DEVELOPMENTS IN ELECTRICALLY CONDUCTIVE BIO-COMPOSITES FOR USE IN ADDITIVE MANUFACTURING

by

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A thesis submitted in partial fulfillment of the requirements for the degree

of

Master of Science

 in

Mechanical Engineering

MONTANA STATE UNIVERSITY Bozeman, Montana

April 2019

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ACKNOWLEDGEMENTS

This work was made possible through the help of fellow graduate students, and Engineering department faculty. Special thanks goes to :

Dr. Cecily Ryan for her guidance and encouragement through my time as an undergraduate student and into my graduate work. I would like to thank all of the Ryan Lab graduate students that helped me complete my work effectively during my time at Montana State University.

Dr. Stephan Warnat and his lab group for their aid in developing consistent methods. Dr. Stephen Sophie, Dr. Roberta Amendola, and Dr. Rob Walker for aiding the research through allowing use of their equipment and machines. Kathy Campbell, Dagny Mest and the rest of the MSU Dept of Engineering support staff for their guidance and assistance navigating the degree program.

This work was performed in part at the Montana Nanotechnology Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant# ECCS-1542210). Carbon black was generously provided by Cabot Corporation, Billerica MA, USA, through Horn, La Mirada CA, USA. Funding for this work was through startup funds from Montana State University.

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ABSTRACT

With the growth of rapid production methods, such as additive manufacturing, petroleum derived plastics are becoming ever more prevalent in consumer homes and landfills. As the industry grows, research into a more circular approach to designing and using materials is critical to maintaining sustainability. Bioplastics such as poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and poly(lactic acid) (PLA) provide material properties comparable to petroleum derived plastics and are becoming more common in the additive manufacturing field. Biobased fillers, such as bio-derived cellulose, lignin byproducts, and biochar, can be used to modify the thermal, mechanical, and electrical properties of polymer composites. Biochar (BioC), in particular, is of interest for enhancing thermal and electrical conductivities in composites, and can potentially serve as a bio-derived graphitic carbon alternative for certain composite applications. In this work, we investigate a blended biopolymer system: PLA/PHBV, and addition of carbon black (CB), a commonly used functional filler as a comparison for Kraft lignin-derived BioC. We present calculations and experimental results for phase-separation and nanofiller phase affinity in this system. indicating that the CB localizes in the PHBV phase of the immiscible PHBV:PLA blends. The addition of BioC led to a deleterious reaction with the biopolymers, as indicated by blend morphology, differential scanning calorimetry showing significant melting peak reduction for the PLA phase, and a reduction in melt viscosity. For the CB nanofilled composites, electrical conductivity and dynamic mechanical analysis supported the ability to use phase separation in these blends to tune the percolation of mechanical and electrical properties, with a minimum percolation threshold found for the 80:20 blends of 1.6 wt.% CB. At 2% BioC (approximately the percolation threshold for CB), the 80:20 BioC nanocomposites had a resistance of $3.43 \times 10^8 \Omega$ as compared to $2.99 \times 10^8 \Omega$ for the CB, indicating that BioC could potentially perform comparably to CB as a conductive nanofiller if the processing challenges can be overcome. Investigations into alkaline and dealkaline lignin sources have shown that alkaline lignin experiences a significant effect on the thermal stability of PHBV eluding that alternate sources of lignin may provide a solution to the processing challenges mentioned. This work has helped to develop a understanding of the factors that aid in creating sustainable materials sourced from PLA, PHBV, and BioC.

INTRODUCTION

Conductive filaments consist of polymers blended with an electrically conductive media such as graphitized carbon or carbon black (CB). These filaments can be used in an additive manufacturing processes such as 3D printing in order to rapid prototype electrical circuits, wearable electronics, and touch sensitive devices. Furthermore this inclusion of a low density filler allows for the tuning of certain material properties such as strength, thermal conductivity and final part weight. Use of these fillers has created a family of filaments unique in their ability to be custom tailored into flexible, strong, and lightweight electronics. As these materials develop it is beneficial to investigate the substitution of bio-sourced materials for the petroleumbased standard. Biopolymers such as poly(lactic acid) (PLA) have been in common use in the 3D printing field since 2007 [3]. Additionally recent studies of bio-sourced graphitized carbon such as biochar (BioC) have provided new insights into potential replacements for their non-bio based counterparts [4].

3D printing in conjunction with electrically conductive filament has enabled complex designs to be manufactured with relative ease and the added benefit of including circuit design. Parts that were once time and cost intensive to make can now be generated affordably and prototyped effectively. These prints allow for custom sensor design that can be included into fabrics to produce wearable electronics and collect data such as stress, strain, and temperature. These printable electronics play a crucial role in advancing the field of bio mechanics [5]. Larger parts can be produced to provide radio frequency shielding for applications in settings where interference is a concern. This radio frequency shielding capability is due to the ability of the filler material to restrict RF movement through its body. Conductive filaments are a growing field with many promising applications.

Though innovative in their creation and potential applications, there are some notable drawbacks of the currently available conductive filaments. At the time of this paper, the majority of conductive filaments are quite costly in comparison to their non-conductive counterparts. The inclusion of carbon in a filament can cost the user anywhere from nine to eleven cents per gram where standard PLA filament is around two cents per gram. More conductive than neat polymers, conductive filaments are less conductive than solid metals such as copper, lead, or steel. Increasing the amount of carbon included in a polymer blend can increase conductivity however, even at its highest possible volume percents, carbon black infused conductive filaments lack the free electron field that allows for electricity to move through materials like metals. When carbon is included at lower volume percents it can have adverse effects on the filament such as micro-cracking and brittleness. These effects cause substantial issues in applications, as a tightly wound filament spool can often break during its feeding into a 3D printer. Carbon infused filament can also cause long term damage to the 3D printer's nozzle due to its abrasive nature. Long term, this problem can cause many issues for a printer and its operators. After the material has been purchased, handled, and printed with, market available conductive filaments are not able to be recycled or disposed of in a sustainable manner. These filaments do not follow a circular life cycle and must be disposed of thoughtfully due to there high carbon inclusion. Industry sized applications present serious questions to the sustainability and functionality of conductive filaments. Some of these questions can be answered by substituting the materials in use.

Industrial pursuit towards a more sustainable future has driven great advancements in material science and engineering, including unique bio-sourced replacements for petroleum based materials. Bio-sourced materials like PLA and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) have made substantial impacts on the polymer industry over the last few years [1]. PLA has become a common installation in the additive manufacturing field while PHBV has sparked significant interest as an attractive additive in PLA blends [1]. In composites, bio-sourced carbon or BioC has drawn significant attention in its practicality as an additive in soils to aid in carbon sequestration [2]. There has also been a substantial amount of work that suggests that BioC possess attractive material and electric properties when produced at high temperatures [4]. As the temperature of production rises, so does the degree of graphitization and thus the ability of electron exchange between the particles. This ability thus enhances the filler material's conductivity improving its use in conductive filament. These developments suggest that the inclusion of a bio-based filler material into bio-based polymers has the potential to replace the industrially available conductive filaments.

The incorporation of BioC into bio sourced polymers can provide a sustainable alternative to their synthesized relatives. In order for large scale production of these materials to be successful, research must discover the solutions to their manufacturing methods. The following research objectives explore the parameters surrounding the use of BioC in PLA:PHBV blends:

- 1. Develop a method of predicting blend morphology of PLA:PHBV while also predicting CB localization in the blend.
- 2. Determine the percolation constant of PLA:PHBV blends with CB used as the filler material.
- 3. Determine and quantify effects of adding BioC to PLA:PHBV blends.

To understand the effects nanoparticulates have on polymer blends, CB was added to three principal mixtures of PLA:PHBV blends (10:90, 20:80, 40:60). These composites were produced in a mini extruder and injection molded into dynamic mechanical analysis (DMA) bars for testing. To monitor how conductivity changes as filler is added, impedance spectroscopy is run on each sample. When filler material is added to a blended polymer, there are likely changes in the material's crystallinity, polymer morphology, and mechanical properties such as strength and modulus. Using differential scanning calorimetry (DSC) reveals how the melting temperature (T_m) , glass transition temperature (T_g) , and crystallinity of each blend changes with increasing filler content. These effects on morphology are investigated visually through field emission scanning electron microscopy (FE-SEM), and predicted via contact angle analysis with Owens-Wendt theory. Filler effects on modulus and strength are monitored through DMA in a three point bending configuration.

The initial results revealed that BioC has substantial effects to PHBV:PLA blends. To investigate these effects, neat alkaline lignin (AL) and dealkaline lignin (DAL) were added to PHBV and PLA individually. These samples were evaluated for effects on crystallinity through DSC, thermal stability through thermogravimetric analysis (TGA), and molecular weight through gel permeation chromatography (GPC).

BACKGROUND

Trash production in the United states has steadily increased from 88 million tons in 1960 to 251 million tons in 2012, an 185% increase in 52 years. Only 35% (87 million tons) of that waste was recycled. Of the plastic products used in 2012 only 30% of polyethylene terephthalate (PET) and 28% of high density polyethylene (HDPE) was recycled [6]. Though thermoplastics are considered a recyclable material, their consumer application sometimes hinders their recyclability. Most of recyclable petrol-plastics are used and disposed of into landfills, sewage, waterways, or in the soil as general litter. Like petrol-plastics bio-derived plastics can be recycled, however the 70% that finds its way to the land fill is degraded by the environment into non-toxic products [7]. Bio-derived polymers have the potential to replace many industrially available plastics, including in applications such as electrically conductive filament.

This review discusses the current state of PLA:PHBV blends, production of BioC, conductive filaments, and the the potential for using bio-sourced materials as a replacement for the industry available. PLA, an already popular material for conductive filament, can be combined with other bio-sourced materials such as PHBV to reduce the amount of filler used, leading to tune-able material properties. Reducing the filler content while maintaining sufficient conductivity is a method of tuning a composites conductivity while also reducing material cost. Similarly, increasing the conductivity of the BioC allows for a reduction in the amount of filler material used and a product's subsequent cost. This increase in conductivity is created by increasing the temperature at which BioC is produced through a slow pyrolosis process . In slow pyrolosis, a material is gradually heated ($10^{\circ}C/min$) to a final high treatment temperature (HTT) under an oxygen free environment. The conductivity of BioC has been shown to increase with slow pyrolosis HTT above 800°C [2]. Market-available

conductive filaments typically do not take advantage of this potential tune-ability of blends though recent research has shown that conductivity of petroleum polymers can be tuned by manipulating morphology and blend ratios, the same should be possible with bio-sourced polymers.

Materials

Composites and Additives

Composite materials are becoming more popular in applications where a combination of stiffness, durability, weight, and cost are of concern; growing in all industries from aerospace applications to household appliances. These composites involve a combination of a polymer matrix with reinforcement of fiber mats, strands, or spherical particles. Typically, the matrix used is a thermoset, however it is also common to see thermoplastics used in the composite industry. The matrix provides the bulk support while additives increase strength and stiffness leading to engineered material properties magnitudes larger than their individual constituents. The scope of the work covered in this paper involves particle nanocomposites where the matrix is a polymer blend, and the particles are select sources of nanometer-sized fillers.

PHBV/PLA Blends

PHBV is a member of the poly(hydroxyalkanoate) (PHA) family which is a group of bio-plastics produced in nature by bacterial fermentation of sugars and lipids [1,8]. PLA is a common bio-sourced material that is known for its relatively high modulus and strength [8]. When blended together, these two polymers begin to show significant benefits to their material properties. The inclusion of PLA in at ratios of 50:50 and above with PHBV has been shown to steadily increase the tensile strength and modulus of the blend [1]. Additionally, the inclusion of PHBV

Formulation		Flexural strength	Flexural modulus		
	[in wt%]	[MPa]	GPa]		
	neat PHBV	30.2 ± 0.56	1.2 ± 0.02		
	neat PLA	94.1 ± 1.92	3.6 ± 0.09		
	PHBV/PLA(50:50)	62.5 ± 1.10	2.4 ± 0.03		
	PHBV/PLA(60:40)	61.0 ± 2.32	2.2 ± 0.06		
	PHBV/PLA(70:30)	53.7 ± 1.44	1.9 ± 0.11		

Table 2.1: Mechanical Properties of PHBV have been show to improve through blending with PLA, reproduced from Nanda et al. [1].

in PLA can increase the crystallinity of the PLA regions, thus inducing a brittle to ductile transition in the blend [8]. Most significantly, blends of PHBV:PLA are immiscible in all ratios and combinations, meaning that PLA will occupy a sea-island structure in the PHBV matrix [1,8]. This structure is especially important to polymer nanocomposites as it allows for three potential regions for the filler to inhabit. As nanofiller is mixed in with PHBV:PLA blends it will localize only in the PHBV region, the PLA region, or the interphase between them. This localization is driven by the entropic nature of the filler to find the region of least resistance which can be characterized through the particulate's wettability.

Bio Carbon Production

Agriculture has taken advantage of carbon rich charcoal or BioC to enhance soil for many generations, and recent research has expanded its potential applications into the electrically conductive realm [2]. BioC can be defined as a charcoal produced from biomass through the process of pyrolysis. In this process select bio-mass materials are heated up to a HTT in the absence of oxygen. Pyrolosis under nitrogen allows the biomass to convert into BioC without combustion or ashing of the material. The most influential parameters when producing conductive BioC are the ramp rate, the value of the HTT, and the source. If these factors are manipulated properly, the degree of carbonization increases thus increasing conductivity [2,4].

With the increase of pyrolysis HTT the conductivity of BioC has been shown to increase due to carbonization [2, 4, 9, 10]. During slow pyrolysis, more volatiles are released as the temperature climbs, leaving a higher wt% of carbon behind. As can be seen in Figure 2.1 eventually the carbon will reach a graphitic organization around 1000°C and increase in order as temperature rises [2]. Rhim et al. were able to break this microstrucural evolution into 5 regions based on the materials reaction to AC or DC electrical current [10]. Specifically they found that in region IV (600-1000°C), DC conductivity is observed and continues to increase with HTT as carbon clusters grow. In Region V (1200-2000°C), the DC conductivity ceases to increase as the bio-mass reaches a fully percolated state and its max potential conductivity. In order to maximize the conductivity of bio-sourced carbon particulates without further alteration, the HTT must be as near to Region V as possible.

Though not as influential as the HTT, the source of the material plays a considerable role in the feasibility and sustainability of BioC. Lignin derived as a waste product from the kraft paper process has several attractive attributes for BioC production. With nearly 60 wt% carbon content, lignin begins the process with a significant advantage [11]. Available from nearly any plant source, lignin is readily available and continually being produced. The type of lignin used in pyrolosis (alkali lignin, dealkaline lignin, Klason lignin, bio-refinery sources) can also have significant effects on the end product as their chemical make up is different. In an investigation of alternate macro sources of lignin (sugar maple, oak, hickory, and bamboo), Gabhi et al. found that across all forms of sourced material, a HTT of 950°C for 8 hours



Figure 2.1: Illustration from *BioChar for Environmental Management* showing with increase in HTT there is (a) increased proportion of aromatic carbon, Highly disordered in amorphous mass;(b)growing sheets of conjugated aromatic carbon, turbostaticly arranged;(c) structure becomes graphitic with order in the third dimension [2]

had a greater effect on conductivity than changing sources. In summary, the source of the lignin or material used in BioC is an important consideration during production, although the primary factor is the HTT.

Conductive Filaments

Incorporating conductive fillers such as CB or graphene into petroleum based polymer blends increases their conductivity [12,13]. As more filler material is added to the blend, the resistance decreases until the blend reaches a maximum conductivity. At this point the filler material percolates through the polymer blend forming a conductive network through the matrix, reducing the resistivity to near that of the filler material alone [14]. Attempts to manipulate this percolation threshold can allow for the reduction of filler material used, and increase a blends conductivity [13, 14].

One potential method of controlling the percolation threshold takes advantage of phase-separation in immiscible blends. These binary or ternary blends allow for the separation of a filler material into specific regions due to the different surface energies of the two or more polymers. Zhang et al. discovered that when blended, thermoplastic polyurethane (TPU) spread at the interface of the two major phases of polyoxymethylene/polyamide copolymer (POM/COPA) allowing for a shell and core morphology of the ternary blend [13]. As CB is added to this mixture it is found to localize in the shell region (TPU) of the blend. This localization in the shell region permitted a significant drop in the percolation threshold as the CB was able to form connective networks through the bulk of the material, yet reduce its occupation to only the minor TPU phase. By controlling the amount of TPU in the blend connective roads can be built through the material allowing for a significant drop in filler material used while still retaining sufficient conductivity.

The ability to manipulate polymer blends through their immiscibility is powerful,

yet not limited to petroleum based polymers, allowing for discoveries made in these polymer to carry over into bio-based polymers. Notably PHBV:PLA composites have been shown to be immiscible due to their surface energies [1, 15, 16]. Snowdon et al. was able to create a shell and core morphology of PLA and PHBV in a matrix of polypropylene similar to the COPA/TPU blends discovered by Zhang et al. As Zhang showed, manipulating the immiscibility can also manipulate the conductivity of the blend through preferentially locating the conductive filler material. This filler material is traditionally a synthesized CB however as mentioned above, BioC may be a sufficient replacement. As material science progresses to a more circular life cycle design for all materials, sustainable and renewable plastics research affords an opportunity to advance the field of conductive filaments.

INCORPORATION OF CARBON NANOFILLERS TUNES MECHANICAL AND ELECTRICAL PERCOLATION IN PHBV:PLA BLENDS^1

Contribution of Authors and Co-Authors

Manuscript in Chapter 3: Incorporation of carbon nanofillers tunes mechanical

and electrical percolation in PHBV:PLA blends

Author: Jesse Arroyo

Contributions: Fabricated samples and conducted contact angle, FE-SEM, impedance, DMA, and DSC experiments and analysis. Equally contributed to the preparation of the manuscript.

Co-author: Cecily Ryan

Contributions: Conducted Raman experiments and analysis and oversaw and contributed to all analyses. Conceived and designed the research. Equally contributed to the preparation of the manuscript.

¹This chapter is a manuscript published in a special issue of *Polymers: Recent Advances in Bioplastics*

Manuscript Information

Jesse Arroyo, Cecily Ryan

Polymers

Status of Manuscript:

□ Prepared for submission to a peer-reviewed journal

□ Officially submitted to a peer-reviewed journal

 \square Accepted by a peer-reviewed journal

 \boxtimes Published in a peer-reviewed journal

Publisher: MDPI, Published, DOI: https://doi.org/10.3390/polym10121371

Introduction

Increasing concern for the environment and volatile petroleum prices has led to growth of bio-based and biodegradable materials as alternatives to petroleum Plastics from bio-derived sources, or bioplastics, can be derived plastics [17]. processed from a variety of feedstock including raw and refined plant sources and methane gas from biological degradation processes [7]. One class of bioplastics, poly(hydroxyalkanoates) (PHAs), such as poly(hydroxybutyrate) (PHB) and its industrially-produced copolymer poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), is synthesized by microorganisms as a storage polymer and can be harvested to produce a usable plastic [18]. PHBV has mechanical properties most similar to polypropylene, however thermal processing of PHBV is challenging due the proximity of the thermal decomposition temperature to the melting temperature [19, 20]. Poly(lactic acid) (PLA) is another important bioplastic, that can be produced through renewable resources, and has mechanical properties most similar to that of polystyrene [20]. Alone, both bioplastics are brittle, with relatively poor impact strength and low thermal degradation temperatures. The toughness and processability of these bioplastics can be improved through multiphase blends of PHBV and PLA, resulting in attractive material properties not obtainable in the neat biopolymers [1, 7].

One growing application space for bioplastics is additive manufacturing, and an emergent area of this space is conductive filament. Conductive filament is used in the rapid prototyping and production of electrically conductive components on a variety of 3D printers [?,12]. This production method enables various applications from low cost sensors to conductive traces, branching into electromagnetic and radio frequency shielding [21,22]. Typically, conductivity in thermoplastics is achieved through the addition of a conductive filler, such as silver nanoparticles, carbon black nanofillers, or graphene [22,23]. In addition to electrical conductivity, these value-added composites can reduce cost and weight, add color, provide anti-static potential at low volume percent, and enhance the mechanical and thermal properties over that of the neat polymer [15]. Of these fillers, the majority of conductive filaments are produced with carbon black (CB), a commercially available petroleum-derived filler.

Though CB offers many positive benefits to polymer blends, when designing biobased composites having a renewable source for and considering the fate of filler materials is also important. Biochar (BioC) carries many of the same benefits as CB, but comes from renewable plant-derived sources and, as a widely applied agricultural amendment, is compatible with the bioplastic's ability to biodegrade. This bio-sourced form of carbon is produced in a similar way to charcoal. Thermal decomposition of biomass in the absence of oxygen results in roughly 35% syngas, 30% bio-oil, and 35% BioC [2]. The electrical conductivity of lignin sourced BioC has been shown to improve with pyrolysis at high treatment temperatures (over 800°C) [4, 24, 25].

The bulk of the work exploring conductive nanocomposites, including with polymer blends, consists of polymers mixed with CB, graphene, carbon nanotubes (CNTs), or other graphite fillers [?, 12–14, 26]. The conductivity of PLA-based composites has been successfully modified with CNTs [27, 28], graphene [29–32], and CB [33, 34]. Conductive filament made from PLA and conductive fillers (CB, graphene) is commercially available [35, 36]. Fewer conductivity studies have been done with PHB and PHBV-based carbon nanocomposites; this work has been primarily with CNTs and graphene or graphene oxide, with conductivities in the range of ~ 0.1 S/m to 30 S/m with loadings above the percolation threshold [37–39].

Studies of conductive polymer blends have shown that nanofillers lower the percolation threshold of the blend over that of nanofiller incorporated into a single polymer, due to the ability to reside in either the minor or major phase, or the interfacial region [13]. This partitioning of the nanofiller produces higher conductivity at lower weight percent filler than in their non-blended counterparts. Phase-separation has been used to control nanofiller localization in blended PLA composites [27–29, 40]. Differences in nanofiller aspect ratio contribute to the phase-localization behavior in addition to phase separation in these composite blends [34, 41, 42]. The studies of BioC involve particulate in a single polymer, conductivity of non-incorporated monolithic BioC, or large (microns to millimeters) fillers in a polymer blend [4, 15, 43, 44].

This study provides a novel investigation into the localization of CB and BioC nanofiller in biopolymer blends, and the resultant impact on mechanical and electrical properties of nanocomposites of interest for 3D printing. The focus is to investigate: (i) nanofiller localization and resultant morphology in a blended biopolymer system, PHBV:PLA, (ii) electrical and mechanical percolation of the nanofilled composites, and *(iii)* the impact of the two nanofillers on processing and melt rheology. To elucidate how nanofiller localization would be expected to occur in the blends, we predict the interfacial energies of the blends using contact angle measurements and calculations of surface tension and verify these predictions using field emission scanning electron microscopy (FE-SEM). We then use impedance spectroscopy, Raman spectroscopy, and dynamic mechanical analysis (DMA) to evaluate the electrical and mechanical properties of the nanocomposites and calculate the percolation threshold in blended and non-blended systems. We use melt rheology during compounding and differential scanning calorimetry (DSC) to evaluate the impact of nanofiller addition during processing and how these interactions impact blend microstructure, thermal stability, and processability.

Theory

Polymer blend phase separation and incorporation of nanofillers can be described through the use of the Owens-Wendt theory [45]. The thermodynamics of phase behavior of polymers in a blend is governed by the surface tension of the polymers. The surface tension is comprised of polar and dispersive components, and is typically measured using the contact angle between the polymer surface and liquids with known polar and dispersive values. The Owens-Wendt theory combines the Goods equation (3.1) with the Young's equation (3.2) to create the linear form (3.3) [45]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_l^d \gamma_s^d} - 2\sqrt{\gamma_l^p \gamma_s^p} \tag{3.1}$$

$$\gamma_s = \gamma_{sl} + \gamma_l \cos(\theta) \tag{3.2}$$

$$\frac{\gamma_l \cos(\theta+1)}{2\sqrt{\gamma_l^d}} = \gamma_s^p \frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}} + \sqrt{\gamma_s^d}$$
(3.3)

Substituting into the linear form (y = mx + b) gives:

$$y = \frac{\gamma_l \cos(\theta + 1)}{2\sqrt{\gamma_l^d}} \tag{3.4}$$

$$m = \gamma_s^p \tag{3.5}$$

$$x = \frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}} \tag{3.6}$$

$$b = \sqrt{\gamma_s^d} \tag{3.7}$$

where γ_l is the overall surface tension of the wetting liquid, γ_s is the overall surface energy of the solid, the polar and dispersive components are represented by γ_s^p, γ_l^p and γ_s^d, γ_l^d respectively, γ_{sl} represents the interfacial tension between the solid and the liquid, and θ is the contact angle between the liquid and the solid. A solid's unknown polar and dispersive components (γ_s^p, γ_s^d) are calculated using contact angles with liquids of a known polar and dispersive component (γ_l^p, γ_l^d). This calculation is done by plotting contact angle data (x, y: equations 3.6 and 3.4) and using a line of best fit to determine a slope and y-intercept [46]. This form of the Harmonic Mean Method requires a minimum of two liquids for which surface tension data is well known to develop a best fit line.

In general, binary polymer blends exhibit either a blended morphology representative of miscibility, or they may exhibit a sea-island structure representative of an immiscible blend. For binary polymer composites, there are typically three potential locations of the nanofiller: it may exist in the major phase, the minor phase, or in the interfacial region between the two. The interfacial tension between the blended polymers and the nanoparticulates was calculated using the Harmonic Mean Equation (3.8), and used to predict the morphology of the system [46].

$$\gamma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}$$
(3.8)

To determine miscibility of the polymer blend, the spreading coefficient λ_{ij} was calculated for phase *i* on phase *j* (3.9). A positive λ_{ij} indicates that polymer *i* will spread and is miscible on *j*, while a negative number indicates immiscibility between i on j [46].

$$\lambda_{ij} = \gamma_j - \gamma_i - \gamma_{ij} \tag{3.9}$$

The localization of the nanofiller in the blend can be predicted by determining the wetting coefficient of the polymer on the particulate, ω_{ij} . This coefficient is given in equation (3.10), where $\gamma_{i,NF}$ represents the interfacial tension of the nanofiller on polymer *i* [46].

$$\omega_{ij} = \frac{\gamma_{i,NF} - \gamma_{j,NF}}{\gamma_{ij}} \tag{3.10}$$

By this definition, if ω_{ij} is greater than 1 the particulate will localize in the *j* phase of the polymer blend. In turn, if ω_{ij} is less than -1 it will localize in the *i* phase and finally if ω_{ij} is between 1 and -1 the particulate will localize in the interfacial region between the blends.

The contact angle between the polymers during molten flow can be characterized by equation (3.11) and used to predict the shape of the minor phase in the major [46].

$$\theta_{ij} = \cos^{-1} \left(\frac{\gamma_j - \gamma_{ij}}{\gamma_i} \right) \tag{3.11}$$

Materials and Methods

Materials

Commercially available PHBV (ENMAT Y 1000p, >98% purity) in pellet form was provided by Tianan (Nigbo City, China). PLA (2003D), also in pellet form, was supplied by Nature Works (Minnetonka, USA). Powdered CB (Vulcan XCMAX22) with a density of 0.19 g/cm³ was provided by Cabot Chemical Corporation (Boston, USA). Kraft lignin, with a density of 1.3 g/cm^3 at 25° C, was purchased from Sigma Aldrich and used to produce the BioC. All materials were stored in a desiccator prior to composite fabrication.

BioC Production

BioC was produced through slow pyrolysis of ball milled kraft lignin. Powdered kraft lignin (20g) was milled with zirconia media for 24 hrs at 60 rpm. The media were removed and the milled lignin was stored at 105°C to remove moisture. Prior to pyrolysis in a tube furnace, nitrogen gas was purged through the tube at 0.95 CCM for 15 minutes to establish an oxygen free environment. After the initial purging, nitrogen flow was reduced to 0.55 CCM and heating began at 10°C/min to 750°C. After one hour at 750°C the temperature was ramped to 950°C at a rate of at 10°C/min and held for an hour. The sample was then allowed to cool to room temperature while still under nitrogen flow. Post pyrolysis, samples were stored at 105°C.

Composite Fabrication

Composites were prepared by melt compounding in a Thermofisher Scientific HAAKE Minilab II dual screw extruder at 50 rpm and 190°C for 5 min. During this time, rheology data were collected and viscosity was calculated from Minilab outputs as shown in Appendix B. After mixing, blends were extruded into a Thermofisher scientific Minijet Pro injection molder. Initial injection pressure was 600 bar for 10 s followed by 450 bar for 60 s. Injection temperatures were 190°C in the gun and 60°C in the mold, as established through prior optimization. All composites were injected into a DMA sample mold (Thermofisher Scientific 557-2295) with dimensions of 60x10x1 mm³. Table 3.1 gives the blend ratios used for the PHBV:PLA blends and blends with nanofillers. CB nanofilled blends were made with all PHBV:PLA blend ratios, while samples of BioC were produced as feasible due to viscosity challenges during

Table 3.1: PHBV:PLA composite blend ratios with CB and BioC nanofiller

	Vol	.% o	f Ble	nd			Wt.?	% of '	Total	
PHBV	100	90	80	60	Nanofiller (CB, BioC)	2	6	10	14	18
PLA	0	10	20	40	PHBV:PLA blend	98	94	90	86	82

processing. Nanofiller was measured as a weight fraction of the total polymer blend.

Characterization

Interfacial parameters, polymer blend morphology, moduli, thermo-mechanical, and electrical properties were evaluated by video contact analysis, FE-SEM, DMA, DSC, Raman spectroscopy, and 4-point probe impedance spectroscopy measurements.

<u>Contact Angle Analysis</u> To better understand the interactions of the polymer blends during mixing, polar and dispersive components of polymer surface tensions were calculated by measuring contact angles with deionized water and diiodomethane (MI). Contact angles were measured using a video contact angle system with drop sizes of $2.45 \pm .5 \ \mu$ L and a minimum of 5 measurements. Angles were divided into their dispersive and polar components using the Owens-Wendt relationship as described in Section 3 (equations (3.1-3.3)). Table 3.2 shows the known dispersive and polar components of water and MI used as the contact liquid. Matlab code was developed to analyze the surface tensions and predict interfacial interactions, phase separation, and nanofiller localization in the polymer blends and nanofilled composites [47].

It is particularly difficult to consistently measure contact angles for nanofillers in order to determine surface energies. Instead, alternate methods such as absorption and heat of immersion are standard techniques and have been explored in previous studies which provided the literature values for CB used in this study [48, 49].

Liquid	γ	γ^p	γ^d
Water	72.8	51.0	21.8
MI	50.8	0.4	50.4

Table 3.2: Surface tensions for water and diiomethane

<u>Dynamic Mechanical Analysis</u> Dynamic mechanical measurements were conducted on a TA instruments Q800 DMA. A multi frequency-strain experiment in the 3-pt bending configuration was run at a frequency of 1 Hz, amplitude of 20 μ m, and a force track of 125%. The temperature was equilibrated at -40°C for five minutes and increased to 150°C at a constant rate of 5°C/min. During the temperature ramp, storage modulus, loss modulus, and $tan \delta$ data were collected.

Differential Scanning Calorimetry A TA Instruments Discovery DSC (Serial Number DSCI-0220) was used to assess the impact of the nanofillers on the polymers and blends. The nitrogen flow rate was 50 mL/min, as optimized in previous work [50]. Samples were encapsulated in aluminum pans with a target sample weight of 5 mg \pm 2 mg, and heated from -20°C to 180°C in the first heating cycle at a rate of 10°C/min. After equilibrating to 190°C, they were held at 190°C for 2 minutes prior to cooling at 10°C/min to -20°C. The samples were then heated at 10°C/min to 195°C in the second and final heating cycle. The glass transition temperature (T_g) was taken to be the midpoint of the heat capacity change, the melting temperature (T_m) was measured as the minimum of the endothermic peak upon heating, the cold crystallization temperature (T_{cc}) was measured as the maximum of the exothermic peak (when present) upon heating, and the crystallization temperature (T_c) was taken the maximum temperature of the exothermic peak upon cooling (in between the first and second heating cycles).

The percent crystallinity of the PHBV and PLA in the matrix, χ_P , was determined using a modification to the standard equation for single phase composites [51]:

$$\chi_P \left[\%\right] = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^\circ} \left(\frac{1}{W_P}\right) \cdot 100\%$$
(3.12)

where ΔH_m and ΔH_{cc} are the enthalpies of melting and cold crystallization measured upon heating, W_P is the weight fraction for the PHBV or PLA, and ΔH_m° is the reference value for 100% crystalline polymer: 146 J/g or 12.5 kJ/mole [52, 53] for PHB and 93.7 J/g for PLA [54]. As a reference, a typical value for the crystallinity of annealed PHB samples measured by Barham was 86% *et al.* [52]. To convert between volume and weight percent, densities of 1.24 g/cm³ for PHBV and 1.25 g/cm³ for PLA were used. Sample density was measured using a Mettler Toledo XS205DU Excellence series analytical balance with the Mettler Toledo Density determination kit for Excellence XP/XS analytical balances. The measurement is a buoyancy technique based on the Archimedes' principle.

To evaluate the effect of BioC on each of the individual biopolymers, DSC was used to evaluate neat PHBV and PLA compared with each of the polymers with BioC. BioC was added on top of each of the biopolymers prior to the first heating cycle. The melting endotherms of the neat polymers were compared to the endotherms of the first and second heating cycles in the BioC nanofilled biopolymers.

<u>Scanning Electron Microscopy</u> To obtain a cross section of the nanofilled blends, samples were cryo-fractured using liquid nitrogen. Examination of fracture surfaces though FE-SEM was conducted on a Supra 55VP System 2512 at 1 kV with an SE2 detector. Samples were uncoated. Nanofiller and matrix microstructure were characterized and the particle-matrix interfaces were imaged along with assessing potential localization of the nanofillers.

<u>Impedance Spectroscopy</u> The polymers' resistivity, impedance, capacitance, and phase angle were measured using a Hioki 3522-50 LCR HiTester in the 4 point configuration at room temperature. Each data point is the average of 3 measurements taken from 0.1 Hz to 10^5 Hz. The percolation threshold for the composites was calculated using a Sigmoidal–Boltzmann function [55]:

$$\rho = \rho_l - \left(\frac{\rho_l - \rho_u}{1 + e^{\frac{\varphi - \varphi_c}{\Delta\varphi}}}\right) \tag{3.13}$$

where ρ is the measured resistivity, ρ_l is the lower limit for resistivity, ρ_u is the upper limit for resistivity, φ is the percentage of CB in the blend, φ_c is the percolation threshold, and $\Delta \varphi$ is the slope in proximity to the percolation threshold. The data for resistivity from impedance spectroscopy at 10³ Hz were fitted using the curve fitting toolbox in Matlab R2018b.

<u>Raman Spectroscopy</u> A fully integrated high resolution Raman microscope for confocal Raman analysis, Horiba LabRam HR Evolution NIR, was used to evaluate CB, BioC, and nanofilled composites for graphitic content. The confocal microscope was used for optical images of the composite samples at 20xLWD and 50xLWD. During Raman spectral acquisition, Raman spectra were acquired at 50xLWD and 100x, the stigmatic spectrometer was used with a grating of 1800 gr/mm, and the 532nm 100mW laser at 1%. To reduce the impact of heating in the samples, the acquisition time was 3 s, and the spectra were accumulated for 3 acquisitions. Raman spectra were recorded between 1000 and 1800 cm⁻¹, which corresponds to the spectral region that provides data on the microstructure of carbons giving a measure of the graphite band at 1530-1610 cm⁻¹ (G) and the disorder-induced band at 1320-1370
	Contact	Angles	Surface Tensions			
	θ H ₂ O θ MI		$\gamma~(20^{\circ}{ m C})$	$\gamma~(190^{\circ}{ m C})$	γ^d	γ^p
	\deg°	\deg°	$(\mathrm{mJ/m}^2)$	$(\mathrm{mJ/m}^2)$	$(\mathrm{mJ/m}^2)$	$(\mathrm{mJ/m}^2)$
PHBV	$64.55 \pm (1.06)$	$47.24 \pm (0.98)$	45.095	35.195	32.365	12.729
PLA	$64.00 \pm (0.66)$	$62.02 \pm (3.05)$	40.996	31.096	23.892	17.104
CB [48, 49]	-	-	98.1	87.9	84.1	3.2

Table 3.3: Contact angles and surface tensions using the Owens-Wendt model

cm⁻¹ (D) [30, 56, 57]. The cftool in Matlab was used to fit gaussian exponentials to the CB and BioC peaks observed in this region to determine the peak locations for D and G peaks and the intensity ratio, I_D/I_G [58].

Results and Discussion

Evaluation of Blend Morphology and Nanofiller Localization

<u>Predictions from Interfacial Tension</u> Contact angle analysis with water revealed that the two polymers exhibit hydrophilic characteristics as contact angles were below 90°. In addition, evaluation with MI showed that both PHBV and PLA exhibit dispersive dominate components (Table 3.3).

Table 3.4 shows predictions of miscibility of the polymer blends and the localization of the nanofiller within the blends made from equations (3.9) and (3.10). A negative spreading coefficient between PHBV on PLA suggests that the PHBV phase is immiscible with the PLA phase. The tension between the CB and PHBV is significantly lower than that between the CB and PLA, suggesting that the CB will preferentially localize in the PHBV phase. This predicted separation is further

	Compo	Component Interfacial tensions mN		s
			\overline{m}	
	PHBV/	PLA	1.924	
	PHBV	/CB	5.187	
_	PLA/	СВ	8.682	
Blend (i:j)	Spreading Coef	$ heta_{ij}^{o}$	Wetting Coef	Particulate localization
PHBV:PLA	-6.0072	29.918	-7.4971	PHBV
PLA:PHBV	2.1592	150.08	7.4971	PHBV

Table 3.4: Interfacial tensions and spreading coefficients between polymers and nanofiller

supported by the negative wetting coefficient between CB on the PHBV major phase, and a positive wetting coefficient with the PLA major phase. These equations predict that for the blends studied here, PLA will form an immiscible structure within PHBV while CB will reside in the PHBV phase.

<u>Verification of Nanofiller Partitioning and Blend Morphology</u> Figure 3.1 shows FE-SEM micrographs of an 80:20 PHBV:PLA blend with and without CB and BioC nanofiller. Immiscibility of PLA in PHBV is seen in its sea-island structure (Figure 3.1a), as predicted by the surface tension results. As CB is added to the blend (Figure 3.1b), it appears to localize in the major PHBV phase while the PLA phase is left absent of nanofiller. This morphology observed via FE-SEM shows a granularity characteristic of the CB nanofiller, and is comparable to other studies where SEM observation of carbon black localization was verified with transmission electron microscopy (TEM) [59,60]. Furthermore, the addition of CB does not alter the immiscibility of the two polymers. The effects of adding BioC to the blend



Figure 3.1: FESEM Images of 80:20 PHBV:PLA with: (a) no nanofiller, (b) 6% CB, and (c) 6 wt% BioC.

can be seen in Figure 3.1c. In the blend with BioC, there is no visual distinction between the two polymer phases. Based on this observation and additional supporting evidence through mixing experiments, rheology, and DSC, we hypothesize that BioC reacts with the biopolymers, potentially preferentially depolymerizing the PLA phase. Previous studies have observed that reduced molecular weight PLA is miscible in PHBV and vice versa [8,61–64]. Therefore, the lack of observable phase separation in FE-SEM is potentially indicative of this molecular weight reduction. In summary, the partitioning of the CB nanofiller behaves as predicted. The interactions of the BioC with the polymer blend are more complex and are discussed in additional detail in Sections 3 and 3.

For the surface energy and partitioning predictions made in Section 3 to be accurate, the filler particle size should be smaller than the minor phase regions of the blend. The as-received lignin yielded BioC with an average particle size of approximately 100 μ m, larger than the 1-3 μ m domains of the PLA in the PHBV (Figures 3.1a & b and 3.2a). The milled lignin yields BioC with a comparable particle size to that of the CB (Figure 3.2). This nano size enables the filler material to reside in either the minor or the major phase of the blend.

Electrical and Mechanical Percolation of Nanofillers



Figure 3.2: FE-SEM of (a) un-milled BioC, (b) milled BioC, and (c) CB shows that the size reduction of the BioC after milling is comparable to the particle size of the CB.



Figure 3.3: Probe orientation on Samples

Impedance Spectroscopy of Polymer Blends Impedance (Z) is defined as the effective resistance of a component to an alternating current made up of real (Z') and imaginary (Z") components (Z = Z' + jZ"). The real and imaginary components of impedance are classified as resistance and reactance respectively. As frequency is increased, Z' will rapidly decrease in insulators and remain constant in conductive materials. Figure 3.4 shows the resistance, R, and impedance, Z, by weight percent CB (Figures 3.4a and 3.4b) and by volume percent PLA (Figures 3.4c and 3.4d). Figure B.1 in Appendix C shows the full spectrum data collected from impedance spectroscopy. For blends with CB filler content below 18%, there is a significant decrease in Z around frequencies of 10^4 Hz (shown in Appendix Figure B.1). This

frequency is considered the characteristic frequency (f_c) at which a dependency on frequency forms. Insulators below f_c behave independently of frequency until frequency is increased above f_c where they become frequency dependent. Samples above 18% CB did not experience this drop off and were considered to behave independent of frequency.

As expected, increasing the percentage of CB added to the matrix increased the conductivity of the nanofilled blend. Using the Sigmoidal-Boltzmann function to fit the resistivity showed that with increasing volume percent of PLA, the percolation threshold (φ_c) shifted from 3.6 % in neat PHBV to a minimum of 1.6 % for 80:20 PHBV:PLA. Table 3.5 gives the values for φ_c with the PLA percentage of the blend. Depending on the conditions for the selective localization of CB at the interface or in one of the polymer phases, in this case PHBV, φ_c changes with the relative amounts of the polymer phases in the system [65, 66]. Other researchers have seen a similar optimization in the mechanical properties for a related 80:20 system [67].

The 80:20 PHBV:PLA 2% BioC sample that was fabricated and measured, had a resistance of $3.43 \times 10^8 \Omega$ as compared to $2.99 \times 10^8 \Omega$ for the 2% CB samples, indicating that BioC has the potential to perform similarly to CB when the BioC is produced via the method described herein, provided that challenges during composite fabrication (Section 3) can be overcome. Converting the measured resistance to resistivity, at 18 wt.% CB the resistivity of the PHBV:PLA nanocomposites ranges from 128 $\Omega \cdot cm$ to 167 $\Omega \cdot cm$, which is comparable to commercially available filament (~ 0.5–115 $\Omega \cdot cm$) [35, 36].

<u>Polymer-Nanofiller Interactions</u> Raman spectroscopy provided insight both into the graphitic content of the BioC as well as the polymer-nanofiller interface in the blends. Table 3.6 gives the D and G bands for BioC as compared to previously

PHBV:PLA	$arphi_c$		
vol.%	wt.% CB		
100:0	3.6 ± 0.02		
90:10	2.4 ± 0.90		
80:20	1.6 ± 0.60		
60:40	2.4 ± 0.01		

Table 3.5: Percolation threshold, φ_c , with volume percent PLA

characterized CB [56]. As expected, for both CB and BioC, only partial graphitization is present, as evidenced by the contribution of the D band which corresponds sp^3 carbon and is attributed to a higher proportion of defects [57, 68]. The intensity ratio between the D and G bands (I_D/I_G) is similar between CB and BioC, potentially indicating similarities in the graphitic and disordered carbon content, although this relationship is complex and is also linked to pyrolysis conditions [69–71]. Raman spectroscopy does support the formation of sp^2 states in the lignin-derived BioC which contribute to electrical conductivity.

Raman spectra provide insight into the polymer-nanofiller interaction via excitation energy shifts upon being incorporated into composites [72]. The Raman spectra corresponding to the D and G bands of both nanofillers were clearly observable in the composites. The CB nanofilled composites had a minimal downshift in the G and D peak intensities upon incorporation of the CB. The BioC showed a more significant upshift in the G band of 39 cm⁻¹. This G-band shift is often observed in chemical modification of the carbon, the presence of electron-donor or acceptor impurities, and surface interactions at the polymer-filler interface [72,73]. Given that



Figure 3.4: Four point impedance spectroscopy of PHBV:PLA blends with increasing CB nanofiller percentages at 10^{3} Hz: (a) resistance versus CB%, (b) impedance versus CB%, (c) resistance versus PLA fraction, and (d) impedance versus PLA fraction.

there is a complex relationship between the biopolymers and the lignin-derived BioC (Section 3), this shift can likely be attributed to that interaction.

	D	G	$I_{\rm D}/I_{\rm G}$
	$(1320-1370 \text{ cm}^{-1})$	$(1530\text{-}1610 \text{ cm}^{-1})$	
CB [56]	1359	1604	1.12
BioC	1366	1534	1.13
80:20, 6% CB	1342	1599	1.08
80:20, 6% BioC	1368	1573	1.03

Table 3.6: Graphitic (G) and disordered (D) bands and peak intensity ratio (I_D/I_G) in CB and BioC nanofilled blends

<u>Dynamic Mechanical Analysis</u> Figure 3.5 shows the mechanical analysis of a subset of the PHBV:PLA:CB nanocomposites for blends below or near the percolation threshold (2% CB) and above the percolation threshold (10% CB). At low temperatures, below the T_g for PLA, there is an increase in elastic modulus of ~ 5500 MPa ± 1695 MPa for the high versus low nanofilled composites. This increase is likely due to the combined increase in PHBV and PLA crystallinity between the 2% and 10% CB composites (Figure 4.1a). At high temperatures, the storage modulus of the composites is primarily affected by the blend ratio (PHBV:PLA).

The loss modulus is related to the material's ability to dissipate mechanical energy and the loss tangent $(tan \ \delta)$, or the ratio between the loss and storage moduli, is related to damping. In composites these values can be linked to interfacial interactions and toughness [74, 75]. Both were influenced by the CB content and blend ratio, with the loss modulus at high temperature increasing slightly in the high nanofilled composites while decreasing with increasing PLA content. There is not a clear dependence of $tan \ \delta$ on CB or blend ratio except for around T_g . All blends show a prominent peak in $tan \ \delta$ around 65.5 °C ± 2.3 °C for 2% CB and shifted upwards to 70.4 °C ± 1.3 °C for 10% CB. The observed peak is near the T_g for PLA, however as even the 100% PHBV composite shows this peak, there is also a contribution due to the presence of the nanofiller. For blends with PLA, the magnitude of the $tan \delta$ peak decreased between the low and high CB composites, indicating that the presence of additional nanofiller reduced material damping around T_g . For all of the blends there was a shift in $tan\delta$ towards higher temperatures with increasing CB content, which can be attributed to the increased nanofiller content inhibiting chain movement [76,77]. This shift can also indicate increased thermal stability in the nanofilled composites. The nanofilled composites also improved temperature stability in the loss and storage moduli over that of neat PHBV (data not shown), which started to decrease around 105 °C as compared to ~120°C for the nanofilled composites. Like the electrical percolation of the nanofiller through the polymer blends, the increases in storage modulus and $tan \delta$ can be linked to the intercalation of the nanofiller through the matrix.

Nanofillers and Fabrication

The behavior of the nanofillers during fabrication was highly dependent on the nanofiller type, CB or BioC. Melt rheology during compounding showed that the melt viscosity of the CB blends increased with increasing nanofiller content, while the viscosity of the BioC blends decreased significantly with the addition of the nanofiller. This effect became more pronounced with increased addition of BioC. DSC showed a modest effect on the melting temperature (T_m) and crystallinity (χ) upon the addition CB to the blends. In the case of BioC, the addition of small amounts of nanofiller had a pronounced effect on both T_m and χ .

<u>Rheology During Extrusion</u> In addition to modifying the electrical and mechanical properties of the solid composites, the nanofillers had disparate effects on the melt



Figure 3.5: A subset of the DMA data (for 2% and 10% CB) showing: (a) storage modulus, (b) loss modulus, and (c) loss tangent (tan δ) for PHBV:PLA = 100:0, 90:10, 80:20, and 60:40.

rheology of the blends during mixing. For CB, the rheology measurements during the mixing cycle of the extruder were largely as expected. Early in the mixing cycle, viscosity peaks prior to full mixing of the nanofilled biopolymer blends. As filler and polymers mix, the viscosity of the system begins to decrease until it plateaus. This plateau indicates that the nanofillers are incorporated and melt blending has stabilized, which occurred by 5 minutes for all CB samples. Also as expected, as CB increased in the blends, the melt became more viscous (Figure 3.6). This effect is

attributed to the added amount of filler in the mixture. Alternatively, the viscosity of BioC blends drops to zero nearly immediately as the filler is added, resulting in a polymer blend that is too fluid for extrusion and injection molding. Due to this rapid reduction in melt viscosity and underlying material causes for the reduced viscosity, BioC nanofilled blends above 2 wt.% could not reproducibly be processed into dimensionally stable composites. The unexpected effect of the BioC on melt viscosity is likely due to chemical reactions with the polymer matrix, as described in Section 3 and Appendix B.



Figure 3.6: Melt rheology of the 80:20 PHBV:PLA blends during melt blending. Increasing wt% of CB causes an increase in the viscosity of blends during mixing.

<u>Differential Scanning Calorimetry</u> Figure 3.7 shows the DSC results for the melting peaks of the blended polymers with increasing wt.% CB. In Figure 3.7a for neat PHBV with CB, the melting peak shifts slightly towards lower temperatures with increasing CB. With increasing PLA content in the blend, Figures 3.7b-3.7d, the impact on the melting behavior becomes more pronounced. Figure 3.7d for the blend (black line) clearly displays the split melting peak, PHBV (170.1 °C) and PLA (149.3 °C), anticipated for a phase-separated blend [1, 64, 75]. With increasing CB,

there is a reduction in the main melting peak areas for both components, which results in a decrease in crystallinity, χ , attributed to these primary peaks. This reduction is shown in Figure 4.1a (solid lines, PLA 10%-40%), with the reduction of χ for PHBV. After an initial increase at low CB%, the crystallinity of the PLA phase remains largely unchanged with increasing CB, Figure 4.1a (dashed lines), due in part to attributing the shoulder peaks to the PLA phase. This increase in peak shoulders and the shift toward lower temperatures (e.g. Figure 3.7d) is indicative of decreased crystallite size and order likely due either to molecular weight reduction in the PHBV component, PLA component or both, or nanofiller-induced disruption of the crystalline phases [?,?,50].

Another feature, most clearly observable for Figures 3.7c and 3.7d, is the presence of a cold crystallization peak, which is most pronounced for CB *wt.*% of 10% and above. This peak shows a general trend of shifting towards lower temperature with increased CB (Figure 4.1b, dashed lines). The presence of cold crystallization indicates barriers to full crystallization during cooling. Because PLA has a cold crystallization peak in the region of the transition observed in the nanofilled composites, we attribute this cold crystallization to the PLA phase (Appendix C, Table B.1) [78]. The presence of cold crystallization with increased CB supports nanofiller disruption of the crystallization process in the blends. Appendix C, Table B.1 gives the complete DSC data for the CB nanofilled blends.

In addition to the reduction in crystallinity in the PHBV phase due to the CB content, there is a more pronounced reduction with the increase in PLA content. Also, while the PLA phase shows a reduction in the cold crystallization peak, the crystallization peak of the blend has an initial increase due to the presence of the nanofiller and then remains largely independent of CB content. Therefore, while χ shows some effect due to the nanofiller, the PHBV phase is influenced primarily by

the vol% of PLA. Toughness and physical effects of aging in PHBV:PLA blends have been shown to improve above that of the neat polymers, because of this tailoring of crystallinity and phase interactions, indicating the potential of these blends for enhanced stability and mechanical properties [8,67].

In contrast, the effects of adding BioC to the blends were significantly different. As discussed in Section 3, when added to the melt, the viscosity decreased substantially. To explore this effect, Figure 3.9 shows a comparison between neat PHBV, neat PLA and BioC added to PHBV and PLA prior to the heating cycles in the DSC. BioC has a substantial effect on the melting endotherm for both PLA and PHBV. PLA:BioC exhibits a melting peak around 150°C on the first cycle, as would be expected in neat PLA. PHBV:BioC also has a melting peak similar to the neat polymer on the first cycle. After mixing with BioC and undergoing a thermal cycle, PLA:BioC exhibits no melt peak implying that PLA no longer has crystalline regions. A similar effect takes place in the PHBV:BioC, with a significant reduction in the area of the peak. These results indicate that the significant material changes in the blend upon addition of this lignin-based BioC are likely due to a reaction between the BioC and the polymers. This reaction renders use of BioC prepared from this source difficult for use in extrusion and injection molding. Additional evidence of this reaction is given in Appendix B, Figure B.1.



Figure 3.7: Stacked DSC (endo up) of the melting peak of PHBV:PLA blends with increasing wt.% of CB: (a) PHBV:PLA = 100:0, (b) PHBV:PLA = 90:10, (c) PHBV:PLA = 80:20, and (d) PHBV:PLA = 60:40.



Figure 3.8: DSC results summarizing: (a) the percent crystallinity (χ) as determined through DSC for (solid lines) the PHBV phase of the blend and (dashed lines) the PLA phase of the blend. The impact of the *vol.*% of the polymer within the blend is more significant in determining crystallinity than the wt% of CB; (b) the shift in crystallization temperature, T_c , with increasing CB for the PHBV phase of the blend (solid lines) and the shift in cold crystallization temperature, T_{cc} for the PLA phase of the blend (dashed lines). For the PLA phase, T_{cc} decreases with increasing wt% of CB.



Figure 3.9: DSC of the melting peak (endo up) of (blue) PHBV and (green) PLA showing (a) the neat polymer, (b) the neat polymer upon adding BioC in the first heating cycle, and (c) the same sample as in b, in the second heating cycle. The effects of mixing BioC with neat polymers is evident in the reduction of both melting peaks, resulting in the absence of a crystalline melting peak for PLA.

Conclusions

Conductive nanofiller localization was tailored through phase separation in the PHBV:PLA blends. The partitioning of the nanofiller for the phase-separated morphology of the blends was calculated from surface energies derived from contact angle analysis. FE-SEM was used to verify the location of the nanofillers; CB localized within the PHBV phase as predicted by our calculations. The lignin-derived BioC had a more complex reaction with the biopolymers, as evidenced by the change in blend morphology as observed via FE-SEM, a rapid reduction in melt upon addition of BioC, and DSC results that show a significant reduction in the PHBV melting peak and the absence of a melting peak for the PLA phase. These material changes upon the addition of BioC are likely due to a reaction occurring between the biopolymers and BioC, potentially due to residual species from the Kraft lignin process. The rapid reduction in melt viscosity and source of lignin-BioC/polymer interaction will be critical to implementing BioC as a potential alternative to CB.

The impedance of CB in PHBV:PLA blends was measured for weight percentages of 0, 2, 6, 10, 14, and 18 *wt.*% CB and PHBV:PLA blends of 100:0, 90:10, 80:20, and 60:40. The phase-separated blends also modified the percolation threshold, which varied between 3.6% and 1.6% CB with the maximum value for 100% PHBV and the minimum for the 80:20 blend. When comparing CB composites with BioC composites with 2% nanofiller (approximately at the percolation threshold), the 2% BioC had a resistance of $3.43 \times 10^8 \Omega$ as compared to $2.99 \times 10^8 \Omega$ for the CB, indicating that BioC could perform comparably to CB as a conductive nanofiller if the processing challenges can be overcome. Results at higher BioC loading would be required to establish if this comparable behavior is present for more conductive samples. Both nanofillers exhibited graphitic content individually and incorporated into PHBV:PLA blends, as determined via Raman spectroscopy, which is necessary for a conductive network of nanoparticles. These results further support the use of nano sized lignin-derived BioC as an electrically conductive nanofiller in biocomposites.

INVESTIGATING EFFECTS OF LIGNIN ON PHBV AND PLA

Introduction

Feed stock choice for BioC production has a significant impact on its final conductivity, and while lignin exhibits processing issues such as thermal instability and reduction of crystallinity in PHBV blends it remains one of the best sources for highly conductive BioC. Containing around 60 wt% carbon in its natural form, lignin holds a significant advantage over other less carbon available sources [11]. Lignin is the second most abundant natural polymer available in the world, being readily produced as a by-product of the paper and pulp industry [79,80]. Industry typically discards or burns lignin as a fuel creating a potential need to develop value -added lignin products. Employing lignin as a source of BioC harnesses much more of the material's potential and can additionally provides significant benefits as a filler in polymer blends.

Processing issues surrounding the addition of lignin sourced BioC to PHBV:PLA has been attributed to several potential causes but have left several unanswered questions [80–84]. When lignin is added to PHBV it can have deleterious effects on the polymer by increasing the temperature of crystallization, hindering the average size of the lammellar stacks [82,83]. Specifically, when alkaline lignin (AL) is added to PHBV it is found to enhance nucleation but hinder growth of the crystalline region and decrease thermal stability at elevated temperatures [82]. In contrast, blending PLA and AL has been shown to increase the thermal stability of PLA and prevent hydrolytic degradation though it still does not favor the crystallization of the polymer [84]. These effects are not specifically attributed to the alkalinity of the filler material and similar experiments have not been conducted on dealkaline lignin (DAL). Investigating the possible effects that the alkalinity of the filler has on the polymer blend will provide a substantial grown in understanding of the composites compatibility.

DSC, thermogravimetric analysis (TGA), and gel permeation chromatography (GPC) are used to better understand the effects that DAL and AL have on polymers PHBV, PLA. and their blends. In particular effects on polymers crystallinity, thermal stability, and molecular weight when combined with AL and DAL are investigated.

Materials and Methods

Materials

Both DAL (CAS: 9005-53-2 Tokyo Chemical Industry co. LTD) and AL (CAS:3068-05-1 Tokyo Chemical Industry co. LTD) are purchased from Sigma Aldrich (St. Louis, USA) and stored in a furnace at 105°C prior to investigation. Commercially available PHBV (ENMAT Y 1000p, >98% purity) in pellet form is provided by Tianan (Nigbo City, China). PLA (2003D), also in pellet form, is supplied by Nature Works (Minnetonka, USA).

Methods

Several methods used to characterize the effects of AL and DAL on PHBV and PLA are hot plate observations, DSC, GPC, and TGA. Hot plate observations are initially conducted in an effort to develop a visual representation of how the filler effects the polymers. DSC is conducted to observe how the filler material effect the crystallinity of the polymer and its effects on thermal properties such as T_g and T_m . To develop an understanding of how AL and DAL might effect the thermal degradation of the polymers, TGA is conducted on the blends. Additionally, TGA is used to analyze neat AL and DAL samples to understand relative regions of mass loss while the lignin is heated up to 1000 °C during BioC production. To investigate the potential for depolymerization reactions initiated by the filler, GPC is run on blended bio-polymer lignin and CB samples to observe any potential drop in molecular weight.

<u>Hot Plate Observations</u> In an effort to gain a preliminary understanding of the effects of lignin on polymers, the fillers and polymer blend were mixed and heated on a hot plate. Polymers are brought to their melting temperatures and held for 1 minute before adding 16 wt% filler material. As filler material is added and thoroughly mixed, the blend is raised to 250°C while observations are made of the sample. As the blend reaches a final temperature, the sample is allowed to cool to room temperature and weighed to to determine mass loss during heating.

Differential Scanning Calorimitry (DSC) TA Instruments Discovery DSC (Serial Number DSCI-0220) is used to assess the impact of the nanofillers on the polymers and blends. The nitrogen flow rate is 50 mL/min, as optimized in previous work [50]. Samples are encapsulated in aluminum pans with a target sample weight of 10 mg \pm 2 mg, and heated from 20°C to 180°C in the first heating cycle at a rate of 10°C/min. After equilibrating to 180°C, they are held at 180°C for 2 minutes prior to cooling at 10°C/min to -20°C. The samples are then heated at 10°C/min to 230°C in the second and final heating cycle. The T_g is taken to be the midpoint of the heat capacity change, the T_m is measured as the minimum of the endothermic peak upon heating, the T_{cc} is measured as the maximum temperature of the exothermic peak upon cooling (in between the first and second heating cycles). The high temperature during the second cycle is chosen in an effort to observe the effects of lignin on the polymers as the temperature is increased. Crystallinity of the polymers is calculated using the same method as mentioned above by Arroyo et al. [16]. <u>Gel Permeation Chromatography (GPC)</u> To observe the effects of lignin on the molecular weight of the polymers , GPC (Agilent HPLC 1260 series, Waters Styragel HR 4 (7.8 × 300 mm, Milford, MA,USA) column (part No. WAT044225), THF (HPLC grade) mobile phase with a flow rate of 0.5 mL/min at 40 °C, UV detector set at 280 nm.) is conducted on neat PLA, PHBV:PLA:CB (80:20:16 wt%) , and PHBV:PLA:BioC (80:20:16 wt%) samples as prepared in [16]. All samples are dissolved at a concentration of 10 mg/ml in tetrahydrofuran (THF) at 60 °C using stir bar agitation at 100 rpm for 1 hour. BioC and CB samples are centrifuged at 4000 rpm for 5 min to allow for particulate separation from the polymer. The solution is then filtered twice through 0.2 μ m filters before loading into GPC. PHBV is only partially soluble in THF so there is only conclusive investigation on the interaction of the PLA component and the filler material.

<u>Thermogravimetric Analysis (TGA)</u> TGA (TA instruments discovery TGA) is conducted on AL and DAL mixed with each of the polymers individually. Samples are heated at a rate of 10 $^{\circ}$ C/min up to 320 $^{\circ}$ C where it is held for 2 mins. Air is used as the gas and mass loss is measured across the entire range.

Results and Discussion

Hot Plate Observations

As an initial approach to observe the effects of lignin on polymers, hot plate mixing provided valuable observations. Most notably, a visual understanding of how the polymer reacts to higher temperatures, and how its degradation changes with addition of filler material can be developed. As the polymer is heated up to its melting temperature the solid can be seen melting into a liquid. Once in the liquid phase and filler material added, there is a significant difference in reaction depending on the filler material and polymer used.

PHBV exhibits the largest reaction as filler material is added. When AL is mixed with molten PHBV, a violent reaction involving smoke and severe burn off of the polymer is noticed at 180°C, and by 200°C the polymer has completely burned off with only lignin remaining. In contrast, when DAL is added to molten PHBV, the reaction is not nearly as severe, and does not occur until 215°C while final burn off occurs near 240°C. As a comparison, the neat sample displays browning and bubbling at 230°C with full burn off near 240°C.



Figure 4.1: Hot plate observations showing: (a) PLA:AL exhibiting no reaction as it is heated up to 240° C; (b) PHBV reacting with AL as evidenced by bubbling and smoking near 190° C.

PLA experiences little to no reactions when mixing with different filler materials. When AL is added to molten PLA no reaction is noticed as it is heated up to 250°C. Similarly, no reaction or burn off is noticed as DAL is added to molten PLA. As neat PLA is heated up to 250°C, there is only slight burn off around 230°C.

The hotplate method provides a quick and effective tool to evaluate how the components of polymer and filler blends react with each other and provided a visual guide to the process occurring during melt compounding. However, there are some limitations when utilizing this method. The temperatures given are effective in their relativity to each other but not comparable to values outside of this experiment. This variation can be attributed to the inaccuracies of measuring surface temperatures of a hot plate with a probe and making the assumption that it is consistent through the polymer blend. While this method was effective for developing an understanding of decreases in viscosity and melt behavior of the blends, DSC was used to quantify changes in melt and crystallization behavior.

Differential Scanning Calorimitry

Figures 4.3 and 4.5 show the effects of adding both AL, and DAL to PHBV and their affects on the polymer's thermal degradation and crystallinity. AL's degradation effects can initially be seen by the change in heat flow occurring around 210°C on the AL sample where it is absent in the neat sample and only present but substantially less severe in the DAL sample. This exothermic heat flow is likely due to the lignin catalyzing the thermal degradation of the polymer. Upon reviewing the cooling cycle in figure 4.3 the effect of this degradation is seen in the significant decrease of the crystallization peak. As a result, the crystallinity of the PHBV:AL with drops 10% from its neat value (Table 4.1). The PHBV:DAL sample experienced only slight degradation around 230°C and a 1% decrease in crystallinity.

In contrast, the PLA experienced little to no change in the T_g and T_m . The PLA used in this experiment had a high amorphous content, >90%, which made observation of crystallization effects on the polymer from the filler material challenging.



Figure 4.2: Cooling crystallization peaks of PHBV with the addition of AL and DAL. The effect of AL can be seen as a reduction in the crystalline peak of the polymer (green line).



Figure 4.3: Crystallization peaks upon cooling for PHBV with the addition of AL and DAL Pre high temp treatment pre high temp treatment needs to be clarified and also watch capitalization.



Figure 4.4: Heating melt peaks of PHBV with the addition of AL and DAL. The effect of AL can be seen as a reduction in the temperature required to drive thermal degradation of the polymer (green line, 220°C).



Figure 4.5: Heating melt peaks of PLA with the addition of AL and DAL. The effect of AL can be seen as a slightly increased melting peak, shifted T_g and trend toward thermal degradation.

Composition	particle $\%$	Tg	Tcc	Tc	Tm	dHm	dHcc	Xc
		°C	$^{\circ}\mathrm{C}$	°C	°C	(J/g)	(J/g)	%
PHBV	0	2.75	-	111.49	174.73	93.379	0.00	64
PHBV/ AL	16	3.22	-	87.64	170.75	66.351	0.00	54
PHBV/ DAL	16	-1.95	-	109.74	170.64	77.517	0.00	63
PLA	0	58.72	-	-	153.10	1.70	0.00	2
PLA/AL	16	55.10	-	-	152.00	2.73	0.00	3
PLA/ DAL	16	60.10	-	-	154.01	0.81	0.00	1

Table 4.1: DSC of polymers mixed with filler materials shows the degree to which the blends are altered.

Gel Permeation Chromotography

To test the hypothesis that there was a reaction between lignin and BioC that caused a de-polymerization of both of the polymers, GPC analysis of the PHBV:PLA:CB and PHBV:PLA:BioC composites is conducted. As mentioned on page 45, the samples are dissolved in THF in which PHBV is only partially soluble. Though this insolubility is not an issue in the PLA sample, it will cause error in the blended samples. The number average molecular weight (M_n) is the ordinary average of the molecular masses of the individual macro molecules, where weight average molecular weight (M_w) is the mass average molar mass, and the polydispersity index (PDI) is a measure of the ratio of M_w/M_n .

Sample	M_w	M_n	PDI
PHBV:PLA:BioC	9157	2605	3.52
PHBV:PLA:CB	7287	1998	3.65
PLA	1449	1358	1.07

GPC revealed that there is likely not a significant drop in molecular weight in the PLA due to the inclusion of BioC when compared to the inclusion of CB. The significantly higher M_w of the blended samples can be attributed to the partial dissolution of PHBV in the and its higher molecular weight. When observing the blended samples through GPC it is seen that the BioC is not likely reducing the degree of polymerization of the PLA, but the effects on the blend as a whole are unknown due to PHBV insolubility. The relatively large PDI is consistent with some larger PHBV chains present in the blended samples. It should be understood that these results are strictly preliminary and need to be re-done in a suitable solvent such as chloroform.

Thermogravimetric Analysis

TGA allows for a more in-depth explanation of how filler materials effect the thermal degradation of the composites. Previous work with similar materials supports the theory that AL may catalyze the thermal degradation of PHBV but not effect PLA as severely.

The thermal stability of both PLA and PHBV is decreased by the addition of filler material from that of the neat polymer. AL, when heated with PHBV decreased the initiation of thermal degradation from roughly 250°C to 220°C. The DAL sample increased the initiation temperature however the final degradation temperature was decreased to 280°C meaning a much more severe burn off of the Figure 4.7. PLA has a much higher temperature of thermal degradation that was not fully explored in this work due to its irrelevance to temperatures experiences during the injection molding process. Again, AL demonstrated much more significant effects than the DAL sample. When heated with PLA, AL decreased initiation of thermal degradation from roughly 310°C to 260°C. The DAL sample exhibited little to no effect on PLA prior to 320°C Figure 4.7.



Figure 4.6: TGA of PHBV with the addition of AL and DAL. The addition of both filler materials decreases the thermal stability with AL having the greater effect.



Figure 4.7: TGA of PLA with the addition of AL and DAL. Though less substantial than the effects on PHBV, AL still has a significant effect on PLA.

Discussion

Alone, each investigation presented here provides interesting results, but together a crucial understanding of how AL and DAL will behave in PHBV and PLA is formed. Previous work shows that there is a decreased crystallinity and thermal degradation between AL and PHBV. Hot plate investigations visually confirmed that the filler material might be reacting with PHBV and not as severely with PLA. This reaction was further shown in DSC, which suggests that there is a slight shift in the Xc and T_m peaks in PHBV but less significant results in the PLA samples. Of those shifts, the larger is influenced by AL. When M_w is investigated though GPC there does not seem to be a significant drop in the PLA samples suggesting that depolymerization is not taking place in in PLA samples, though these results are only preliminary. TGA provided the most significant results as to what might be occurring in the polymer blends while at temperatures relevant for the extrusion and injection molding process. As AL is heated with PHBV and PLA, both samples show signs of thermal degradation with PHBV:AL composites being the most pronounced.

It is likely that a combination of factors led to the complete degradation of PHBV:PLA:BioC composites at 190°C. Lignin samples provide a baseline understanding of potential effects, though its pyrolized state may even further decrease the thermal stability of the blend with less organic material to inhibit degradation. There is also the possibility that a nano-sized filler material has more potential to catalyze degradation with a higher surface area as the filler in this study was not ball milled. Most significantly, it is likely that the mixing process of injection molding ensured that the BioC was affecting the PHBV by lowering its thermal decomposition temperature to a range required for PLA to melt. TGA showed that AL dropped the initiation temperature of thermal degradation to nearly 220°C for PHBV and it is possible that the combination of nano-particulate sizing, pyrolysis of the BioC, and

the mixing environment would decrease that degradation to the 190°C range.

Conclusions

Thorough analysis of the effects of AL and DAL on PHBV and PLA provided a significant understanding of what might have been causing issues in the study outlined by Arroyo and Ryan [16]. Hot Plate observations, DSC, GPC, and TGA have shown that AL can have severe impacts on PHBV specifically. PLA was minimally impacted by the inclusion of AL and DAL during blending. It is likely that the issues encountered during the Arroyo study are due to the increased temperature of the blend (required to melt PLA) and the alkalinity of the lignin used in the sample. This study allows for the recommendation of DAL in use of polymer blends incorporating PHBV with polymers of higher melt temperature. Based on the results of this study DAL is the preferred source of BioC for use in PHBV based composites .

MODELING WORK RELEVANT TO NANOFILLED COMPOSITES

Flow Modeling of Nanofilled Polymer Composites

Introduction

Recent advancements in nanocomposites have greatly expanded the potential application of particle filled polymer blends. Furthermore, the evolution of additive manufacturing allows for these complex materials to reach applications far beyond the lab environment. As these fields grow in popularity, predictions of nanofiller localization and their resulting material parameters, such as conductivity and modulus, are extremely beneficial.

Currently there are a significant number of polymer melt flow simulations available to the public, though their ability to model nanofiller movement is lacking. Solidworks Polymer is an industry standard injection molding software that allows the user to model polymer melt flow into molds and predict points of common issue such as flash and weld lines. Solidworks' parent company, Dassalt studios, also offers another program called BIOVIA which predicts the miscibility of polymer blends, though it neglects all considerations of the extrusion process and effect of nanofillers on the blends. ANSYS provides a nearly all encompassing program, poly flow, that uses CFD techniques to model polymer blends during extrusion, though there is no specification for the ability to incorporate nanofiller.

Hypothesis

If the melt flow phase of polymer nanocomposites can be represented through conventional CFD methods then predictions of nanofiller localization in the overall blend can be made.



Figure 5.1: The open mixing chamber shows the "cycle" channel in blue and the "flush" channel in red.



Extrusion exit port



Port with 2mm die installed

Figure 5.2: Exit conditions of the extruder

Assumptions

- The Polymer melt will "Flash Cool" not altering the morpohology of the blend
- The melt flow does not expand as it leaves the extruder

Methods

<u>Building the Flow Region</u> The flow region of interest can be described by a cylindrical region of diameter d and length l (Figure 5.3). This region represents the polymer flow out of the HAAKKE minilab extruder in a semi-molten state. The diameter is selected based on the extrusion die diameter while the length is selected to be long enough allowing for proper blend modeling but not to long to allow for



l = 20mm

Figure 5.3: Section was drawn and meshed in ANSYS





extended computation time. The part was drawn in ANSYS and meshed there as well.

To further explore the effects of the HAAKE minilab extruder die geometries, the "flush" channel of the machine can be modeled. This region is of interest as there are significant geometrical changes that will have adverse affects on the polymer flow during extrusion. Initially for flow simplicity the machine has a rectangular cross section that leaves the cycle region and is compressed to a smaller region before finally being forced through a circular cross section. <u>Modeling Air flow through the Solver</u> This Project was solved in three distinct steps. First plain PHBV was run through the solver, second a PHBV/PLA blend was run through the solver to examine the accuracy of the blending, third, particulate was included into the blended phase in an effort to understand its location. Below the general solver parameters are outlined, where Tables 5.1,5.2 and, 5.3 outline any differences between the methods.

Governing Equations and Numerical methods

The Model was setup in ANSYS for polymer flow through the section to evaluate its validity. A Pressure based solver was used due to the low mach flow. This solver was chosen in-part due to pressure projection scheme being appropriate for an incompressible flow. The incompressible assumption is valid due to the low velocity and mach number of the problem.

<u>Material Selection</u> For this solver the default values of air were modified to follow ideal gas behaviour. Non-Newtonian-Power law parameters were selected from similar polymer blends such as HDPE and LDPE while surface tension values for the PHBV/PLA polymers were provided from previous research. Carbon was selected for the particulate as a pre-defined Fluent material.

<u>Boundary Conditions</u> The boundaries were selected as the inlet and outlet as defined in the meshing process. The Inlet velocity was set to 0.70 $\frac{m}{s}$, which is a reasonable velocity for these extrusions. The volume fraction of the blends varied during the troubleshooting process and was finalized at 1 indicating a full flow of phase 1.

<u>Considerations</u> Modeling of Figure 5.3 shows an expected velocity and pressure profile of the air as it moves at 0.7 $\frac{m}{s}$ through the cross section, however it does not reveal much about what external effects might have on the flow path. Though these results are interesting, they do not fully reflect the model of polymers moving though



The area on the construction with we

Pressure Profile of the entire section

Focus on the constriction with velocity vectors

Figure 5.5: Exit conditions of the Extruder under air flow

air in a 3mm spectrum as in real world extrusion, but rather air moving through an aluminum tube. Due to this realization, the Aluminum tube solver will not be presented for the rest of the report.

It can be seen in Figure 5.5 that the more influential flow obstruction occurs in the constriction from the outflow channel of the extruder into the 2mm diameter die.

<u>Single polymer flow Modeling of PHBV</u> The primary step in solving the larger problem was to see if the polymer of interest could be modeled through the region of interest. This step was fairly basic requiring few alterations (Table 5.1) to the code including the definition of a Non-Newtonian fluid (Figure 5.6).

/define/models/viscous/turbulence-expert> turb-non-newtonian Enable turbulence for non-Newtonian fluids? [no] yes

/define/models/viscous/turbulence-expert>

Figure 5.6: Code entered into Fluent command line
Table 5.1: Fluent parameters used for PHBV flows

Setup		
General	Solver type	Transient, Pressure-based
	Model:	Multiphase,VOF
	Viscous:	K- ϵ Turbulent
	***	Activate Non-Newtonian Flow in command line
Material	Solid:	Aluminum
	Fluid:	Phase 1: Air
	Fluid:	Phase 2: PHBV (non-Newtonian power-law)
		k=2E4 \textit{Pas}^n , n= .41 , $\nu_{min}{=}.001$, $\nu_{max}{=}1000$
B.C.'s	Inlet:	As described, $V_{f1}=0, V_{f2}=1$
		variable density par.= $1.225 \frac{kg}{m^3}$
		$v_{mixture} = 0.7 \frac{m}{s}$
	Outlet	No back flow(ie: backflow $V_{f2} = 0$)

Solution

Initialization	Type	Hybrid
	Patch	@ t=0
		$V_{f2}=0$ (ie: 100% air in the sys)
Calc. Activities	Sol. Data. export	CFD-Post Compatible
		Select domain and quantities desired to view in results
Run Calc	Solver selections	t_s =.001, N_t =100, Max Iter= 50



Figure 5.7: Volume fraction of Single polymer moving through the extruder

<u>Modeling of blended Polymer flow</u> For the blended phase the model was switched to a mixture in order to prepare for the inclusion of particles. ANSYS's reference database recommends that VOF models are used for two or more immiscible fluids where the mixture model is more appropriated for particulate in mixed flows. This change required that the IC's be set as velocity profiles for each phase and a initial pressure specified as zero. Additionally phase data for the PLA flow was included noting that for the power-law relationship LDPE variables were selected. A surface tension was included as it was calculated in lab via contact angle analysis and the Owens-Wendt relationship. The Volume fraction was set to 80% PHBV and 20%PLA to resemble results produced in lab. In order for ANSYS to recognize the difference between the inlet materials two separate inlet domains must be defined. This domain definition was done by expanding the model toward the screws as can be seen in Figure 5.1 and Figure 5.8.

\mathbf{Setup}		
General	Solver type	Transient, Pressure-based
	Model:	Multiphase, Mixture
	Viscous:	K- ϵ Turbulent
	***	Activate Non-Newtonian Flow in command line
Material	Solid:	Aluminum
	Fluid:	Phase 1: Air
	Fluid:	Phase 2: PHBV (non-Newtonian power-law)
		k=2E4 \textit{Pas}^n , n= .41 , $\nu_{min}{=}.001$, $\nu_{max}{=}1000$
	Fluid:	Phase 3: PHBV (non-Newtonian power-law)
		k=2E4 \textit{Pas}^n , n=.39, $\nu_{min}{=}.001$, $\nu_{max}{=}1000$
	Interactions	Surface tension: $1.924 \frac{mN}{m}$
B.C.'s	Inlet:	As described, $V_{f1}=0$, $V_{f2a}=1$, $V_{f3b}=1$
		variable density par.= $1.225 \frac{kg}{m^3}$
		$v_1 = 0.7 \frac{m}{s}, v_2 = 0.7 \frac{m}{s}, P_o = 0$ Pa
	Outlet	No back flow (ie: backflow $V_{f2,3} = 0$)

Solution

Initialization	Туре	Hybrid
	Patch	@ t=0
Calc. Activities	Sol. Data. export	$V_{f2,3}=0$ (ie: 100% air in the sys) CFD-Post Compatible
	Ĩ	Select domain and quantities desired to view in results
Run Calc	Solver selections	t_s =.001, N_t =50, Max Iter= 50

Table 5.2: Fluent parameters used for PHBV/PLA flows with changes from single flow boxed.



Figure 5.8: New Meshed Shape

<u>Modeling of Particulate flow</u> Initially this portion of the problem was solved using a Mixtures model however through troubleshooting it was realized that a Eulerian model would be more appropriate. The new meshed shape was modified to induce more miking within the blend while the particulate injection was made at the center of the polymer entrance.

Setup		
General	Solver type	Transient, Pressure-based
	Model:	Multiphase, Eularian
	Viscous:	K- ϵ Turbulent
	Discrete Phase	ON, Carbon phase-4
	***	Activate Non-Newtonian Flow in command line
Material	Solid:	Aluminum
	Fluid:	Phase 1: Air
	Fluid:	Phase 2: PHBV (non-Newtonian power-law)
		k=2E4 \textit{Pas}^n , n= .41 , $\nu_{min}{=}.001$, $\nu_{max}{=}1000$
	Fluid:	Phase 3: PHBV (non-Newtonian power-law)
		k=2E4 \textit{Pas}^n , n= .39 , $\nu_{min}{=}.001$, $\nu_{max}{=}1000$
	Interactions	Surface tension: $1.924 \frac{mN}{m}$
B.C.'s	Inlet:	As described, $V_{f1}=0, V_{f2a}=1, V_{f3b}=1$
		variable density par.= $1.225 \frac{kg}{m^3}$
		$v_1 = 0.7 \frac{m}{s}, v_2 = 0.7 \frac{m}{s}, v_4 = 0.7 \frac{m}{s}$ $P_o {=} 0$ Pa
	Outlet	No back flow (ie: backflow $V_{f2,3} = 0$)

Solution

Initialization	Туре	Hybrid
	Patch	@ t=0
		$V_{f2,3}=0$ (ie: 100% air in the sys)
Calc. Activities	Sol. Data. export	CFD-Post Compatible
		Select domain and quantities desired to view in results
Run Calc	Solver selections	t_s =.001, N_t =50, Max Iter= 50

Table 5.3: Fluent parameters used for $\rm PHBV/PLA/Carbon$ flows with changes from Blended flow boxed .

<u>Conclusions</u> Through step by step development of these methods, a Fluent model that provides some visual aid to how particles effect polymer blends was produced. The results listed above support the hypothesis stated that if the melt flow phase of polymer nanocomposites can be represented through conventional CFD methods then predictions of nanofiller localization in the overall blend can be made. However there are significant limitations to the solver and methods used. There are significant blurry boundary lines with in the flow region, and the ability to include a wettability coefficient for the particulate was not readily found. Going forward it would be beneficial to this project if a wettability coefficients were able to be defined, the ability to create a solid interface investigated, and finally develop more globular style blends in the polymer. This project provides a reasonable approach to understanding how the physics of injection molding effects particulate location in ternary polymer blends.

Future work in Computational Fluid Dynamic Predictions of Polymer Blend Morphology in Droplet Microfluidics

Introduction

Microfluidic droplet generation devices have been used to produce consistent droplets of immiscible blends repeatably in industry and research applications that have exciting potential in the field of polymer science [85, 86]. Typically the droplet branch of microfluidics involves separating a heterogeneous sample into many microsized droplets suspended in a carrier fluid [86]. This blend is usually a combination of a water based material suspended in oil, however there is potential that this method is applicable to immiscible polymer blends. Immiscible polymer blends at their melting point may be able to replicate droplet formation allowing for consistent and custom tailored material properties in binary and ternary polymer blends.

Variability of polymer surface characteristics and interactions can further complicate this process, however there are methods to address and predict interactions within the blend. The Owens Went theory in conjunction with the harmonic mean method can provide insight into polymers miscibility, and where a select filler material might localize within the blend. Though this insight provides substantial progress in understanding the polymers miteractions, there is still some uncertainty in how exactly the melted polymers might behave in the droplet process. Numerical models have been able to accurately develop an understanding of the droplet formation process [87–89]. If surface tensions can be measured for the polymers individually then their miscibility and performance in droplet micro fluidics can also be predicted allowing for custom tailoring of droplet extruded polymers.

Formulation

The Incompressible form of the Navier-Stokes equations Multiphase 2D flow is a well studied case, the following method is one that has been explored in particular by Desjardins et al. [90]. A common method of solving two phase flows begins with the incompressible form of the Navier-Stokes Equations,

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho} \nabla p + \frac{1}{\rho} \nabla \cdot (\mu [\nabla \mathbf{u} + \nabla \mathbf{u}^{t}]) + \mathbf{g}$$
(5.1)

Where **u** is the velocity field, ρ is Density, p is the pressure, and **g** is the gravitational force. Continuity of the flow region can be described by:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho = 0$$
(5.2)

In the case of a multiphase flow, Γ defines the separation between phases. In phase 1,

the material properties are consistent through the media ($\rho = \rho_1, \mu = \mu_1$) until at the phase boundary. At this point the material properties experience a jump in properties that can be defined as $[\rho]_{\Gamma} = \rho_1 - \rho_2$ and $[\mu]_{\Gamma} = \mu_1 - \mu_2$ while the velocity field across the interface is considered continuous $[\mathbf{u}]_{\Gamma} = 0$. Pressure across the interface is not considered continuous and can be modeled by:

$$[p]_{\Gamma} = \sigma k + 2[\mu]_{\Gamma} \mathbf{n}^{t} \cdot \nabla \mathbf{u} \cdot \mathbf{n}$$
(5.3)

where σ is the surface tension, k the interface curvature, and **n** the interfacial normal.

<u>The Level Set Method</u> The level set method defines the interface as an iso-surface of a smooth function [90,91]. This method allows for automatic handling of topology changes, no need to track the interface, and efficient parameterization. There are two types of level set methods solving, the distance function as proposed by Chopp and the hyperbolic tangent function developed by Olsson and Kreiss [91,92].

Implementing the level set method begins with initializing the interface as a zero level set of a smooth function ϕ .

$$|\phi(\mathbf{X},t)| = |\mathbf{X} - \mathbf{X}_{\gamma}| \tag{5.4}$$

In this form \mathbf{X}_{γ} is the closest point on the interface from a point \mathbf{X} . In one material ϕ is represented as negative, positive in the other and zero at the interface. From this smooth representation of the interface the normal vector \mathbf{n} and curvature of the surface (k) can be computed with ...

$$\mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|} \tag{5.5}$$

$$k = -\nabla \cdot \mathbf{n} \tag{5.6}$$

To transport this interface the advection diffusion partial differential equation can be applied to ϕ .

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = 0 \tag{5.7}$$

Though simple this method of transporting the interphase will cause distortions in ϕ away from the interface which was previously smooth. To re-establish the smoothness of ϕ and ensure stability of the interface ϕ can be re-initialized by a distance function such as the Hamilton-Jacobi equation:

$$\frac{\partial \phi}{\partial \tau} + S(|\nabla \phi| - 1) = 0$$
(5.8)

Where S is a modified sign function, and τ is a psuedo time. Though functional, this re-initialization method has drawbacks in its volume conservation which can lead to innacuracies in the mass of the polymer blend transported.

As opposed to the signed distance function proposed by Chopp, Olsson and Kreiss implement a hyperbolic tangent function to define the phase region reinitialization [92]. This re-initialization addresses the smoothing inaccuracies in the interface during transport.

$$\psi(x,t) = \frac{1}{2} \left(\tanh\left(\frac{\phi(x,t)}{2\epsilon}\right) + 1 \right)$$
(5.9)

 ϵ defines the thickness of the interface profile and ϕ is the signed distance level set. Transport can now occur through the same method of applying eq 5.7 to ψ . In this configuration the interface is now defined at $\psi = .5$ where it was previously at $\phi = 0$. In conservative form with a solenoidal velocity ($\nabla \cdot \mathbf{u} = 0$) transport becomes:

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\mathbf{u}\psi) = 0 \tag{5.10}$$

To ensure that the hyperbolic tangent profile of ψ remains, the level set function must be re-initialized to maintain the shape of the profile.

$$\frac{\partial \psi}{\partial \tau} + \nabla \cdot (\psi (1 - \psi)\mathbf{n}) = \nabla \cdot (\epsilon (\nabla \psi \cdot \mathbf{n})\mathbf{n})$$
(5.11)

Where again τ is advancing the equation in psuedo time. Solving this equation should allow for the proper transport of the defined region.

One significant point of this study lies in the initialization of the flow shape. With most immiscible blends like oil and water, a circular shape can be assumed, however with polymer flows it is possible that the shape may trend to be more ellipsoidal. Droplet shape is something that can be assumed to be circular during development of the numerical model and then simply corrected to fit the actual flow region based on experimental results.

Methods

Though there are many different forms of droplet generators, this work focuses on a simple geometry as seen in Figure 5.9. This geometry was chosen as it develops a basic representation of the flow region which will consist of only two polymers, PHBV as the major phase and PLA as the minor. Initially the flow region will be solved for a simple oil and water mixture and compared to experimental results.

Solving this complex problem will begin by modeling a single drop of minor phase hovering in the major phase by using the level set method. Once the phase region can be verified and the solution determined stable, a uniform velocity in the x



Figure 5.9: As fluid 1 enters the junction it occludes fluid 2 flow until pressure build causes severance in fluid 1 creating uniform droplets. The red box represents the region in which the project will be focusing.

direction will be applied to the flow region to ensure that it responds adequately to movement. After movement of the minor phase through the major has been validated a flow field can be generated and applied to the region. This flow field will be solved through the use of the incompressible Navier Stokes Equations.

<u>Initialization of 2D Hyperbolic</u> After the mesh has been defined, the shape of the minor phase must be specified. For most polymer flow the shape of the minor phase can be initialized through the use of a simple circle equation:

$$r^{2} = (x - h)^{2} + (y - k)^{2}$$
(5.12)

where the radius is defined by r and circle center at (h, k). If experimental results show that the droplet exhibits alternate shapes such as an ellipsoid or other geometries, they too can be defined in this setting. Initialized with symbolic variables this equation can then be plugged into eq 5.9 and solved over the mesh region. This solution should yield the initialized flow region with a hyperbolic tangent transition from phase 1 to 2, and interface Γ located at 0.5.

<u>Re-initialization of the 2D Hyperbolic</u> Now that the 2D shape has been defined, its stability in space must be addressed. The shape must be looped over time ensuring that its location in space is consistent and that any interactions between phases are smooth. The normal vector and curvature of the surface can now be determined as in eq 5.5 and 5.6. Determination of these values is crucial to the pressure solution across the interface.

<u>Transport of the 2D Hyperbolic</u> As stability across time is determined the interface can now be translated by eq 5.10. A delta τ must be calculated with its compression and diffusive components and surface normal used from above. Initially a uniform velocity field (**u**=1) should be applied to the 2D hyperbolic. As the shape is translated across a region of unit length, the solution should take exactly 1 unit of time ensuring a accurate solution.

<u>Application Of the Navier stokes solver</u> Once the shape's transport has been determined stable and accurate in a uniform velocity field, a Navier Stokes field can be generated to transport the shape. This is done by including the Level set method in the Navier Stokes solver, and applying the corrected velocity field to the droplet.

Going Forward

While still in its early stages, this work still allows for a greater understanding of the necessary steps to create a flow model for binary polymer blends in droplet formulation. The governing equations and interfacial solving methods have been defined, regions of interest developed, and plan of solution laid out. Future work should finish the solver as defined here, verify the methods used and their proper application, and vary the materials used in an effort to see if polymer regions and pressure will change greatly with altering surface tensions. Finally, once fully developed the work should incorporate a particle tracker and attempt to predict the localization of a filler material within the binary droplets enabling a time and cost saving understanding of the nano-filled composite droplet production process.

CONCLUSIONS AND DIRECTION FOR FUTURE WORK

Results of this study as related to the research objectives:

1. Develop a method of predicting blend morphology of PLA:PHBV while also predicting CB localization in the blend.

Blend morphology predictions were made through a combination of the Goods Equation the Harmonic mean equation, and contact angles of the polymers with two liquids of known polar and dispersive components (Chapter 3). This evaluation allows for the prediction that PLA will be immiscible in PHBV for all weight percentages and should form a sea-island structure in the blend. By using literature derived surface energies for the CB it was predicted that the filler material would localize in the PHBV matrix for all amounts of the blend. Values obtained using this method were verified by comparison with relevant research and justification through experimental methods. Furthermore, FE-SEM images provided visual verification of the blends' predicted state and an understanding of the polymers' morphology.

2. Determine the percolation constant of PLA:PHBV blends with CB used as the filler material.

Evaluation of three blends of PHBV:PLA with five wt%'s of CB provided a development of the polymer blended percolation value. A minimum percolation threshold was found in the 80:20 blend to be roughly 1.6 wt% CB. Though issues persisted with BioC filler material, comparable resistivity values were measured between the 2 wt% blends indicating a promising potential for the replacement of CB with BioC if these issues are resolved.

3. Determine and quantify effects of adding BioC to PLA:PHBV blends.

When added to PHBV:PLA blends, AL sourced BioC has negative effects that yield unsatisfactory composites. Hot plate mixing, DSC, and TGA show that AL based impacts are specifically a decrease in thermal stability and crystallinity in the PHBV samples with little noticeable effects in the PLA. Effects observed by Arroyo et al. can likely be attributed to pyrolized AL decreasing the thermal stability of PHBV in a well mixed sample. This degradation occurred in the polymer blend as the extrusion temperature was elevated to accommodate the higher melting temperature of PLA.

Ongoing studies into these composites should address the following:

1. Effects of processing parameters such as high treatment temperature (HTT) and feed-stock source on the final conductivity of BioC samples and their compatibility with PHBV:PLA blends.

Follow up work covered in this project investigated the effect of lignin sources on the PHBV and PLA which provided insight into how its BioC product might alter the composite. This follow up work neglects the effects of slow pyrolysis on the lignin and its application as a conductive BioC. Future work should investigate the how altering HTT and alkalinity of the BioC alters its conductivity and its compatibility with PHBV and PLA.

2. Investigate the use of other bio-polymers and particulate localization using the phase localization code developed in this project.

Particle localization predictions provided insight into how PHBV and PLA would react in a blend, and where certain fillers would localize in this composite. This method is easily repeatable with various types of plastics that can be parameterized through contact angle analysis. Though filler localization in the matrix phase is beneficial as discovered in this work, there is potential that interfacial localization may further lower the percolation threshold of the composite. Predictions of what materials might exhibit this phenomena can be made through the methods outlined in Chapter 3. Future work should explore alternate sources of BioC and utilize Owens-Wendt theory to predict the tuneability of the composite.

3. Investigate the use of droplet microfluidics to control particulate localization in the blended composite.

Immiscible polymer blends allow for the manipulation of composite morphology. However there is little to no control of the exact shape, size, and distribution of the minor phase. Advancements made in the field of droplet microfluidics allow for the control of immiscible blend mixing and may allow for similar control in the polymer field. Future work should investigate the ability to control minor phase size, distribution, and shape with in the major through experimental and numerical methods. REFERENCES

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87 Acronyms

- ${\cal M}_n\,$ number average molecular weight
- M_w weight average molecular weight

AL alkaline lignin

 BioC biochar

 ${\bf CB}\,$ carbon black

 ${\bf CNT}\,$ carbon nanotube

DAL dealkaline lignin

DMA dynamic mechanical analysis

DSC differential scanning calorimetry

FE-SEM field emission scanning electron microscopy

GPC gel permeation chromatography

 ${\bf MI}$ diiodomethane

PDI polydispersity index

PHA poly(hydroxyalkanoate)

PHB poly(hydroxybutyrate)

PHBV poly(hydroxybutyrate-co-hydroxyvalerate)

PLA poly(lactic acid)

TGA thermogravimetric analysis

THF tetrahydrofuran

APPENDICES

CODE USED TO DEVELOP PREDICTIONS

APPENDIX A

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This work used the following MATLAB code to produce predictions of the blend morphology.

```
%% Prediction of Ternery Blend Morphology and CB localization
\% this code predicts the morphology of 3 phase polymer blends and
   the \ localization
\% of a nano-particulate using the geometric mean equation, and
   contact
% angles of each polymer
% Inputs: Contact angles of Polymer and liquid
% Outputs: interfacial tension, spreading coef
clc
clear
TI=190;%temperature the Blend is made at (C)
TM=25; % temperature Contact Angle is run at (C)
dt=TI-TM;
% Polymer(i) (CORE)
namei='PGA';
%Contace angels in H20 and DIIMETH
P1 = (72.4 + 66.7 + 56.1 + 67.3 + 75) / 5;\% H20
P2 = (52.7 + 60.1 + 59.5 + 59.6 + 60.3) / 5;\% DIO
[Gi, Gid, Gip, Gim] = OwensWendt (P1, P2, TI, namei, TM); % SURFACE
   tension From owens wendt
dgdti = .06; \%(mj/M^2C)
% These are write over values from a paper to compare too****
Gid = 17.094;
Gip = 8.206;
Gi = 20.546;
Gim=Gi-(dgdti*(TI-TM));
\% Polymer(j) (SHELL)
namej='PLA';
PL1 = (63.15 + 63.25 + 64.7 + 64.4 + 64.5) / 5; \% H20 62.66; \%
PL2 = (65.7 + 59.55 + 65.8 + 59.15 + 59.9) / 5;\% DI; 63.10;\%
[Gj, Gjd, Gjp, Gjm] = OwensWendt (PL1, PL2, TI, namej, TM); % SURFACE
   tension From owens wendt
dgdtj = .06; \%(mj/M^2C)
```

```
% Polymer(k)= (MATRIX)
namek='PHBV';
Pk1=(63.3+65.35+65.55+65.35+63.2)/5;% H20 67.46
```

```
Pk2 = (46.85 + 46.15 + 46.4 + 48.5 + 48.3) / 5;\% DIO 46.34;
[Gk, Gkd, Gkp, Gkm] = OwensWendt (Pk1, Pk2, TI, namek, TM); % SURFACE
   tension From owens wendt
dgdtk = .06; \%(mj/M^2C)
\% Filler CB =
namef='BC';
PF1=86.82;
PF2 = 59.13;
[Gcb, Gcbd, Gcbp, Gcbm] = OwensWendt (PF1, PF2, TI, namef, TM); %
   SURFACE tension From owens wendt
\% Gcbt=98.1; \% as measured at room temp
\% Gcbd = 84.1;\% (200C, mJ/m^2) \%
% Gcbp = 3.2;\% (200C, mJ/m^2)
dgdtcb = .06; %(mj/M^2C)
% ------ Harmonic Mean EQN------
%Interfacial tension
Gij=Gi+Gj-(4*Gid*Gjd)/(Gid+Gjd)-(4*Gip*Gjp)/(Gip+Gjp);
Gik=Gi+Gk-(4*Gid*Gkd)/(Gid+Gkd)-(4*Gip*Gkp)/(Gip+Gkp);
Gkj=Gj+Gk-(4*Gjd*Gkd)/(Gjd+Gkd)-(4*Gjp*Gkp)/(Gjp+Gkp);
```

```
\% spreading coefficient
```

```
Likj=Gkj-Gik-Gij; %spreading coef for I over J In K
Lijk=Gik-Gkj-Gij; %spreading Coef for J over I in K
Ljik=Gij-Gik-Gkj; %spreading Coef for K Over J in I
```

```
if Likj >0
    fprintf('%suwilluuspreaduoveru%suinu%s.u\n', namei, namej, namek)
elseif Likj <0
    fprintf('%suwillubeaduupuatutheuinterfaceuofu%suinu%s.u\n',
        namei, namej, namek)
end</pre>
```

```
if Lijk >0
    fprintf('%suwilluspreaduoveru%suinu%s.u\n',namej,namei,namek)
elseif Lijk <0</pre>
```

```
end
```

```
\% Wetting \ coeff with CB
wij = (Gicb - Gjcb) / Gij; \% PHBV - PLA
wik=(Gicb-Gkcb)/Gik; %PHBV-PP
wkj = (Gkcb - Gjcb) / Gkj; \% PP - PLA
%-----
if wij>1
    phasei = namej;
elseif wij <-1
        phasei=namei;
else
    phasei='Interface';
end
%-----
                       _____
if wik>1
    phasej= namek;
elseif wik <-1
    phasej=namei;
else
    phasej='Interface';
end
%-----
if wkj>1
    phasek= namej;
elseif wkj <-1
    phasek=namek;
else
    phasek='Interface';
end
%---
%
```

Component={namei; namej; namek; namef};% I J K CB

```
makeup={'Shell';'Core';'Matrix';'Fiber'};
ST = [Gi; Gj; Gk; Gcb];
STmelt = [Gim; Gjm; Gkm; Gcbm];
Dispersive = [Gid; Gjd; Gkd; Gcbd];
Polar= [Gip;Gjp;Gkp;Gcbp];
dgdt = [dgdti; dgdti; dgdtk; dgdtcb];
TT= table ( makeup, Component, ST, STmelt, Dispersive, Polar, dgdt);
disp(TT)
%
S='/';
IJ = [namei S namej];
IK=[namei S namek];
JK=[namej S namek];
IF=[namei S namef];
JF=[namej S namef];
KF=[namek S namef];
JI= [namej S namei];
KJI=[namek S namej S namei];
ComponentCouple={IJ;IK;JK; IF;JF;KF};
InterfacialTension= [Gij;Gik;Gkj;Gicb;Gjcb;Gkcb];
Blend={IJ; JI; KJI; 0; 0; 0};
SpreadingCoefficient = [Likj; Lijk; Ljik; 0; 0; 0];
WettingCoefficient = [wij; wik; wkj; 0; 0; 0];
FillerLocalization = { phasei ; phasej ; phasek ; 0; 0; 0 } ;
T=table (ComponentCouple, InterfacialTension, Blend,
   SpreadingCoefficient , WettingCoefficient , FillerLocalization );
\operatorname{disp}(T)
    The above code references the following Owens-Wendt function.
function [Sigs, sigsd, sigsp, Sigm, d, p] = OwensWendt(A1, A2, Temp,
   name, RT)
% Owens Wendt Theory for Surface Enegry Calculation
% Using water and Diiodomethane
% change liquids as necessary
TM Temp; % Melt temp concerned about mixing at
          %Room Temperature
RT = RT:
% Insert Liquid data here
sigl = [72.8]
              % water
       50.8]; %DIMETH
```

%known surface tension values for liquid at room temp

```
% Break into 2 component model
% Liquid on PTFE.. Polar component= 0 Dispersive= 18 mJ/m^2
%thetaPTFE= [113.7
% 100.7 ]; %DIIMETH
% Liquid contact angle on PTFE
```

```
% Computing the Dispersive and Polar components of each
sigld = [21.8 % water%(sigl.^2.*(cosd(thetaPTFE)+1).^2)/72;
50.4]; % DIMETH
% Dispersive component
siglp = [51.0
.4];% sigl-sigld Polar component
```

```
% Insert contact angles for Polymer in question
theta1=(A1); % water
theta2=(A2); % glycerol
```

```
plot(X,Y,'o',X,fit,'-')
legend('data','Linear_Fit')
```

```
% using the slope and the slope intercept to fing the surface
tension
sigsp=(P(1))^2; % slope ie: polar
sigsd=(P(2))^2; % Intercept ie: Dispersive
Sigs= sigsp+sigsd;
fprintf('Surface_Tension_for_')
fprintf(name)
fprintf('\n\n')
fprintf('\unuununununAT_ROOM_TEMPERATURE\n')
fprintf('Overall_surface_Energy_=_%3.3f_mj/m^2_u\n', Sigs);
fprintf('Dipsersive_component_uu=_%3.3f_umj/m^2_u\n', sigsd);
fprintf('Polar_component_uu=_%3.3f_umj/m^2_u\n', sigsp);
```

% Ratio Method of determining the Melt polar and Dispersive components

```
dgdt=.06;% accepted value in Ohmega paper % (11/9)* Go/Tc*(1-(20/
Tc))^(2/9);
Sigm= Sigs-(dgdt*(TM-RT));
d=(sigsd/Sigs)*Sigm;
p=(sigsp/Sigs)*Sigm;
```

```
 \begin{array}{l} fprintf(`\_\_\_\_\_At\_\%3.0f\_degrees\_Celcius\n',TM);\\ fprintf(`Overall\_surface\_Energy\_=\_\%3.3f\_mj/m^2\_\_\n', Sigm);\\ fprintf(`Dipsersive\_component\_\_=\_\%3.3f\_\_mj/m^2\_\n',d);\\ fprintf(`Polar\_component\_\_\_=\_\%3.3f\_\_mj/m^2\_\n',p);\\ end \end{array}
```

<u>APPENDIX B</u>

SUPPLEMENTAL OBSERVATIONS AND METHODS
BioC Modifications to Melt Viscosity

In order to investigate the large reduction in melt viscosity with increasing addition of biochar (BioC), we heated a blend of 80:20 poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV):poly(lactic acid) (PLA) with BioC on a hot plate at a controlled temperature ramp. Figure B.1 shows the visual results of this experiment. Upon initial melting there was an apparent reaction with bubbling and rapid liquefaction of the melt as compared to the blend without BioC. These observations prompted experiments with differential scanning calorimetry (DSC) (Appendix C, Table B.1).



Figure B.1: Reaction of 80:20 PHBV:PLA with BioC. Reaction occurs in close proximity to the melting temperature.

Supplemental processing methods

In order to accurately calibrate the shear rate (γ^*) and viscosity (η^*) during mixing, we measured the volumetric flow rate of our primary phase, PHBV, and applied mixing chamber geometry provided by ThermoFisher Scientific for the HAAKE Minilab II to calculate γ^* and η^* . The Minilab is equipped with a back flow channel designed as a slit capillary with a pressure transducer in the capillary entrance and one pressure transducer at the capillary exit (Figure B.1).

- Distance between the transducers: $\Delta L = 64 \text{ mm}$
- Depth of the flow channel: h = 1.5 mm
- Width of the flow channel: w = 10 mm



Figure B.1: Flow channel of the HAAKE Minilab, provided by ThermoFisher Scientific. The circles denote the pressure transducers.

The pressure transducers measure the pressure drop in the capillary. From the capillary geometry and the pressure drop the shear stress (τ) is calculated:

$$\tau = \left(\frac{h}{2\Delta L}\right) \Delta P = (0.01171875) \Delta P \tag{B.1}$$

where h and ΔL are defined as above, and ΔP is the pressure change between the two pressure transducers. Because the Minilab does not measure the absolute volume of the flow, the values for γ^* and η^* are calculated from the apparent flow volume through the capillary. This apparent flow volume, \dot{V} , is proportional to the screw speed, n:

$$V = C * n \tag{B.2}$$

where the correlation factor, C, was determined experimentally for PHBV by measuring mass flow rate out of the extruder: $C = 2x10^{-7}$. From the volume flow \dot{V} and the capillary geometry, the apparent shear rate (γ^*) was calculated:

$$\gamma^* = \left(\frac{6}{wh^2}\right) = (2.\overline{6}x10^8)\dot{V} \tag{B.3}$$

and from this result the viscosity (η^*) was calculated:

$$\eta^* = \frac{\tau}{\gamma^*} = \frac{wh^3}{12 * \Delta L} \frac{\Delta P}{\dot{V}} = (4.3945 x 10^{11}) \left(\frac{\Delta P}{\dot{V}}\right) \tag{B.4}$$

APPENDIX C

SUPPLEMENTAL DATA

Supplemental Data

Impedance measurements for all frequencies

Figure B.1 shows the data for the poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV):poly(lactic acid) (PLA) blends at carbon black (CB) percentages of 2%, 6%, 10%, 14%, and 18%.

Differential scanning calorimetry

Table B.1 gives the thermal transition temperatures and enthalpies for the complete set of PHBV:PLA:CB blends. As observed in our work and prior studies of blends [64], the ΔH_m of the individual components of the blends can be measured by splitting the melt peak (endothermic) into two main regions and assuming the exothermic ΔH_{cc} peak due to cold crystallization can be attributed to the PLA phase. The resulting crystallinity for each phase of the blend was calculated as described in Section 3.



Figure B.1: Four point impedance testing of PHBV:PLA blends at increasing CB nanofiller percentages: (a) impedance, (b) resistance, (c) angle, and (d) capacitance versus frequency.

Composition	Filler	T_{a}	T_{cc}	T_c PHBV:PLA	T_m	ΔH_m	ΔH_{cc}	X_c
-	wt.% CB	$^{\circ}{}^{g}{}^{\circ}{}$	°Ĉ	°C	°C	J/g	J/g	%
100:0	0	-	_	122	172	92.0	_	63
100:0	2	-	-	126	169	81.7	-	57
100:0	6	-	-	125	171	89.7	-	65
100:0	10	-	-	125	172	85.1	-	65
100:0	14	-	-	126	171	81.8	-	65
100:0	18	-	-	124	171	76.6	-	64
PLA Component								
90:10	2	51.97	113.44	_	152.00	16.24	3.47	13.6
90:10	8	51.36	107.90	-	152.00	16.11	3.38	13.6
90:10	10	54.12	113.29	-	152.00	14.00	3.46	11.2
90:10	14	51.69	104.55	-	152.00	12.70	1.76	11.7
90:10	18	51.28	99.41	-	152.00	16.73	1.79	15.9
80:20	0	57.21	123.17	-	150.00	10.52	3.31	7.7
80:20	2	52.30	0.00	-	153.00	10.46	0.00	7.9
80:20	8	53.19	106.57	-	153.00	14.87	3.04	12.0
80:20	10	53.44	102.46	-	153.00	14.83	3.60	13.2
80:20	14	53.30	105.28	-	153.00	12.56	2.47	11.7
80:20	18	52.18	97.80	-	153.00	16.65	1.60	7.5
60:40	0	52.37	121.60	-	149.00	14.59	9.59	5.3
60:40	2	52.65	117.85	-	153.00	14.06	5.79	8.8
60:40	8	50.66	98.54	-	153.00	21.85	9.39	13.3
60:40	10	53.76	102.00	-	153.00	16.01	7.05	9.6
60:40	14	54.58	100.48	-	155.00	15.30	6.26	9.7
60:40	18	53.74	102.22	-	155.00	14.88	4.08	11.5
PHBV Component								
90:10	2	-	_	125.74	166.88	69.88	-	47.87
90:10	8	-	-	125.13	167.04	65.32	-	44.74
90:10	10	-	-	125.71	169.04	63.78	-	43.69
90:10	14	-	-	125.24	169.08	61.20	-	41.92
90:10	18	-	-	124.74	166.15	55.40	-	37.95
80:20	0	_	_	119.03	170.08	63.96	_	43.81
80:20	2	-	-	125.00	168.03	48.57	-	33.27
80:20	8	-	-	124.83	167.17	55.44	-	37.98
80:20	10	-	-	124.18	166.39	51.97	-	35.60
80:20	14	-	-	124.84	168.13	53.26	-	36.48
80:20	18	-	-	123.14	163.81	40.38	-	27.66
60:40	0	-	-	116.37	168.42	45.85	-	31.40
60:40	2	-	-	123.30	168.72	45.40	_	31.10
60:40	8	-	-	121.96	163.05	30.89	_	21.16
60:40	10	-	-	123.40	167.79	37.18	_	25.47
60:40	14	-	-	121.60	168.12	34.13	_	23.38
60:40	18	-	-	119.65	166.85	28.82	-	19.74

Table B.1: Differential scanning calorimetry of the PHBV:PLA blended polymers.