

WOOD FIBER REINFORCED BACTERIAL BIOCOMPOSITES: EFFECTS OF
INTERFACIAL MODIFIERS AND PROCESSING ON MECHANICAL AND PHYSICAL
PROPERTIES

By

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ABSTRACT

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Derived from renewable resources, polyhydroxybutyrate (PHB) exhibits good mechanical properties relative to its polyolefin based counterparts. Reinforcing PHB with wood fiber (WF) results in a biodegradable composite with costs significantly decreased. In this study, PHB/WF composites are produced with percentages of wood fiber comparable to current commercial wood plastic composites (WPCs). In order to improve mechanical and physical properties, interfacial modifiers were added to the PHB/WF composites and processed through injection molding at levels of 1, 2, and 4% on total. Tensile, impact, density, and water absorption properties were investigated for composites modified with maleic anhydride-grafted PHB (MA-PHB), D.E.R., Uralac, and poly(methylene diphenyl diisocyanate) (pMDI). All interfacial modifiers demonstrated improvements in mechanical and physical properties, however composites modified with pMDI displayed properties far superior from the rest. Fracture morphology has been investigated through scanning electron microscopy (SEM) and indicates enhanced fiber adhesion. Morphological studies utilizing dynamic scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), suggest that pMDI is serving to increase

mechanical properties not by crosslinking of the PHB matrix, but rather through interactions at the fiber-PHB interface. Parallel formulations were also produced through 35-mm extrusion to investigate composite differences due to processing. The mechanical and physical properties of unmodified and modified (at levels of 4% on total) were contrasted for both injection molded and extruded composites through tensile, impact, density, and water absorption testing. Results indicated similar trends in tensile properties for all modified composites through both processing methods. Because of a pre-compounding step through a twin-screw extruder, the injection molded samples indicated higher stiffness and strength due to better dispersion. Differences in density were detected and found to have a significant impact on stiffness and strength. Water absorption tests showed similar trends across modifying agents from injection molding to extrusion. However, variation in fiber orientation within injection molded samples resulted in surface cracking and increased water uptake of specimens.

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Dedication

This thesis is dedicated to my wife Tracie, my parents, and my sister.

CHAPTER 1 - INTRODUCTION

1.1 Background

A new era in environmental consciousness has risen. This is an era in which politicians are considering the effects of energy expenditure and emissions on the effect of global warming, stories of climate change are being reported from all corners of the world, and geopolitical influences are generating concerns over the cost and availability of non-renewable fossil fuels. Since the death of the steam-engine, our society has relied on petro-chemical resources for both energy, and the make-up of much of our consumer products. The U.S. Environmental Protection Agency estimates that in 2005, plastics comprised 11.9% of municipal solid waste. Plastics are surpassed in waste tonnage only by paper products and yard trimmings. Within the more environmentally progressive European market, in 2005, 99.9% of plastics produced were petro-chemically derived (Toloken, S., 2007).

Currently filling niche applications such as utensils, food packaging, grocery bags, and mulch films, biopolymers fill an insignificant share in the current marketplace. However, due to the fact that biopolymers are biodegradable and are produced from renewable resources, much attention has been focused on expanding the market for biopolymers. Japan's government for instance wants 20% of the country's plastic to come from bio-based sources by the year 2020 (Toloken, S., 2007).

Biopolymers are natural polymeric materials either grown by or derived from renewable resources. The former series of biopolymers includes soy protein, starch, and cellulose. The latter includes Polylactic acid (PLA), vegetable oil-based polyurethane, and Polyhydroxyalkanoates (PHAs). PHAs are a class of biopolymers grown by bacteria in the fermentation process with

sugars or enzyme-thinned starch. Many different monomers can be produced through within this class of biopolymer. PHAs can be homopolymers or co-polymers, and depending on the monomer used, the mechanical properties of PHAs can be tailored from rubbery to rigid properties. Of PHAs, polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) are most commonly used. PHB exhibits strength and stiffness comparable to that of polypropylene (PP) (Velde and Kiekens, 2002). The PHBV co-polymer may be used with varying hydroxyvalerate (HV) content to increase the toughness of the PHB polymer. Biodegradation of PHAs can occur with aerobic and anaerobic bacteria and fungi. The end product of PHA degradation in aerobic conditions are carbon dioxide and water, while methane is a further product in anaerobic conditions. It has been shown that a 1mm molding of PHBV was completely degraded after 6, 75, and 350 weeks in anaerobic sewage, soil, and sea water, respectively (Lee, 1996).

Although PHAs have a desirable mechanical properties and environmentally friendly characteristics, the biopolymer is still not used extensively in commercial applications. The limited use of PHAs is primarily due to their high cost relative to polyolefins (such as PP). Currently, PHBV produced from Chinese supplier Tianan Biologic Material Co. Ltd, sells for \$2.36 per pound. With production capabilities expanding, Tianan has projected that their price for PHBV can reach \$1.60 per pound (Grace, 2007). While this is a drastic improvement, even \$1.60 per pound does not compare well with \$0.80 - \$0.95 per pound for polyethylene (PE) or PP. While many researchers are excited about the possibilities PHB hold, concerns have been raised about the true energy costs of producing PHB. It has been shown that the energy expenditure (in fossil fuels) required in the production of PHAs exceeds that required to produce an equal mass of polystyrene by 5.7% (Gerngross 1999).

By reducing the quantities of polymeric material required, incorporating filler or fibers with biopolymers is an effective method of reducing effective end-product costs. Fibers or fillers used in compositing processing may be distinguished as either inorganic or organic. In terms of inorganic fibers and fillers, glass, carbon black, calcium carbonate, and talc are commonly used with thermoplastic matrices (Yoshida, 2006; Kalaitzidou, 2007; Leong, 2004). Alternatively, organic, or natural fillers and fibers have become a strong competitor to inorganic fillers. Inclusion of fibers such as flax, hemp, kenaf, bamboo, cellulose, and wood fiber have shown promise in reducing the cost and mechanical properties from that of neat polymers (Herrmann, 1998; Qian, 2006; Bledzki and Gassan, 1999). In addition to reducing costs and improving mechanical properties such as stiffness and strength, and in contrast to inorganic fillers, natural fibers are non-abrasive to processing equipment, and are derived from annual renewable resources. One of the most common natural fibers currently used in commercial production is wood fiber (WF), or wood flour. Wood plastic composites (WPCs) are commonly produced with polyolefin matrices such as PP, polyethylene (PE), and polyvinylchloride (PVC) (Clemons 2002). Current applications of WPCs include decking, siding, window framing, and fencing.

Through the production of PHB WPCs, natural composites (or biocomposites) can be aimed directly at a developed market saturated with polyolefin based WPCs. Recent research has looked into further solutions for PHB/WF composites. It has been estimated that ca. 30-40% of the energy expenditure in the production of PHAs is a result of the extraction of cellular biomass from PHA (Gerngross, 1999). Coats et al (2007) has shown that the utilization of unpurified PHB in WF composites is possible and does not significantly affect the stiffness of the composite (in comparison to pure PHB/WF). However, since the polymer content incorporated in the PHB-WF composite is reduced with the inclusion of biomass, the strength is drastically reduced. By

using 40% cellulose fiber in composites produced through injection molding, Gatenholm et al (1992) have shown that PHB/cellulose fiber composites are very competitive with both PP/WF and Polystyrene/WF composites in stiffness, displaying moduli of 6.2, 3.7, and 6.3-GPa respectively. While these are promising values, PHB/WF composites have shown to be less than competitive with polyolefin WPCs in terms of strength. Singh and Mohanty (2007) studied the mechanical properties of injection molded PHBV/WF composites with 30 and 40% WF and reported tensile strengths of 17 and 16.75-MPa, respectively. In contrast, Bledzki and Faruk (2003), showed that PP/WF composites produced through injection molding with 50% WF exhibited strengths ranging from 20-25-MPa, depending on wood fiber size. Further, when coupled with maleic anhydride-polypropylene copolymer, strengths ranging from 35-40-MPa were achieved (and stiffness was increased to 6-GPa).

1.2 Problem Statement

Current consumer WPC products are primarily produced with high percentages of wood fiber (ca. 60-70% WF). As of this time of publication, only one study has been published that investigates the mechanical properties of PHB/WF composites at percentages above 40% WF. Dufresne (2003) studied composites made from PHB and plasma modified ground olive stone at fiber loading levels up to 70%. Unfortunately ground olive stone is not a resource commonly exploited in the North American WPC market.

Further, as the percent of wood fiber is increased, the role of polymer-fiber adhesion on strength is dramatically increased. This holds true for both polyolefin/WF composites (Correa, 2007), and has been shown for PHB/WF composites as well. Singh and Mohanty (2007) report that the tensile strength continually decreases from 21.42-MPa to 16.75-MPa when increasing wood fiber levels from 0-40% on PHBV, respectively. In order to assess the viability of

PHB/WF composites for residential, decking, siding, window framing, and fencing applications (in direct competition with polyolefin based WPCs), studies must be done on PHB/WF composites with higher percentages of wood fiber, and methods of strengthening the polymer-fiber interface must be introduced.

1.3 Approach

Thanks to the hydrophobic-hydrophilic disparity between conventional polyolefins (PP, PE, PVC) and wood fiber, many different solutions have been investigated to improve the adhesion between polymers and wood fibers. Most commonly, additives are included that are designed to interact with both the polymer phase and the wood fiber by either chemically or physically bonding, or through polymer entanglement. In this study, four different interfacial modifiers have been selected to improve upon the mechanical properties of PHB/WF composites; maleic anhydride-grafted PHB (MA-PHB), a low molecular weight solid epoxy resin, or D.E.R., a low molecular weight carboxylic terminated polyester, or Uralac, and poly(methylene diphenyl diisocyanate) (pMDI).

Maleic anhydride grafted-polyolefins are the most prevalent interfacial modifier used in WPCs today. By processing PP/WF composites through injection molding, Kim et al (2007) showed that the addition of 3% maleic anhydride-polypropylene (MAPP) on total could improve tensile strength from 33-MPa to 44-MPa (Kim, 2007). The authors also showed that effectiveness of MAPP was strongly influenced by the percentage of maleic anhydride grafting as well as the molecular weight of the MAPP. Maleic anhydride is suggested to bond at the wood fiber interface through esterification reaction and hydrogen bonding (Correa, 2007). Given the hydroxyl functionality of PHB, it is expected that MA-PHB would show similar improvements in strength to PHB/WF composites

Similar in character to the function of maleic anhydride-grafted polyolefins, two novel interfacial modifiers were employed; a low molecular weight polyester with carboxyl terminated groups, Uralac, and low molecular weight epoxy, D.E.R. Both the epoxy, and the carboxyl groups are expected to chemically bond with the hydroxyl-rich functionality of the wood fibers.

For many years, pMDI has been used as an adhesive in oriented strand board composites (Frazier and Ni, 1997). More recent studies utilizing pMDI grafted stearic anhydride as an interfacial modifier for PE/WF composites (Geng, 2005), and pMDI incorporated into PHB/Bamboo fiber composites (Qian, 2006) report significant improvements in both strength and stiffness over the respectively unmodified composites.

In order to conserve PHB supplies, composites with the aforementioned interfacial modifiers were processed through injection molding. Although a two step process is employed (pre-compounding and then injection molding), the semi-continuous injection molding process allows for finished and uniform test specimens to be manufactured with little waste. Because processing can affect many variables of composite material properties (fiber alignment, crystallization, density, etc.), the effect of processing the same modified PHB/WF composites was studied. Most commercial WPCs are processed through extrusion processes (Clemons, 2002), and so the effects of injection molding on PHB/WF composites were contrasted with those of extrusion.

1.4 General Objectives

- Investigate the effects of interfacial modifiers on improving mechanical and physical properties of the resultant composites.

- To determine the morphological effects of the most promising modifier on PHB/WF morphology.
- To compare mechanical and physical properties of PHB/WF composites, as processed through injection molding and extrusion.
- To isolate possible differences between injection molding and extrusion that may influence interpretation for studies intended to be scaled up.

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CHAPTER 2 - EFFECT OF INTERFACIAL MODIFIERS ON MECHANICAL AND PHYSICAL PROPERTIES ON PHB/WF AND THEIR EFFECT ON COMPOSITE MORPHOLOGY

2.1 Abstract

As the social costs for fossil fuels are increasing and environmental concerns regarding climate change and sustainability are growing, the need for truly biodegradable and environmentally friendly consumer products has increased. Polyhydroxybutyrate (PHB) has received considerable attention as a bacterially derived biopolymer with attractive mechanical properties. Processing PHB with wood fiber (WF) reduces cost and improves mechanical properties. To explore the commercial viability of PHB/WF composites, systems were produced at industry-standard levels of fiber loading. Further, four interfacial modifiers were selected to improve upon the mechanical properties of PHB/WF composites. The composites were processed by injection molding of pre-compounded and palletized formulations. Interfacial modifiers studied include maleated PHB (MA-PHB), a low molecular weight epoxy, D.E.R., a low molecular weight polyester, Uralac, and polymethylene-diphenyl-diisocyanate (pMDI). Mechanical properties were characterized through tensile testing (ASTM D638), notched impact testing (ASTM D256), and water absorption tests. Results show improvements in strength properties with the use of all the modifiers studied, however, pMDI showed the highest improvements. With the addition of 4% pMDI, PHB/WF composites displayed an increase in strength of 57%, and an increase in Young's modulus of 21%. The pMDI modifier also improved water uptake of the composites. Studies of the fracture interface showed signs of improved fiber bonding, as do morphological studies by dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). Interpretation of the DSC and DMA results indicate

possible reaction with lubricant, and interaction between PHB and wood fibers with the addition of pMDI.

2.2 Introduction

For some time now, natural fibers have received considerable attention as a reinforcing material for commercial thermoplastics. Wood fibers (WF) are attractive because of their low cost and high specific properties. Commercial wood plastic composites (WPCs) have been successfully developed utilizing polyolefins such as polypropylene and polyethylene (Clemons, 2002). While composite manufacturers use varying degrees of recycled polypropylene or polyethylene, many manufacturers still use 100% virgin polyolefin for the manufacturing of WPCs.

In an effort to reduce societies dependence on fossil fuels, biopolymers have been proposed as a viable alternative to polyolefins as matrix material in WPCs. Polymers such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA) have been identified as possible alternatives to petrochemically derived polymers (Manju, 2005; Gatenholm, 1992).

PHAs are a class of polymers synthesized and grown by a wide range of bacteria through fermentation of sugars and lipids. In addition to being produced by bacteria, PHAs are also biodegradable through enzymatic degradation. Of the PHAs, considerable attention has been focused on polyhydroxybutyrate (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). With tensile strength and tensile modulus reported to be from 20-25 MPa, and 600-800 MPa, respectively, PHB is comparable to polypropylene for many applications (Zhang, 2004).

While various PHB-based natural fiber composites have been evaluated in the literature, as of yet, no studies have studied the composite produced with industry-standard levels of fiber

loading (Reinsch and Kelley, 1997; Gatenholm, 1992). Four interfacial modifiers have been selected to encourage PHB/WF interaction. Maleated systems have been well recognized for their potential in WPCs and have been developed for use in both PP and PE composites (Sombatsompop, 2005; Lu, 2005). Maleic anhydride has even been coupled with neat PHB to improve properties such as thermal stability (cold crystallization temperature, decomposition temperature, Chen, 2002). In this study, maleic anhydride grafted PHB (MA-PHB) was produced for use in a PHB/WF composite. In addition, two novel interfacial modifiers are used in this study. D.E.R. is a low molecular weight solid epoxy resin and Uralac is a low molecular weight polyester with carboxyl end groups. In both situations, it is hypothesized that the reactive end groups will chemically bond with the wood fibers and facilitate compatibility with the PHB matrix, forming a superior bond. Finally, polymeric isocyanates have long been used as adhesives for wood. First used in wood-strand composites, isocyanates are now considered for their application in WPCs (Zhang, 2005; Geng, 2005). Isocyanates have even been shown to be effective on PHB-based natural fiber composites. Qian (2006) showed that 3% polymethylene-diphenyl-diisocyanate (pMDI) can be used to improve the strength of PHB/Bamboo fiber composites from 40 MPa to 50 MPa, and the stiffness from 5 GPa to 9 GPa. Illustrated in Table 2.1 is the chemical structure for each modifying agent and the anticipated reaction at the hydroxyl-functioned wood fiber surface. With MA-PHB, D.E.R., and Uralac, it is expected that the modifier becomes entangled with the PHB matrix thus forming a matrix-fiber linkage. In the case of pMDI it is possible that the pMDI may react to form a polyurethane which may entangle and hydrogen bond with the PHB matrix.

The focus of this study is to develop viable formulations for PHB/WF composites. The objectives of this study are to 1) investigate the effects of interfacial modifier type on improving

mechanical and physical properties of the resultant composites, 2) to evaluate the modifying efficiency at the interface, and 3) to determine the morphological effects of the most promising interfacial modifier on PHB/WF morphology.

2.3 Materials

The WPC composites were composed primarily of PHB (Tianan Biologic Material Co., Ltd., Ningbo, China) and 60-mesh ponderosa pine wood fiber (American Wood Fibers, Schofield, WI). Because of the slow crystallizing nature of PHB, boron nitride (BN) in platelet form (Carbotherm PCTF5, obtained from Saint Gobain Advanced Ceramics Corporation, Amherst, NY) was included to promote homogeneous nucleation (Qian, 2007). Previous research has shown that the use of Glycolube WP2200 (provided by Lonza Inc., Allendale, NJ) may serve as an effective lubricant and produce composites with improved mechanical properties (Anderson, 2007a). Talc (Nicon 403 obtained from RioTinto of Centennial, CO) was used to improve processing and water uptake of the highly filled composites. Multiple interfacial modifiers were evaluated in the study. The pMDI (Mondur G541), supplied by Bayer MaterialScience (Pittsburgh, PA), contained 31.5 mass % NCO. Uralac P5142, a low molecular weight polyester was supplied by DSM Resins US, Inc (Augusta, GA). D.E.R. 662E, a low molecular weight solid epoxy resin was supplied by DOW (Midland, MI). Finally, to produce the maleated-PHB, dicumyl peroxide (98% purity) and maleic anhydride (95% purity) were obtained from Aldrich (St. Louis, MO).

2.4 Methods

2.4.1 Preparation of composites

PHB-WF compounds containing different interfacial modifiers were prepared by dry blending and then melt mixing in a twin screw extruder and granulated for use in injection molding. In preparation for mixing, PHB was first dried in an oven at 100°C for 12 hours. Pine wood flour was dried by steam tube to a moisture content of 2.8 mass %. Blends were prepared with 35 parts PHB, 57 parts WF, 8 parts Talc, 0.2 parts BN, 3 parts WP2200, and either 0, 1, 2 or 4 parts interfacial modifier. To produce the interfacial modifier MA-PHB, 95 parts PHB, 5 parts maleic anhydride, and 0.5 parts dicumyl peroxide (used as an initiator) were processed in a torque rheometer (Haake PolyLab 3000P) at 180°C and 50 rpm for 40 minutes. The ungrafted maleic anhydride was removed by vacuum oven in 100 °C for 12 hours.

Except in the case of blends containing pMDI, all formulations were premixed by manually tumbling the components in a plastic bag for 5 minutes. In the case of blends containing pMDI, the liquid modifier was added to the PHB powder and dispersed using a standard kitchen blender for 1 minute. Melt mixing and pre-compounding were accomplished through a co-rotating twin screw extruder (Leistritz ZSE-18) fed by a volumetric feeder. The screw diameter was 17.8 mm and the L/D ratio was 40.

Extrusion temperatures for pre-compounding were independently controlled on eight zones along the extruder barrel. A declining temperature profile was chosen to reduce thermal degradation and improve melt strength (Zhang, 2004). From the feed throat to the die adapter, the temperatures were set as follows; 170°C, 175°C, 170°C, 165°C, 164°C, 163°C, 162°C, and 160°C. The formulations were introduced into the extruder throat with a screw-driven starve

feeder. The extruder screw was maintained at a speed of 125 rpm. The resulting residence time was estimated to be approximately 1.5 minutes. After exiting the die, the extrudate was air cooled and granulated.

2.4.2 Preparation of test specimens

Standard ASTM D638, type I tensile specimens and 12 x 3 x 127-mm flexure bars were produced by injection molding (Sumitomo SE 50D). Temperature zones were independently controlled at 175°C, 180°C, 175°C, 165°C from the feeding end to the nozzle. The mold temperature was held constant at 60°C. The filling pressure was set for 1700-kgf/cm² and the packing pressures were set to 1275-kgf/cm² and 1360-kgf/cm² for the 1st and 2nd stage, respectively. Residence times were consistently measured around 5 minutes.

Test specimens for impact testing were cut from the center (length-wise) of the flexure specimens and notched using a XQZ-I Specimen Notch Cutter (Chengde Jinjian Testing Instrument Co., Ltd.). Specimens for water absorption tests and DMA tests requiring specimen sizes differing from those produced through injection molding were milled on a manual milling machine to dimensions of 11 x 2.5 x 125-mm and 2 x 12 x 52-mm, respectively.

2.4.3 Mechanical and physical property testing

Tensile tests were performed in accordance with ASTM D638 using a screw driven Instron 4466 Standard with a 10-kN electronic load cell. Tests were performed at a crosshead speed of 5-mm/min and strain was measured with a clip-extensometer with a 25 mm gage length (MTS model # 634.12E-24). Sample geometry was measured on all samples prior to testing and density was calculated from the resulting volume (length x width x thickness) and the sample

mass. Fractured tensile specimens were sputter coated with gold for observation by scanning electron microscopy (SEM) on a Hitachi S-570.

Notched impact testing was performed according to ASTM D256, method A. The test frame was configured with a load head corresponding to a maximum impact of 2.7-J. Water absorption tests were performed in a temperature controlled, distilled water bath held at room temperature. The surface moisture was blot-dried with a towel, and the specimens were allowed to air dry for 10 minutes prior to measurement. Moisture content was calculated on a mass percent basis using the following equation:

$$MC = \frac{(M - M_o) \times 100}{M_o} \quad (1)$$

Where MC is the moisture content (mass %), M is the mass of the specimen at time t, and M_o is the initial (dry) weight of the specimen.

2.4.4 Statistical Analysis

The influence of various formulations variables on the physical and mechanical properties of the composite was assessed using an analysis of variance (ANOVA). When the influence of density on mechanical properties was significant, density was accounted for as a covariate. This changed the analysis to an analysis of covariance (ANCOVA). All analyses were conducted using statistical software (SAS, Version 6.9.1, SAS Institute Inc., Cary, NC). Since data sets were unbalanced, the general linear model was employed. Significance was set for the $\alpha = 0.01$ level.

2.4.5 Testing of thermal properties

Dynamic mechanical properties of the modified systems were analyzed with a Rheometric Scientific RSA II using three-point-bending configuration. Before the temperature ramp tests were conducted, the linear viscoelastic range was determined through a strain sweep. Further experiments were conducted under a constant frequency of 1 Hz and a strain amplitude of 0.03% for dynamic temperature sweep tests from -30°C to 125°C.

The melting and crystallization behavior of the modified systems were examined using a differential scanning calorimeter (DSC) (Mettler Toledo, DSC 822e). Samples were taken from an exact location on the tensile-bar specimens and weighed from 3-6 mg. Aluminum crucibles (40- μ l) were hermetically sealed to contain the specimens. Each sample was heated from 30°C to 180°C at 20°C/min, held for 2 minutes to erase the previous thermal history, and cooled at 20°C/min to -30°C. Following the cool down, samples are re-heated to 180°C at 20°C/min to collect the final DSC trace used to determine melt behavior.

2.5 Results and Discussion

2.5.1 Statistical analysis of mechanical and physical properties

Density has been shown by others to have a very large influence on mechanical properties in wood plastic composites. Micromechanical models that have been verified for natural fiber reinforced composites predict that composite stiffness may be increased by increasing the density of the composite (Facca, 2006). In wood-plastic composites, increases densities may be the result of better dispersion of fiber bundles, polymer penetration of the hollow fibers, or better bulk packing due to increased fiber alignment. Any of these scenarios would manifest itself in improved stress transfer between fiber and polymer phases, resulting in

the potential of improved mechanical properties. Because fiber alignment is largely influenced by the shear gradient in a die, it is likely that the various composites in this study have comparable fiber alignment. Therefore, changes in density would likely be a function of increased fiber dispersion or polymer penetration of the fibers.

Figure 2.1 presents the composite density when produced with various levels and types of modifier. For all systems, a step increase in density occurs from 0% to 1%, possibly resulting from improved fiber wetting leading to better polymer impregnation of the fiber lumens. An analysis of variance (ANOVA) was conducted to determine if the type of level of modifier produced a statistically significant affect on the composite density:

$$Y_{ij} = \beta_0 + \mu_i m_i + \lambda_j l_j + \varepsilon_{ij} \quad (2)$$

Where:

Y_{ij} = response value (density)

β_0 = model intercept

μ_i = coefficient of the main effect for the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

m_i = the Boolean variable for the main effect of the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

λ_j = coefficient of the main effect for the level of modifier (j = 0, 1, 2, or 4%)

l_j = the Boolean variable for the main effect of the level of modifier (j = 0, 1, 2, or 4%)

ε_{ij} = error associated with response value

Interpretation of the ANOVA results (Table 2.2) suggests significant differences in the composite density when incorporating different modifier types and levels. Using the Duncan

groupings, it becomes apparent that these differences are largest between 0% and 1% modifier level, and between the composites produced with the Uralac and MA-PHB modifier types.

Given the differences in density and its potential to influence mechanical properties, it is appropriate that we look at the mechanical properties normalized to a mean density, so as to remove any variation in properties due to changes in density. To standardize mechanical properties for a mean density, an analysis of co-variance (ANCOVA) model was utilized. The main effects of both the type and level of modifier was considered, and density will be used as a covariate. The model statement will thus be composed as follows:

$$Y_{ij} = \beta_0 + \mu_i m_i + \lambda_j l_j + \tau(\rho_{ij} - \bar{\rho}_{..}) + \varepsilon_{ij} \quad (3)$$

Where:

Y_{ij} = response value (E or σ_{\max})

β_0 = model intercept

μ_i = coefficient of the main effect for the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

m_i = the Boolean variable for the main effect of the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

λ_j = coefficient of the main effect for the level of modifier (j = 0, 1, 2, or 4%)

l_j = the Boolean variable for the main effect of the level of modifier (j = 0, 1, 2, or 4%)

τ = coefficient for the effect of covariate density

ρ_{ij} = the variable density corresponding to Y_{ij}

$\bar{\rho}_{..}$ = grand mean of density

Because density is a continuous and uncontrolled property in this experiment, the density coefficient (τ) reflects an assumed linear relation between changes in density and the response

value (i.e. either E or σ_{\max}). Using this linear relationship, each individual modulus or strength measurement may be adjusted by its deviation from the mean density.

2.5.2 *Stiffness of modified composites*

The adjusted values for Young's modulus as a function of modifier type and level are represented in Figure 2.2. Interpretation of the results indicates that pMDI as a modifier is highly effective at improving stiffness. Even at levels of 1% pMDI added on total, the modulus shows an increase 13% over that of the control. The performance improvement with the addition of pMDI appears to be a near linear trend through to 4% pMDI added on total. With 4% pMDI added to the composite, stiffness is increased to 9.9-GPa (or 21% over the control). The low molecular weight polyester Uralac showed mild signs of improvement over the control, while the low molecular weight epoxy, D.E.R., and maleated PHB showed no practical improvements in stiffness at any level.

The results from the ANCOVA of Young's modulus (Table 2.3) lead us to determine that both modifier type and level of modifier has a significantly different effect on stiffness. By examining the Duncan's grouping of modifiers, we can see that the stiffness of pMDI-modified systems is significantly higher than that of Uralac, which is higher than D.E.R. and MA-PHB. The Duncan's grouping also suggests that all levels of modifiers show a significantly different effect on stiffness.

The significant interaction of the type and level of modifier most likely results from the different slopes depicted in Figure 2.2 for each modifier. With increasing levels, pMDI has a much more pronounced effect than Uralac, and D.E.R. and MA-PHB have no effect.

Comparisons of the control composite to other PHB/natural fiber composites may be made if the effect of increased fiber percentages are taken into account. Gatenholm (1992) studied composites with 40% cellulose fiber processed through injection molding with various polymeric matrices. In tensile testing of PP/cellulose composites, the Gatenholm (1992) reported a Young's modulus of 3.7-GPa, polystyrene/cellulose composites had a modulus of 6.3-GPa, and PHB/cellulose composites had a modulus of 6.2-GPa. Previous studies by the authors on the effect of wood fiber loading on PHB also agree with trends noted in stiffness (Anderson, 2007b). Unmodified, and filled with only 40% fiber, the PHB/cellulose composite exhibited much higher stiffness than the PP/cellulose composite. This is consistent with results reported by Beg and Pickering (2006) who studied injection molded PP/WF composites with 60% WF. The PP/WF composites were tested in accordance with ASTM D638, and exhibited a modulus of 2.2-GPa. When coupled with 2% maleated PP (MAPP), the modulus was increased to 5.2-GPa. Alternatively, this study has shown that when PHB/WF is coupled with 2% pMDI, the stiffness may be increased to 9.4-GPa.

2.5.3 Strength of modified composites

The effect of modifier type and level on the tensile strength of the composite is depicted in Figure 2.3. Unlike the varying effect of modifiers on stiffness, their addition appear to have a positive influence on strength. However, yet again pMDI shows the most drastic of improvements; reaching a maximum strength of 34.5-MPa with 4%, followed by Uralac. D.E.R. and MA-PHB both show modest improvements over the unmodified composite; reaching 28.2-MPa and 25.2-MPa, respectively.

Looking at Table 2.4 for the results of the ANCOVA on tensile strength it can be seen that again, both modifier type and level has a significant effect on strength. The corresponding

Duncan groupings show us that all types of modifiers and levels of modifiers are significantly different from each other with the pMDI producing the highest properties followed by Uralac, D.E.R and MA-PHB.

With respect to strength, PHB/WF composites without interfacial modifier performed comparably to PP/WF composites. In this study, a maximum strength of 22-MPa for the control formulation was achieved. Similarly, Beg and Pickering (2006) reported a tensile strength of 19.9-MPa. Now, a direct comparison cannot be made, because Beg and Pickering used wood fibers treated with a NAOH solution, and used no talc or lubricant. However, as an estimate, this comparison suggests that strength properties may not be significantly different. Once modified with 2% MAPP, the PP/WF composite shows drastic improvements in strength to 45.5-MPa. In contrast, 2% of pMDI added to PHB/WF composites improved the strength to 27.8-MPa. It must be noted, however that in this study, the full potential of pMDI has not been realized. For both stiffness and strength, with the addition of pMDI, each further percent increment of pMDI has only resulted in further improvements. The point at which higher levels of pMDI starts to decrease mechanical properties has not been realized.

2.5.4 Failure strain and impact properties of modified composites

The failure strain of modified composites was recorded as a measure of ductility. Because of the originally brittle nature of PHB and the addition of high wood fiber levels, all recorded failure strains were low for any practical purpose. The control formulation fractured at 0.37% strain and addition of MA-PHB, D.E.R., and Uralac did little to change the failure strain of the composites. While still low, pMDI did exhibit a slight effect on failure strain, increasing it from 0.37% to 0.47% strain with 4% pMDI added on total. Impact properties were also measured. The

type and level of modifiers did not significantly affect the notched impact energy of the composites, which ranged from 3.2 to 3.7-kJ/m².

2.5.5 Water uptake of modified composites

Because of the hydrophilic nature of wood fibers and the environmental conditions WPCs are often exposed to in application, understanding of the water uptake behavior in WPCs is beneficial. The transport of liquids and gases through a solid medium is often described by Fickian diffusion. Fick's second law describes the transport of molecules through a medium in which the diffusion flux and concentration gradient at a particular point change with time. Under conditions of non-steady state diffusion, the apparent diffusion constant, D_A may be described by:

$$D_A = \pi \left[\frac{h}{4M_{sat}} \right]^2 \left[\frac{\partial M_t}{\partial \sqrt{t}} \right]^2 \quad (4)$$

Where h is the thickness of the sample, M_{sat} is the moisture uptake at saturation, and $\partial M_t / \partial \sqrt{t}$ is the slope of the moisture uptake versus square root of time (Chowdhury and Wolcott, 2007). Water absorption plots exhibit Fickian behavior when M_t / \sqrt{t} exhibits a linear relationship. Deviation from Fickian behavior can occur when approaching saturation, or when composite defects (such as cracks) are present (Roy and Xu, 2001). Formation of micro-cracks may be caused by induced stresses arising from hygrothermal swelling. It is also possible that the presence of these cracks to increase the moisture content at saturation by the addition of surface area or facilitating capillary uptake of moisture.

The percentage of water uptake as a function of the square root of time is plotted in Figure 2.4 for the 4% level of modified composites. During testing, cracking was visually

observed and recorded for each specimen (as shown in Figure 2.5). The time recorded for the onset of cracking coincided with the inflection in the water absorption slope and increased with the addition of interfacial modifiers. Because of the damage to the composites, the realistic calculation of diffusion coefficients is difficult, as the saturated moisture content and the moisture uptake rate are likely increased.

The point of deviation from Fickian behavior was estimated for each formulation. The inflection point for the control was around $400\text{-s}^{1/2}$, 4% MA-PHB, D.E.R., and Uralac were estimated to change in slope around $500\text{-s}^{1/2}$, and the water uptake slope for 4% pMDI inflected around $725\text{-s}^{1/2}$. Since the cracking is most likely due to hygrothermal expansion of the fibers resulting in a residual stress on the composite, it is reasonable that the pMDI modified composites took the longest to crack. Further, prior to cracking, the slope of the water uptake curve is lowest for the composites modified with 4% pMDI. It is possible that pMDI helps to reduce moisture transport under Fickian conditions as well. The water uptake behavior was also recorded for composite modified with 1% and 2% pMDI. While not shown, the effect of increasing pMDI content from the control composite to the 4% pMDI had the effect of reducing the initial water uptake slope, and increasing the time before cracking and deviation from Fickian behavior occur. Similar results were noted in the study of the effect of pMDI on polyethylene/WF composites. The addition of pMDI has been shown to reduce the water uptake rate and saturated moisture content of polyethylene/WF composites (Zhang, 2005).

2.5.6 Influence of modifiers on fracture morphology

After tensile testing, the fracture surface of the composites was imaged. Micrographs of representative fibers for each composite modified at the 4% level are shown in Figure 2.6. In the first image, the control formulation displays a fiber drawn clean from the matrix with no signs of

polymer adhesion. When comparing this to the composites modified with 4% MA-PHB, 4% D.E.R., and 4% Uralac, it can be seen that these composites again show signs of fiber pull-out, but upon close examination, the fibers reveal some degree of polymer adhesion as is evidenced by the irregular surface of the standing fibers. Images of the fiber surface for a composite modified with 4% pMDI do not show fiber pull-out, but rather a clean fracture that likely propagated from the matrix straight through the fiber. For these pMDI modified composites, it appears that the adhesion between the PHB and the fiber is strong enough fracture the fiber and matrix before failing at the interphase.

Examining the macroscopic scale of the composites reveals the same trends. Taken at 300x, Figure 2.7 displays micrographs of the composites produced with, and without 4% interfacial modifier. Consistent with the microscale view of the control surface, Figure 2.7a shows a micrograph of the unmodified composite with many examples of fiber pull-out and clean, exposed fibers. Composites modified with 4% MA-PHB, 4% D.E.R., and 4% Uralac all display fiber pull-out, however it is important to note that as the images progress from MA-PHB to D.E.R. to Uralac, the exposed fibers become shorter and the fiber and matrix domains become more difficult to distinguish from one another. In contrast, in micrographs of the 4% pMDI modified composite, no fibers are visible, and the domains between fiber and PHB are indistinguishable, suggesting crack propagation through PHB and fiber and not through the interphase.

With the addition of pMDI to PHB/WF composites mechanical testing has shown a 17% increase in Young's modulus and a 53% increase in tensile strength. Water absorption tests show decreased water uptake and suggest increased resistance to cracking through residual stresses. Observations of the fracture surface also indicated great improvements in adhesion.

While the other modifiers (MA-PHB, D.E.R., and Uralac) showed improvements in physical and mechanical properties, for practical purposes and for the purposes of this research, continued investigation will be focused upon pMDI as a modifier.

2.5.7 Effect of pMDI on polymer morphology

While the PHB/WF composites are primarily composed of WF, much can be gained from the understanding of the polymer crystal morphology. The modifying agent pMDI may be serving to chemically or physically bond the PHB to the fiber, crosslink the PHB, or both. The polymer crystalline structure may be assessed through the use of DSC which may yield insight into changes in the polymer crystal perfection (through T_m measurements) or the degree of crystallization.

Displayed in Figure 2.8 is a representative DSC trace for the unmodified PHB/WF composite. On the initial heating scan, a double melt-peak is evident where crystals with a low degree of perfection melt, anneal, and then melt again. However, this feature is not evident in the second heating scan where the cooling rate is likely slow enough to yield a more homogeneous and ordered crystal structure. This double melting phenomena has been recorded through other literature (Qian, 2007) and through the use of a faster heating rate (20°C/min) it is possible to further minimize the effect of recrystallization. Further, by focusing further interpretation on the second heating and first cooling trace, variability in measurements due to differences in thermal history of the samples can be minimized.

The PHB/WF composites are produced from multiple polymeric components, with each manifesting their unique thermal transitions. To fully understand the different features evident in the scans of the composite material, the behavior of the individual components were examined.

Figures 2.9 and 2.10 show DSC thermograms for wood fiber, lubricant (WP2200), and the PHB (with boron nitride). Included at 3%, the lubricant displays a melting temperature (T_m) of 148°C, and a crystallization temperature (T_c) of 141°C. The wood fibers show a very broad thermal transition when cooling at ca. 145°C, while the PHB shows a melt temperature of 166°C and a crystallization temperature of 106°C. The thermal signatures of each component can be distinguished in the DSC trace of the composite material (Figure 2.8). Shown in Figure 2.9 is an illustration of how the heat of fusion was measured through this study the measurements for all composites were standardized by the mass of PHB within the specimen. The heat of crystallization was similarly measured.

When comparing the melt temperatures of the PHB/BN (Figure 2.9) with that of the control PHB/WF composite (Figure 2.8) it can be seen that the incorporation of wood fibers has the effect of decreasing the melt temperature of the PHB by 10°C. Research by Reinsch and Kelley (1997) on PHB/cellulose composites show that the reduction in T_m is due to the reduced crystalline perfection of crystals nucleated on the fiber surface. Studies by Harper (2003) correlate decreases in T_m with the onset of a transcrystalline layer (TCL), or a distinct crystalline structure that forms the fiber surface.

Because the possibility exists that pMDI may react with both the lubricant and the PHB, two additional composites were produced for analysis by DSC. One composite was a control produced without lubricant, and the other was a composite modified with 4% pMDI and without lubricant. The properties obtained through DSC traces for composites without lubricant are displayed in Table 2.5. The addition of 4% pMDI increases T_m from 159.9°C to 163.0°C, while the T_c decreases from 106.4°C to 104.9°C and no considerable changes in either the heat of fusion or the heat of crystallization were noted. If pMDI reacts with PHB to form a crosslinked

network, the degree of crystallization would likely decrease. Because no changes were noted in ΔH_f or ΔH_c between the modified and unmodified composite, the addition of pMDI had no effect on the degree of crystallization. However, the T_m and T_c did change with the addition of pMDI. Increases in T_m suggest that the perfection of the polymer crystals through the entire composite is increasing. Further, decreases in T_c suggest a decreased ability of the polymer to crystallize. If pMDI is acting at the interface in a manner similar to that of MAPP (Hristov and Vasileva, 2003), it is possible that strong interaction between the pMDI-PHB grafted polymer and the wood fiber is inhibiting the PHB from nucleating on the wood fiber surface. Because crystallites grown from fiber are energetically less stable than spherulitic crystal structures, a macro-scale decrease in the crystallization on the fiber surface would result in an increase in the crystal perfection and the T_m . Similarly, increased interaction between the fiber and the polymer matrix could reduce the mobility of the polymer surrounding the fiber, decreasing the ability of the fiber to act as a nucleation site. Hristov and Vasileva (2003) reported similar findings with PP/WF and rubber-toughened PP/WF composites with the addition of MAPP. The addition of MAPP to PP/WF was shown in this study to prohibit heterogeneous nucleation on the fiber, and thus allow for more spherulitic growth.

However, the composites examined through tensile testing, water absorption, and fracture morphology were all processed with 3% lubricant included in the formulation. With crosslinked polymers, the glass transition temperature (T_g) increases with increased crosslink density due to the restriction of polymer mobility within, and surrounding the crosslinked network. In addition to assessing the melting and crystallization behavior by DSC, DMA was used to assess changes in the T_g . The thermal behavior of these composites modified with 0, 1, 2, and 4% pMDI is illustrated in Figures 2.11 and 2.12 for the heating and cooling traces, respectively. Scans of the

same composites through DMA are shown in Figure 2.13. The DMA traces indicate increases in T_g as measured by the onset of the plateau (around 20°C) in the dampening ($\tan(\delta)$) trace. Further, an increase in storage modulus (E'), and decreases in both loss modulus (E'') and dampening levels can be seen with increases in pMDI content. As seen in Figures 2.11 and 2.12, the addition of pMDI to the composite increases T_m and T_c , and decreases ΔH_m and ΔH_c .

Increases in storage modulus reflect the trends observed for tensile testing of the same composites, that stiffness increases with increased levels of pMDI. Decreases in dampening levels may indicate increased interfacial adhesion of polymer-WF composites (Correa, 2007). In situations where fiber adhesion is limited, the dampening of a composite should be comparable to that of just the polymer. If fiber adhesion is high, the ability of the polymeric phase to accommodate deformation is limited, and the mechanical dampening of the composite is reduced. Similarly, if adhesion is high, the mobility of polymer chains is limited and the temperature at which the glass transition occurs should increase. The same logic holds for increases in matrix crosslinking as well. If crosslinked networks are present, the ability of the polymeric phase to accommodate deformation is limited, and the mechanical dampening of the composite is reduced. While results indicate increased T_g and dampening, the effects of crosslinking and increased fiber adhesion cannot be distinguished from each other with the given information.

Increases in T_m are possibly the same reflection of increased fiber adhesion discussed for composites without lubricant. Changes in crosslinking should result in an decreased percentage of polymer crystals this would have an effect on the heat of fusion and the heat of crystallization, as there would be fewer crystals to melt, or less polymer available for crystallization. First, the effects of just lubricant on crystallization should be examined. Table 2.5 also gives the thermal

properties for composites processed with lubricant. If the composites processed with and without lubricant are compared, it can be seen that the addition of lubricant decreases the ΔH_m and ΔH_c slightly. However, if pMDI is added to the composite with lubricant, both ΔH_m and ΔH_c show further signs of decreasing (Table 2.6). This suggests that the matrix system of pMDI, lubricant, and PHB are crosslinking in some manner, reducing the degree of crystallinity in the composite. It is apparent that the inclusion of lubricant allows for crosslinking of the PHB-pMDI system, but without information on the proprietary structure of the lubricant, no further speculation as to the mechanism of crosslinking may be made at this time.

The T_c also shows a significant increasing trend with the addition of pMDI. Other studies have reported increases in crosslinking, with increases in T_c in the use of isocyanate based interfacial modifiers, but have attributed the phenomena to an increased nucleation effect of the isocyanate (Lee and Wang, 2006). This justification does not fit with the results presented here because a decreased nucleation effect was noted in the composites with no lubricant and pMDI. Based on the results currently available, no viable explanation can be made at this time to fit this phenomena.

2.6 Conclusion

Biopolymers have been limited in use to packaging applications since their introduction into consumer products. In an effort to develop PHB for competition in the wood plastics industry with applications such as decking, siding, and fencing, composites of PHB and WF were produced with wood levels comparable to those used for WPC applications. The composites were processed through injection molding to conserve raw materials and produce uniform test specimens. Tensile testing of the unmodified PHB/WF composites resulted in an average Young's modulus of 8.1-GPa, and Ultimate strength of 21.9-MPa. Interpretation of

results suggests that PHB/WF composites have high stiffness compared to PP/WF composites, and are more comparable in stiffness with PS/WF composites. The strength of PHB/WF composites was suggested to be comparable with that of PP/WF.

The addition of interfacial modifiers was found to have a positive influence on both stiffness and strength. The most promising interfacial modifier was pMDI. At levels of 0, 1, 2, and 4%, pMDI improved tensile properties more effectively than Uralac, D.E.R., and MA-PHB. The addition of 4% pMDI coincided with a 57% increase in ultimate strength, and a 21% increase in Young's modulus. Similarly, water absorption tests indicate increased resistance to water uptake with the addition of interfacial modifiers with pMDI showing the greatest improvements.

Improved fiber adhesion was suggested with the addition of pMDI, and observed through SEM micrographs. Micrographs of the control showed a large degree of fiber pull-out, and fully exposed fibers. Composites modified with D.E.R. and Uralac showed signs of improved fiber adhesion, and pMDI exhibited complete fiber-matrix coherency.

Investigations into the effect of pMDI on the polymer morphology of PHB/WF composites Showed signs of increased T_m , T_g , and decreased ΔH_m and ΔH_c in the control composite (which included lubricant). Interpretation of these results suggests improved fiber adhesion and possible crosslinking within the PHB-lubricant-pMDI system.

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2.8 Tables

Modifier	Structure	WF Interaction
MA-PHB		Esterification
D.E.R.		Etherification
Uralac		Esterification
pMDI		Urethane linkage

Table 2.1 Structure of interfacial modifiers and possible reactions with the wood fiber surface.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Modifier	3	0.0045	0.0015	10.09	<0.0001
Level	3	0.1568	0.0523	352.05	<0.0001
Modifier*Level	9	0.0067	0.0007	5.01	<0.0001

Modifier	Uralac	pMDI	DER	MA-PHB
Duncan Grouping	A	A B	B	C
Mean (g/cm ³)	1.402	1.400	1.398	1.392

Level	1	4	2	0
Duncan Grouping	A	B	B	C
Mean (g/cm ³)	1.415	1.410	1.408	1.36

Table 2.2 Type III ANOVA and Duncan grouping for effect of modifiers and levels of modifiers on density ($R^2 = 78.8\%$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Modifier	3	1.01	0.34	5.40	0.0012
Level	1	7.26	7.26	116.17	<0.0001
Modifier*Level	3	12.58	4.19	67.10	<0.0001
Density	1	4.82	4.82	77.08	<0.0001

Modifier	pMDI	Uralac	MA-PHB	DER
Duncan Grouping	A	B	C	C
Mean (GPa)	9.15	8.63	8.36	8.33

Level	4	2	1	0
Duncan Grouping	A	B	C	D
Mean (GPa)	8.93	8.76	8.64	8.14

Table 2.3 Type III ANCOVA and Duncan grouping for effect of modifiers and levels of modifiers on tensile modulus ($R^2 = 79.3\%$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Modifier	3	531.43	177.14	625.36	<0.0001
Level	1	1457.24	485.75	1714.80	<0.0001
Modifier*Level	3	422.15	46.91	165.59	<0.0001
Density	1	2.70	2.70	9.53	0.0022

Modifier	pMDI	Uralac	MA-PHB	DER
Duncan Grouping	A	B	C	D
Mean (MPa)	27.53	25.95	24.83	23.78

Level	4	2	1	0
Duncan Grouping	A	B	C	D
Mean (MPa)	29.82	25.99	24.58	21.95

Table 2.4 Type III ANCOVA and Duncan grouping for effect of modifiers and levels of modifiers on tensile strength ($R^2 = 97.3\%$).

% Lubricant	% pMDI	Melt		Crystallization	
		T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
0	0	159.9	9.96	106.4	8.72
0	4	163.0	10.04	104.9	8.45
3	0	157.3	9.02	97.7	7.90

Table 2.5 Effects of 4% pMDI on and lubricant thermal properties of composites. Heat is measured in J/g of PHB.

% pMDI	Melt		Crystallization	
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
0	157.3	9.02	97.7	7.90
1	158.2	8.46	98.2	7.59
2	158.4	7.98	98.9	7.39
4	159.0	7.15	100.2	6.69

Table 2.6 Effects of pMDI on thermal properties of PHB/WF including lubricant. Heat is measured in J/g of PHB.

2.9 Figures

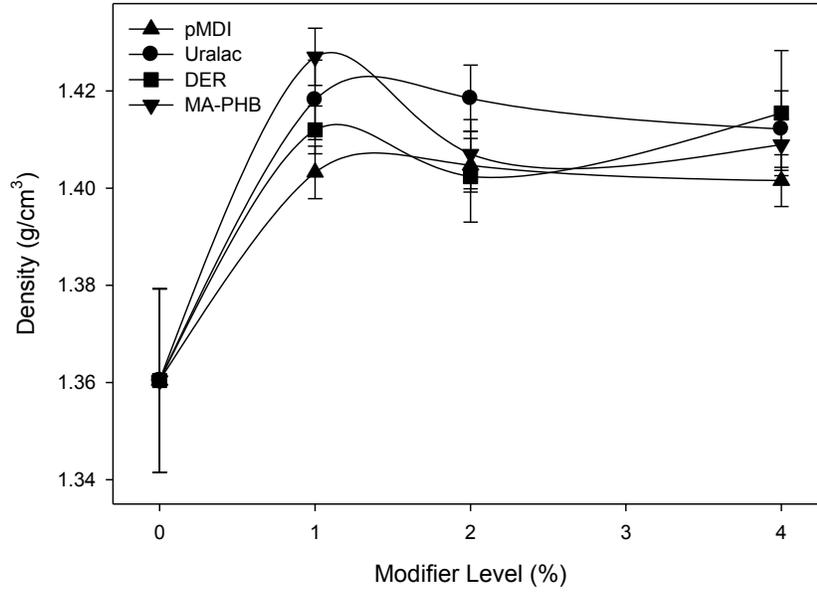


Figure 2.1 Effect of modifiers on density.

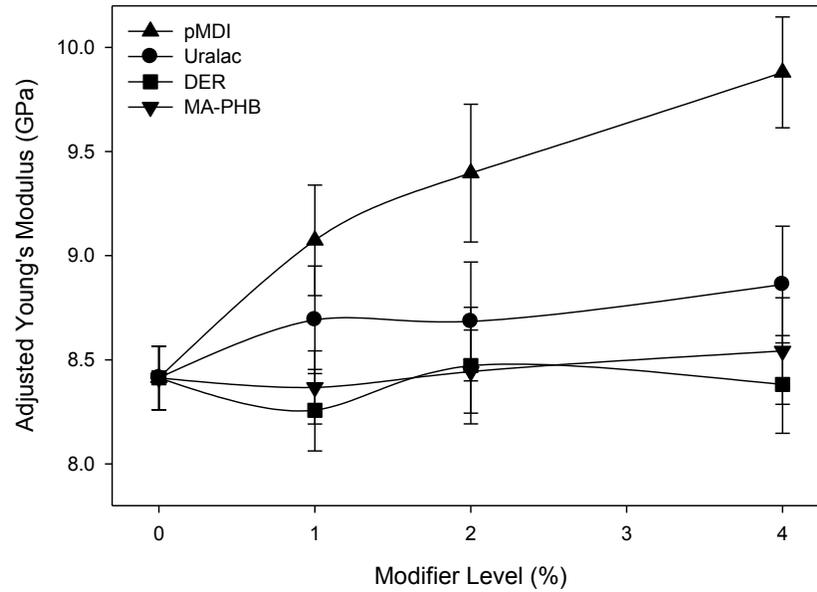


Figure 2.2 Tensile modulus of PHB/WF and PHB/WF modified composites.

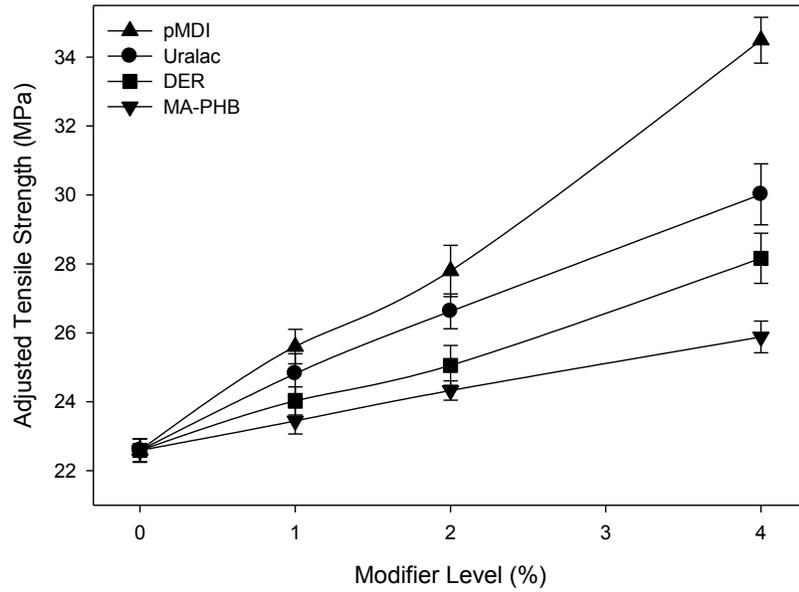


Figure 2.3 Tensile strength of PHB/WF and PHB/WF modified composites.

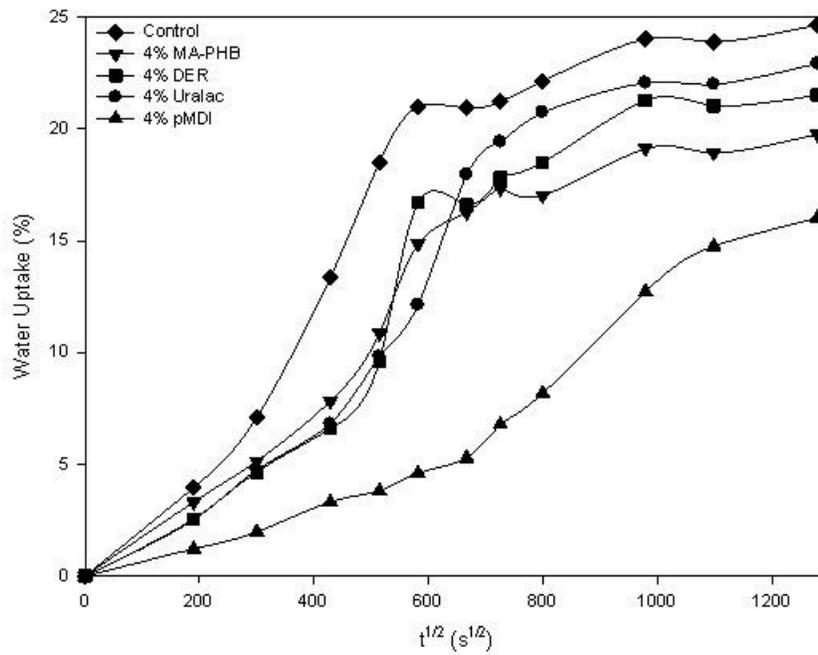


Figure 2.4 Water absorption of PHB/WF and PHB/WF modified composites at 4% on total, plotted against the square root of time.



Figure 2.5 Water absorption of PHB/WF and PHB/WF modified composites at 4% on total plotted against the square root of time.

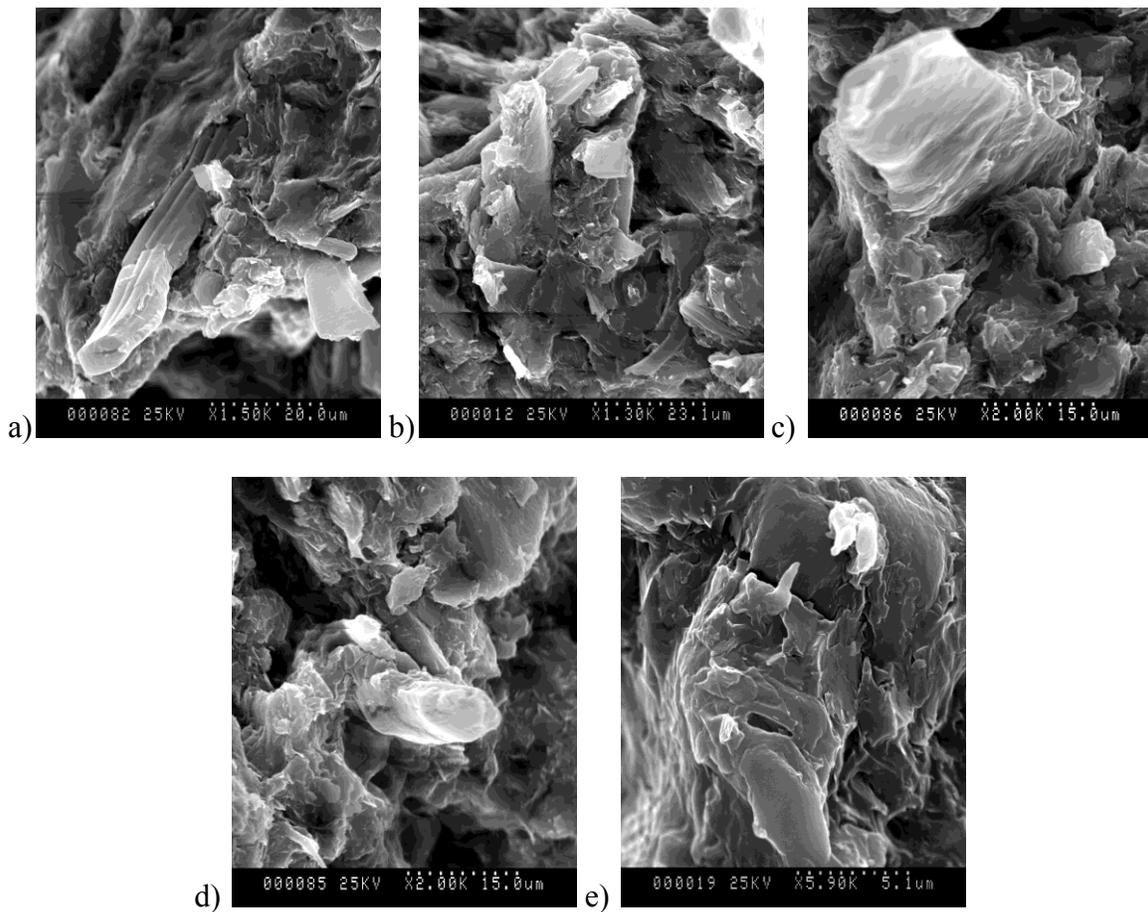


Figure 2.6 SEM micrograph of tensile-fractured PHB/WF: a) Unmodified, and modified with b) 4% MA-PHB, c) 4% D.E.R., d) 4% Uralac, and e) 4% pMDI.

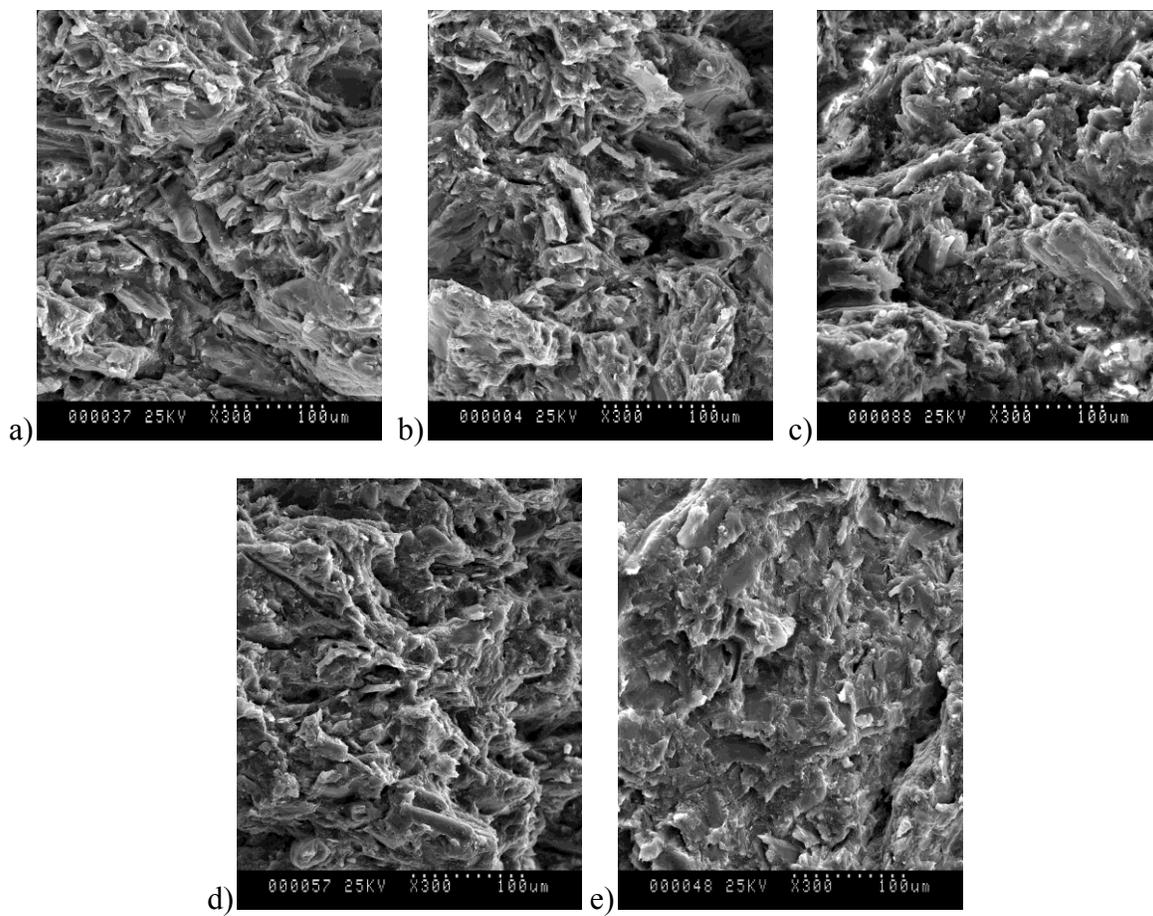


Figure 2.7 SEM micrograph of tensile-fractured PHB/WF, taken at 300x. The composites are; a) Unmodified, and modified with b) 4% MA-PHB, c) 4% D.E.R., d) 4% Uralac, and e) 4% pMDI.

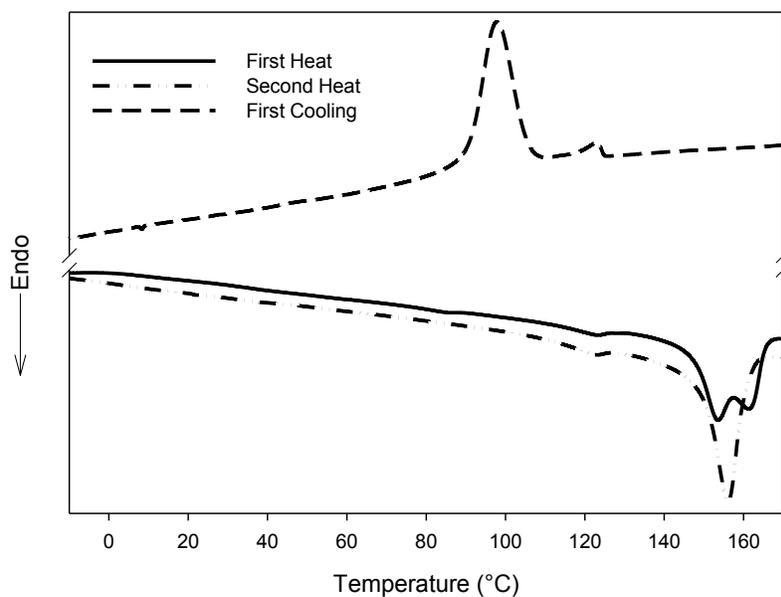


Figure 2.8 DSC thermogram of one full heat treatment of PHB/WF. Includes 1st heat, cooling, and 2nd heat.

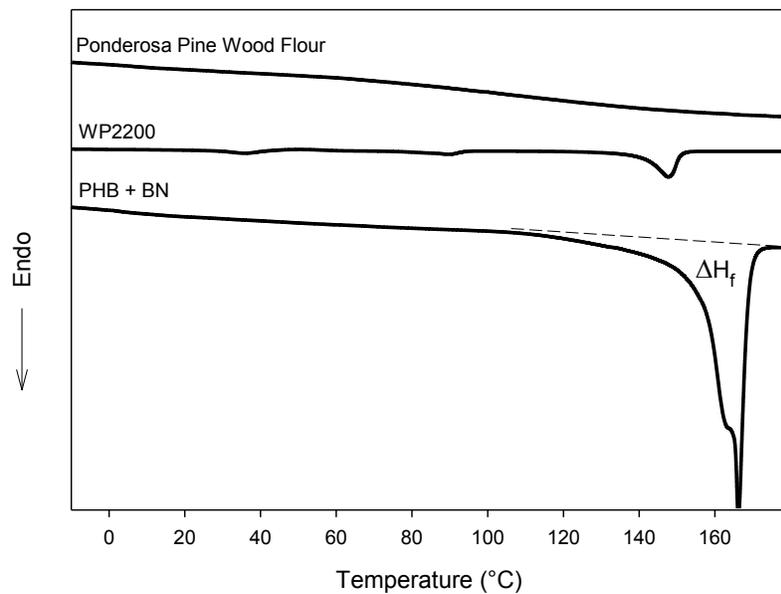


Figure 2.9 Example DSC thermograms of the neat polymeric components used to produce the various composites. The area used to measure values for ΔH_f is indicated.

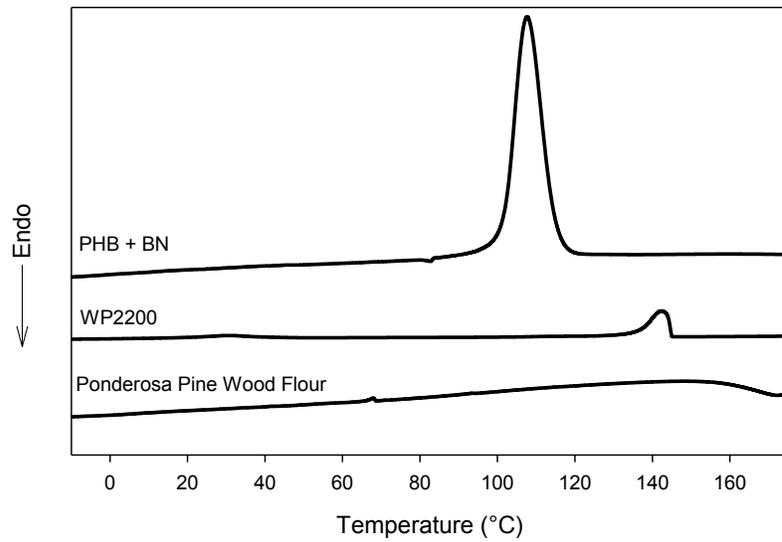


Figure 2.10 Example DSC thermogram of the cooling of neat polymeric components used to produce the various composites after 2 min at 180°C.

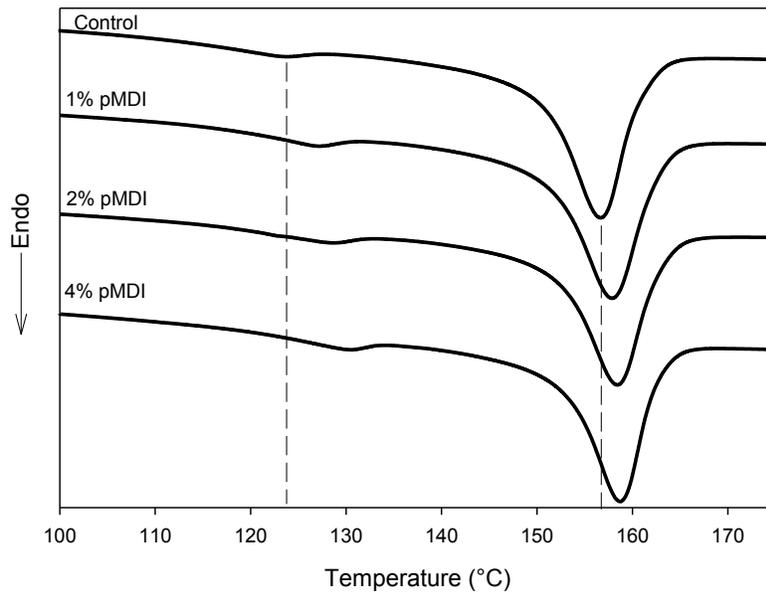


Figure 2.11 DSC thermogram of PHB/WF systems modified with pMDI including lubricant. Heat is measured in J/g of PHB.

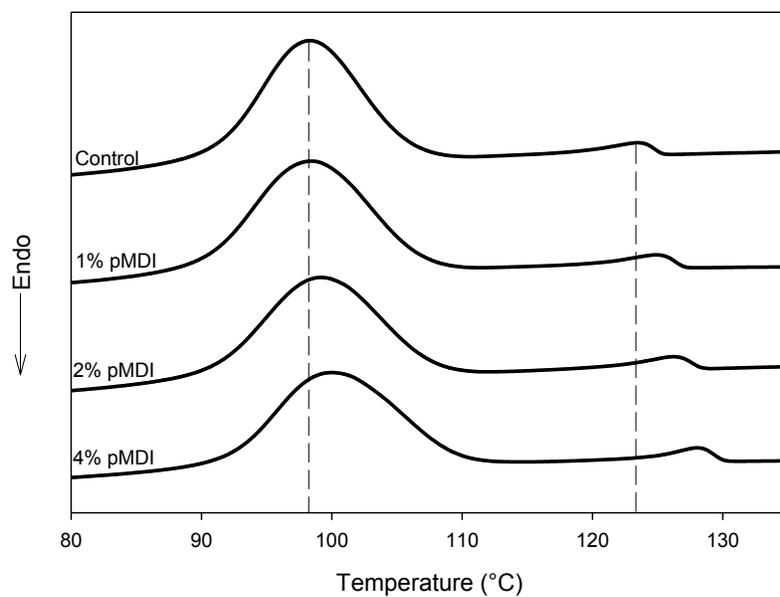


Figure 2.12 DSC thermogram of PHB/WF systems modified with pMDI including lubricant, cooling after 2 min at 180°C. Heat is measured in J/g of PHB.

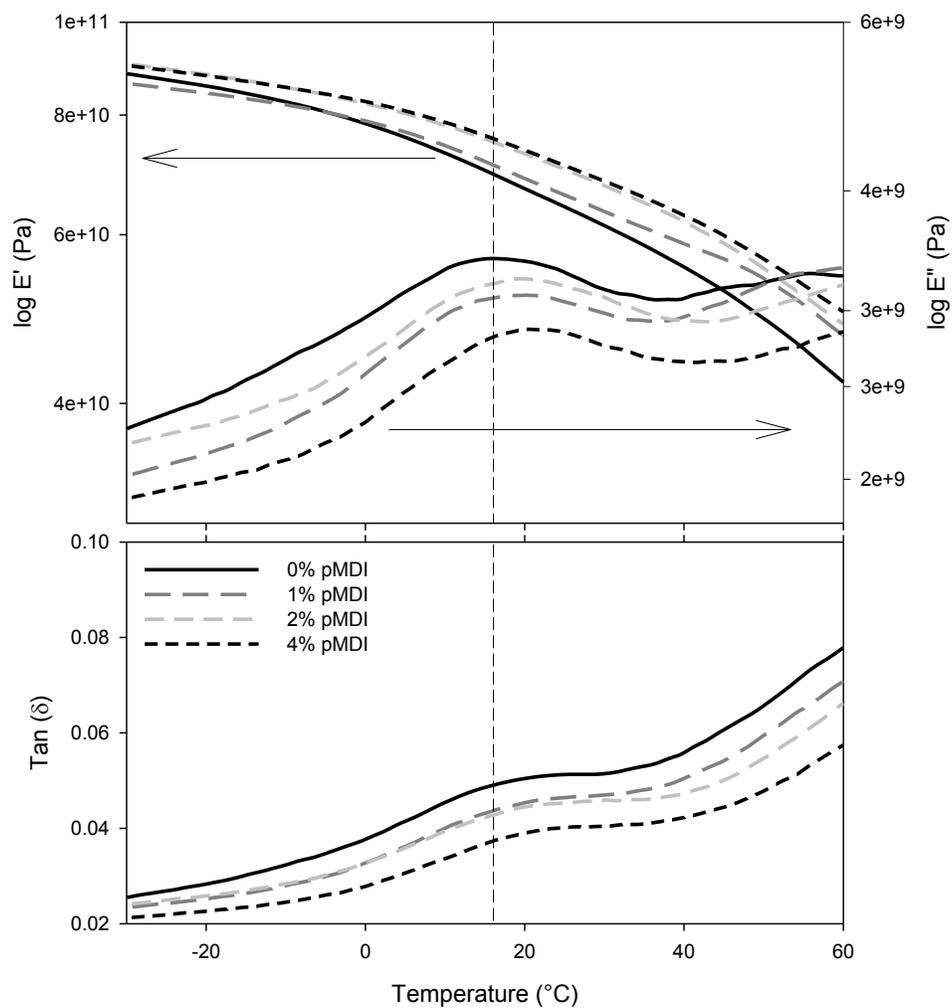


Figure 2.13 DMA scan of PHB/WF systems modified with pMDI (including WP2200).

CHAPTER 3 - EFFECT OF PROCESSING ON PHYSICAL AND MECHANICAL PROPERTIES OF PHB/WF COMPOSITES

3.1 Abstract

Composites made from polyhydroxybutyrate (PHB) and wood fiber (WF) have been shown to exhibit excellent mechanical properties. Unfortunately no studies have, as of yet investigated PHB/WF composites as processed through extrusion processes. This is significant because extrusion is preferred processing method for wood plastic composite (WPC) products such as decking and siding. This study utilizes parallel formulations of composites to investigate the influence of interfacial modifiers and processing method. Mechanical and physical properties were investigated through tensile, impact, density, and water absorption tests. It was found that injection molding produced composites of a higher density, and that differences in density produced a direct effect on stiffness and strength of the composites. The stiffness and strength of injection molded formulations was higher than that of the same formulations processed through extrusion. Both processing methods displayed similar trends in mechanical properties with the increasing effectiveness of incorporated interfacial modifiers. Water absorption tests showed similar trends across modifying agents from injection molding to extrusion. However, hygrothermal strains within the higher density injection molded samples resulted in surface cracking and increased water uptake of specimens. Changes in all of the physical and mechanical properties investigated suggest better dispersion of the injection molded specimens when compared to the same formulations processed with extrusion. The difference in dispersion may result from the pre-compounding step prior to injection molding, and density differences from the high packing pressures used during injection molding. Microtomed surfaces of the composites were viewed through scanning electron microscopy (SEM), and show further

evidence of improved fiber dispersion from injection molding. Differential scanning calorimetry (DSC) was used to investigate differences in crystallization. While results indicate that extrusion processing resulted in a greater degree of crystal perfection from that of injection molding, no correlations may be made regarding the implications on mechanical properties at this time.

3.2 Introduction

Polymer/natural fiber composites have increasingly been utilized for consumer products (Smith and Wolcott, 2006). Most predominantly, wood plastic composites have made their way into the home construction industry. Utilized in products such as decking, siding, window framing, and fencing, WPCs have proven to be cost-effective, environmentally friendly, and durable alternatives to wood lumber (Smith and Wolcott, 2006). For most of these products, extrusion processes are employed (Clemons, 2002). Due to growing environmental concerns, however, the use of natural fiber composites is rapidly expanding into other markets. Non-structural automotive parts, food storage/utensils, and packaging for consumer products have started to emerge as natural fiber composite products (Bledzki and Gassan, 1999). Such new applications for natural fiber composites require the ability to manufacture complex, three dimensional shapes. While extrusion processes can produce components with constant cross section, injection molding may be used to produce many complicated shapes. Much experimental development on composite material properties has been undertaken through both means of processing. Studies employing the extrusion process are commonly conducted at fiber loading levels of at least 50%, and more commonly 60-70% (Chowdhury and Wolcott, 2007). Conversely, fiber composite formulations designed for injection molding commonly contain at most 50% fiber, and more commonly 10-40% fiber (Singh and Mohanty, 2007). With injection

molding, lower fiber loading levels are preferred to achieve good flow and surface properties through the mold (Kato, 1999).

Often, studies aimed at improving composite properties for materials destined for specific applications utilize processing methods used commercially to create the consumer product. For example, a study investigating the use of a compatibilizer system to improve the mechanical properties of polyethylene/wood fiber (PE/WF) composites used a compression molding machine to produce test specimens (Geng, 2006). The same study was aimed at improving the properties of wood plastic composites (WPCs) that have applications in decking and siding. Because processing methods such as injection molding and compression molding are a semi-continuous processing method from which test coupons may directly be formed, such processing methods are often preferred for laboratory scale research.

While basic research on compatibilizers and interfacial modifiers is necessary, it is possible for variation in processing methods to have a tremendous effect on physical and mechanical properties (Chambers, 2001; Stark, 2004). Further, the effect of the interfacial modifier may alter the rheology or wetting of fibers which, depending on processing conditions may, or may not have an influence on composite properties of the test coupon.

In their early stage of commercial development, PHB and other PHAs are relatively expensive, but with advances in production technology, the price is anticipated to continuously decrease (Esposito, 2005). Owing to their easier crystallization and relatively higher crystallinity than that of PLA, PHB and some PHBVs show higher heat distortion temperatures (HDT) and higher resistance to diffusion. In recent years, PHAs and their composites have received extensive study from both academia and industry for cost effectiveness and performance

enhancement (Esposito, 2005; Chen, 2003). Thus far, all studies published involving PHB and natural fibers have employed either injection molding, or compression molding for processing of composites (Singh and Mohanty, 2007; Fernandes, 2004). For the laboratory setting, these processes are particularly useful because only limited quantities of raw material are necessary to produce a suitable number of processed coupons for testing. Nevertheless, information lacks on the properties of extruded PHB or other PHA/natural fiber composites.

Previous research (Anderson, 2007) has found that interfacial modifiers have a positive influence on composite mechanical and physical properties. Inclusion of all interfacial modifiers at levels of 4% on the total mass of the composite resulted in higher strength, decreased moisture transport, and in one case, improved stiffness. While high levels of wood fiber were used for these studies, a practical comparison of mechanical and physical properties with wood composites similar to those used in WPC applications still cannot be made. In this study, the mechanical and physical properties of extruded PHB/WF composites will be presented, and the properties of parallel formulations, as processed through injection molding will be compared.

3.3 Objectives

The focus of this study is to determine the effects of scale-up in the processing of PHB/WF composites and to determine the viability of commercial PHB based WPCs. The objectives of this study are to:

- Improve the mechanical and physical properties of extruded PHB/WF composites using interfacial modifiers.
- Compare mechanical and physical properties of PHB/WF composites, as processed through injection molding and extrusion.

- Isolate possible differences between injection molding and extrusion that may influence interpretation for studies intended to be scaled up.

3.4 Approach

Formulations of PHB/WF composites were produced with, and without interfacial modifiers through both injection molding and extrusion processes. Composites were modified with maleated PHB (MA-PHB), low molecular weight epoxy resin, D.E.R., low molecular weight polyester, Uralac, and polymethylene diphenyl diisocyanate (pMDI). Previous studies (Anderson, 2007) showed improvements in mechanical and physical properties with the addition of these interfacial modifiers. The authors of this study wanted to compare not only the properties of PHB/WF through different processes, but to determine differences as PHB/WF composites are modified as well. Composites were processed at comparable temperatures and standard cooling methods were used for each processing method. Mechanical properties were investigated through tensile and flexural testing, notched impact testing, and water absorption tests.

3.5 Materials

PHB (Tianan Biologic Material Co., Ltd, Ningbo, China) and 60-mesh ponderosa pine wood flour (American Wood Fibers, Schofield, WI) were used to form the basis of the wood composites. To improve processing by both injection molding and extrusion, lubricant in the form of Glycolube WP2200 (Lonza, Inc., Allendale, NJ) and talc (Nicon 403 obtained from RioTinto of Centennial, CO) were used as additives. Further, because PHB has been known to crystallize slowly, nucleating agent was employed to speed up nucleation and reduce secondary crystallization (Qian, 2007). Based results reported by Qian (2007), fine boron nitride (BN) in platelet form was chosen as a nucleating agent (Carbotherm PCTF5, obtained from Saint Gobain

Advanced Ceramics Corporation, Amherst, NY). Interfacial modifiers shown previously (Anderson, 2007) to improve mechanical properties were incorporated at the 0, or 4% level. The use of interfacial modifiers allowed the authors to investigate differences in processing due to differences in fiber wettability and/or melt viscosity. The modifiers include pMDI (Mondur G541, supplied by Bayer MaterialScience, Pittsburgh, PA), MA-PHB, D.E.R. 662E (DOW, Midland, MI), and Uralac P5142 (DSM Resins US, Inc, Augusta, GA). Finally in order to produce MA-PHB, maleic anhydride (95% purity) and dicumyl peroxide (98% purity) were obtained from Aldrich (St. Louis, MO).

3.6 Methods

3.6.1 Grafting of MA-PHB

Qian (2006) described production of MA-PHB through reactive extrusion. Based on this report, MA-PHB was produced through reactive grafting in a torque rheometer (Haake PolyLab 3000P). The raw components consisted of 95 parts PHB, 5 parts maleic anhydride, and 0.5 parts dicumyl peroxide. These were mixed in a torque rheometer at 180°C and 50 rpm for 40 minutes. Following reactive processing, a vacuum oven (100°C for 12 hours) was used to remove the residual maleic anhydride not grafted to the PHB.

3.6.2 Premixing

Composites of wood fiber reinforced PHB were produced with ca. 60% wood fiber in order to reflect industry standard levels of reinforcement for products such as WPC decking. Higher levels of reinforcement increase melt pressures in extrusion such that the composites may retain their shape after exiting the die. To remove moisture prior to processing, PHB was dried for 12 hours at 100°C, and the wood flour was dried by steam tube to a moisture content of 2.8-

mass % (based on oven dry weight). Composite compositions were as follows: 35 parts PHB, 57 parts WF, 8 parts Talc, 0.2 parts BN, 3 parts WP2200, and 4 parts interfacial modifier.

The raw components were assembled and dry blended by tumbling the mixture in a plastic bag (for injection molded quantities), or by tumbling in a drum mixer for 10 minutes (for extrusion on the Cincinatti Milicron CM 35). Prior to dry blending, pMDI was dispersed in small quantities of PHB using a standard kitchen blender for 1 minute. The pMDI-rich PHB was then dispersed back into the bulk PHB for use in the WF composites modified with pMDI.

3.6.3 Processing by injection molding

Preparing samples through injection molding is a two step process. It is often desirable to compound composites using a twin screw extruder in order to ensure good distribution and mixing of composite components. For compounding, a co-rotating twin screw extruder equipped with a volumetric feeder was utilized (Leistritz ZSE-18). The screw diameter was 17.8-mm, and the L/D ratio was 40. Extrusion temperatures were independently controlled on eight zones along the extruder barrel. A reverse temperature profile was chosen in order to reduce thermal degradation and improve melt strength (Zhang, 2004). From the feeding throat to the die adapter, the temperatures were set as follows; 170°C, 175°C, 170°C, 165°C, 164°C, 163°C, 162°C, and 160°C. The screw speed was maintained at 125 rpm, and the resulting residence time was measured to be around 1.5 minutes. After exiting the die, the extrudate was discharged into air and cooled naturally. Finally, the extrudate was ground into granules using a granulator fitted with a 6 mm pore-size screen (Nelmor, G810M1).

Standard tensile (ASTM D638, type I) specimens and flexure bars (12 x 3 x 127 mm) were produced by injection molding (Sumitomo SE 50D). The temperature zones of the injection

molding machine were independently controlled at 175°C, 180°C, 175°C and 165°C from the feeding end to the nozzle. The mold temperature was held constant at 60°C, and the average cycle time was 50 seconds. The filling pressure was set for 1700-kgf/cm² and packing pressures were set to 1275-kgf/cm² and 1360-kgf/cm² for the 1st and 2nd stage, respectively. Residence times were consistently measured around 5 minutes.

3.6.4 Processing by extrusion

After dry blending in a drum mixer for 10 minutes, composite blends were fed through a conical co-rotating twin screw extruder (Cincinnati Millicron CM 35). The screw diameter is tapered from 35-mm at the feeding throat to the die, and the length-to-diameter ratio of the extruder was 22. A slit die with cross section dimensions of 3.7 x 0.95-cm was used to produce rectangular bars. The temperature zones were independently controlled through 3 barrel zones, 2 die zones, and through the screw at 170, 175, 163, 162, 160, and 160°C, respectively. Melt pressures ranged from 4.5 to 7.5-MPa, and residence times averaged around 5 minutes. Upon exiting the die, the extrudate was cooled through a cold water bath.

3.6.5 Preparation of test specimens

For tensile testing, the injection molded bars were used as received (type I geometry). Extruded samples were trimmed by a shaper to match the geometry for type III tensile tests. Flexure tests were also conducted using the rectangular specimens as received from injection molding, and the as received profile extrusion specimens (cut to 20 cm in length). For impact testing, the test specimens were prepared in accordance with ASTM D256. The straight bars produced through injection molding were cut to 62 mm lengths from both ends of the bar (and were labeled accordingly). The specimens were notched using a V-shaped specimen notch cutter with a 0.25-mm notch radius (XQZ-I, Chengde Jinjian Testing Instrument Co., Ltd.). The

extruded samples were milled down to the core such that the long axis of the impact specimen matched that of the extrusion direction with dimensions of 62 x 12.5 x 3-mm (to match the size of the injection molded specimens). Extruded samples were similarly notched.

Specimens for water absorption tests were milled on a manual milling machine to dimensions of 11 x 2.5 x 125-mm. Both the injection molded and extruded specimens were milled from the exterior skins towards the core. It was necessary to mill the injection molded specimens in order to remove any polymer-rich cap, and it was necessary to mill the extruded specimens such that the process of moisture transport happened on the same scale as with the injection molded specimens.

3.6.6 Mechanical and physical properties

Tensile tests were performed on all composites in accordance with ASTM D638. Specimens were of type I and type III geometry for injection molded specimens, and extruded specimens, respectively. All specimens were conditioned 48 hours prior to testing. Testing was performed using a screw driven Instron 4466 Standard with a 10-kN electronic load cell. The crosshead speed was 5-mm/min, and the initial strain was measured with a clip-extensometer with a 25-mm gage length (MTS model # 634.12E-24). The geometry (length, width, and thickness) and weight were measured on all samples and density was calculated on a weight/volume basis. Flexural testing was executed in accordance with ASTM D790. The support span was set to be equal to 16 times the specimen depth.

To investigate the fiber dispersion and/or fiber breakdown of the composites, cross sections of the composite surface were cut using Reichert Ultramicrotome fitted with a glass knife. Water was used to facilitate smooth cuts to the composite surface. After removing the

surface moisture under a hot light the specimens were placed in a desiccator to further reduce the surface moisture content. The dried specimens were then sputter coated with gold for observation by scanning electron microscope (SEM) on a Hitachi S-570.

Because improvements in interfacial modification in polymer-fiber composites may reveal improved toughness and resistance to crack propagation, notched impact tests were performed to assess differences in interfacial adhesion, or processing method. Notched impact tests were performed in accordance with ASTM D256, method A. The Izod pendulum impact test frame was configured for a maximum impact energy of 2.7-J.

Immersion test ASTM D570 was in part, adopted to measure the water absorption of the composites. Specimens were soaked in a bath of distilled water held at room temperature. Prior to taking measurements, specimens were blot-dried with a towel and allowed to naturally dry in air for 10 minutes. The moisture content (MC) was calculated on a mass percent basis using the following equation:

$$MC = \frac{(M - M_o) \times 100}{M_o} \quad (1)$$

Where M is the weight of the specimen at time t, and M_o is the initial (dry) weight of the specimen.

3.6.7 Statistical Analysis

To help sort the influence of processing vs. interfacial modifiers, mechanical properties were assessed using an analysis of variance (ANOVA). When significant, the influence of density was accounted for as a covariate. The resulting analysis of covariance (ANCOVA) helped to account for the variability in mechanical properties due to variance in density. A

general linear model with significance, $\alpha = 0.01$ was employed through SAS statistical software (SAS Version 6.9.1, SAS Institute Inc., Cary, NC).

3.6.8 Thermal Properties

Properties of the polymer melt and crystallization for the composites were examined using a differential scanning calorimeter (DSC) (Mettler Toledo, DSC 822e). Injection molded samples were taken from tensile specimens in a specific location in the center of the specimen. Extruded DSC samples were taken from the bulk of the cross section (2-mm from the edges). All tested specimens weighed from 3-6-mg and were hermetically sealed in 40- μ l aluminum crucibles. Each sample was heated from -30°C to 180°C at 20°C/min in order to obtain information for the polymer crystal morphology post processing. All samples were aged similarly, post processing.

3.7 Results and discussion

3.7.1 Effect of processing on density

In the processing of materials through injection molding, most systems employ two stages for applying pressure to force the molten material into the mold cavity. Initial injection of the material is controlled by the injection pressure. This stage is used to force a set volume of material (as determined by the injection shot size) into the mold cavity (Osswald, 2006). Once the mold cavity has been filled, additional material is forced into the cavity to compensate for shrinkage of the material as it cools on contact with the cool mold wall. This excess pressure to compensate for material contraction is specified by the packing pressure (Kamal, 1977).

Conversely, extrusion processes rely on normal stresses developed due to the pressure of the melt being forced into smaller volumes by the screw. This normal stress forces the extruded

material to take the shape of the die (White, 1977). Depending on the formulation, the melt pressures of the PHB/WF composites through extrusion ranged from 5.1-MPa to 7.2-MPa. In contrast, the filling pressure for injection molding was held constant at 167-MPa, and the packing pressure was held at ca. 128-MPa. Given the differences in processing pressures, it would be apparent that these two methods would lead to differences in composite density.

As is depicted in figure 3.1, the two processing methods do result in differing densities. For the unmodified PHB/WF composite the results show a jump in density from 1.29-g/cm³ to 1.36-g/cm³ for the extruded and injection molded composites, respectively. These differences in density are within reasonable limits, as HDPE/WF composites processed by injection molding and extrusion have exhibited densities of 1.40-g/cm³ and 1.26-g/cm³, respectively (Stark, 2004).

3.7.2 Statistical analysis of stiffness and strength

Previous studies have shown that the influence of density on mechanical properties is very strong (Facca, 2006). An analysis of covariance (ANCOVA) is a general linear model with which the power of an analysis of variance (ANOVA) is combined with the features of a linear regression. The ANCOVA describes main effects after removing the variance in the response variable due to the variance in the continuous covariate. If the effect of the covariate is found to be significant, then equal regression slopes are assumed. This assumption allows for a single regression relationship to be estimated between the covariate and the response variable. Using either Young's modulus or tensile strength (E, or σ_{max} , respectively) the ANCOVA model statement was constructed as follows:

$$Y_{ij} = \beta_0 + \varphi_i p_i + \mu_j m_j + \tau(\rho_{ij} - \bar{\rho}_{..}) + \varepsilon_{ij} \quad (2)$$

Where:

Y_{ij} = response value (E or σ_{\max})

β_0 = model intercept

φ_i = coefficient of the main effect for processing method (i = Injection Molded, Extruded)

p_i = the Boolean variable for the main effect for processing method (i = Injection Molded, Extruded)

μ_j = coefficient of the main effect for the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

m_j = the Boolean variable for the main effect of the i^{th} interfacial modifier (i = MA-PHB, DER, Uralac, pMDI)

τ = coefficient for the effect of covariate density

ρ_{ij} = the variable density corresponding to Y_{ij}

$\bar{\rho}_{..}$ = grand mean of density

Using τ , subsequent adjustments may be made to the original response variable in order to express them at a common density. Since the extruded specimens all exhibited lower density than the injection molded specimens, the general effect of adjusting to a mean density is that the stiffness and strength for the extruded specimens is raised relative to the injection molded specimens.

The high packing pressures applied on the part while solidifying in the mold helps the densification of the materials and wetting of fiber by the polymer. With extrusion, the increases in fiber affinity with more effective modifiers may allow for better fiber disintegration. As fiber bundles are broken down, the interfacial area across which stress may be transmitted is increased. As is shown in Figure 3.2, this has the effect of increasing the composite stiffness of the extruded specimens from that of the unmodified composite.

In contrast, composites produced through injection molding display comparable moduli, with the exception of the composite modified with pMDI. Where different modifiers improved stiffness of composites processed through extrusion, the same composites show little difference in stiffness processed through injection molding. It is possible that the effects of increased fiber wetting have no benefit in light of the high-shear pre-compounding process, and the high pressures of the injection molding process. However, the high stiffness of the pMDI is no fluke, as was shown previously (Anderson, 2007), increasing amounts of pMDI added to PHB/WF composites consistently resulted in higher composite stiffness. It is likely that in addition to better wetting of the wood fibers, pMDI is helping to physically or chemically improve the PHB-fiber adhesion.

Interpretation of the ANCOVA results (Table 3.2) for stiffness suggests that all factors have a significant effect on stiffness. Examination of the Duncan groupings does not indicate differences between the Uralac and the MA-PHB, as well as the D.E.R. from the control. However, the mean value separation of the Duncan groupings are taking into account the mean from both injection molding and extrusion processes. Similarly, in averaging the effect of different modifiers, the Duncan grouping also suggests a significant difference between injection molding and extrusion.

The results from the ANCOVA lead us to conclude that all effects for tensile strength are significant. The effect of processing is still highly significant, but less so than with stiffness because of the convergence in strength properties with the addition of more effective modifiers. The Duncan groupings also support the notion of significant differences in strength between all modifiers and between both injection molding and extrusion processes.

The adjusted values for tensile strength as a function of processing method and modifier type are represented in Figure 3.3. Interpretation of the results suggests that the tensile strength of composites processed by injection molding is generally higher than that of composites processed by extrusion. However, as the modifiers increase in effectiveness, the differences between composites processed by different methods decreases. This behavior suggests two competing effects; the first is that the addition of the interfacial modifier improves fiber wetting and as a result facilitates fiber dispersion through the composite, the second effect is that the high shear rate involved in pre-compounding (a twin screw speed of 125-rpm) followed by the high shearing of the composite during injection molding facilitates better mixing and fiber dispersion. With the control formulation a large difference in strength can be seen between the extruded and the injection molded samples, here injection molding is likely dispersing fibers more thoroughly through the composite allowing for stress to be shared equally among the fibers. With the addition of 4% pMDI, no practical difference in strength is present between the composites processed by both methods.

While no other studies have used PHAs in composites reinforced with wood fiber at levels of 60% WF, data from other fiber composites, or differing wood levels can help to gauge reasonable levels for mechanical properties. Gatenholm (1992) studied PHB, PP, and polystyrene (PS) composites reinforced with 40% cellulose fiber, processed through injection molding. Stiffness was measured for each system in terms of Young's modulus and was found to be 3.7-GPa, 6.3-GPa, and 6.2-GPa, for the PP, PS, and PHB composite systems, respectively. While the reported values in this study seem high for tensile modulus, they seem to be consistent in that PHB composites yield much higher stiffness than those of PP. Summarized in Table 3.4 are tensile stiffness and strength for composites modified with 60% WF, produced through injection

molding. The results indicate that in comparison with unmodified PP/WF composites, PHB/WF composites exhibit much higher stiffness, and comparable strength. When modified with equal levels of MAPP, or pMDI, the strength of the PP/WF composites exceeds that of the PHB/WF composites, and PP/WF is exceeded by PHB/WF in stiffness.

Through extrusion the differences in flexural properties are not as drastic as those just described for injection molded composites. Shown in Table 3.4 are values for PP, PE, and PHB/WF composites produced through extrusion with ca. 60% WF. The values suggest that strength values of PP and PHB/WF composites are relatively comparable for both modified and unmodified composites. Further, the stiffness of PHB/WF composites is higher than that of PP/WF for both the modified and unmodified composites. Finally, both the stiffness and the strength are higher than those values reported for PE/WF composites. However, because these composites were produced with different additives, and through different extruders these comparisons should be made lightly, as results may differ for a contiguous study conducted on PP/WF, PE/WF, PHB/WF composites.

3.7.3 Composite toughness

As measures of ductility and resistance to crack propagation, both failure strain (under tensile loading) and the impact energy (by notched Izod tests) were recorded for both processing methods and interfacial modifiers. Because of the brittle nature of the composites, no differences were noted in fracture energy as a function of either processing method or modifier type. All composites indicated fracture energies ranging from 3.0 to 3.5-kJ/m². Similarly, the failure strain of all the composites was low. Values for failure strain by tensile testing ranged from 0.3 to 0.6%. An ANCOVA similar to the model described for stiffness and strength was analysed. The effect of the covariate density was not found to be significant. As a result, tensile strain has not

been adjusted to a mean density and is displayed in its raw form in Figure 3.4. The results pictured in Figure 3.4 suggest no overall difference in failure strain between injection molding and extrusion processes. However, the extruded samples seem to have a larger spread of failure strains as function of modifier type than that of the injection molded samples. This is most likely due to the varying effect of wetting due to modifier type, was earlier suggested to have a strong influence on properties through extrusion.

3.7.4 Effect of processing on water uptake of composites

PHB/WF composites of similar size were tested for water uptake when fully immersed. Water uptake is often described non-steady state diffusion (or Fickian behavior). Under conditions of non-steady state diffusion, the concentration gradient of a molecule diffusing through a medium changes with respect to time and results in a net accumulation in mass. A direct solution to Fick's second law by which an apparent diffusion coefficient D_A may be calculated is described by the following equation:

$$D_A = \pi \left[\frac{h}{4M_{sat}} \right]^2 \left[\frac{\partial M_t}{\partial \sqrt{t}} \right]^2 \quad (4)$$

Where h is the thickness of the sample, M_{sat} is the water uptake percentage at saturation, and $\partial M_t / \partial \sqrt{t}$ is the slope of the water uptake versus square root of time (Chowdhury and Wolcott, 2007). Fickian diffusion may then be described by a linear relationship of $\partial M_t / \partial \sqrt{t}$. When the composites immersed in water approach saturation, deviation from Fickian diffusion will occur. Further, if composite defects are present or form, fast diffusion paths are created within the composite that also result in deviation from steady state diffusion (Roy and Xu, 2001).

Depicted in Figures 3.5 and 3.6, the water uptake behavior is plotted as a function of time^{1/2} for both extruded and injection molded specimens respectively. It can be seen through Figure 3.6, that modified and unmodified composites exhibit an inflection point in the slope of the curves. Further, with increasing modifier effectiveness, this inflection point occurs later in testing. It was observed that the inflection in the plots coincided with the visual observation (Figure 3.7) of the injection molded composites cracking. As a result, it may be determined that steady state diffusion occurs until the inflection point (due to composite damage).

In contrast, the extruded samples exhibited steady state behavior until saturation. It is possible that this difference in behavior is due to the higher average density of the injection molded specimens. With larger quantities of fiber and matrix enclosed within the same volume, it would be expected that the hygrothermal strains due to fiber swelling would be greater in the composite with a higher density. The increase in hygrothermal strains due to an increase in density may cause debonding, which may lead to cracking of the composite.

To calculate representative diffusion coefficients, Rao (1988) proposed a correction that considers edge the edge effects of diffusion through a specimen. The apparent diffusion coefficient may be adjusted as follows to calculate the true diffusion coefficient (D):

$$D = \frac{D_A}{\left(1 + \frac{h}{L} + \frac{h}{W}\right)^2} \quad (5)$$

Where W is the specimen width and L is the specimen length. The average diffusion coefficients were calculated for the control, 4% MA-PHB, 4% D.E.R., 4% Uralac, and 4% pMDI, and were found to be 3.94e-6, 2.44e-6, 2.96e-6, 2.23e-6, and 8.86e-7 mm²/sec, respectively. It was found that incorporation of more effective modifiers reduced the diffusion

coefficient of the PHB/WF composites. The diffusion coefficients calculated for PHB/WF are higher than results reported for PE/WF (60%) extruded composites, which ranged from $6.29\text{e-}7$ to $8.07\text{e-}7$ mm^2/sec (Chowdhury and Wolcott, 2007).

3.7.5 Effect of processing on composite morphology

Since we are only able to view a 2-d slice of the composite, it is not easy to get a global image of the fiber bundles however, looking at the two extreme cases (of 4% pMDI modified composites vs. the control) will give us the best estimation of the bulk differences. Figure 3.8 displays SEM micrographs of the microtomed surface of the control and 4% pMDI composite, processed through both methods. With the control composites a large discrepancy in the fiber morphology is present across processing methods. The extruded control specimen displays fiber bundles that are fully in-tact. Conversely, the injection molded control shows little evidence of fiber bundles, and fibers are evenly dispersed through the matrix. When looking at composites modified with 4% pMDI, little differences in fiber morphology between processing methods are visible. Both injection molded and extruded composites display fibers that are dispersed and collapsed. This processing/modifier effect on fiber morphology supports results described from tensile testing. The stronger fiber affinity of the pMDI modified composites has the effect of dispersing fibers in extrusion similar to that in injection molding. Conversely, the hydrophobic PHB matrix in the control composite does not wet the fiber bundles adequately. As a result, when processed through extrusion, fiber bundles remain in-tact, and when processed with high pressure in injection molding, fiber bundles are broken down by the high shear forces.

3.7.6 Effect of processing on polymer crystalline structure

The mechanical properties of PHB have been shown to be greatly influenced by aging time, and thermal treatment, or annealing (de Koning and Lemstra, 1993; Biddlestone, 1996).

Since crystallization kinetics are greatly influenced by cooling parameters from the melt, and aging has been shown to be a mechanism of secondary crystallization (de Koning and Lemstra, 1993), differences in crystallinity are likely to arise when looking at the composite from the as-processed state. Because PHB is prone to recrystallization effects resulting in bimodal melting, (Qian, 2007), a rapid heating rate was used to minimize this effect.

Figure 3.9 illustrates representative DSC heating thermograms of unmodified composites processed and cooled through injection molding (with a mold temperature of 60°C), and through extrusion (cooled by a water bath). In order to avoid differences in polymer content, DSC samples were taken from the core of the extruded profile instead of the polymer-rich skin. The injection molded specimen displays a bimodal melting system, while the extruded specimen does not. Because of the larger cross-section size of the extruded bars, and the fact that DSC specimens were taken from the bulk material, it is likely that the tested material underwent cooling at a rate so slow enough to allow for a higher degree of crystallization which allowed for less secondary crystallization. This resulted in a more homogeneous crystal structure, unlike the injection molded specimens which were cooled relatively rapidly. Further, Table 3.5 indicates no significant difference in crystallinity by cooling method as is measured by the heat of fusion.

These differences in crystallization are likely to have an effect on mechanical and physical properties. However, given the multitude of other variables taking effect on these properties, the direct effect of crystallization cannot be isolated through these studies.

3.8 Conclusion

To further investigate the viability of PHB/WF composites for use in commercial WPC applications, PHB/WF composites have been extruded with modifiers previously shown to

significantly improve mechanical properties. Further, the effects of processing PHB/WF composites through injection molding and extrusion processes have been compared. Raw formulations have been prepared similarly for both processes with various interfacial modifiers, and resulting mechanical and physical differences examined. Tensile testing of composites showed higher values of Young's modulus and ultimate tensile strength for injection molded specimens over extruded specimens. Similar composite specimens showed higher density from injection molding processes than from extrusion processing. The variation in mechanical properties was accounted for through statistical analysis of density as a covariate in an ANCOVA using processing methods and interfacial modifier types as main effects. Further differences in mechanical properties were attributed to fiber dispersion within the matrix. Micrographs of the composite surfaces from SEM suggested decreased size in fiber bundles with injection molded composites. Regardless of processing method, the type of interfacial modifier added to the composite formulations was suspected to have an influence on fiber dispersion, likely through better fiber wetting.

Mechanical properties of PHB/WF composites processed through extrusion were shown to be competitive with coupled PP/WF composites. PHB/WF composites modified with pMDI indicated higher stiffness, and comparable strength to MAPP coupled PP/WF composites at the same percentage of modifiers.

Water absorption of the composites processed by different methods displayed considerable differences in behavior. Cracking of the injection molded specimens was observed and suggested to be a result of the higher composite density. Extruded specimens displayed characteristics only of water uptake and saturation. Prior to cracking, moisture transport was more limited in injection molded specimens than that in extruded specimens.

Interpretation of DSC traces suggested differences in crystal perfection between injection molded and extruded specimens. The degree of crystallization, as measured through the heat of fusion and the heat of crystallization was unchanged respective to processing method.

3.9 References

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3.10 Tables

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Processing	1	0.233	0.233	1338.00	<0.0001
Modifier	4	0.075	0.019	107.85	<0.0001
Processing*Modifier	4	0.004	0.001	6.42	<0.0001

Processing	Injection Molding	Extrusion
Duncan Grouping	A	B
Mean (g/cm ³)	1.40	1.33

Modifier	4%Uralac	4% pMDI	4% DER	4% MA-PHB	Control
Duncan Grouping	A	A	A	B	C
Mean (g/cm ³)	1.39	1.38	1.38	1.37	1.33

Table 3.1 Table 3.1 Type III ANOVA and duncan grouping for effect of processing and modifiers on density ($R^2 = 91.6\%$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Processing	1	4.938	4.938	38.41	<0.0001
Modifier	4	24.591	6.148	47.83	<0.0001
Processing*Modifier	4	4.658	1.165	9.06	<0.0001
Density	1	1.913	1.913	14.88	0.0002

Processing	Injection Molding	Extrusion
Duncan Grouping	A	B
Mean (GPa)	8.77	7.13

Modifier	4% pMDI	4% Uralac	4% MA-PHB	4% DER	Control
Duncan Grouping	A	B	C	C	D
Mean (GPa)	9.06	8.32	7.90	7.84	7.33

Table 3.2 Type III ANCOVA and duncan grouping for effect of modifiers and processing method on tensile modulus ($R^2 = 89.8\%$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Processing	1	23.167	23.167	10.03	0.0019
Modifier	4	1542.548	385.637	166.94	<0.0001
Processing*Modifier	4	105.646	26.411	11.43	<0.0001
Density	1	98.475	98.475	42.63	<0.0001

Processing	Injection Molding	Extrusion
Duncan Grouping	A	B
Mean (MPa)	28.20	21.30

Modifier	4% pMDI	4% Uralac	4% DER	4% MA-PHB	Control
Duncan Grouping	A	B	C	D	E
Mean (MPa)	33.00	27.77	25.59	21.86	18.13

Table 3.3 Type III ANCOVA and duncan grouping for effect of modifiers and processing method on tensile strength ($R^2 = 94.7\%$).

Matrix	Modifier	Extruded, 60% WF		Injection Molded, 40% WF	
		MOE (GPa)	MOR (MPa)	E (GPa)	σ_{max} (MPa)
PHB	-----	5.3	28	2.2	19.9
PHB	2% pMDI	7.0	42	5.2	45.5
PP	-----	4.1*	33*	8.1 [†]	22.0 [†]
PP	2% MAPP	4.3*	48*	9.4 [†]	27.8 [†]
PE	-----	2.9*	18*	-----	-----
PE	2% MAPE	2.6*	39*	-----	-----

Table 3.4 Tensile properties of WPCs injection molded with ca. 60% WF (*Reference: Beg and Pickering, 2004).

Processing Method	Melt Crystallization		Melting				
	T _c (°C)	ΔH _m (J/g)	T _{m1} (°C)	1 st Scan T _{m2} (°C)	ΔH _m (J/g)	2 nd Scan T _m (°C)	ΔH _m (J/g)
Ext	100.4	22.3	NA	163.1	-23.8	160.1	-24.7
IM	98.3	23.3	154.2	162.1	-24.9	156.8	-26.6

Table 3.5 Effects of processing on thermal properties of PHB/WF (control formulation).

3.11 Figures

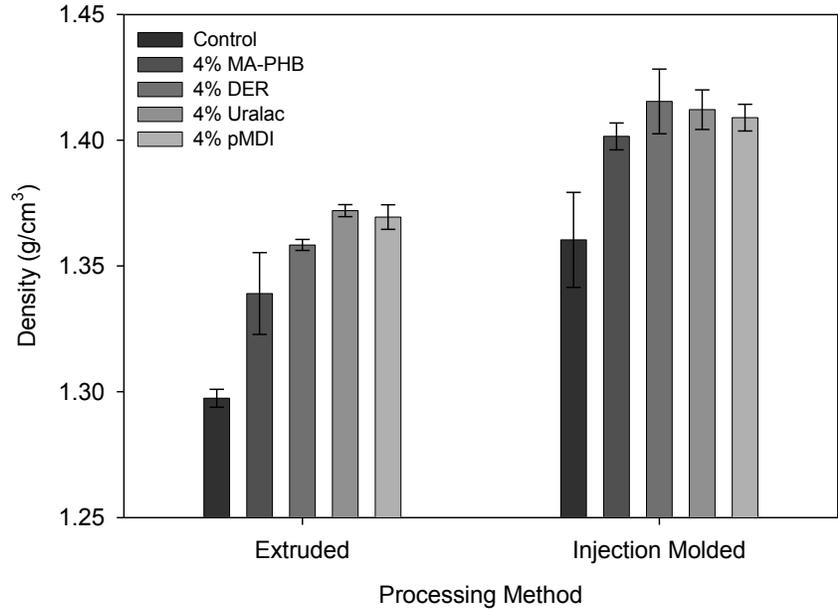


Figure 3.1 Density of PHB/WF modified composites processed through extrusion and injection molding.

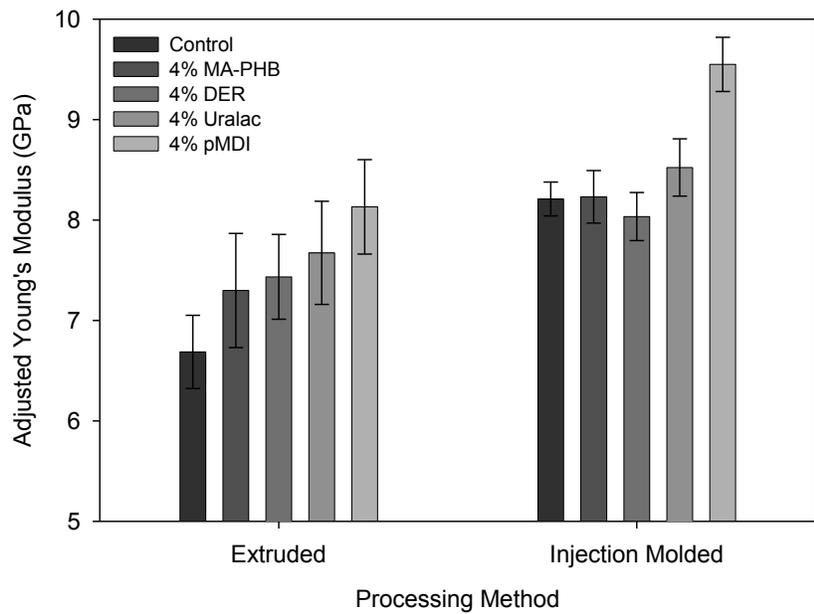


Figure 3.2 Tensile modulus of PHB/WF and PHB/WF modified composites processed through extrusion and injection molding.

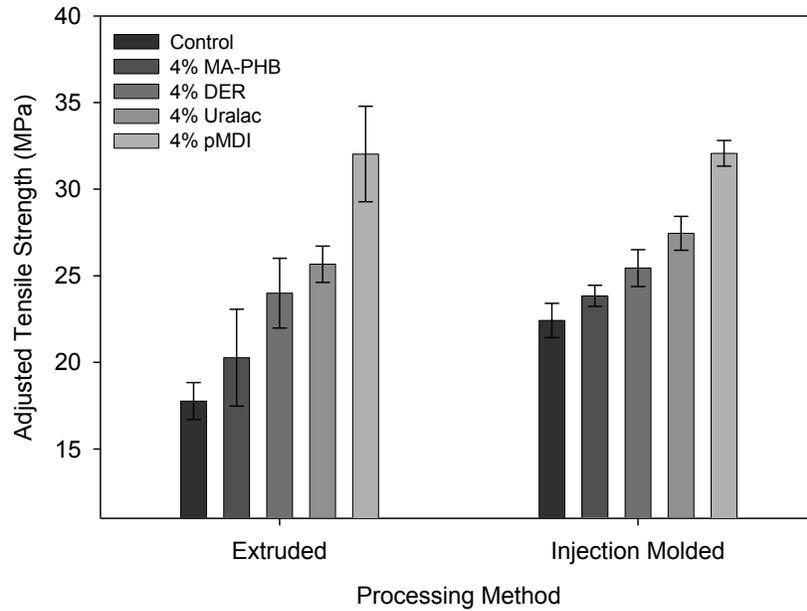


Figure 3.3 Tensile strength of PHB/WF and PHB/WF modified composites processed through extrusion and injection molding.

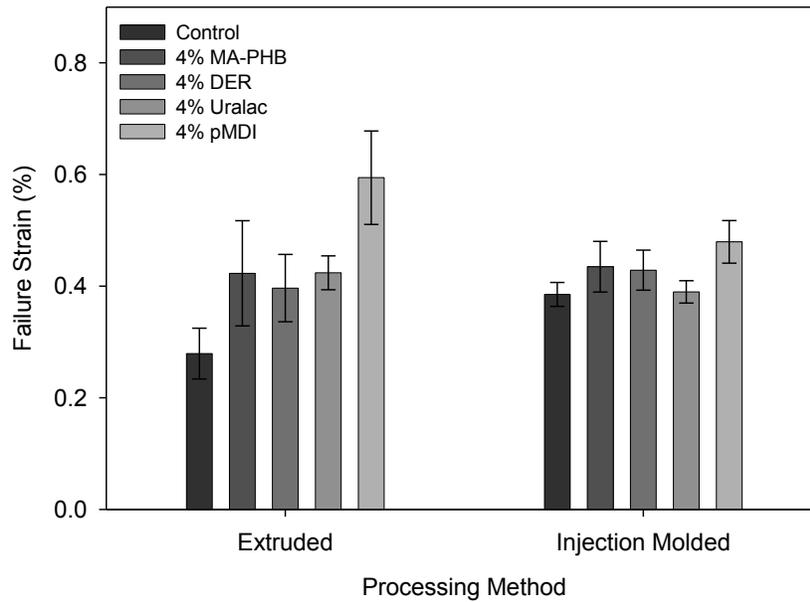


Figure 3.4 Failure strain of PHB/WF and PHB/WF modified composites processed through extrusion and injection molding.

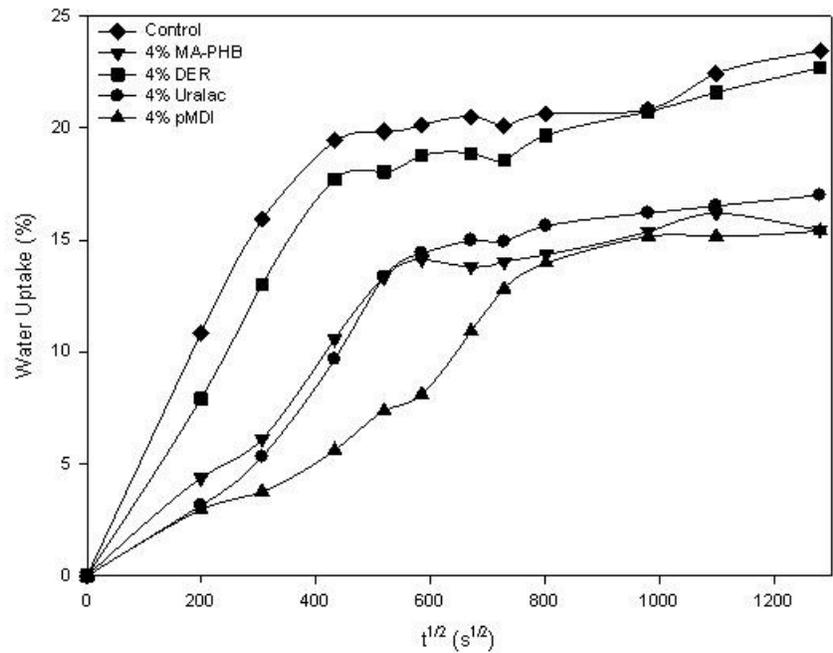


Figure 3.5 Water absorption of PHB/WF and PHB/WF modified composites processed through extrusion.

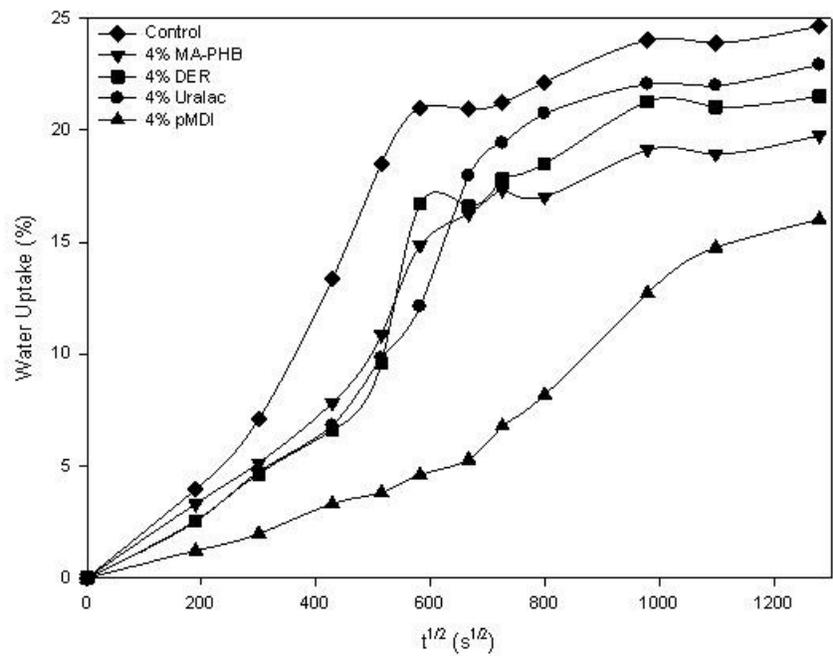


Figure 3.6 Water absorption of PHB/WF and PHB/WF modified composites processed through injection molding (Anderson, 2007).



Figure 3.7 Photograph of an injection molded PHB/WF composite (control formulation, immersed for 4 days) (Anderson, 2007).

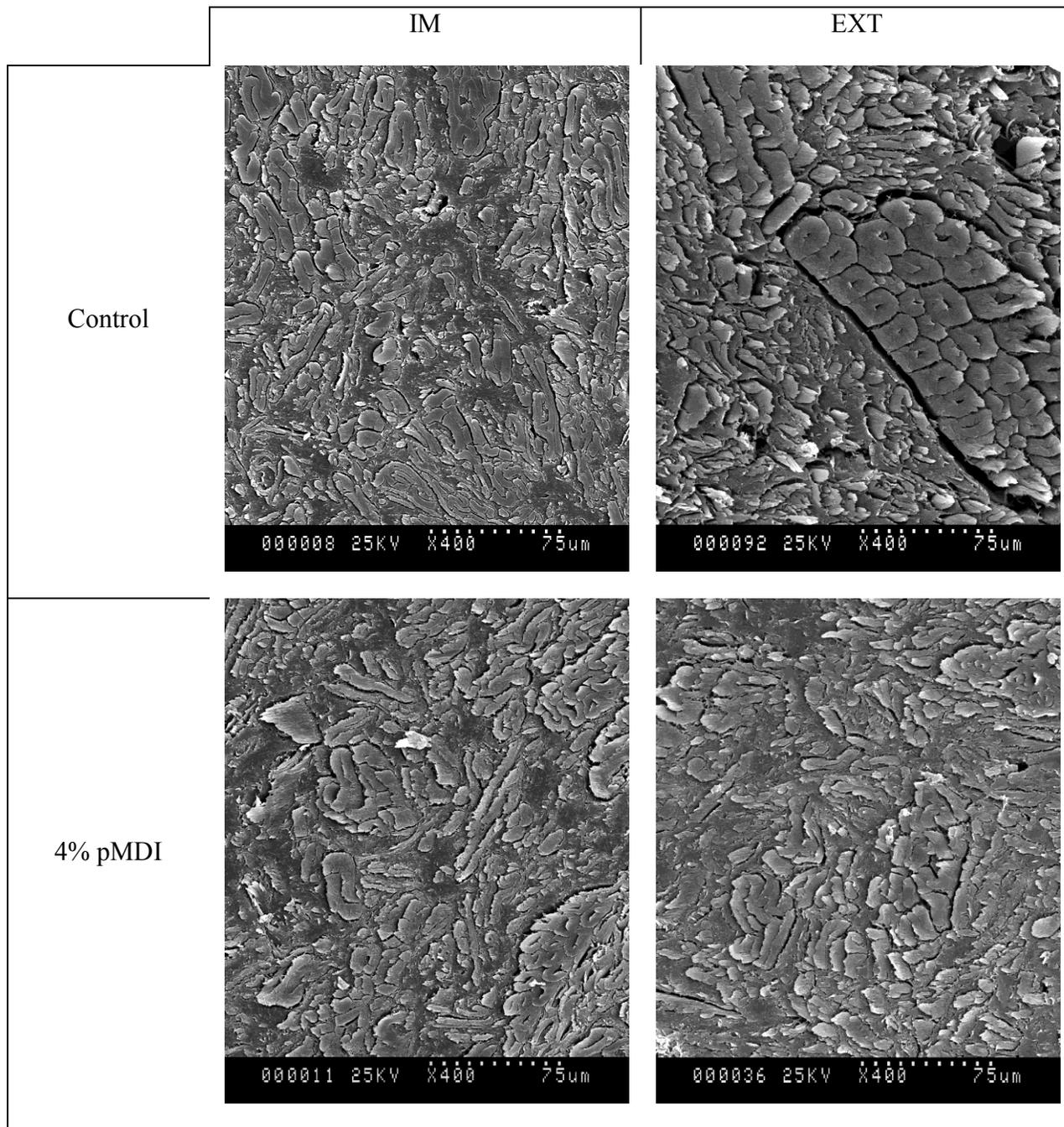


Figure 3.8 SEM micrograph of microtomed PHB/WF, processed through injection molding and extrusion.

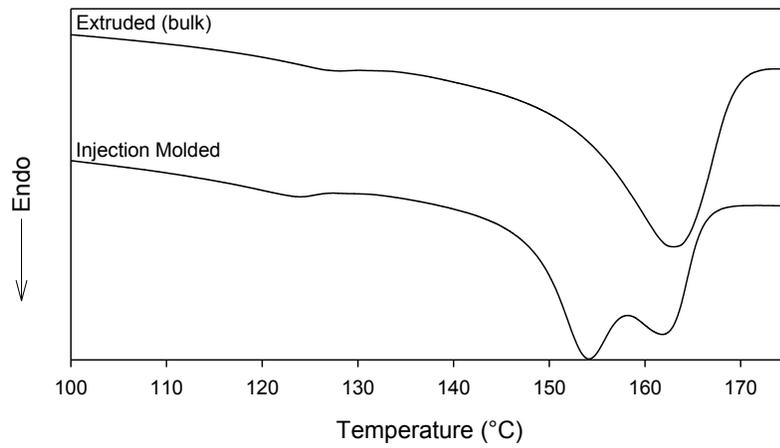


Figure 3.9 DSC thermogram of the first heating after processing of PHB/WF (control formulation) processed through injection molding and extrusion.

4. CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

Concerns mounting over the dependence on fossil fuels and foreign oil supplies paired with increasing awareness over global warming are growing. As a result, the market for bio-based materials is growing as well. Biocomposites made from polyhydroxybutyrate and wood fiber (PHB/WF) offer a viable alternative to polyolefin based -wood plastic composites (WPCs). To date, composites based on petrochemically derived polyolefins have been extensively studied for use in WPCs and have applications in decking, siding, and fencing. Effective solutions to improve the polymer-fiber adhesion have been developed and offer improvements on mechanical and physical properties. In contrast, no studies have yet reported solutions to improve the mechanical properties of PHB/WF composites. Further, PHB/WF composites have yet to be produced with formulations comparable to those used for the aforementioned applications, nor be processed by similar methods. Therefore, the intent of this research was two-fold. First, to examine the mechanical and physical properties of formulations similar to those used for polyolefin/wood fiber home construction materials, and utilizing additives aimed at improving mechanical properties of the composites through injection molding. Secondly, to investigate the differences in processing PHB/WF composites through extrusion (commonly used for mass production of WPCs), and injection molding (commonly used for research purposes).

Potential agents to modify interfacial adhesion of PHB/WF composites were first screened. Reports of maleated PHB (MA-PHB), and poly(methylene diphenyl diisocyanate) (pMDI) suggested the potential to improve the mechanical properties of PHB/WF composites. In addition, two novel interfacial modifiers were identified as possible candidates for improvements. The composites were produced with ca. 60% wood fiber (WF) through injection

molding. Tensile tests of the composites revealed great improvements in stiffness and strength with the addition of pMDI at levels of 0, 1, 2, and 4%. While the strength was improved with all interfacial modifiers, the effect was most pronounced with pMDI. Water absorption tests showed improvements in the water uptake of all composites, but was most pronounced again with those modified by pMDI. Scanning electron microscopy (SEM) micrographs of the tensile fractured surfaces suggested increased fiber adhesion with the addition of 4% pMDI to the PHB/WF composites through decreased fiber pullout and increased compatibility between the fiber and the matrix from that of the control specimens. Interpretation of thermal properties suggested increased fiber adhesion, paired with possible crosslinking of the PHB, lubricant, and pMDI.

When processed through extrusion, the same formulations resulted in lower stiffness and lower strength. Injection molded specimens resulted in higher densities than extruded specimens. The variation in mechanical properties due to differences in density was accounted for through statistical analysis, and subsequent differences in mechanical properties were attributed to differences in fiber dispersion. SEM images of microtomed surfaces revealed a cross-section of fibers incorporated in the polymer matrix, and provided further evidence for higher fiber dispersion through injection molding than extrusion processes. Water absorption tests of composites processed by different methods displayed considerable differences in behavior. Cracking of the injection molded specimens was observed and suggested to be a result of higher composite density. Extruded specimens displayed characteristics only of water uptake and saturation. Prior to cracking, moisture transport was more limited in injection molded specimens than that in extruded specimens. Processing of composites through injection molding also had the effect of decreasing the crystal perfection over that of extrusion processing. Because of the

differences in geometry of finished parts, the bulk of the extruded specimens were allowed to cool more slowly and resulted in a greater degree of crystal perfection.

This research has provided direction on some promising interfacial modifiers that effectively work to improve the mechanical properties of PHB/WF composites. This study has shown that PHB/WF composites may be manufactured with mechanical properties comparable to those of coupled PP/WF composites. Work has begun in understanding the influence of pMDI on improving mechanical properties, but is not yet conclusive. Since a basis has been established in understanding the differences in processing of these composites, further studies may be able to better predict the effects of scaling up in processing from injection molding to extrusion.

4.2 Future work

In order to further the viability of PHB/WF composites, the raw material cost of PHB must still be reduced. This may be accomplished by the utilization of PHB-rich biomass and the elimination of PHB purification from the processing of raw PHB. Further studies on PHB-rich biomass and WF composites modified with pMDI may show competitive improvements in PHB/WF composites in both cost, and performance criteria. Further, the effects of pMDI on improving the polymer-fiber adhesion between PHB and WF are still not clear. Direct studies of the crystal morphology, using polarized optical microscopy (POM) and studies of chemical interactions at the interface using fourier transform infrared spectroscopy (FTIR) may be beneficial in further understanding the mechanisms of improvements in mechanical properties.

APPENDIX A – STUDY OF VARIOUS LUBRICANTS ON PHB/WF COMPOSITES

A.1 Introduction

As the viscosity of wood-plastic composites increases with higher wood content, the selection of a lubricant suitable for the polymer matrix becomes very important. The proper selection of lubricant can improve the surface quality of extruded products and allow for faster processing speeds. The following research includes an extensive study on lubricant packages was conducted to determine the most effective system for polyhydroxybutyrate/wood fiber (PHB/WF) composites.

A.2 Methods and Materials

Wood plastic composites (WPCs) based on PHB were produced with the same control formulations and materials reported previously (Anderson, 2007). No interfacial modifiers were used and a variety of lubricants in addition to Glycolube WP2200 (Lonza, Inc, Allendale, NJ) were tested; EBS (N,N'-ethylene-bisstearamide from GE Specialty Chemicals), Zinc Stearate (ZnSt) (DLG-20B from Ferro Corp., Cleveland, OH) in a blend of 2:1 ZnSt/EBS, Optipak 100 (OP100) (Honeywell, Morristown, NJ), oxidized polyethylene (OPE) (A-C 629 from Honeywell, Morristown, NJ), and Struktol 306 (Struktol Co. of America, Stow, OH) were included in PHB/WF composites at 3% on total. The formulations were mixed in a drum blender for 10 minutes and then processed through twin screw extrusion (Cincinnati Milicron CM 35). The temperatures for extrusion processing were controlled through 3 barrel zones, 2 die zones, and through the screw at 170, 175, 163, 162, 160, and 160°C, respectively. The extrudate was cooled through a cold water bath after exiting the die. Flexural testing was performed on the as-received rectangular specimens cut to 20-cm in length, in accordance with ASTM D790 on a screw driven Instron 4466 Standard.

A.3 Results and Discussion

Based on mechanical performance, Figure A.1 shows that composites processed with the lubricant Glycolube WP2200 performed exceptionally in both stiffness and strength when compared to the performance of the composites with other lubricant systems. The flexure strength of all of the composites except those with WP2200 fluctuates from 20-23-MPa, whereas using WP2200 resulted in a 36% increase to 30-MPa. Similarly, for flexural stiffness, the use of WP2200 instead of other lubricants resulted an increase of roughly 21%. While visual observation are subjective, there was some variation in the quality of the surface of the extruded bars that coincided with the variation in lubricant packages, both Glycolube WP2200 and OPE appeared to perform well.

A.4 Conclusions

From these results it is apparent that Glycolube WP2200 helps to produce PHB/WF composites with superior mechanical properties. Both stiffness and strength displayed strong improvements over all other lubricant systems studied. All further investigations will make use of this investigation by utilizing WP2200 just as shown presently, at levels of 3% on total.

A.5 References

Anderson, S.P. "Effect of Interfacial Modifiers on Mechanical and Physical Properties on PHB/WF and Their Effect on Composite Morphology." Washington State University, Masters Thesis, Ch. 2, Dec. 2007.

A.6 Figures

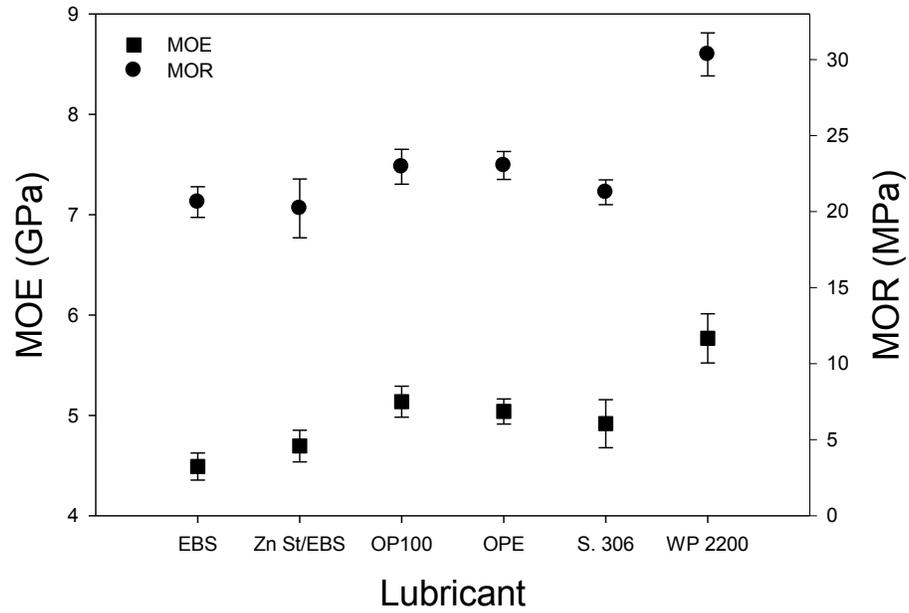


Figure A.1 Comparison of lubricant systems in PHB/WF composites on flexural stiffness and strength.

APPENDIX B –VARIED WOOD FIBER LEVELS AND HV CONTENT ON PHB/WF COMPOSITES

B.1 Introduction

In current literature, polyhydroxyalkanoate/wood fiber (PHA/WF) composites are produced with varying variables, making comparisons to other research difficult. Studies of PHA composites have utilized various wood contents (Coats, 2007), and various types PHAs (Gatenholm. 1992). As was shown by Facca (2006), variation in the fiber content on high density polyethylene (HDPE) can have a strong effect on both stiffness and strength. Gatenholm (1992) also showed that variation in hydroxyvalerate (HV) content on polyhydroxybutyrate-co-hydroxyvalerate (PHBV) can also have a strong effect on both the stiffness and strength of composites. In this study, the effects of both variation in wood flour content, and HV content on the mechanical properties of PHA/WF composites are investigated.

B.2 Methods and Materials

Polyhydroxybutyrate (PHB), and PHBV containing 8 and 12% HV in fine powder form were provided by Tianan Biologic Material Co. (Ningbo, China), and Metabolix Inc. (Cambridge, MA), respectively. Boron nitride (BN) powder (Carbotherm PCTF5, obtained from Saint Gobain Advanced Ceramics Corporation, Amherst, NY) was used as a nucleating agent at levels of 0.5% on total polymer weight. Ponderosa pine wood flour (60-mesh) was obtained from American Wood Fibers (Schofield, WI) and was dried by steam tube.

Prior to precompounding, the PHA/WF mixes were manually tumbled in a plastic bag for 5 minutes. Precompounding was performed through a Leistritz ZSE-18 twin screw extruder. The extrudate was cooled in a water bath and then pelletized and oven dried for injection molding.

Tensile specimens in accordance with ASTM D638 (type I) standards were produced through injection molding (Sumitomo SE 50D). The temperature zones of the injection molding machine were independently controlled at 180°C, 185°C, 175°C, and 165°C from the feeding end to the nozzle, respectively. The mold temperature was held constant at 60°C. Tensile specimens were tested on a screw driven Instron 4466 Standard with a 10-kN electronic load cell. The crosshead speed was 5-mm/min, and the initial strain was measured with a clip-extensometer with a 25 mm gage length (MTS model # 634.12E-24).

B.3 Results and Discussion

Produced with 40% wood flour, the effect of PHBV composites with varying HV content on mechanical properties is shown in Figure B.1. An increased HV content in PHB yields a slight increase in strength at 8% HV, and a subsequent decrease with 12% HV. As has been suggested from previous literature, the stiffness of the PHB/WF composite decreases with increasing HV content (Gatenholm, 1992). This may be due to the decrease in the degree of crystallization suggested by Qian (2007) with increases in HV content.

Composites utilizing PHB as the matrix material were also tested with varying wood content from 20-60% WF. It was found that increases in reinforcement resulted in a linear increase in Young's modulus (Figure B.2, $R^2 = 97.3\%$). This linear trend in Young's modulus is consistent with results reported by Facca (2006) who studied the mechanical properties of HDPE/Oak Fiber (20 and 40-mesh) composites. This is also consistent with predictions from

micromechanical models such as Rule of Mixtures (ROM) and Halpin-Tsai, which predict that composite stiffness is increased with increased fiber loading. Also represented in Figure B.2 is the effect of fiber loading on the strength of PHB/WF composites. Composites display increases in strength with low fiber loadings, transitioning to decreases in strength at higher levels. This trend is also consistent with the findings of Facca (2006).

B.5 Conclusions

From this study we have a basis to compare PHB/WF composites produced at varying levels of wood fiber. This is important because no studies as of yet have produced PHB/WF composites at WF levels higher than 40%. Further, it has been identified that utilization of PHB in wood fiber composites displays good strength and stiffness when compared to PHBV8 and PHBV12. Further studies will involve the use of PHB because of its availability and respectable mechanical properties.

B.6 References

Coats E.R., Loge, F.J., Wolcott, M.P., Englund, K., McDonald, A.G. "Production of Natural Fiber Reinforced Thermoplastic Composites Through the Use of Polyhydroxybutyrate Rich Biomass." *Bioresource Technology*, In Press, 2007.

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Qian, J., Zhu, L., Zhang, J., and Whitehouse, R.S., "Comparison of Different Nucleating Agents on Crystallization of Poly(3-hydroxybutyrate-co-3-hydroxyvalerates)." *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 45, pp. 1564-1577, 2007.

B.7 Figures

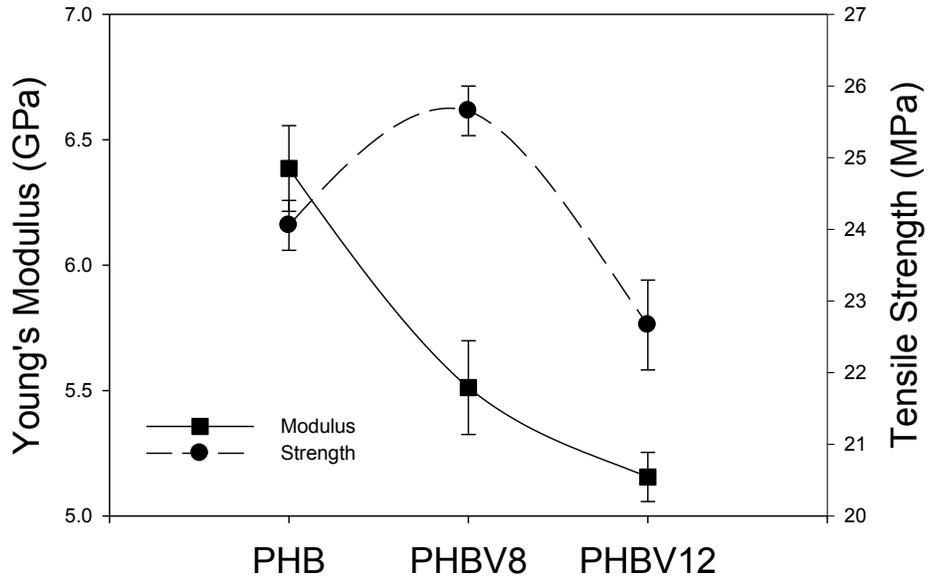


Figure B.1 Effect of HV content in PHB compounded with WF on tensile stiffness and strength

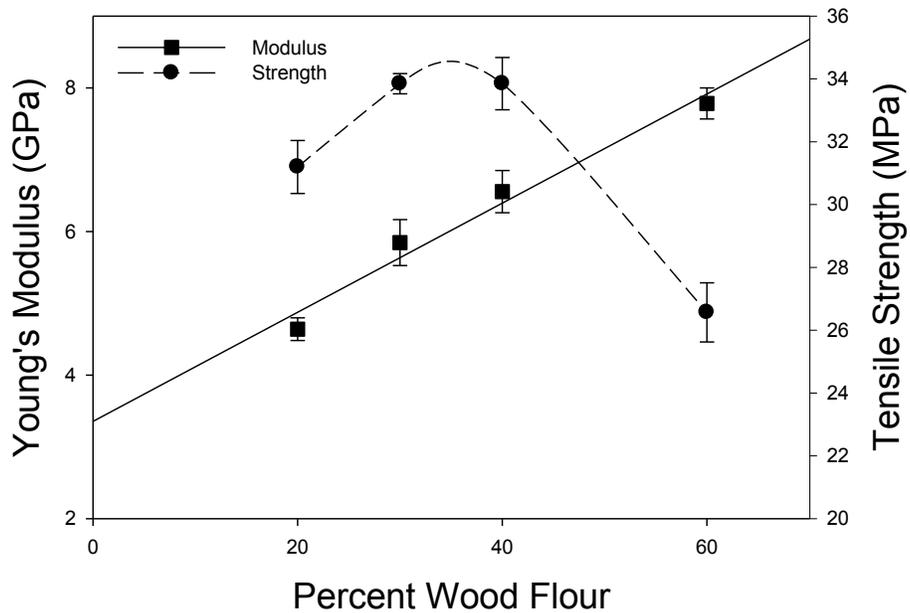


Figure B.2 Influence of varied wood fiber loading in PHB/WF composites on tensile strength and stiffness