Development of Polylactic Acid (PLA) based Durable Blends and Biocomposites: Routes for Improving Performance

by

Vidhya Nagarajan

A Thesis
presented to
The University of Guelph

In partial fulfillment of requirements
for the degree of
Doctor of Philosophy
in
Engineering

Guelph, Ontario, Canada

© Vidhya Nagarajan, August, 2016
ABSTRACT

DEVELOPMENT OF POLYLACTIC ACID (PLA) BASED DURABLE BLENDS AND BIOCOMPOSITES: ROUTES FOR IMPROVING PERFORMANCE

Vidhya Nagarajan
University of Guelph, 2016

Advisor: Prof. Amar K. Mohanty
Co-Advisor: Prof. Manjusri Misra

Use of synthetic plastics derived from petroleum is challenged due to extremely well-known issues of greenhouse gas (GHG) emissions causing climate change. Bioplastics are emerging as a new paradigm, focusing on renewability and sustainability. Replacing the fossil carbon present in plastics and products with renewable carbon allow to reduce the carbon footprint and GHG emissions. Polylactic acid (PLA) is one of the widely studied renewable resource based bioplastic with huge potential to be on a par with synthetic plastics. However, common commercial grades of neat PLA is yet to gain a strong commercial standpoint in applications other than cold food packaging due to its poor toughness and low heat resistance.

This thesis demonstrated feasible routes to fabricate PLA based blends and biocomposites with desirable morphology and crystallinity for durable applications. Two promising directions were considered; one based on PLA as a major phase and the other based on PLA as a minor phase. A three step approach was followed while pursuing both research directions. First, binary blends were studied to have a fundamental understanding regarding how the properties of the blends change by varying the blend ratio. Next, a suitable compatibilizer containing a reactive functional group was added to the optimum binary blend to achieve better properties through a reactive extrusion technique. The developed ternary blends showed
improvement in toughness depending on the type of functionalized terpolymer. In the third and final step, fabrication of biocomposites and the effect of addition of different fillers, additives, and processing strategies were investigated in an aim to increase the crystallinity and heat resistance. Through a combination of univariate and statistical optimizations, biocomposites containing PLA either as a major or minor phase, having a stiffness-toughness balance and a higher heat resistance were developed. Successful property improvements obtained in the developed materials has so far been unattainable for injection molded PLA biocomposites. Polymer and additive combinations investigated in this thesis are novel. Property attainment elaborated here enriches the existing body of literature concerning PLA based durable materials.
Dedicated to the four most important men who made this happen

Dr. Krishnaraj Sambath, *My beloved Husband*

Mr. Nagarajan Venkatachengan, *My Father*

Mr. William Keith Mclean, *My God Father*

Dr. Amar Kumar Mohanty, *My Advisor*
Acknowledgments

First and foremost, I sincerely thank Prof. Amar K. Mohanty and Prof. Manjusri Misra for encouraging me to pursue Ph.D. I express my sincere gratitude to them for their valuable guidance, sage advice, strong encouragement and support all these years. I appreciate their time, and effort in making my experience as a graduate student very productive and stimulating. I am privileged to have been a part of bioproducts discovery and development centre (BDDC) and seen its transformation over the past few years. I would also like to thank Prof. Mohanty and Prof. Misra for giving me several unique opportunities to work on project proposals, patent drafting, conference planning, and various exciting BDDC outreach activities. I am not sure there are enough words of thanks to express fully the gratitude I have for my advisors.

I will forever be indebted to Prof. Abdul Kader (B.S.A. Crescent Engineering College, India) for encouraging me to apply for graduate studies at University of Guelph. Special thanks go to Dr. Kunyu Zhang, for inspiring a part of my thesis work. I would like to thank my advisory committee members Prof. Mohammad Biglarbegian and Prof. Alfons Weersink for providing valuable advice on the thesis work. I would also like to thank my examination committee members, Prof. Michele Oliver, Prof. Karen Gordon and Prof. Ramani Narayan (Michigan State University) for their constructive comments and suggestions on the thesis.

I greatly acknowledge the financial support from (1) the Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA)- University of Guelph Bioeconomy-Industrial Uses Theme (Project # 200245, 200358, 200425); (2) the Ontario Research Fund, Research Excellence Program; Round-7 (ORF-RE07) from the Ontario Ministry of Research and Innovation (MRI), currently known as the Ontario Ministry of Research, Innovation and Science (MRIS) (Project # 052644 and # 052665); (3) the Natural Sciences and Engineering Research Council (NSERC)
Canada Discovery Grants (Project # 401111); and the NSERC Network of Centres of Excellence (NCE) AUTO21 Program (Project # 460372 and 460373). I am grateful to School of Engineering and Plant Agriculture department administration staff, particularly, Laurie Gallinger (for the much needed hugs!), Martha Davies, Tara Israel and Jennifer Kingswell for always being pleasant and ready to help.

My good friend, lunch buddy and a recent PhD graduate from BDDC, Dr. Vida Poursorkhabi, thank you for all your companionship, support, and advice. That witty sense of humor you have has lightened me up on multiple occasions. I have learnt a lot working with you on several assignments including ISBBB 2014 conference. I would like to thank all the past and present members of BDDC who have taught me valuable things and given me experiences worth remembering for life: Dr. Nima Zarrinbakhsh (my primary source for getting research questions answered); Dr. Tao Wang (the knowledgeable expert in microscopy, I would be more than happy to host you in Chennai); Dr. Singaravelu Vivekanandan (for his help with report writing and advice on character building), Dr. Rajendran muthuraj (for always being available to help with material handling, and occasional tamil conversations), Dr. Yury Yurev (for his help with understanding atomic force microscopy); Dr. Ramesh Kumar Petla (for helping me out during my initial days in Guelph). I would also like to thank all those who have shared the office space with me: Dr. Mohammad Abdelwahab and Dr. Petri Myllytie (lignin docs.), Dr. Simonet Torres (the green eyed photographer), Akpene Afenyadu (the ‘self-talk’er), Shujath Khan (the wedge heels master). I have enjoyed both, the research and not so research related conversations with you all. Thanks to Dr. Arturo Rodriguez, for always being kind and available when I needed help with processing. Big thanks to BDDC technician, Zack Jamha for helping with all semi-pilot scale processing and for being available for various lab related help. I would also like to thank
fellow PhD students in BDDC: Ehsan, Emmanuel, Oscar, Ghodsieh, Ryan and Michael, I have benefitted largely from the insightful discussions about our research, they helped in strengthening my understanding of the field. I have also had the pleasure of working with numerous other post docs, graduate students and summer students who have come through the lab.

My heartfelt thanks go to my family. Thank you for being very supportive and understanding during the course of this degree. This tough pursuit could not have been possible without your support and constant encouragement. Sorry Nana (Dad), I had to pick an argument with you 4 years back to continue grad studies in Canada, but I am sure I have made you proud. Thank you in all sincerity for believing in me. And amma (Mom), I know I was responsible for your countless sleepless nights, but you can be proud now as your second daughter will also be a ‘Dr.’ although not in the same sense as akka (sister). Akka, you have been a biggest motivation for my life, thank you for standing by me, when I decided to continue grad studies. Athamma (mother-in-law), you are loved and appreciated for so many reasons, my world is happier today because it includes you as my second mother. I thank you for all the pranic healing and blessings, and above all for being a big part of my support system. Big hugs and thanks to my landlord, William, who has been my God Father all these years. Thank you for all the valuable life lessons you have given me, for all your love, positivity, encouragement, and stupendous support. The enthusiasm and passion you have for research is contagious. You have made the past six years of my stay in Canada very special and memorable.

Thank you Janani and Farhan for instilling enthusiasm in pursuing graduate studies in Canada during my undergraduate years in India. It was one unforgettable first trip to Banff in winter 2011, thank you for introducing me to the real Canadian winter, Janani. Nishat, Iryna,
Gurvinder, Shirley, John, Harpreet, and Kelly thank you for making 2013 as one of the best years at school, our UC lunch times and sushi nights are some of my fond grad life memories. With you guys, I was able to venture out more, not just with courses but with social experiments – ranging from food to music. I still laugh when I reminisce about the times we played taboo. Thank you again for all the tea parties, pasta and lasagna nights, we now will have to count on google hangouts. I would like to thank my wonderful roommates Chuck, Maria, Sibel, and Toey for all the cultural experience. Thank you Sibel for all your encouragement and the Turkish coffee, I am happy your mission of making me drink coffee was eventually accomplished. I enjoyed how 351 Cole road at one point was a BDDC house. My time at Guelph was more enjoyable because of all you guys becoming a part of my life. I would also like to thank Guelph public transit and all the pleasant drivers who operate the routes 6 and 7, specifically driver Clint, whose last night bus service I took to go home several times after long nights of thesis writing.

Very special thanks to my loving, patient, immensely supportive and understanding husband, Krishna. My deepest appreciation goes to you for giving me the grit to persevere and succeed, and for bringing ultimate happiness into my life. This thesis could not have happened without you being my tower of strength. I am no poet, but I would like to borrow the lines of Madhan Karky to best express what you do for me, “neer vizhchi pole nindravan, naan neendha oru odai aanaai; vaan muttum malayai pondravan, naan aada oru medai aannai”
# Table of Contents

Acknowledgments........................................................................................................... v
List of Tables ..................................................................................................................... xiv
List of Figures ................................................................................................................... xv
List of Abbreviations ........................................................................................................ xx
List of Publications ........................................................................................................... xxiv

**Chapter 1: Thesis Overview** ...................................................................................... 1
1.1 Research Motivation and Background .................................................................. 2
1.2 Thesis Goal ............................................................................................................. 3
1.3 Thesis Title Rationale .......................................................................................... 4
1.4 Research Direction ............................................................................................... 4
1.5 Objectives and Hypothesis .................................................................................. 5
1.6 Synopsis of Thesis Chapters ............................................................................... 7

**Chapter 2: Introduction to Biobased Materials** ...................................................... 10
2.1 Biobased Materials ............................................................................................... 11
2.2 Biopolymers ......................................................................................................... 11
2.3 Biocomposites ....................................................................................................... 14
2.4 Natural Fibers: Classification and Composition .................................................. 16
   2.4.1 Advantages and attributes of natural fibers .................................................. 18
   2.4.2 Challenges in adapting natural fibers for composite applications .............. 19
2.5 Biochar (i.e Biocarbon) ....................................................................................... 20
   2.5.1 Attributes and advantages of biocarbon ..................................................... 22
References ..................................................................................................................... 24

**Chapter 3: Literature Review** .................................................................................. 27
3.1 Polylactic acid (PLA) for Durable Materials ....................................................... 28
3.2 Toughness: Definitions and Mechanisms ............................................................ 29
3.3 Super Toughened PLA Blends ............................................................................. 31
   3.3.1 Reactive compatibilization with functional monomers ............................... 31
Chapter 4: PLA Binary and Ternary Blends

4.1 Introduction

4.2 Materials and Methods

4.2.1 Materials

4.2.2 Melt blending

4.2.3 Testing and characterization

4.3 Results and Discussion

4.3.1 Mechanical properties

4.3.2 Morphology of the binary blends

4.3.3 Ternary blend morphology and toughening mechanism

4.3.4 FTIR spectra

4.3.5 Rheology

4.3.6 Differential scanning calorimetry (DSC)

4.3.7 Dynamic mechanical analysis (DMA)

4.5 Conclusion

References
Chapter 5: Crystallization Behavior of PLA with Aromatic Sulfonate Derivative

5.1 Introduction
5.2 Materials and Methods
  5.2.1 Materials
  5.2.2 Sample preparation
  5.2.3 Testing and characterization
5.3 Results and Discussion
  5.3.1 Non-isothermal crystallization behavior
  5.3.2 Isothermal crystallization kinetics
  5.3.3 Wide angle x-ray diffraction (WAXD)
  5.3.4 Heat deflection temperature (HDT)
  5.3.5 Spherulite morphology from optical microscopy
  5.3.6 Rheology
  5.3.7 Scanning electron microscopy (SEM)
5.4 Conclusion
References

Chapter 6: PLA Biocomposites

6.1 Introduction
6.2 Materials and Methods
  6.2.1 Materials
  6.2.2 Biocomposite fabrication
  6.2.3 Testing and characterization
6.3 Results and Discussions
  6.3.1 Non-isothermal crystallization behavior
  6.3.2 Isothermal crystallization behavior
  6.3.3 Wide angle x-ray diffraction (WAXD)
  6.3.4 Mechanical properties and heat deflection temperature (HDT)
  6.3.5 Optical microscopy
  6.3.6 Morphology of optimized PLA biocomposites
  6.3.7 Composition, particle size and dispersion of nucleating agents
References
6.3.8 Dynamic mechanical analysis (DMA) ................................................................. 175
6.3.9 Thermogravimetric analysis (TGA) ................................................................. 178
6.4 Conclusions ............................................................................................................ 180
References .................................................................................................................... 182

Chapter 7:  Reactive Extrusion of PTT-PLA Blends using a Terpolymer ................. 186

7.1 Introduction ............................................................................................................. 187
7.2. Materials and Methods ....................................................................................... 188
    7.2.1 Materials ......................................................................................................... 188
    7.2.2 Blend preparation ............................................................................................. 189
    7.2.3 Testing and characterization ............................................................................ 189
    7.2.4 Factorial design of experiments .................................................................... 190
7.3 Analysis of Variance (anova) for Factorial Design of Experiments ............... 192
    7.3.1 Main effects and interactions plot ................................................................. 194
7.4 Discussion on Compatibilization, Morphology and Mechanical Properties ...... 196
    7.4.1. Axial force curves from reactive extrusion ................................................. 196
    7.4.2 Compatibilization reactions and FTIR spectra ............................................. 198
    7.4.3 Morphology of the blends ............................................................................. 201
    7.4.4 Impact and tensile properties ........................................................................ 204
7.5 Model Fitting ......................................................................................................... 206
    7.5.1 Goodness of model fit...................................................................................... 208
    7.5.2 Contour plots and response optimization ..................................................... 212
7.6 Conclusion .............................................................................................................. 214
References .................................................................................................................... 215

Chapter 8:  Size-Fractionated Biocarbon Composites ............................................. 218

8.1 Introduction ............................................................................................................. 219
8.2 Materials and Methods ....................................................................................... 219
    8.2.1 Materials ......................................................................................................... 219
    8.2.2 Size-fractionation of biocarbon ................................................................. 221
    8.2.3 Processing of biocomposites ........................................................................ 222
List of Tables

Table 3-1: Impact strength results for super toughened PLA blends................................. 43
Table 3-2: PLA blends with improved heat resistance – summary of literature results .......... 54
Table 3-3: PLA blends with concurrent improvement in impact strength and heat resistance ... 57
Table 4-1: Physical properties of blending polymers .......................................................... 89
Table 4-2: Mechanical properties of PLA/HYT/terpolymer blends ...................................... 94
Table 5-1: Thermal characteristics of PLA and PLA with different concentration of Lak ...... 121
Table 5-2: Isothermal crystallization kinetics parameter obtained from Avrami plots .......... 126
Table 5-3: HDT for PLA/Lak Formulations molded at different temperatures....................... 132
Table 6-1: Differential scanning calorimetry data ............................................................... 156
Table 6-2: Elemental composition of different nucleating agents ......................................... 174
Table 6-3: Decomposition temperature of PLA biocomposites............................................. 179
Table 7-1: Factorial design of experiments with mechanical property results ....................... 192
Table 7-2: ANOVA for notched Izod impact strength (J/m) .................................................. 193
Table 7-3: ANOVA for tensile strength (MPa) ........................................................................ 194
Table 7-4: Mechanical properties of neat polymers and PTT70-PLA30 blend ................. 204
Table 7-5: Regression model summary for response variables ............................................. 207
Table 8-1: Differential scanning calorimetry data ............................................................... 243
Table 9-1: Production capacities and growth rate of PLA and PTT ...................................... 254
Table 9-2: Cost of polymers, additives and fillers ................................................................. 255
Table 9-3: Cost estimate for selected polymer blends and composites ............................... 256
Table C-1: Mechanical properties and HDT of PTT-PLA blends ........................................ 279
Table C-2: DSC results for PTT-PLA binary blends ............................................................. 282
List of Figures

Figure 1-1: Research direction for thesis ................................................................. 5

Figure 2-1: Classification of polymers based on source and biodegradability .............. 12

Figure 2-2: Schematic differentiating compostable and durable biopolymers ................ 13

Figure 2-3: Biocomposite terminologies .................................................................... 14

Figure 2-4: Natural fiber types, surface treatment options and challenges .................... 17

Figure 2-5: Raw material, technology and potential application for biocarbon .............. 22

Figure 2-6: Schematic showing microstructure of sieved miscanthus biocarbon and their favorable attributes ........................................................................................................... 23

Figure 3-1: Components, morphology and impact strength of supertoughened PLA blends..... 34

Figure 3-2: Notched impact strength PBSA blends .......................................................... 35

Figure 3-3: A simple schematic of a possible mechanism by which ACR toughens PLA ....... 37

Figure 3-4: (a) Notched Izod impact strength of neat and dynamically vulcanized PLA/NR blends, (b) SEM Images of dynamically vulcanized PLA/NR (65/35) ......................... 40

Figure 3-5: Morphology of the PLA/EVA50 (80/20) blends after impact testing: (a) initial impact bars, (b) optical images, and TEM images of (c) un-deformed part, (d)–(d") the stress whitening zone at different magnifications .................................................................. 42

Figure 3-6: Effect of molding temperatures on crystallinity (Xc) developed for PLA with 5% acetyl triethyl citrate (ATC) and 1% talc ........................................................................................................ 51

Figure 3-7: (a) Sample deflection recorded during creep tests for the sample PLA (squares), PA11 (diamonds), PLA70 (circles), and PLA70-C3 (triangles). ................................. 55

Figure 3-8: Distortion temperature under load (DTUL) of PLA-crushed Kenaf fiber .......... 63

Figure 3-9: Timeline of previous studies on biochar composites ........................................ 65
Figure 4-1: Tensile properties of PLA/HYT blends ......................................................... 92
Figure 4-2: Impact strength and elongation of PLA/HYT blends ..................................... 93
Figure 4-3: Impact Fracture Behavior of PLA Ternary Blends ........................................ 95
Figure 4-4: Impact fracture surface morphology of PLA/HYT blends ......................... 97
Figure 4-5: Impact fracture surface morphology of PLA/HYT/GMA terpolymer blends .... 98
Figure 4-6: Impact fracture surface morphology of PLA/HYT/MaH terpolymer blends .... 99
Figure 4-7: Cryogenic fracture surface morphology of PLA/HYT/Terpolymer blends .... 101
Figure 4-8: FTIR Spectra for the individual blend components ........................................ 102
Figure 4-9: FTIR spectra for PLA ternary blends ............................................................ 103
Figure 4-10: Reaction of GMA and MaH with functional groups of PLA ......................... 104
Figure 4-11: (a) Complex viscosity and (b) storage modulus of PLA/HYT blends ........ 106
Figure 4-12: Flow curve and viscosity curve for the PLA ternary blends ...................... 107
Figure 4-13: DSC Melting traces of PLA/HYT blends (from 2nd heat cycle) .................. 109
Figure 4-14: Storage modulus and Tan δ for (a) binary blends and (b) ternary blends ...... 111
Figure 5-1: DSC melting traces of PLA and PLA with Lak from second heating cycle .... 120
Figure 5-2: (a-d) Relative crystallinity plots for PLA with different wt% of Lak .............. 123
Figure 5-3: (a-d) Avrami Plots for PLA with different wt% of Lak ................................. 125
Figure 5-4: Crystallization rate vs. crystallization temperature for PLA with Lak ............ 129
Figure 5-5: WAXD pattern for neat PLA and PLA with different concentration of Lak .... 130
Figure 5-6: Polarized optical microscopy images of PLA and PLA with 0.5 % Lak ........ 134
Figure 5-7: (a-b) Variation in complex viscosity, storage modulus and loss modulus of PLA/Lak with increasing Lak content as a function of frequency ........................................ 135
Figure 5-8: SEM Images of Lak-301 at 200x and 1000x magnification .......................... 137
Figure 5-9: SEM Images of (a,b) PLA+0.25 % Lak; (c,d) PLA+0.5 % Lak; (e,f) PLA+0.75 % Lak; (g,h) PLA+1 %Lak ................................................................. 138

Figure 6-1: DSC thermograms of neat polymers and PLA1blend........................................... 151

Figure 6-2: DSC thermograms of first heating scans ............................................................... 153

Figure 6-3: Plot of relative crystallinity vs. time and crystallization half time of composites with different nucleating agents at two different temperatures ............................................. 158

Figure 6-4: WAXD profile of raw materials and biocomposites without nucleating agents molded at low and high mold temperature. ................................................................. 160

Figure 6-5: WAXD profile of different nucleating agents and their composites molded at different temperatures ........................................................................................................ 161

Figure 6-6: Impact strength and HDT of PLA biocomposites with and without Lak molded at different mold temperatures and injection cycle time .................................................. 163

Figure 6-7: Impact strength and HDT of PLA biocomposites with different nucleating agents molded at 110°C mold temperature ........................................................................... 166

Figure 6-8: Tensile and Flexural properties of selected PLA biocomposites ......................... 167

Figure 6-9: Optical microscopy images of PLA1blend/MS (90/10)-top row and PLA1blend/MS/Lak (89/10/1)-bottom row at 50x magnification ......................................................... 169

Figure 6-10: SEM images of PLA biocomposites with and without nucleating agent......... 171

Figure 6-11: SEM with EDS points for PLA biocomposites ..................................................... 174

Figure 6-12: Effect of mold temperature on the storage modulus and tan delta of the PLA biocomposites .................................................................................................................. 175

Figure 6-13: Effect of different nucleating agents on the (a) storage modulus and ............... 177

Figure 6-14: TGA Thermograms for selected PLA biocomposites molded at 110°C ............... 179
Figure 7-1: Main effects plot for (a) impact strength (b) tensile strength of the blends........... 195

Figure 7-2: Interaction plot for impact strength of the blends........................................ 196

Figure 7-3: Axial force vs. time curves for PTT70-PLA30/EMAGMA blends......................... 197

Figure 7-4: Reaction of PTT/PLA end groups with epoxy functional group of EMAGMA..... 198

Figure 7-5: FTIR Spectra for PTT70-PLA30/EMAGMA blends (a) full range- stacked (b) zoomed region between 1200 and 850 cm⁻¹ ................................................................. 200

Figure 7-6: PTT70-PLA30 blend at 5000x and 8000x magnification................................. 201

Figure 7-7: Cryo fractured surface morphology of PTT70-PLA30/EMAGMA (85/15) blends at (a) 100 rpm, (b) 200 rpm and (c) 0.5 phr CE, 200 rpm ......................................................... 202

Figure 7-8: Cryo fractured surface morphology of PTT70-PLA30/EMAGMA (80/20) blends at (a) 100 rpm, (b) 200 rpm and (c) 0.5 phr CE, 200 rpm ......................................................... 202

Figure 7-9: Normal probability plot of the residuals for (a) impact strength and (b) tensile strength ............................................................................................................ 209

Figure 7-10: Residuals against fitted values for (a) impact strength and (b) tensile strength ... 210

Figure 7-11: Residuals against observed order for (a) impact strength and (b) tensile strength 211

Figure 7-12: (a-c) Individual and overlaid contour plots of strength properties assessing the combined effect of EMAGMA and screw speed................................................................. 213

Figure 7-13: Response optimization for individual predictor variables ............................ 214

Figure 8-1: FTIR spectra for ‘as received’ biocarbon ....................................................... 220

Figure 8-2: Schematic of sieve setup on a Ro-Tap sieve shaker ....................................... 221

Figure 8-3: Particle size distribution based on the mass retained in the sieves ............... 226

Figure 8-4: SEM images of biocarbon sieved to different particle size range ................. 227
Figure 8-5: Particle size distribution along the longest and shortest dimension for size-fractionated biocarbon

Figure 8-6: Particle size distribution along the longest dimension for 20-75 μm and <20 μm.

Figure 8-7: Morphology of composites with different size-fractionated biocarbon

Figure 8-8: Morphology of composites with (a) 20-75 μm BC; (b) <20 μm BC; (c) 20-75 μm BC after etching; (d) <20 μm BC after etching; (e) 20-75 μm BC and 0.5phr CE (f) <20 μm BC and 0.5phr CE

Figure 8-9: (a) Tensile and (b) flexural properties of size-fractionated biocarbon composites showing the effect of varying size range, mold temperature and CE

Figure 8-10: Impact strength and HDT for biocarbon composites

Figure 8-11: Shear rate vs. viscosity for size-fractionated biocarbon composites

Figure 8-12: (a) Storage modulus and (b) Tan delta graphs for PTT biocomposites with size-fractionated biocarbon

Figure 8-13: (a) Storage modulus and (b) Tan delta graphs for PTT biocomposites with 20-75 μm biocarbon

Figure 9-1: Cost vs. biobased content of developed materials (a) PLA as major phase (b) PLA as minor phase

Figure B-1: Tensile and flexural properties of neat PLA, blends and biocomposites

Figure B-2: Impact strength and HDT of selected blends and composites

Figure C-1: SEM Images for PTT/PLA blends. Composition: 90/10, 80/20, 70/30

Figure C-2: SEM Images for PTT/PLA blends. Composition: 60/40 and 50/50
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACR</td>
<td>Acrylic impact modifiers</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile (butadiene styrene)</td>
</tr>
<tr>
<td>BA</td>
<td>Butyl acrylate</td>
</tr>
<tr>
<td>BC</td>
<td>Biocarbon</td>
</tr>
<tr>
<td>Bio-PA</td>
<td>Biobased polyamide</td>
</tr>
<tr>
<td>Bio-PET</td>
<td>Biobased polyethylene terephthalate</td>
</tr>
<tr>
<td>C$\infty$</td>
<td>Characteristic chain ratio</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CE</td>
<td>Chain extender</td>
</tr>
<tr>
<td>CF</td>
<td>Crystalline fraction</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>COP21</td>
<td>Conference of Parties (COP) or 2015 Paris Climate Conference</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl peroxide</td>
</tr>
<tr>
<td>DDGS</td>
<td>Distillers dried grains with solubles</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis/analyzer</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative thermogravimetry</td>
</tr>
<tr>
<td>EBAGMA</td>
<td>Ethylene butyl acrylate glycidyl methacrylate</td>
</tr>
<tr>
<td>EBAMaH</td>
<td>Ethylene butyl acrylate maleic anhydride</td>
</tr>
<tr>
<td>EGMA</td>
<td>Ethylene glycidyl methacrylate</td>
</tr>
<tr>
<td>EMAGMA</td>
<td>Ethylene methyl acrylate glycidyl methacrylate</td>
</tr>
<tr>
<td>EMAMaH</td>
<td>Ethylene methyl acrylate maleic anhydride</td>
</tr>
</tbody>
</table>
EMAA-Zn Ethylene methacrylic acid based zinc ionomer
EN European Standard
ENR Epoxidized natural rubber
EVA Ethylene-co-vinyl acetate
FTIR Fourier transform infrared
GHG Greenhouse gas
GMA Glycidyl methacrylate
$H_m$ Enthalpy of melting
$H_c$ Enthalpy of crystallization
HDPE High density polyethylene
HDT Heat deflection temperature
HYT Hytrel
LEED Leadership in Energy and Environmental Design
LDPE Low density polyethylene
LTI Lysine triisocyanate
Lak Lak-301, commercial nucleating agent
MAF Mobile amorphous fraction
MAPE Maleated polyethylene
MAPP Maleated polypropylene
MFI Melt flow index
MMA Methyl methacrylate
MS Miscanthus
NR Natural rubber
NOx Mono-nitrogen oxides
PBAT Poly (butylene adipate-co-terephthalate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>Poly (butylene succinate)</td>
</tr>
<tr>
<td>PBSA</td>
<td>Poly (butylene succinate-co-adipate)</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybutylene terephthalate</td>
</tr>
<tr>
<td>PC</td>
<td>Poly (carbonate)</td>
</tr>
<tr>
<td>PCL</td>
<td>Poly (ε-caprolactone)</td>
</tr>
<tr>
<td>PDLA</td>
<td>Poly (d-lactide)</td>
</tr>
<tr>
<td>PE</td>
<td>Poly (ethylene)</td>
</tr>
<tr>
<td>PEA</td>
<td>Poly (ester amide)</td>
</tr>
<tr>
<td>PEE</td>
<td>Poly (ether ester) elastomer</td>
</tr>
<tr>
<td>PEBA</td>
<td>Poly (ether-block-amide)</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PGA</td>
<td>Poly (glycolic acid)</td>
</tr>
<tr>
<td>PHA</td>
<td>Poly (hydroxyalkanoate)</td>
</tr>
<tr>
<td>PHB</td>
<td>Poly (hydroxybutyrate)</td>
</tr>
<tr>
<td>PHBV</td>
<td>Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)</td>
</tr>
<tr>
<td>Phr</td>
<td>Parts per hundred</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly (lactic acid)</td>
</tr>
<tr>
<td>PLLA</td>
<td>Poly (l-lactide)</td>
</tr>
<tr>
<td>PMAOD</td>
<td>Poly (maleic anhydridealt-octadecene)</td>
</tr>
<tr>
<td>PMDI</td>
<td>Polymeric Methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
</tr>
<tr>
<td>POE</td>
<td>Polyethylene octene</td>
</tr>
<tr>
<td>PP</td>
<td>Poly (propylene)</td>
</tr>
<tr>
<td>PPC</td>
<td>Polypropylene carbonate</td>
</tr>
<tr>
<td>PTAT</td>
<td>Poly (tetramethylene adipate-co-terephthalate)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PTT</td>
<td>Poly (trimethylene terephthalate)</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>PUEP</td>
<td>Polyurethane elastomer prepolymer</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly (vinyl alcohol)</td>
</tr>
<tr>
<td>RAF</td>
<td>Rigid amorphous fraction</td>
</tr>
<tr>
<td>RPM</td>
<td>Rotation per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SG</td>
<td>Switchgrass</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>$T_{cc}$</td>
<td>Cold crystallization temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis/analyzer</td>
</tr>
<tr>
<td>TPSA</td>
<td>Thermoplastic starch acetate</td>
</tr>
<tr>
<td>TPV</td>
<td>Thermoplastic vulcanizate</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nation Framework Convention on Climate Change</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>$\nu_e$</td>
<td>Entanglement density</td>
</tr>
<tr>
<td>VST</td>
<td>Vicat softening temperature</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide angle x-ray diffraction</td>
</tr>
<tr>
<td>Wt.</td>
<td>Weight</td>
</tr>
</tbody>
</table>
List of Publications

**Patent**

**Book Chapters**


**Peer Reviewed Journal Articles**


Chapter 1: Thesis Overview

Thesis overview starting with research motivation, thesis goal and research directions are provided in this chapter. Specific objectives and related hypothesis in accomplishing the thesis goal are listed. This is followed by synopsis of other thesis chapters.
1.1 Research Motivation and Background

Since the inception of human kind, activities related to finding food, shelter and clothing started with minimum amount of modification of already existing natural materials. Exploitation of renewable resources is not novel in this context. However, the development of renewable resource based macromolecules was setback with 20th century petrochemical revolution. Soon after, petroleum based plastics became ubiquitous and indispensable synthetic materials. Using non-renewable source like petroleum as a raw material is associated with greenhouse gases emissions. Anthropogenic CO₂ emissions are unequivocally warming the planet. Leading scientific organizations worldwide endorse climate change is real; related resources can be found on NASA’s webpage on global climate change. Intensive research and development efforts are therefore focused on using carbon strategically, without emitting more greenhouse gases and causing extensive environmental damage. Renewable resources (like biomass) are becoming increasingly important alternative to satisfy our demand. Bioeconomy moves away from the fossil economy that runs on petroleum and encompasses the sustainable production of biomass into food, feed and biobased products. Use of biobased materials represents a holistic strategy to reduce the material carbon footprint and mitigate climate change.

Major industries and business operations are recognizing how sustainable sourcing and use of renewable materials can impact their carbon footprints. Automotive industry is one of the major sectors driving the demand for biobased materials to meet performance and sustainability challenges. Stringent corporate average fuel economy (CAFÉ) standards in US and standards for CO₂ emissions per km per average vehicle in Europe are arguably driving the need for lightweight biomaterials. Automotive manufacturers are showing interest in conducting high-
profile demonstrations of biobased materials to help accelerate innovation and market acceptance. Biobased materials can provide significant opportunities for weight savings, strength and versatility in automotive interior parts. This will allow automakers to meet new standards without sacrificing quality and performance.

1.2 Thesis Goal

In the realm of bioplastics, poly (lactic acid), PLA has been undoubtedly the most researched material. Commercial PLA produced by NatureWorks LLC., under the tradename Ingeo™ is world’s foremost 100% biobased, biodegradable compostable plastic. PLA contributes to commercially viable products with significantly lower CO₂ emissions and material carbon footprint compared to traditional fossil fuel based plastics. Current global production capacity of PLA by NatureWorks is 150,000 and is expected to increase further by 75,000 tons per year with Carbion Purac’s new plant in Thailand set to open in second half of 2018. Research and development efforts to harness the potential of PLA for a broad range of applications are therefore of great interest and value to society. Current use of PLA is almost entirely limited to transparent food containers, blister packaging, cold drink cups, and cutlery. Inherent brittleness and low heat resistance of PLA prevents it from serving as a sustainable alternative for a wide range of possible applications. Attempts to enhance the performance of PLA beyond standard levels so far in injection molded applications have generated formulations with either higher heat resistance or greater impact strength, but seldom both. This is mainly because of the inverse relationship existing between impact strength and heat resistance properties of PLA. Main goal of this thesis therefore was to develop durable, high performance PLA based blends and composite materials, specifically showing concurrent improvements in impact strength and heat resistance. Stiffness-toughness balance was also a critical aspect of the developed materials.
1.3 Thesis Title Rationale

PLA, being a biobased, compostable polymer is generally used for making compostable products. However, in this thesis, PLA based blends and composite materials that are non-compostable are developed by blending with other synthetic, non-biodegradable/non-compostable additives to improve PLA’s performance and to extend its reach into markets for biobased durable products. The non-compostable PLA materials developed in this thesis are therefore referred to as ‘durable’ and hence the thesis is titled as “Development of PLA based durable blends and biocomposites: Routes for improving performance”.

1.4 Research Direction

Thesis goal was accomplished by pursuing two different research directions. In the first, PLA was used as major phase; the resulting materials had high percentage of PLA. In the second, PLA was used as minor phase; the resulting materials had lower percentage of PLA. In each of the proposed direction, three steps were followed to accomplish the goal: Fabrication and performance evaluation of PLA based (i) binary blends (ii) ternary blends and (iii) biocomposites. The research direction is shown schematically in Figure 1-1.

In the first part PLA was blended with a thermoplastic copolyester elastomer (TPCE) and then a functionalized terpolymer was added as a compatibilizer and impact modifier. This resulted in a super toughened PLA blend which was used as the matrix system for the incorporation of natural fibers. Biocomposites created in this way showed high impact and heat resistance compared to neat PLA.
Similarly in the second part of the thesis, PLA was blended with another partially biobased engineering thermoplastic, polytrimethylene terephthalate (PTT) which also has similar drawbacks as PLA, low impact and heat resistance. Binary blend ratio of PTT-PLA was optimized, to which a terpolymer was added to improve the toughness. Developed blend was then used as a matrix for the incorporation of biocarbon. Resulting biocomposites were again proved to have higher impact strength and heat resistance compared to the neat polymers, PLA and PTT.

Methodologies and different materials used were identified based on critical review of the literature. Rational for selection of different blending components, fillers and additives used in part 1 and part 2 are explained in the main chapters.

1.5 Objectives and Hypothesis

Specific objectives and hypothesis set out to accomplish the thesis goal in each of the chapters are explained below:
Part 1, Chapter 4

Objective 1: Evaluate the mechanical, thermal and rheological properties of PLA – TPCE binary blends. Hytrel, a commercially available TPCE belonging to the family of poly (ether ester) was selected.

Hypothesis: Blending PLA with a tough polymer such as Hytrel will result in blends having high impact toughness.

Objective 2: Improve the properties of PLA binary blends by reactive extrusion using a functionalized terpolymer. Different kinds of functionalized terpolymers were selected.

Hypothesis: Reactive extrusion will result in highly toughened PLA ternary blends.

Part 1, Chapter 5

Objective 3: To study the crystallization kinetics of aromatic sulfonate derivative, a new commercial nucleating agent

Hypothesis: Crystal nucleating agent can improve the crystallization rate of PLA thereby improving heat deflection temperature (HDT).

Part 1, Chapter 6

Objective 4: Achieve concurrent improvement in impact strength and heat resistance of PLA biocomposites. Effect of different nucleating agents, fiber types and processing strategies were investigated.

Hypothesis: Nucleation agent or fiber alone cannot provide the necessary improvements in crystallinity and heat resistance of PLA.

Part 2, Chapter 7

Objective 5: Optimize the properties of PTT, PLA and EMAGMA blends using statistical design of experiments.
Hypothesis: Shear rate and amount of additives have an effect on the resulting morphology of the reactive compatibilized blends.

Part 2, Chapter 8

Objective 6: Explore the use of biocarbon as renewable filler for PTT-PLA blends, and achieve concurrent improvements in impact strength and HDT.

Hypothesis: Particle size of the fractionated biocarbon affects the properties of the biocomposites. High mold temperature enhances the crystallization of PTT.

1.6 Synopsis of Thesis Chapters

Chapter 2 presents a broad introduction to biobased materials including biopolymers, biocomposites, natural fibers and biochar. Classification of biopolymers and natural fibers are discussed. Different terminologies related to biocomposites are clarified followed by a brief introduction to biochar (i.e biocarbon).

Chapter 3 reviews the related literature and advances readers’ understanding on the current research status of PLA based materials for durable applications. Focus of this review chapter is on the fundamental understanding of the major sought after properties – toughness and heat resistance. It also serves to identify the research gap in literature.

Chapter 4 presents the properties of PLA binary blend with Hytrel at different weight ratios and discusses the performance of multi-component blend containing PLA, Hytrel, and a series of functionalized terpolymers. Discussions based on results from various characterization techniques helps in understanding the strong co-relation between morphology and its significant effect on imparting property improvement.
**Novelty:** Reactive blending of the ternary blend components has resulted in a super toughened PLA blends.

Chapter 5 investigates the isothermal and non-isothermal crystallization behavior of PLA with a commercial nucleating agent Lak-301, belonging to the family of aromatic sulfonate derivatives.

**Novelty:** For the first time in literature, this study established the crystallization kinetics and spherulite morphology of PLA with Lak-301.

Chapter 6 proposes a novel combination of PLA blend, nucleating agent, natural fiber and a high mold temperature to attain PLA biocomposites with improved impact strength and heat deflection temperature (HDT). Discussion presents the effect of different nucleating agents, fiber types and mold temperatures on the biocomposite properties.

**Novelty:** Property improvement reported in this chapter had been unattainable so far in injection molded PLA biocomposite materials and we believe this work is first in the field.

Chapter 7 demonstrates the effectiveness of adopting a statistical design of experiments approach in opposition to traditional univariate approach in optimizing the properties of PTT-PLA-EMAGMA ternary blend system while varying the additives content and screw rpm. This chapter discusses the analysis of variance (ANOVA) results of the selected mixed level full factorial design and development of linear regression model.

**Novelty:** This study is one of the first successful attempts to compatibilize PTT-PLA blends and achieve property improvements.
Chapter 8 explores the use of size-fractionated biocarbon as effective renewable filler for the developed blends of PTT and PLA with moderate toughness. Particle size analysis of biocarbon is presented and correlated with the resulting mechanical, thermal and rheological properties.

**Novelty:** This study establishes the importance of biocarbon particle size in achieving desired property improvements.

Chapter 9 provides a general overview of the sustainability and market development aspects of the biopolymers and biocomposites followed by a preliminary cost analysis.

Chapter 10 concludes this thesis with overall summary, significant contributions and recommendations for future works.
Chapter 2: Introduction to Biobased Materials

Use of biobased materials is gaining increased importance with environmental concerns mounting worldwide over the use of nonrenewable resources. In recent years, many industries across various manufacturing sectors have acknowledged the need to adapt environmentally friendly manufacturing technologies and products. The scope for materials and technologies based on renewable resources is vast; extensive research and laboratory demonstrations have repeatedly proved the technical, environmental, and economical benefits of such innovative materials. This chapter gives a broad introduction to biobased materials including biopolymers, biocomposites, natural fibers and biochar. Classification of biopolymers and natural fibers are discussed. Different terminologies related to biocomposites are clarified followed by a brief introduction to biochar (i.e. biocarbon).
2.1 Biobased Materials

Bio- in Greek means life. ‘Biomaterial’ or ‘biobased material’ is defined as any material made from living organisms. Although this definition is broad, within the scope of plastics and plastic products, it typically refers to materials that are derived from renewable agricultural or forestry materials. This excludes fossilized materials. Products partly or wholly made from biobased materials are referred to as biobased products. Because they are derived from renewable raw materials such as plants, bio-based products can help reduce CO₂ emissions and offer other advantages such as lower toxicity or novel product characteristics for e.g. biodegradability. Multiple industrial adaptations and exploration of innovative biobased materials are underway to meet environmental concerns. Past decade has seen a remarkable surge of research interest in developing biopolymer blends and composites for durable applications in automotives, electronics, and semi structural parts.

2.2 Biopolymers

Generally accepted definition for biopolymers is they are macromolecules derived from renewable resources such as plants, trees, bacteria, or algae. In scientific terms, specifically, biopolymers refer to either biodegradable polymers, derived from non-renewable and renewable resources, or non-biodegradable polymers derived from renewable resources [1]. In other words for a polymer to be called a biopolymer, it has to be either biodegradable, bio-based or both. Classification of biopolymers based on source and biodegradability is shown in Figure 2-2. Biopolymers are often also referred as bioplastics in many published literatures.
‘Compostable’ and ‘biobased, durable’ are different but interrelated concepts of bioplastics. The focus of compostable bioplastics is to offer biodegradability as end of life option under compostable conditions, immaterial of the carbon source and reduce the solid waste stream ending up in landfill. In case of durables, the focus is to reduce the material carbon footprint by replacing fossil carbon with renewable carbon. Durable materials are targeted for long term applications in automotive interior parts, electronics, semi-structural parts and such. Performance of bioplastics in general is not on a par with petroleum-based plastics. Bioplastics such as PLA are therefore blended with other synthetic, non-biodegradable polymers and additives to extend
their reach into markets for biobased durable products. The concept of ‘compostable’ and ‘durable’ biopolymers are explained in schematic shown in **Figure 2-2**.

![Schematic differentiating compostable and durable biopolymers](image)

**Figure 2-2: Schematic differentiating compostable and durable biopolymers**

Although the potential of certain bioplastics were identified in the early 1900s, only recently they have emerged as a viable material for large-scale commercial use. Global bioplastics production capacity is set to quadruple from 1.7 million tonnes in 2014 to 17 million tonnes in 2020 [2]. Production of bioplastics like polylactic acid (PLA), polyhydroxy alkanoate (PHA) and starch based blends are projected to increase from 0.7 million tonnes in 2014 to over 1.2 million tonnes in 2019 [2]. The global production of bioplastics in 2014 was dominated by bio-based, non-biodegradable polymers (bio-polyethylene, bio-polyamide, etc) at 60.9 % while the biodegradable plastics accounted for 39.1 % with PLA scoring highest (12.2 %) in this category [2]. Market share of biobased polymers was 1.4 % in 2011 and is expected to reach more than 4 % in 2020 [2]. The biobased share is growing at a tremendous rate compared to the global polymer production. Automotive sector is the second most dynamic market segment after packaging.
2.3 Biocomposites

Composite is a heterogeneous combination of two or more different phase constituents (matrix, load bearing or reinforcement elements, fillers and compatibilizers) [3]. Reinforcements and fillers can be long, short, continuous, discontinuous, or spherical particles [3]. In this context, natural fibers are of definite interest to fabricate composites. When at least one of the constituent in the composite system is either biobased or biodegradable, it is described as a biocomposite. This term is also synonymous with ‘green composites’. Terminologies related to biocomposites are schematically represented in Figure 2-3.

![Figure 2-3: Biocomposite terminologies](image)
‘Natural fiber composite (NFC)’ is used to refer to composites containing natural fiber as the second discontinuous phase. Biocomposites made from biobased, biodegradable plastics and plant-derived filler/reinforcement is termed ‘all green composites’ to indicate the final formulations will be 100% biobased and biodegradable. Composites with more than one type of natural fiber or combination of natural fiber with other biobased filler are referred to as ‘hybrid biocomposites’.

For the past two decades, comprehensive research has been conducted on biocomposites and numerous research articles have been published addressing various challenges in the fabrication of biocomposites. Final goal has always been achieving composites with desired level of mechanical performance and cost attributes for specific industrial uses. Synergistic combination of natural fibers and plastics can result in a material having favorable level of performance, quality and cost, and therefore possessing immense potential and prospects for serving different industries and applications. Natural fiber composites based on polyolefins such as polyethylene (PE), polypropylene (PP) have been widely researched and are successful in finding applications in development of interior parts for automotive industries [4-7]. Certain renewable resource based biopolymers have the potential to be an important component of a continuously emerging new line of low carbon footprint materials. Combining biopolymers with natural fibers is a strategy to produce advanced composite materials. This strategy enables research scientists to design and engineer materials according to the requirements of the end user while keeping sustainability, economic feasibility and environmental considerations within the design framework.
2.4 Natural Fibers: Classification and Composition

Natural fibers are abundantly available and are relatively inexpensive. Natural fibers are mainly classified as vegetable fibers, animal fibers and mineral fibers (e.g. asbestos) depending on the origin [8]. Vegetable fibers are further classified as wood (soft and hard) fibers and non-wood fibers. Five basic types of non-wood fibers with few representative examples are,

- **Bast**: hemp, flax, jute, kenaf and ramie
- **Leaf**: sisal, pineapple, abaca
- **Seed/fruit**: coir, kapok, coconut
- **Straw**: wheat, rice, soy and corn straw
- **Grass/reed**: switchgrass, miscanthus

Figure 2-4 shows the general classification of lignocellulosic natural fibers, surface treatment methods and challenges which are discussed in later sections of this chapter. Generally, bast fibers are preferred in applications requiring high tensile strength, stiffness and modulus. They are available in chopped, non-woven and mat forms. Bast and leaf fibers find application in particle boards, fiberboards, automotive components, products for housing and infrastructure [9]. Leaf fibers and coir are employed as cordage materials, cotton in apparels and jute in carpeting and sacking. Other lignocellulosic residues such as sugarcane bagasse, coffee chaff, hulls and residues resulting from agricultural and industrial processing also represent a major fiber source for the development of renewable resource based biocomposites for industrial applications. Distillers dried grains with solubles (DDGS), a coproduct of corn ethanol industry, and lignin, a co-product of bioethanol, pulp and paper industry are also gaining increased interest for creating new value added biocomposite materials [10].
Natural Fibers

Figure 2-4: Natural fiber types, surface treatment options and challenges

The universe of natural fiber is very broad; even so, the basic chemical constituents are similar only their composition varies depending on the type and origin of the fiber. Natural fiber contains rigid, crystalline cellulose micro fibrils and hemicellulose in a matrix of amorphous lignin. They also contain pectin, waxes, and some water-soluble compounds. Cellulose is the most abundant organic compound available in earth. Plant cell walls get their strength, stiffness and stability from this main structural component, cellulose. The amount of cellulose present in a fiber has a significant influence on the properties and performance of resulting composite
materials produced for various applications. The compositions of various natural fibers have been listed in detail in several review articles and book chapter [11,12]. The mechanical properties of resulting composite materials are highly dependent on the source of natural fiber mainly because of variation in composition. For example, two composites made of jute and flax, with similar host matrix and equal concentrations even after identical treatments will not essentially show the similar mechanical performance [1]. Nagarajan et al. [13] investigated the effect of fiber composition and fiber length on biocomposites containing perennial grasses and agricultural residues and concluded these factors had a complementary effect on the performance of biocomposites. Research and development is directed more towards in situ compatibilization and reactive extrusion techniques for injection molding type of biocomposites.

2.4.1 Advantages and attributes of natural fibers

Principal advantages of using natural fibers in fabrication of composites are listed below [1,11].

- Renewability, biodegradability and CO₂ neutrality nature of natural fibers makes it environmental friendly. Carbon sequestration helps in reducing GHG emissions and its implications on climate change.

- Reinforcing synthetic and biopolymers with natural fibers can reduce dependence on petro based materials. Typically up to 50 wt. % of the matrix can be replaced with natural fibers for several injection molded applications. Weight percentages of natural fiber in compression molded composites could be higher than 50 % depending on the matrix system and compatibilizers used for certain target application.

- Natural fibers are available at a lower cost; therefore they can help in offsetting the cost of matrix. Final cost of the parts can be cheaper or on a par with the synthetic counterparts.
• Natural fibers can be an effective substitute for synthetic fibers such as E-glass fibers in certain applications. This advantage will be well received by industries as several countries have imposed severe restriction on disposal of products made with glass fibers and use of asbestos has also been banned in several parts of the world.

• When composites with natural fibers are incinerated for energy recovery process, only harmless residues are released without any trace of heavy metals.

• Natural fibers have environmentally benign production process and disposal options compared to synthetic fibers. They can be processed in conventional processing equipment with reduced dermal and respiratory irritation. Unlike glass fibers, natural fibers are non-abrasive to processing machinery used for manufacturing the composite materials, resulting in overall better efficiency.

• Certain categories of natural fiber have high specific modulus, strength, and low density compared to E-glass fibers.

• Natural fiber composites are lightweight materials; for automotive applications this translates to weight saving advantage and improved fuel efficiency. Natural fibers also exhibit good acoustic and sound abatement properties.

2.4.2 Challenges in adapting natural fibers for composite applications

Several challenges are encountered while developing composites from natural fibers and they all need to be effectively addressed to elevate the performance and market acceptability of biocomposites. Challenges discussed below are interconnected and good control over these factors is important to create composites meeting the desired level of performance set by the industries. Knowledge on physical characteristics of fibers such as fiber architecture, strength, variability and crystallinity are necessary to design composite formulations with desired
performance attributes. Unfortunately, in most cases the natural fiber composite do not possess same level of performance as glass fiber composites due to the incompatibility between hydrophobic polymer matrix and hydrophilic natural fiber. Although, this issue can be solved by adequate physical and / or chemical modification (as listed in Figure 2-4), the risk of chain degradation and cost increment is a major thrust area for research.

Natural fibers can withstand a maximum processing temperature of 200 °C. Poor thermal stability beyond this temperature limits their use in engineering plastics which are usually processed above 230 °C. In general, natural fiber composites have higher susceptibility to moisture absorption. The moisture content is usually dependent on the composition of non-crystalline parts and presence of voids on the fiber surface. Appropriate drying methods have to be established before processing the material with polymer matrix. Other dominant barriers are aesthetics, undesirable odor during melt processing and in final product. This problem can be neutralized by adding suitable odor control additives. Variability in fiber characteristics and properties depending on harvest conditions and seasonal changes also affect the composite properties. Production patterns affecting the properties of the fibers are being surveyed over longer time periods to acquire an understanding of producing fibers with consistent qualities [8].

2.5 Biochar (i.e. Biocarbon)

Intensive research and development efforts are focused on using carbon strategically, without emitting more greenhouse gases and causing extensive environmental damage. Recently, an article published in nature communications provided an estimated potential of biochar to mitigate climate-change when it is produced using pyrolysis technology and stored in soil in a sustainable manner [14]. According to this study, annual emissions of CO₂, nitrous oxide and
methane could be reduced by 12 %, offsetting 1.8 Pg CO$_2$-C equivalent of current 15.4 Pg CO$_2$-C (1 Pg =1 Gt). This study used different scenarios and criterion for sustainable biochar production and storage to provide this estimate [14].

Biochar is defined as ‘a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment’ by International Biochar Initiative (IBI) [15]. Initially it was designated to be used for environmental management, especially in soil amendment. However, the range of application for biochar is widening from cascade of uses in animal farming, to water treatment, to additives in cosmetics, textile, electronics, construction and composite applications [16]. Carbon contained in the biomass, taken from the atmosphere in the form of CO$_2$ during plant growth is stored for long period of time when biochar is used in any of these applications. Biochar is therefore an excellent source for carbon sequestration. Much of the knowledge regarding the use of biochar in soil amendment comes from the pioneering work of Lehmann et al [17].

Different terminologies surrounding biochar exist such as char, charcoal, porous carbon, activated carbon, pyrolyzed carbon, black C and biocarbon. Production process along with intended use forms the basis for the naming convention [17]. Biochar denotes carbon rich charred organic matter used for soil amendment, remediation or other environmental services. Relatively new term ‘Biocarbon’ is adopted in this thesis to denote the carbon produced through thermochemical conversion process and used for composite applications. This term emphasizes the biological origin of carbon, distinguishing it from synthetic fillers like carbon black. Raw material or feedstock, production process and potential applications for biocarbon are summarized in Figure 2-5.
Renewable sources including different kinds of wood and wood waste [18-22], agricultural residues [23,24], perennial grasses like switchgrass and miscanthus [25,26], pine saw dust [27], poultry litter [27], coconut shells [28], spent coffee ground [29], and lignin [30] have been used thus far in making biocarbon.

2.5.1 Attributes and advantages of biocarbon

Attributes of biocarbon (Figure 2-6) such as relatively high surface area, carbon content (50-80 %), and hydrophobic nature compared to natural fibers makes it desirable filler for composites [31]. Biocarbon can also act as reinforcement based on its aspect ratio, strength and stiffness. It offers a wide processing window when combined with engineering plastics, unlike most other natural fibers that degrade above 200 °C. Thermal stability of the final composites is also higher compared to natural fiber composites. Chemical and physical properties of biocarbon have an effect on the final properties of the composites. Feedstock, particle size, and pyrolysis temperature are some of the factors governing the final properties of biocarbon. Slow pyrolysis process can provide higher biocarbon yield. Formation of pores provides the biocarbon with overall surface area and pore volumes. The surface area is known to increase with production temperature, activation and reduction in particle size.
Characteristics of biocarbon are also contingent on the type of pre-processing operation. Grinding and milling operations could result in biocarbon with different particle sizes which can then be used to advantage depending on final property requirements. Apart from these advantages, biocarbon has a great potential to replace carbon black, commonly used as a filler in automotive tires and as a black pigment in most automotive interior parts, electronic casings, and agricultural mulch films (for UV-resistance). Commodity carbon black is produced by subjecting coal or petroleum based feedstock to high temperatures under controlled combustion. Emissions from this process include sulfur compounds, particulate matter, polycyclic organic matter, NOx, organics, CO, and trace elements [32]. Due to the non-renewable origin of carbon black and a recent drive to replace it with biobased materials, biocarbon is being proposed as a sustainable alternative with potential economic benefits.
References


(10) Lamontagne, N. D., New Natural-fiber Composites find their roles’, Plastics Engineering, June 2013.


(32) US DOE Identification and Selection of Major Carbon Dioxide Stream Compositions

Chapter 3: Literature review

Last decade has seen a remarkable surge of research interest in developing poly lactic acid (PLA) based blends and composites for durable applications in automotive, electronics, and semi structural parts. This chapter summarizes the most recent developments in achieving super toughened and heat resistant PLA blends and composites. Exhaustive literature available on these topics are organized based on the strategies and approaches taken to resolve the material problems. Various factors governing toughness and heat resistance of blends and composites are discussed. Morphology and crystallinity that individually contribute to toughness and heat resistance have also been elucidated. Later part of this chapter reviews the blends of PLA with engineering plastics. Research works reported so far on poly trimethylene terephthalate (PTT) and PLA blends are detailed followed by a section on composites containing biocarbon. Last section lists the contributions of this thesis in bridging some of the research gaps existing in PLA blends and composites.

1 Version of this chapter is published as ‘Perspective on Polylactic Acid (PLA) based Sustainable Materials for Durable Applications: Focus on Toughness and Heat Resistance’ in ACS Sustainable Chemistry & Engineering, 2016, 4 (6), 2899–2916.
3.1 Polylactic acid (PLA) for Durable Materials

PLA is a biodegradable thermoplastic polyester produced by condensation polymerization of lactic acid, which is derived by fermentation of sugars from carbohydrate sources such as corn, sugarcane, or tapioca [1,2]. From energy consumption, CO\textsubscript{2} emissions and end of life options, PLA is superior to many petroleum-based polymers [1]. Depending on the D-lactide content, PLA can be either amorphous or crystalline. Melting temperature of semi-crystalline PLA, with low content of D-lactide is in the range of 170-180 °C and glass transition temperature (\(T_g\)) is around 60 °C. Crystallization rate of semi-crystalline PLA is very slow compared to other commercial polymers such as polypropylene and polyethylene. PLA already serves as an alternative to certain petroleum based plastics in commercial applications thanks to its high volume availability in the market at a price on a par with common plastics like polypropylene. Market demand for PLA has grown dramatically over the past decade with much of it being in the packaging industry [2]. PLA was initially promoted for single use packaging applications, given the key benefit of short life cycle due to its compostable nature. The application areas for PLA are widening with usage in durable structural parts generating particular high demand. Besides property enhancement with suitable additives, when the final formulations are intended for compostable applications, the materials should satisfy the compostability standards set forth in ASTM D6400 or EN 13432. On the flip side, there are not many cost effective and compostable additives available to substantially raise the performance level of PLA while retaining its compostability. Industries are therefore seeing a major shift in the marketplace from ‘compostability’ to ‘renewability’. However, being compostable and being renewable are not dependent or in conflict with each other, each has its own advantages.
Current research around the world on PLA modification and application is focused on producing high performance partially renewable materials which can compete with conventional plastics. However, much like other synthetic plastics, PLA has its own inherent weakness which prevents it from being widely adopted for durable applications, in particular its low toughness and heat resistance. PLA has very slow crystallization rate, while a high level of crystallinity is desirable in finished products as it dictates most of the mechanical and thermal properties. The toughness and ductility of PLA have been improved with multiple strategies including copolymerization, plasticization, and melt blending with different tough polymers, rubbers and thermoplastic elastomers [3-9].

3.2 Toughness: Definitions and Mechanisms

Toughness is a complicated property; it is defined in terms of ‘impact strength/toughness’, the ability to absorb sudden impact energy without breaking and ‘tensile toughness’, the ability to absorb energy while being pulled apart or stretched. Emphasis is on the ability to absorb energy before fracture. PLA is a brittle polymer with low crack initiation energy (measured by unnotched impact test) and low crack propagation energy (measured by notched impact test); it fails by crazing. While it may be relatively easy to improve the ductility (elongation at break), it is much more challenging to increase the impact toughness of PLA.

Impact toughness depends on many extrinsic (notch, temperature, loading mode, specimen geometry, fracture behavior) and intrinsic (phase morphology, chain structure and entanglements) variables. The responsiveness of a particular polymer to be rubber toughened is also said to depend on entanglement density \( \nu_e \) and characteristic chain ratio \( C_\infty \), these two will decide the fracture behavior of crazing and yielding [10]. Readers are referred to Wu’s work [10] for detailed understanding of these concepts.
Toughening mechanisms including shear yielding, multiple crazing and a combination of both have been reported for toughened PLA blends [4]. According to toughening theories [10-14], stress concentration due to the presence of spherical rubbery particles is the first step to complex toughening process. Multiple crazing occurs when the stress required for craze initiation is less than the yield stress. In this situation, maximum triaxial stress concentrations at the dispersed particles initiate crazes. Craze termination is the next natural step in this mechanism through the formation of small multiple crazes leading to crack propagation. New surfaces generated during the creation of multiple crazes consume more energy than a small number of large crazes. Shear yielding occurs when the stress required for craze initiation is greater than yield stress. Toughening by this mechanism is usually achieved by hydrostatic tension in the dispersed particles acting as shear band initiators. When the yield stress and craze initiation stress are comparable or when there are interactions between the shear bands and crazes formed in the matrix, combination of shear yielding and multiple crazing becomes the predominant mechanism. Cavitation is another important precursor phenomenon to any toughening mechanism. Two types of cavitation have been observed in PLA toughened with a rubbery phase: (i) internal cavitation, which occurs when the interfacial bonding is strong between the rubber domains and matrix (ii) debonding cavitation, which occurs when there is poor interfacial bonding strength. To prevent the localization of strain, cavities formed either in the rubber particle (internal) or the matrix (debonding) alters the triaxial stress state and favors the formation of shear bands ultimately leading to shear yielding of the matrix. Combination of internal and debonding cavitation is also a possible mechanism. The particle size, shape and distribution of toughening agent can be tailored to substantially reduce the amount of impact modifiers or elastomers required for a desired toughness. Multicomponent blends containing
reactive copolymers are therefore being developed to tune the phase morphology in interesting ways and obtain blends with moderate stiffness and sufficient toughness by employing techniques like in situ reactive compatibilization and dynamic vulcanization. These processes increase interfacial strength by promoting chemical reactions between blending components establishing a strong bridge for transmission of stresses.

3.3 Super Toughened PLA Blends

PLA blends with drastic improvement in impact toughness are being referred to as ‘super toughened’ PLA. This term was first known to be used by Wu [10] for convenience to arbitrarily denote blends having notched impact strength higher than 10 ft/\text{lb} or \sim 530 \text{ J/m} (energy lost per unit width, North American standard) which is approximately equal to 53 \text{ kJ/m}^2 (energy lost per unit cross-sectional area, European standard) depending on the dimension of the sample. Research work specifically focused on achieving super toughened PLA blends (impact strength beyond 35 \text{ kJ/m}^2) is reviewed in this section. They are categorized according to the type of reactive toughening polymers and techniques used. Range of impact properties thus far obtained in super toughened PLA blends are summarized in Table 3-1. Most of the articles discussed in this section were focused on achieving super toughness and have not investigated the effect on crystallinity or heat resistance.

3.3.1 Reactive compatibilization with functional monomers

Successful application of reactive compatibilization technique has provided enormous opportunities to compatibilize otherwise immiscible and incompatible blends. Reactive compatibilization is therefore seen as a powerful technique to effectively enhance the compatibility of PLA with other tough polymers. Melt blending PLA with other suitable polymers in the presence of a reactive monomer forms a graft copolymer at the interphase,
decreases the interfacial tension of the immiscible polymer components and promotes interfacial adhesion. Finer phase morphology developed in the blends facilitates stress transfer between the two phases thereby improving the properties of the blends. Maleic anhydride, glycidyl methacrylate, isocyanate, and epoxy, are some of the widely investigated reactive monomers proving to be successful in compatibilizing the blends of PLA with other bio and petro-based polymers. In the work of Harada et al.[15] 0.5 % lysine triisocyanate (LTI) was found to increase the impact strength of PLA/PBS (90/10) blend from 18 kJ/m² to 50-70 kJ/m². These improvements were attributed to effective interfacial reactions accomplished between the isocyanate functionalities of LTI and carboxyl, hydroxyl end groups of the blending polymers.

Glycidyl methacrylate (GMA) is one of the versatile functional monomer tailored to meet a variety of applications and a great number of PLA super toughening work reports use of GMA in one or other form to facilitate compatibility by reacting with functional end groups of PLA. Effectiveness of GMA in improving the toughness of PLA is explored mainly through these three routes: (i) Addition of GMA monomers or copolymers such as ethylene glycidyl methacrylate (EGMA), ethylene methyl acrylate glycidyl methacrylate (EMAGMA), and ethylene butyl acrylate glycidyl methacrylate (EBAGMA); (ii) Addition of tough polymers grafted with GMA to facilitate compatibility between the blending components (two step process of grafting followed by reactive compatibilization) and (iii) Addition of tough thermoplastic elastomers in combination with GMA copolymers in one step reactive extrusion. Factors drastically affecting the toughening behavior of PLA blends containing GMA are the reactive extrusion screw rpm and residence time which in turn affects important morphological aspects such as dispersed phase size and inter-particle distance. Increasing the screw rpm from 30 to 200 in low molecular weight PLA containing 20 % EGMA was found to have a drastic effect on
elongation [16], as the value went up from 26 % to > 200 %. However, a super toughened PLA blend with 72 kJ/m\(^2\) of impact strength was achieved only after annealing the processed samples at 90 °C for 2.5h. Another parameter appearing to have a significant effect on the resulting toughening is GMA grafting content. Polyethylene octene (POE), a metallocene catalyzed thermoplastic polyolefin elastomer grafted with different percentage of GMA (1.8 and 0.8 %) was used to toughen PLA [17,18]. To achieve impact strength of 55 kJ/m\(^2\), 45 wt. % of POE-g-GMA (1.8 %) had to be blended with PLA [17], whereas in another study [18], 20 wt. % of POE-g-GMA (0.8 %) was sufficient to attain super toughness of over 80 kJ/m\(^2\). These super toughened blend systems were proved to be efficient in absorbing external energy through a combination of crazing and shear yielding mechanisms. Poly (ether-block-amide), PEBA a commercial class of thermoplastic copolyester elastomer from Arkema is seen as an efficient impact modifier for brittle polymers as it is highly resistant to sudden impact even at very low temperatures (~40 °C). In spite of such favorable properties [19], 30 wt. % PEBA was required to improve the impact strength of PLA to 60 kJ/m\(^2\). Zhang et al. [20] used EMAGMA as a reactive interfacial compatibilizer for blends of PLA/PEBA and achieved impact strength up to 500 J/m, while maintaining tensile strength at 50 MPa (Figure 3-1).
Performance improvements in these ternary blends were attributed to their unique morphology of partial encapsulation of PEBA by EMAGMA in PLA matrix. Interfacial cavitation and good adhesion between phases resulted in massive shear yielding of PLA matrix. Vachon et al. [21] used EMAGMA and poly (maleic anhydride-alt-octadecene) (PMAOD) to compatibilize PLA and thermoplastic poly (ether ester) elastomer, PEE. Sharp transition in impact strength values to 650 J/m was noticed in PLA ternary blends containing 12 % of PEE and 12 % of EMAGMA, with EMAGMA being more efficient compared to PMAOD. Recently, Zhou et al. [22] investigated the effect of adding GMA grafted PEBA (PEBA-g-GMA) as impact modifier for PLA and thermoplastic starch acetate (TPSA). This work showed notched Izod impact strength of ~60 kJ/m² could be achieved for PLA/TPSA/PEBA-g-GMA (70/15/15) blend.
TPSA esterification degree of 0.04 % was needed to improve the compatibility between TPSA and PLA/PEBA-g-GMA.

Properties of polymers are influenced to a greater extent by the length of the macromolecule. When the macromolecular chain is longer, the molar mass and entanglement degree is higher, which increases the melt temperature and viscosity. Adding a chain extender (CE) to PLA increases the molar mass of PLA by connecting the short and long polymer chains via a reactive functional end groups present in the CE. When a multifunctional epoxy based chain extender, Joncryl® was used for in situ reactive compatibilization of PLA and poly (butylene succinate-co-adipate), PBSA, the alteration of blend structure from linear to long branched chains enhanced the impact strength of PLA/PBSA (60/40) blend [23,24] as shown in the Figure 3-2.

![Figure 3-2: Notched impact strength as a function of PBSA content and Joncryl weight fraction.](image)

The schematic depicts the modification of the PLA/PBSA blend interface by Joncryl through the formation of non-linear copolymer. [Reprinted from Polymer, Vol 80, V. Ojijo, S.S. Ray, Supertoughened biodegradable Polylactide blends with non-linear copolymer interfacial architecture obtained via facile in-situ reactive compatibilization, 1-17, Copyright © 2015, with permission from Elsevier, License number: 3794351260132]
Particle size of PBSA dispersed phase reduced by 74% with the addition of 0.6% Joncryl and further reduction was noticed with increase in Joncryl content owing to effective compatibilization. Dong et al. [25] have also reported Joncryl is effective in increasing the ductility and percentage elongation of PLA/PBAT blends, to a maximum of 500%. As previous studies [24] have established the presence of induction time for reactivity of Joncryl, effect of increasing the temperature to increase the reactivity of Joncryl can be an interesting aspect of future investigations.

3.3.2 Acrylic copolymers and core-shell impact modifiers

Acrylic polymers such as poly (methyl methacrylate), PMMA and poly (butyl acrylate), PBA have been found to be partially miscible with PLA; therefore, they have been used to toughen PLA [26,27]. Achieving significant increase in impact strength is however a challenge in simple binary blends of PLA with such polymers [26-28]. Researchers have looked into core shell acrylic copolymers such as methyl methacrylate - butadiene styrene, acrylonitrile-butadiene styrene and methyl methacrylate-butyl acrylate copolymers to super toughen PLA [29-35]. The rubbery core provides impact resistance while the glassy shell imparts rigidity. Outer shell can be designed specifically to be compatible with the PLA matrix. Core-shell composition, particle diameter and its distribution, grafting percentage and crosslinking degree are all important factors to achieve the necessary toughening and they have all been investigated in detail in PLA matrix. Acrylic impact modifiers (ACRs) containing different ratios of methyl methacrylate, MMA (hard/shell monomer) and butyl acrylate, BA (soft/core monomer) were used to super toughen PLA [31,32]. Impact strength and elongation at break gradually increased with increase in the amount of soft monomer in the ACR. In PLA/ACR (90/10) containing BA/MMA in the ratio of 90/10, unnotched impact strength was significantly increased to 68 kJ/m² compared to 17
kJ/m$^2$ for the neat PLA. Tensile and flexural properties were not drastically reduced as the ACR content was only 10 % [31]. As the concentration of MMA hard shell monomer increased, the impact strength initially increased and then decreased, signifying the presence of critical concentration of MMA. Highest notched Izod impact strength of 77.1 kJ/m$^2$ was achieved when the ACR core–shell ratio was optimized at 79.2/20.8 for the 80/20 PLA/ACR blend [32]. With increase in BA content, the interactions between ACR and PLA were believed to get stronger and the interface between these phases was indistinct. Internal and debonding cavities in the ACR domains induced crazes and shear bands in the PLA making the matrix around the ACR particles to deform easily to achieve shear yielding as shown in the schematic [31], **Figure 3-3**.

*Figure 3-3: A simple schematic of a possible mechanism by which ACR toughens PLA*


Poly (ether glycol) methyl ether acrylate, abbreviated as AcrylPEG has been most effective in imparting super toughness to PLA thus far. Two different approaches were investigated by Kfoury et al. [33]: (i) polymerization of AcrylPEG to poly (AcrylPEG) using free
radical initiator, Luperox and (ii) direct one step reactive extrusion with PLA, where in situ grafting of AcrylPEG onto PLA backbone was achieved. Substantial improvement of notched Izod impact strength to 102 kJ/m² was achieved for PLA with 20 wt. % AcrylPEG, and 35 kJ/m² for PLA with poly (AcrylPEG). Commercial non-biodegradable acrylic impact modifiers available under the tradename Paraloid™ BPM-500 [34] and KM-365 [35] from Rohm and Haas, and Biomax® Strong [36] from DuPont are also available to toughen PLA. PLA blends with Paraloid™ BPM-500 [34] possessed good flexibility compared to neat PLA, impact strength however did not improve beyond 40 J/m. PLA has been reported to show brittle to ductile transitions when KM-365 and Biomax® Strong are added beyond 20 wt. %. In some cases, impact modifiers were observed to hinder the crystallization of PLA and decrease the tensile properties of the blends.

3.3.3 Dynamic vulcanization

Dynamic vulcanization is one of the most versatile areas of polymer modification. It is a process in which selective vulcanization of elastomer with nonvulcanizing thermoplastic is achieved during shearing in melt mixing leading to the formation of two-phase material where particulate crosslinked elastomeric phases are dispersed in the plastic matrix [37]. Zhang et al. [38] introduced a super toughened PLA ternary blends with moderate tensile strength and modulus by melt blending PLA with ethylene n-butyl acrylate GMA (EBAGMA) and ethylene methacrylic acid based zinc ionomer (EMAA-Zn). Unlike other blends, in addition to reactive compatibilization between PLA and EBAGMA, dynamic vulcanization of EBAGMA was also achieved. Ternary blends containing EMAGMA/Ionomer weight ratio ≥ 1, Zn metal ion, higher percentage of MMA functionality and increased degree of neutrality were found to have enhanced interfacial compatibility and hence higher impact strength [39-41]. Morphological
analysis based on SEM images demonstrated that with the increase in EMAA-Zn content, the occluded subinclusion phase of EMAA-Zn turned to continuous phase within the ‘salami’ like dispersed domains. This morphology was not dependent on reactive blending temperature, however higher reactive extrusion temperatures resulted in unfavorably higher degree of crosslinking in EBAGMA which was resisting internal cavitation.

Polyurethane elastomer prepolymer (PUEP) with isocyanate (–NCO) terminal groups vulcanized to a rubber phase has been shown to toughen PLA [42]. The –NCO groups reacted with hydroxyl, carboxyl end groups of PLA to form urethane linkages in addition to vulcanization reaction of the PUEP. These reaction products bridged the PLA phase with vulcanized rubber phase of PUEP. Predominant internal cavitation in dynamic vulcanized blends imparted major toughening effect to PLA/PEUP (70/30) blends with impact strength of 55 kJ/m² and elongation values reaching over 400 %. In another recent work, researchers have developed super tough PLA materials through in situ reactive blending with poly ethylene glycol based diacrylate (PEGDA) monomers [43]. The crosslinking of acrylate groups resulted in phase separated morphology with PEGDA as the dispersed phase. Sea-island morphology had been the typical, predominant morphology of thermoplastic vulcanizates (TPVs) but Chen [44,45] and Yuan et al. [46,47] discovered it is possible to achieve continuous crosslinked rubber phase in peroxide induced dynamic vulcanization of PLA with natural rubber (NR) and epoxidized natural rubber (ENR). Impact strength results and SEM morphology of dynamic vulcanized PLA/NR (65/35) [44] are shown in Figure 3-4. After cryofracture and etching of PLA phase, formation of continuous honeycomb like network structure by the NR phase was clearly visible. Extensive plastic deformation of the surrounding PLA deformed the rubber domains due to heterogeneous stress fields and enhanced the toughness. Brittle ductile transition was observed at
PLA/ENR (60/40) blend ratio with notched Izod impact strength of 47 kJ/m², which was 15 times higher compared to 3 kJ/m² for neat PLA [45]. At dicumyl peroxide (DCP) content beyond 0.03 phr, interfacial adhesion between phases was enhanced and a higher degree of crosslinking was achieved in ENR. ‘Fully biobased and super tough PLA TPV’ displaying a quasi-co-continuous morphology with vulcanized unsaturated polyester elastomer (UPE) is yet another successful effort to super toughen PLA using dynamic vulcanization [48]. Tensile and impact strength of PLA/UPE TPVs improved from 3.2 MJ/m3 and 16.6 J/m to 99.3 MJ/m3 and 586 J/m, respectively. Other researchers have also experimented with the dynamic vulcanization technique on PLA blends of biobased polyester elastomers (BPE) [49], ethylene co-vinyl acetate (EVA) [50] and ultrafine fully vulcanized powder rubber (UFPR) [51]. They have been successful in achieving tremendous improvements in elongation at break (>400 %) however; the impact strength is either not reported or very low in the case of UFPR.

![Figure 3-4](image)

**Figure 3-4:** (a) Notched Izod impact strength of neat and dynamically vulcanized PLA/NR blends, (b) SEM Images of dynamically vulcanized PLA/NR (65/35)

[Reprinted with permission from ACS applied materials & interfaces, Vol 6, Chen, Y., Yuan, D., & Xu, C, Dynamically vulcanized biobased Polylactide /natural rubber blend material with continuous cross-linked rubber phase, 3811-3816, Copyright © 2014, American Chemical Society]
3.3.4 Melt blending with random aliphatic copolyesters, and other toughening polymers

In a series of studies, Joziasse [52] and Odent et al. [53-55] synthesized random biodegradable copolyester: CL with d,l-lactide, (P[CL-co-LA]) and CL with δ-Valarectone (VL), (P[CL-co-VL]) has been used as impact modifiers for PLA. When silica nanoparticles (10 %) were added to PLA blends containing these copolyesters, spherically dispersed domains converted to co-continuous morphology, increasing the impact strength to 39.7 kJ/m² vs 2.7 kJ/m² for neat PLA [55]. Li et al.[56] prepared sliding graft copolymer (SGC) where PCL side chains are bound to polyrotaxane (PR) cyclodextrin rings and used them to toughen PLA. Methylene diphenyl diisocyanate (MDI) was used as the reactive compatibilizer. Blends of PLA/SGC/MDI displayed super toughening with impact strength values as high as 48.6 kJ/m². Unfortunately, preparing such copolymers is not currently economically viable for adoption by the industry for wide scale production.

Unique combination of toughness, durability and flexibility makes thermoplastic polyurethane elastomers (TPU) a suitable material to blend with PLA. Addition of 30 % TPU to PLA resulted in blends with impact strength of 315 J/m and elongation at break of 363 % [57]. Liu et al.[58] noticed toughening PLA by in situ polymerization of PEG and PMDI to form crosslinked polyurethane (CPU) was successful, where the impact strength of PLA with 30 % CPU increased from 16 to 546 J/m. Liu et al.[59] introduced PDLA into PLLA/TPU blends to form stereocomplex crystals that can dramatically improve the melt viscosity and change the sea-island morphology of PLLA/TPU to a unique network like structure. High levels of crystallinity in these blends were achieved by injecting the samples into a preheated mold at 130 °C and post annealing. This resulted in PLLA/TPU/PDLA (70/15/15) blends with remarkable improvement in impact strength up to 63.2 kJ/m². Ethylene-co-vinyl acetate (EVA) with different vinyl
contents and ethylene acrylic elastomer (EAE) has also been found to impart super toughness to PLA at 20 wt. % [60,61], Figure 3-5.

![Figure 3-5: Morphology of the PLA/EVA50 (80/20) blends after impact testing: (a) initial impact bars, (b) optical images, and TEM images of (c) un-deformed part, (d)–(d'') the stress whitening zone at different magnifications


Formation of shear bands initiated by the internal cavitation of EVA resulted in shear yielding type of fracture behavior in the blend, no crazing or interfacial debonding occurred. As a consequence of numerous internal cavitations, stress whitening was noticed on a macroscopic scale as shown in the Figure 3-5.
Table 3-1: Impact strength results for super toughened PLA blends

<table>
<thead>
<tr>
<th>Technique / Additives</th>
<th>Range of Impact Strength Achieved</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GMA based copolymers, thermoplastic elastomers and GMA grafted copolymers:</strong> EGMA, POE, POE-g-GMA, PEBA, PEE EMAGMA, PEBA-g-GMA</td>
<td>Notched Charpy: 46.1 - 72 kJ/m² Notched Izod: 40-80 kJ/m², 450-650 J/m</td>
<td>16-22</td>
</tr>
<tr>
<td><strong>Compatibilizers and chain extenders for PLA blends with PBS, PBSA, PBAT:</strong> LTI, Joncryl, TPP</td>
<td>Notched Izod: Non-break Notched Charpy: 16 – 40 kJ/m²</td>
<td>15, 23, 24</td>
</tr>
<tr>
<td><strong>Acrylic impact modifiers and acrylic copolymer with GMA:</strong> MBS, ABS-g-GMA, AcrylPEG, ACR with different BA and MMA content, KM-365 and Paraloid BPM 500 from Rohm and Haas, Biomax® strong from DuPont</td>
<td>Notched Izod: 35 – 120 kJ/m² 540 J/m</td>
<td>26-36</td>
</tr>
<tr>
<td><strong>Dynamic Vulcanization:</strong> EBAGMA, EMAA based ionomers, PUEP, NR, ENR, UPE</td>
<td>Notched Izod: 480 -800 J/m (Non-break) 38 – 60 kJ/m²</td>
<td>37-51</td>
</tr>
<tr>
<td><strong>Random aliphatic copolyesters, polyurethanes, and other flexible polymers:</strong> P(CL-co-LA), P(CL-co-VL), TPU, CPU, EVA</td>
<td>Notched Izod: 40- 83 kJ/m² 450 -550 J/m</td>
<td>52-61</td>
</tr>
</tbody>
</table>
3.4 Evaluation of Factors Affecting Toughness

In any rubber toughened factors such as rubber content, type, particle size, particle size distribution and interparticle distance are closely interrelated and greatly affect the resulting toughening effect. Majority of investigations concerning super toughened PLA have reported the existence of an optimum loading level of the toughening agent and beyond this level fracture toughness ceases to improve or in some cases starts to decline. This might be due to several intrinsic factors related to the microstructure and the efficiency of rubber to support any kind of toughening mechanism at high rubber contents when there is not much matrix material to undergo plastic deformation. Toughness improvements can be expected only in a certain rubber content range, in which the rubber is dispersed in desired particle sizes and size distribution to effectively cavitate or fibrillate for maintaining a substantial degree of structural integrity in response to impact. The experimental evidences reported for such a limit is 20-30 wt. % of rubber content, therefore modelling and theoretical work can be developed to predict and explain this limit in future. The rubbery phase added as a toughening agent is generally preferred to be compatible with PLA to such an extent that there is satisfactory dispersion and wetting but not completely miscible to result in a single homogeneous phase morphology. When the two phases are miscible as in PEG- plasticized PLA with, the elongation ratio (percentage) is improved tremendously but the inability of the second phase to act as stress concentrator does not favor multiple crazing or shear yielding resulting in blends with only moderate toughness. Similarly low toughness was reported for PLA with in situ formed PU containing non-crosslinked product which acted as a plasticizer [58]. In the case of PLA/EVA blends, toughness improvements were marginal because of the formation of homogeneous morphology below 20 wt. % EVA [60].
Toughness improvement is also the highest at an optimum rubber particle size. When the dispersed phase is incompatible with the matrix, it would exist as spherical particles to reduce surface tension. If the components in the blend have good compatibility, uniform dispersion of the rubbery toughening agent with relatively small particle size can be expected. With an overlap in stress fields around the well dispersed particles, plastic deformation can propagate through entire matrix giving rise to effective energy dissipation. Reactive compatibilization has been found to reduce the particle size of the thermoplastic elastomer or rubbery copolymer considerably [15,18,24,58] and in some cases their shape evolves from spherical to distinct co-continuous morphology [24,56]. The shape and size of the dispersed particles are dependent on the dynamic viscosity, the shear rate of melt blending, and the interfacial tension. The dispersed particles will have the smallest average size when the viscosity ratio of the two phases is closer to unity and when the interfacial tension is lower [12]. Higher shear rate generated by increasing the screw rotation speed in an extruder can drastically reduce the particle size of the rubber. For example, increasing the screw rpm from 30 to 200 significantly decreased the particle size of EGMA in high molecular weight PLA (PLA-H) compared to low molecular weight PLA (PLA-L) [16]. Proximity of viscosity ratio to unity in the case of PLA-H reduced the particle size to 50-100 nm while in PLA-L it was reduced to 100-300 nm [16]. However, very small particle size may not be beneficial for achieving super toughness as small particles may not effectively absorb the energy of the external force. Other researchers who quantified the particle size of dispersed phase in super toughened PLA also have established the fact that having optimum particle size had resulted in superior toughening effect [15,18,58]. Based on the theories of Wu [11], the entanglement density, υe is recognized to be one of the main factors governing the deformation mechanism. For brittle polymers in general super toughening is predicted to occur at an optimum
ve of 0.1mmol/cc, as massive crazing and yielding of the matrix occurs at this level of \( v_e \) [11]. Depending on composition, PLA is predicted to have ve in the range of 0.12-0.14 mmol/cc [52,62]. Using Wu’s relationship [11] between optimum rubber particle size, \( d_o \) and \( v_e \),

\[
\log d_o = 1.19 - 14.1 v_e \quad (3.1)
\]

The \( d_o \) for PLA can be calculated to be in the range of 0.16-0.31 \( \mu \)m. Based on theoretical investigations, this range can be expected to be the guiding value of particle size in future PLA work aiming at achieving successful super toughening effect. However, if the dispersed rubber phase contains rigid sub-inclusions as in the case of core-shell or salami like morphology in ternary blends, the inclusion phase can anchor the load bearing fibrils to the matrix which can effectively reduce premature cavitation. Therefore in an alternative view, particle size range required to achieve optimum toughness also depends on other factors such as strain rate, morphology of the dispersed particles, rubber content and the rubber shear modulus.

Unfortunately, PLA super toughening studies have not delved into the effect of particle size distribution. Bimodal particle size distribution was observed when P[CL-co-VAc] with high molar mass was used to toughen PLA samples prepared by compression molding [54]. Although super toughening effect was not achieved, compression molded samples containing P[CL-co-VAc] in bimodal particle size distribution attained higher impact strength compared to their injection molded counterparts. Such improvements in compression molded samples were thought to be because of the relatively larger size of the micro-domains in them compared to the morphology of injection molded samples and the authors did not provide further explanation behind this experimental observation. Smaller particles can toughen the localized shear bands formed in between the large particles [63]. This makes the crack tip region sustain higher fracture load by maintain a higher critical stress level. If this critical stress level generates greater
triaxial stress ahead of the crack tip, it causes higher degree of cavitation in the larger particles; consequently, the adjacent matrix undergoes shear yielding before fracture [63]. Optimum size and bimodal distribution would be necessary to achieve synergistic super toughening. There is great scope for interesting future work on examining the effects of such bimodal particle size distribution.

Another factor to consider for efficient rubber toughening is the average interparticle distance, L. According to toughening theories [13,64], L should be below a value, L_c, in order for the rubbery particles to effectively initiate plastic deformation in the surrounding matrix, despite L being directly related to rubber particle size and content. In PLA toughened with POE-g-GMA [18], when the rubber content and particle size was increased, interparticle distance was reduced. The critical value, L_c for effective toughening of the blend was found to be 0.5 μm [18]. However, there is no unique agreement between researchers whether L_c is more important than content and size. If so, the ultimate goal of manipulating the content and size will be to drive the L below the L_c. On the other hand, observations reporting very small particle size but no substantial toughening effect do not follow this theory on L and L_c Further studies are needed to establish any possible relationships.

3.5 Heat Resistance

‘Heat resistance’, can be defined as the ability of a material to maintain properties of interest at a desired level at the maximum service temperature for a prolonged period of time. Having a certain level of heat resistance is one of the principal criteria for material selection. The heat resistance of PLA depends on its level of crystallinity and crystallization behavior. The crystallization model suggests the chain segments of semi-crystalline PLA co-exist in three different forms: (i) crystalline fraction (ii) rigid amorphous fraction (RAF), and mobile
amorphous fraction (MAF) [65]. Crystalline fraction is where the chain segments are all in ordered crystalline state. Random long molecular chains of amorphous fraction co-exist with the crystalline chains [65,66]. When a polymer approaches its glass transition temperature, \( T_g \), molecular chains of crystalline region are unlikely to move due to strong intermolecular interactions but chains of amorphous phase move freely. Within the amorphous region, some chain segments are rigid, consequently hindering free movement of the entire long chain. This fraction is referred to as rigid amorphous fraction (RAF) and the remaining long molecular chains in the amorphous region are known as MAF [65-67]. PLA with very low degree of crystallinity has a great proportion of its chains in the MAF which has high mobility near its \( T_g \) and therefore exhibits very low heat resistance, with distortion temperatures often occurring close to \( T_g \). When the crystallization of PLA is facilitated with external aids such as nucleating agents, the proportion of the crystalline and rigid amorphous fraction is increased, which impedes chain mobility and resists heat induced distortions, resulting in enhanced heat resistance [66,67].

Heat resistance is often quantified by the detection of a softening point under a certain load. The two most commonly adopted techniques measure: Heat Deflection or Distortion Temperature (HDT) and Vicat Softening Temperature (VST). HDT is defined as the temperature at which a specimen deflects 250 \( \mu \)m, under a specified load and thickness at a heating rate of 2 \( ^\circ\)C per min. The two common loads used are 0.46 MPa (66 psi) and 1.8 MPa (264 psi). VST is defined as the temperature at which the specimen is penetrated to a depth of 1 mm by a flat-ended needle with a 1 mm\(^2\) cross-sectional area. Common loads are 10 and 50N with heating rates of either 50 or 120 \( ^\circ\)C per hour depending on the standards followed [68,69]. It is generally understood VST is the temperature at which a material loses its form-stability and HDT is the
temperature at which material loses its load bearing capacity. However, the difference in assessing the softening point by HDT or VST is mainly a matter of defining the ‘end point’ [69]. VST values are usually higher than the HDT values and the difference is quite modest in the case of PLA which shows HDT of ca. 55 °C and VST of 65 °C. Various techniques and methods have been explored to improve the crystallinity and heat resistance of PLA. This section reviews the state-of-the-art technologies for improving the heat resistance of PLA by (i) addition of nucleating agents and stereocomplex; (ii) adopting different processing strategies; (iii) blending with heat resistant polymers; and (iv) fabrication of biocomposites with natural fibers and nano reinforcements. A summary of PLA blends with improved HDT/VST is presented in Table 3-2.

3.5.1 Nucleating agents and processing strategies

Nucleating agents can effectively promote crystallization by providing nucleation sites around which the polymer chains can crystallize. Shorter crystallization half time achieved with the addition of nucleating agents can help to increase the crystallinity while shortening the molding cycle times. Nucleating agents for PLA include, but are not limited to, talc,[70,71] N,N'-ethylene bis-stearamide (EBS) [72], carbon nanotubes [73], metal salts of phenylphosphonic acid [74], multiamide and hydrazide compounds [75-80], barium sulfate [81], titanium dioxide [81], calcium carbonate (CaCO₃) [81], nano CaCO₃ [82], and orotic acid [83]. Although numerous investigations have been conducted on improving crystallization of PLA with the help of nucleating agents, only a handful of them co-relate the increase in crystallinity due to nucleation to increase in heat resistance measured through HDT/VST. Recently, TMC-328, a commercial heterogeneous multi-amide nucleating agent, has been found to greatly enhance the heat resistance of PLA at a very small concentration (0.2 %) [67]. Benoylhydrazide (BH) compounds, in particular octamethylenedicarboxylic dibenzoylhydrazide, (OMBH) and
decamethylenedicarboxylic dibenzoylhydrazide (DMBH) are known to impart enhancement in the crystallization of PLA [79], [84]. The nucleation ability ($T_c$ and $\Delta H_c$) of OMBH was found to be higher than DMBH, and ethylenebis (12-hydroxystearylamide), EBH/ talc mixture at 1 wt% loading in PLA [79]. In addition to using hydrazide nucleating agent, high molding temperature of 110 °C was adopted to achieve substantial improvements (results are in Table 3-2). In spite of the successful enhancement of the crystallization rate of PLA through the addition of nucleating agents, obtaining injection molded articles of PLA with high crystallinity remains difficult with a fast mold cooling rate. Nucleated PLA molded in room temperature molds with fast cooling (>100 °C/min) does not show substantial improvement in HDT. Therefore, the effect of performing annealing post processing on the mechanical and thermal properties, and the fracture behavior of PLA has been studied. The crystallinity of PLA has been found to increase consistently through annealing in most of the studies and the increase lead to an improvement in its heat resistance and overall mechanical performance. Park et al. [85] and Nascimento et al. [86] performed annealing of PLA under various conditions to obtain microstructures with different spherulite sizes and density. The heat resistance of PLA was markedly improved when its crystallinity was increased by annealing. PLA with 1 % EBH molded at room temperature and then annealed for 1, 2, 4, 10 and 20 min at 105 °C showed increasing HDT with increasing annealing time. A sharp step change in HDT was noticed when the crystallinity went 25 %, indicating a threshold for crystallinity content [72]. However, annealing adds a post processing step, which may not be economical or industrially feasible.

As an alternative to annealing, researchers [79,87,88] have looked at increasing the mold temperature during the injection molding process which is seen as an in-mold annealing process as the cooling time is increased to facilitate effective demolding of the samples. Harris and Lee
[87] increased the injection mold temperature to 110 °C and were successful in obtaining PLA molded articles with high percentage of crystallinity and high HDT. However, the problem with this step is cycle time of ~2 mins due to higher cooling time as demolding of the processed components would be difficult with short cooling cycle. Li and Huneault [88] also observed similar effect of mold temperature on crystallinity as shown in **Figure 3-6**.

![Figure 3-6: Effect of molding temperatures on crystallinity (Xc) developed for PLA with 5% acetyl triethyl citrate (ATC) and 1% talc.](image)

At mold temperatures below 50 °C, low crystallinity level was observed, and crystallinity reached maximum level at 80 °C mold temperature with a combination of 5 % plasticizer and 1 % talc. In most of the above reviewed works [67,72,79,84] addition of nucleating agent in combination with annealing or high temperature molding was helpful in increasing the mechanical properties. Increase in crystallinity increased the tensile and flexural modulus. In
some cases, increased number of spherulite structures with low spherulite size was believed to consume more energy and thus increase the impact strength of PLA samples containing nucleating agents.

In opposition, Vadori et al. [89] have showed increasing the mold temperature of PLA decreases the impact toughness and percentage elongation of high impact PLA. Unique approach of using epoxy-based PolyJet mold instead of steel mold for conventional injection molding to produce PLA parts with high crystallinity has been proposed to offer promising results (Table 3-2) [90]. Due to low thermal conductivity of epoxy-based PolyJet mold, PLA parts containing nucleating agents produced from this mold had significantly higher level of crystallinity, thermal and mechanical properties compared to PLA samples molded from steel molds. When PLA is injected into 23 °C steel mold, it is cooled below its $T_g$ in 15s due to high thermal conductivity of the steel mold, whereas, in PolyJet mold, PLA material stays above $T_g$ for around 66s, allowing the material to crystallize. As a result, VST of PLA molded in 23 °C PolyJet mold increased to 118-124 °C compared to VST of 60-65 °C for PLA samples obtained from 23 °C steel mold. Use of such PolyJet molds show promise in achieving higher levels of crystallinity for PLA at room temperature molding conditions.

3.5.2 Blending with heat resistant polymers, stereo complexation, and use of nano fillers

Blending PLA with heat resistant engineering polymers such as polycarbonate [91], poly (acrylonitrile-butadiene-styrene) [92], nylon [93], polyoxymethylene [94] can improve the HDT of PLA when there is good compatibility between the blending polymers. Biodegradable ternary blends of PLA, PHBV and PBS with balanced stiffness and toughness attained HDT of ~72 °C with 30 wt. % PLA in the blend [95]. Polyoxymethylene, POM has a high HDT of 160 °C and it crystallizes fast with 70-80 % crystallinity content [94]. Nonetheless, having POM as a dispersed
phase in PLA did not help in improving the HDT; to achieve desired improvements in HDT, POM should be the major phase in the blend as significant improvements were observed with phase inversion, beyond 40 % [94]. Two different monomers, d-lactide and l-lactide exist due to chirality of PLA. Homopolymers of d- and l-lactide (PDLA and PLLA) have faster crystallization and higher melting points compared to common PLA which has small percentage of d -lactide with atactic stereo regularity in a majority of l-lactide. Stereocomplex of two polymers with same structure but different configuration has melting temperature between 190-230 °C. Stereocomplex (SC) PLA can work as nucleating agent promoting the formation of ordered structures. Various mixtures of PLLA and PDLA have been investigated [96-99] and 50-50 blend with stereocomplex crystalline structure improved the HDT to 150 °C. Nevertheless, high cost of PDLA is a bottleneck to stereocomplexation due to difficulty in production of D-lactide and hence PDLA. In a recent publication, Yin et al. [100] used high melting point PLLA homocrystallites (hPLLA) as nucleating agent to improve the thermomechanical properties of PLA. About 20 °C difference in melting point between PLA (4032D, Ingeo™ NatureWorks) and hPLLA helped to keep hPLLA crystallites unmelted at the processing temperature of 170 °C. Presence of 5 % hPLLA accelerated PLLA crystallization at a remarkable rate compared to PLA containing same amount of talc and SC PDLA. PLLA, with and without talc and PDLA were noticed to deform in less than 2 mins when placed in an oven at 70 °C for 5 mins under a constant load of 50gm, whereas PLLA with hPLLA crystallites showed no visible deformation for 5 mins, HDT/VST needs to be measured for any practical comparisons. This work however has contributed to new ways of tailoring the crystallization of PLLA without involving any post processing techniques and more importantly without compromising the biodegradable nature of the polymer.
Incorporation of nanoparticles into PLA is a relatively new strategy that researchers are exploring to improve the heat resistance of PLA. While addition of 2 wt. % talc to PLA resulted in 3 °C HDT improvement [101], addition of 8 wt. % montmorillonite (MMT) to PLA increased its HDT by 28 °C [102]. Layered silicate nanocomposites offer desired improvement in HDT only when the silicate layers of the clay are intercalated, stacked and well distributed in PLA.
matrix [103,104]. While 7% of organomodified montmorillonite (OMMT) containing trimethyl octadecyl ammonium cation increased the HDT of PLA to ~112 °C [104], 10wt % of organically modified synthetic fluorine mica (OMSFM) increased the HDT of PLA to ~117 °C [103], under a deflection load of 0.98MPa. Dicyclopentadiene (DCPD) filled urea formaldehyde microcapsules added to arrest the crack propagation and promote self-healing in PLA was observed to act as nucleating agent [105]. Formation of stable cocontinuous morphologies of heat resistant polymer with the aid of well intercalated nanoparticle is a recently explored promising strategy to increase the crystallinity. PLA phase interpenetrated with a continuous framework of nylon (30 wt.%) and 3phr OMMT showed resistance to temperature up to ~160 °C (Figure 3-7), however the HDT at 0.25 mm was same as that of neat PLA [93].

Figure 3-7: (a) Sample deflection recorded during creep tests for the sample PLA (squares), PA11 (diamonds), PLA70 (circles), and PLA70-C3 (triangles)

The pictures show the samples PLA70 (b) and PLA70-C3 (c) at the end of the test, that is after the temperature had reached ≈160 °C [Reprinted from Macromolecular Materials and Engineering, Vol 299, A. Nuzzo, S. Coiai, S. C. Carroccio, N. Dintcheva, C. Gambarotti, G. Flippone, Heat resistant fully biobased nanocomposite blends based on poly (lactic acid), 31-40, Copyright © 2013, with permission from Elsevier, License number: 3794371367676]
3.6 PLA Blends with Concurrent Improvements in Toughness and Heat Resistance

Having higher crystallinity in a semicrystalline polymer sometimes negatively affects the impact strength, hence the inverse relationship between HDT and impact strength. Perkins [14] explained that crystallites in the polymer can act as stress concentrators, thereby causing the stress acting on a small volume of the material to grow much higher than the average stress applied to the entire sample. As a result, material breaks at a stress value typically less than the expected critical value. Shear yielding and multiple crazing are also observed to decrease due to the presence of crystallites. Unfortunately, little attention has been paid to achieving PLA blends with balanced toughness and heat resistance because it is still a challenge to simultaneously control phase structure and matrix crystallization of blends. Perhaps the most useful work towards the search for such PLA blends are confined to using non-biodegradable engineering polymers such as polycarbonate (PC) having high impact strength and heat resistance. Several commercial PLA/PC blends [106-109] have been developed, which are seen as environmentally benign materials containing over 50% biodegradable and renewably sourced polymer, PLA. Addition of over 40% PC to PLA have shown some promise in increasing the impact strength of PLA, however, increasing the heat resistance of this blend has remained a challenge without the use of compatibilizers. Hashimi et al. [91] developed a four component super toughened blend containing PLA/PC/EGMA/SEBS (40/40/15/5) where SEBS toughened PLA in the presence of EGMA and a further improvement in toughness and heat resistance was achieved through the incorporation of PC in the blend. Wang et al. [110] investigated the effect of compatibilizers, epoxy (EP) resin and poly (butylene succinate-co-lactate), PBSL for PLA/PC binary blends. Combination of PBSL (10%) and EP (10%) in the presence of catalyst, tetrabutyl ammonium bromide (TBAB, 1%) in 50/50 blend of PLA/PC resulted in significant and concurrent
improvement in impact strength and heat resistance, the values are listed in Table 3-3. Chain extenders such as Joncryl® and tetruglycidyl-4,4’-diaminodiphenylmethane (TGDDM) in combination with small percentage of acrylic impact modifiers (BPM-520) have been used to improve the interfacial interactions in PLA/PC blends [111,112]. Although PLA/PC blends showed phase separated morphology and there were no sign of PLA-PC chain entanglements, interfacial connection was established between the chain extender and blending polymers which increased the impact strength and heat resistance upon annealing.

**Table 3-3: PLA blends with concurrent improvement in impact strength and heat resistance**

<table>
<thead>
<tr>
<th>PLA Blend Formulations</th>
<th>Notched Izod Impact Strength</th>
<th>HDT at specified load and deflection</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/PC/EGMA/SEBS(40/40/15/5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C mold temperature</td>
<td>65.9 kJ/m²</td>
<td>0.45MPa, 0.36mm</td>
<td>0.45MPa, 0.36mm 91</td>
</tr>
<tr>
<td>80 °C mold temperature</td>
<td>63.3 kJ/m²</td>
<td>88.6 °C</td>
<td>91</td>
</tr>
<tr>
<td>PLA/PC/PBSL/EP/TBAB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50/50/5/0/0)</td>
<td>36.6 kJ/m²</td>
<td>0.45MPa, 0.25mm</td>
<td>94.8 °C</td>
</tr>
<tr>
<td>(50/50/10/0/0)</td>
<td>65.1 kJ/m²</td>
<td></td>
<td>76.8 °C</td>
</tr>
<tr>
<td>(50/50/10/10/0)</td>
<td>25.4 kJ/m²</td>
<td>82.5 °C</td>
<td>94.2 °C</td>
</tr>
<tr>
<td>(50/50/10/10/0.1)</td>
<td>34.0 kJ/m²</td>
<td></td>
<td>94.2 °C</td>
</tr>
<tr>
<td>PLA/PC with Joncryl or TGDDM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(70/30/0.3phr)</td>
<td>~30 kJ/m² (Joncryl)</td>
<td>1.82MPa, 0.32mm</td>
<td>94 °C (Joncryl) 111</td>
</tr>
<tr>
<td>Room temperature molding followed by annealing</td>
<td>~13 kJ/m² (TGDDM)</td>
<td></td>
<td>~81 °C (TGDDM)</td>
</tr>
<tr>
<td>at 120 °C for 6h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA/PC/BPM/Joncryl (85/10/5/0.3phr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample molded at room temperature</td>
<td>~10 kJ/m²</td>
<td>0.45MPa, 0.32mm</td>
<td>57 °C</td>
</tr>
<tr>
<td>sample annealed at 120 °C for 6h</td>
<td>~40 kJ/m²</td>
<td></td>
<td>135 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>112</td>
</tr>
</tbody>
</table>
3.7 PLA Blends with Other Engineering Plastics

Having covered PLA/PC blends in previous section this section is focused on PLA blends with other engineering plastics like polyamide (PA), and polytrimethylene terephthalate (PTT). PLA blend with acrylonitrile butadiene styrene (ABS) have also been covered within the sections on ‘super toughened PLA blend’ based on the strategies used to toughen the blend. Renewable resource based polyamide (PA 610) was blended with PLA in the presence of a low molecular weight epoxy resin based on bisphenol-A as a compatibilizer by Pai et al [113]. Compatibility between PLA and PA 610 was reported to improve based on copolymer formation at the interface due to ester–amide interchange reactions. Although non-break un-notched impact behavior was observed in PLA/PA 610 (50/50) blends with 2-3 phr of compatibilizer, the notched impact strength was very low, with only 25 J/m. Mechanical and thermal properties of biobased PA11 and PLA in the presence of titanium isopropoxide catalyst was investigated by Patel et al. [114]. They did not find any evidence for transesterification reaction between PLA and PA11, despite the use of high amount of catalyst, high temperature and residence time. Thermal degradation of PLA was believed to preclude the interchange reactions; as a result property enhancement was not achieved. Feng and Ye [115] reported a tremendous improvement in tensile elongation (> 150 %) when a PA terpolymer (PA6/PA66/PA610) above 15 % was added, showing ductile fracture with yielding and necking. In this study impact toughness was not reported. Rashimi et al. [116] also reported similar improvements in PLA/PA11 blends when halloysite nanotubes (2-6 %) were added; however notched Izod strength did not seem to improve.
3.7.1 Polytrimethylene terephthalate (PTT) and PLA blends

PTT is a semicrystalline polymer produced from condensation of 1,3, propane diol (PDO) with terephthalic acid or dimethyl terephthalate, joining the PET and PBT (poly ethylene and butylene terephthalate) family of polyesters. Renewable 1,3, propane diol (PDO) is used as one of the monomer building blocks for PTT. Recent technological breakthroughs have made PTT production an economical process, offering opportunities in textile, carpet, packaging and other engineering applications. PTT has been shown to be a promising engineering plastic with unique combination of properties such as good tensile strength, elastic recovery, fast crystallization rate, electrical insulation, dimensional stability, and chemical resistance while retaining ease of processing [117,118]. Very much similar to PLA, application of PTT in areas requiring resistance to sudden load is quite limited due to their low impact toughness. Motivation for investigating blends of PLA/PTT is to develop a material that will have high biobased content for durable applications by taking advantage of each of the blending component properties. PLA/PTT blends have been shown to be miscible based on a composition-dependent single glass transition temperature (T_g) [119]. Percentage of elongation at break and tensile strength of the PTT/PLA blend were reported to decrease with the increase in PLA content. Increasing PLA content has a negative effect on the crystallization rate as well; higher activation energy was needed for the crystallization process, mainly because of very slow crystallization rate of PLA [120]. On the flip side, PTT/PLA blends showed higher thermal stability compared to neat PTT [120]. Lin and Cheng [121] have looked into improving the compatibility of PTT/PLA blends by adding methyl methacrylate-butadiene-styrene copolymer (MBS). As opposed to the work of Zou et al. [119], clear phase separation between PTT and PLA with spherical PTT particles of 120 μm was observe in PTT/PLA (50/50) blend ratio. With the addition of MBS, compatibility
of PTT/PLA blends was shown to improve as the dispersed PTT particle size reduced to 40-25 μm. However, impact strength of the blends reduced with the addition of MBS. Authors concluded this to be due to the crystallization of PTT at the interface which favored the disentanglement of MBS from the PTT [121]. There is however a great knowledge gap in developing PTT/PLA blends with improved properties by adding a third component such as compatibilizer.

### 3.8 PLA Biocomposites

Biocomposite is a multiphase system, where plant-derived fiber or mineral/synthetic filler is dispersed in the biopolymer matrix; either the matrix or the reinforcement phase is biobased [122,123]. Toughened PLA biocomposites has a far greater potential for minimizing the limitations of PLA hence major research efforts are being taken to develop and commercialize them. Numerous research works have been conducted in the field of PLA composites however most of the work report only marginal improvements in impact strength and HDT [124-129]. Scope of this section has been limited to reviewing the research progress in injection molded PLA biocomposites that used tough PLA blends as the matrix for incorporation of fibers and fillers. The increase in fracture toughness observed for PLA biocomposite is not as high as in the case of the neat PLA. For instance, improving the toughness of neat PLA by 20 fold might increase the fracture toughness of the composite by 3-6 folds only. Such poor translation of matrix toughness into the composite is due to the presence of fiber, which is a constraint that suppresses elastic deformation of the matrix at the crack front. However having a toughened PLA blend as a starting material to incorporate fibers can be a good way to achieve a balanced performance. Furthermore, cost of developing such blends can be offset to certain extent by adding less expensive lignocellulosic fibers.
PLA blended with tough biopolymers such as PBAT and PCL have been explored as a matrix system to incorporate natural fibers [130-132]. In most cases, surface treatment has proved to be effective in promoting interfacial interactions between the relatively hydrophobic matrix and hydrophilic filler. Having 30 wt. % PBAT in PLA-PBAT/Alkali treated saw dust (70/30) composites improved the unnotched Izod impact strength by 50 % [130]. Surface of Kenaf treated with 2 % silane coupling agent was observed to become hydrophobic with the ability to bind active groups of the polymer [131]. Chemical interactions formed between hydroxyl, silanyl and alkoxy groups increased the impact strength of the PLA-PBAT biocomposites by 22 %, [131]. By treating ramie fiber with silane coupling agent (KH550) for in situ polymerized PLLA-PCL matrix, tensile and impact strength increased from 12.14 MPa, 30.0 J/m to 23.45 MPa, and 88.9 J/m, respectively [132]. Incorporation of Cordenka fiber at 25 wt. % has been shown to triple the impact strength of PLA without any tough component being present; however more research is needed towards the effect of this fiber on HDT [133]. While addition of 5 wt. % lignin resulted in toughness improvement in PLLA [134] from 8.2 to 12.5 kJ/m², addition of 5 wt. % of lignin-g-rubber-g-PDLA to PLLA exhibited a seven-fold enhancement in toughness (from stress–strain curves) compared with neat PLLA. This improvement is significant considering the copolymer contains only 3.8 wt. % of rubber [135].

In the case of PLA/pine wood floor composites, notched Charpy impact strength was found to increase gradually with increase in addition of wood floor and further increment in impact strength was achieved by toughening the PLA matrix with styrene-butadiene-styrene (SBS) block copolymer [136]. Use of reactive impact modifiers can form ductile interface between PLA and fiber thus increasing the resultant properties. With this hypothesis, ethylene acrylate copolymer (Biomax®) was used as an impact modifier (IM) for PLA/kenaf fiber (KF)
composites [137]. Impact strength and elongation at break increased but only at a high loading level of 40 % with substantial reduction in tensile strength and modulus. Liu et al. [138] compared the toughening effect of three different reactive elastomers: polyoxyethylene grafted with maleic anhydride (POE-g-MAH), ethylene–propylene–diene rubber grafted with maleic anhydride (EPDM-g-MAH), and ethylene-acrylate-glycidyl methacrylate copolymer (EAGMA) on PLA/Basalt fiber composites. EAGMA at 20 wt. % imparted the most toughening effect by recording a value of 33.7 kJ/m² for unnotched Charpy impact strength [138].

Other mineral fillers such as barium sulfate [139] and calcium sulfate [140,141] have also been reported to increase the toughness of the PLA composites. PLA based nanocomposites prepared by incorporation of nano fillers such as cellulose nanofibers and nano whiskers [142], nano-calcium carbonate [143-145], nano and mesoporous silica [146-149], halloysite nanotubes [150,151], nano clay [151-154], and titanium oxide nanoparticles [155] exhibited good improvement in toughness, mechanical and barrier properties however none of these studies have reported the heat resistance of the developed materials. Although the hybridization of PLA with impact modifier and nanoparticle can offer a toughened composite material, challenges exists in achieving good level of dispersion and distribution of the nanoparticles, its compatibility with the matrix and ease of processing.

On the flip side, considerable number of research investigations has shown the heat resistance of injection molded PLA biocomposites to increase with fiber/filler incorporation in spite of affecting impact strength negatively. Crushed kenaf fiber [156] has been reported to significantly increase the HDT of injection molded PLA composites when added beyond 10 wt. %, as shown in Figure 3-8.
Stiffness and HDT of the PLA was improved with the addition of newspaper fibers/talc hybrid with drastic reduction to impact strength [157,158]. HDT of the PP-PLA composites could be increased to 120 °C with 30 % Oat hull but in a major phase of PP, with a drastic reduction in impact strength [159]. Incorporating 30 wt. % agricultural residues like soy stalk, corn stalk, wheat straw and their hybrids in PLA matrix did not provide desired increase in HDT, only the modulus of the composites increased while impact strength remained essentially the same as virgin or neat PLA [160]. In such cases, addition of fibers alone would not be sufficient to increase the HDT, a combinatorial approach of adding nucleating agents and use of high mold temperature could be beneficial.
3.9 Biocarbon in Composites

Biocarbon based composites can provide significant opportunities for weight savings, strength and versatility in automotive interior parts. This will allow automakers to meet stringent standards without sacrificing quality and performance. However, only limited research has been conducted in promoting biocarbon based composites for such applications. Figure 3-9 shows the timeline of previous studies that looked into using biocarbon in different polymer matrices. The timeline is categorized based on bamboo charcoal and biocarbon from other resources because of the high temperature (1000 °C) involved in obtaining bamboo charcoal. Polyethylene terephthalate (PET)/polypropylene (PP) blends [161], chitosan [162], PP and polyethylene (PE) [163], polyaniline [164], low density polyethylene (LDPE) [165], ultrahigh molecular weight PE [166] and polylactic acid [167,168] have been investigated so far as the matrix for the incorporation of bamboo charcoal. These research articles mainly looked at morphology, mechanical and thermal properties of the composites. Early work exploring the potential of biocarbon in automotive parts comes from Peterson et al associated with United States Department of Agriculture. They are investigated on biocarbon from different sources with varying carbon content and particle size as a potential replacement for carbon black in styrene butadiene rubber (SBR) and natural rubber (NR) [169-172]. Mohanty et al from University of Guelph was the first to investigate the effect of biocarbon on engineering plastics like polytrimethylene terephthalate (PTT) [173,174] and Nylon [175,176]. Other researchers in the field have studied the effect of different biocarbon on Epoxy [177], polyvinyl alcohol (PVA) [178] and PP [179] matrix. Recently, Sharma et al [180-185] have published a series of research articles on using biocarbon in combination with wood floor to develop ‘wood plastic biochar composites’.
Figure 3-9: Timeline of previous studies on biochar composites categorized based on bamboo charcoal and biocarbon from other renewable sources.
Although original driving force for adding fillers to polymers was to reduce the overall cost of the final formulations, fillers also modify certain matrix properties favorably. All of the above published literature agrees with the stiffening effect of biocarbon. Key understanding underpinning the information in these publications is the importance of carbon content, particle size, pyrolysis temperature, and surface area in enhancing the performance of the biocarbon composites.

3.10 Research Gap

Extensive research effort has been devoted to developing PLA blends and biocomposites with desirable morphology and crystallinity for durable applications. Around 50 research articles have directly contributed to super toughened PLA and 35 of them have been published in the past three years, during the course of this thesis. However, achieving feasible and economical manufacturing processes for mass production of such materials has been quite a challenge. Enhancing matrix crystallization has been reported to be an effective strategy towards creating heat resistant PLA blends. Both thermal annealing and nucleating agent induced matrix crystallization could significantly enhance heat resistance of the blends, while maintaining or further increasing the toughening efficiency. However, increasing matrix crystallinity alone cannot guarantee toughness improvement in most cases because suitable morphology must be obtained for PLA matrix to undergo plastic deformation. Specifically, optimum elastomer content, particle size, and interparticle distance are identified to be the most important deciding factors for toughening PLA.

Attempts to enhance PLA performance beyond standard levels so far had generated formulations with either higher heat deflection temperature (HDT) or greater impact strength but seldom both. This inverse relationship in PLA prevents it from serving as a sustainable
alternative. This needs to be addressed for the success of PLA in other durable applications. Effect of adding thermally stable fillers like biocarbon to engineering polymer blends are also significantly lacking. Technological developments focusing on the emergence and exploitation of renewable carbon based fillers for PLA materials are needed to serve the demand for ‘light weight’, ‘carbon neutral’ durable materials.

This thesis intended to bridge the research gap existing in the PLA blends and composites by:

- Investigating the effect of thermoplastic elastomer and different reactive functionalized terpolymer in achieving super toughened blends of PLA (Chapter 4)
- Establishing the crystallization kinetics of PLA with a new nucleating agent, aromatic sulphonate derivative (Chapter 5)
- Using supertoughened blends as a matrix for PLA biocomposite fabrication (Chapter 6)
- Achieving concurrent improvements in impact strength and HDT of PLA by adding nucleating agents and natural fiber in combination with a high mold temperature (Chapter 6). 
- Blending PLA in minor phase with engineering plastic, PTT and resolving the contradictory conclusions in the literature regarding the miscibility of these blends (Appendix C).
- Improving the compatibility of PTT-PLA blends with the help of a reactive compatibilizer through a statistical design of experiments approach (Chapter 7).
- Studying the effect of size fractionated biocarbon on the microstructure and properties of PTT ternary blends. Effect of particle size and shape, chain extender and high mold temperature were also investigated (Chapter 8).
References


(4) Odent, J.; Raquez, J.; Dubois, P., Eds.; In Biodegradable Polyesters; Fakirov, S., Ed.; Highly Toughened Polylactide-Based Materials through Melt-Blending Techniques; Wiley-VCH Verlag GmbH & Co. KGaA: 2015; .


(65) Ma, Q.; Georgiev, G.; Cebe, P. Constraints in semicrystalline polymers: Using quasi-isothermal analysis to investigate the mechanisms of formation and loss of the rigid amorphous fraction. Polym., 2011, 52 (20), 4562-4570.


(68) Biron, M. Thermoplastics and thermoplastic composites; William Andrew: 2012; .


(75) Bai, H.; Zhang, W.; Deng, H.; Zhang, Q.; Fu, Q. Control of crystal morphology in poly (L-lactide) by adding nucleating agent. Macromolecules, 2011, 44 (6), 1233-1237.


(100) Yin, H.; Wei, X.; Bao, R.; Dong, Q.; Liu, Z.; Yang, W.; Xie, B.; Yang, M. Enhancing Thermomechanical Properties and Heat Distortion Resistance of Poly (L-lactide) with High Crystallinity under High Cooling Rate. ACS Sustainable Chem. Eng., 2015, 3 (4), 654-661.


(125) Petinakis, E.; Yu, L.; Edward, G.; Dean, K.; Liu, H.; Scully, A. D. Effect of matrix–
particle interfacial adhesion on the mechanical properties of poly (lactic acid)/wood-flour micro-


(127) Bledzki, A. K.; Jaszkiewicz, A.; Scherzer, D. Mechanical properties of PLA composites

(128) Bledzki, A.; Franciszczak, P.; Meljon, A. High performance hybrid PP and PLA
biocomposites reinforced with short man-made cellulose fibres and softwood flour. Composites,
Part A, 2015, 74 , 132-139.

(129) Ho, M.; Lau, K.; Wang, H.; Hui, D. Improvement on the properties of polylactic acid

(130) Nomai, J.; Jarapanyacheep, R.; Jarukumjorn, K. Mechanical, Thermal, and Morphological
Properties of Sawdust/Poly (lactic acid) Composites: Effects of Alkali Treatment and Poly

(131) Sis, A. L. M.; Ibrahim, N. A.; Yunus, Wan Md Zin Wan Effect of (3-aminopropyl)
trimethoxysilane on mechanical properties of PLA/PBAT blend reinforced kenaf fiber. Iran.

(132) Xu, H.; Wang, L.; Teng, C.; Yu, M. Biodegradable composites: Ramie fibre reinforced
663-670.

(133) Ganster, J.; Fink, H.; Pinnow, M. High-tenacity man-made cellulose fibre reinforced
thermoplastics—Injection moulding compounds with polypropylene and alternative matrices.


(135) Sun, Y.; Yang, L.; Lu, X.; He, C. Biodegradable and renewable poly (lactide)–lignin
composites: synthesis, interface and toughening mechanism. J. Mater. Chem. A, 2015, 3 (7),
3699-3709.

(136) Qiang, T.; Yu, D.; Gao, H.; Wang, Y. Polylactide-based wood plastic composites


(140) Murariu, M.; Ferreira, A.; Duquesne, E.; Bonnaud, L.; Dubois, P. Polylactide (PLA) and Highly Filled PLA-Calcium Sulfate Composites with Improved Impact Properties. Macromolecular symposia. 2008, 272, 1-12.


(151) Murariu, M.; Dechief, A.; Ramy-Ratiarison, R.; Paint, Y.; Raquez, J.; Dubois, P. Recent advances in production of poly (lactic acid)(PLA) nanocomposites: a versatile method to tune crystallization properties of PLA. Nanocomposites, 2015, 1 (2), 71-82.


Chapter 4: PLA Binary and Ternary Blends

This study is an attempt to explore the effectiveness of thermoplastic copolyester elastomer (TPCE) as a toughening agent for improving the impact strength of PLA. Hytrel® thermoplastic copolyester of polyether glycol and polybutylene terephthalate was selected as the TPCE of choice for this study. Blends of PLA/Hytrel at varying weight ratios were prepared using extrusion followed by injection molding technique. Optimal synergies of two polymers were found in the PLA/Hytrel (70/30) blend, showing impact strength of 234 J/m, a 6 fold increase compared to neat PLA. Effect of different functionalized terpolymers was also analyzed in providing super toughening behavior. A series of functionalized terpolymers, ethylene methyl acrylate-glycidyl methacrylate (EMAGMA), ethylene butyl acrylate-glycidyl methacrylate (EBAGMA), ethylene methyl acrylate-maleic anhydride (EMAMaH) and ethylene butyl acrylate-maleic anhydride (EBAMaH) were added to accomplish reactive compatibilization. GMA containing copolymers showed better properties in terms of impact toughness compared to MaH copolymer containing blends. Super toughening effect observed only in blends based on EMAGMA is attributed to the different morphology obtained in the ternary blends.

---

2 Version of this chapter is submitted for publication as ‘Blends of polylactic acid with thermoplastic copolyester elastomer: Effect of functionalized terpolymer type on reactive toughening’ in Polymer Engineering and Science, June 2016 (under review).
4.1 Introduction

Numerous approaches and techniques have been explored to increase the crystallization and toughness of PLA, such as plasticization and/or nucleation, block copolymerization, chemical modification and blending with suitable flexible polymers. Combining nucleating agents with plasticizers has showed an improvement in PLA’s mechanical properties and crystallization kinetics. However, with long usage period plasticizers are susceptible to migrate to the surface of the product, which causes embrittlement of the polymer. Furthermore, the low glass transition temperature \( (T_g) \) of plasticized PLA makes it difficult to process and obtain final commercial products. Chemical modification is typically complex, technically demanding, and expensive due to the cost of required catalysts and/or monomers. Among all the approaches taken to combat the issues of PLA, blending PLA with flexible rubbery polymers seems to be a promising direction towards achieving the required level of performance.

Binary blends of PLA with other flexible polymers like poly (ε-caprolactone) PCL, poly (butylene terephthalate) PBAT, poly (hydroxyalkanoate) PHAs have been widely studied in literature. Thermoplastic copolyester elastomers (TPCE), block copolymers composed of hard and soft segments, have attracted considerable attention in various fields ranging from commodity plastics to engineering ones because they combine the processability of thermoplastics and the physical properties of elastomers. Poly (ether-block-amide) copolymer (PEBA) is an important class of commercial thermoplastic elastomers with unique physical and processing properties. PEBA is a segmented block copolymer consisting of an aliphatic polyamide as the hard block, a polyether as the soft block and a di-acid serving as the joint between the two blocks [1]. The unique chemical and segment structure of PEBA offers a wide range of excellent performances including good mechanical properties, biocompatibility and
processibility, etc. In particular, low glass transition temperature of the polyether-rich phase makes PEBA highly resistant to impact even at temperature as low as -40 °C, and can therefore be used as an impact modifier for the brittle thermoplastic polymers.

In our previous work [2], we focused on reactive blending of PLA with a series of renewable resources based PEBA and a functionalized terpolymer, ethylene methyl acrylate-glycidyl methacrylate (EMAGMA) to fabricate super-toughened PLA ternary blends. To the best of our knowledge, this was the first study to report the reactive melt blending of PLA and renewable elastomer based multiphase blends. Varying composition of binary blends PLA/PEBA, PLA/EMAGMA and ternary blends PLA/PEBA/EMAGMA were studied in detailed. Super-toughened PLA blend showing impact strength of ca. 500 J/m with partial break impact behavior was achieved at an optimized blending ratio of 70 wt. % PLA, 20 wt. % EMAGMA and 10 wt. % PEBA. Brief summary of the results are presented in literature review section. Knowledge gained from this empirical research has been useful in extending the work to results reported in the current chapter.

Hytrel® is a TPC-ET composed of poly (butylene terephthalate) as a hard segment and poly (ether glycol) as soft segment, commercialized by DuPont. Recently, grades with 35-65 % bio-based content of this polymer are available from DuPont under the trade name Hytrel RS®. Hytrel has outstanding mechanical properties [3-4] at temperatures up to 130 °C combined with very good flexibility at low temperature. It shows good impact, and tear resistance, in addition to resistance against creep and abrasion. It is said to possess excellent oil, hydraulic fluids and grease resistance too. Because of its outstanding properties such as distinguished flexural fatigue and a broad service temperature, Hytrel has been used to modify many brittle polymers such as PC (polycarbonate), phenoxy, PET (polyethylene terephthalate), and PVC (polyvinyl chloride)
However, to the best of our knowledge, the systematic blending study of PLA and Hytrel has not been reported in detail so far.

This chapter therefore presents the investigation of mechanical, thermal and rheological properties of PLA/Hytrel blends at blending ratio of 90/10, 80/20, 70/30, 60/40 and 50/50 wt. %. In addition, effect of different functionalized terpolymers on further enhancing the properties of the ternary blend was compared. Functionalized terpolymers chosen to achieve super toughening are: ethylene methyl acrylate-glycidyl methacrylate (EMAGMA), ethylene butyl acrylate-glycidyl methacrylate (EBAGMA), ethylene methyl acrylate-maleic anhydride (EMAMaH) and ethylene butyl acrylate-maleic anhydride (EBAMaH). Blending ratio of 70 % PLA, 10 % HYT and 20 % terpolymer was selected for the comparison study based on results from previous work. Phase behavior and mechanical performance of the binary and ternary blends were thoroughly investigated. Toughening mechanism in the blends is established by analyzing the structure-property relationship.

4.2 Materials and Methods

4.2.1 Materials

PLA, Ingeo™ 3001D was purchased from NatureWorks LLC, USA. Hytrel® RS 40F3 NC010 used was purchased from DuPont, ON, Canada. This particular grade of Hytrel contains at least 50 % biobased ingredients by weight, which corresponds to the polyether glycol in the soft segment. Henceforth, Hytrel will be referred to as HYT. EBAGMA under the trade name Elvaloy PTW was supplied by DuPont, ON, Canada. EMAGMA (Lotader AX 8900) product of Arkema Inc. was obtained from Quadra Chemicals, ON, Canada. EBAMaH (Lotader 3410) and
EMAMaH (Lotader 3410) were kindly supplied by Arkema Inc., PA, USA. In preparation for blending, PLA and HYT were dried in hot air oven for 12 hours at 80 °C and the terpolymers were dried for 12 hours at 60°C. Physical properties of these polymers from datasheet are presented in Table 4-1 and the Chemical structures are presented of selected polymers can be found in Appendix A.
<table>
<thead>
<tr>
<th>Material Properties</th>
<th>PLA</th>
<th>Hytrex</th>
<th>EMAGMA</th>
<th>EBAGMA</th>
<th>EMAMaH</th>
<th>EBAMaH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>62</td>
<td>20</td>
<td>4</td>
<td>5.2</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Tensile Elongation, %</td>
<td>3.5</td>
<td>650</td>
<td>1100</td>
<td>950</td>
<td>750</td>
<td>700</td>
</tr>
<tr>
<td>Notched Izod Impact, (J/m)</td>
<td>16</td>
<td>NB</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Flexural Modulus (MPa)</td>
<td>3600</td>
<td>50</td>
<td>&lt;30</td>
<td>--</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td>HDT/VST (°C)</td>
<td>55 (HDT)</td>
<td>50 (HDT)</td>
<td>&lt;40 (VST)</td>
<td>--</td>
<td>45 (VST)</td>
<td>47 (VST)</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.24</td>
<td>1.11</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>MFR, g/10 min (190 °C, 2.16kg)</td>
<td>22 (210 °C)</td>
<td>20 (210 °C)</td>
<td>6</td>
<td>12</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Melting Temperature (°C)</td>
<td>180</td>
<td>205</td>
<td>65</td>
<td>72</td>
<td>84</td>
<td>89</td>
</tr>
</tbody>
</table>
4.2.2 Melt blending

Neat PLA, binary and ternary blends with varying compositions were melt-processed using a micro-compounder (DSM Xplore®, Netherlands). The length and L/D of the screws are of 150 mm and 18, respectively. The barrel volume of the machine is 15 cm$^3$. Extrusion was performed at a 205 °C barrel temperature and 100 rpm screw speed. After a total residence time of 2.5 min, a preheated cylinder was used to transfer the molten blend to a preheated DSM micro 12 cc injection molding machine. Samples were molded at 30 °C mold temperature.

4.2.3 Testing and characterization

Mechanical properties were measured after the test specimens were conditioned in standard laboratory atmosphere for 40 h at 23 °C and 50 % relative humidity (ASTM D 618-08, Procedure A- 40/23/50). Instron (Norwood, MA, USA) Instrument Model 3382 was used to study the tensile and flexural properties of the blends according to ASTM standards D638 and D790 respectively. The tensile properties of blends were tested at 50 mm/min. The flexural specimens of the matrix were tested at a crosshead speed of 14 mm/min. Notched Izod impact strength was measured with the help of Testing Machine Inc. (TMI) instrument according to ASTM D256. At least six notched samples were measured for impact strength and five samples for tensile properties. Average values with standard deviations are reported.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted through the use of a Thermo Scientific Nicolet 6700 spectrometer with a resolution of 4 cm$^{-1}$ and 64 scans per sample.

Rheological characterization was conducted using an Anton Paar MCR302 rheometer (Anton Paar GmbH, Graz, Austria) using a parallel plate configuration. The plate diameter used
was of 25 mm, with a measurement gap distance set at 1 mm. Dynamic sweep analysis were conducted for all samples to determine linear viscoelastic ranges. These tests were conducted at a strain of 1% for oscillation measurements. Frequency sweep analysis was conducted from 0.1-100 rads at 220 °C under nitrogen atmosphere.

*Differential scanning calorimetry (DSC)* was performed by heating the samples to 210 °C with heating rate of 10 °C/min, followed by a 3 min isothermal step to erase the thermal history and then cooled to -50 °C with a cooling rate of 5 °C/min. Same temperature profile used for first heating scan was followed for second heating scan as well. Glass transition temperature ($T_g$), cold crystallization temperature ($T_{cc}$), crystallization temperature ($T_c$), melting temperature ($T_m$) were determined from the DSC graphs. Percentage crystallinity ($\chi_c$) was calculated using the equation,

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{f \Delta H_m^0} * 100\% \quad (4.1)$$

Where, $\Delta H_m$ is the enthalpy of melting, $\Delta H_{cc}$ is enthalpy of cold crystallization, $\Delta H_m^0$ is the enthalpy of melting of 100% pure PLA, 93.7 J/g. $f$ is the weight fraction of PLA in the blend.

*Dynamic mechanical analysis (DMA)* was conducted on a DMA Q800 from TA Instruments using a dual-cantilever clamp with a mode of frequency sweep/temperature ramp at the frequency of 1 Hz and oscillating amplitude of 15 μm. The samples were heated from -50 to 120 °C at a heating rate of 3 °C/min.

*Morphology* and phase behavior was observed by scanning electron microscopy (SEM), Phenom ProX (Phenom World BV, Netherlands) equipped with a back scattering electron (BSE). Cressington sputter coater 108 was used to gold coat the samples for 15 s under an argon atmosphere.
4.3 Results and Discussion

4.3.1 Mechanical properties

Tensile properties, elongation and impact strength for PLA/HYT blends are shown in Figure 4-1 and Figure 4-2. Neat PLA deformed in a typical brittle fashion without obvious yielding under tensile stress. The tensile strength of the PLA was above 70 MPa, while the elongation at break was only around 4%.

![Figure 4-1: Tensile properties of PLA/HYT blends](image)

Compared to the neat PLA, the ductility of PLA was improved as the amount of HYT loading was increased with a gradual step reduction in tensile strength and modulus. Such reduction in strength is a fairly common observation while adding a softer second component. Blends with HYT content higher than 20 wt. % underwent distinct yielding followed by considerable cold drawing during the tensile test, indicating the change in fracture behavior of PLA from brittle to ductile in PLA/HYT blends. Stiffness of a polymer depends on its resistance to flexibility and chain mobility. HYT has glass transition temperature (Tg) well below the room
temperature. Therefore at ambient temperature of testing, HYT imparts mobility to the molecular structure of the blends. Accordingly, elastic modulus or Young’s modulus (E) determined by tension tests decreased gradually with increasing HYT content. Notched Izod impact strength of these blends increased with increasing content of HYT. Having higher amount of HYT in the blends helped in absorbing more impact energy by transmitting the stresses between the dispersed HYT particles.

**Figure 4-2: Impact strength and elongation of PLA/HYT blends**

When HYT content was increased beyond 30% the blend exhibited non-break behavior. SEM observations reported later in this chapter supports such transition in fracture behavior due to the dispersed phase becoming co-continuous.

Mechanical properties of PLA ternary blends comparing the effect of different terpolymer are provided in Table 4-2. Tensile strength and modulus of ternary blends containing different terpolymers are all in the same range. Flexural strength of GMA based terpolymers are
lower compared to the MaH based terpolymers. This could be attributed to the relatively higher stiffness of MaH based compatibilizers.

Table 4-2: Mechanical properties of PLA/HYT/Terpolymer blends

<table>
<thead>
<tr>
<th>Blend Formulation</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elong. At break (%)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Impact Strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/HYT/EMAGMA</td>
<td>40±1.06</td>
<td>2.4±0.21</td>
<td>52±3.29</td>
<td>55±0.94</td>
<td>2.2±0.03</td>
<td>Non-break</td>
</tr>
<tr>
<td>PLA/HYT/EBAGMA</td>
<td>43±2.49</td>
<td>2.4±0.03</td>
<td>43±0.78</td>
<td>55±0.73</td>
<td>2.2±0.03</td>
<td>214±21.7</td>
</tr>
<tr>
<td>PLA/HYT/EMAMaH</td>
<td>42±0.81</td>
<td>2.5±0.12</td>
<td>44±4.02</td>
<td>60±0.85</td>
<td>2.2±0.04</td>
<td>111±16.6</td>
</tr>
<tr>
<td>PLA/HYT/EBAMaH</td>
<td>42±0.60</td>
<td>2.4±0.06</td>
<td>41±2.55</td>
<td>60±1.84</td>
<td>2.2±0.05</td>
<td>108±13.9</td>
</tr>
</tbody>
</table>

Drastic difference is noticed only in the impact strength of the ternary blends. GMA based terpolymers have imparted relatively higher impact strength, with EMAGMA showing super toughening effect (non-break behavior). The impact strength of blends with MaH based compatibilizers is lower than the binary blends of PLA containing 30 % HYT. Elongation at break (%) was higher for EMAGMA, while blends with other terpolymers show same range of values at around 42 %. It is well known that the tensile testing is usually performed at a constant low strain-rate condition and the impact testing is carried out at remarkably high speed [9]. Good level of interfacial adhesion would be required to withstand sudden loading in notched test samples. In addition, phase morphology of the blend also plays a significant role in deciding the toughness of the blends. Fracture behavior of the ternary blends is further explained in detail with reference to the morphologies in the next section.
Figure 4-3 shows the impact fractured samples of different ternary blends. Blends with GMA based terpolymers showed a stress whitening zone, blends with MaH did not show any signs of stress whitening. The term stress whitening denotes a macroscopic phenomenon that produces a cloudy, whitened appearance in polymer samples when they are subjected to mechanical stresses due to fatigue, impact or tensile loading [10]. It is the result of localized changes in the matrix which alters the refractive index of the polymer. Many studies have attributed rubber particle cavitation, crazes and micro voids to be the primary mechanism for stress whitening which subsequently results in large plastic deformation of the matrix [11-13].

In our case, the volume of material involved in stress whitening phenomena is different between the EMAGMA and EBAGMA based blends. Crescent shaped stress whitening was observed in EMAGMA blends, while a smaller and relatively straight zone along the fracture line was observed in the EBAGMA blends. The area fraction of stress whitening zone indicating where the fracture occurred on the impact surface can be directly related to the amount of

Figure 4-3: Impact Fracture Behavior of PLA Ternary Blends
improvement in the toughness of the blends. Such co-relations have also been put forward by other researchers [14-15].

4.3.2 Morphology of the binary blends

Impact fractured surface morphology of neat PLA and binary blends containing varying amount of HYT are shown in Figure 4-4. Although craze bands was noticed in neat PLA, its localized nature resulted in brittle failure, which is also indicated by smooth fracture. When immiscible polymers are melt blended, two major morphologies can be expected: the sea-island or matrix-droplet morphology and a co-continuous morphology [16-18]. The latter kind of morphology is preferred as it offers better combination of the component properties. However, most often, higher amount of the second phase would be required to achieve such morphologies and the recent trend is to add nano fillers to achieve co-continuity [19]. SEM images for blends shown in Figure 4-4 clearly indicate that HYT was immiscible with PLA. Typical phase separated sea-island morphology was observed in blends containing lower amount of HYT, where PLA occupied the continuous phase and HYT, the dispersed phase. In PLA/HYT (90/10) blend, HYT domains were observed as spherical droplets with fibrillar threads between the particles. As HYT content increased to 20 and further to 30 % the spherical droplets changed to elliptical and were highly deformed with discernible fibrils and pullouts. This was the impact energy dispersing mechanism in blends containing lower amount of HYT. Beyond 30 % HYT, the morphology changed to co-continuous morphology which is distinctly visible in 50/50 blend. Here the HYT phase assumed an elongated structure, preferable along the extrusion and molding direction, making it much effective in absorbing the impact load. This kind of co-continuous structure is generally formed near a composition where phase inversion can be expected [20].
Figure 4-4: Impact fracture surface morphology of PLA/HYT blends (Magnification: 3000x)
4.3.3 Ternary blend morphology and toughening mechanism

Morphology of ternary blend with different terpolymers in low and high magnifications is shown in Figure 4-5 and 4-6. Distinctly dispersed particles in PLA matrix is observed with cavitation and fibril between the dispersed particles.

![Image of fracture surface morphology](image)

**Figure 4-5: Impact fracture surface morphology of PLA/HYT/GMA terpolymer blends (Magnification: 5000x and 10000x)**
Cavitation is an important precursor phenomenon to any toughening mechanism. Two types of cavitation have been observed in PLA toughened with a rubbery phase: (i) internal cavitation (within the rubber particle), which occurs when the interfacial bonding is strong between the rubber domains and matrix (ii) debonding cavitation (between the rubber particle and matrix), which occurs when there is poor interfacial bonding strength. To prevent the localization of strain, cavities formed either in the rubber particle or the matrix alters the triaxial stress state and favors the formation of shear bands ultimately leading to shear yielding of the matrix. All of the ternary blends exhibited debonding cavitation denoted by the gap between the

Figure 4-6: Impact fracture surface morphology of PLA/HYT/MaH terpolymer blends (Magnification: 5000x and 10000x)
particle and the matrix around it. However, only in the case of PLA/HYT/EMAGMA blends, massive shear yielding was observed (Figure 4-3). This also supports the super toughening effect and larger stress whitening that was observed only in these blends. Morphologies observed in the ternary blends can be summarized under three types.

- Type 1: Debonding cavitation followed by massive shear yielding and large area of stress whitening (EMAGMA blend)
- Type 2: Debonding cavitation followed by moderate shear yielding with fibrils and small areas of stress whitening (EBAGMA blend)
- Type 3: Debonding cavitation with fibrils, no yielding and stress whitening (MaH terpolymer blends)

Although void formation due to debonding cavitation is a factor contributing to toughness, it only leads to small amount of energy dissipation, consequently resulting in only moderate improvement in toughness. Cavitation plays an important role in further activation of matrix plastic deformation. Despite cavitation observed in all the ternary blends, it is interesting to note that only in the case of EMAGMA blends the cavitation process has promoted massive shear yielding and super toughening. To further elucidate this behavior, cryogenically fractured surface of the blends were studied under SEM. The images are shown in Figure 4-7. From these SEM images and previously shown ones it is hard to distinguish between the HYT and terpolymer domains. The fact that cavitation was absent in PLA/HYT blends, and the higher amount of terpolymer (20 %) in the blend compared to HYT (10 %) leads us to the assumption that the larger domains could be the terpolymer. Cryofractured surfaces show quite a difference in the dispersed particle size. In the case of EMAGMA based blends, there appears to be large number of particles in smaller size compared to other blends. When the volume fraction of the cavitation
formed are sufficiently high, it is easier for the neighboring matrix to yield, stretch and strain harden under imposed mechanical load. Such varying results observed in the dispersion and particle size of these blends could be attributed to the difference in physical properties, interfacial affinity, and viscosity of the components and how they react under the melt blending.

Figure 4-7: Cryogenic fracture surface morphology of PLA/HYT/Terpolymer blends (Magnification: 5000x)

4.3.4 FTIR spectra

Characteristic FTIR peaks of PLA, HYT and the different polymers are shown in Figure 4-8 and Figure 4-9 shows the FTIR spectra of the ternary blends.
Figure 4-8: FTIR Spectra for the individual blend components (arrows show the characteristic peaks of the reactive groups)

Characteristic peak observed for PLA were: CH$_3$ stretching at 3000-2940 cm$^{-1}$, symmetric C=O carbonyl stretching at 1710 and 1746 cm$^{-1}$, CH$_3$ bending at 1357 cm$^{-1}$, and C-C(O)-O stretching of ester bonds at 1180-1043 cm$^{-1}$. The peak values coincide with literature peak values reported for PLA [21]. Based on literature [22] characteristic IR bands for the butylene terephthalate segment of HYT were identified to be C=O vibration 1712 cm$^{-1}$, CH$_2$ bending at 1452 cm$^{-1}$, C-O vibration at 1267 cm$^{-1}$ and C=O bending around 916 cm$^{-1}$. In addition, peaks at 2796-2937 corresponding to C-H stretching were also observed. GMA based terpolymers can be characterized by epoxide ring vibration at 911 cm$^{-1}$; C-O stretching vibrations at 1105 cm$^{-1}$ and 1192 cm$^{-1}$; -C=O stretching vibration at 1734 cm$^{-1}$; -C-H vibrations at
Characteristic absorption bands of MaH based terpolymers are -C-C- skeleton vibration at 940 cm\(^{-1}\); -C=O carbonyl stretching at 1730 cm\(^{-1}\); symmetric C=O stretching of anhydride functions at 1785 cm\(^{-1}\) and -CH- symmetric and asymmetric stretching at 2950 cm\(^{-1}\) and 2996 cm\(^{-1}\), respectively [24].

**Figure 4-9: FTIR spectra for PLA ternary blends (arrows show the disappearance of characteristic peaks of the reactive groups)**

The reaction (Figure 4-10) that is expected to occur between the epoxide functional group of GMA terpolymer and the functional groups of PLA (-COOH and/or -OH) [25] can be detected from the disappearance or decreasing intensity of the characteristic peak of epoxy or oxirane group at 911 cm\(^{-1}\). Similarly, the reaction between maleic anhydride functional group of MaH based terpolymers and PLA can be detected from the disappearance or decreasing intensity of the maleic anhydride characteristic peak at 1785 cm\(^{-1}\). In the spectra of the ternary blends
Figure 4-9) these characteristic peaks disappeared indicating the functional groups were consumed during reactive extrusion process. Similar observations have been reported in other reactive extrusion studies that have used these terpolymers [26-27]. Although disappearance of epoxy and maleic anhydride functional groups in blends were observed, it is hard reach quantitative conclusions regarding the effectiveness of different functionalities.

![Chemical structure images](image)

*Figure 4-10: Reaction of GMA and MaH with functional groups of PLA*

### 4.3.5 Rheology

Rheological properties of blends are related to their morphology/phase structure and the interaction between the components. Rheological response measured can precisely reflect changes in the structure [28]. Results for binary blend complex viscosity and storage modulus
obtained as a function of angular frequency from oscillatory tests is shown in Figure 4-11a and b. Frequency sweep experiments were conducted in a linear viscoelastic range at a strain of 10%. Complex viscosity refers to the total resistance to dynamic shear, whereas storage modulus (elastic component) and loss modulus (viscous component) denote the temporarily stored energy and irrecoverable lost energy while initiating flow [29]. Neat HYT exhibits power-law behavior similar to PLA but with higher elasticity and viscosity compared to PLA in both high and low frequency region. Newtonian plateau of complex viscosity observed in PLA and blends with lower amount of HYT reduced with increase in HYT content. Rheological behavior of HYT and blends with higher amount of HYT resembles characteristic yield stress behavior, whereby the material does not flow unless the applied stress exceeds a certain value. At lower frequencies, complex viscosity of the blends are reported to be strongly affected by the elastic property of the rubber, this is in accordance with the trend observed in blends containing higher amounts of HYT. All the binary blends also exhibited shear thinning behavior and showed an intermediate behavior between neat PLA and HYT. From Figure 4-11b, storage modulus (G’) for the blends was also observed to increase with increase in HYT content and angular frequency. At higher frequencies the behavior is not much different between the neat polymers and the blends. Compared to PLA, HYT has flexible molecular chain and is easier for it to form entanglements. This higher degree of entanglements associated with HYT leads to higher amount of reversible elastic deformation which is reflected in the storage modulus curves of the blends.
Figure 4-11: (a) Complex viscosity and (b) storage modulus of PLA/HYT blends
During production process, polymer blends are most often subjected to high amount of deformation and shear linked to the non-linear region. Hence after having an idea regarding the behavior of binary blends in linear viscoelastic region, the behavior of ternary blends are analyzed in both linear and non-linear range for relative comparison. Flow behavior is generally represented using the flow curves and viscosity curves. Figure 4-12 shows the mutual dependence of shear stress, $\tau$ vs. shear rate, $\dot{\gamma}$ and viscosity vs. shear rate, $\dot{\gamma}$ on a double logarithmic scale.

Figure 4-12: Flow curve and viscosity curve for the PLA ternary blends
The flow curves show a Newtonian region (until the dashed line) where the stress vs. strain rate is a straight line, and the viscosity is not affected by the changes in shear rate. Beyond this limit, the blends exhibit pseudoplasticity where the fluids become thinner as shear rate increases (shear thinning). The Newtonian plateau observed in the viscosity curve is referred to as zero shear viscosity. MaH based blends show lower zero shear viscosity compared to GMA based ones with PLA/HYT/EMAGMA showing the highest of all. With increasing shear rates, the chains can disentangle, orient or stretch themselves parallel to the direction of driving force. Therefore in non-linear region the sample is deformed to a point where in the molecular structure is destroyed and shear thinning takes place. The difference in flow behavior of the ternary blends can be attributed to the sensitivity of individual components, any interactions between them and the blend morphology.

4.3.6 Differential scanning calorimetry (DSC)

Melting thermograms obtained for the binary and ternary blends after erasing the thermal history are presented in Figure 4-13. Crystallization, melting and glass transition temperatures of PLA remained the same indicating PLA-HYT blends are immiscible. The cold crystallization peak and melting peak intensity of PLA decreased with increasing concentration of HYT in the blend. This is an expected behavior as the PLA chain proportions in the blend are reduced. Glass transition temperature \( T_g \) of HYT was observed around 0 °C and a corresponding second \( T_g \) was observed in blends containing HYT higher than 30 %. Similarly crystallization peak also appeared for these blends at around 160 °C corresponding to the poly (butylene terephthalate) hard segment in HYT. Melting peak corresponding to HYT in the blends appeared at 205 °C.
Figure 4-13: DSC Melting traces of PLA/HYT blends (from 2\textsuperscript{nd} heat cycle)
Cold Crystallization peak temperature was reduced in binary and ternary blends compared to neat PLA, except in the case of EMAGMA. This indicates hindrance to the crystallization of PLA chains and is interesting to note that this behavior is similar to plasticization effect. The small endothermic peak appearing before the melting peak of PLA corresponds to the pre-melt crystallization. Similar observations in PLA have been reported previously by other researchers [29].

4.3.7 Dynamic mechanical analysis (DMA)

Figure 4-14 (a, b) shows the storage modulus (E’) and Tan δ curves for the neat polymers, binary and ternary blends. Storage modulus behavior of HYT was drastically different from that of PLA, due to its elastomeric nature. Blends followed the rule mixture in exhibiting modulus between that of neat components. The tan δ curves clearly shows the T_g of HYT and the binary blends with higher percentage of HYT also showed a two-step modulus reduction around the T_g of the blending components. Damping behavior of the blends has also monotonically increased with increasing elastomer content in the blends. In the case of ternary blends, storage modulus and tan δ curves exhibited β transition in the sub-zero temperature in addition to α transition (T_g). When the temperature was increased beyond 90 °C, cold crystallization of PLA occurred which is manifested as increase in storage modulus values. As opposed to different cold crystallization temperature obtained for EMAGMA based blends in DSC, all of the blends showed increase in E’ around the same temperature range. Compared to PLA/HYT (70/30) blend, PLA/HYT/Terpolymer (70/10/20) blend showed higher values of storage modulus. Again while comparing the E’ of blends with different polymers, EMAGMA based ternary blends show relatively higher values.
Figure 4-14: Storage modulus and Tan δ for (a) binary blends and (b) ternary blends.
4.5 Conclusion

PLA-HYT blends with content of HYT varying between 0 and 50 % are phase separated blends in which high viscosity HYT was dispersed as domains in the low viscosity continuous matrix of PLA up to 40 wt. % HYT concentration. Co-continuous morphology was observed at PLA-HYT blend ratio of 50/50. Tensile strength and modulus of the binary blends steadily decreased with increase in HYT content. Addition of 30 wt. % HYT resulted in blends showing impact strength around 250 J/m. A series of functionalized terpolymers, EMAGMA, EBAGMA, EMAMaH and EBAMaH were added to accomplish reactive compatibilization. The ternary blend ratio was selected based on previous studies. GMA containing copolymers showed better properties in terms of impact toughness compared to MaH copolymer containing blends. The domain size of the dispersed phase in the ternary blends was found to be bigger in all the cases except the blends containing EMAGMA. In addition, a greater stress whitening zone was observed in the impact fractured surface of PLA/HYT/EMAGMA. Compared to having 250 J/m in PLA-HYT (70/30) blends, suitable compatibilization resulted in PLA/HYT/EMAGMA (70/10/20) blends with high impact toughness showing non-break impact behavior. The difference in effectiveness between EBAGMA and EMAGMA could possibly due to the processing temperature range selected. EMAGMA could have relatively lower induction time which might help in achieving good reactivity and hence a favorable morphology in the blends.

References


19. PLA/Nylon/ Nanofiller –from Lit Rev chapter


Chapter 5: Crystallization Behavior of PLA with Aromatic Sulfonate Derivative

This chapter provides a detailed investigation of crystallization behavior and morphology of polylactic acid (PLA) in the presence of a nucleating agent: potassium salt of 5-dimethyl sulfoisothalate, an aromatic sulfonate derivative (Lak-301). Isothermal crystallization kinetics of PLA melt mixed with Lak at concentrations of 0.25 - 1 wt. % was investigated at a range of crystallization temperature, 140-150 ºC. To gain further insight on the effect of Lak, non-isothermal differential scanning calorimetry (DSC), wide angle x-ray diffraction (WAXD), polarized optical microscope (POM), heat deflection temperature (HDT) and rheology were also performed. At 0.25 wt. % Lak, crystallinity of PLA increased from 10 % to 45 %, and in 1 wt. % Lak, maximum crystallinity of 50 % was achieved. With 1 wt. % Lak, crystallization half time reduced to 1.8 min from 61 min for neat PLA at 140 ºC. The isothermal crystallization kinetics was analyzed using Avrami model. Values of the Avrami exponent for PLA with Lak were mainly in the range of 3 indicating a three dimensional crystal growth is favored. Crystallization rate was found to increase with increase in Lak content. Observation from POM confirmed that the presence of Lak in the PLA matrix significantly increased the nucleation density.

3 Version of this chapter is published as 'Crystallization behavior and morphology of polylactic acid (PLA) with aromatic sulfonate derivative’ in Journal of Applied Polymer Science, 2016, 133 (28).
5.1 Introduction

Much of the current research pertaining to PLA is directed towards overcoming its two major drawbacks: low impact strength and slow crystallization rate. Successful modification of these properties in cost efficient ways will greatly widen the use of PLA in packaging containers, agricultural, biomedical and engineering materials. Depending on the D-lactide content, PLA can be either amorphous or crystalline. Melting temperature of semi-crystalline PLA, with low content of D-lactide is in the range of 170-180 °C and glass transition temperature ($T_g$) is around 60 °C. Crystallization rate of semi-crystalline PLA is very slow compared to other commercial polymers such as polypropylene and polyethylene [1]. Therefore, it is difficult to achieve high crystallinity without changes to formulation or processing conditions. PLA remains almost amorphous under practical processing and molding conditions adopted for injection molding processes with high rate of super cooling. Difficulty in demolding and ejection of parts made of PLA is also attributed to its slow crystallization. In the context of heat deflection temperature (HDT), increasing the crystallization rate of PLA is of great importance as higher amount of crystalline form contributes to high HDT at service temperatures above $T_g$ [2].

Major strategies that are known to increase the crystallinity of PLA are (i) formation of stereo-complex crystals, (ii) use of nucleating agents, alone or in combination with plasticizers; (iii) in some cases epitaxy has also shown to be an effective way to speed crystallization of PLA [3,4]. Nucleation and crystallization mechanisms are however different in each of these cases. Incorporation of a nucleating agent is the most economical and widely used method for accelerating the crystallization process and increasing the crystallinity content. Presence of a nucleating agent in a virgin polymer can influence the kinetics and crystalline morphology by offering nucleation sites for initializing the crystallization process [5]. Lowering the
crystallization half time with the addition of a nucleating agent can help shorten the molding cycle times. Numerous investigations have been conducted on improving the crystallization of PLA; they are all reviewed in the literature review section.

In this chapter, we have investigated the effectiveness of an aromatic sulphonate derivative (potassium salt of 5-dimethyl sulfoisothalate), commercially available as Lak-301 in increasing the crystallization rate of PLA. To the best of our knowledge, isothermal crystallization kinetics and nucleation behavior of Lak-301 at different concentration in PLA have not been investigated in detail. Intent of this chapter is therefore to investigate the effect of Lak concentration and crystallization temperature on the overall crystallization rate of PLA with Lak.

5.2 Materials and Methods

5.2.1 Materials

PLA, Ingeo 3001D with 1.5 % D-lactide content was purchased from NatureWorks LLC, USA. Potassium salt of 5-dimethyl sulfoisothalate commercially available as Lak-301 was purchased from Takemoto Oil & Fat Co, Japan. Nucleating agent will be referred as Lak in the article. Neat PLA was oven-dried at 80 °C for at least 12 hours.

5.2.2 Sample preparation

Samples of neat PLA and PLA with different concentrations of Lak (0.25, 0.5, 0.75 and 1 wt. %) were fabricated through melt extrusion and injection molding. 15 cc, co-rotating twin screw micro extruder and 12 cc micro injection molding machine (DSM Research, Netherlands) were used. Processing temperature of 180 °C, screw rpm of 100 and residence time of 2 min was adopted for all the samples. Melt from the extruder was collected and transferred to the injection molder through a preheated collecting device. Holding pressure and time was set to 9 bar and
18s, respectively. Samples were molded to disc shape for rheology testing at a molding temperature of 30 °C. Neat PLA was also processed under identical conditions to possess similar thermal history.

5.2.3 Testing and characterization

**Differential Scanning Calorimetry (DSC):** Non-isothermal DSC was performed under heat-cool-heat cycle. Heating profile of 0 to 190 °C with heating rate of 10 °C/min was adopted for first and second heat cycle. 3 min isothermal step was included between cycles to erase the thermal history. Cooling cycle was run at 5 °C/min. Isothermal DSC was performed by heating the samples to 190 °C with heating rate of 10 °C/min followed by isothermal step at desired crystallization temperature for 30 mins. Samples of 3-5 mg for both isothermal and non-isothermal DSC were prepared from specimens molded at 30 °C. TA Instruments (New Castle, DE) DSC Q200 was used for the analysis.

**Wide angle x-ray diffraction (WAXD):** WAXD profiles of the samples were collected at room temperature from SuperNova Agilent single-crystal diffractometer equipped with a microfocus CuKα (λ=1.54184 Å) radiation source and Atlas CCD detector. X-Ray diffraction images were collected from four different angular positions of the goniometer using φ-scans to generate a 1D powder pattern within 2θ range of 5 and 100°. Images were processed using CrysAlisPro software. Plots of the powder pattern were generated from the original images with a step of 0.02° in 2θ.

**Heat Deflection Temperature (HDT):** Dynamic Mechanical Analyzer (DMA) Q800 from TA Instruments was used for measuring the HDT by heating the samples at 2 °C/min under a preload force calculated to match 0.455 MPa as per ASTM D648. HDT reported is the temperature corresponding to 0.1889 % strain; results are an average of two samples.
**Scanning electron microscope (SEM):** Phenom ProX (Phenom World BV, Netherlands) SEM equipped with a back scattering electron (BSE) detector was used to study the morphology of PLA samples with nucleating agent. Processed, non-isothermal samples were used for the analysis.

**Polarized optical microscope (POM):** POM from Nikon Instruments Inc., Canada equipped with a hot stage from Linkam Scientific Instruments Ltd., UK was used to perform a qualitative analysis of the crystallization process. Samples were melted at 180 °C, and a maximum cooling rate of 50 °C/min was used to bring the samples to desired isothermal temperature.

**Rheological characterization:** Anton Paar MCR302 rheometer (Anton Paar GmbH, Graz, Austria) with a parallel plate configuration (22mm plate and 1 mm measurement gap) under nitrogen atmosphere was used for rheological characterization. Frequency sweep analysis was done between 0.1-600 rad/s, at 190 °C and 1 % strain rate.

### 5.3 Results and Discussion

#### 5.3.1 Non-isothermal crystallization behavior

Effect of Lak on crystallization of PLA under non-isothermal conditions were studied and the DSC thermograms of melting from second heating cycle for neat PLA and PLA with increasing concentration of Lak are presented in **Figure 5-1**.
Figure 5-1: DSC melting traces of PLA and PLA with Lak from second heating cycle

Melting ($T_m$), cold crystallization ($T_{cc}$), and crystallization ($T_c$) peak temperatures, melting enthalpy ($\Delta H_m$), glass transition temperature ($T_g$) and percentage crystallinity ($\chi_c$) calculated from second heating cycle are provided in Table 5-1. PLA exhibited its characteristic cold crystallization, melting peaks and glass transition temperature ($T_g$). First obvious observation from Figure 5-1 is the cold crystallization peak which reflects the materials ability to crystallize below the melting temperature. The presence of cold crystallization peak in the second heating cycle of neat PLA indicates some of the semi-crystalline chains were still capable of rearranging or recrystallizing before melting. The absence of cold crystallization peak in PLA/Lak is a good indication Lak acts as an effective nucleating agent in promoting the crystallization process.
Table 5-1: Thermal characteristics of PLA and PLA with different concentration of Lak

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_{cc}$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>169.5±0.1</td>
<td>41.1±0.1</td>
<td>117.8±0.2</td>
<td>105.3±0.3</td>
<td>63.0±0.3</td>
<td>10.6±0.3</td>
</tr>
<tr>
<td>PLA+0.25 % Lak</td>
<td>168.9±0.3</td>
<td>40.9±0.1</td>
<td>--</td>
<td>132.3±0.2</td>
<td>62.9±0.1</td>
<td>44.8±0.2</td>
</tr>
<tr>
<td>PLA+0.5 % Lak</td>
<td>168.9±0.1</td>
<td>40.1±0.2</td>
<td>--</td>
<td>133.6±0.4</td>
<td>62.9±0.1</td>
<td>45.1±0.4</td>
</tr>
<tr>
<td>PLA+0.75 % Lak</td>
<td>169.1±0.2</td>
<td>41.8±0.1</td>
<td>--</td>
<td>134.2±0.2</td>
<td>62.7±0.2</td>
<td>48.3±0.1</td>
</tr>
<tr>
<td>PLA+1 % Lak</td>
<td>169.7±0.3</td>
<td>42.8±0.2</td>
<td>--</td>
<td>134.6±0.2</td>
<td>62.6±0.1</td>
<td>50.8±0.2</td>
</tr>
</tbody>
</table>

In previously published literature on crystallization of PLA with other nucleating agents, reduction in cold crystallization peak and in some cases disappearance has been reported and this behavior has been concluded to signify the efficiency of nucleating agent in enhancing the crystallization process [6,7]. The crystallization peak temperature, $T_c$ of PLA showed drastic improvement from 105 to 134 °C with the addition of Lak. Also, $T_c$ showed an increasing trend with increasing concentration of Lak again suggesting Lak is an efficient nucleating agent, supported by literature [6-8]. Presence of nucleating agent favors heterogeneous nucleation which would decrease the free enthalpy and increase the nucleation rate in the high temperature region and shift the $T_c$ value to higher temperature [9]. Percentage crystallinity ($\chi_c$) of PLA and PLA/Lak formulations were calculated using the equation,

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{f \Delta H_m^0} \times 100 \% \quad (5.1)$$

$\Delta H_m$ is the melting enthalpy and $\Delta H_{cc}$ is cold crystallization enthalpy, both taken from second heating cycle. $\Delta H_m^0$ is 100 % crystalline PLA’s melting enthalpy, 93.7 J/g [10] and $f$ corresponds to the weight fraction of PLA. With the disappearance of cold crystallization peak in the presence of Lak, crystallinity as high 50 % was achieved. Like $T_c$, percentage crystallinity also showed an increasing trend with increase in Lak concentration.
5.3.2 Isothermal crystallization kinetics

Isothermal crystallization behavior of PLA with different levels of Lak was examined at a range of temperatures between 140 and 150 °C. Literature suggests the crystallization temperature of PLA to be in the range of 105-120 °C [1,11,12]. In this study we have selected 120 and 140 °C as isothermal crystallization temperature (T_{c-is}) for pure PLA. In the case of PLA containing Lak, it was difficult to conduct the isothermal study at temperatures less than 140 °C as some of the crystals were already formed at temperatures below 140 °C while cooling from melt condition, even when a maximum cooling rate of 50 °C was used. When the polymer melt is rapidly cooled from melt to predetermined T_{c-is}, there is a time interval before the start of crystallization. This time is termed induction time, during which nucleation and growth process has been suggested to take place. Efficient nucleating agent shortens the induction time and enhances the overall rate of transformation from the molten state to the crystalline solid state. For instance, in the case of PLA with 1 % Lak, induction time was noticed to be 2s at 140 °C, whereas for neat PLA, induction time was 6 min at 120 °C. Such shortening of induction times in the presence of Lak is understandable, as PLA does not have to undergo self-nucleation.

Isothermal crystallization can be better understood by evaluating the relative degree of crystalline conversion or relative crystallinity (X_t) as a function of time at different crystallization temperatures selected. Relative crystallinity is expressed as the ratio of the area of the crystallization time, t, to the total area of the exotherm peak,

\[ X_t = \frac{\int_{t_0}^{t_f} (dH/dt)\,dt}{\int_{0}^{\infty} (dH/dt)\,dt} \quad (5.2) \]

Where, dH/dt is the rate of heat flow during the crystallization process at time t.

**Figure 5-2 (a-d)** shows the evolution of relative crystallinity with time for PLA with different levels of Lak at a range of isothermal crystallization temperatures.
Sigmoid nature of the relative crystallinity curves, with time dependence is obvious. These figures clearly depict the increase in crystallization time as the crystallization temperature increases from 140 to 150 °C. There is a critical $T_{c,\text{iso}}$ where the crystallization rate is the fastest. Below this critical temperature, the crystallization rate is dominated by crystal nucleation and above this critical temperature crystal growth rate is the dominant mechanism due to the increase in molecular mobility [13].
Avrami theory is the most common and widely used method to analyze and describe the isothermal crystallization kinetics. Avrami method relates relative crystallinity, $X_t$, to crystallization time, $t$, by the equation,

$$1 - X_t = \exp (-kt^n)$$  \hspace{1cm} (5.3)

or

$$\ln[-\ln(1 - X_t)] = n \ln(t) + \ln(k)$$  \hspace{1cm} (5.4)

Where $k$ is the crystallization rate constant involving both nucleation and growth rate parameters. $n$ is the Avrami exponent, dependent on the nature of nucleation and crystal growth dynamics [8]. By plotting $\ln[-\ln(1 - X(t))]$ versus $\ln(t)$, the Avrami exponent $n$, and the logarithm of the kinetic constant $\ln k$, can be determined from the slope and intercept, respectively. In general, these double log plots show deviations from linearity towards the beginning and end of crystallization due to initial and secondary crystallization [6]. Secondary crystallization is considered to occur due to crystal perfection and/or impingement of spherulites [9]. Therefore, only 20-80% of relative crystallinity linear portion data was used to fit the equation to obtain $n$ and $k$ values.

Avrami plots $\ln[-\ln(1 - X(t))]$ versus $\ln(t)$ for PLA with different concentrations of Lak at a range of crystallization temperatures is shown in Figure 5-3 (a-d). Almost parallel nature of the lines for a given sample in these plots indicates a good fit. Results evaluated from the plots are summarized in Table 5-2.
For neat PLA, the values of n range from 2.1 to 2.4 which are similar to literature values of 2.1-2.4 at $T_{c_{iso}} = 120-140 \, ^\circ C$ by Xu et al.[7]; 2.0-2.3 at $T_{c_{iso}} = 114-126 \, ^\circ C$ by Zhang et al.[14]; 2.5-2.9 at $T_{c_{iso}} = 90-140 \, ^\circ C$ by Tsuji et al. [15]; 2.4-2.8 at $T_{c_{iso}} = 120-140 \, ^\circ C$ by Weng et al.[16]. In case of PLA with Lak the n values have shifted from the range of 2 for pure PLA to range of 3 with 0.25, 0.5 and 0.75 % Lak and back to the range of 1.5-3 for PLA with 1 % Lak. This strongly indicates conditions such as, presence of the nucleating agent Lak, its concentration, and the crystallization temperature, have strong influence on the crystallization mechanism of PLA.
<table>
<thead>
<tr>
<th>Sample</th>
<th>ln(k)-intercept</th>
<th>k</th>
<th>Standard error</th>
<th>n</th>
<th>Standard error</th>
<th>Half Time (t½)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120 °C</td>
<td>-4.8</td>
<td>0.007</td>
<td>0.004</td>
<td>2.1</td>
<td>0.002</td>
<td>8.3</td>
</tr>
<tr>
<td>140 °C</td>
<td>-10.1</td>
<td>0.000</td>
<td>0.000</td>
<td>2.4</td>
<td>0.002</td>
<td>60.1</td>
</tr>
<tr>
<td>PLA+ 0.25 % Lak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140 °C</td>
<td>-3.7</td>
<td>0.023</td>
<td>0.003</td>
<td>3.1</td>
<td>0.002</td>
<td>2.9</td>
</tr>
<tr>
<td>142 °C</td>
<td>-3.8</td>
<td>0.020</td>
<td>0.004</td>
<td>3.0</td>
<td>0.004</td>
<td>3.1</td>
</tr>
<tr>
<td>144 °C</td>
<td>-6.1</td>
<td>0.002</td>
<td>0.001</td>
<td>3.6</td>
<td>0.001</td>
<td>4.9</td>
</tr>
<tr>
<td>146 °C</td>
<td>-6.1</td>
<td>0.002</td>
<td>0.003</td>
<td>3.1</td>
<td>0.002</td>
<td>6.2</td>
</tr>
<tr>
<td>148 °C</td>
<td>-6.7</td>
<td>0.001</td>
<td>0.003</td>
<td>3.2</td>
<td>0.001</td>
<td>7.2</td>
</tr>
<tr>
<td>150 °C</td>
<td>-8.7</td>
<td>0.000</td>
<td>0.004</td>
<td>3.5</td>
<td>0.002</td>
<td>10.5</td>
</tr>
<tr>
<td>PLA+ 0.5 % Lak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140 °C</td>
<td>-3.1</td>
<td>0.044</td>
<td>0.006</td>
<td>3.2</td>
<td>0.007</td>
<td>2.3</td>
</tr>
<tr>
<td>142 °C</td>
<td>-3.2</td>
<td>0.038</td>
<td>0.007</td>
<td>2.2</td>
<td>0.005</td>
<td>3.6</td>
</tr>
<tr>
<td>144 °C</td>
<td>-3.3</td>
<td>0.035</td>
<td>0.007</td>
<td>1.8</td>
<td>0.004</td>
<td>5.1</td>
</tr>
<tr>
<td>146 °C</td>
<td>-5.5</td>
<td>0.004</td>
<td>0.004</td>
<td>2.9</td>
<td>0.002</td>
<td>7.6</td>
</tr>
<tr>
<td>148 °C</td>
<td>-8.4</td>
<td>0.000</td>
<td>0.002</td>
<td>3.5</td>
<td>0.001</td>
<td>9.9</td>
</tr>
<tr>
<td>150 °C</td>
<td>-7.3</td>
<td>0.001</td>
<td>0.003</td>
<td>3.0</td>
<td>0.001</td>
<td>10.1</td>
</tr>
<tr>
<td>PLA+ 0.75 % Lak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140 °C</td>
<td>-2.3</td>
<td>0.098</td>
<td>0.004</td>
<td>3.1</td>
<td>0.006</td>
<td>1.8</td>
</tr>
<tr>
<td>142 °C</td>
<td>-2.2</td>
<td>0.110</td>
<td>0.002</td>
<td>3.2</td>
<td>0.002</td>
<td>1.9</td>
</tr>
<tr>
<td>144 °C</td>
<td>-3.3</td>
<td>0.036</td>
<td>0.002</td>
<td>3.0</td>
<td>0.002</td>
<td>2.6</td>
</tr>
<tr>
<td>146 °C</td>
<td>-5.3</td>
<td>0.005</td>
<td>0.003</td>
<td>3.1</td>
<td>0.002</td>
<td>4.8</td>
</tr>
<tr>
<td>148 °C</td>
<td>-5.5</td>
<td>0.004</td>
<td>0.002</td>
<td>3.0</td>
<td>0.001</td>
<td>5.5</td>
</tr>
<tr>
<td>150 °C</td>
<td>-7.8</td>
<td>0.000</td>
<td>0.003</td>
<td>3.3</td>
<td>0.001</td>
<td>9.2</td>
</tr>
<tr>
<td>PLA+ 1 % Lak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140 °C</td>
<td>-2.0</td>
<td>0.127</td>
<td>0.009</td>
<td>2.8</td>
<td>0.013</td>
<td>1.8</td>
</tr>
<tr>
<td>142 °C</td>
<td>-3.1</td>
<td>0.041</td>
<td>0.005</td>
<td>3.1</td>
<td>0.005</td>
<td>2.4</td>
</tr>
<tr>
<td>144 °C</td>
<td>-3.5</td>
<td>0.028</td>
<td>0.010</td>
<td>2.3</td>
<td>0.007</td>
<td>3.8</td>
</tr>
<tr>
<td>146 °C</td>
<td>-3.8</td>
<td>0.021</td>
<td>0.010</td>
<td>2.0</td>
<td>0.005</td>
<td>5.7</td>
</tr>
<tr>
<td>148 °C</td>
<td>-3.5</td>
<td>0.028</td>
<td>0.007</td>
<td>1.6</td>
<td>0.004</td>
<td>6.8</td>
</tr>
<tr>
<td>150 °C</td>
<td>-3.5</td>
<td>0.030</td>
<td>0.005</td>
<td>1.5</td>
<td>0.002</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Avrami exponent, n usually range from 1-4, the lower values (1-2) are associated with two dimensional growth with instantaneous and sporadic nucleation while the higher n values (3-4) denotes three dimensional growth of spherulites with just sporadic or combination of simultaneous and sporadic nucleation [17]. n values in the range of 2 obtained for pure PLA indicates mainly homogeneous nucleation with two dimensional crystal growth was favored in the absence of nucleating agents. n values in the range of 3 obtained for PLA with 0.25, 0.5 and 0.75 % Lak indicates that at particular concentration of Lak, three dimensional crystal growth is favored.

The drop in n value with increase in Lak concentration (1 %) can be attributed to increased nucleation density which could result in a large number of partially developed spherulites impinging with each other at very early stage of crystallization thus resulting in sheaf like structures or truncated spherulites. Presence of such intermediate sheaf like crystal geometry has been reported to decrease the Avrami exponent from 3 [18,19]. Values of k with unit min^{-n} are dependent on n, and n varies with T_{c-iso} therefore, k values are not directly compared. Hence crystallization kinetics is discussed based on crystallization half time (t_{1/2}), crystallization rate (\tau_{1/2}) and activation energy. Crystallization half time, t_{1/2} is defined as the time required to achieve 50 % of the final crystallinity of the sample at a given T_{c-iso}, expressed by the equation

$$T_{1/2} = (\ln 2/k)^{1/n} \quad (5.5)$$

The reciprocal of t_{1/2} is denoted as the crystallization rate, \tau_{1/2}. Parameter k is a temperature-dependent factor; it is denoted in the Arrhenius form for isothermal transformation as

$$\ln(k) = \ln(k_0) - \frac{E}{RT} \quad (5.6)$$
The activation energy for overall crystallization can be determined by plotting \( \ln(k) \) vs \( 1/T \) and \( \ln(k) \) is directly related to the activation energy. For neat PLA, the \( \ln(k) \) value is -10.7 at 140 °C, comparing this to PLA with Lak, the \( \ln(k) \) values and thus the activation energy is reduced in the presence of Lak. Another notable point is the increase in \( \ln(k) \) value (activation energy) of PLA/Lak with increase in crystallization temperature. Calculated values of \( t_{1/2} \) are listed in Table 5-2.

With the addition of Lak the crystallization half time reduced significantly and showed an increasing trend with increase in crystallization temperature. Lowest crystallization half time was achieved for PLA with 1 % Lak at 140 °C. These observations suggest Lak is effective in enhancing the isothermal crystallization behavior of PLA and the level of improvement is dependent on the crystallization temperature. Based on the explanations of Gao et al.[20] and Kang et al.[21] the change in \( t_{1/2} \) with the addition of nucleating agent is based on the nucleation rate which is controlled by free enthalpy of formation of nuclei of critical size, and free energy of the activation governs the diffusion of polymer segments across the phase boundary. In the high temperature region, free enthalpy is the dominant factor controlling nucleation rate; whereas in the low temperature region, free energy of activation has a greater influence on the nucleation rate. They have attributed higher \( t_{1/2} \) of neat PLA to high free enthalpy and hence slow crystallization. With the addition of nucleating agent, free enthalpy reduces which in turn enhances primary nucleation.

For more clarity, dependence of crystallization rate (\( \tau_{1/2} \)) on isothermal crystallization temperature is explained by plotting \( 1/ t_{1/2} \) as a function of \( T_{c-iso} \) in Figure 5-4. It is clear from this graph that the crystallization rate is gradually decreasing with increase in \( T_{c-iso} \) and a progressive increase is observed with increase in the concentration of Lak. At temperatures
between 142 and 148 °C, 0.75 % Lak shows higher crystallization rate compared to PLA with 1 % Lak. These observations suggest Lak is effective in accelerating the overall isothermal crystallization process.

![Figure 5-4: Crystallization rate vs. crystallization temperature for PLA with Lak](image)

**Figure 5-4: Crystallization rate vs. crystallization temperature for PLA with Lak**

### 5.3.3 Wide angle x-ray diffraction (WAXD)

In order to study the effect of addition of Lak on the crystal forms of PLA, WAXD patterns were recorded for neat PLA and PLA with different Lak content, and they are shown in Figure 5-5. Depending on different crystallization conditions, PLA is known to crystallize in three different crystal modifications: α, β, and γ forms [22,23]. Among the three crystal forms, α form is the most commonly observed crystal structure for crystals developed from melt crystallization at Tc higher than 120 °C, and α’ form for Tc less than 100 °C [22-24]. In our study,
samples were not crystallized and the WAXD pattern obtained reflect the crystallization structure developed during processing of samples at the specified molding conditions (30 and 110 °C).

![WAXD pattern](image)

**Figure 5-5: WAXD pattern for neat PLA and PLA with different concentration of Lak**

From **Figure 5-5**, it is evident that Neat PLA exhibited a broad hollow ascribed to the amorphous nature and a weak reflection peak at $2\theta = 16.84^\circ$, revealing the semicrystalline nature. Addition of Lak at different levels did not change this behavior, however a slight increase in the intensity of the peak was observed with increase in the concentration of Lak from 0.25 to 1%. With increase in mold temperature to 110 °C, Lak enhanced the crystallization of PLA and hence two strong peaks appeared at $2\theta = 16.84^\circ$ and $2\theta = 19.1^\circ$. These two peaks indexed as (200/110) and (203) are characteristic peaks for a typical $\alpha$ and $\alpha'$ crystal forms of PLA.24
5.3.4 Heat deflection temperature (HDT)

As discussed in the introduction section, adding nucleating agents to improve the crystallization of PLA is one of the efficient ways to improve the short term heat resistance property of PLA indicated by HDT. Current study has established the effectiveness of Lak-301 in improving the crystallinity of PLA; hence it is natural to expect that it would also significantly improve the HDT. However, in spite of successful enhancement in crystallization rate of PLA through addition of nucleating agents, obtaining injection molded articles of PLA with high crystallinity remains difficult due to very high mold cooling rate. HDT results obtained in this study, presented in Table 5-3, also support this practical limitation of using Lak for samples molded at low mold temperature.

Main reason for this observation is the insufficient level of crystallinity developed in nucleated PLA molded at room temperature. Typical cooling rates for conventional injection molding at room temperature (20–25°C) can be as high as 200 °C/min depending on the holding time. This leads to insufficient level of crystallinity in molded products. Hot mold (80–120°C) can be used to reduce the quench rate and to crystallize the part within the mold by applying in-mold-annealing time by extending the cooling time. In our case, as the mold temperature was increased, tremendous improvements were observed, especially in samples containing higher amounts of Lak molded at 110 °C. Based on the target applications, suitable molding conditions have to be adopted for desired HDT in final formulations. These results further corroborate with crystallinity profiles obtained from WAXD.
Table 5-3: HDT for PLA/Lak Formulations molded at different temperatures

<table>
<thead>
<tr>
<th>PLA/Lak Formulations at different mold temperatures</th>
<th>HDT (°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA + 0.25 % Lak at 30 °C</td>
<td>56.1 ± 0.2</td>
</tr>
<tr>
<td>PLA + 0.5 % Lak</td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>56.1 ± 0.3</td>
</tr>
<tr>
<td>60 °C</td>
<td>56.8 ± 0.1</td>
</tr>
<tr>
<td>90 °C</td>
<td>58.0 ± 0.2</td>
</tr>
<tr>
<td>110 °C</td>
<td>88.3 ± 0.3</td>
</tr>
<tr>
<td>PLA + 0.75 % Lak</td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>56.1 ± 0.1</td>
</tr>
<tr>
<td>60 °C</td>
<td>56.2 ± 0.1</td>
</tr>
<tr>
<td>90 °C</td>
<td>58.7 ± 0.2</td>
</tr>
<tr>
<td>110 °C</td>
<td>116.0 ± 0.2</td>
</tr>
<tr>
<td>PLA + 1 % Lak</td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>56.2 ± 0.1</td>
</tr>
<tr>
<td>60 °C</td>
<td>56.4 ± 0.2</td>
</tr>
<tr>
<td>90 °C</td>
<td>58.7 ± 0.1</td>
</tr>
<tr>
<td>110 °C</td>
<td>140.8 ± 1.2</td>
</tr>
</tbody>
</table>

5.3.5 Spherulite morphology from optical microscopy

In the case of neat PLA, nucleation and subsequent crystal growth was difficult to observe at temperatures higher than 130 °C, where as in the case of PLA containing nucleating agent Lak, the crystals were already partially formed at this temperature while cooling from melt state. Therefore, the optical microscope images shown in Figure 5-6 were captured at 120 °C for neat PLA and 140 °C for PLA with Lak. Images for only PLA with 0.5 % Lak are shown as similar crystallization behavior was noted invariable of the content of Lak. At melt state, optical microscopy image for PLA was completely dark but in other formulations with Lak, the Lak
particles were visible as bright spots. Nucleation and spherulites growth occurred rather slowly in neat PLA compared to PLA containing nucleating agents.

The spherulites sizes were large and were impinging on each other. An efficient nucleating agent is expected to provide a surface conducive to nucleation and increase the nucleation density by reducing the surface free energy barrier for primary nucleation.[9] Based on the above explanation, Lak can be an effective nucleating agent as the nucleation density increased with much smaller spherulites size but with larger number of spherulites. The crystallization appears to be complete by 3-4 min in the presence of Lak at 140 °C. These observations further confirm that incorporation of Lak is a promising means to improve the crystallization of PLA at appropriate molding conditions.
Figure 5-6: Polarized optical microscopy images of PLA (top row) and PLA with 0.5 % Lak (bottom row) at 20 x magnifications
5.3.6 Rheology

Rheology is of fundamental and practical interest as it can reveal changes in macromolecular chain structure with the addition of nucleating agents based on the variation in melt viscosity. Figure 5-7 (a-b) presents the storage modulus ($G'$) and complex viscosity ($\eta$) of neat PLA and PLA/Lak formulations at 190 °C as a function of angular frequency.

Figure 5-7 (a-b): Variation in complex viscosity, storage modulus and loss modulus of PLA/Lak with increasing Lak content as a function of frequency
Complex viscosity of PLA and PLA with Lak exhibited Newtonian behavior at lower frequencies and shear thinning behavior at higher frequencies. It can be seen, at lower frequencies, complex viscosity of PLA containing Lak was less than neat PLA and this behavior was pronounced at concentrations of 0.75 % and 1 % Lak. Such reduction in complex viscosity could be attributed to reduction in free volume as the nucleating agent increases the crystallinity of PLA, or just the presence of Lak particles which could interfere with physical process of chain entanglements in PLA melt. Similar behavior has been reported previously by other researchers in nucleated systems with PLA as matrix [25,26]. The storage modulus, $G'$ and loss modulus $G''$ of PLA with Lak was almost the same as neat PLA and at certain concentrations slightly lower than PLA. A characteristic terminal flow behavior of $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ was expected for PLA and it was observed to follow this behavior fairly well. The slopes of $G'(\omega)$ and $G''(\omega)$ calculated from angular frequencies lower than 10 rad/s for neat PLA was 1.93 and 0.96 respectively. These values are consistent with values reported by other researchers for PLA [25-27]. Addition of Lak did not seem to affect the shape and slope of storage modulus and loss modulus curves indicating chain dynamics were not drastically affected by the presence of Lak.

5.3.7 Scanning electron microscopy (SEM)

SEM of Lak-301 is shown in Figure 5-8 at low and high magnifications. Irregular trapezoidal crystal structures with particle size ranging from approximately 5 to 200 μm were observed. Some of the large size particles were noticed to be agglomerated. Fractured surface morphology of PLA with Lak is shown in Figure 5-9.
Figure 5-8: SEM Images of Lak-301 at 200x and 1000x magnification
Figure 5-9: SEM Images of (a, b) PLA+0.25 % Lak; (c, d) PLA+0.5 % Lak; (e, f) PLA+0.75 % Lak; (g, h) PLA+1 %Lak
Magnification: 1000x.
The fractured surface was obtained by breaking the extruded strands of PLA containing different concentrations of Lak. SEM micrographs on the top row show the distribution of Lak particles in PLA matrix. As the concentration of Lak is increased, more particles were seen on the surface, and hence a propensity for higher nucleation density. At 0.25 % Lak concentration, the fracture surface of PLA is smooth, characteristic of PLA brittle fracture. As the concentration increased to 1 %, a rough fracture surface with some fibrils was observed. SEM micrographs in the bottom row show the development of spherulites structures in PLA/Lak formulations. The sizes of the spherulites were in the order of 100 μm. The spherulites observed here seems to have formed from an aggregate of lamellae radiating from the center outward. They appear to have a Lak particle as a central nucleating entity which has initiated the crystal growth in all directions. Thus the different crystals are nucleated separately and grow uncorrelated. Also, the spherulites developed have distinct boundaries, and are noticed to impinge on each other. The size of the spherulite is reduced and is smaller in the case of PLA with 1 % Lak. Another notable observation is spherulitic structures which have formed only around certain Lak particles. This could be due to the wide range of variation in the Lak particle size or simply not enough time to undergo complete crystallization process under the adopted processing conditions. This SEM morphology shown here gives an idea of the morphology that is likely to develop in PLA formulations under non-isothermal conditions with fairly high cooling rates from melt temperature.

5.4 Conclusion

PLA with different concentration of Lak was prepared through melt extrusion and injection molding. The isothermal and non-isothermal crystallization behavior, isothermal crystallization kinetics, spherulitic morphology and crystalline structure of PLA and PLA with
Lak were investigated in detail. The addition of even small amounts of Lak significantly enhanced the non-isothermal crystallization peak temperature of PLA from 105 to 134 °C. The isothermal crystallization kinetics study revealed the overall crystallization rate to be much faster in PLA nucleated with Lak and the rate was found to be highest at 0.75 wt. % Lak. Crystallization rate however decreased with increasing crystallization temperature indicating the presence of critical isothermal crystallization temperature. Crystallization half time as low as 1.8 min was obtained while adding 0.75-1 % Lak at isothermal crystallization temperature of 140 °C. The values of the Avrami exponent of the neat PLA indicated two dimensional crystal growths. In the case of PLA/Lak formulations, at Lak concentration of up to 0.75 % the n values were around 3 indicating a three dimensional crystal growth. With further increase in Lak concentration to 1 wt. % Avrami exponent value reduced, this is believed to be due to increased nucleation density which could result in a large number of partially developed spherulites impinging on each other. Therefore, at early stage of crystallization sheaf like structures or truncated spherulites are expected to be developed. The observations from POM showed greater nucleation density in PLA/Lak blends with numerous small size spherulites compared to larger and sparse spherulite structures developed in PLA. WAXD profiles showed both neat PLA, and PLA with Lak was having mainly α and α’ form of crystal structure and hence we can conclude Lak did not modify the crystal structure but enhanced the process of crystallization. In summary, Lak can be effective in providing the required crystallizability for PLA, which could help in extending the practical range of PLA applications, when the products are molded at higher molding temperature.
References


Chapter 6: PLA Biocomposites

This work is a successful attempt in achieving Polylactic acid (PLA) biocomposites showing concurrent improvements in impact strength and heat deflection temperature (HDT). Biocomposites were fabricated from super toughened ternary blend of PLA, poly (ether-b-amide) elastomeric copolymer (PEBA) and ethylene-methyl acrylate-glycidyl methacrylate (EMAGMA), and miscanthus fibers. Effect of varying the processing parameters and addition of various nucleating agents were investigated. Crystallinity was controlled by optimizing the mold temperature and cycle time of the injection process. With the addition of 1 wt. % aromatic sulfonate derivative (Lak-301) as nucleating agent at mold temperature of 110 °C, PLA biocomposites exhibited dramatic reduction in crystallization half time to 1.3 min with crystallinity content of 42 %. Mechanical and thermal properties assessment for these biocomposites revealed a 4 fold increase in impact strength compared to neat PLA. HDT of PLA biocomposites increased to 85 °C from 55 °C again compared to neat PLA. Crystallization behavior was studied in detail using differential scanning calorimetry (DSC) and was supported with observations from wide angle x-ray diffraction (WAXD) profiles and polarized optical microscopy (POM). Presence of nucleating agent did not alter the crystal structure of PLA, however, a significant difference in spherulite size, crystallization rate and content was observed. Fracture surface morphology and distribution of nucleating agent in the PLA biocomposites were investigated through scanning electron microscopy (SEM).

Version of this chapter is published as ‘Overcoming the fundamental challenges in improving the impact strength and crystallinity of PLA biocomposites: influence of nucleating agent and mold temperature’ in ACS applied materials & interfaces, 2015, 7(21), 11203-11214.
6.1 Introduction

Poly (lactic acid) (PLA) is an aliphatic thermoplastic polymer obtained from renewable resources. PLA has high strength, modulus, biocompatibility and transparency. Large scale availability of PLA at a reasonable price has opened up more common applications areas like packaging, fiber materials, and other commodity materials [1-3]. Wide scale applications of PLA are however significantly hindered by its poor impact resistance, slow crystallization rate and low heat deflection temperature (HDT), especially in areas that require high level of mechanical strength, high resistance to temperature and sudden impact [3]. Only the crystalline PLA phase that exists above the glass transition (T_g) temperature, around 55 °C is known to impart useful mechanical properties [4]. Crystalline form of PLA is therefore important to achieve required improvements in HDT. On the other hand, the impact strength of semicrystalline polymers like PLA usually varies inversely with the percent crystallinity [5]. Attempts to enhance the performance of PLA biocomposites beyond standard levels so far for injection molded applications had generated formulations with either higher HDT or greater impact strength, but seldom both.

In our previous work [6], super toughened PLA ternary blends were formulated by adding a functionalized polyolefin, ethylene methyl acrylate glycidyl methacrylate (EMAGMA) to PLA and polyether block amide (PEBA) blend. Reactive functional groups on the E-MA-GMA reacted with carboxyl and hydroxyl end groups present in the PLA and PEBA thereby improving the toughness of the ternary blend dramatically. Although non-break impact behavior was observed in the PLA ternary blends, HDT remained typically same as that of neat PLA. The
aim of this chapter was to improve crystallinity and heat resistance by formulating biocomposites.

Increase in PLA’s total percentage crystallinity can effectively improve HDT, stiffness, and chemical resistance [7]. Due to high crystallization half time resulting from slow crystallization rate of PLA, obtaining an injection molded article with high crystallinity remains a challenge. Therefore, to obtain a molded component with increased crystallinity and maximized mechanical and physical performance, Harris and Lee [8] increased the mold temperature during injection molding to over 100 °C. However, the problem with this step is higher cycle time of ~2 mins would be required. Demolding of the processed components would be difficult in short cycle time due to higher cooling time required.

Presence of nucleating agents in a virgin polymer can have positive effect on crystallization kinetics and morphology by offering nucleating sites for initializing the crystallization process. Lowering of crystallization half time achieved with the presence of a nucleating agent can help in shortening the molding cycle times [9]. Another approach to increase crystallinity is by adding natural fibers to the polymer matrix. This approach serves dual purpose; they can increase the stiffness and heat resistance of a polymer while decreasing the cost of resulting composite materials as they replace a certain percentage of relatively expensive matrix material. Miscanthus, a perennial grass has been recently studied as effective filler in biopolymers [10,11] owing to their multiple advantages including its availability at very low cost. Besides increasing the crystallinity and heat resistance, natural fibers and nucleating agents can curtail the toughness of PLA as these properties negatively impact each other. But by using super toughened ternary PLA blends as a matrix material, the resulting biocomposites would still have higher impact strength and HDT compared to neat PLA. This chapter therefore proposes a
novel combination of PLA ternary blends, nucleating agents and natural fibers to formulate PLA biocomposites that are injection molded at different mold temperature to accomplish the desired results. The effect of adding different nucleating agents and the effect of varying the process parameters on the PLA biocomposites are summarized by investigated mechanical, thermal, thermomechanical properties and morphology by various characterization techniques.

Super toughened blends of PLA/HYT/EMAGMA of developed in the Chapter 4 were a later extension of the previous ternary blend work discussed in reference [6]. Therefore optimization of composite properties was carried out using the super toughened blend of PLA/PEBA/EMAGMA as a matrix. However, the biocomposites with PLA/HYT/EMAGMA and oat hull fibers fabricated using the conditions optimized in this chapter are presented in Appendix C.

6.2 Materials and Methods

6.2.1 Materials

PLA, Ingeo 3001D with 1.5% d-lactide content was purchased from NatureWorks LLC, USA. PLA 3100 HP with increased crystallizability was also purchased from NatureWorks LLC, USA. Polyether block amide (PEBA), Pebax® Rnew 35R53 having renewable carbon content of 28-32% was purchased from Arkema Company. EMAGMA terpolymer containing 8% of glycidyl methacrylate, commercially available as Lotader AX 8900 from Arkema Company was obtained from Quadra Chemicals, Canada. Nucleating agents used are (1) Aromatic sulphonate derivative (potassium salt of 5-dimethyl sulfoisothalate), commercially available as Lak-301 from Takemoto Oil & Fat Co, Japan; (2) magnesium oxysulphate, sold as HPR-803i by Milliken Chemical. Ltd., USA and (3) precipitated calcium carbonate sold by Specialty Minerals Inc., as
Emforce®bio. Miscanthus fibers were supplied by New Energy Farms, Leamington, ON, Canada. Polymers, nucleating agents and fiber will henceforward be abbreviated in the text and figures as noted: PLA 3001D as PLA1; PLA 3100HP that is said to contain about 1 % of Lak-301 as PLA2 and blends containing these PLAs will be referred to as PLA1 blend and PLA2 blend. Miscanthus will be abbreviated as MS; Lak-301 as Lak; HPR-803i as HPR and Emforce®bio as Emf. At few places for brevity, nucleating agents will be abbreviated as NA.

6.2.2 Biocomposite fabrication

Matrix material was a blend of PLA/EMAGMA/PEBA (70/20/10), optimization of the blend ratio was done in our earlier work and the details can be found in our previous publication.[6] Based on preliminary examinations, weight percentage of miscanthus in the biocomposite was decided to be 10 %, beyond which it is difficult to achieve required impact strength in the biocomposites. PLA and miscanthus were dried in oven for at least 12 hours at 80 °C while PEBA and EMAGMA were dried at 60 °C. Micro 15 cc co-rotating twin screw extruder and micro 12 cc injection molder from DSM Research, Netherlands were used to fabricate all the test samples. Biocomposites were extruded and injection molded at 190 °C, however, to investigate the effect of varying the processing temperature, 170 °C and 180 °C were also used. Residence time and screw rpm was maintained at 2.5 mins and 100, respectively. A preheated collector connected to the injection molder was used to transfer the extrudate for molding. Injection pressure used for 1st and 2nd stage are 3 and 6 bar, respectively.

It is known from the wealthy of literature that the crystallization temperature for PLA is approximately around 105 to 130 °C, therefore different mold temperatures (30, 60, 90, 110 and 120 °C) was adopted and the properties were examined systematically at these molding
temperatures. Cooling time of 30s was adopted for 30 °C mold temperature and 60s for higher temperatures to facilitate complete cooling before demolding of the samples without distortion. In order to provide a comparison with non-nucleated biocomposites and to emphasize the individual effect of high mold temperature and presence of nucleating agents, PLA1blend/MS (90/10) was molded at low and high temperature (30 and 110 °C). Furthermore, to investigate the effect of other nucleating agents such as HPR and Emf in comparison with Lak, the performance of PLA1blend/MS/HPR, PLA1blend/MS/Emf was studied at 110 °C. Results of varying the concentration of Lak in the biocomposite between 1 and 2 % are also reported as no significant difference was observed in the intermediate concentrations. For list of formulations please refer to Table 5-1 (column1) on DSC data.

6.2.3 Testing and characterization

Properties were tested after the molded specimens were conditioned according to ASTM D 618-08, Procedure A- 40h, 23 °C and 50 % relative humidity. Mechanical properties reported are an average result of five samples. Differential scanning calorimetry (DSC) was performed in DSC 200 from TA instruments. 5 mg of sample was prepared by cutting a thin slice from molded sample conditioned at laboratory atmosphere. Heat-cool-heat cycles with following conditions were used. Heat cycle: -50 °C to 190 °C at 10 ºC/min, cool cycle: 190 °C to -50 °C at 5 ºC/min. First heat cycle was followed by a 3 min isothermal step to erase the thermal history. Glass transition temperature ($T_g$), crystallization temperature ($T_{mc}$), cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$) were determined from the DSC graphs. Percentage crystallinity ($\chi_c$) was calculated using the using the equation,

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{f \Delta H_m^0} * 100 \% \quad (6.1)$$
Where, $\Delta H_m$ is the enthalpy of melting, $\Delta H_c$ is enthalpy of cold crystallization, $\Delta H^0_m$ is the enthalpy of melting of 100 % pure PLA, 93.7 J/g as mentioned in the literature. $f$ is the weight fraction of PLA in the composite. Wide angle x-ray diffraction (WAXD) profiles were obtained at room temperature using a SuperNova Agilent single-crystal diffractometer equipped with a microfocus CuKα ($\lambda=1.54184$ Å) radiation source and Atlas CCD detector. X-Ray diffraction images were collected goniometer using $\phi$-scans placed at four different angular positions to generate a 1D powder pattern within 2$\theta$ range of 5 and 100°. The images were processed using CrysAlisPro software. Step of 0.02° in 2$\theta$ was used to generate powder pattern plots.

Instron Instrument Model 3382 was used to measure the tensile and flexural properties by adapting ASTM standards D 638 and D 790, respectively. Tensile test conditions are, gauge length: 50 mm; crosshead speed: 50 mm/min for the blends and 5mm/min for the biocomposites. Flexural test of blends and composites were done at crosshead speed of 14 mm/min and span length of 52 mm. TMI 43-02 Monitor Impact Tester with a 5 ft-lb pendulum was used to measure the notched Izod impact strength (ASTM D 256) at room temperature. Dynamic mechanical properties (storage and loss modulus and tan $\delta$) were studied using DMA Q800, TA Instruments. Temperature range: -50 to 130 °C; ramp rate: 3 °C/min. HDT was also measured in DMA Q 800 with three point bending clamp in DMA controlled force mode at a stress of 0.455 MPa and ramp rate of 2 °C/min. Deflection was evaluated at 250 μm (0.1889 % strain). Thermal stability of biocomposites in nitrogen atmosphere was accomplished using a TGA Q 500, TA Instruments. Experimental temperature range: 25 ± 3 °C to 600 °C; heating rate: 20 °C/min. Fractured surface morphology was observed by Scanning electron microscope (SEM) SEM, Inspect S 50, FEI Netherlands. Samples were gold coated for 30 s under an argon atmosphere using Cressington sputter coater 108. Phenom ProX SEM (Phenom World BV, Netherlands)
equipped with a back scattering electron (BSE) detector and energy dispersive spectroscopy (EDS) was used to illustrate the composition of different nucleating agents. SEM images were captured at an accelerating voltage of 10 keV. Polarized optical microscope (POM) equipped with a hot stage (Nikon Instruments Inc., Canada, Linkam Scientific Instruments Ltd., UK) was used to perform a qualitative analysis of the crystallization process.

6.3 Results and Discussions

6.3.1 Non-isothermal crystallization behavior

Non-isothermal crystallization behavior of neat polymers and PLA biocomposites were studied using differential scanning calorimetry (DSC) to investigate the effect of processing parameters and effect of different nucleating agents in promoting the crystallinity. DSC melting curves for neat PLA, PEBA, GMA and PLA blend are presented in Figures 6-1.

![DSC thermograms of neat polymers and PLA blend](image)

*Figure 6-1: DSC thermograms of neat polymers and PLA1blend*
PLA exhibited its characteristic cold crystallization and melting peaks and glass transition temperature (T_g). PEBA is seen to melt at 140 °C with a shallow melting peak; the T_g was around -15 °C. EMAGMA also showed a very shallow melting peak at 60 °C, seen mostly as a flat line in Figure 6-2. Several trends were noticed from the first heating scans obtained from DSC for PLA biocomposites with and without nucleating agents at different mold temperatures. The first heating scan is preferred here as it best reflects the effect of different processing temperature profiles used for processing the samples on the resulting crystallinity content. First obvious observation from Figure 6-2 is the cold crystallization peak which reflects the materials ability to crystallize below the melting temperature. Cold crystallization peak was present in all the composites except the ones containing Lak molded at temperatures higher than 90 °C. This indicates that some of the semicrystalline chains were still capable of rearranging or recrystallizing before melting and that the particular processing parameter used did not allow complete reorganization of the chains while processing. General trend noted here was decrease in T_{cc} of biocomposites with Lak as the molding temperature increased. The absence of cold crystallization peak in PLA1 blend/MS/Lak (89/10/1) at 110 °C, 120 °C and PLA2 blend/MS (90/10) at 110 °C is a good indication that Lak at higher molding temperatures acts as an effective nucleating agent in promoting the crystallization process compared to other nucleating agents (HPR, Emf). From observations noted on T_{cc}, individual effects of high mold temperature and presence of Lak at 30°C molding were not sufficient in eliminating the process of cold crystallization. This emphasizes the combination effect of having high mold temperature and the presence of effective nucleating agent like Lak in facilitating crystallization such that the crystal are in a stable form and does not show any recrystallization.
Percentage crystallinity could quantify the effectiveness of different nucleating agents in combination with elevated mold temperatures which is discussed in subsequent paragraphs.

From the Figure 6-2, several peculiarities were noticeable in the melting peaks of first heating scan. Small exothermic peak just before the melting peak was noticed in all the biocomposites except the one containing Lak molded at higher mold temperatures. Another event is the occurrence of double melting peaks which was distinct in PLA biocomposites with Lak (1 and 2
% molded at 110 °C, where the small exothermic peak was absent. Multiple melting peaks usually indicate the presence of imperfect crystals that have the tendency to melt at lower temperatures [12]. In fact, the phenomenon of multiple melting peaks is attributed to a variety of factors including the presence of different crystal morphologies and modifications, possibility of crystallization induced molecular segregation; orientation and reorganization process occurring during DSC and the heating rates of DSC experiment [12-17]. Detail analysis of multiple melting peaks in PLA by several researchers reveal that these phenomena can be correlated with crystallization condition requirements for the formation of α’ and α crystal [14-16]. When the PLA biocomposite crystallizes at temperatures below 120 °C, α’ crystals are formed which are disordered crystal with same conformation as α form but with loose packing. The exothermic peak appearing just before the melting peak in our results can be associated with the transformation of disordered α’ crystals to more ordered α crystals. When the PLA biocomposite crystallizes at temperatures that favor the simultaneous formation of α’ and α crystals, a double melting peak appears.

Single melting peaks are associated with the formation of α crystals alone at higher crystallization temperature [14]. This behavior can also be explained in terms of low and high melting temperature crystallites. The presence of low melt temperature crystallites in larger quantities reduces the fraction of material competing with the formation of high temperature crystallites, at least within the temperature zone where the low temperature crystal phase is stable and there is potential to nucleate the high temperature crystal phase. As a result, increasing the molding temperature would increase the concentration of the low temperature crystallites and thus the lower melting peak has a more significant presence on the DSC thermogram. Slight reduction in melting temperature of PLA biocomposites containing Lak molded at higher
temperatures supports the imperfection in crystal structure. PLA2 containing Lak in masterbatch has high melt temperature and single melting peak indicating the presence of stable crystal structure. Ke and Sun [18] have also noticed similar behaviors in their work on PLA and starch composites. They have attributed the appearance of small exothermic peak to the additional crystallization that had occurred at a higher temperature during the DSC heating scan than the initial temperature at which the first crystallization occurred, which is quite possible in our case as well.

Melting temperature ($T_m$), melt crystallization and cold crystallization temperature ($T_{mc}$ and $T_{cc}$), percentage crystallinity ($\chi_c$) and glass transition temperature ($T_g$) data are provided in Table 6-1. Two different glass transition temperatures were observed for PLA biocomposites under 1st heating cycle (represented by inverse triangles in Figure 6-2). First $T_g$ appeared at around 42-45 °C which was manifested by a typical inflection in the base line towards the endothermic side. The second $T_g$ noticed around 60 °C showed a very sharp transition almost like an endothermic melting peak in some of the biocomposite formulations. The sharpness observed is often related to the relaxation kinetics of the polymer chains subjected to heating at a constant rate [19]. This phenomena of double $T_g$ has been reported previously for PLA based materials and are attributed to the presence of some of the amorphous polymer chains of the PLA being located in two different regions, one region is where all the amorphous polymer chains are situated far from the crystalline ones and the next region is where the immobilized polymer chains are situated closer to the crystallites [19]. The double $T_g$ behavior disappeared in the second heating scan suggesting that the relaxation behavior of the samples could have changed by erasing the thermal history.
Table 6-1: Differential Scanning Calorimetry Data

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Percentage crystallinity, $\chi_c$</th>
<th>Melt temp, $T_m$ (°C)</th>
<th>Cold Crys temp, $T_c$ (°C)</th>
<th>Melt Crys temp, $T_m$ (°C)</th>
<th>Glass trans temp, $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation</td>
<td>1st cycle</td>
<td>3rd cycle</td>
<td>1st cycle</td>
<td>3rd cycle</td>
<td>1st cycle</td>
</tr>
<tr>
<td>Composites without nucleating agent at different mold temp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA1 blend-MS (90/10) at 190 °C, 30 °C, 30 s</td>
<td>17.22</td>
<td>8.02</td>
<td>170.23</td>
<td>170.45</td>
<td>93.93</td>
</tr>
<tr>
<td>PLA1 blend-MS (90/10) at 190 °C, 110 °C, 30 s</td>
<td>31.35</td>
<td>15.27</td>
<td>168.84</td>
<td>170.30</td>
<td>99.31</td>
</tr>
<tr>
<td>Composites with nucleating agent at different mold temp and diff loading level</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 190 °C, 30 °C, 30 s</td>
<td>14.94</td>
<td>49.01</td>
<td>170.06</td>
<td>170.14</td>
<td>94.85</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 190 °C, 60 °C, 60 s</td>
<td>19.08</td>
<td>51.04</td>
<td>172.63</td>
<td>171.63</td>
<td>96.51</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 190 °C, 90 °C, 60 s</td>
<td>27.09</td>
<td>52.17</td>
<td>170.41</td>
<td>170.71</td>
<td>91.31</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 190 °C, 110 °C, 60 s</td>
<td>42.25</td>
<td>58.94</td>
<td>171.61</td>
<td>169.77</td>
<td>--</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 190 °C, 120 °C, 60 s</td>
<td>41.11</td>
<td>57.38</td>
<td>167.26</td>
<td>169.41</td>
<td>--</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (88/10/2) at 190 °C, 110 °C, 60 s</td>
<td>43.98</td>
<td>47.68</td>
<td>172.59</td>
<td>169.55</td>
<td>--</td>
</tr>
<tr>
<td>Composites with nucleating agent at different melt temp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 180 °C, 110 °C, 60 s</td>
<td>41.88</td>
<td>58.73</td>
<td>174.24</td>
<td>171.78</td>
<td>--</td>
</tr>
<tr>
<td>PLA1 blend-MS- Lak (89/10/1) at 170 °C, 110 °C, 60 s</td>
<td>31.34</td>
<td>56.57</td>
<td>169.88</td>
<td>169.68</td>
<td>--</td>
</tr>
<tr>
<td>Composites with other nucleating agents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA2 blend-MS (90/10) at 190 °C, 110 °C, 60 s</td>
<td>39.42</td>
<td>54.71</td>
<td>179.14</td>
<td>177.42</td>
<td>--</td>
</tr>
<tr>
<td>PLA1 blend-MS- HPR (89/10/1) at 190 °C, 110 °C, 60 s</td>
<td>18.00</td>
<td>5.60</td>
<td>170.23</td>
<td>170.68</td>
<td>98.36</td>
</tr>
<tr>
<td>PLA1 blend-MS- Emf(89/10/1) at 190 °C, 110 °C, 60 s</td>
<td>22.52</td>
<td>9.71</td>
<td>169.27</td>
<td>170.17</td>
<td>97.05</td>
</tr>
</tbody>
</table>
Dramatic difference in melt crystallization temperature was observed with the addition of Lak which shifted the $T_{mc}$ from ~96 to ~134 °C. $T_{mc}$ peak was absent in biocomposites containing HPR and Emforce, due to inability of the material to crystallize at the programmed cooling rate (5 °C/min), indication of the material being in amorphous state when cooled down from molten state. Similar observations have been reported previously by Jiang et al. [20] and Suskut et al. [13] in PLA/CaCO$_3$ system. Difference of ~ 40 °C in $T_{mc}$ of biocomposites with Lak strongly suggests that there is an increase in the concentration of nucleation sites induced by the addition of nucleating agent, Lak. However, PLA2blend/MS biocomposites showed only ~8 °C improvement in crystallization temperature.

6.3.2 Isothermal crystallization behavior

Degree of crystallinity relative to the maximum achievable crystallinity level is referred to as relative crystallinity.[17] It is often more desirable to know the rate at which crystallization occurs at a fixed temperature and a measure of which is crystallization half time. It is the time taken by a sample to reach half the final crystallinity. Crystallization behavior of composites with different nucleating agents were studied under two different temperatures. Figure 6-3 is a plot of relative crystallinity against time. It shows the crystallization behavior and half time of PLA biocomposites with different nucleating agents (Lak, Emforcebio and HPR803i).

Non-isothermal crystallization revealed that Lak was increasing the crystallization temperature significantly, therefore 140 °C was selected for isothermal crystallization study but this temperature was very high that no crystal formation was observed in composites containing other nucleating agents even when subjected to isothermal condition for more than 3 hours. Therefore, efficiency of other nucleating agents was analyzed at 120 °C. This temperature is not
very appropriate for Lak as most of the crystals would have formed by the time the samples are quenched to 120 °C however a comparison is provided in Figure 6-3.

![Figure 6-3: Plot of relative crystallinity vs. time and crystallization half time of composites with different nucleating agents at two different temperatures](image)

Many studies have reported the strong dependence of crystallization rate on the selected isothermal crystallization temperature. Neat PLA is known to have very slow crystallization rate, and depending on the temperature selected in the range of 105 to 130 °C PLA has shown to have crystallization half times between 5 and 40 min [8,21,22]. As listed in Figure 5-3, crystallization half time for PLA blend was noticed to be 12 min and with the addition of fibers, it slightly decreased to 11 min, which could be attributed to the presence of miscanthus. Multiple studies have reported the ability of cellulose in natural fibers to act as nucleating agents and sometimes presence of fibers could promote transcrrystallinity [23,24]. Striking difference in crystallization
rate was observed in case of Lak with ~40 fold increase at 120 °C and ~10 fold increases at 140 °C. Very low half time of 0.28 mins for composites containing Lak isothermally crystallized at 120 °C could be an indication that crystal formation might have already started while cooling down from melt temperature. HPR had increased the half time to 14.24 min indicating that addition of HPR has actually hindered the crystallization process and is not effective in offering nucleation sites for the polymer to crystallize. Emf nucleating agent had decreased the half time to 9.33 mins however not as effective as Lak. In comparison, it can be said that Lak is very efficient in imparting desired level of crystallinity within a short period of time which is of great value to maintain short cycle times during the injection molding.

The effectiveness of different nucleating agents tested here can mainly be attributed to their physical nature and the nucleation mechanism. HPR (magnesium oxysulfate) and Emf (precipitated calcium carbonate) are inorganic materials, which when added as nucleating agents act as heterogeneities on which the crystallizing polymer crystallizes when cooled down from unoriented molten state giving rise to heterogeneous nucleation mechanism [25]. On the other hand, Lak is a salt of organic sulphonic acid which makes it an organic nucleating agent. Chemical nucleation behavior is mostly favored by organic NAs, where they are said to cause the chain scission in polyesters and form ionic chain ends and then ionic clusters which acts as the true nuclei [26]. Under the conditions studied in this work, organic nucleating agent (Lak) has been found to impart high level of crystallization in PLA.

6.3.3 Wide angle x-ray diffraction (WAXD)

To obtain further information on crystallization, the crystalline nature of matrix, fiber and biocomposites were analyzed WAXD. Figure 6-4 demonstrates the profiles obtained for neat PLA, PLA blend matrix, miscanthus and biocomposites at low and high mold temperature (30
and 110 °C). Neat PLA exhibited a broad hollow ascribed to the amorphous nature and a week reflection peak at $2\theta = 16.84$ revealing the semi-crystalline nature. In addition to the above characteristic peaks, blends and composites molded at 30 °C exhibited a small diffraction peak at around $2\theta = 20.8$ which could be ascribed to poorly formed crystals of PEBA [27]. On the other hand, same broad hollow of PLA was noticed in biocomposites molded at 30 °C indicating the inability of PLA to form perfect crystals at this molding temperature. However, when molded at 110 °C and in the absence of nucleating agent, the intensity of the PLA characteristic peak at $2\theta = 16.84$ strongly increased and a shoulder appeared at $2\theta = 19.13$ indicating the increase in crystallization of PLA under this molding condition. These peaks are two strong reflections of 200/110 ($2\theta = 16.84$) and 203 ($2\theta = 19.13$). These peak values are in accordance with values reported in literature [16,28,29].

![WAXD profile of raw materials and biocomposites without nucleating agents molded at low and high mold temperature.](image)

**Figure 6-4:** WAXD profile of raw materials and biocomposites without nucleating agents molded at low and high mold temperature.
Therefore, the two same reflections seen in our WAXD profile, along with DSC data supports the formation of mixture of $\alpha'$ and $\alpha$ crystal phases in our biocomposite system. **Figure 6-5** compares the x-ray diffraction profiles of different nucleating agents, PLA biocomposites nucleated with Lak at different mold temperatures and biocomposites with HPR and Emf molded at 110 °C. PLA1blend /MS/Lak (89/10/1) at low mold temperatures (30 and 60 °C) were similar to the patterns of biocomposites without nucleating agent at low mold temperature except the peak at $2\theta = 5.37$ which comes from the characteristic peak of Lak. With the increase in mold temperature from 90 to 120 °C the crystalline peak intensity of PLA increased significantly.
and the highest intensity was recorded for the biocomposites molded at 120 °C. With the increase in content of Lak from 1 to 2 % the peak intensity was not significantly affected and it was much similar to the one containing 1 % molded at 110 °C. While comparing PLA1blend/MS/Lak molded at 110 °C with HPR and Emf, again the ones with Lak showed higher intensity of reflection associated with the crystalline part. Approximate peak maxima, 2θ (d spacing) values obtained for PLA1blend/MS/Lak (89/10/1) molded at 110 °C is 5.37 (16.46), 12.35 (7.16), 14.80 (5.98), 16.84 (5.26), 19.13 (4.64), 22.33 (3.98). In all of the above discussed biocomposites the 2θ values for the crystalline peak remained the same indicating that the addition of nucleating agent and the increase of mold temperature has increased the crystallizability of PLA without affecting its inherent crystal structure. Similar result has been previously reported by Xiao et al.[30] in PLA with triphenyl phosphate and talc as nucleating agents.

6.3.4 Mechanical properties and heat deflection temperature (HDT)

As discussed previously, impact strength and HDT are the two most important deciding factors for commercializing PLA for wide scale applications. Therefore, the effect of nucleating agents and processing parameters on the impact strength and HDT were first determined and the optimizations were done based on the balance of these two properties. Figure 6-6 shows the trend in impact strength and HDT of PLA biocomposites with and without nucleating agents at various mold temperatures. Neat PLA has impact strength of 20 J/m and HDT of 55 °C. PLA blends containing PEBA and EMAGMA showed non-break behavior which was attributed to the unique morphology development in this particular blend formulation as noted in our previous publication [6]. However, the HDT of blends remained the same as that of neat PLA. From Figure 5-6 it is noticeable that the addition of 10 % miscanthus reduced the impact strength to ca.
120 J/m, this is considered to be common as the ductility of the matrix is reduced by the addition of fibers that restrict the molecular mobility of the polymer chains.

Nagarajan et al. [10] have previously reported such reduction in impact strength with the addition of miscanthus fibers in a different matrix system. Nonetheless, the level of impact strength is still 300% higher compared to the neat PLA. But the HDT of this formulation was found to be at 58 °C, meaning the incorporation of natural fiber alone in the blend matrix system did not help in increasing the HDT tremendously mainly because there was no significant change in crystallinity as discussed in the ‘crystallization behavior’ section. Nyambo et al. [31] studied the effect of adding agricultural residues in PLA and noticed no improvement in HDT even at 30wt % fiber loading.

**Figure 6-6: Impact strength and HDT of PLA biocomposites with and without Lak molded at different mold temperatures and injection cycle time**

A- PLA1 blend / MS (90/10) at 30 °C, 30 s; B-PLA1 blend/MS (90/10) at 110 °C, 60 s; C- PLA1 blend/MS/Lak (89/10/1) at 30 °C, 30 s; D-PLA1 blend/MS/Lak (89/10/1) at 60 °C, 60 s; E-PLA1 blend/MS/Lak (89/10/1) at 90 °C, 60 s; F-PLA1 blend/MS/Lak (89/10/1) at 110 °C, 60 s; G-PLA1 blend/MS/Lak (89/10/1) at 120 °C, 60 s
Increasing the mold temperature is one of the effective and proven strategies to improve the crystallizability of PLA. Vadori et al. [32] have recently published an investigation on the effect of mold temperature on the performance of PLA where a 90 °C mold temperature was found to impart maximum crystallinity. In our study, when the PLA biocomposites without any nucleating agent was molded at high mold temp of 110 °C, the impact strength was maintained while the HDT increased from 58 °C to 64 °C which was only a limited improvement. This observation revealed that incorporation of fiber and high mold temperature alone is not sufficient to achieve the required balance of properties, which can again be well supported with crystallinity results from DSC experiments. Hence, addition of nucleating agents becomes important.

Effectiveness of nucleating agent, Lak-301 was studied by varying the mold temperature from 30, 60, 90, 110 and 120 °C. From Figure 6-6 it can be said that the increase in mold temperature in presence of Lak has had minor influence on the impact strength up to a temperature of 90 °C, but the HDT has improved to 65 °C at a molding temperature of 90 °C. Once the temperature was increased beyond 90 °C, drastic difference in both impact strength and HDT was noticed. This could be well related to the marked improvement in crystallinity achieved at different mold temperatures. This result is also an indication of nucleated material having faster crystallization rates. Once the percentage crystallinity of PLA in the biocomposites is over 40 % it plays a dramatic role in influencing the material properties. Although the HDT reached a plateau over 110 °C mold temperature, the impact seemed to reduce further with the increase in mold temperature. Therefore, depending on the property requirements, the crystallinity level needed to achieve those requirements can be controlled by selecting appropriate mold temperatures. Another noteworthy point here is demolding of the samples at
high mold temperatures; without the nucleating agent the samples were hard to remove from the mold in spite of having miscanthus fibers which imparted certain amount of stiffness to the composites. However, with the addition of Lak, the samples did not warp and were easy to remove from the mold without causing any potential deformation. This factor is important from industrial processing point of view, as cooling time higher than 60s would not be preferred as it will affect the overall production efficiency and cost, defeating the very purpose of making these materials available at an affordable cost. Suryanegara et al. [9] have also made similar observation where the presence of combination of microfibrillated cellulose and phenyl phosphonic acid zinc (NA) helped in easy demolding of the samples processed with 90 °C mold temperature.

Effectiveness of two other additives as nucleating agents (HPR 803i and Emforcebio) and PLA containing Lak-301 nucleating agent, (PLA 3100 from Natureworks, referred as PLA2) in providing the required balance of impact strength and HDT was tested at a mold temperature of 110 °C and has been compared with biocomposites containing Lak, results are shown in Figure 6-7. Addition of HPR and Emforcebio nucleating agents have not influenced the properties significantly, the impact strength remained same as that of biocomposites without any nucleating agents molded at higher mold temperatures and the HDT increased to just above 60 °C. On the other hand PLA2 system already containing Lak additive showed better performance compared to the other two additives but still lower than adding Lak separately during processing as in PLA1 system. Depending on the property requirements and in a way to achieve the cost vs performance balance, using PLA containing the Lak additive might be a better choice.
A- PLA1 blend/MS/Lak (89/10/1); B- PLA1 blend/MS/HPR (89/10/1); C- PLA1 blend/MS/Emf (89/10/1); D- PLA2 blend/MS (90/10); E- PLA1 blend/MS/Lak (88/10/2)

**Figure 6-7: Impact strength and HDT of PLA biocomposites with different nucleating agents molded at 110°C mold temperature**

Yu et al. [33] studied the effect of adding talc on thermal and mechanical properties of PLA. They have reported that talc did not bring about any significant difference in HDT till 5 wt. % loading and the maximum increment achieved was 3 °C at 18 wt. % talc loading beyond which the HDT plateaued. Sinha et al. [34] have reported a significant enhancement in HDT of PLA when organically modified synthetic fluorine mica was added and when the injection-molded specimens were annealed at 120 °C for 30 min. Therefore, based on literature and experimental evidence we can conclude that organic nucleating agents in combination with high temperature molding/annealing are being very efficient in crystallizing PLA and increasing the HDT effectively. Our results suggest that the crystallinity strongly dictates the balance that could be achieved between impact strength and HDT. In other words, by controlling the crystallinity through mold temperature and the type of nucleating agents, control of impact strength and HDT could be achieved. Increase in HDT with increase in crystallinity has also
been reported by Tang et al. [35]. They have noted that the crystallinity threshold for achieving improvements in HDT is about 20-25%. With the increase in content of Lak from 1% to 2%, improvement in properties seem to have reached a plateau as only a slight increase in HDT and a slight decrease in the impact strength was noticed, therefore we can conclude that 1% was sufficient to impart the required level of crystallinity that positively changed the impact strength and HDT.

Tensile strength, tensile modulus, flexural strength and flexural modulus were also investigated. **Figure 6-8** shows the results obtained for selected PLA biocomposites with and without nucleating agents at different mold temperatures.

![Figure 6-8: Tensile and Flexural properties of selected PLA biocomposites](image)

A- PLA1 blend / MS (90/10) at 30 °C, 30 s; B- PLA1blend/MS (90/10) at 110 °C, 60 s; C- PLA1 blend/MS/Lak (89/10/1) at 30 °C, 30 s; D-PLA1 blend/MS/Lak (89/10/1) at 110 °C, 60 s; E- PLA1 blend/MS/HPR (89/10/1) at 110 °C, 60 s; F-PLA1 blend/MS/Emf (89/10/1) at 110 °C, 60 s; G- PLA2 blend/MS (90/10) at 110 °C, 60 s
Tensile modulus was found to increase slightly with increase in mold temperature, immaterial of the nucleating agent being present in the composite and this trend was more prevalent in flexural modulus. Most of the studies have also reported increase in modulus with increase in degree of crystallinity [36]. The difference in tensile strength between different mold temperature and nucleating agents are considered to be within the standard deviation. However, a slight increase in flexural strength is seen with increase in mold temperature in biocomposites with and without Lak which can be correlated with the increase in percent crystallinity. In the case of biocomposites with HPR and Emf the observed increase in flexural cannot be correlated with crystal formation, therefore it is believed to be due to the possible reinforcing effect offered by these additives.

6.3.5 Optical microscopy

In the case of PLA1blend/MS (90/10) biocomposites, spherulite growth was difficult to observe at temperatures higher than 120 °C whereas in the case of biocomposites with Lak nucleating agent, the crystals were already formed at 120 °C as we discussed in previous results that Lak has effectively increased the crystallization temperature of PLA. Therefore, the optical microscopy images of biocomposites with and without Lak are compared at different temperatures. PEBA and EMAGMA present in the matrix as dispersed particles were clearly visible along with a large fiber particle when the composites without Lak was melted at 200 °C. In the case of biocomposites with Lak, the dispersed phase was noticeable however, not very clear as observed in composites without Lak. Main observation was regarding the crystalline content. In the absence of Lak, the spherulite size was very large and the rate at which they were forming was relatively slow and this is clearly visible from the images in Figure 6-9.
Figure 6-9: Optical microscopy images of PLA1blend/MS (90/10)-top row and PLA1blend/MS/Lak (89/10/1)-bottom row at 50x magnification
In the case of PLA1blend/MS/Lak (89/10/1), densely packed spherulites impinged on one another were observed and the spherulite formation was occurring at a much faster rate. The crystallization process was almost complete in 1.5 mins as shown in Figure 6-9. Although both samples with and without nucleating agent exhibited spherulitic morphology, there was a dramatic difference in spherulite size, crystallization rate and content. Tang et al. [35] have also reported such reduction in average diameter of the spherulites when ethylenebishydroxy-stearamide (EBH) was added as nucleating agent for PLA.

6.3.6 Morphology of optimized PLA biocomposites

The mechanical properties of composites largely depends on the phase morphologies, therefore, SEM was employed to study the phase structure. Figure 6-10 shows impact fractured surface morphology of biocomposites with and without Lak nucleating agent. The micrographs of impact fractured surface of the biocomposites largely showed ductile fracture, evident from rough fracture surface and the presence of longer fibrils and cavitations indicating matrix deformation. Energy dissipation process in biocomposites can be grouped into matrix related (microvoiding or cavitation, crazing, shear bending and yielding) and fiber related (debonding, fiber pullout and breakage) [37]. Toughening mechanism observed in the super toughened PLA ternary blend used as a matrix here has been reported in detail in our previous work.[6] Synergistic effect of good interfacial adhesion and cavitations followed by massive shear yielding of the PLA matrix was said to have contributed to the enormous toughening effect observed in the ternary blends [6]. Fiber pull out and debonding was also observed on the impact fractured surfaces of the biocomposites mainly because of the absence of any compatibilizer that could improve the interfacial adhesion between the fiber and the matrix.
PLA1blend/MS (90/10) at (a) 30 °C mold temperature (b) 110 °C mold temperature; (c) PLA2blend/MS (90/10) at 110 °C mold temperature, (d) and (e) PLA 1 blend/MS/Lak (89/10/1) at 110 °C with different magnifications, (f) PLA 1 blend/MS/Lak (89/10/1) at 110 °C from SEM with back scattering electron (BSE) detector. Magnification: (a)-(d) 2000x; (e) 5000x (f) 2500x

**Figure 6-10**: SEM images of PLA biocomposites with and without nucleating agent
In the presence of Lak, PLA was expected to be well nucleated however spherulitic morphology was not noticeable in the SEM micrograph but the number of voids or cavitation was found to be higher in the nucleated matrix. The reduction in impact strength with the simultaneous increase in mold temperature and addition of nucleating agent could be attributed to the enhanced crystallization ability of the well nucleated samples which diminished the capability of PLA in the blend matrix to accommodate the interfacial debonding.

### 6.3.7 Composition, particle size and dispersion of nucleating agents

SEM with EDS data for biocomposites with different nucleating agents are shown in Figure 6-11 and Table 6-2. Intensity of the back scattered electron (BSE) signal which is related to the atomic number of the material, can provide meaningful insight on chemical composition and distribution of various elements. Compositions of nucleating agents were identifiable through EDS. As mentioned before Lak-301 is potassium salt of dimethyl 5-sulfoisophthalic acid, hence a strong peak for potassium and sulfur was observed.

The particle size of Lak in PLA1blend/MS/Lak composites was fairly high, between 10-20 μm. The surface of Lak particles was noticed to be very rough. In the case of PLA2blend/MS system, Lak particles were of 1-2 μm and were hard to spot. Also, when scanned for composition, only the concentration of potassium was obtainable. This could be because of the fairly small particle size, making it difficult to detect. X-rays usually come deeper from the surface, therefore the concentration of other elements could have masked the insignificant amount of sulfur in the Lak at the particular scanned point. Rod-like morphology was observed for HPR (Magnesium oxysulfate) and Emf (precipitated calcium carbonate). HPR seemed to possess the highest aspect ratio which supports our previous claims of it acting more as a reinforcing agent. Emf was hard to visualize at same magnification used for other composites.
therefore a comparison is provided at higher magnification. The particle size of Emf was measured to be around 1-3 μm. No agglomerates were noticed in biocomposites with different NAs, they were all well distributed. In addition to the difference in nucleating agent nature, i.e., organic or inorganic, particle size and shape could also have an effect on the nucleation efficiency. Nucleation density, distribution and size of spherulites are dependent on the particle size of NA and a fine particle size is known to possess higher nucleation tendency [38]. However in our case, Lak with larger particle size has been the efficient nucleating agent, leading us to believe that there is a factor that is outplaying the effect of particle size of NA. In order to increase the rate of crystallization, molecular interactions between polymer and surface of NA are important [39]. From all our investigation and experimental results we can conclude that Lak was efficient in reducing the interfacial free energy barrier for nucleation and hence increased the crystallization rate significantly.
(A) PLA1 blend/MS/Lak (B) PLA2 blend/MS (C) PLA1 blend/MS/HPR at a magnification of 5000x (D) PLA 1 blend/MS/Emf, all biocomposites molded at 110 °C mold temperature, magnification of 12000x

Figure 6-11: SEM with EDS points for PLA biocomposites

Table 6-2: Elemental composition of different nucleating agents

<table>
<thead>
<tr>
<th>Element Number, Symbol, Name</th>
<th>PLA1 blend/MS/Lak Lak-301</th>
<th>PLA2 blend/MS Lak-301</th>
<th>PLA1 blend/MS/HPR HPR-803i</th>
<th>PLA 1 blend/MS/Emf Emforcebio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, C, Carbon</td>
<td>59.5 (0.9)</td>
<td>62.8 (0.8)</td>
<td>45.1 (0.9)</td>
<td>66.8 (0.9)</td>
</tr>
<tr>
<td>8, O, Oxygen</td>
<td>26.8 (0.2)</td>
<td>30.7 (0.0)</td>
<td>45.7 (0.0)</td>
<td>28.1 (0.0)</td>
</tr>
<tr>
<td>12, Mg, Magnesium</td>
<td>--</td>
<td>--</td>
<td>8.2 (0.0)</td>
<td>--</td>
</tr>
<tr>
<td>16, S, Sulfur</td>
<td>4.6 (0.1)</td>
<td>--</td>
<td>1.0 (0.1)</td>
<td>--</td>
</tr>
<tr>
<td>19, K, Potassium</td>
<td>9.0 (0.0)</td>
<td>6.6 (0.0)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>20, Ca, Calcium</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5.1 (0.1)</td>
</tr>
</tbody>
</table>
6.3.8 Dynamic mechanical analysis (DMA)

Effect of mold temperature and different nucleating agents on the storage modulus and tan delta of the PLA biocomposites are presented in Figure 6-12 and Figure 6-13(a) and (b).

![Dynamic mechanical analysis graph](image)

**Figure 6-12: Effect of mold temperature on the storage modulus and tan delta of the PLA biocomposites**

With the increase in mold temperature from 30 to 110 °C for PLA1blend/MS/Lak composites, significant increase in storage modulus was noticed and the increase was observed to be a gradual step increase between the mold temperatures due to the increase in crystallinity. At room temperature the maximum storage modulus obtained for the biocomposites molded at 110 °C was found to be 2458 MPa. At sub-zero temperatures also the storage modulus for the biocomposites with Lak nucleating agent molded at 110 °C was distinctly higher. While comparing the storage modulus of biocomposites with different NA, PLA1blend/MS/Lak composites still performed significantly better. The maximum storage modulus at room temperature for PLA1 blend /MS composites molded at 110 °C without any nucleating agent was
2103 MPa while for rest of the biocomposites with different NA, the storage modulus was ca. 2120 MPa, which is only a slight increase compared to the one without any nucleating agent processed at the same molding temperature. Increase in storage modulus trend can be well correlated with the crystallinity results from DSC as the crystalline structures in combination with fibers decrease the mobility of the chains in the amorphous region thereby increasing the composite stiffness [40]. A sharp reduction in storage modulus was noticed at the glass transition zone which is associated to the softening of the composites. Almost all samples touched a zero value except PLA1 blend/MS/Lak molded at 90 and 110 °C and PLA2 blend/MS. This is because the large amount of amorphous region in the composites having low crystallinity is not capable of storing energy above the glass transition zone [41] and similar behavior has been reported in neat PLA molded at different mold temperature by Vadori et al. [32]. In most of the biocomposites with and without NA processed at different mold temperatures, the storage modulus was noticed to increase after 90 °C which was typical of recrystallization [41]. In the case of PLA1 blend/MS/Lak molded at 110 °C, the modulus was deteriorating throughout the investigated range of temperature without touching zero. This indicated that there was no amorphous region incapable of storing energy and the crystal structures are already in a stable state therefore there was no apparent increase in storage modulus due to recrystallization.

The temperature at which maximum of tan δ occurs is referred to as dynamic Tg of the system. In our case we noticed two tan δ peaks, one occurred at low temperature corresponding to the rubbery components present in the matrix while the other peak at high temperatures corresponds to the PLA matrix. The magnitude of the tan δ peak depends essentially on two factors, the relative concentration of the components and the nature of the phase, whether
dispersed or continuous [41]. In low temperature range, the smaller tan δ peak denotes the component with lower T_g to be in the dispersed phase which is true in our case.

Figure 6-13: Effect of different nucleating agents on the (a) storage modulus and (b) tan delta of the PLA biocomposites molded at 110 °C
From the tan δ curve shown in the inset graph in Figure 6-13, it is clear that the damping peak height is significantly reduced and the peak temperature, dynamic $T_g$ has shifted significantly from 71.5 °C for samples molded at 30 °C to 78.1 °C for samples molded at 110 °C. While comparing the tan δ graphs of biocomposites without NA and with different NA, the peak height is almost same for all biocomposites except the one containing Lak at mold temperatures higher than 90 °C. However, the peak temperature values are significantly different. Interestingly, the $T_g$ values from tan δ peak for biocomposites with HPR and Emforce NA were noticed to be less than that of the biocomposites without any NA. This behavior could again be related to the difference in crystallinity content observed for these biocomposites and the resulting restriction in molecular movement which lowered the damping in transition zone. DMA results corroborate well with results obtained from mechanical properties and DSC thus showing the effectiveness of Lak in providing required performance.

6.3.9 Thermogravimetric analysis (TGA)

TGA thermograms of neat PLA, PLA blend, and composites with and without nucleating agents at mold temperature of 110 °C are presented in Figure 6-14. Decomposition temperature of the biocomposites is provided in Table 6-3. Neat PLA showed one step degradation behavior with highest initial thermal stability of all. With the addition of blend components like PEBA and EMAGMA, the degradation temperature at onset and $T_5$ for the PLA blends was considerably reduced while $T50$ increased. With the addition of 10 % miscanthus, the stability further reduced which is expected due to lower stability of the lignocellulosic fibers added to the matrix system. Interestingly, addition of Lak has significantly increased the thermal stability of the biocomposites, predominantly between 320 and 350 °C. When PLA2 (PLA containing Lak
masterbatch) was used, thermal stability was again noted to increase however, not to an extent of adding 1 % Lak during the processing step.

![TGA Thermograms for selected PLA biocomposites molded at 110 °C](image)

**Figure 6-14: TGA Thermograms for selected PLA biocomposites molded at 110 °C**

**Table 6-3: Decomposition temperature of PLA biocomposites**

<table>
<thead>
<tr>
<th>Biocomposite formulation</th>
<th>Decomposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>294.17</td>
</tr>
<tr>
<td>PLA 1 blend</td>
<td>270.56</td>
</tr>
<tr>
<td>PLA 1 blend/MS (90/10) at 30 °C mold T, 30 s cooling</td>
<td>267.15</td>
</tr>
<tr>
<td>PLA 1 blend/MS (90/10) at 110 °C mold T, 60 s cooling</td>
<td>236.13</td>
</tr>
<tr>
<td>PLA 1 blend/MS/Lak (89/10/1) at 30 °C mold T, 30 s cooling</td>
<td>227.10</td>
</tr>
<tr>
<td>PLA 1 blend/MS/Lak (89/10/1) at 110 °C mold T, 60 s cooling</td>
<td>246.08</td>
</tr>
<tr>
<td>PLA 1 blend/MS/HPR (89/10/1) at 110 °C mold T, 60 s cooling</td>
<td>230.00</td>
</tr>
<tr>
<td>PLA 1 blend/MS/Emforce (89/10/1) at 110 °C mold T, 60 s cooling</td>
<td>253.68</td>
</tr>
<tr>
<td>PLA 2 blend/MS (90/10) at 110 °C mold T, 60 s cooling</td>
<td>247.26</td>
</tr>
</tbody>
</table>
It is shown that the degradation temperatures of biocomposites with HPR and Emforce were significantly decreased especially in the case of HPR. This may be due to the reduction in molecular weight of the polymer matrix occurring during the mixing stage. Similar results have been reported by Liu et al. [42] when they studied the effect of inorganic nucleating agents on the properties of PLA. Another important reason for the drastic reduction in thermal stability of biocomposites containing HPR (magnesium oxysulfate) could be due to the characteristic of HPR to release crystalline water at temperatures around 250 °C [43]. Increase in mold temperatures did not show a particular trend in affecting the thermal stability of the composites. In the case of PLA1 blend/MS/Lak (89/10/1) molded at 110 °C, thermal stability close to that of PLA blends were obtained in the $T_{50}$ region.

6.4 Conclusions

PLA biocomposites with higher levels of impact strength and HDT has been successfully developed. Such improvements in the mechanical performance of injection molded PLA biocomposites were accomplished using a super toughened blend system as matrix and by enhancing the crystallinity using nucleating agents and preheated mold during injection molding. Compared to neat PLA, 4 fold increase in impact strength and HDT of 85 °C was observed for PLA biocomposites. Lak-301 was found to be an effective nucleating agent compared to others used in this work. Combined effect of appropriate nucleating agents and optimized process parameters not only increased the crystallization rate and content but also reduced the molding time. Fastest crystallization rate was achieved in the case of biocomposites with 1 % Lak molded at 110 °C. Also, the molded PLA biocomposite samples were able to be ejected without any distortion. Compared to HPR and Emf, Lak was efficient in reducing the free energy barrier for nucleation. DMA results clearly articulated the increase in crystallinity through a gradual step
increase in storage modulus as the mold temperature was varied from 30 °C to 110 °C for PLA1blend/MS/Lak biocomposites. Densely packed spherulitic morphology of the nucleated biocomposites was clearly observed under optical microscopy. Increase in HDT was moderate while PLA2 (PLA 3100 HP containing 1 % Lak, from NatureWorks) was used in the blend matrix, however, our results suggest that based on the property requirements set for the final molded part, Lak-301 could either be added separately during processing to PLA or PLA 3100HP could be used. SEM with EDS was helpful in analyzing the distribution and size of nucleating agents in the composite system. Lak was found to possess larger particle size compared to other nucleating agents.

This study has effectively demonstrated that PLA biocomposites with improved impact and heat resistance, possessing sufficient moldability can provide a solution to overcome the impediments in adapting PLA for a variety of commercial applications. Biocomposites showing higher level of crystallinity, enhanced mechanical and thermal performance are expected to show improvements in durability as well. This is the subject of our current investigation and future publication.
References


(9) Kalita, B. Life cycle assessment of switchgrass (Panicum virgatum L.) biomass production in Ontario, University of Guelph, Guelph, Canada, 2012.


Chapter 7: Reactive Extrusion of PTT-PLA Blends using a Terpolymer

A reactive extrusion route was employed to compatibilize blends of PTT and PLA by the addition of a random terpolymer of ethylene, methyl acrylate, and glycidyl methacrylate (EMAGMA) and multifunctional epoxy chain extender (CE). Mixed level full factorial design was used to investigate the strength properties of the resulting blends. Using analysis of variance (ANOVA), main and interaction effects of EMAGMA, chain extender and screw speed on impact strength and tensile strength of the compatibilized blends were investigated. Multiple linear regression models were developed to predict the strength properties and their adequacy was verified by checking residual plots. Most influencing factor for tensile strength was the terpolymer EMAGMA, while the impact strength was significantly affected by all three factors and one of the interaction effects. Phase morphology indicated a two-phase structure in which PLA phase was dispersed as domains in the continuous PTT matrix. Coalescence behavior was much less prominent in compatibilized blends having EMAGMA. Domain size of the dispersed phase was found to decrease with the increasing concentration of the EMAGMA at higher shear rates. Reduced interparticle distance was believed to be the main mechanism behind impact toughening in the blends. PTT70-PLA30/EMAGMA (85/15) blends with 0.5 phr CE processed at 200 rpm with impact strength of 122 J/m and tensile strength of 44 MPa has been selected as the optimum blend formulation.

5 Version of this chapter is published as ‘Reactive Compatibilization of Poly Trimethylene Terephthalate (PTT) and Polylactic Acid (PLA) Blends: Factorial Design Optimization of Mechanical Properties’ in Materials & Design, 2016, 110, 581-591.
7.1 Introduction

As the technical feasibility and cost effectiveness of adopting bio-route for the synthesis of monomers improves, biobased polymers with completely different performance characteristics are being developed. Use of a renewable 1,3, propane diol (PDO) as one of the monomer building blocks for an engineering plastic, poly trimethylene terephthalate (PTT) is one such advancement. Background details on PTT are provided in literature review, chapter 3, section 3.7.1. Similar to PLA, PTT has low impact strength and heat resistance. Adding PLA in minor phase to PTT may not help in overcoming these drawbacks; however the motivation for investigating such blends is development of a material having high biobased content for durable applications.

PTT and PLA blends in varying blend ratio were investigated to gain fundamental understanding regarding the morphology and resulting properties of the binary blends. These blends were completely immiscible with typical phase separated sea-island morphology. The results are presented in Appendix C. In literature review section, it was identified there is a wide knowledge gap in developing PTT/PLA blends with improved properties by adding a third component such as compatibilizer. Based on several other studies and work explained in the previous chapters, ethylene methyl acrylate glycidyl methacrylate (EMAGMA), a reactive terpolymer with epoxy functional groups could be a good compatibilizer for PTT-PLA blends as well. Hitherto, there are no published studies investigating the effect of EMAGMA as an impact modifier and compatibilizer for PTT/PLA blends. Work detailed in this chapter is the first attempt at successful improvement in PTT/PLA blend properties through reactive compatibilization using EMAGMA. Joncryl ADR 4368, a chain extender containing multiple epoxy groups was added to the blends to facilitate melt stabilization and further
compatibilization in the blend. In opposition to traditional univariate approach, statistical design of experiment has been followed by generating a mixed level full factorial design to investigate the effect of different parameters on mechanical properties and morphology. Conventional univariate approach may take a higher number of experiments to find the optimum conditions; if significant interactions are present between the factors, conclusions from these experiments may be unsound or even misleading. Through factorial design of experiments, multiple controlling parameters can be systematically varied to study their effects on the response variable [1, 2]. A major advantage of the factorial design is the precise estimation of main effects of each factor and their interactions in fewer experiments [1].

7.2. Materials and Methods

7.2.1 Materials

PTT available under the tradename Sorona® 3301 BK 001 was kindly supplied by DuPont (Wilmington, DE, USA). DuPont™ Sorona® contains 35 wt. % renewable resource content derived from corn. Weight average molecular weight ($M_w$) of Sorona is 56,300 g/mol. Ingeo™ PLA 3001D with 1.4% D-lactide content and $M_w$ of 220,000 g/mol was purchased from NatureWorks LLC (Minnetonka, MN, USA). Melting point of PLA is 170°C and PTT is 228°C (from technical data sheet). Lotader AX 8900 (EMAGMA) product of Arkema (Colombes, France) was purchased from Quadra Chemicals, Canada. Joncryl ADR-4368, an epoxy functionalized chain extender (CE) was obtained from BASF (Ludwigshafen, Germany). Prior to processing, 12 hours drying protocol for PTT at 105 °C, PLA at 80 °C and EMAGMA at 60 °C were followed.
7.2.2 Blend preparation

Reactive extrusion of PTT, PLA, and EMAGMA, with and without CE was accomplished in a twin screw co-rotating micro compounder (Xplore®, DSM Research, The Netherlands). A DSM micro injection molder was used to mold test samples. PTT-PLA blend ratio of 70-30 was selected for compatibilization based on preliminary screening of mechanical and thermal properties of PTT-PLA blends at ratios varying in steps of 10 up to 50 wt. % PLA. Reactive extrusion temperature was collectively controlled at 250 °C and screw rpm was varied for different formulations based on the standard order suggested by the factorial design of experiments. Polymer pellets in the calculated blend ratio was fed to the extruder and were melt mixed for 2.5 mins to facilitate reactive compatibilization. In the following steps, melt mixed hot extrudate was collected through a heated piston cylinder assembly connected to the injection molding machine and the test samples were molded at 30 °C. Injection pressure for injection and holding stages was set at 3 and 6 bar, respectively; total injection time was 20 secs. Samples were conditioned for 48 hours at room temperature and 50 % relative humidity prior to any testing.

7.2.3 Testing and characterization

Tensile and Impact Tests: Tensile samples of type IV were tested in Instron 3382 Universal Testing Machine (Norwood, MA, USA) according to ASTM standard D638 at 50 mm/min crosshead speed. Notched Izod impact strength of processed blends was measured using 43-02-01 Monitor Impact Tester from Testing Machines Inc. (New Castle, DE, USA) with 5 ft. lb pendulum according to ASTM standard D256. Average measurement of 6 samples for impact test and 5 samples for tensile test are reported with standard deviations. Fourier transform infrared spectroscopy (FTIR) spectra were collecting using Thermo Scientific Nicolet™ 6700
(Waltham, MA, USA) under an attenuated total reflection infrared mode in the frequency range of 500 cm\(^{-1}\) and 4000 cm\(^{-1}\), averaging 32 scans. Scanning electron microscope (SEM) Phenom ProX (Phenom World BV, Netherlands) equipped with a back scattering electron (BSE) detector was used to observe the blend morphology. Impact fractured and cryogenically fractured surfaces before SEM imaging were gold coated using Cressington sputter coater 108 auto under an argon atmosphere for 15 secs.

7.2.4 Factorial design of experiments

Control of processing parameters and additives amount is the key to obtaining a compatibilized blend with optimum level of properties. It is therefore essential to identify the controlling parameters which predominantly determine performance of the blends produced. In some cases, effect of one parameter on the final properties could be different when other parameters are not varied or set at a different value, giving rise to interaction effects. Conventional univariate approach may take a higher number of experiments to find the optimum conditions; if significant interactions are present between the factors, conclusions from these experiments may be unsound or even misleading. Through factorial design of experiments, multiple controlling parameters can be systematically varied to study their effects on the response variable [17-18]. A major advantage of the factorial design is the precise estimation of main effects of each factor and their interactions in fewer experiments [17]. In this work, mixed level full factorial design was selected. Such a design would take all possible combinations of the varying levels of the factor into account and increase the design resolution without confounding any effects. The following control factors and their adjustment levels have been selected for this design.
(i) Control Factors: EMAGMA (5, 10, 15), CE (0, 0.25, 0.5), Screw rpm (100, 200)
(ii) Response Variables (y): Impact strength (MPa), Tensile Strength (MPa)

Control factors established in this study were selected based on preliminary screening experiments. Processing temperature is usually considered to have an effect on the reactive extrusion of the blends. Preliminary experiments revealed the difficulty in extruding PTT at temperatures below 250 °C because of the die zone being at lower temperature than the set barrel (processing) temperature. Preliminary Taguchi design revealed no significant effect when temperature was varied at the levels of 250, 255 and 260 °C in combination with various levels of screw rpm and additives content. There could be several reasons for this observation. Reaction kinetics may not be sensitive to temperature in the above selected range or the interfacial tension was not changed in this window of 10 °C. Properties were beginning to decline when processed at 270 °C indicating possible thermal degradation of the polymers. Therefore, processing temperature was held constant at 250 °C. Chain extender (CE) was added to the blend system mainly to offer melt stability to the polyesters and the maximum loading was limited to 0.5 phr based on preliminary experiments. Maximum screw speed of 200 rpm was selected once the preliminary experiments indicated a drastic decline in properties of the blends processed at 250 rpm. This could be attributed either to the potential increase in internal barrel temperature due to high shear or the opposing nature of dispersion and coalescence effects, this aspect is discussed further in reference to morphology of the blends. Therefore, a full factorial mixed level design with high design resolution was selected for this study. Minitab® software was used to generate and analyzing the design of experiments. Design array and the process responses (objective functions) are presented in Table 7-1. Experiments were conducted in randomized order as suggested by the run order in the table to prevent any bias and nuisance factors affecting the
processing and testing of blends. Only impact strength and tensile strength were considered as response variable in optimizing the blend formulations.

Table 7-1: Factorial design of experiments with mechanical property results

<table>
<thead>
<tr>
<th>Std Order</th>
<th>Run Order</th>
<th>EMAGMA</th>
<th>CE</th>
<th>Screw Speed</th>
<th>Impact Strength (J/m)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>% Elong. at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>10</td>
<td>0</td>
<td>100</td>
<td>34.3±4.1</td>
<td>50.8±0.3</td>
<td>2.3±0.16</td>
<td>34.9±4.0</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>10</td>
<td>0</td>
<td>200</td>
<td>51.1±1.7</td>
<td>50.4±0.4</td>
<td>2.3±0.08</td>
<td>59.1±5.1</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>0.25</td>
<td>100</td>
<td>40.2±4.1</td>
<td>50.5±1.3</td>
<td>2.4±0.09</td>
<td>41.7±8.6</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>10</td>
<td>0.25</td>
<td>200</td>
<td>69.4±5.7</td>
<td>49.1±0.8</td>
<td>2.1±0.04</td>
<td>61.6±4.5</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>100</td>
<td>50.4±5.3</td>
<td>50.3±0.5</td>
<td>2.3±0.07</td>
<td>38.3±8.2</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>10</td>
<td>0.5</td>
<td>200</td>
<td>69.9±3.0</td>
<td>50.4±0.7</td>
<td>2.3±0.13</td>
<td>48.4±5.7</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>15</td>
<td>0</td>
<td>100</td>
<td>49.8±8.8</td>
<td>43.9±1.4</td>
<td>2.3±0.12</td>
<td>35.8±4.6</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>15</td>
<td>0</td>
<td>200</td>
<td>67.8±7.1</td>
<td>44.9±1.6</td>
<td>2.1±0.37</td>
<td>68.6±3.0</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>15</td>
<td>0.25</td>
<td>100</td>
<td>91.4±9.4</td>
<td>44.9±1.4</td>
<td>2.2±0.07</td>
<td>60.9±1.4</td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td>15</td>
<td>0.25</td>
<td>200</td>
<td>108.2±2.6</td>
<td>43.7±0.3</td>
<td>2.1±0.07</td>
<td>53.5±2.9</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>15</td>
<td>0.5</td>
<td>100</td>
<td>91.4±4.0</td>
<td>46.3±0.3</td>
<td>2.3±0.09</td>
<td>42.7±2.3</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>15</td>
<td>0.5</td>
<td>200</td>
<td>122.9±2.7</td>
<td>44.2±0.7</td>
<td>2.0±0.13</td>
<td>59.3±3.2</td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>20</td>
<td>0</td>
<td>100</td>
<td>57.2±6.3</td>
<td>37.8±0.7</td>
<td>2.0±0.11</td>
<td>42.7±2.3</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>200</td>
<td>150.9±7.1</td>
<td>36.5±0.9</td>
<td>1.7±0.05</td>
<td>68.0±8.0</td>
</tr>
<tr>
<td>15</td>
<td>13</td>
<td>20</td>
<td>0.25</td>
<td>100</td>
<td>130.2±10.6</td>
<td>38.5±0.5</td>
<td>1.8±0.09</td>
<td>41.7±5.5</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>20</td>
<td>0.25</td>
<td>200</td>
<td>169.2±5.2</td>
<td>38.2±1.4</td>
<td>1.8±0.10</td>
<td>49.2±5.5</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>20</td>
<td>0.5</td>
<td>100</td>
<td>120.2±5.9</td>
<td>38.8±0.8</td>
<td>1.9±0.06</td>
<td>40.6±6.1</td>
</tr>
<tr>
<td>18</td>
<td>14</td>
<td>20</td>
<td>0.5</td>
<td>200</td>
<td>205.1±13.6</td>
<td>37.5±0.64</td>
<td>1.8±0.07</td>
<td>45.6±6.3</td>
</tr>
</tbody>
</table>

7.3 Analysis of Variance (anova) for Factorial Design of Experiments

ANOVA can be used to investigate the factors which are hypothesized to influence strength properties. Since there were several factors involved in our experiment, there were also several hypotheses to be tested; three for each of the main factors and one for interaction effect.
Null hypothesis (Ho) for each of the main factor is: there is no significant difference in mean strength when the ‘factor’ level is increased. For the interaction factors, null hypothesis, Ho: there is no interaction between the factors. ANOVA was performed by comparing the variability between groups (mean squares, MS) to the variability within groups (mean square error, MSE). Assumptions of normality and equal variance (homoscedasticity) are the key requirements for ANOVA [1]. If these assumptions hold for the ANOVA model, F-statistic will follow F-distribution with corresponding degree of freedom (DF). Table 7-2 and 7-3 shows the ANOVA for impact and tensile strength. P-values were compared with a $\alpha$ level of 0.05 to determine whether the observed data for each of the factors were statistically significant to reject the null hypothesis. Referring to ANOVA tables, all of the factors had significant effect on the mean impact strength, while only EMAGMA was significant for tensile strength. Interactions of the factors did not seem to affect tensile strength but, EMAGMA and screw speed interaction did have significant effect on the impact strength.

Table 7-2: ANOVA for notched Izod impact strength (J/m)

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of Freedom (DF)</th>
<th>Sum of Squares (SS)</th>
<th>Mean Squares (MS)</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMAGMA</td>
<td>2</td>
<td>21616.5</td>
<td>10808.2</td>
<td>84.32</td>
<td>0.001</td>
</tr>
<tr>
<td>Chain extender (CE)</td>
<td>2</td>
<td>5596.7</td>
<td>2798.3</td>
<td>21.83</td>
<td>0.007</td>
</tr>
<tr>
<td>Screw Speed</td>
<td>1</td>
<td>7171.6</td>
<td>7171.6</td>
<td>55.95</td>
<td>0.002</td>
</tr>
<tr>
<td>EMAGMA*CE</td>
<td>4</td>
<td>1040.6</td>
<td>260.2</td>
<td>2.03</td>
<td>0.255</td>
</tr>
<tr>
<td>EMAGMA*Screw Speed</td>
<td>2</td>
<td>2907.8</td>
<td>1453.9</td>
<td>11.34</td>
<td>0.022</td>
</tr>
<tr>
<td>CE*Screw Speed</td>
<td>2</td>
<td>158.1</td>
<td>79.1</td>
<td>0.62</td>
<td>0.584</td>
</tr>
<tr>
<td>Error</td>
<td>4</td>
<td>512.7</td>
<td>128.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>39004.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table 7-3: ANOVA for tensile strength (MPa)

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of Freedom (DF)</th>
<th>Sum of Squares (SS)</th>
<th>Mean Squares (MS)</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMAGMA</td>
<td>2</td>
<td>456.94</td>
<td>228.47</td>
<td>358.78</td>
<td><strong>0.000</strong></td>
</tr>
<tr>
<td>Chain extender (CE)</td>
<td>2</td>
<td>0.88</td>
<td>0.44</td>
<td>0.70</td>
<td>0.551</td>
</tr>
<tr>
<td>Screw Speed</td>
<td>1</td>
<td>2.84</td>
<td>2.84</td>
<td>4.46</td>
<td>0.102</td>
</tr>
<tr>
<td>EMAGMA*CE</td>
<td>4</td>
<td>2.87</td>
<td>0.71</td>
<td>1.13</td>
<td>0.455</td>
</tr>
<tr>
<td>EMAGMA*Screw Speed</td>
<td>2</td>
<td>0.20</td>
<td>0.10</td>
<td>0.16</td>
<td>0.858</td>
</tr>
<tr>
<td>CE*Screw Speed</td>
<td>2</td>
<td>0.75</td>
<td>0.37</td>
<td>0.59</td>
<td>0.596</td>
</tr>
<tr>
<td>Error</td>
<td>4</td>
<td>2.54</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>467.04</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 7.3.1 Main effects and interactions plot

**Figure 7-1 (a-b)** shows main effect of the selected parameters on the impact and tensile strength of the blends. A main effect is the difference between the mean responses of a factor measured in the levels specified. In other words, it is the change in strength properties when the levels of EMAGMA, CE and screw speed are changed. When the difference between the maximum and minimum values of the average strength corresponding to each factor is higher, the effect of that factor on the resulting properties is higher. As shown in Figure 6-1a, EMAGMA has the most effect followed by screw speed and CE in increasing the impact strength. As established by ANOVA table for tensile strength, only EMAGMA had a significant effect; varying the CE and screw speed had no effect on the average tensile strength of the blends.
Based on the ANOVA results we can see the main effects plot adequately describes the relationship between the factors and the tensile strength of the blends. In the case of impact strength, ANOVA results suggested a strong interaction between EMAGMA content and screw speed; hence the interaction plots for impact strength are examined. Interaction here refers to the effect of one factor being dependent on the level of other factor. Each point in the interaction plot shown in Figure 7-2 depicts the mean impact strength at different combinations of screw speed, EMAGMA and CE content. Interaction is present between the factors when the lines are not parallel, i.e. slope of the lines is different. Interaction plot of EMAGMA*Screw speed indicates that processing of blends at a screw speed of 200 rpm seems to have a higher effect on impact.
strength when the EMAGMA content is 20 wt. % as the slope of the 200 rpm line is steeper beyond 15 % of EMAGMA. There were no interactions seen between CE and screw speed. Slope of the blends containing 0.25 and 0.5 phr CE were different from the ones without CE, however these interactions were shown to be of no significance in ANOVA results.

![Interaction plot for impact strength of the blends](image)

*Figure 7-2: Interaction plot for impact strength of the blends*

### 7.4 Discussion on Compatibilization, Morphology and Mechanical Properties

#### 7.4.1. Axial force curves from reactive extrusion

Using the data acquisition software of the vertical twin screw extruder, axial force exerted on the material to push it downwards towards the die was measured. Recorded force values are plotted against time in *Figure 7-3* for selected formulations. This force value is an indirect measure of the melt viscosity of the blends at different conditions; it can also indicate
degradation or any other reactions occurring in the blends [3]. Increase in viscosity during mixing is an indication of the reactions occurring in the blend. Initial steep increase in force value for 15 secs noticed after the 50 sec mark and steep decrease after 255 sec is due to feeding of the polymers and collection of the extrudate. After showing initial increase in force values, PTT 70-PLA30/EMAGMA (90/10) at 100 rpm plateaued indicating no further reaction and constant viscosity in the system as noticed in the binary blend. As the screw rpm and EMAGMA content was increased, gradual increase in the axial force values were observed. This increase in force is due to the compatibilization reactions occurring at the interface, which are aimed at bringing down the interfacial tension thereby promoting intermixing and increase in viscosity. Further increase in force value was observed when CE was added to the blend containing 20 % EMAGMA. Values did not reach a plateau within the selected range of residence time, indicating further reaction and increase in properties may be possible.

![Axial force vs. time curves for PTT70-PLA30/EMAGMA blends](image-url)

*Figure 7-3: Axial force vs. time curves for PTT70-PLA30/EMAGMA blends*
Advantages of having higher shear rates in the reactive extrusion process is clearly evident from looking at the force curves for PTT70-PLA30/EMAGMA (90/10) blend at 100 and 200 rpm. With increase in screw rpm, induction time for compatibilization reactions was reduced and the viscosity was increased. The residence time was however held constant at 2.5 mins to minimize the overall cycle time of the process. Complex flow field in co-rotating twin screw extruder may offers better mixing in lesser time. Higher shear stress resulting from higher screw speed may increase internal temperature and result in degradation of shear sensitive components. Although PLA is shear sensitive, force curves suggest no potential degradation.

### 7.4.2 Compatibilization reactions and FTIR spectra

Reactive extrusion allows for the generation of in situ copolymer at the interfaces directly during melt blending. As shown through axial force curves previously, reaction between carboxyl, hydroxyl end groups of PTT/PLA and epoxide group of EMAGMA and CE proceeds within the time scale of melt processing. Well established reaction scheme [4-9] is shown in Figure 7-4.

![Reaction scheme](image)

*Figure 7-4: Reaction of PTT/PLA end groups with epoxy functional group of EMAGMA*
Efficiency of these reactions was assessed by FTIR spectroscopy. Figure 6-5a compares the PTT70-PLA30/EMAGMA blend processed at different conditions. EMAGMA can be characterized by epoxide ring vibration at 911 cm\(^{-1}\); C-O stretching vibrations at 1105 cm\(^{-1}\) and 1192 cm\(^{-1}\); -C=O stretching vibration at 1734 cm\(^{-1}\); -C-H vibrations at 2851 cm\(^{-1}\) and 2921 cm\(^{-1}\) [7]. In blends, the 1746 cm\(^{-1}\) bands are assigned to ester -C=O carbonyl stretching. PTT shows characteristic peaks at 1504 and 1408 cm\(^{-1}\) assigned to the C-C stretching modes, while the peak at 723 cm\(^{-1}\) is due to C–C rocking vibrations [10]. PLA shows -C-C- stretching at 867 cm\(^{-1}\) and 955 cm\(^{-1}\). Peaks at around 1087 cm\(^{-1}\), 1127 cm\(^{-1}\) and 1180 cm\(^{-1}\) are for -C-O-stretching of the polyesters [11]. Characteristic peak for epoxy in oxirane ring (911 cm\(^{-1}\)) were not found in the compatibilized blend as shown in Figure 7-5b, this can be assumed to be due to complete consumption of epoxy groups during the reactive extrusion process. Similar observations have been reported by various other researchers to confirm the compatibilization of blends using reactive terpolymers [8]. C-O-C stretching bonds pointing to the compatibilization reactions are overlapped with the characteristic peaks of the polyesters, however, changes in peak intensities were noticed. A small shift and broadening in the peaks related to the symmetric stretching of the C-O-C bonds was observed in the compatibilized blend as shown in Figure 6-5b. Quantitative determination of the epoxide conversion by IR spectroscopy is challenging. It is therefore safe to conclude based on the axial force values that the reaction was not complete within the selected processing time range for certain compositions and the residual epoxy groups present in the blends is hard to detect through FTIR.
Figure 7-5: FTIR Spectra for PTT70-PLA30/EMAGMA blends (a) full range- stacked   (b) zoomed region between 1200 and 850 cm⁻¹
7.4.3 Morphology of the blends

Morphology has a strong influence on the mechanical, physical and rheological properties of polymer blends [12]. Ratio of the blending components, interfacial tension between them, viscosity ratio and the shear force involved in the processing operations are some of the major factors deciding the blend morphology [12,13]. Figure 7-6 shows the morphology of impact fractured PTT70-PLA30 blend, with clear indication of phase separation.

![Figure 7-6: PTT70-PLA30 blend at 5000x and 8000x magnification](image)

Two or more particles of PLA were merging together exhibiting coalescence. Such sea-island morphology is typical for immiscible blends. Cryogenic fracture surface of PTT70-PLA30/EMAGMA (85/15) and (80/20) blends processed at 100 and 200 rpm are show in Figures 7-7 and 7-8. Figure 7-7c and 7-8c displays the morphology of these blends with 0.5 phr CE at 200 rpm.
Figure 7-7: Cryo fractured surface morphology of PTT70-PLA30/EMAGMA (85/15) blends at (a) 100 rpm, (b) 200 rpm and (c) 0.5 phr CE, 200 rpm

Figure 7-8: Cryo fractured surface morphology of PTT70-PLA30/EMAGMA (80/20) blends at (a) 100 rpm, (b) 200 rpm and (c) 0.5 phr CE, 200 rpm
Electron beam was found to etch away the PLA particles in spite of having a layer of gold coating; this is rather helpful in drawing meaningful conclusions. Reduction in PLA particle size was obvious in PTT70-PLA30/EMAGMA (85/15) blend when the screw speed was increased from 100 to 200 rpm. After the addition of CE, PLA particle size is clearly observed to reduce further. As the amount of EMAGMA increased to 20 wt. % in the blends, coalescence of the PLA particles were predominant. Reduction in particle size of the PLA is believed to be caused by a combination of two different phenomena [14]: (i) suppression of PLA particle coalescence and (ii) reduction in interfacial tension between PTT and PLA. Cigana et al. [15] have showed when the dispersed phase concentration is between 20 to 30 %, the decrease in particle size with the addition of compatibilizer is mainly due to reduction in coalescence. Increase in mixing shear rate is also accepted to promote finer blend morphology through droplet breakup, and this supports morphological observations in the ternary blends processed at low and high screw speed.

At higher concentration of compatibilizer, reduction in particle size levels-off and the equilibrium concentration at which it occurs is referred to as critical concentration [13]. In our case, at 15 % EMAGMA might have already reached the critical concentration, which could be why further reduction in particle size was not observed in PTT70-PLA30/EMAGMA (80/20) blends processed at 100 rpm, instead coalescence was noticed. Above the critical concentration, compatibilizer much like a surfactant may not modify the interface very much but form micelles or smaller droplets [9] in the bulk phase. Although thermodynamically EMAGMA should prefer to be in the interphase, the shear forces may not be enough to breakup these droplets [14] resulting in coalescence as noticed in Figure 6-8a. Such observations have also been reported to occur when the number of collisions between dispersed particles resulting in coalescence is
higher than the droplet breakage [16]. With increase in screw speed, breakup of droplets is promoted to suppress coalescence and results in reduction in PLA particle size for PTT70-PLA30/EMAGMA (80/20) blend processed at 200 rpm. With the addition of CE at higher screw speed further reduction in particle size was observed which could be attributed to interfacial tension effects as epoxy group of CE reacts with PTT and PLA. Enthalpy of mixing and interfacial free energy is reduced as the reaction product of epoxy with carboxyl/hydroxyl functional groups anchors itself at the interface [13].

7.4.4 Impact and tensile properties

Impact and tensile properties of the neat polymers and uncompatibilized PTT70-PLA30 blend are given in Table 7-4 for comparison against data in Table 7-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>% Elongation at break</th>
<th>Impact Strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PTT</td>
<td>60.9 ±1.17</td>
<td>2.80 ±0.027</td>
<td>57.93 ±10.02</td>
<td>21.70 ±3.84</td>
</tr>
<tr>
<td>Neat PLA</td>
<td>78.1 ±2.07</td>
<td>3.70 ±0.03</td>
<td>4.91 ±0.86</td>
<td>31.57 ±2.32</td>
</tr>
<tr>
<td>PTT70-PLA30</td>
<td>67.1 ±1.55</td>
<td>3.15 ±0.095</td>
<td>3.15 ±0.35</td>
<td>20.60 ±3.28</td>
</tr>
</tbody>
</table>

Interfacial adhesion and morphological parameters have interrelated effects on the impact strength. Uniform dispersion of the minor phase in the matrix can be promoted by increasing the interfacial adhesion. When interfacial adhesion is same between the samples, difference in morphological parameters greatly influence the impact strength [17]. Surface-to-surface interparticle distance or matrix ligament $\tau$, proposed by Wu [18] combines the effect of particle size, distribution and volume fraction of the dispersed particles in a single parameter. For
toughening to occur, $\tau$ must be smaller than the critical value, $\tau_c$. By satisfying this criterion, shear yielding is promoted in the matrix which results in effective toughening. Sample showing higher value of interparticle distance is likely to be brittle where yielding cannot propagate [18]. Linking our SEM observations to impact strength results, spatial distribution of particles has a consequential influence on the impact strength of the PTT70-PLA30/EMAGMA blends. Decrease in particle size and uniform distribution reduced the interparticle distance thereby increasing the impact strength through matrix yielding. Average of 20-30 J/m increase in impact strength values are observed in blends with or without chain extender when the screw speed is changed from 100 to 200 rpm. Exception to this trend is blends with 20% terpolymer, at 0 and 0.5 phr chain extender. Between these two formulations, although the final impact value is higher for blends with chain extender, the magnitude of increase is higher for 80/20 blends without chain extender. One possible reason for this could be the change in blend viscosity with the incorporation of the chain extender and how it affects the coalescence and interfacial tension between the blending polymers. High screw speed and high chain extender content is effective in suppressing coalescence thereby reducing the dispersed particle size of 80/20 blends as explained in morphology section.

Tensile strain at fracture, usually called the elongation is a conventional measure of ductility. Although no direct relationship exists between the ductility and performance in service, it serves as a good indicator of changes in formulations or processing conditions. Comparing the percentage elongation of neat polymers, uncompatibilized and compatibilized blends from table 6-1 and 6-4, we can say the ductility of the PTT70-PLA30 blend is substantially increased with the addition of EMAGMA. This could be attributed partly to the process of compatibilization and partly to the mere presence of a third component with higher intrinsic ductility. In the
absence of chain extender, percentage elongation was observed to almost double when the screw speed was increased from 100 to 200 rpm. However, with the addition of chain extender such incremental trend was not observed in blends processed at low and high screw speed. This could be attributed to the increased density of crosslinked chains in the matrix resulting from the chain extension effect.

On the other hand, increase in EMAGMA content causes the blends to yield at lower applied stress. Few possible explanations for such reduction in tensile strength with higher amount of compatibilizer could be put forward. (i) Presence of discontinuities in the phase separated blends merely reduces the cross-section of the matrix available for external load transmission. (ii) After crossing a critical compatibilizer concentration, only part of the EMAGMA enters the interface, the rest forms small droplets [19], which could coexist with relatively larger PLA particles. With strong interfacial adhesion to transmit stress between these three components, a monotonic dependence in tensile strength characterizing the individual blend components is observed [20]. Similar trends in tensile strength of rubber modified polymers have been reported previously in the literature [21]. Modulus is also seen to decrease linearly with increase in softer EMAGMA. Immaterial of compatibilization, interfacial adhesion present in the blends are sufficient to transmit the stress at small strain under which the modulus is generally measured. Hence modulus is always a monotonic function of the composition of the blends [20].

7.5 Model Fitting

ANOVA table and factorial plots have assisted in determining which of the factors are important in affecting the strength properties; the next step is to model the effect of these significant factors. Method of least squares is typically used for estimating parameters and model
fitting. In general, the response variable, y, can be related to predictor variables by a first order multiple linear regression model,

$$ y = \beta_0 + \beta_1(A_i) + \beta_2(B_i) + \beta_3(C_i) + ... \beta_i(A_i^2B_i)... + \beta_i(A_i^3C_i)... + \beta_i(B_i^2C_i)... + \epsilon_i $$

The deviations, $\epsilon_i$, are assumed to follow a normal distribution with mean zero and standard deviation $s$. For regression model in our case, y represents mean strength; $\beta_i$ refer to the regression coefficients. $A_i$, $B_i$, and $C_i$ represents the factors terpolymer, chain extender and screw speed respectively. Three different levels of the factors A and B, two different levels of factor C are represented by the subscript $i$. Only second order interaction terms are included in the model; third order interaction terms are not included on the assumption they are negligible and they are used to get an estimate of the random variation in response variable, strength. Based on the significant factors affecting each of the strength properties, models developed are expressed in Table 7-5.

**Table 7-5: Regression model summary for response variables**

<table>
<thead>
<tr>
<th>Response</th>
<th>Regression Equation</th>
<th>$R^2$ (%)</th>
<th>$R^2_{adj}$ (%)</th>
<th>$R^2_{pred}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact strength (J/m)</td>
<td>IS = 92.79 - 40.22 $A_1$ - 4.14 $A_2$ + 44.36 $A_3$ - 24.23 $B_1$ + 7.00 $B_2$ + 17.22 $B_3$ - 19.96 $C_1$ + 19.96 $C_2$ + 9.04 $A_1C_1$ - 9.04 $A_1C_2$ + 8.93 $A_2C_1$ - 8.93 $A_2C_2$ - 17.97 $A_3C_1$ + 17.97 $A_3C_2$</td>
<td>95.61</td>
<td>92.54</td>
<td>85.78</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>TS = 44.281 + 5.978 $A_1$ + 0.369 $A_2$ - 6.347 $A_3$</td>
<td>97.84</td>
<td>97.55</td>
<td>96.89</td>
</tr>
</tbody>
</table>

In the above models the contrast coefficients for each level of the factor are normalized to make their sum zero. While predicting for one level of a factor other levels for the factor are taken as zero.
7.5.1 Goodness of model fit

$R^2$ is a goodness-of-fit statistic determining how well the model fits the data. $R^2$ denotes the percentage variation in the response variable explained by the developed model, it is always between 0 and 100 %. Calculated values shown for $R^2$ in Table 7-5 are closer to 100 % which explains almost all the variability in strength around its mean in the developed models. $R^2_{adj}$ is adjusted for the number of predictors in the model. $R^2_{pred}$ indicates how well the developed regression model predicts the strength properties for new observations [22]. $R^2_{pred}$ values in Table 7-4 indicate the models can predict valid responses for new observations very well. $R^2_{pred}$ for impact strength is lower than the $R^2$; reason for this could be due to higher number of terms in the model. Residual plots in Figure 7-9 to 7-11 have been used to show the goodness of model fit by checking the normality and equal variance assumptions.

Satisfying the assumptions is necessary to produce unbiased estimates of the coefficients. Residuals refer to the difference between the experimental values and fitted or predicted values. Normal probability plot of residuals for tensile and impact strength of blends shown in Figure 6-9a and 6-9b falls on the straight line indicating the residuals are normally distributed. Residuals versus fitted values plot for tensile and impact strength of blends in Figure 6-10a and 6-10b shows random pattern of residuals as expected, ensuring the linear model adequacy.
Figure 7-9: Normal probability plot of the residuals for (a) impact strength and (b) tensile strength
Figure 7-10: Residuals against fitted values for (a) impact strength and (b) tensile strength

Standardized residuals were used as they are better indicators of outliers due to their constant variance as in this case the value of a residual is divided by an estimate of its standard deviation. Standardized residuals greater than 2 and less than -2 are usually considered outliers. Spread of residual values in the plots fall within this range and on both sides of 0 indicating no outliers in the data collected for strength values at different factor levels. Residual versus order of data plot shown in Figure 7-11a and 7-11b depicts all residuals in the data collection order.
This plot is useful to ascertain the residuals are uncorrelated, no time or space related effects were noticed. Residuals were exhibiting normal random noise and were equally distributed with both positive and negative values around the horizontal line (residual is 0).

**Figure 7-11: Residuals against observed order for (a) impact strength and (b) tensile strength**
7.5.2 Contour plots and response optimization

Contour plots are used to graphically explore the three-dimensional relationship between variables in two dimensions. In the contour plots shown in Figure 7-12, EMAGMA and screw speed are plotted on the x- and y-scales and the strength values are represented by contours while holding the CE value at 0.5 phr. Analysis in the previous section revealed EMAGMA content to be the only significant factor to affect the tensile strength of the blends, accordingly a proportional decrease in strength can be seen as the EMAGMA content increases. Contours in Figure 7-12a clearly show the possibility of achieving impact strength over 160 J/m at screw speed higher than 150 rpm and EMAGMA content higher than 18%. Both the contour plots are overlaid in Figure 7-12c, the white region is where balanced tensile and impact strength can be achieved. The lower and upper bounds of the optimal values are shown in the legend. Depending on the requirements for a target application appropriate formulations can be selected to achieve desired performance.

Response Optimization tool from Minitab software was used to find the global optimum points for each combination of EMAGMA, chain extender, and screw speed. Value of 1 was selected to give equal emphasis to the target values of impact strength and tensile strength. Response optimizer works by searching for predictor variable combinations optimizing both the responses by satisfying the requirements set for each of them. Individual desirability (d) for impact and tensile strength are obtained first which are then combined to maximize the composite desirability (D) to provide optimum points of predictor variables. Goal for both impact and tensile strength was set to maximize but a compromise of one variable is required due to the inverse relationship in these properties with increasing content of EMAGMA.
Figure 7-12 (a-c): Individual and overlaid contour plots of strength properties assessing the combined effect of EMAGMA and screw speed.
Optimization of the responses is shown in Figure 7-13, the red solid line points to the optimum level; blue dotted line is the maximum average response for impact and tensile strength.

![Figure 7-13: Response optimization for individual predictor variables](image)

Optimum levels predicted for content of additives and screw speed to yield highest impact and tensile strength are 15 wt. % EMAGMA, 0.5 phr CE and 200 rpm for screw speed at a composite desirability of 0.5571.

### 7.6 Conclusion

Parameters influencing the reactive compatibilization of PTT70-PLA30/EMAGMA blend and the resulting strength properties are modelled using a mixed level full factorial design. This method allowed for the detection of statistically significant variation in mean impact and tensile
strength upon varying the EMAGMA, CE content and screw speed. Most influencing factor for tensile strength is EMAGMA, while the impact strength is significantly affected by all three factors and one of the interaction effects. Based on the requirement to strike a balance between the stiffness and toughness of the blends, PTT70-PLA30/EMAGMA (85/15) blends with 0.5 phr CE processed at 200 rpm has been selected as the optimum formulation. The phase morphology of PTT70-PLA30/EMAGMA blends was investigated as a function of screw rpm and compatibilizer concentration. Morphology indicated a two-phase structure in which PLA phase was dispersed as domains in the continuous PTT matrix. The coalescence behavior was much less prominent in compatibilized blends having EMAGMA. The compatibilizing action of EMAGMA was associated with the reaction between the glycidyl epoxy group of EMAGMA with hydroxyl and carboxyl group of PTT and PLA leading to the formation of a graft copolymer at the blend interface. The domain size of the dispersed phase was found to decrease with the increasing concentration of the EMAGMA at higher shear rates. Reduced interparticle distance was believed to be the main mechanism behind impact toughening in the blends. Appropriate selection of additives and processing parameters in this work has resulted in blends with good balance of properties compared to previous works on PTT-PLA blends.

**References**


(2) Coelho, A. M.; Estrela, V. V.; de Assis, J. T.; de Carvalho, G. In Methodology for Optimization of Polymer Blends Composition; Sanguansat, P., Ed.; Principal Component Analysis – Engineering Applications; InTech: Croatia, 2012; pp 41.


Chapter 8: Size-Fractionated Biocarbon Composites

This chapter investigated the effect of adding 10 wt. % size-fractionated biocarbon to a biobased blend of PTT and PLA. Particle size classification for biocarbon was done based on sieve analysis and particle size distribution was measured based on image analysis within each of the selected ranges. Biocarbon particle size and shape was found to profoundly change the properties of the composites. Depending on the particle size of the biocarbon used, microstructure of the polymer blend matrix changed. Composites having biocarbon particle size range of 20-75 µm resulted in a morphology showing better dispersion of the blend components. Furthermore, addition of epoxy based multifunctional chain extender was found to result in much finer morphologies having very small size dispersed polymer particles. Impact strength was found to increase significantly in composites which possessed such morphologies favoring high energy dissipation mechanisms. Maximum impact strength of 85 J/m was achieved in certain composite formulations, which is impressive considering the inherent brittleness of PTT and PLA. By increasing the injection mold temperature, fast crystallization of PTT was achieved which increased the heat deflection temperature to 80 °C. From rheological observations, incorporation of biocarbon increased viscosity, but the shear-thinning behavior of the matrix was preserved. Anomalous reduction in impact strength of composites containing biocarbon less than 20 µm are explained based on morphology-rheology correlations.

Version of this chapter is submitted for publications as ‘Biocomposites with size-fractionated biocarbon: Influence of microstructure on macroscopic properties’ in ACS Omega, August 2016.
8.1 Introduction

Aim of the current work was to investigate the effect of size-fractionated biocarbon on the resulting macroscopic properties of the composites, which would enable selection of biocarbon with appropriate sizes for target applications. PTT-PLA blend moderately toughened with ethylene methyl acrylate glycidyl methacrylate (EMAGMA) was selected as the matrix material. Composition of the matrix was PTT-PLA/EMAGMA (85-15). Ratio of PTT/PLA was 70/30 wt.% and amount of biocarbon was kept constant at 10 wt.%. By adding biocarbon to the above matrix, cost effective composite formulations can be developed if favorable properties are obtained. As both PTT and PLA have low impact and heat resistance, goal of this work was to develop a formulation that will show improvement in the above mentioned properties, relative to the neat polymers. Because of the general tendency of fillers to reduce the impact strength at higher filler content, preliminary investigation reported here was conducted by adding only 10 wt.% biocarbon. Effect of different size-fractionated biocarbon obtained through mechanical sieving was investigated by studying the microstructure, mechanical, thermal and rheological properties. Effect of adding chain extender and increasing the mold temperature was also investigated. Final properties of the composites are critically dependent on the size and shape of the particles themselves. Therefore, particle size distributions through image analysis for different size-fractionated biocarbon particle were also performed.

8.2 Materials and Methods

8.2.1 Materials

PTT available under the tradename Sorona® 3301 BK 001 was kindly supplied by DuPont (Wilmington, DE, USA). This grade of Sorona® contains 35 wt. % of renewable
resource content derived from corn. NatureWorks Ingeo™ PLA 3001D with 1.5 % D-lactide content was supplied by NatureWorks LLC (Minnetonka, MN, USA). Lotader AX 8900 (EMAGMA) product of Arkema (Colombes, France) was purchased from Quadra Chemicals, Canada. Epoxy functionalized chain extender (CE) used in this work was Joncryl ADR-4368, product of BASF (Ludwigshafen, Germany). Miscanthus based biocarbon (BC) hammer milled to below 1/64 in. was received from Competitive Green Technologies, Leamington, ON, Canada. This biocarbon was produced through a low temperature pyrolysis process, as the functionalities are noticed to be still present in the Fourier transform infrared (FTIR) spectra shown in Figure 8-1. Bands between 1200 and 1000 cm\(^{-1}\) are due to the stretching of C-O-C and C-O bonds from cellulose, indicating the biocarbon maintains characteristic spectral features of cellulose. Broad OH stretching bands also appear at 3500-2700 cm\(^{-1}\). Peaks in the region 1100 - 1600 cm\(^{-1}\) are for aromatic skeletal vibrations and aromatic CH deformations are around 750-880 cm\(^{-1}\).

![FTIR spectra for 'as received' biocarbon](image)

**Figure 8-1: FTIR spectra for ‘as received’ biocarbon**
Prior to processing, 12 hours drying protocol for PTT at 105 °C, PLA at 80 °C and EMAGMA at 60 °C were followed. Moisture content of the polymers before processing was measured to be 0.045 ± 0.007 %. Moisture content of biocarbon stored in the oven at 105 °C was measured to be 1.6 ± 0.15 %.

8.2.2 Size-fractionation of biocarbon

Size-fractionation of biocarbon was performed using a nest of WS Tyler test sieves having opening of 300, 212, 150, 125, 75, and 20 µm. The coarse and fine sieves were assembled on a Ro-tap® sieve shaker (WS Tyler, OH, USA) and agitated for 10 min. Schematic sieve setup is shown in Figure 8-2 along with the particle size range selected for this study.

![Schematic of sieve setup on a Ro-Tap sieve shaker](image)

Figure 8-2: Schematic of sieve setup on a Ro-Tap sieve shaker

Oscillating and tapping action of Ro-tap throws the particles in the air so the particles find the openings. After the sieving was complete, mass retained over different sieves was collected, weighed and analyzed. Percent mass retained on each sieve was calculated from three replications of sieving. In order to obtain substantial amount of biocarbon below 20 µm, ‘as
received’, hammer milled biocarbon was further subjected to ball milling for 3 hours at 300 rpm. Planetary ball mill (Retsch GmbH, Haan, Germany) was used for size reduction. Stainless steel grinding jar was charged with 40 gm of biocarbon and the milling media contained of 64 small zirconium oxide balls of diameter 10 mm and 1 stainless steel ball of diameter 40 mm. Once clamped, the grinding jar rotates about its own axis and in the opposite direction around the common axis of the sun wheel. Combination of impact and frictional forces resulting from grinding ball movements results in high degree of size reduction. Milled biocarbon was then sieved with Retsch air jet sieving machine, AS 200 to obtain biocarbon primarily below 20 µm. High performance industrial vacuum cleaner setup generates vacuum inside the sieving machine. As a result, the suction pulls the ambient air through the slotted nozzle and collects the material. Sieving time and speed was set to 1 min and 30 rpm respectively.

8.2.3 Processing of biocomposites

Biocomposites were fabricated in a micro-compounder (DSM Xplore®, Netherlands) by adding all the blend components and size-fractionated biocarbon of required composition in a one step process. The length and L/D of the screws are of 150 mm and 18 mm, respectively. The barrel volume of the machine is 15 cm3. Extrusion was performed at 250 °C barrel temperature and 200 rpm screw speed. After a total residence time of 2 min, a preheated cylinder was used to transfer the molten blend to a DSM micro 12 cc injection molding machine. Injection pressure for injection and holding stages was set at 4 and 8 bar, respectively; total injection time was 18 sec. Samples were molded at 30 °C mold temperature. For selected biocomposites, samples were also molded at 60 and 90 °C. Injection time was increased to 60 sec to facilitate cooling and easy sample removal without distortion when high mold temperature was used. Effect of chain
extender and mold temperature was investigated only in composites with 20-75 µm BC and less than 20 µm BC for concise presentation of the experimental results. Mold temperatures, 30, 60 and 90 °C was adopted for 20-75 µm BC composites. Based on the initial assessment of mechanical properties and heat resistance of these composites, only 30 and 90 °C was selected to be investigated for less than 20 µm BC composites. To show the effect of chain extender (CE) in combination with mold temperature, CE was added to 20-75 µm BC composites molded at 30 and 90 °C. For comparison, properties of less than 20 µm BC composites containing CE molded at only 90 °C is provided.

8.2.4 Testing and characterization

Morphology of individual biocarbon particles and fractured surface was observed by scanning electron microscopy (SEM), Phenom ProX (Phenom World BV, Netherlands) equipped with a back scattering electron (BSE). Cressington sputter coater 108 was used to gold coat the composite samples for 15 s under an argon atmosphere. Selected composites were etched in chloroform for 30 min at 50 °C to remove the PLA and EMAGMA phase. ImageJ, a public domain image processing and analysis program developed by the National Institute of Health (NIH), USA was used to measure the particle size of biocarbon. Around 300 particles were measured in longest (length) and shortest (width) dimensions for biocarbon obtained from sieve opening above 75 µm. For 20-75 µm BC and less than 20 µm BC, around 1000 particles were measured for longest dimension.

Mechanical properties were measured after the test specimens were conditioned in standard laboratory atmosphere for 40h at 23 °C and 50% relative humidity (ASTM D 618-08, Procedure A). Instron Instrument Model 3382 was used to study the tensile and flexural
properties of the biocomposites. ASTM standard D638 with type IV sample was followed for
tensile test. Flexural test was done following the ASTM D790 procedure B. The tensile
properties of biocomposites were tested at 5 mm/min. The flexural specimens were tested at a
crosshead speed of 14 mm/min. Notched Izod impact strength was measured with the help of
Testing Machine Inc. (TMI) instrument according to ASTM D256. At least six notched samples
were measured for impact strength and five samples for tensile and flexural properties. Average
values with standard deviations are reported.

Rheological characterization was conducted using an Anton Paar MCR302 rheometer
(Anton Paar GmbH, Graz, Austria) using a parallel plate configuration. The plate diameter used
was of 25 mm, with a measurement gap distance set at 1 mm. Shear rate was varied between
0.01 and 1000/s. The test was conducted at 250 °C under nitrogen purge.

Differential scanning calorimetry (DSC) was performed by heating the samples to 240 °C
with heating rate of 10 °C/min, followed by a 3 min isothermal step to erase the thermal history
and then cooled to -50 °C with a cooling rate of 5 °C/min. Same temperature profile used for first
heating scan was followed for second heating scan as well. Glass transition temperature (T_g),
cold crystallization temperature (T_cc), crystallization temperature (T_c), melting temperature (T_m)
were determined from the DSC graphs. Percentage crystallinity (χ_c) was calculated using the
using the equation,

\[ \chi_c = \frac{\Delta H_m - \Delta H_{cc}}{f \Delta H_m^0} \times 100 \% \]  

(8.1)

Where, \( \Delta H_m \) is the enthalpy of melting, \( \Delta H_{cc} \) is enthalpy of cold crystallization, \( \Delta H_m^0 \) is the
enthalpy of melting of 100 % pure PTT, 145.5 J/g. f is the weight fraction of PLA in the blend.
Dynamic mechanical analysis (DMA) was conducted on a DMA Q800 from TA Instruments using a dual-cantilever clamp in frequency sweep/temperature ramp mode at the frequency of 1 Hz and oscillating amplitude of 15 μm. The samples (dimensions 12.7 × 63.5 × 3.2 mm) were heated from -50 to 120 °C at a heating rate of 3 °C/min. Heat deflection temperature (HDT) was also measured in DMA Q 800 with a three-point bending clamp in DMA controlled force mode at a stress of 0.455 MPa and ramp rate of 2 °C/min. Deflection was evaluated at 0.1889 % strain.

8.3 Results and Discussion

8.3.1 Particle size analysis and shape classification

Common method of particle size distribution (PSD) analysis is done by mechanical sieving of the particulate materials using sieves having standard size. It is the method adopted by the American Society of Agricultural and Biological Engineers (ASABE) for analyzing the particle size of forage materials in chopped form [1]. Other methods reported in use are laser diffraction, acoustic spectroscopy, and light scattering. However, these techniques are expensive and most often assume spherical geometry while analyzing irregular particles. SEM is another widely used technique for measuring the particle size and is listed on the methods suggested by the ASTM standard issued for characterization of particles [2]. Because of the differences in particle sizes obtained from different techniques, the results are usually viewed as quantitative comparisons to establish the significance of a process or method used to obtain the particles. PSD from sieve shaker provides the percentage of particles retained on different sized sieves as shown in Figure 8-3.
A maximum weight percentage distribution was achieved in the range of 20-75 µm. Hammer mill is known to breakdown the biomass or in this case biocarbon, due to the action of shear and friction [3]. Milling screen size, motor speed and material feeding method are mentioned to be key variables determining the resulting particle size and particle size distribution [3]. As we can see from Figure 8-3, this kind of distribution provides a broad range of particle size based on the selected sieve. Therefore, particle sizes in longest and shortest dimension within each of these ranges were measured from SEM images. In addition to providing relatively precise particle size distribution, SEM can also provide useful information regarding the shape of the particles. Representative SEM images used for the analysis are shown in Figure 8-4 and the particle size distribution is presented in Figures 8-5 and 8-6. Size-fractionated biocarbon are differentiated based on the sieve openings.
Figure 8-4: SEM images of biocarbon sieved to different particle size range
Using standardized nomenclature is encouraged for describing the particulate materials and they are provided in ASTM F1877–05, appendix x2 [2]. Shape of the biocarbon in the first four particle size ranges, above 75µm resembles the structure of chopped miscanthus fibers from which the biocarbon was pyrolyzed. Based on the above standard, they could be classified under ‘sharps or shards- rectangular fibers’. Particles of biocarbon in the 20-75 µm range have sharp edges and can be called as ‘sharps or shards-cuttlefish’. Shape of the particles less than 20 µm can be described to be a mixture of ‘granular, irregular – smooth and angulated’.

Figure 8-5: Particle size distribution along the longest and shortest dimension for size-fractionated biocarbon
Broad particle size distribution can be observed for particle length (longest dimension) compared to particle width (shortest dimension) distribution histograms shown in Figure 8-5. This can be explained based on the characteristics of mechanical sieving. In general, the sieving process is described as width-based separation process, where the particles having width higher than the sieve opening size cannot pass through in any given orientation [4]. However, when the sieves are under tapping motion, longer particles can ‘fall-through’ or ‘nose-dive’ into smaller sieve openings [4]. This tipping action results in larger inconsistencies in length based separation processes, which is reflected as broad distribution when particle length is measured. Particles having dimensions much higher than the maximum sieve opening can be observed from Figure 8-5. However, as the sieve opening size reduces the distribution becomes narrower. Although majority of the particle width is within the sieve opening range, presence of smaller particles cannot be avoided as they tend to agglomerate and cling to one another during sieving.

Figure 8-6: Particle size distribution along the longest dimension for 20-75 µm and less than 20 µm
Only length based particle size distribution is provided for the 20-75 µm and less than 20 µm sieve in Figure 8-6, due to the difficulty in measuring the width for the particles laying edge-wise showing thickness, the third dimension. Also, as the particle size reduces, length and width for granular shaped particles coincides. Majority of the biocarbon belonging to the 20-75 µm sieve range has particle length of less than 75 µm. The size-fractionation process through mechanical sieving resulted in lesser amounts of biocarbon below 20 µm (Figure 8-3), therefore to obtain substantial amount of biocarbon in this range to fabricate composites, ‘as received’ biocarbon was subjected to ball milling process (conditions described in methods section). The milled biocarbon was sieved to below 20 µm without fractionation in an air jet sieve. Majority of the particles were under 2 µm indicating ball milling process has resulted in greater size reduction. This also explains the shape of these particles being quite different from other biocarbon of higher sieve opening ranges. Such differences in shapes and sizes of the biocarbon are expected to have significant effect on the matrix, resulting in different morphologies and macroscopic properties.

8.3.2 Morphology

Impact fractured surface morphology of composites containing different size-fractionated biocarbon are shown in Figure 8-7 and 8-8, the arrows point to biocarbon particles. Biocarbon particles are randomly oriented in planes parallel to the surface and are visibly well distributed over the entire section of the matrix for composites shown in Figure 8-7. Morphology of the matrix in composites with biocarbon above 125 µm do not show any phase separated blend components, PLA and EMAGMA. With reduction in BC particle size to less than 125 µm, roughly spherical domains of dispersed PLA-EMAGMA are noticed, where the blend retains its
sea-island morphology. This morphology is predominant in composites with 75-125 and 20-75 µm range and can be viewed from the higher magnification section.

**Figure 8-7: Morphology of composites with different size-fractionated biocarbon**

For composites with less than 20 µm BC, the morphology changes again from sea-island structure to a morphology with elongated bands of coalesced PLA-EMAGMA as shown in **Figure 8-8**. In order to clearly present the change in composite microstructure, the fractured surfaces were etched in chloroform at 50°C for 30 min. Chloroform etched both PLA and EMAGMA phase leaving the PTT phase intact. In **Figure 8-8**, etched images of these composites are presented in lower magnification to show the distinct difference.
Figure 8-8: Morphology of composites with (a) 20-75 µm BC; (b) <20 µm BC; (c) 20-75 µm BC after etching; (d) <20 µm BC after etching; (e) 20-75 µm BC and 0.5phr CE (f) <20 µm BC and 0.5phr CE
Flow-induced microstructure changes continuously due to a complex interplay between break-up and coalescence. In composites with less than 20 µm biocarbon, the bands are made of coalesced PLA and EMAGMA particles. This difference in morphology could be attributed to change in (i) viscosity, (ii) biocarbon particle shape with milling, or (iii) free energy of mixing which alters the interaction and interfacial tension between the blend components. These results demonstrate morphology of the composites is contingent not only on the particle size and distribution, but also on particle shape and how the matrix viscosity is affected.

Effect of chain extender was assessed only in composites with 20-75 µm BC and less than 20 µm BC for simple comparison. On addition of CE to these composites, the morphology changed again; dispersed domain sizes were further reduced to very small size, most likely due to the change in viscosity and interfacial tension between the dispersed blend components. The epoxy based chain extender has been effective in breaking apart the PLA phase to very small particles in both the composite formulations. Addition of CE was able to promote droplet breakup and overcome the effect of coalescence observed in less than 20 µm biocarbon composites. Fine dispersion of the particles in the matrix helps in increasing the toughness as the interparticle distance or ligament thickness is reduced, facilitating yielding of the matrix. Because the matrix used is a ternary blend system, it is important to control the blend inclusion size to achieve desired morphologies which will decide the majority of macroscopic properties. Effect of colloid particles on stabilizing the morphology of emulsions has been an intense field of investigation for more than a century. Immiscible polymer blends are like highly viscous emulsions. Addition of nano fillers has been found to suppress the coarsening process and stabilize cocontinuous structure of the blends through accumulation at the interface. Based on this strategy, many nano fillers including carbon black has been used to stabilize the
cocontinuous morphology [5, 6]. Lipatov et al. [7] proposed that filler can stabilize the blend morphology by adsorbing either of the blending polymers on their surface. In order for this interfacial stabilization to occur, the inorganic fillers should have highest surface area and be dispersed very well in the blend. Based on our morphological observations, biocarbon with less than 20 µm is expected to have high surface area compared to other particle size range, which could help in suppressing the breakup of polymer particles. However, addition of chain extender overpowers this suppression effect and facilitates very fine dispersion of PLA-EMAGMA particles in the matrix.

8.3.3 Mechanical properties and HDT

Incorporation of particulate fillers can modify the mechanical properties of polymers in many ways depending on the particle size, loading, particle-matrix interfacial adhesion and the microstructure of the composites [8]. Maximum strength a micro-particulate composite can sustain under uniaxial tensile loading mainly depends on the effective stress transfer between the matrix and filler particles. In composites with poor bonding or wetting, debonding occurs at the interphase and the particles are unable to carry the load. As a result, tensile strength of the composites reduces when fillers are added to the polymer matrix. Biocarbon composites studied in this work did not show drastic improvement in tensile strength as the particle size range reduced; results are shown in Figure 8-9. However, a slightly increasing trend is observed but with the values still being lower than the matrix strength. With the addition of CE, and high molding temperature (90 °C), tensile strength of the composite is close to that of the blend processed at 30 °C. In addition to the chain extension effect, joncryl has been reported to reduce interfacial tension between the blending components thus reducing the size of the dispersed phase, in this case PLA and EMAGMA.
Figure 8-9: (a) Tensile and (b) flexural properties of size-fractionated biocarbon composites showing the effect of varying size range, mold temperature and CE.
From morphological examinations discussed in previous section reduction in dispersed phase size was found to be true for these blends. PLA with reduced phase size in PTT blend can now act as efficient hard filler particles having relatively stronger adhesion with the matrix compared to the biocarbon particles thereby increasing the stress transfer.

Flexural strength is a material’s ability to resist deformation under a combination of compressive and tensile stresses. Hence, values reported for flexural strength are usually higher than tensile strength. From Figure 8-9b it can be seen flexural strength remains almost the same for biocomposites until the particle size range reaches 75-125 µm. Beyond this range slight increase is observed for composites with 20-75 µm BC. For composites containing less than 20 µm BC, flexural strength was observed to decrease. This anomalous observation can be explained with reference to the morphology of the composites containing less than 20 µm biocarbon. The cocontinuous bands of PLA-EMAGMA probably resulted in more flexibility thus reducing the composites’ overall ability to resist deformation. Prominent increase in flexural strength is observed when the mold temperature is increased from 30 °C to 60 °C and then to 90 °C. This could be related to the increase in crystallinity of PTT which enhances secondary bonding through closely packed molecular chains [9].

Addition of 10 wt. % biocarbon has increased the elastic and flexural modulus of the composites. However, the modulus was seen to be not affected by the difference in particle size range of biocarbon. It is not surprising as several studies in literature have reported similar observations [10, 11]. However, there are some theoretical predictions and experimental evidences which report increase in modulus when the particle size is roughly below 30 nm [12, 13]. Based on these observations, there seems to be a critical particle size beyond which there is no effect on composite modulus. As seen previously, the particle size of biocarbon is well above
the 30 nm range proposed, hence the modulus of biocomposites fabricated in this study are insensitive to the difference in the range of particle size examined. When the mold temperature was increased to enhance the crystallization rate of PTT, flexural modulus values increased indicating the increase in stiffness of the composites. When CE was added to composites containing 20-75 and less than 20 µm BC, initial reduction in modulus, especially flexural was observed. When the mold temperature was increased to 90 °C, similar to previous observation in composites without CE, the flexural modulus slightly increased.

For composites, impact strength is a complex correlation due to the presence of fillers their orientation and distribution, the filler-matrix adhesion and the resulting morphology. In order to have high impact strength or toughness, large volume of the material should be able to absorb the energy dissipated. Values of impact strength observed are usually correlated to the energy dissipation mechanism preferred by the fracturing surface. Crack initiation and propagation are important in determining the impact strength of the composites. Same mechanism of pull out and debonding which increases the impact strength of composites tends to have a negative effect on breaking strength. This is sometimes the reason for the inverse relationship between breaking strength and impact strength. Figure 8-10 shows the initial reduction in notched Izod impact strength indicating the decreased ease of crack propagation in the presence of larger biocarbon particle. Impact fractured surface morphology revealed a change in morphology as the size of the biocarbon particles reduced. As the blend components were dispersed in the matrix, impact strength increased, showing values closer to the level of the matrix. Impact strength of 70 J/m was achieved in the case of composites with 75-125 and 20-75 µm BC. Corroborating with morphological observations, impact strength of composites with less than 20 µm biocarbon dropped to 40 J/m. This again can be attributed to the inability of the
coalesced structure to dissipate much energy or the absence of resistance to crack propagation and crack pinning effect.

Figure 8-10: Impact strength and HDT for biocarbon composites

With the addition of CE to composites containing 20-75 µm and less than 20 µm biocarbon, impact strength increased to 85 J/m. This again could be related to the very fine dispersed polymer particle morphology observed in the presence of CE which favored a high energy dissipating mechanism. When a suitable interparticle distance between the dispersed polymers is reached, the matrix can yield easily thus improving impact strength. Another possible toughening mechanism is crack pinning. The finely dispersed and well bonded PLA particles can facilitate crack pinning mechanism by impeding crack propagation. The crack tends
to bow out between particles and forms secondary cracks which consume extra energy. This toughening mechanism has been noted in epoxy filled with rigid glass spheres [14].

As crystallization of PTT is promoted by increasing the mold temperature, impact strength of the composites containing 20-75 µm BC remained the same. However, in the presence of CE, samples molded at 90 °C showed reduction in impact strength. Increase in crystallinity sometimes negatively affects the impact strength when the crystallites act as stress concentrators. It causes the stress acting on a small volume of the material to grow much higher than the average stress applied to the entire sample [15]. It is possible this behavior is prominent only in the presence of CE due to the dispersion of PLA-EMAGMA in very small and fine particles. In addition to the crystalline structure, the crystalline superstructure which includes the spherulite size, crystalline form, and percentage crystallinity also influences the mechanical properties of semicrystalline polymers [16].

**Figure 8-10** also shows the heat deflection temperature for the matrix and composites with different size-fractionated biocarbon. Incorporation of fillers is known to increase the HDT of semicrystalline polymers depending on the type of polymer and its crystallization rate, type and amount of filler loading. It also depends on processing conditions like mold temperature which affect mechanical behavior and presence of nucleating agents enhancing crystallization. HDT is closely related to the flexural modulus of the filled composite [11]. Addition of different size-fractionated biocarbon has increased the HDT of the composites by at most 4 to 7 °C. This temperature is still very low for any engineering polymer based material to be stated as upper value of dimensional stability. Therefore, effect of mold temperature in increasing the crystallization and HDT was investigated. Gradual increase in flexural modulus noticed while increasing the mold temperature from 30 to 90 °C corresponds with the observed increment in
HDT. Highest average HDT of 80 °C was obtained for composites with 20-75 µm and less than 20 µm molded at 90 °C. Improvement in HDT values at higher mold temperature are attributed to the enhanced stiffness and percentage of PTT crystallization.

8.3.4 Rheology

Incorporation of solid particulates can critically alter the flow characteristics, influencing melt processing and properties of the final composites [17]. Key factors changing the rheological behavior of composites are: filler size, shape, concentration, and the interactions between filler particles [18]. In general, for a composite system, viscosity increases with filler concentrations and reduction in filler particle size. Fillers with smaller particle size facilitate the formation of filler network or structural skeleton within the polymer matrix, resulting in a very sharp rise in viscosity at a low shear rate. Defining yield stress behavior has been reported for nanoparticles forming such network structures [19]. Yield stress is not observed in polymers filled with larger particles because hydrodynamic interaction dominates the response to shear deformation rather than particle–particle interaction [19]. As the material is subjected to higher shear rate, the filler network structure is destroyed and the effect of filler on viscosity becomes minimal [20].

To elucidate the molecular origins of viscosity changes, rheological response of biocarbon filled composites in linear and non-linear region was studied. Figure 8-11 shows the dependence of viscosity, \( \eta \), on log shear rate, \( \dot{\gamma} \). PTT blend matrix exhibits zero shear viscosity plateau indicating Newtonian behavior at low shear rate and power law behavior at higher shear rate. Upon the addition of size-fractionated biocarbon (up to 75 µm), viscosity of the composites in the limit of Newtonian region was observed to increase. Highest viscosity was achieved at 20-75 µm range, implying there is tighter packing between particles potentially resisting relative motion. Surprisingly, with further reduction in particle size, viscosity of the composites dropped
below the matrix viscosity. It is important to mention, this reduction in viscosity was reproducible and may not be attributed to the matrix degradation.

![Shear rate vs. viscosity for size-fractionated biocarbon composites](image)

**Figure 8-11 Shear rate vs. viscosity for size-fractionated biocarbon composites**

Such conspicuous reduction in viscosity has been reported previously for polymer composites with nanoparticles [19]. Dilution of the polymer chain entanglement density, selective adsorption of high molecular weight polymer chains on the surface of the particles, increased excluded free volume induced around the particles, slip between the sample and geometry during rheological testing, and the degradation of the matrix are some of the reasons attributed to this behavior [19]. Extended set of experimental results is required to decide which of these factors are responsible for the observed reduction in viscosity of the <20 µm BC composites.
At higher shear rates, the chains can disentangle, orient or stretch themselves parallel to the direction of driving force. Therefore, in non-linear region the sample is deformed to a point where in the molecular structure is destroyed and shear thinning takes place with drastic drop in viscosity. In summary, incorporation of biocarbon affects the viscosity based on the particle size and shape at low shear rates but the basic shear thinning behavior of the polymer matrix is not affected. The observed increase or decrease in viscosity of the composites at low shear rates depends on the polymer inclusion phase present in the matrix and how they are affected based on the particle size range of biocarbon.

### 8.3.5 Differential scanning calorimetry (DSC)

The non-isothermal crystallization behavior of PTT blend and biocomposites was studied using DSC to investigate the effect of size-fractionation, mold temperature and chain extender. **Table 8-1** shows the values obtained for glass transition temperature \((T_g)\), melting temperature \((T_m)\) and enthalpy \((H_m)\), cold crystallization temperature \((T_{cc})\) and corresponding enthalpy \((H_{cc})\) from 1st heating cycle, crystallization temperature \((T_c)\) from cooling cycle. \(T_g\) of PTT and PLA in biocomposites have increased slightly with addition of biocarbon, CE and change in mold temperature compared to the \(T_g\) of these components in the blend. Addition of size-fractionated biocarbon, CE and increase in mold temperature has slowed down the local dynamics of polymer chain, hence the increase in \(T_g\) of PTT and PLA in composites. Average melting temperature for PTT and PLA remained the same throughout the entire range of formulations tested.
Table 8-1: Differential Scanning Calorimetry Data

<table>
<thead>
<tr>
<th>Composite Formulations</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$H_c$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>% Crys</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PTT</td>
<td>PLA</td>
<td>PTT</td>
<td>PLA</td>
<td>PTT</td>
<td>PLA</td>
<td>PTT</td>
</tr>
<tr>
<td>PTT blend, 30°C Mold</td>
<td>43.42</td>
<td>55.8</td>
<td>226.5</td>
<td>164.8</td>
<td>33.0</td>
<td>7.4</td>
<td>68.1</td>
</tr>
<tr>
<td><strong>Effect of size-fractionation at mold temperature of 30 °C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC 212-300 µm</td>
<td>48.1</td>
<td>56.5</td>
<td>227.0</td>
<td>163.1</td>
<td>36.0</td>
<td>8.0</td>
<td>69.5</td>
</tr>
<tr>
<td>BC 150-212 µm</td>
<td>46.7</td>
<td>57.3</td>
<td>228.7</td>
<td>164.5</td>
<td>32.2</td>
<td>5.0</td>
<td>70.1</td>
</tr>
<tr>
<td>BC 125 - 150 µm</td>
<td>47.0</td>
<td>57.0</td>
<td>228.2</td>
<td>164.7</td>
<td>32.1</td>
<td>8.0</td>
<td>69.8</td>
</tr>
<tr>
<td>BC 75-125 µm</td>
<td>50.5</td>
<td>58.6</td>
<td>226.7</td>
<td>166.0</td>
<td>30.1</td>
<td>7.5</td>
<td>67.7</td>
</tr>
<tr>
<td>BC 20-75 µm</td>
<td>45.3</td>
<td>57.8</td>
<td>228.9</td>
<td>166.3</td>
<td>30.1</td>
<td>7.6</td>
<td>69.3</td>
</tr>
<tr>
<td>BC &lt;20 µm</td>
<td>49.2</td>
<td>59.6</td>
<td>228.1</td>
<td>165.6</td>
<td>28.0</td>
<td>7.0</td>
<td>69.1</td>
</tr>
<tr>
<td><strong>Effect of mold temperature</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC 20-75 µm, 60 °C</td>
<td>46.0</td>
<td>60.6</td>
<td>228.1</td>
<td>165.7</td>
<td>31.7</td>
<td>7.2</td>
<td>67.5</td>
</tr>
<tr>
<td>BC 20-75 µm, 90 °C</td>
<td>46.5</td>
<td>60.2</td>
<td>227.2</td>
<td>165.5</td>
<td>31.0</td>
<td>6.9</td>
<td>--</td>
</tr>
<tr>
<td>BC &lt;20 µm, 90 °C</td>
<td>46.6</td>
<td>59.8</td>
<td>226.9</td>
<td>165.0</td>
<td>28.8</td>
<td>7.6</td>
<td>--</td>
</tr>
<tr>
<td><strong>Effect of CE and mold temperature</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC 20-75 µm, 0.5 phr CE 30 °C Mold</td>
<td>45.6</td>
<td>60.5</td>
<td>227.5</td>
<td>164.7</td>
<td>29.7</td>
<td>5.8</td>
<td>69.1</td>
</tr>
<tr>
<td>BC 20-75 µm, 0.5 phr CE 90 °C Mold</td>
<td>46.6</td>
<td>60.7</td>
<td>227.0</td>
<td>164.9</td>
<td>27.2</td>
<td>4.7</td>
<td>--</td>
</tr>
<tr>
<td>BC &lt;20 µm, 0.5 phr CE 90 °C Mold</td>
<td>46.1</td>
<td>60.1</td>
<td>227.6</td>
<td>163.7</td>
<td>28.0</td>
<td>6.0</td>
<td>--</td>
</tr>
</tbody>
</table>
Although $T_{cc}$ of PTT and PLA remained the same, an interesting trend was observed in the enthalpy values ($H_{cc}$). As the particle size range of biocarbon decreased, $H_{cc}$ of PTT increased and PLA decreased. Larger fraction of PTT chains were not able to crystallize during the molding process as the biocarbon particle size and the inclusion phase size decreased. However, $T_{cc}$ of PTT disappeared with increase in mold temperature indicating faster and complete crystallization of PTT achieved during high temperature molding. PLA exhibited its characteristic cold crystallization at around 100 °C. Increase in this temperature to ~110 °C indicated slower crystallization rate in the presence of chain extender. Increase in mold temperature did not seem to have any effect on $T_{cc}$ of PLA. Previously we discovered the $T_{cc}$ of PLA to disappear only at mold temperature of 120 °C (Chapter 5).

As expected, PLA phase did not exhibit melt crystallization upon cooling due to its very slow crystallization rate. $T_c$ of PTT in certain composite formulations was increased to higher temperature, compared to the value observed for the blend. Percentage crystallinity calculated for composites with different size-fractionated biocarbon is seen to decrease with decrease in the particle size range. This is expected as the cold crystallization enthalpy increased. Increase in mold temperature for composites with 20-75 µm and <20 µm BC increased the crystallinity by 20 % and this was directly reflected in HDT values. Although composites with BC >150 µm had similar high values of crystallinity, the HDT were observed to be low. As the mold temperature increased, it is possible that higher fraction of amorphous chains were arranged closer to the crystalline fraction. Consequently, this arrangement hinders free movement of the entire long chain, resists heat induced distortions, resulting in enhanced HDT.
8.3.6 Dynamic mechanical analysis (DMA)

Storage modulus, G’ and damping factor, tan δ with temperature for different size-fractionated biocarbon is shown in Figure 8-12 (a-b). Overlaid storage modulus and tan δ graphs for 20-75 um biocarbon in the presence of CE and at different mold temperature are shown in Figure 8-13. First obvious observation is the increase in storage modulus of the composites compared to the blend matrix due to the addition of biocarbon. All of the composites showed similar values of storage modulus. Drop in storage modulus in subzero temperature is characterized by the transition of EMAGMA phase in the blends and composites. At the plateau region above 0 °C and below T_g, rapid short range diffusion motions dependent on the chain entanglement take place. Drastic drop in storage modulus occurs when the material passes through the T_g of PTT and PLA, showing α transition relaxation peak.

*Figure 8-12: (a) Storage modulus and (b) Tan delta graphs for PTT biocomposites with size-fractionated biocarbon*
Beyond 90 °C, transition assigned to polymer chain rearrangement in the crystalline domain and across the amorphous-crystal interphase occurs. This temperature coincides well with cold crystallization temperature observed for PLA from DSC. 20-75 µm biocarbon composites containing CE showed reduced storage modulus, with values less than that of the matrix. As the mold temperature was increased from 30 to 90 °C, gradual step increase in storage modulus was observed corroborating with other test results. The vertical magnitude of the tan δ peak gives the information regarding the damping behavior of the biocarbon on the motion of polymer chains. Reduction in tan δ peak indicates restricted molecular movement due to polymer-particle interactions. In our case, the peak height was only slightly varied between different size-fractionated biocarbon and at <20 µm, the tan δ peak magnitude was higher than the matrix. This particular composite seems to have experienced higher viscoelastic energy
dissipation. Composites with 20-75 µm BC at higher mold temperature showed greater degree of damping compared to the ones molded at 30 °C.

8.4 Conclusion

In this work, biocomposites were made from PTT blend and size fractionated biocarbon using melt extrusion and injection molding. Ethylene methyl acrylate glycidyl methacrylate (EMAGMA) was added as a toughening agent for the blends. Composition of the blends and composites were kept constant. 10 wt. % biocarbon was added to PTT 70/PLA 30 - EMAGMA blend (85-15). Biocarbon between size ranges of 212-300 µm, 150-212 µm, 125-150 µm, 75-125 µm, 20-75 µm and < 20 µm were fractionated by sieving using Tyler sieves having corresponding sieve opening size. Inconsistencies in length based particle size distributions are explained based on the sieving action promoting a fall-through effect. Biocarbon milled to particle size < 20 µm was observe to take a different particle shape and was classified under granular irregular particles having smooth and angulated surface. Fractured surface morphology of the composite revealed good dispersion of the biocarbon at higher particle size ranges. Depending on the particle size of the biocarbon used, microstructure of the polymer blend matrix changed. Blend retains its primary sea-island morphology with roughly spherical domains of PLA-EMAGMA dispersed phase in composites with 75-125 and 20-75 µm biocarbon. At larger particle size range, biocarbon offered hindrance to the dispersion of the blend components during processing. The change in morphology of composites with < 20 µm biocarbon was attributed to the good dispersion of the particles that could stabilized the blend morphology showing coalesced PLA-EMAGMA particles. Addition of chain extender was effective in suppressing the coalescence and dispersed the PLA-EMAGMA particles in much smaller and finer morphologies. This morphology was favorable in achieving higher impact strength by a
combination of yielding and crack pinning mechanism. In an attempt to improve the crystallinity of PTT, the mold temperature was increased. This promoted faster PTT crystallization consequently increasing the HDT to around 80 °C in some of the formulations when the mold temperature was 90 °C. The stiffening effect achieved with increasing mold temperature was further supported by the increase in flexural modulus. Viscosity of different polymers measured from rheological tests supported the morphology and mechanical properties observed for the biocomposites. As the morphology generated during processing has significant effect on the resulting properties, this study presents a way to control the morphology of the composites by selecting biocarbon having appropriate size and shape. In addition to achieving desired properties, cost reduction involved in using biocarbon can also contribute to the success of these composites in finding high performance applications.

References


Chapter 9: Sustainability and Preliminary Cost Analysis

Discussion in this chapter is focused on the general sustainability and supply chain management aspects of the biomaterials. Market development scenario is discussed. Preliminary cost analysis based on raw material and a fixed compounding cost was conducted. Estimated costs provided in this chapter for the developed formulations are helpful for qualitative comparisons against the cost of neat resin.
9.1 Sustainability of Biopolymers and Renewable Fillers

Sustainability combines environmental, societal, and economic considerations in product development. Sustainability of a biomaterial depends on a variety of key factors, including source material, production process, and material management after end of useful life. Sustainable biomaterials collaborative (SBC) formed to spur biomaterial development lists several other key principles and goals to achieve true sustainability [1]. While there are still unsettled concerns over the GHG emissions, overall energy use and implications of crop production, biopolymer production is an immature technology with significant opportunities for improvement. Concerns regarding recycling and disposal of products made out of biopolymers also needs to be addressed to maximize the benefits without impeding their commercial viability. Sorting technologies like near-infrared and low-cost alternatives like black light illumination are being explored for unique identification of biopolymers in recycling waste streams [2].

PLA uses less than 1/25th of 1 % (0.04 %) of the annual global corn production; therefore there is no immediate impact on food prices or supply [2]. To be more precise, 2.5 lbs. of corn is required to produce one pound of PLA, as per NatureWorks process [2]. Currently dextrose from corn is used as the major raw material, however, in the future other sugar sources such as cellulosic raw materials, agricultural wastes and non-food plants are expected to be used [2]. Carbon footprint of PLA is reported to be 75 % lower than traditional PS or PET [2,3]. On the other hand, production of PTT consumes around 30-40 % less energy and results in 56-63 % lower GHG emissions compared to petroleum based polymers like nylon 66 and nylon 6 [4]. PTT can be 37 wt. % biobased and can potentially be recycled in PET waste stream. Production of biobased propylene diol (PDO), the renewable monomer for PTT is said to consume up to 40 % less energy and 40 % reduction in GHG emissions compared to petroleum based PDO [5].
Advantages of using natural fiber began to spread in early 1990s. However, at the time, quantitative results demonstrating their potential were significantly lacking. United Nations Conference on Trade and Development together with International Jute Organization started addressing the positive environmental attributes of different bast fibers in 1996 [6]. Later, Dam and Bos [7] investigated the environmental impact of natural fibers in industrial applications and reported “natural fiber production requires less than 10% of the energy originally consumed for the production of PP fibers (around 90GJ/tonne)”. In another review, production of china reed fibers were reported to show around 15% lower energy consumption when compared to the production of glass fibers [8]. The inherent advantages of natural fibers and their characteristics like biodegradability and low carbon footprint add to the sustainability of the production, distribution, consumption and disposal. However, ecological sustainability needs to be addressed in an unambiguous manner through independent studies involving entire life cycle of the biobased product. Life cycle analysis (LCA) can be used to effectively quantify the environmental impacts of bioproducts starting from raw material to processing and to final product disposal [9]. In this regard, composites containing natural fibers have a distinct advantage in relation to energy consumption, toxicity, emission of effluent, ease of disposal options, etc. [9].

9.2 Supply Chain Management

Reliable and continuous availability of natural fibers/biomass is extremely important for any successful commercial development of composite materials. Performance of the supply chain largely depends on the degree of integration and coordination between individual entities. Farmers producing biomass for composite applications want to see solid markets and grantees; while on the other hand, industries want to have a guarantee of sustainable biomass supply.
Therefore, it is imperative to strike a balance between the needs of farmers and industries. Intermittent high volumes of agricultural residues available over a period for use in composite applications could affect the year round production of biocomposite materials. There is essential need to control the fluctuating supply throughout the year; therefore one important aspect in biomass supply chain is the logistics. Several studies [10-12] have used mathematical models to assess the complete energy cost involved in the use of biomass along the entire supply chain (development, establishment, production, harvest, storage and transport to facilities manufacturing the end use products). On the basis of these studies numerous cost reduction strategies have been proposed. Reduction in logistics cost could have a major impact on the regional and domestic competitive positioning. Therefore, the presence of industrial biocomposite manufacturing facility in the vicinity of farm lands and agricultural production areas can have great economic advantages. This has been one of the main reasons for the development of small and localized bio-refineries demonstrating the concept of regional sustainable manufacturing [13]. This ensures biomass is locally sourced, as close as possible, to avoid high transportation costs and to keep feedstock cost to a minimum while increasing sustainability of the manufacturing process [13]. Another strategy that can effectively address the fiber supply concerns is the hybridization of two or more different fiber that can ease the demand on just one fiber type.

9.3 Market Development

Production capacity of biopolymers is growing at an impressive rate, and is expected to triple from 5.7 million tonnes in 2014 to nearly 17 million tonnes by 2020 [14]. Compound annual growth rate (CAGR) for biopolymers is 20% but CAGR of traditional polymers is only 3–4% [14]. Production capacities and CAGR for PLA and PTT are listed in Table 9-1.
Table 9-1: Production capacities and growth rate of PLA and PTT [14]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Biobased content</th>
<th>No. of producing companies in 2014 and until 2020</th>
<th>No. of locations in 2014 and until 2020</th>
<th>Production capacities (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>100 %</td>
<td>27</td>
<td>33</td>
<td>180,000</td>
</tr>
<tr>
<td>PTT</td>
<td>35 %</td>
<td>2</td>
<td>3</td>
<td>90,000</td>
</tr>
</tbody>
</table>

NatureWorks LLC is the largest producer of PLA with their Blair, Nebraska manufacturing facility having production capacity of 300 million pounds (140,000 metric tons). Shell and DuPont are the major producers of PTT under the trade name Corterra and Sorona, respectively.

In addition to being renewable resource based and reducing dependence on fossil fuels, several other factors contribute toward enhancing the market developments and opportunities for bioproducts. Legislative provisions are backing up the production/manufacturing processes, and use of specific consumer goods developed with intentions to reduce the environmental damage. Norway is considering evaluating tax incentives for biobased polymers and imposing new taxes on petroleum-based CO₂ content in polymers with an aim to increase market demand for biobased products [15]. Such an initiative proposed by Norway is first of its kind, and is expected to be followed by other countries of the world [15]. There are more international platforms available now for discussing the market issues and current status of bioproducts. Example of few such organizations includes Food and Agriculture Organization of the United Nations (FAO), European Bioplastics, Biotechnology Industry Organization (BIO), Cluster Industrielle Biotechnologie (CLIB) 2021, etc. Aside from the above mentioned factors, an
important player determining the future prospects of biocomposites are the research institutions and centers located around the world. They are dedicated to finding most promising areas of commercial applicability, thereby elevating the status of biobased materials to a new pedestal while considering the balance between performance, economics and sustainability.

### 9.4 Preliminary Cost Analysis

Cost of the polymers, additives and fillers are listed in Table 9-2. These costs were obtained through email conversations with technical sales representatives of respective companies. Cost for PLA, PTT and Hytrel were obtained based on truck load pricing (~20,000 kg). Cost for other additives were list prices provided by the company. Some of the distributors wave the freight charges based on the quantity of materials ordered; therefore the price listed in Table 9-2 does not include freight charges.

#### Table 9-2: Cost of polymers, additives and fillers

<table>
<thead>
<tr>
<th>Polymer/Additive</th>
<th>Company</th>
<th>Cost (US $/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA 3001D</td>
<td>NatureWorks LLC.</td>
<td>1.32</td>
</tr>
<tr>
<td>PTT Sorona 3001 BK 001</td>
<td>DuPont</td>
<td>3.36</td>
</tr>
<tr>
<td>Hytrel RS 40F3 NC010</td>
<td>DuPont</td>
<td>5.68</td>
</tr>
<tr>
<td>EMAGMA, Lotader AX8900</td>
<td>Arkema</td>
<td>4.67</td>
</tr>
<tr>
<td>Lak-301</td>
<td>Takemoto Oil &amp; Fat Co., Ltd.</td>
<td>19</td>
</tr>
<tr>
<td>Joncryl ADR 4368 (CE)</td>
<td>BASF</td>
<td>11.75</td>
</tr>
<tr>
<td>Miscanthus (chopped)</td>
<td>Competitive Green Technologies</td>
<td>0.09 (CAD 240/ton)</td>
</tr>
<tr>
<td>Biocarbon (hammer milled)</td>
<td>Competitive Green Technologies</td>
<td>0.46 (CAD 0.6/lb)</td>
</tr>
</tbody>
</table>

Cost of miscanthus available in bales is around CAD 110 per ton. Cost quoted in the table is for miscanthus fibers in chopped form, ready for composite applications. Biocarbon cost given in Table 8-2 is based on the raw material miscanthus (chopped form) and also includes the cost
of hammer milling. The cost of biocarbon is expected to vary significantly based on the raw material used for its production. For example, if the biocarbon is produced from coffee chaff, a co-product, which currently does not have any market value, biocarbon cost will include only the cost associated with the production process (pyrolysis and hammer milling) and hence will be cheaper.

Preliminary cost estimated for selected polymer blends and composites developed in this work are shown in Table 9-3.

Table 9-3: Cost estimate for selected polymer blends and composites

<table>
<thead>
<tr>
<th>Selected Formulations</th>
<th>Cost in US $/lb (Material and compounding)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/HYT/EMAGMA (70/10/20) - ‘PLA blend’</td>
<td>2.57</td>
</tr>
<tr>
<td>PLA blend/Miscanthus/Lak (89/10/1)</td>
<td>2.50</td>
</tr>
<tr>
<td>PLA blend/Miscanthus/Lak (84/15/1)</td>
<td>2.38</td>
</tr>
<tr>
<td>PTT70-PLA30/EMAGMA (85/15) - ‘PTT blend’</td>
<td>3.18</td>
</tr>
<tr>
<td>PTT70-PLA30/EMAGMA/CE (85/15/0.5phr)</td>
<td>3.24</td>
</tr>
<tr>
<td>PTT blend/Biocarbon/CE (90/10)</td>
<td>2.92</td>
</tr>
<tr>
<td>PTT blend/Biocarbon/CE (90/10/0.5phr)</td>
<td>2.97</td>
</tr>
</tbody>
</table>

As most of the polymers and additives cost was provided in USD, the estimated cost of the formulations are also expressed in USD to avoid distortions due to exchange rates. This cost analysis was performed solely based on raw material cost and by assuming a fixed compounding cost of USD 15 cents per pound. This number was arrived based on personal conversation with CEO of Competitive Green Technologies, who suggested CAD 20-25 cents to be a good estimate for compounding. As an example, cost calculation for ‘PLA blend’ is shown below.

\[(0.7\times1.32) + (0.1\times5.68) + (0.2\times4.67) + (0.15) = 2.57\]
Owing to the low price of PLA, any modifications done by adding additives like impact modifier and nucleating agents adds to the cost of the resulting formulations. As can be seen from Table 8-3, higher percentage of natural fiber incorporation is advantageous in bringing down the overall cost of the composites. In the case of PTT blends and composites, cost of the developed formulations is lower than the cost of the neat PTT as it is priced higher. Choice of additives, fillers and optimization of the fabrication process has helped in attaining the cost vs. performance balance. Figure 9-1 shows the balance between cost and biobased content of the developed materials.

![Figure 9-1: Cost vs. biobased content of developed materials (a) PLA as major phase (b) PLA as minor phase](image)

Although the starting material, neat PTT was only 35 % biobased, the composite formulations can be up to 51 % biobased. In the case of PLA composites, maximum biobased content of 76 % can be achieved depending on the percentage of natural fibers incorporated in the matrix.
References


Chapter 10: Conclusions and Outlook

10.1 Conclusion

Evolution of bioplastics industry has changed directions dramatically since the early 90s. The latest generation is moving towards ‘durable’ (non-biodegradable) bioplastics having high biobased content; it is the current trend. Main objective is to replace ‘fossil carbon’ with ‘renewable carbon’, a holistic strategy to mitigate climate change by minimizing the environmental impact of a product throughout its life cycle. Durable bioplastics are desired for multi-use long term application in automotive, electronics and other industries. One necessary requirement for them is to be both tough and strong yet the two attributes are often mutually exclusive. Does this mean a biobased and biodegradable polymer such as PLA with its high strength but low toughness cannot be adopted for durable applications? – Well, not exactly, this is where the concept of controlling the properties of PLA to achieve stiffness-toughness balance along with acceptable heat resistance comes into play. This thesis was set out to explore the possibilities of developing PLA based blends and biocomposites having optimum balance of properties for durable applications. Hypothesis outlined in Chapter 1 were tested, inference based on empirical findings are summarized for all the chapters.

Part 1, Chapter 4: PLA binary and ternary blends

PLA binary blends

Synopsis: Blend of PLA with Hytrel (HYT), a thermoplastic copolyester elastomer with poly (butylene terephthalate), hard segment and poly (tetramethylene ether) glycol soft segment at varying weight ratios was investigated.
**Hypothesis:** Blending PLA with a tough polymer such as HYT will result in blends having high impact toughness.

**Inference:** Brittle-ductile transition occurred at HYT content greater than 20 wt. %, impact strength of 230 J/m was achieved with 30 wt. % HYT and with further increase in amount of HYT, non-break impact behavior was observed. Desired toughness improvements were achieved at higher HYT content, however the tensile strength was observed to decrease with increase in rubber content.

**PLA ternary blends**

**Synopsis:** Functionalized terpolymers, EMAGMA, EBAGMA, EMAMaH and EBAMaH were selected as the reactive compatibilize for PLA-HYT blend. Properties were compared for PLA-HYT-terpolymer (70-10-20) blend ratio.

**Hypothesis:** Reactive extrusion will result in highly toughened PLA ternary blends.

**Inference:** Only ternary blends with EMAGMA resulted in super toughened blends. Out of the 4 terpolymers tested, the hypothesis was true only in the case of EMAGMA. Impact toughness values obtained for other blends were lower compared to PLA-HYT (70-30) binary blends. The difference in level of resistance to impact was attributed to the morphology of the ternary blends.

**Part 1, Chapter 5: Crystallization behavior of PLA with aromatic sulfonate derivative**

**Synopsis:** Isothermal and non-isothermal crystallization behavior of PLA having different amounts of aromatic sulfonate derivative, a new commercial nucleating agent, Lak-301 was investigated

**Hypothesis:** Crystal nucleating agent can improve the crystallization rate of PLA thereby improving heat deflection temperature (HDT).
**Inference:** Lak-301 was efficient in improving the crystallization rate of PLA under isothermal conditions however higher injection mold temperature was required to achieve desirable improvement in HDT.

**Part 1, Chapter 6: PLA biocomposites**

**Synopsis:** PLA super toughened blend was used as a matrix to incorporate miscanthus (10 wt. %) and different nucleating agents such as Lak-301 (aromatic sulfonate derivative), HPR-803i (magnesium sulphate), Emforce-bio (precipitated calcium carbonate). Different mold temperature was also investigated as a means to increase the crystallinity of PLA biocomposites.

**Hypothesis:** Nucleation agent or fiber alone cannot provide the necessary improvements in crystallinity and heat resistance of PLA.

**Inference:** As hypothesized, having only miscanthus or nucleating agent did not increase the crystallinity very much and hence the HDT was only a few degrees higher compared to neat PLA. Combination of miscanthus, nucleating agent, Lak, and a high molding temperature of 110 °C was necessary to achieve fast crystallization of PLA during molding. This resulted in increase of HDT to around 80 °C, while maintaining impact strength of around 100 J/m. From different types of nucleating agents tested, only Lak-301 showed superior ability to crystallize PLA and provide necessary improvements in HDT.

**Part 2, Chapter 7: Reactive Extrusion of PTT/PLA blends**

**Synopsis:** Blend of PTT with PLA minor phase (30 wt. %) was selected for addition of reactive compatibilizer EMAGMA. Statistical design of experiments was used to optimize the level of EMAGMA, screw speed and chain extender.
**Hypothesis:** Shear rate and amount of additives have an effect on the resulting morphology of the reactive compatibilized blends.

**Inference:** With increase in extrusion screw speed from 100 rpm to 200 rpm (high shear rate) and addition of chain extender, effective dispersion of PLA and EMAGMA in PTT matrix was obtained. Dispersion size and related morphology were observed to change significantly at different loading levels of EMAGMA, chain extender and screw speed. Although blends with 20 wt. % EMAGMA resulted in highest improvement in impact strength, 15 wt. % was selected as the optimum based on the stiffness-toughness balance for incorporation of fillers.

**Part 2, Chapter 8: Size-fractionated biocarbon composites**

**Synopsis:** PTT is an engineering thermoplastic with high melting temperature and the processing of the blends are accomplished at 250 °C. Adding natural fibers to PTT based blends having PLA in a minor phase would result in thermal degradation of fibers during processing. Hence renewable carbon based filler, biocarbon, was selected as the suitable filler for composite fabrications. Effect of different particle range on the microstructure of the resulting composites and macroscopic properties were investigated.

**Hypothesis:** Particle size of the fractionated biocarbon affects the properties of the biocomposites. High mold temperature enhances the crystallization of PTT.

**Inference:** Depending on the particle size of the biocarbon used, microstructure of the polymer blend matrix changed and hence the properties were affected. Composites having biocarbon particle size range of 20-75 µm resulted in a morphology showing better dispersion of the blend components. Furthermore, addition of epoxy based multifunctional chain extender was found to
result in much finer morphologies having very small size dispersed polymer particles. Impact strength was found to increase significantly in composites which possessed such morphologies favoring high energy dissipation mechanisms. Maximum impact strength of 85 J/m was achieved in certain composite formulations, which is impressive considering the inherent brittleness of PTT and PLA. By increasing the injection mold temperature, fast crystallization of PTT was achieved which increased the heat deflection temperature to 80 °C.

10.2 Recommendation for Future Work

Following recommendations are provided based on the results and knowledge obtained from carrying out this thesis research.

 PLA-HYT binary blends

Commercial chain extender, Joncryl has similar multifunctional epoxy groups like EMAGMA. Effect of adding this chain extender to binary blends could be explored to investigate if it promotes compatibilization and reduce interfacial tension which can result in good improvement in mechanical and thermal properties. If this route works, there is a potential to obtain higher toughness with low amount of elastomeric impact modifiers like Hytrel.

Super toughened PLA blends

Although different reactive functionalized terpolymers were investigated, only EMAGMA was found to provide super toughening effect. Studying the effect of high temperature processing conditions with the help of chain extender and melt stabilizer could give valuable conclusions regarding the reactivity of these terpolymers at higher melt blending temperature.
**PLA biocomposites**

Additives that could help in reducing the long term hydrolysis and thus improving the durability of the blends were identified and used in PLA biocomposite formulation. However, experimental investigation on long term durability and hydrolysis stabilization needs to be pursued to quantify the effect of these additives.

Investigating the effect of adding biocarbon to the super toughened PLA blends will be another line of interesting future investigation.

**PTT ternary blends**

Experimental observations from increase of axial force during the reactive extrusion process revealed a potential to achieve further improvement in properties of PTT-PLA/EMAGMA blends by melt mixing for higher residence time. It would be interesting to investigate the effect of different screw configuration in a twin screw extruder to achieve the better dispersion in lesser time.

**PTT-PLA biocarbon composites**

Optimum properties were achieved at a biocarbon particle size range of 20-75 µm. Maintaining the balance in biocomposite properties by adding higher percentage of this biocarbon can be investigated to further improve the cost vs. performance attributes of these biocomposites for future industrial applications.
10.3 Outlook

We live in a fossil-based economy. We depend on oil for our energy, transport, and materials. Use of such unprecedented levels of fossil resources has resulted in ever higher levels of greenhouse gasses causing climate change. Renewable resources like biomass are therefore becoming increasingly important alternative to satisfying our demand. The bio-economy moves away from the fossil economy that runs on petroleum and encompasses the sustainable production of biomass into food, feed and bio-based products such as bioplastics. Use of biobased materials represents a holistic strategy to mitigate climate change and minimize the environmental impact of a product throughout its life cycle. Many major industries and business operations are moving towards sustainable sourcing and use of renewable materials. Principles of green chemistry, sustainability and engineering are being integrated in the research and development efforts to achieve a good balance of product performance and environmental friendliness. Biobased content is now an important driver in development of durable biopolymer blends and composites. Switching from fossil carbon to bio/renewable carbon minimizes the carbon footprint of the materials and the products created from them. Any renewable resource (such as biomass) when used as a raw material for product manufacturing helps in achieving a balanced carbon cycle. Use of agricultural, lignocellulosic residues for high volume applications can bring in new source of income for farmers while extending the value chain of the crops. This can help in job creation in rural farming communities.

Finally, one might ask when and where durable PLA materials may find application. Before answering, we should consider the evolution of bioplastics industry which has had multiple shifts in direction. First phase was focused on biodegradable and/or compostable characteristics, primarily intended for single use packaging applications. The second phase
offered compostable and renewable resource based alternative for non-degradable petro-based commodity plastics. The current trend is the development of durable bioplastics. Commercialization arguably marks the success of research and development efforts, but the timeline should not be compared to that of mature technologies. Although PLA based materials are aimed for high volume applications in interior automotive parts and other structural and semi-structural applications, they will initially find application in consumer goods such as cell phone casings, personal and home care products. This thesis is a small step towards driving the bioplastics technology to market for durable bioproducts application.
Appendix A: Chemical structure of the blend components

1. Poly (lactic acid), PLA

2. Poly (trimethylene terephthalate), PTT

3. Thermoplastic copolyester elastomer
   3a. Poly (ether amide) block copolymer, PEBA [Pebax Rnew, product of Arkema]
   3b. Poly (ether ester) block copolymers, HYT [Hytrel RS, product of DuPont]

Poly (butylene terephthalate), hard segment  Poly (tetramethylene ether) glycol, soft segment
4. Functionalized terpolymer

4a. Ethylene methyl acrylate glycidyl methacrylate, EMAGMA

MA content: 24 %, GMA content: 8 %

4b. Ethylene butyl acrylate glycidyl methacrylate, EBAGMA

BA content: unknown, GMA content: 4 to 5 %
4c. Ethylene methyl acrylate maleic anhydride, EMAMaH

MA content: 15 %, MaH content: 3.1 %

4d. Ethylene butyl acrylate maleic anhydride, EBAMaH

BA content: 17 %, MaH content: 3.1 %

5. Chain extender

Jongrlyl
R1–R5 are H, CH3, a higher alkyl group, or combinations of these, R6 is an alkyl group, and x, y and z each lie between 1 and 20.

Bioadimide [specific structure not known]
General structure for aromatic monomeric carbodiimide

\[
\begin{array}{c}
\text{N} \\
\text{R}_1 \\
\text{N} \\
\text{C} \\
\text{R}_2 \\
\text{N} \\
\text{C} \\
\text{R}_3 \\
\text{N} \\
\text{R}_4 \\
\text{N} \\
\text{C} \\
\end{array}
\]

R1 to R4 independently of one another are H, C1- to C20-alkyl, C3- to C20-cycloalkyl, C6- to C15-aryl or a C6- to C15-aralkyl radical which optionally may also contain heteroatoms.
Appendix B: Mechanical properties and HDT of biocomposites containing PLA/HYT/EMAGMA blend and Oat hull fibers

Investigation on mechanical properties and HDT of biocomposites developed from PLA/HYT/EMAGMA blend and Oat hull fibers is presented in this appendix. The processing conditions, type and amount of nucleating agent selected are based on the results of optimized formulations developed in Chapter 4 and Chapter 5.

Aspects that are different compared to the biocomposites developed in Chapter 5 are:

- Matrix: PLA/HYT/EMAGMA
- Fiber type: Oat hull
- Fiber content: 15 and 20 \%
- Addition of chain extender and hydrolysis stabilizer

Materials

- PLA- Ingeo\textsuperscript{TM} 3001D, NatureWorks LLC, USA.
- HYT- Hytrel\textsuperscript{®} RS 40F3 NC010, DuPont, USA.
- EMAGMA - Lotader AX 8900, Arkema, USA.
- Nucleating agent - Lak-301, Takemoto Oil & Fat Co, Japan.
- Chain extender (CE) - BioAdimide XT 500, Rhein Chem, USA.
- Fiber - Oat hull (OH), New Energy Farms, Leamington, ON, Canada.

All the polymers and fibers were dried in hot air oven for 6 hours at 80°C except E-MA-GMA which was dried at 60 °C.

Methods

Fabrication of blends and biocomposites involved extrusion followed by injection molding. A micro 15 cc co-rotating twin screw compounding, manufactured by DSM Research,

\textsuperscript{7} Part of this study is published in proceedings of 20th International Conference on Composite Materials (ICCM), ‘Polylactic acid based blends and biocomposites with improved Performance: Influence of reactive compatibilization, process parameters and nucleating agents’ July 2015.
Netherlands was used for extrusion. The processing temperature was set to 190 °C and was collectively controlled from the feeding end to the nozzle to avoid degradation of the polymer matrix. The extruded molten material was collected and transferred through a preheated collector built with piston cylinder assembly to a DSM micro 12 cc injection molding machine. Blends were molded at 30 °C mold temperature. Biocomposites were injection molded at 110 °C. Test specimens were conditioned at laboratory conditions (room temperature and 50 % relative humidity) for at least 42 hours before testing for properties.

**Testing and characterization**

Instron Instrument Model 3382 was used to study the tensile and flexural properties of the blends and composites according to ASTM standards D638 and D790 respectively. The tensile properties of blends were tested at 50 mm/min and biocomposites were tested at 5 mm/min. The flexural specimens of the matrix were tested at a crosshead speed of 14 mm/min. Heat deflection temperature was tested in dynamic mechanical analyzer, DMA Q 800 from TA Instruments, USA. Tests were conducted using three point bending clamp by applying a load of 0.455 MPa. The blends were heated from room temperature to a desired temperature (60 °C for neat PLA and blends, 110 °C for biocomposites) at a ramp rate of 2 °C/min. HDT was recorded at 0.1889% strain.

**Results and discussion**

**Tensile and flexural properties**

Tensile and flexural properties of neat PLA, binary and ternary blends and biocomposites are summarized in **Figure B-1 and B-2**. With the addition of HYT and EMAGMA to PLA in the
binary and ternary blends, the tensile strength was observed to decrease. PLA being a hard and brittle polymer breaks in a brittle fashion showing high tensile strength of around 70 MPa.

Figure B-1: Tensile and flexural properties of neat PLA, blends and biocomposites

A-Neat PLA; B- PLA-HYT (90/10) C- PLA-HYT-EMAGMA (70/10/20); D- PLA ternary blend/OH/Lak (84/15/1); E- PLA ternary blend/OH/CE (82/15/1/2); F- PLA ternary blend/OH/CE (77/20/1/2)
But with the addition of HYT and EMAGMA having a soft rubbery phase, the ductility of PLA is improved which was reflected as an increase in the % elongation noticed in PLA binary and ternary blends. Elongation at break for neat PLA was 4 % whereas with 10 wt. % HYT addition it increased to 13 % and a further increase to 50 % was achieved in the case of ternary blends. Tensile strength was observed to reduce further in biocomposites which was believed be due to poor stress transfer between the added oat hull fibers and PLA blend matrix. Significant improvement in Young’s modulus was achieved with incorporation of fibers and nucleating agent. Addition of chain extender to the biocomposites did not bring about any increase in tensile strength but did decrease the modulus, owing to the increased segmental mobility of the chains in the presence of chain extender. Flexural properties followed similar trend as tensile properties except one case where the flexural strength of the ternary blends and biocomposites were in the same range. The addition of fibers and nucleating agents on to the blend matrix did not have a significant adverse effect on the stress transfer ability when the biocomposite samples were subjected to a combination of loads under flexural test. On increasing the content of oat hull from 15 to 20 % in biocomposites containing the chain extender, the tensile and flexural properties were maintained and this indicated that with the addition of chain extender the fiber content in biocomposites could be increased to 20 %, however, this was found to be detrimental in case of impact strength as explained in next section.

**Impact strength and heat deflection temperature**

Neat PLA has impact strength of 20 J/m and HDT of 55 °C. In PLA/HYT (90/10) blends, the impact strength increased to 72 J/m and PLA blends containing HYT and EMAGMA exhibited a non-break behavior, which was attributed to the unique morphology development in this particular blend formulation, discussed in chapter 4. The synergistic effect of good
interfacial adhesion and cavitations followed by massive shear yielding of the PLA matrix is believed to have contributed to the enormous toughening effect observed in the ternary blends.

The HDT of blends however remained the same as that of neat PLA. From Figure B-2, it is noticeable that the addition of 15% oat hull reduced the impact strength to 98 J/m. This is considered to be common, as the ductility of the matrix is reduced by the addition of fibers that restrict the molecular mobility of the polymer chains. Nonetheless, the level of impact strength is still 300% higher compared to the neat PLA. But the HDT of this formulation was found to be at 58 °C when the injection molding was done at 30 °C. Incorporation of oat hull in the blend matrix system did not help in increasing the HDT as no significant change in crystallinity was
observed. By increasing the mold temperature to 110 °C, HDT as high as 88 °C was achieved. This was mainly due to the increase in PLA crystallinity facilitated by the presence of nucleating agent. In chapter 5, biocomposites based on a different matrix and fiber system containing Lak as nucleating agent, it was shown that both high molding temperature and a presence of nucleating agent was important in achieving such high increments in crystallinity and HDT. With the addition of chain extender, the impact strength increased close to 110 J/m. This could be attributed to the presence of chain extender which helped to reconnect the cleaved chains thereby increasing the molecular weight, and melt strength of the biocomposites. In a next step, the fiber content in biocomposites were increased to 20 %, although this increase did not seem to affect the tensile properties, there was a significant but undesirable reduction in impact strength of the biocomposites. This could be attributed to the insufficient and low energy path for crack initiation and propagation due to high fiber content. Such reduction in impact strength with increase in fiber content is a fairly common observation reported by a multitude of studies. HDT was observed to reduce as a result of chain extension effect which reduced the percentage crystallinity of biocomposites. Increasing the fiber content to 20 % helped in improving the HDT mainly due to increase in stiffness from the addition of fibers, the increase was however not to an extent of biocomposites without chain extender.
Appendix C: Polytrimethylene terephthalate (PTT) and polylactic acid (PLA) binary blends

This appendix chapter provides the baseline data investigating the mechanical and thermal properties of PTT-PLA binary blends at varying blend ratios.

Materials
PLA- Ingeo™ 3001D, NatureWorks LLC
PTT – Sorona® 3301 BK001, DuPont

Methods

Instron Instrument Model 3382 was used to study the tensile and flexural properties of the blends and composites according to ASTM standards D638 and D790 respectively. The tensile properties of blends were tested at 50 mm/min The flexural specimens of the matrix were tested at a crosshead speed of 14 mm/min. Heat deflection temperature was tested in dynamic mechanical analyzer, DMA Q 800 from TA Instruments, USA. Tests were conducted using three point bending clamp by applying a load of 0.455 MPa. The blends were heated from room temperature to a 70 °C a ramp rate of 2 °C/min. HDT was recorded at 0.1889 % strain. Results reported are average of 5 samples for mechanical properties and 2 samples for HDT.

Results and discussion

Mechanical Properties and heat deflection temperature

Tensile and flexural properties showed increasing trend with increase in the amount of PLA added to PTT. This is expected as PLA has higher strength and modulus; however beyond 30 wt. % drop in the properties was noted. Impact strength was reduced slightly with the incorporation of PLA and HDT seemed to increase slightly with the addition of PLA. This could
be due to the improvement in crystallinity of PTT with the addition of PLA. As addition of impact modifier/compatibilizer might affect the strength and modulus properties while improving the toughness, it might be beneficial to use low processing temp and control the crystallinity.

Table C-1: Mechanical properties and HDT of PTT-PLA blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength</th>
<th>Tensile Modulus</th>
<th>Elong. @brk</th>
<th>Flexural Strength</th>
<th>Flexural Modulus</th>
<th>Impact Strength</th>
<th>HDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>60.9±1.17</td>
<td>2.80±0.027</td>
<td>57.9±10.0</td>
<td>108.7±3.04</td>
<td>3.30±0.063</td>
<td>21.7±3.84</td>
<td>46.6±1.23</td>
</tr>
<tr>
<td>PTT-PLA (90/10)</td>
<td>62.0±1.13</td>
<td>2.88±0.072</td>
<td>17.8±2.82</td>
<td>100.0±2.87</td>
<td>3.27±0.072</td>
<td>15.9±2.33</td>
<td>58.4±1.25</td>
</tr>
<tr>
<td>PTT-PLA (80/20)</td>
<td>63.4±0.71</td>
<td>2.97±0.076</td>
<td>5.03±1.35</td>
<td>105.1±1.26</td>
<td>3.46±0.042</td>
<td>15.2±0.02</td>
<td>58.6±1.71</td>
</tr>
<tr>
<td>PTT-PLA (70/30)</td>
<td>67.1±1.55</td>
<td>3.15±0.095</td>
<td>3.15±0.35</td>
<td>106.8±2.69</td>
<td>3.37±0.088</td>
<td>17.6±3.28</td>
<td>60.2±1.64</td>
</tr>
<tr>
<td>PTT-PLA (60/40)</td>
<td>64.8±1.00</td>
<td>3.18±0.062</td>
<td>2.56±0.35</td>
<td>102.2±0.94</td>
<td>3.20±0.063</td>
<td>30.5±4.72</td>
<td>53.8±2.12</td>
</tr>
<tr>
<td>PTT-PLA (50/50)</td>
<td>57.1±1.10</td>
<td>3.26±0.029</td>
<td>1.99±0.08</td>
<td>106.7±0.89</td>
<td>3.43±0.048</td>
<td>14.1±1.03</td>
<td>56.5±0.89</td>
</tr>
</tbody>
</table>

**Morphology**

Phase morphology of impact fractured blends is shown through SEM images in Figure C-1 and C-2 for varying blend ratios. PTT-PLA blends showed typical sea-island morphology of immiscible polymer blends. Lower particle size and uniform distribution was observed for dispersed PLA, when added in smaller amounts. Once the ratio of PLA in the blend was increased to 30 wt. % and beyond, the dispersed droplets were coalescing leading to formation of bigger droplet size. With further increase in PLA to 50 wt. %, matrix-droplet morphology was disappearing and the blends were beginning to go through a phase inversion process.
Figure C-1: SEM images for PTT/PLA blends. Composition: 90/10, 80/20, 70/30
Magnification: 3000 and 5000x
Thermal properties

Thermal properties of PTT-PLA blend from differential scanning calorimetry (DSC) are provided in Table C-2. Melting temperature values of PTT and PLA have not changed, indicating that there is no degradation. However, the melting enthalpy of PTT (not shown here) followed a decreasing trend with increase in the weight content of PLA which is expected.

Figure C-2: SEM images for PTT/PLA blends. Composition: 60/40 and 50/50

Magnification: 3000 and 5000x
The crystallization temperature \( T_c \) of PTT shifted to higher temperature with the addition of 10 and 20 wt. % PLA indicating such amounts of PLA is aiding in crystallization of PTT at higher temperature. Crystallinity of PTT has also increased with the addition of PLA with a maximum of 37.3 % of 70/30 blend. These values directly reflect the HDT results, where a higher HDT value was observed for 70/30 blend.

**Table C-2: DSC results for PTT-PLA binary blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_m ) of PTT (°C)</th>
<th>( T_m ) of PLA(°C)</th>
<th>( T_{cc} ) of PTT(°C)</th>
<th>( T_{cc} ) of PLA(°C)</th>
<th>( T_c ) of PTT(°C)</th>
<th>( T_c ) of PLA(°C)</th>
<th>( \chi ) of PTT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTT</td>
<td>228.42</td>
<td>--</td>
<td>67.09</td>
<td>--</td>
<td>181.79</td>
<td>--</td>
<td>29.97</td>
</tr>
<tr>
<td>PTT-PLA (90/10)</td>
<td>228.35</td>
<td>167.51</td>
<td>67.98</td>
<td>--</td>
<td>188.66</td>
<td>--</td>
<td>34.25</td>
</tr>
<tr>
<td>PTT-PLA (80/20)</td>
<td>228.25</td>
<td>168.53</td>
<td>68.35</td>
<td>--</td>
<td>188.14</td>
<td>--</td>
<td>35.13</td>
</tr>
<tr>
<td>PTT-PLA (70/30)</td>
<td>228.24</td>
<td>168.24</td>
<td>68.91</td>
<td>110.7</td>
<td>183.29</td>
<td>--</td>
<td>37.32</td>
</tr>
<tr>
<td>PTT-PLA (60/40)</td>
<td>228.48</td>
<td>168.94</td>
<td>66.56</td>
<td>113.2</td>
<td>182.3</td>
<td>97.96</td>
<td>34.98</td>
</tr>
<tr>
<td>PTT-PLA (50/50)</td>
<td>228.21</td>
<td>168.23</td>
<td>70.58</td>
<td>113.2</td>
<td>182.56</td>
<td>96.86</td>
<td>35.46</td>
</tr>
</tbody>
</table>