The repeated failure of the test occurred also for oxygen and carbon dioxide permeation measurements for these blends and was attributed to minor cracks in the material. Ecoflex is a biopolymer with higher hydrophilicity than PHBV, which might compromise the barrier property. This factor has a detrimental effect on WVP [108]. Furthermore, similar behavior was observed by Suyatma et al. PLA, a hydrophobic polymer, was incorporated in chitosan decreasing WVP. With an increase of PLA to 10% wt., water vapor barrier was better than the blends with PLA contents of 20% and 30% [155].

Additionally, the effect of incorporation of both TiO_2 and Ecoflex was studied. The PHBV/Ecoflex/TiO_2 blends, with PHBV/Ecoflex/TiO_2 ratios of 79/20/1, 69/30/1, and 49.5/49.5/1, had WVP of $4.43\times10^{-6}\pm3.8\times10^{-7}$, $5.41\times10^{-6}\pm2.1\times10^{-7}$, and $5.56\times10^{-6}\pm2.0\times10^{-7}$ kg.m/m^2.s.Pa, respectively. WVPs of the blends were not significantly different from each other or from the PHBV/Ecoflex 50/50 blend. However, they were much higher than for the neat PHBV. Adding TiO_2 in the PHBV/Ecoflex/TiO_2 79/20/1 and 69/30/1 blends did result in sheets for which the permeability coefficient could be measured, unlike the blends without TiO_2 for which measurements failed, as discussed earlier.

Plasticizers in polymers also influence permeability of the material. In this study, the permeability of the PHBV/TEC blend could not be measured. This is because TEC leached out to the surface of the material, resulting in an oily surface and inability to attach to the aluminum mask for the permeation test. However, the study of Munoz et al., showed that the incorporation of glycerol as a plasticizer in glutenin-rich film strikingly increased WVP of the film at higher than 40%wt of glycerol. The plasticizer in the blend created free volume and increased molecular movement and the matrix was less dense [156].

Grafting also can alter the permeability of the polymer. WVPs of the grafted PHBV with 2HEMA are indicated in Table 4.4. The presence of 2HEMA content of 20 % wt. did not significantly increased WVP of the grafted PHBV compared to the neat PHBV. However, sheets with 30 wt. % 2HEMA (30 %wt.) in the grafted material had significantly higher WVP than both neat PHBV and grafted PHBV with 20 % wt. of 2HEMA. Grafting of 2HEMA created a branched chain PHBV matrix, which hindered the crystallization of PHBV,

contributing to free volume for water vapor passing through [147]. Additionally, 2HEMA is a water-soluble monomer, which has polar affinity [157]. Thus, the grafted PHBV is more water-favorable. With an increase of 2HEMA, the WVP barrier was compromised. This result was in agreement with the chitosan/HEMA membrane produced by Li et al. HEMA in the material increased hydrophilicity of chitosan leading to higher permeation [158].

Other than the modifications reported earlier, crosslinking is another way to modify polymers for suitable applications. WVP of the crosslinked PHBV with a help of L101 as an initiator in this study was $8.18\times10^{-6}\pm9.8\times10^{-7}$ kg.m/m^2.s.Pa, which is higher than that of the neat PHBV. In general, crosslinking decreases permeation since molecular chains are restricted and linked by covalent bonds in a three-dimensional array, contributing to limited movement of the molecules and a dense structure. This decreases the permeability. According to Frederick, crosslinked protein-pullulan films with alginate derivative propyleneglycol alginate (PGA) as a crosslinker had decreased WVP when compared to the un-crosslinked [159]. In addition, crosslinked gliadin-rich fraction film prepared by Hernandez-Munoz et al. had significantly higher water barrier than the un-crosslinked film [160]. In this study, in contrast, higher WVP of the crosslinked PHBV might be because covalent bonds in the crosslinking network impeded the crystallinity of the PHBV, creating free volume (voids), which was a preferable path for water vapor.

4.3.4.2 Oxygen and carbon dioxide permeability

Oxygen and carbon dioxide are common gases used in measuring gas barrier properties of polymeric materials. Oxygen and carbon dioxide permeation through materials are crucial to food shelf life. So, oxygen and carbon dioxide permeation are essential to plastic packaging selection. Oxygen and carbon dioxide permeation of PHBV in this study were 2.26×10^{-18} $\pm3.4\times10^{-19}$ and $2.06\times10^{-17}\pm8.5\times10^{-18}$ kg.m/m^2.s.Pa, respectively. According to Thellen et al., PHBV possesses high barrier to oxygen [161]. This could be due to high crystallinity and less amorphous area creating fewer pathways for the gases to pass through. In addition, according to Costamagna, et al., a crystalline structure is an impermeable barrier. It takes longer for gases to travel along the interface of crystalline and amorphous regions (tortuous path) than in amorphous regions, resulting in lower gas permeability [162]. Inclusion of both the inorganic compound and the polymer in PHBV also affected the permeation of oxygen and carbon dioxide. According to Ray et al. PLA-layered silicate nanocomposite was prepared by adding montmorillonite modified with octadecylammonium cation in PLA in melt extrusion. The PLA nanocomposite blend had lower O_2 permeation than the neat PLA [163]. Fabrication of PLA/TiO_2 nanocomposite films as reported by Zhu et al. had a lower O_2 permeability coefficient than pure PLA [126]. Matteucci et al. stated that gas (CO_2 H_2, N_2 and CH_4) permeation of poly(1-trimethylsilyl-1-propyne) added with TiO_2 was lower at low TiO_2 content whereas the permeation increased with a high content of TiO_2 due to the higher void fraction in the material [164]. In this study, PHBV/TiO_2 had O_2 and CO_2 permeation of $2.60\times10^{-18}\pm1.0\times10^{-19}$ and $2.91\times10^{-17}\pm1.3\times10^{-18}$ kg.m/m^2.s.Pa, respectively. These values were not significantly greater than PHBV. This indicates the presence of TiO_2. 1%wt. did not affect

O_2 and CO_2 permeability of the neat PHBV. In contrast, the presence of Ecoflex in PHBV/Ecoflex 50/50 %wt. decreased the O_2 and CO_2 barrier properties when compared to the neat PHBV. This might be due to the fact that Ecoflex somewhat impeded the crystalline formation of PHBV, leading to a less dense matrix and gases could travel through the free volume of the polymer. For PHBV/Ecoflex 80/20 and 70/30 %wt%, the gas permeation, both O_2 and CO_2, could not be measured, as stated earlier.

In the PHBV/Ecoflex/TiO_2 systems, the O_2 and CO_2 permeation were also higher than PHBV, as shown in Table 4.4. CO_2 permeation for PHBV/Ecoflex/TiO_2 79/20/1 and 69/30/1 %wt. could not be measured as the CO_2 quantity was beyond the range of the instrument. A possible explanation is minor cracks occurred in the test samples but that did not occur for the WVP and O_2 samples so the cause is uncertain. O_2 and CO_2 permeation of PHBV/Ecoflex/TiO_2 49.5/49/5/1 %wt. were not statistically different from those of PHBV/Ecoflex 50/50 %wt.

The O_2 and CO_2 permeation coefficients of PHBV-g-2HEMA 90/10 and 70/30%wt are shown in table 4.4. It was found that O_2 permeation coefficient for PHBV-g-2HEMA 90/10 and 70/30 were not significantly different from that of the neat PHBV. However, there was a difference between PHBV-g-2HEMA 90/10 and 70/30. Grafting with a low content of 2HEMA decreased O_2 permeation compared to the neat PHBV, as opposed to grafting with a higher 2HEMA load. CO_2 permeation in the neat PHBV and PHBV-g-2HEMA 90/10 were not significantly different whereas PHBV-g-2HEMA 70/30 had greater CO_2 permeation than both the neat PHBV and PHBV-g-2HEMA 90/10. According to Costamagna et al. [162], grafting poly(acrylic acid) onto LDPE decreased O_2 permeation when compared to the ungrafted

polymer [162]. Huang and Kanitz stated that polyethylene-styrene graft copolymer fabricated by γ radiation of LDPE in a styrene-methanol solution had a decrease in O_2 and CO_2 permeability with increase in grafting from 20-30% and both gas permeabilities increased again above 30%. This was because, in low grafting, the free volume decreased due to less mobility of LDPE chains creating cohesion forces resulting in lower permeability. Above 30%, polystyrene chains disrupted crystalline areas of LDPE [165]. In this study, at lower 2HEMA of 10% wt., grafting did not influence the permeability of either of the gases. With an increase of 2HEMA, greater CO_2 permeability was obtained even though the increase in O_2 permeation was not significant, compared to the neat PHBV. This is because grafting initiated branching of the molecules in the polymer matrix and made the polymer matrix less crystalline. Thus, gases were able to diffuse through the polymer.

For gas permeation of the crosslinked PHBV in this study, O_2 permeation could not be measured due to failure in the O_2 permeation tester. In this case, the O_2 transmission level increased and did not level off, resulting in a "failed" test. However, CO_2 permeation of the crosslinked PHBV was $2.39\times10^{-17}\pm3.6\times10^{-18}$ kg.m/m^2.s.Pa, which was not statistically different from PHBV. Thus, crosslinking did not influence the CO_2 permeation in the crosslinked material.

4.4 Conclusion

In the effort to modify PHBV, many methods were used for improving PHBV to be effective for use in flexible packaging. The main property that needs to be improved is elongation, which indicates flexibility. PHBV has inherent brittleness, tackiness, high crystallinity, and low melt strength. These drawbacks lead to inability to process in conventional processes such as extrusion cast film and blown film. To overcome the drawbacks, inorganic compound incorporation, blending, incorporation of plasticizer, grafting and crosslinking were applied in order to fabricate a modified PHBV. The resulting modified PHBV materials had lower tensile strength and elongation at break than the neat PHBV except for the crosslinked PHBV. The crosslinked PHBV had elongation at break much greater than the neat PHBV even though its tensile strength was only slightly higher than the neat PHBV. Crosslinking, therefore, was the selected modification method for improving flexibility of PHBV in this study.

5. INFLUENCE OF THE AMOUNT OF INITIATOR ON THE DEGREE OF PHBV CROSSLINKING AND ITS PROPERTIES

5.1 Introduction

The previous study showed that crosslinking is the best way to improve the ductility including flexibility of PHBV thin sheet for packaging applications. Elongation is the crucial property that is of concern in this study. Elongation is the ability of a material to be plastically deformed under load. It is the change in length before failure. The goal was to obtain the optimum content of initiator resulting in the maximum elongation of the crosslinked PHBV. Crosslinking is a potential modification method for polymer materials in order to impart useful properties for suitable applications. It is polymer chain extension by covalently bonding in multiple directions creating a crosslinked network. The covalent bonds in crosslinking can be intramolecular or intermolecular bonds, or both. The crosslinking process is irreversible. Molecular chains in a crosslinked polymer are restricted so that they are unable to move past one another, resulting in elasticity in amorphous areas and reduced crystallinity as well as reduction of free volume. Crosslinking impedes the orderly arrangement of molecular chains in crystalline formations, contributing to elastic behavior at a low degree of crosslinking. Polymeric materials become softer. Crosslinking changes polymer properties to become more durable and resistant to heat, light, chemicals, mechanical load, etc. [60].

5.2 Fabrication of crosslinked polyhydroxybutyrate-co-valerate with different amounts of initiator

PHBV neat resin was placed in the mini twin-screw extruder with L101 as an initiator for the crosslinking reaction. The amount of initiator was varied: 0.5, 1, 2, 3 and 4% wt. The extruder was set at a screw speed of 150 rpm, and temperature of 165 °C in all three temperature zones. In the beginning of the process, the polymer was sticky and hard to mix in the extruder. The force increased sharply as cross-linking began to occur. At the maximum shearing force, the materials were well mixed and the reaction reached a maximum. When the reaction proceeded beyond this point, PHBV experienced thermal degradation and the shear force declined. Therefore the point of maximum shear force was used as a guideline to obtain the maximum extent of cross-linking. The residence time (at the maximum shear force) was 1 min. Figure 5.1 shows the shearing force profile of molten PHBV in the extruder. The crosslinked extrudates were discharged from the extruder in a strand form with low melt strength, stickiness and elastomeric behavior [77]. The extrudates were left at room temperature until they solidified. The solid strands were pelletized. Then, the crosslinked PHBV pellets were placed in a 180×180 mm^2 aluminum frame of thickness 0.25 mm. and sandwiched between aluminum platens in order to form compression molded sheets. The pellets were compression molded at a temperature of 165 °C and 20,000 psi for 5 min. and cooled by tap water flow through the platens for 15 min. The crosslinked PHBV sheets obtained were pre-conditioned at 23 °C, 50 %RH for 48 hrs. and then investigated visually, and tested for mechanical, thermal and permeability properties. Figure 5.2 shows the crosslinked PHBV resins produced with L101 initiator content at 0.5, 1, 2, 3, and 4 %wt.

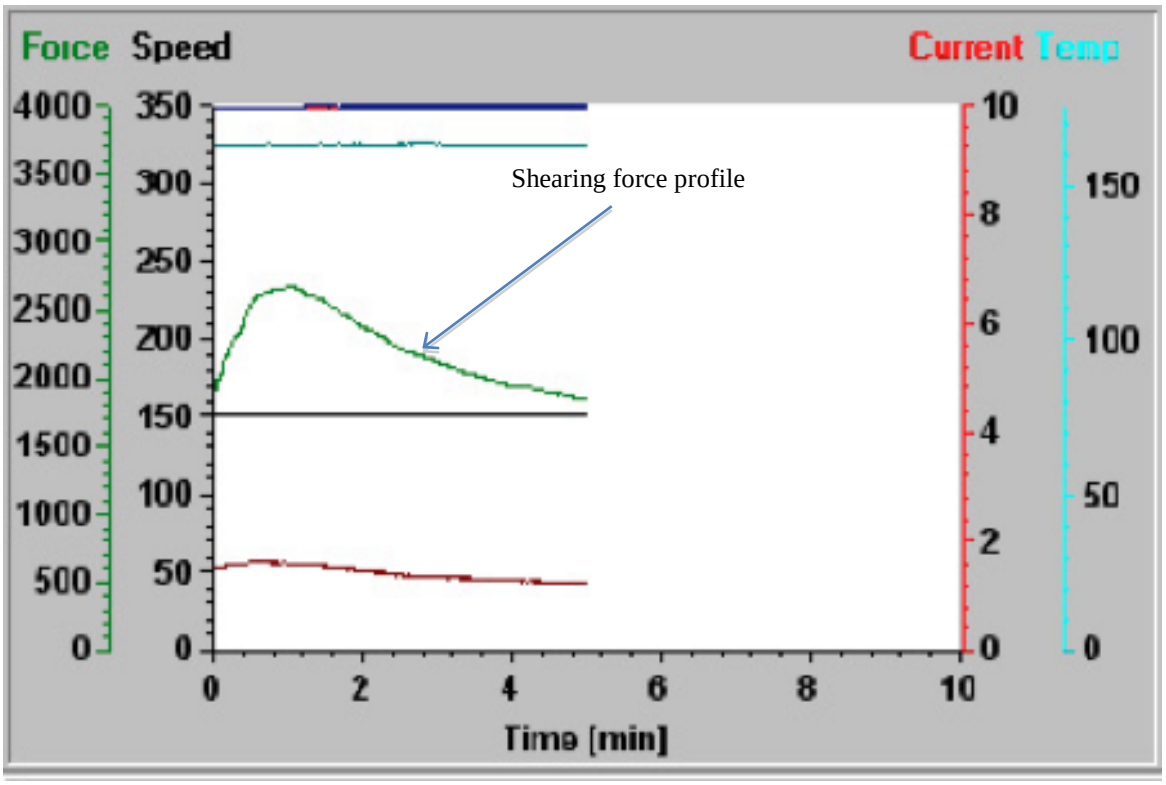


Figure 5.1 Shearing force profile of the molten PHBV crosslinked with a presence of L101 vs. time in the mini twin screw extruder indicating the maximum force of molten polymer reached the highest at reaction time of 1 min.

(a) (b) (c)

(d) (d) (f)

Figure 5.2 PHBV neat resin (a) and crosslinked PHBV with L101 of 0.5 (b), 1 (c), 2 (d), 3 (e), and 4 (f) %wt.

5.3 Results and discussion

5.3.1 Visual characteristics of the crosslinked poly(hydroxybutyrate-co-valerate)s

The PHBV extrudates with L101 at 0.5, 1, and 2 %wt. had low melt strength, elastomeric behavior and tackiness, causing them to stick to surfaces such as the die. The PHBV extrudates with L101 at 3 and 4 %wt., on the other hand, had better melt strength and less tackiness than PHBV and those with L101 at 0.5, 1, and 2 %wt. After cooling down and pelletization, the pellets of PHBV with L101 at 0.5, 1, and 2 %wt., visually similar to neat PHBV, were yellowish in color, had a smooth surface, and were rigid and soft when compressed, similar to rubber. Meanwhile, the pellets of crosslinked PHBV with L101 at 3, 4 %wt. were pale yellow and had air pockets inside, resulting in a structure that resembled a sponge, as can be seen in Figure 5.2. This characteristic was similar to that of crosslinked PHBV with dicumyl peroxide (DCP) as an initiator prepared by Fei et al. The crosslinked PHBV with 3%wt DCP had many bubbles distributed in the material [93]. The pellets were rigid and harder than neat PHBV when compressed. After being molded into sheet form, all the crosslinked PHBV sheets looked similar to one another and to the neat PHBV sheet as well. All the visual characteristics of the crosslinked PHBV polymers are shown in Table 5.1

Table 5.1 Visual characteristics of PHBV and crosslinked PHBV with L101 of 0.5, 1, 2, 3, and 4 %wt.

<table>
<tr><th>Material</th><th>Extrudate</th><th>Disk form</th><th>Sheet form</th></tr>
<tr><td>Neat PHBV</td><td>-</td><td>-</td><td>Yellow,
flexible but brittle when folded</td></tr>
<tr><td>Crosslinked PHBV (L101 0.5%wt)</td><td rowspan="5">Low melt strength,
Sticky when heated,
Rigid when cooled</td><td rowspan="5">Rigid but soft like rubber</td><td rowspan="3">Yellow,
flexible but brittle when folded</td></tr>
<tr><td>Crosslinked PHBV (L101 1%wt)</td></tr>
<tr><td>Crosslinked PHBV (L101 2%wt)</td></tr>
<tr><td>Crosslinked PHBV (L101 3%wt)</td><td rowspan="2">Pale yellow,
flexible but brittle when folded</td></tr>
<tr><td>Crosslinked PHBV (L101 4%wt)</td></tr>
</table>

The residence time of all crosslinked PHBV was 1 min.

5.3.2 Mechanical properties of crosslinked poly(hydroxybutyrate-co-valerate)s

As mentioned earlier, elongation is the property of most concern in this study. It indicates ductility and flexibility of the material. The tensile strength and elongation at break of neat PHBV and crosslinked PHBVs are shown in Table 5.2, Figure 5.3 and Figure 5.4. Tensile strength is the ability of a polymeric material to withstand load. The crosslinked PHBV with L101 at 0.5 and 1 %wt. had lower tensile strength than the neat PHBV whereas tensile strengths of both crosslinked PHBVs with L101 at 2 and 4 %wt. were not statistically significantly different from the neat PHBV. Meanwhile, elongation at break in the crosslinked PHBV was significantly improved. When the amount of L101 was increased, the elongation at break increased until reaching the maximum at L101 2% wt. With an increase of L101 greater than 2 %wt., elongation at break decreased. The crosslinked PHBV with L101 2 % wt. had statistically greater elongation than the neat PHBV, more than two times that of the neat material. L101 in the reaction acts as an initiator or crosslinker for the crosslinking reaction. It initiates free radicals on the PHBV molecular chains, which promptly covalently react to form a multi directional network and the network rapidly grows. The covalent bonds can be intra- and/or intermolecular bonds resulting in molecular chain restriction, so that the molecular chains are unable to move pass one another. In the crosslinked PHBV with L101 less than 2 %wt., the elongation at break increased with an increase of L101 content. This might be because the crosslinker induced more free radicals, which resulted in more molecular chain restriction and more elongation. At PHBV with L101 more than 2 %wt., on the other hand, the large number of free radicals may have led to more restrictions due to a higher crosslink density. PHBV with L101 at 3 and 4 %wt. appeared to be a rigid and hard material. According

to Haene et al., branched PHBV was obtained with a small amount of dicumyl peroxide (DCP) of 0.025-0.3 %wt. as an initiator. At DCP more than 0.2 %wt., elongational viscosity in the crosslinked PHBV melt steeply increased indicating long chain branching [166]. An increase in elongation at break of the crosslinked PHBV in this study agreed with the results of PHBV sheets crosslinked with DCP. At DCP 1 %wt., elongation improved from 4 to 8.9%, and the elongation was far higher with crosslinked PHBV at DCP of 2 and 3%wt. Moreover, the tensile strengths of crosslinked PHBV produced with various amount of DCP were not much different from one another [93]. This corresponds to the tensile strength results for crosslinked PHBV in this study.

Moreover, many studies indicate that crosslinking alters the mechanical properties of polymers. Bigi et al. reported that glutaraldehyde (GTA) crosslinked gelatin film possessed high stress at break and elongation at GTA more than 1%wt as well as low deformation of the film [167]. The crosslinked starch-PVC blend with borax as a crosslinker was fabricated for improving tensile strength and flexibility of the gelatinized starch. Borax initiated covalent bonds in the blend, which promoted intermolecular H-bonds previously present in the blend. The crosslinked material had higher tensile strength than the non-crosslinked starch-PVC blend [168].

Table 5.2 Mechanical properties of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Tensile strength (MPa)	Elongation at break (%)
Neat PHBV	$19.84 \pm 0.54^{a,b}$	15.04 ± 0.59^{c}
Crosslinked PHBV (L101 0.5%wt)	15.42 ± 0.88^{d}	16.37 ± 1.76^{c}
Crosslinked PHBV (L101 1%wt)	17.78 ± 0.63^{c}	28.80 ± 1.35^{b}
Crosslinked PHBV (L101 2%wt)	20.45 ± 0.66^{a}	37.20 ± 2.25^{a}
Crosslinked PHBV (L101 3%wt)	$18.27 \pm 0.62^{b,c}$	28.47 ± 0.85^{b}
Crosslinked PHBV (L101 4%wt)	$19.00 \pm 0.16^{a,b,c}$	$32.77 \pm 3.07^{a,b}$

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time of all crosslinked PHBV was 1 minute

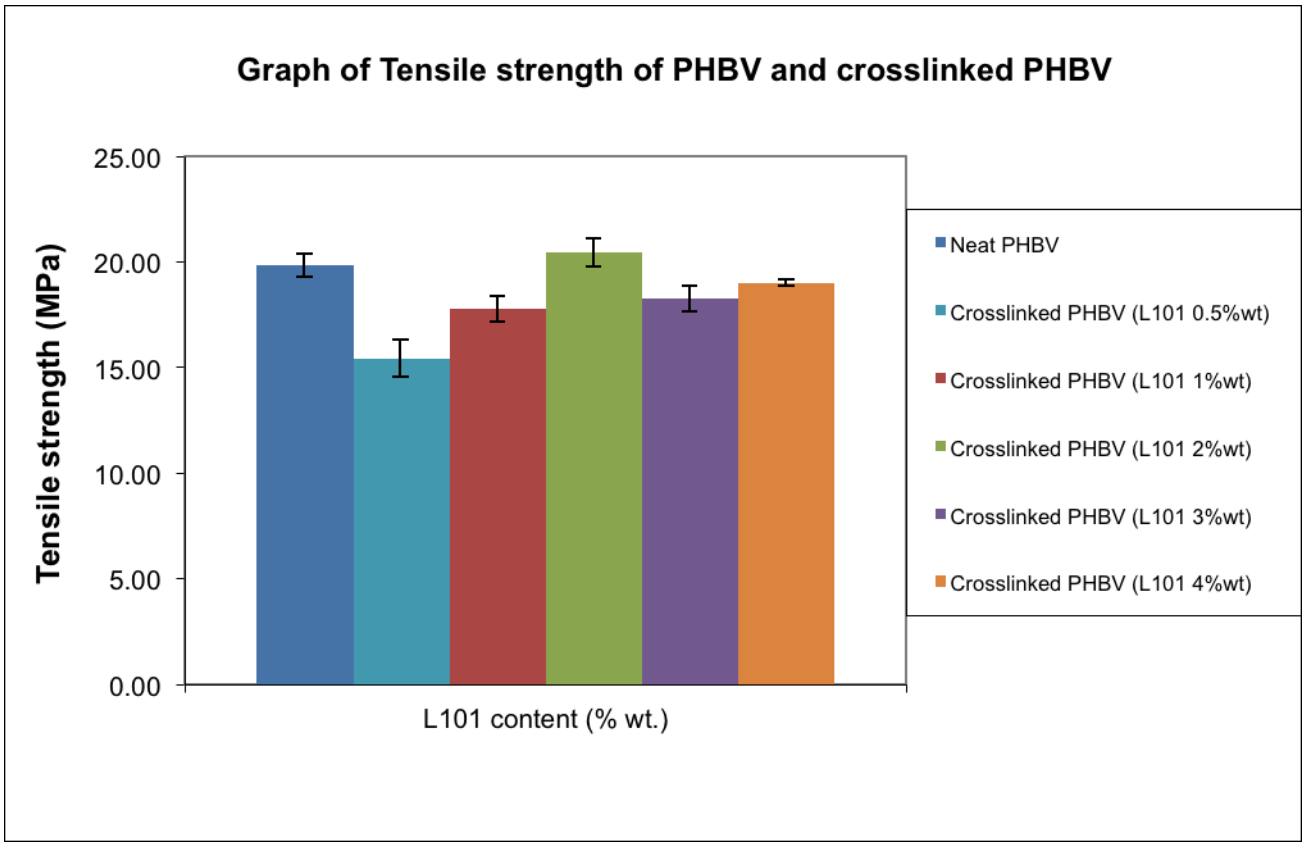


Figure 5.3 Tensile strength of neat PHBV and crosslinked PHBV sheets

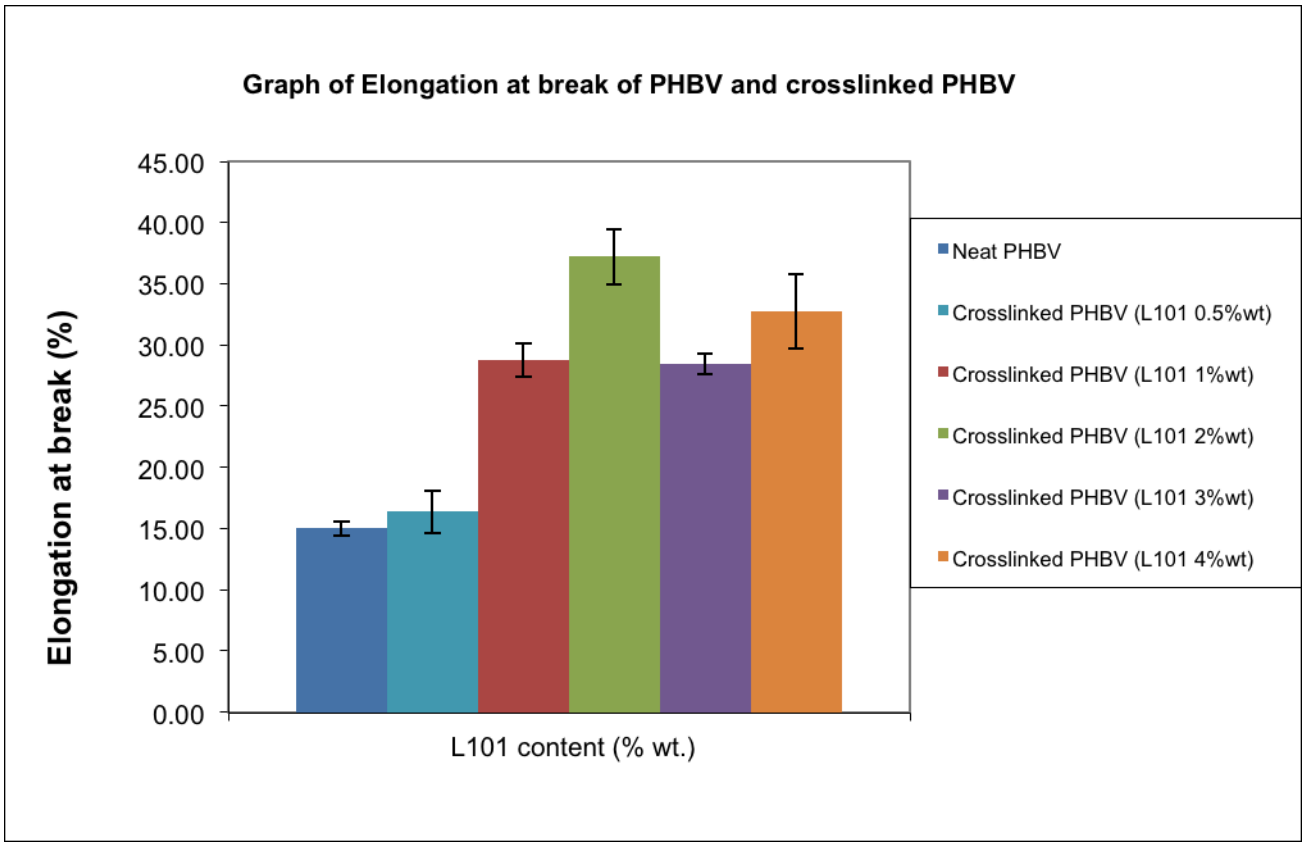


Figure 5.4 Elongation at break of neat PHBV and crosslinked PHBV sheets

5.3.3 Thermal properties of crosslinked poly(hydroxybutyrate-co-valerate)

Thermal properties of crosslinked PHBV were identified by DSC thermograms as shown in Figure 5.5 and Table 5.2. DSC showed that the T_c and T_m of the crosslinked PHBVs were significantly lower than the neat PHBV. The T_gs of PHBV and the crosslinked PHBV were not observed in this study. The crosslinked PHBVs had a covalent network that restricted the molecular movement. This array pattern impeded crystalline formation and decreased crystallinity, as shown in Table 5.2. In addition, the decrease of crystallinity contributed to imperfect and small size crystallite formation beginning at a lower temperature (T_c). The two T_ms were also lower with an increase of L101 content due to higher crosslink density [149, 169]. This result was consistent with crosslinked PHBV with dicumyl peroxide (DCP) as a crosslinker. T_c and T_m of the materials decreased compared to non-crosslinked PHBV [93]. In the work of Yang et al., crosslinked PLA was prepared by adding triallyl isocyanurate (TAIC) and DCP as an initiator. The crosslinked PLA showed a decrease in T_c and T_m when the crosslinker increased resulting in lower crystallinity due to molecular chain motion inhibition [149]. Crosslinked poly(ε-caprolactone) with benzoyl peroxide (BPO) also had the same trend. The presence of BPO decreased T_m and crystallinity of the crosslinked material. However, the T_c of the crosslinked PLA was unexpectedly higher since other substances such as impurities from the processing and catalyst residue acted as nucleating agents, probably initiate crystallization [170].

The heat of fusion (ΔH_m) indicates the energy required by the polymer material in order to melt the crystallites. The heat of fusion of all crosslinked PHBVs was statistically significantly lower than the neat PHBV than the neat PHBV. At lower content of L101 of 0.5 and 1 %wt., ΔH_ms were not significantly different. In addition, ΔH_ms of crosslinked PHBV with L101 at 2, 3 and 4 %wt. were not statistically different but were significantly lower than those of the crosslinked PHBV with L101 0.5 and 1 %wt. This shows that the crosslinking had an influence on the crystallinity of PHBV. With an increase of L101 content in the crosslinked PHBV, crystallinity was slightly decreased. An abrupt decrease in ΔH_m and crystallinity occurred at L101 2%wt. At a content of L101 more than 2%wt. any further decrease in ΔH_m and crystallinity was insignificant. This behavior of crosslinked PHBV indicated that crosslinking disturbed crystallite formation. The decrease in crystallinity in a crosslinked polymer was also reported by Krumova et al. DSC showed that ΔH_m and T_m of poly(vinyl alcohol), PVA, crosslinked with hexamethylene diisocyanate dramatically decreased indicating less crystallinity in the structure [171]. Moreover, ΔH_m and T_m of a crosslinked polyethylene/ethylene vinyl acetate blend with *tert*-butyl cumyl peroxide (BCUP) as an initiator were found to be lower when BCUP increased [172].

The thermal stability of the crosslinked PHBV was investigated using TGA. In this study, the crosslinked PHBV had slightly lower thermal stability than the neat PHBV as can be seen in Figure 5.6. Both experienced one stage weight loss. The onset temperature for the crosslinked PHBVs was around 295 °C which was slightly less than neat PHBV (300°C) and the decomposition was complete at about 330 °C which was lower than the 340 °C for neat PHBV. Generally, the crosslinking process increases thermal stability. According to Yang et

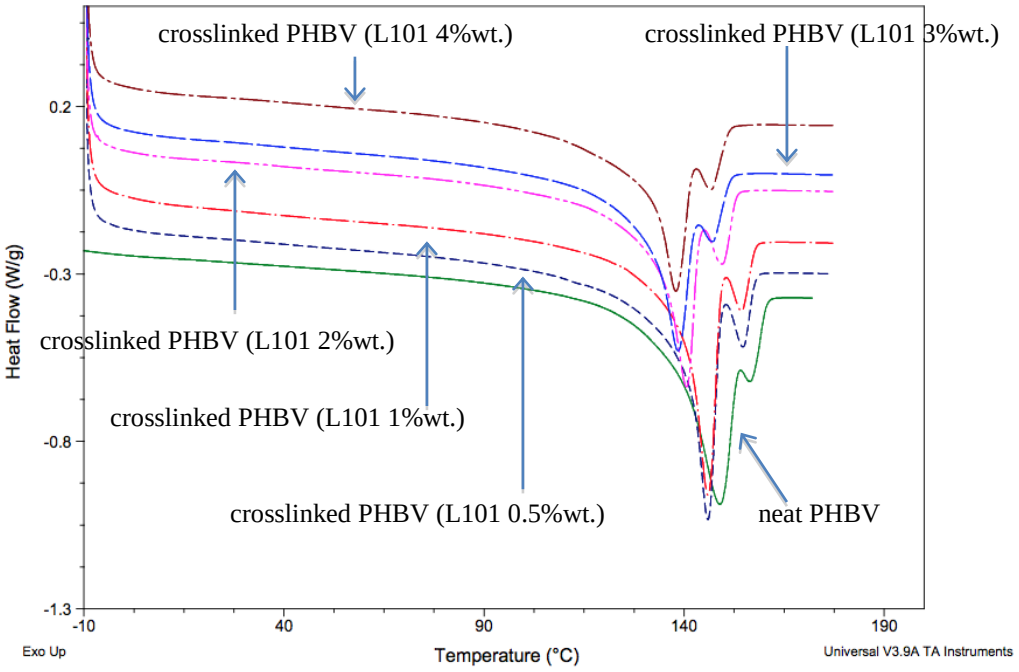
al., the thermal degradation temperature of crosslinked PLA was higher than that of neat PLA. The different in onset temperature was about 70 °C and of the ending decomposition temperature was 65 °C [149]. In addition, crosslinked poly(isobornyl methacrylate-co-butyl acrylate) copolymer possessed greater thermal stability than linear poly(isobornyl methacrylate-co-butyl acrylate) copolymer [173]. However, the thermal stability of the crosslinked PHBVs in this study was not enhanced. The TGA result in Figure 5.6 agreed with TGA of crosslinked PHBV with DCP as a crosslinker prepared by Fei et al [93]. There was no difference observed between PHBV and crosslinked PHBV in thermal decomposition [93].

One possible explanation for this behavior was suggested by Khonakdar et al. Crosslinking reactions induce covalent bonds at tertiary carbons in the polymer molecules, where are more likely to have thermal decomposition [169, 174]. According to Ke et al., benzophenone (BP) was used as an initiator in the presence of UV light, which induced photografting polymerization of polyacrylamide (PAM) onto PHBV. The tertiary hydrogen was abstracted from the PHBV main chain. Thus, PAM was attached onto the PHBV [175].

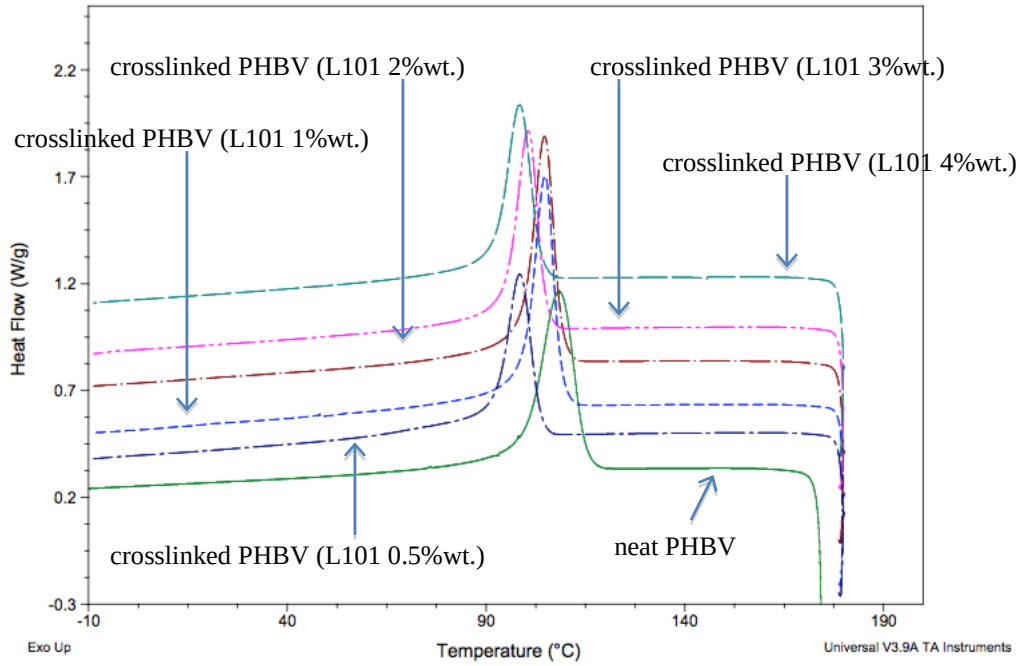
Table 5.3 Thermal properties of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	**T_c (°C)**	**T_m (°C)**		**Heat of fusion, ΔH_m (J/g)**	**PHBV Crystallinity (%)**
Neat PHBV	107.71±0.40[a]	149.31±0.67[a]	156.82±0.56[a]	65.31±0.33[a]	59.92±0.30[a]
Crosslinked PHBV (L101 0.5%wt)	105.33±0.52[b]	146.98±1.04[b]	155.44±0.85[a,b]	60.84±1.86[b]	55.81±1.71[b]
Crosslinked PHBV (L101 1%wt)	104.48±0.30[b]	145.33±0.61[b]	153.78±0.63[b]	59.28±1.17[b]	54.38±1.08[b]
Crosslinked PHBV (L101 2%wt)	100.00±1.24[c]	140.16±0.81[c]	148.89±0.98[c]	51.42±0.32[c]	47.17±0.29[c]
Crosslinked PHBV (L101 3%wt)	99.21±0.89[c]	139.53±1.17[c]	148.34±1.32[c]	50.01±0.66[c]	45.88±0.60[c]
Crosslinked PHBV (L101 4%wt)	99.08±0.54[c]	138.60±0.54[c]	147.06±0.48[c]	49.69±0.68[c]	45.59±0.62[c]

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time of all crosslinked PHBV was 1 minute.



(a)



(b)

Figure 5.5 Endothermic (a) and exothermic (b) profiles of neat PHBV and crosslinked PHBVs with L101 at 0.5, 1, 2, 3 and 4 %wt.

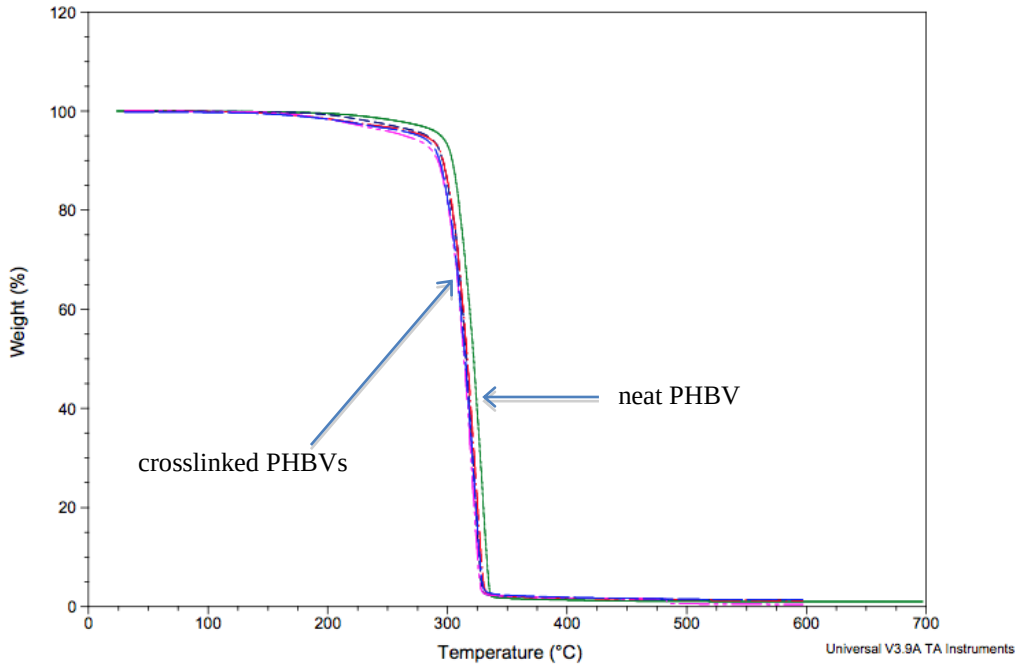


Figure 5.6 Thermal decomposition profiles of neat PHBV and crosslinked PHBVs with L101 at 0.5, 1, 2, 3 and 4 %wt.

5.3.4 Permeation properties of crosslinked poly(hydroxybutyrate-co-valerate)s

Permeability of water vapor, oxygen, and carbon dioxide was used in identifying whether the selected flexible material is suitable to be effectively used in packaging applications. Water vapor permeability (WVP) of all the crosslinked PHBVs was higher than that of neat PHBV as shown in Table 5.4 and Figure 5.7. However, the result in this study was different from many studies. According to Ouattara et al., crosslinked milk protein film by irradiation had lower WVP when compared to the non-crosslinked film [176]. Hernandez-Munoz et al. reported that crosslinked gliadin-rich fraction film had significantly higher water barrier when compared to the un-crosslinked film [160]. Additionally, Coma et al. stated that moisture barrier of crosslinked hydroxypropyl methyl cellulose (HPMC) with citric acid, compared to the un-crosslinked HPMC, was improved from 269±14 g/m^2.day to 221±2 g/m^2.day at 23 °C 50%RH [177]. In this study, PHBV inherently has a high water vapor barrier. The result showed that WVPs of the crosslinked PHBVs with L101 at 1 and 2%wt. were slightly higher than that of the neat PHBV, and WVPs of the crosslinked PHBVs with L101 at 0.5, 3 and 4%wt. were significantly greater than that of the neat PHBV. In fact, the crystalline structure of polymer is impermeable to water vapor and gases [178]. Crosslinking involves reduction of crystallinity as can be seen in Table 5.3 since the crosslinking network contributed to chain restriction, which impeded the crystallinity of the PHBV, creating free volume (voids) for water vapor permeation; further, thermal processing in the extruder may cause some thermal degradation involving chain scission. Then crosslinking did not contribute to improving water vapor barrier.

Table 5.4 Permeability properties of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	**Water vapor permeation, kg.m/m^2.s.Pa**	**Oxygen permeation, kg.m/m^2.s.Pa**	**Carbon dioxide permeation, kg.m/m^2.s.Pa**
Neat PHBV	$1.74\times10^{-6}\pm0.9\times10^{-7c}$	$2.26\times10^{-18}\pm3.4\times10^{-19}$	$2.06\times10^{-17}\pm8.5\times10^{-18b}$
Crosslinked PHBV (L101 0.5%wt)	$1.01\times10^{-5}\pm3.2\times10^{-6b}$	-	$2.44\times10^{-17}\pm3.1\times10^{-18b}$
Crosslinked PHBV (L101 1%wt)	$6.33\times10^{-6}\pm1.3\times10^{-7b,c}$	-	$2.04\times10^{-17}\pm2.8\times10^{-18b}$
Crosslinked PHBV (L101 2%wt)	$8.18\times10^{-6}\pm9.8\times10^{-7b,c}$	-	$2.39\times10^{-17}\pm4.0\times10^{-18b}$
Crosslinked PHBV (L101 3%wt)	$8.95\times10^{-6}\pm1.75\times10^{-6b}$	-	$5.00\times10^{-17}\pm4.8\times10^{-18a}$
Crosslinked PHBV (L101 4%wt)	$2.20\times10^{-5}\pm4.5\times10^{-6a}$	-	-

All measurements were performed in triplicate.
Values are reported as mean ± standard deviation.
Different letter designations for values in the same column indicate significant differences ($p \leq 0.05$).
The residence time of the crosslinked PHBV was 1 min.

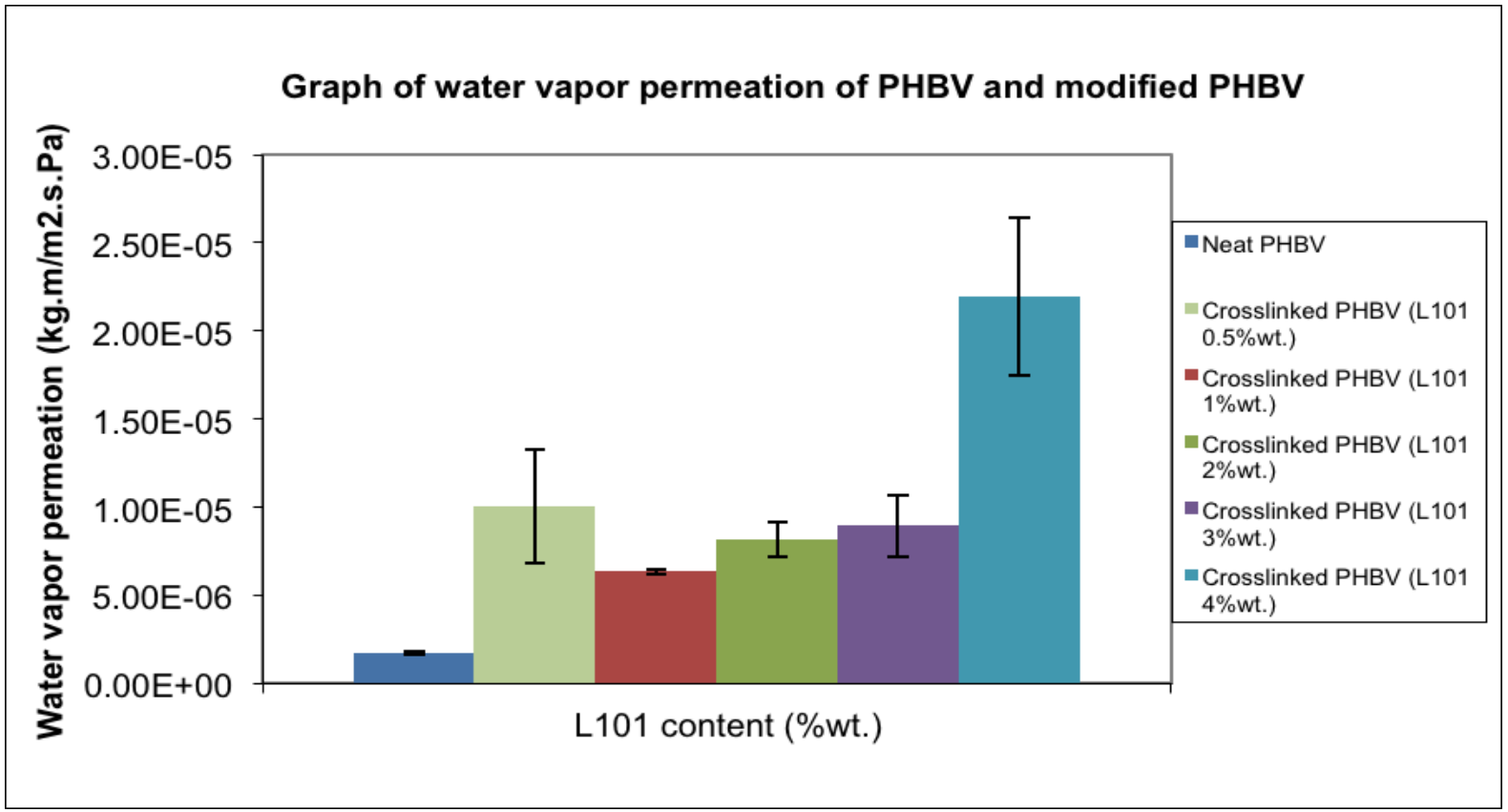


Figure 5.7 Water vapor permeation of neat PHBV and crosslinked PHBV sheets

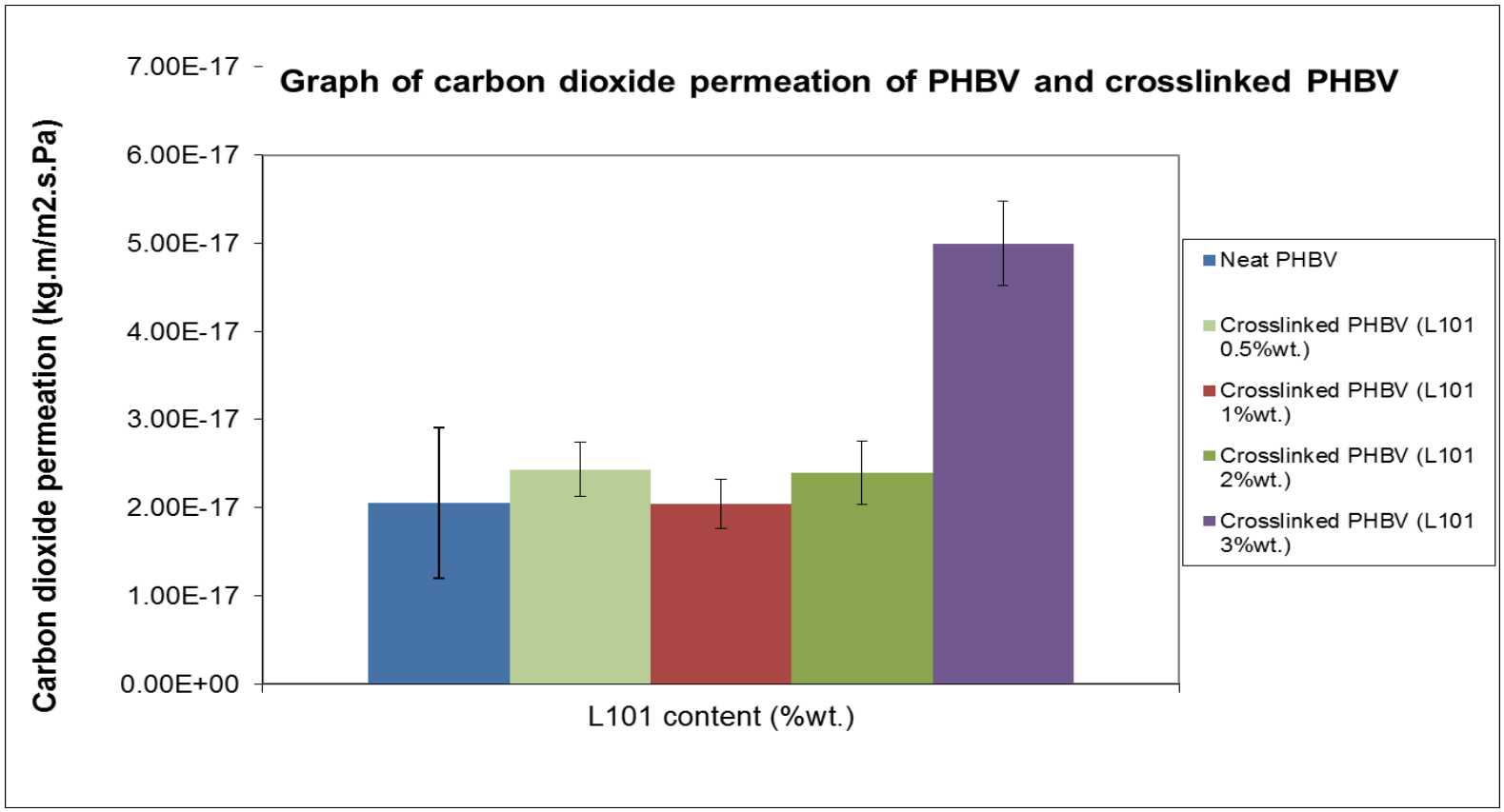


Figure 5.8 Carbon dioxide permeation of neat PHBV and crosslinked PHBV sheets

Oxygen permeation of the crosslinked PHBV could not be determined since the oxygen permeation machine (Mocon Oxtran 2/21) failed to perform the test. This was due to the fact that a high quantity of O_2 passed through the sheet and the measuring values were too high for the machine to quantify. Another possible reason for machine failure was that the crosslinked samples had a defect (small crack) due to its brittleness. In addition, carbon dioxide permeation (CO_2P) for the crosslinked PHBV with L101 4%wt. could not be measured because the amount of CO_2 passing through the sheet was beyond the measuring range of the machine. Generally, crosslinking decreases the CO_2P of polymers since the covalent network blocks free volume resulting in less gas permeation [179]. In this study, CO_2P of the neat PHBV and the crosslinked PHBVs with L101 at 0.5, 1 and 2 %wt. were not statistically significantly different. Meanwhile, CO_2P of the crosslinked PHBV with L101 at 3 %wt. was significantly higher than the neat PHBV and the crosslinked PHBV with L101 at 0.5, 1 and 2 %wt. Thus, crosslinking did not have significant effect on CO_2 permeability of PHBV at L101 content less than 3%wt. The greater CO_2P of crosslinked PHBV with L101 3 %wt., on the other hand, was attributed to chain restriction in the crosslinked network that interfered with the crystallization of the PHBV, creating voids for CO_2 passing through. Therefore, crosslinking worsened the CO_2 barrier of the PHBV at L101 3%wt.

5.4 Conclusion

Crosslinking is a modification method for improving PHBV properties, which tends to be inherently brittle and sticky. In this study, the crosslinking process (chemical reaction) required an initiator or crosslinker (catalyst), L101, in order to drive the reaction. The increase of L101 content in the crosslinked PHBV changed mechanical, thermal and permeability properties of PHBV.

6: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Summary and conclusions

Poly(hydroxybutyrate-co-valerate), PHBV, is a biodegradable polymer which has potential to be used in many areas, especially in packaging applications. However, it has serious inherent drawbacks such as brittleness and lack of elongation. To overcome its downsides, PHBV was modified by various methods in order to permit its use in flexible applications.

6.1.1 Selection of modification method for improving polyhydroxybutyrate-co-valerate properties for compression molding thin sheet

PHBV was blended with titanium dioxide (TiO_2) 1% by weight in order to obtain a toughening effect. The PHBV/TiO_2, compression molded into sheet, exhibited cracks all over the sheet. The sheet had tensile strength and elongation at break of 18.64±0.55 MPa and 10.60±0.50%, respectively, which were less than those of PHBV (19.84±0.54 MPa and 15.04±0.59%). Thermal properties of PHBV/TiO_2 showed lower crystallinity than PHBV due to TiO_2 interfering with the PHBV structure. Permeability of all three gases evaluated (water vapor, oxygen and carbon dioxide) of PHBV/TiO_2 was slightly higher than PHBV since TiO_2 aggregations created voids that gasses can get through. In the second trial, PHBV was blended with poly(butylene adipate-co-terephthalate) (PBAT or Ecoflex) at various ratios of PHBV/Ecoflex (80/20, 70/30, and 50/50 by weight) for flexibility. The compression molded sheets had lower tensile strength and elongation at break at every ratio of the blend (9.64±1.34

MPa and 5.43±1.27% for 80/20, 8.58±0.89 MPa and 8.37±1.74% for 70/30, 4.16±0.45 MPa and 4.47±0.12% for 50/50) when compared to PHBV. Thermal properties indicated that all blends of PHBV/Ecoflex had lower crystallinity than PHBV because Ecoflex impeded PHBV crystalline formation. Permeability of the blend (50/50) for all three gases was greater than PHBV. In the third trial, PHBV was blended with Ecoflex and TiO_2 at different ratios of PHBV/Ecoflex/TiO_2 (79/20/1, 69/30/1 and 49.5/49.5/1 by weight) to obtain combined effects of TiO_2 and Ecoflex. The compression molded sheets had lower tensile strength and elongation at break than PHBV in all ratios of the blend (12.54±1.02 MPa and 3.57±0.65% for 79/20/1, 11.30±1.20 MPa and 3.83±1.29% for 69/30/1, 6.31±0.56 MPa and 6.47±1.07% for 49.5/49.5/1). The PHBV blends had lower crystallinity than PHBV since Ecoflex in the blend interfered with crystallinity as well as TiO_2 aggregation creating non-uniformity, which diminished the crystallinity. The permeability of gasses in all blends was higher than PHBV corresponding to lower crystallinity in the blends. In the fourth trial, PHBV was blended with triethyl citrate (TEC) at a ratio of PHBV/TEC of 80/20 by weight to impart flexibility. The sheet was appeared to have clear liquid on the surface of the sheet due to TEC migration. Tensile strength and elongation at break of the compression molded sheet was lower than PHBV (4.82±1.19 MPa and 2.57±0.31%). PHBV/TEC had less crystallinity than PHBV. Permeability of the blend was not measured due to TEC migration. In the fifth trial, PHBV was grafted with 2-Hydroxyethyl methacrylate (2HEMA) at ratios of PHBV/2HEMA of 90/10 and 70/30 by weight. The sheets had lower tensile strength and elongation at break than PHBV (10.91±0.16 MPa and 7.51±0.02% for 90/10, 12.54±0.21 MPa and 11.40±1.51% for 70/30). Thermal analysis showed lower crystallinity in the blend than PHBV since the grafting process creates branched molecules in PHBV, which impede crystallization.

Permeability of the blends was higher than PHBV due to the branched chains in the matrix. In the final trial, PHBV was crosslinked in the presence of 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (L101). The sheet had significant greater elongation at break than PHBV and tensile strength was slightly higher than PHBV (20.45±0.66 MPa and 37.20±2.25%). The crosslinked PHBV had lower crystallinity than PHBV since the crosslinked network impeded crystalline formation, creating voids for favorable paths for gases resulting in higher permeation.

6.1.2 Influence of the amount of initiator on the degree of polyhydroxybutyrate-co-valerate crosslinking and its properties

Crosslinking was selected for modifying PHBV since it resulted in better elongation at break. In the second part, the amount of L101 in the crosslinking reaction was varied in order to obtain crosslinked material with higher elongation at break. L101 was added for the crosslinking reaction of PHBV at 0.5, 1, 2, 3, and 4 % by weight. The neat PHBV and crosslinked PHBVs sheets were not significantly different in tensile strength. However, elongation at break of crosslinked PHBVs was much greater than for PHBV, especially at a L101 content of 2%wt. where it was two times higher than neat PHBV. Thermal analysis showed that crystallinity of the crosslinked PHBVs were lower than neat PHBV when L101 content increased. Also, the permeability of gases decreased with an increase in L101 content

6.2 Problems and recommendations for future work

PHBV has an advantage of being biodegraded in damp conditions and exposure to microorganisms and its drawback of lack of elongation was improved by a crosslinking process in the presence of an initiator, L101. However, the modified PHBV might change the biodegradation behavior of the neat PHBV. Therefore the biodegradability of the modified PHBV needs to be studied and compared to that of the neat PHBV in order to evaluate the ability to maintain biodegradability of the modified PHBV.

APPENDICES

Appendix A- Mechanical properties of neat PHBV and modified PHBV material sheets

Table A-1 Tensile strength of all compositions of modified PHBV material sheets

Material	Tensile strength (MPa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	20.4402	19.6542	19.4170
Blend of PHBV/TiO_2 nanoparticle 1%wt	18.2131	19.2536	18.4455
Blend of PHBV/Ecoflex : 80/20 %wt	11.1444	9.2290	8.5519
Blend of PHBV/Ecoflex : 70/30 %wt	7.5528	9.0766	9.1117
Blend of PHBV/Ecoflex : 50/50 %wt	4.6721	3.8074	3.9957
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	13.7211	11.9125	11.9939
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	9.9633	12.2717	11.6732
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	6.9391	6.0979	5.8856
Blend of PHBV/Triethyl citrate : 80/20 %wt	4.6052	3.7461	6.0966
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	11.0747	10.7521	10.8969
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	12.7578	12.3455	12.5020
Crosslinked PHBV (L101 2%wt) rxn time 1 min	20.7967	19.6838	20.8691

Table A-2 Elongation at break of all compositions of modified PHBV material sheets

Material	Elongation at break (%)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	14.89	15.69	14.53
Blend of PHBV/TiO_2 nanoparticle 1%wt	10.10	11.10	10.60
Blend of PHBV/Ecoflex : 80/20 %wt	6.80	4.30	5.20
Blend of PHBV/Ecoflex : 70/30 %wt	9.70	6.40	9.00
Blend of PHBV/Ecoflex : 50/50 %wt	4.40	4.40	4.60
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	4.20	2.90	3.60
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	2.90	3.30	5.30
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	5.80	5.90	7.70
Blend of PHBV/Triethyl citrate : 80/20 %wt	2.50	2.30	2.90
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	7.50	7.41	7.62
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	10.90	10.20	13.10
Crosslinked PHBV (L101 2%wt) rxn time 1 min	39.40	37.30	34.90

Table A-3 Tensile strength of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Tensile strength (MPa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	20.4402	19.6542	19.4170
Crosslinked PHBV (L101 0.5%wt)	14.4600	15.6100	16.2000
Crosslinked PHBV (L101 1%wt)	18.4700	17.2400	17.6200
Crosslinked PHBV (L101 2%wt)	20.7967	19.6838	20.8691
Crosslinked PHBV (L101 3%wt)	18.7900	18.4300	17.5900
Crosslinked PHBV (L101 4%wt)	18.8261	19.0295	19.1384

Table A-4 Elongation at break of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Elongation at break (%)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	14.89	15.69	14.53
Crosslinked PHBV (L101 0.5%wt)	18.40	15.40	15.30
Crosslinked PHBV (L101 1%wt)	28.40	30.30	27.70
Crosslinked PHBV (L101 2%wt)	39.40	37.30	34.90
Crosslinked PHBV (L101 3%wt)	29.30	27.60	28.50
Crosslinked PHBV (L101 4%wt)	29.50	33.20	35.60

Appendix B- Thermal properties of neat PHBV and modified PHBV material sheets

Table B-1 Crystallization temperature of all compositions of modified PHBV material sheets

Material	Crystallization temperature, T_c (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	107.58	107.39	108.16
Blend of PHBV/TiO_2 nanoparticle 1%wt	110.02	109.57	110.05
Blend of PHBV/Ecoflex : 80/20 %wt	70.95	70.73	69.04
Blend of PHBV/Ecoflex : 70/30 %wt	67.46	69.51	69.35
Blend of PHBV/Ecoflex : 50/50 %wt	75.63	76.03	75.83
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	84.15	84.78	85.12
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	81.94	81.01	81.75
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	82.80	81.16	83.42
Blend of PHBV/Triethyl citrate : 80/20 %wt	64.45	74.89	71.84
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	104.95	105.20	104.84
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	98.62	102.11	102.38
Crosslinked PHBV (L101 2%wt) rxn time 1 min	100.56	98.57	100.86

Table B-2 The first melting temperature of all compositions of modified PHBV material sheets

Material	Melting temperature, T_{m1} (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	148.87	150.09	148.98
Blend of PHBV/TiO_2 nanoparticle 1%wt	153.12	153.50	152.99
Blend of PHBV/Ecoflex : 80/20 %wt	143.13	143.38	142.37
Blend of PHBV/Ecoflex : 70/30 %wt	142.87	143.12	145.11
Blend of PHBV/Ecoflex : 50/50 %wt	143.55	142.92	143.55
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	146.01	145.61	145.88
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	146.15	145.87	146.00
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	146.54	146.29	146.94
Blend of PHBV/Triethyl citrate : 80/20 %wt	130.28	131.97	130.70
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	149.87	149.42	149.56
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	144.34	147.42	147.62
Crosslinked PHBV (L101 2%wt) rxn time 1 min	140.55	139.23	140.70

Table B-3 The second melting temperature of all compositions of modified PHBV material sheets

Material	Melting temperature, T_{m2} (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	156.40	157.45	156.61
Blend of PHBV/TiO_2 nanoparticle 1%wt	159.55	159.98	159.77
Blend of PHBV/Ecoflex : 80/20 %wt	156.93	157.02	155.97
Blend of PHBV/Ecoflex : 70/30 %wt	156.15	156.81	157.47
Blend of PHBV/Ecoflex : 50/50 %wt	156.69	156.13	156.54
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	157.87	157.66	157.66
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	158.08	157.68	157.87
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	158.20	158.27	158.71
Blend of PHBV/Triethyl citrate : 80/20 %wt	146.55	146.86	146.11
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	158.50	157.87	157.66
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	154.92	157.03	157.03
Crosslinked PHBV (L101 2%wt) rxn time 1 min	149.45	147.76	149.45

Table B-4 Heat of fusion of all compositions of modified PHBV material sheets

Material	Heat of fusion, ΔH_m (J/g)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	65.50	65.50	64.93
Blend of PHBV/TiO_2 nanoparticle 1%wt	59.66	59.25	59.57
Blend of PHBV/Ecoflex : 80/20 %wt	50.90	50.58	50.83
Blend of PHBV/Ecoflex : 70/30 %wt	46.98	46.09	45.28
Blend of PHBV/Ecoflex : 50/50 %wt	31.89	31.54	31.77
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	49.24	48.77	49.06
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	43.51	44.11	44.22
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	31.95	31.69	31.91
Blend of PHBV/Triethyl citrate : 80/20 %wt	37.18	42.46	41.97
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	51.59	54.23	53.39
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	39.44	41.99	41.22
Crosslinked PHBV (L101 2%wt) rxn time 1 min	51.07	51.70	51.49

Table B-5 Crystallization temperature of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Crystallization temperature, T_c (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	107.58	107.39	108.16
Crosslinked PHBV (L101 0.5%wt)	104.85	105.89	105.26
Crosslinked PHBV (L101 1%wt)	104.66	104.65	104.14
Crosslinked PHBV (L101 2%wt)	100.56	98.57	100.86
Crosslinked PHBV (L101 3%wt)	98.45	98.99	100.19
Crosslinked PHBV (L101 4%wt)	98.48	99.21	99.54

Table B-6 The first melting temperature of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Melting temperature, T_{m1} (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	148.87	150.09	148.98
Crosslinked PHBV (L101 0.5%wt)	145.96	148.04	146.95
Crosslinked PHBV (L101 1%wt)	145.94	145.32	144.72
Crosslinked PHBV (L101 2%wt)	140.55	139.23	140.70
Crosslinked PHBV (L101 3%wt)	138.49	139.31	140.79
Crosslinked PHBV (L101 4%wt)	137.99	139.00	138.81

Table B-7 The second melting temperature of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Melting temperature, T_{m2} (°C)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	156.40	157.45	156.61
Crosslinked PHBV (L101 0.5%wt)	154.73	156.39	155.21
Crosslinked PHBV (L101 1%wt)	154.26	154.02	153.07
Crosslinked PHBV (L101 2%wt)	149.45	147.76	149.45
Crosslinked PHBV (L101 3%wt)	147.15	148.10	149.76
Crosslinked PHBV (L101 4%wt)	146.50	147.34	147.34

Table B-8 Heat of fusion of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Heat of fusion, ΔH_m (J/g)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	65.50	65.50	64.93
Crosslinked PHBV (L101 0.5%wt)	58.72	62.21	61.58
Crosslinked PHBV (L101 1%wt)	58.05	60.39	59.39
Crosslinked PHBV (L101 2%wt)	51.07	51.70	51.49
Crosslinked PHBV (L101 3%wt)	49.39	50.70	49.95
Crosslinked PHBV (L101 4%wt)	49.03	50.38	49.66

Appendix C- Permeation properties of neat PHBV and modified PHBV material sheets

Table C-1 Water vapor permeation of all compositions of modified PHBV material sheets

Material	Water vapor permeation (kg.m/m^2.s.Pa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	1.7137×10^{-6}	1.6556×10^{-6}	1.8382×10^{-6}
Blend of PHBV/TiO_2 nanoparticle 1%wt	1.8638×10^{-6}	1.5144×10^{-6}	1.7363×10^{-6}
Blend of PHBV/Ecoflex : 50/50 %wt	5.7988×10^{-6}	5.3421×10^{-6}	5.4455×10^{-6}
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	4.8423×10^{-6}	4.3439×10^{-6}	4.1044×10^{-6}
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	5.1935×10^{-6}	5.6159×10^{-6}	5.4142×10^{-6}
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	5.7446×10^{-6}	5.5777×10^{-6}	5.3460×10^{-6}
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	2.3726×10^{-6}	1.8465×10^{-6}	2.1066×10^{-6}
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	3.2242×10^{-6}	4.4369×10^{-6}	4.7425×10^{-6}
Crosslinked PHBV (L101 2%wt) rxn time 1 min	8.9446×10^{-6}	8.5172×10^{-6}	7.0841×10^{-6}

Table C-2 Oxygen permeation of all compositions of modified PHBV material sheets

Material	Oxygen permeation (kg.m/m^2.s.Pa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	2.5043×10^{-18}	2.4029×10^{-18}	1.8702×10^{-18}
Blend of PHBV/TiO_2 nanoparticle 1%wt	2.4966×10^{-18}	2.6211×10^{-18}	2.6892×10^{-18}
Blend of PHBV/Ecoflex : 50/50 %wt	6.8898×10^{-18}	6.0747×10^{-18}	7.0663×10^{-18}
Blend of PHBV/Ecoflex/TiO_2 : 79/20/1 %wt	5.7426×10^{-18}	5.1542×10^{-18}	4.7701×10^{-18}
Blend of PHBV/Ecoflex/TiO_2 : 69/30/1 %wt	5.9086×10^{-18}	4.8650×10^{-18}	5.3653×10^{-18}
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	6.2619×10^{-18}	6.2645×10^{-18}	6.3630×10^{-18}
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	1.8337×10^{-18}	1.0318×10^{-18}	1.3464×10^{-18}
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	2.8285×10^{-18}	3.1267×10^{-18}	2.6770×10^{-18}

Table C-3 Carbon dioxide permeation of all compositions of modified PHBV material sheets

Material	Carbon dioxide permeation (kg.m/m^2.s.Pa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	1.5858×10^{-17}	1.5437×10^{-17}	3.0438×10^{-17}
Blend of PHBV/TiO_2 nanoparticle 1%wt	2.9089×10^{-17}	3.0316×10^{-17}	2.7815×10^{-17}
Blend of PHBV/Ecoflex : 50/50 %wt	7.7334×10^{-17}	8.0598×10^{-17}	5.8830×10^{-17}
Blend of PHBV/Ecoflex/TiO_2 : 49.5/49.5/1 %wt	8.1706×10^{-17}	6.9323×10^{-17}	8.7477×10^{-17}
Grafted PHBV with 2HEMA : 90/10 %wt (L101 0.1%wt)	3.0511×10^{-17}	3.0696×10^{-17}	3.0488×10^{-17}
Grafted PHBV with 2HEMA : 70/30 %wt (L101 0.1%wt)	5.1475×10^{-17}	5.1051×10^{-17}	5.1084×10^{-17}
Crosslinked PHBV (L101 2%wt) rxn time 1 min	2.7303×10^{-17}	2.4278×10^{-17}	2.0140×10^{-17}

Table C-4 Water vapor permeation of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Water vapor permeation (kg.m/m^2.s.Pa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	1.7137×10^{-6}	1.6556×10^{-6}	1.8382×10^{-6}
Crosslinked PHBV (L101 0.5%wt)	8.5133×10^{-6}	7.8943×10^{-6}	1.37628×10^{-5}
Crosslinked PHBV (L101 1%wt)	6.2113×10^{-6}	6.2959×10^{-6}	6.4711×10^{-6}
Crosslinked PHBV (L101 2%wt)	8.9446×10^{-6}	8.5172×10^{-6}	7.0841×10^{-6}
Crosslinked PHBV (L101 3%wt)	1.03819×10^{-5}	6.9995×10^{-6}	9.4594×10^{-6}
Crosslinked PHBV (L101 4%wt)	1.87391×10^{-5}	2.71214×10^{-5}	2.01022×10^{-5}

Table C-5 Carbon dioxide permeation of crosslinked PHBV at various initiator contents compared to neat PHBV

Material	Carbon dioxide permeation (kg.m/m^2.s.Pa)		
	Replicate 1	**Replicate 2**	**Replicate 3**
Neat PHBV	1.5858×10^{-17}	1.5437×10^{-17}	3.0438×10^{-17}
Crosslinked PHBV (L101 0.5%wt)	2.1176×10^{-17}	2.4524×10^{-17}	2.7356×10^{-17}
Crosslinked PHBV (L101 1%wt)	1.7586×10^{-17}	2.3138×10^{-17}	2.0518×10^{-17}
Crosslinked PHBV (L101 2%wt)	2.7303×10^{-17}	2.4278×10^{-17}	2.0140×10^{-17}
Crosslinked PHBV (L101 3%wt)	4.5930×10^{-17}	5.5278×10^{-17}	4.8726×10^{-17}

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