



Compatibilization improves physico-mechanical properties of biodegradable biobased polymer composites



Nikushi S. Yatigala^{a,*}, Dilpreet S. Bajwa^b, Sreekala G. Bajwa^a

^a Department of Agricultural and Biosystems Engineering, North Dakota State University, 1221 Albrecht Boulevard, Fargo, ND 58102, USA

^b Department of Mechanical Engineering, North Dakota State University, 111 Dolve Hall, Fargo, ND 58102, USA

ARTICLE INFO

Keywords:

- A. Biocomposite
- B. Fiber/matrix bond
- B. Mechanical properties
- B. Thermal properties

ABSTRACT

Biodegradable biobased polymer composites have the advantage of low environmental impact and high sustainability. However, these biocomposites exhibit poor mechanical properties due to poor fiber-matrix bonding. This study evaluated the effect of compatibilization of five biocomposites on their physico-mechanical properties. Composites were prepared with 30 wt% wood fiber and one of the five biodegradable biopolymer: poly(lactic acid) (PLA), polyhydroxybutyrate (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), Bioflex (PLA blend), or Solanyl (starch-based). The composites were compatibilized with 2–3 wt% maleic anhydride, and evaluated for melt flow index, water uptake, hardness, flexural, compressive, impact, and thermal properties. Melt flow index was reduced by 10–16% for compatibilized composites implying the crosslinking of the polymer. Compatibilized composites of PLA, Bioflex, and PHBV exhibited improved thermal and strength properties, and reduced water absorption. These improvements were attributed to the enhanced fiber-matrix interfacial interaction caused by the compatibilizer. However, compatibilization did not work in PHB and Solanyl.

1. Introduction

Biodegradable polymers produced from renewable and biobased resources reduce waste accumulation, do not contribute to CO₂ emissions, and ease dependency on petroleum-based fuels and products. Along with their positive impact to environment, biodegradable biobased polymers have many other desirable properties such as biocompatibility, bioactivity, chemical inertness, high stiffness and strength, good film-forming properties and low toxicity [1,2]. Although biobased polymers have numerous benefits compared to conventional plastics, they usually have high cost, higher crystallinity, sensitivity to thermal degradation, and poor mechanical properties [1,3].

By blending biobased polymers with other biodegradable natural fillers to create a composite, the overall mechanical and degradation properties can be improved while reducing cost [4]. Despite higher mechanical properties of synthetic fibers such as glass fibers, natural fibers are attractive due to growing concern over environmental and ecological impacts and societal preferences. For example, wood fiber (WF) is an inexpensive and readily available byproduct from furniture manufacturing and other wood processing businesses that is reused as a filler in polymer composites [5]. Properties such as specific strength, ease of separation, low density, and CO₂ seizure are beneficial

characteristics of natural fibers over synthetic fibers such as glass or carbon fibers [6]. Natural fibers serve as good reinforcements and fillers in biocomposites for a myriad of reasons including low cost, fewer health hazards during processing, less abrasiveness to processing equipment, and good specific strength, thermal, electric and acoustic properties [7].

Poor interfacial adhesion between the hydrophobic polymer and hydrophilic natural fibers causes decrease in some strength properties and increase affinity to water of the composites [4]. Properties of polymer composites can be improved by introducing reactive functional groups such as compatibilizers and coupling agents [8]. Grafting a compatibilizer into a polymer enhances the miscibility between the polymer and natural fiber, which improves the overall mechanical and thermal properties. One of the most commonly used compatibilizers, maleic anhydride (MA), forms both hydrogen and covalent bonds with hydroxyl groups of the fiber and induce molecular entanglement with the polymer. These bonds improve the adhesion between the polymer and the fiber, and results in a better dispersion.

In this study, five types of MA-compatibilized biocomposites were prepared by compounding wood fiber with five different types of biopolymers: poly(lactic acid) (PLA), Bioflex (BF, PLA blend), Solanyl (SL, starch-based), poly(3-hydroxybutyric acid) (PHB), and poly(3-

* Corresponding author.

E-mail address: sykushi@gmail.com (N.S. Yatigala).

hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Even though there are many studies conducted with several different natural fiber-polymer composites, there is only limited research reported on the effect of MA on these biodegradable biobased polymers with wood fiber (WF) as a filler on the properties that have been tested in this study [9]. No studies have been conducted on effect of MA on Solanyl and Bioflex polymers. Most of the reported work on wood flour/fiber incorporated PLA, PHB and PHBV are generally without any compatibilizers. Therefore, a study was conducted to understand the impact of wood fiber filler and compatibilizer on five biodegradable biopolymers. The following questions were asked in this study.

1. How does incorporating wood fiber filler into five different biobased biodegradable polymers affect their mechanical, thermal, and water absorption properties?
2. Does compatibilization of the biopolymer-natural fiber composites with MA improve their mechanical, thermal, and water absorption properties?

The effect of WF loading and compatibilization on mechanical and physical properties was evaluated using tests for water absorption, melt flow index, hardness, impact fracture energy, compressive strength, and flexural strength and modulus. The influence of compatibilization and WF loading on the thermal degradation, melting behavior and crystallinity of biocomposites was studied using thermo gravimetric analyzer (TGA) and differential scanning calorimetry (DSC).

2. Experimental procedure

2.1. Materials

PLA used in this study was type 2003D from NatureWorks LLC (Minnetonka, MN). PLA is a biodegradable polyester obtained by polymerization of lactic acid. Lactic acid is a sugar fermentation product from corn, sugar beets/cane, or potatoes. The PHB (ENMAT Y3000P) and PHBV (ENMAT Y1000P) were supplied by TianAN Biopolymer (Ningbo City, Zhejiang Province, China). PHB and PHBV are examples of polyhydroxyalkanoates (PHA). PHAs are linear polyesters produced in nature by bacterial fermentation of sugar or lipids. Bioflex (BF) biopolymer (Bio-Flex® F2110) is a PLA blend, and it was obtained from FKUR Plastics (Willich, Germany). Solanyl (SL) biopolymer (Solanyl® C2201) was purchased from Rodenburg Biopolymers (Oosterhout, Netherlands). SL is made from potato starch reclaimed from the food processing industry. Maleic anhydride (63,200), Luperox® P: tert-Butyl peroxybenzoate (TBPB), benzoyl peroxide (BP), and Luperox 101: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (L101) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). The WF used in this study was from oak wood.

2.2. Polymer composite manufacturing

2.2.1. Preparation of grafted polymer

The procedure for biopolymer grafting included mixing each of the polymer with MA and an initiator, and then extruding them with a micro 18 lab-scale twin screw extruder with a 40/1 length to diameter ratio (Leistritz Ltd., Somerville, NJ). Prior to extrusion, all the polymer pellets were dried according to recommended conditions provided by the supplier. The PHB and PHBV polymers were dried at 80 °C for 2 h (h), PLA at 80 °C for 6 h, SL at 45 °C for 4 h, and BF at 60 °C for 3 h. For grafting, 2–3 wt% of Maleic anhydride (MA) and 0.5–1 wt% of a specific initiator (TBPB, BP, or L101) were hand-mixed with each polymer in a zip-lock plastic bag (Table 1). The mixture was then compounded via extrusion, cut into pellets, and dried at 80 °C in an oven for 12 h. Extrusion temperature profiles used for PLA, BF, SL, PHB, and PHBV were all different as shown in Table 2.

2.2.2. Preparation of WF composites

All the composites were manufactured with 30 (wt%) WF loading. For uncompatibilized composites, the WF was hand mixed only with 70 (wt%) neat polymer. For compatibilized composites, WF was hand mixed with grafted polymer and neat polymer pellets. The MA compatibilized PHB and PHBV composites had 65% polymer, 5% MA grafted polymer and 30% WF. All other MA compatibilized composites had 66% polymer, 4% MA grafted polymer and 30% WF. The mixture of WF, polymer, and/or MA grafted polymer were then compounded using the same twin-screw extruder used for the preparation of grafted polymer composites, using the same temperature setting shown in Table 2. All the extruded strands were water cooled, cut into pellets, and dried at 80 °C in an oven for 24 h.

2.2.3. Compression molding

After drying, composite pellets were compression molded into 150 mm square, 5 mm thick sheets using a Carver hot press (model 3856, Carver Inc., Wabash, IN) at 50 atm pressure. The molding temperature was maintained at 180 °C for all polymers except SL, which was kept at 150 °C. The molding time was between 7 and 10 min. The molded sheets were allowed to cool slowly under ambient conditions to prevent cracking.

2.3. Characterization of composites

2.3.1. Differential scanning calorimetry

To determine the thermal properties of composites, approximately 8 mg of each sample was characterized using a Q20 Dynamic Scanning Calorimeter (TA Instruments, New Castle, DE). All samples were first equilibrated at 25 °C, then heated from 25 °C up to 200 °C at the rate of 10 °C/min. About two- four replicates were run for each sample. An empty aluminum pan was used as a reference. All measurements were performed under N₂ atmosphere. From the heating scan, glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melt temperature (T_m), crystallization enthalpy (ΔH_c), and melting enthalpy (ΔH_m) were determined. The degree of crystallinity (X%) of the samples was evaluated as follows (Eq. (1)):

$$X\% = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0(w_p)} 100\% \quad (1)$$

where w_p is the polymer fraction in the composites, and ΔH_m⁰ is the estimated melting enthalpies of their respected pure polymer, which is 93.7 J/g for PLA and BF, and 146 J/g for PHB and PHBV [3,10].

2.3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE). About 5–8 mg of each samples were used with a constant nitrogen flow of 40 mL/min. Heating rate was 20 °C/min and the heating scans were performed in the range of 25–800 °C. The range of temperatures for the thermal degradation was estimated from the first derivative (DTG) curves, while the weight loss was determined from the TG plot.

2.3.3. Melt flow index (MFI)

To measure the changes in MFI that occurred due to fiber loading and compatibilization, composite pellet samples were evaluated using a Tinius Olsen melt flow indexer (model MP1200, Tinius Olsen, Horsham, PA) with a fixed weight of 2.16 kg according to ASTM D1238 [11] standard. The temperature inside the bore of the cylinder was maintained at 210 °C for PLA, 190 °C for BF, 170 °C for SL, and 180 °C for PHB and PHBV.

2.3.4. Water absorption

To measure the water absorption of samples, Eq. (2) was used as specified by ASTM D570 [12] standard. All the test specimens were

Download English Version:

<https://daneshyari.com/en/article/7889748>

Download Persian Version:

<https://daneshyari.com/article/7889748>

[Daneshyari.com](https://daneshyari.com)