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EFFECT OF MATERIAL PARAMETERS ON MECHANICAL PROPERTIES OF BIODEGRADABLE POLYMERS/NANOFIBRILLATED CELLULOSE (NFC) NANOCOMPOSITES

Yottha Srithep[1], Ronald Sabo[2], Craig Clemons[2], Lih-Sheng Turng[1,*], Srikanth Pilla[1], and Jun Peng[1]
[1]*Polymer Engineering Center, Dept. of Mechanical Eng., University of Wisconsin–Madison, Madison, WI 53706, USA*
srithep@wisc.edu; turng@engr.wisc.edu (corresponding author); pilla@wid.wisc.edu; jpeng4@wisc.edu
[2]*USDA Forest Service. Forest Products Laboratory, Madison, WI 53726, USA; cclemons@fs.fed.us; rsabo@fs.fed.us*

Abstract - Using natural cellulosic fibers as fillers for biodegradable polymers can result in fully biodegradable composites. Biodegradable composites were prepared using nanofibrillated cellulose (NFC) as the reinforcement and poly (3-hydroxybutyrate-co-3-hydroxyvalerate, PHBV) as the polymer matrix. The objective of this study was to determine how various additives (i.e., blending PHBV with chain extender (CE) and/or Ecovio—a commercially available PLA/PBAT blend) affect the mechanical properties of injection molded PHBV/NFC nanocomposites. Tensile test bars of PHBV/NFC nanocomposites were produced via a novel process involving freeze drying and high-shear followed by injection molding. A three-variable, two-level, full-factorial design was used to investigate the effects and interactions of CE, Ecovio, and NFC content on the mechanical properties of the nanocomposites. At the level investigated, Ecovio had the largest influence of all of the additives studied on the mechanical properties of PHBV. Two significant interactions between variables were also found. The tensile modulus and strength increased slightly with 3% NFC content in neat PHBV but more considerably in PHBV with Ecovio. Moreover, 1 wt% CE increased the tensile modulus of neat PHBV slightly but had no effect on PHBV with NFC or Ecovio.

Keywords: Nanofibrillated cellulose (NFC), Biobased and biodegradable polymers, nanocomposites, poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV.

Introduction

The development of commercially viable biodegradable plastics is an important effort in preserving and revitalizing our global environment and economy. Polylactide (PLA) and polyhydroxy-alkanoates (PHAs) have attracted much attention over the last two decades mainly due to increasing environmental concerns [1, 2]. Generally, PHBV is less crystalline and more flexible than highly crystalline, extremely brittle, and relatively hydrophobic poly(3-hydroxybutyrate) PHB; however, higher toughness is required for PHBV to broaden its applications.

Poly(butylene adipate-co-terephthalate) (PBAT) is an aliphatic–aromatic copolyester that is bio-degradable [3]. Due to its high toughness and biodegradability, PBAT is an excellent candidate for toughening biodegradable and biobased polymers such as PLA and PHBV. The PHBV/PBAT blends were shown to have decreased tensile strength and modulus; however, their elongation and toughness dramatically increased [4].

Generally, the thermal degradation of PHBV is considered as an inevitable side effect of normal melt processing conditions. Inspired by the work of using chain extenders (CE) to control the degradation of neat PLA and recycled poly(ethylene terephthalate) (RPET) [5, 6], this study employed CE in the material formulation to reduce the effects of thermal degradation on PHBV.

Reinforcing fibers of various sizes and forms have been effectively used in polymer composites as reinforcing agents [7]. Nanofillers, however, are found to be preferable in many applications due to their high surface area-to-volume ratio. Nanofibrillated cellulose (NFC) is a biologically derived nanofiber reinforcer suitable for polymer materials. NFC is an interconnected web with fibrils having diameters in the range of 10 to 50 nm [8]. NFC film has a high Young's modulus (ca. 3.7 GPa as reported in previous study [8],) which makes it a suitable candidate for polymer reinforcement.

This study investigates the effects of adding CE, Ecovio, and NFC, on the mechanical properties of PHBV. Characterization techniques including tensile testing, Gel permeation chromatography (GPC) and scanning electron microscopy (SEM), were employed.

Experimental

Materials

The materials used in this study were PHBV, NFC, Ecovio, and CE. PHBV under the trade name Y1000P was purchased in both pellet and powder forms from Ningbo Tianan Biologic Material, Co. Ltd. NFC was prepared at the U.S. Forest Service Forest Products Laboratory (Madison, WI) according to a procedure described by Saito and Isogai [9]. An aqueous suspension of NFC fibers at 0.4 wt% was used in this study. Ecovio (a compatibilized blend of PLA/PBAT at a weight ratio of 45/55) was obtained

from BASF and had a melt viscosity of 2.5 to 4.5 ml/10 min at 190 °C. The chain extender (Joncryl ADR 4368C) supplied by BASF was a multi-functional reactive polymer with Tg = 55°C, obtained in flake form. Joncryl ADR-4368 used to increase the melt strength of polyesters. The chain extender was used as received.

Experimental Design

A two-level, full-factorial statistical design (DOE) was used to establish the main effects and interactions of three additives on the mechanical properties of PHBV composites (cf. Table 1). Additional PHBV specimens filled with different Ecovio contents, (i.e. 25%, 50%, and 100%) were prepared for comparison.

Table 1: Material compositions (by weight).

Exp. No.	Sample	PHBV (%)	NFC (%)	Ecovio (%)	CE (%)
1	PHBV	100	0	0	0
2	PHBV+3%NFC	97	3	0	0
3	PHBV+75%Ecovio	25	0	75	0
4	PHBV+75%Ecovio+3%NFC	22	3	75	0
5	PHBV+1%CE	99	0	0	1
6	PHBV+1%CE+3%NFC	96	3	0	1
7	PHBV+1%CE+75%Ecovio	24	0	75	1
8	PHBV+1%CE+75%Ecovio+3%NFC	21	3	75	1

Sample Preparation

Composites were prepared using a two-step process. Master batch preparations using a freeze drier were followed by melt compounding, as described below.

Preparation of the master batch

To prepare the composites, the water medium had to be removed from the corresponding aqueous suspension of NFC. PHBV powder was first dispersed in distilled water, stirred for 1 hour, and then mixed with an aqueous suspension of NFC to reach a dry weight ratio of 85% PHBV and 15% NFC. The mixture was then stirred overnight using a magnetic stirrer. Afterwards, this suspension was quickly frozen by liquid nitrogen to prevent the PHBV powder from settling. In addition, rapid freezing might avoid NFC aggregation during freeze drying, as reported by Pääkkö et al. [10].

The frozen mixture was then freeze dried using a 4.5L Labconco FreeZone freeze drier to remove water thoroughly. Dried PHBV/NFC masterbatch was later diluted to 3 wt% NFC content by melt compounding.

Melt compounding and preparation of specimens

The PHBV pellets were combined with the NFC masterbatch, CE, and/or Ecovio in a variety of formulations. PHBV was dried in an oven for 2 hours at 90 °C before processing. Prior to injection molding, materials were melt compounded using a thermokinetic mixer. They were compounded in 50 g batches and discharged when the temperature reached 180 °C. fter discharge, the molten blend was subsequently granulated. Tensile bars (ASTM D638 Type V) were injection molded using a micro injection molding machine (DSM Xplore). The molding was done at 180 ºC with a mold temperature of 25 ºC, a cooling time of 15 seconds, and a holding pressure of 7 bar.

Characterization

Tensile testing

Tensile tests were performed on the injection molded tensile specimens following the ASTM D638 standard. The static tensile modulus, strength, and strain-at-break were measured at atmospheric conditions on an Instron 5865 mechanical testing instrument. The tensile tests were performed using an initial load of 0.5 N and a constant crosshead speed of 1 mm/min. Five specimens of each sample group were tested and the average results were reported.

The significant main effects and interactions of the material variables were determined for the tensile properties. The DesignExpert 6.0.101 software was used in the data analysis.

Gel permeation chromatography (GPC)

The number- and weight-average molecular weights (Mn and Mw, respectively) and the polydispersity index (PDI) for molded PHBV, and molded PHBV + 1 wt% CE were determined. Samples were dissolved chloroform via continuous stirring in a constant temperature sand bath (60 ºC) for 1 hour. The sample solution was filtered through a 0.2 mm PTFE membrane filter. With an eluent flow rate of 1.0 mL/min, 100 mL samples were injected into a Viscotek model VE2001 with Model 302-050 tetra detector array (differential refractive index (RI)).

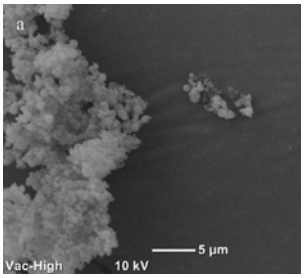
Scanning electron microscopy (SEM)

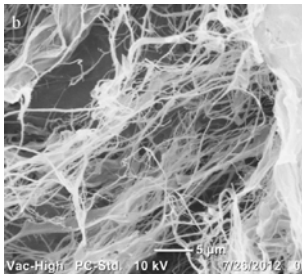
SEM images were examined using an SEM (JEOL Neoscope Benchtop) operated at 10 kV. All specimens were sputter-coated with a thin layer of gold prior to examination.

Results and Discussion

Freeze Dried Aqueous Suspension of NFC

The SEM images of PHBV powder, freeze-dried NFC, and freeze-dried PHBV + 15% NFC masterbatch are shown in Figures 1(a), (b), and (c), respectively. As shown in Figure 1 (a), the individual PHBV powder is smaller than 1 µm. Freeze-dried NFC (Figure 1 (b)) shows an interconnected fibrillar skeleton structure with diameters on the order of 1 µm although some nano-scale fibers were still present and others form 2-dimensional extended sheet-like structures.





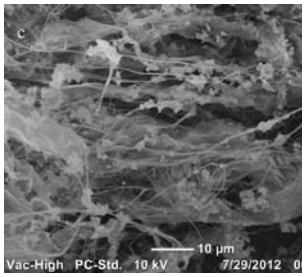


Figure 1: SEM images of: (a) PHBV powder, (b) freeze-dried NFC, and (c) freeze-dried PHBV + 15% NFC.

The observed fibrillar diameter after the freeze-dried process was much larger than what was observed (e.g., 5–10 nm) in the aqueous gels using transmission electron microscopy (TEM) in a previous study [8]. This indicates that some aggregation of nanofibers took place in the process of freeze drying. Similar behavior in freeze drying results has been reported in another study [10]. For the freeze-dried PHBV + 15% NFC, Figure 1 (c) shows that some of the PHBV powder attached to the fibrillar NFC network, while some of it aggregated. This PHBV + 15% NFC was used as the masterbatch in the subsequent melt compounding process.

Tensile Properties

As shown in Figure 2, Ecovio content (at the 75% level) had the largest influence among main effects and interactions. The influence of Ecovio content on modulus, strength and strain, can be seen in more detail in Figure 3, which shows tensile curves for a range of PHBV:Ecovio weight ratios. Strains increased from 3-21% but modulus and strength decreased with an increase in Ecovio content, demonstrating the toughening effect of PBAT in the Ecovio [4]. However, since Ecovio interacted with other variables, its effect was not consistent at different levels of the other variables. Hence, these interactions must be considered to adequately describe the behavior. For example, Figure 4 shows the interaction between Ecovio and NFC content for the modulus measurements. The addition of NFC into PHBV did not significantly change the tensile properties of PHBV. This might be due to the agglomeration of fibers which was confirmed by SEM.

However, NFC did increase the tensile modulus and strength of PHBV +75% Ecovio by 60% and 26%, respectively, suggesting good fiber–matrix adhesion [11]. Nevertheless, the strain at break for PHBV+75% Ecovio reinforced with 3%NFC decreased. Similar effects by other wood fiber on the tensile properties of PBAT, which is the matrix component in Ecovio, have been reported previously [11, 12]. Moreover, as shown in Figure 2 (Exp. Nos. 1 and 5), adding 1 % CE did not cause any difference in the tensile strength but induced a slight increase in the tensile modulus of PHBV by 12% (e.g., Figure 5) though not in the blends of CE with PHBV+75% Ecovio.

GPC results revealed that CE increased the average molecular weight of PHBV slightly. PHBV exhibited a number average molecular weight of 132,000±1500 before processing. After processing, the number average molecular weight decreased by 33%. As discussed, PHBV is susceptible to thermal degradation during melt blending and injection molding. However, the addition of 1% CE increased the number average molecular weight by 10%. The polydispersities of unprocessed PHBV pellets, molded PHBV, and molded PHBV + 1% CE were 2.4, 2.3, and 2.1, respectively.

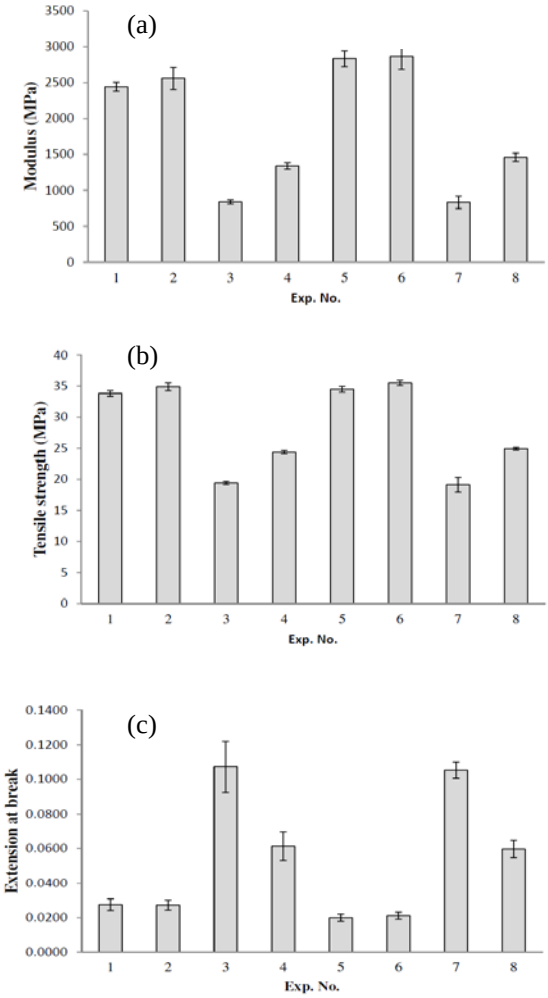


Figure 2: Mechanical properties in terms of (a) tensile modulus (MPa), (b) tensile strength (MPa), and (c) strain-at-break for (1) PHBV, (2) PHBV + 3% NFC, (3) PHBV + 75% Ecovio, (4) PHBV + 75% Ecovio + 3% NFC, (5) PHBV + 1% CE, (6) PHBV + 1% CE + 3% NFC, (7) PHBV + 1% CE + 75% Ecovio, and (8) PHBV + 1% CE + 75% Ecovio + 3% NFC (cf. Table 1).

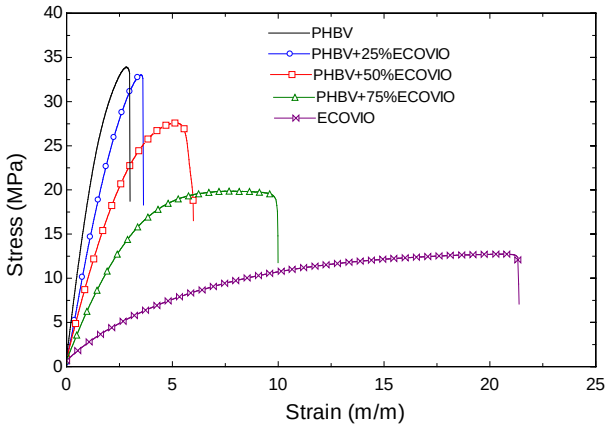


Figure 3: Tensile stress versus strain curves for the PHBV and Ecovio blends.

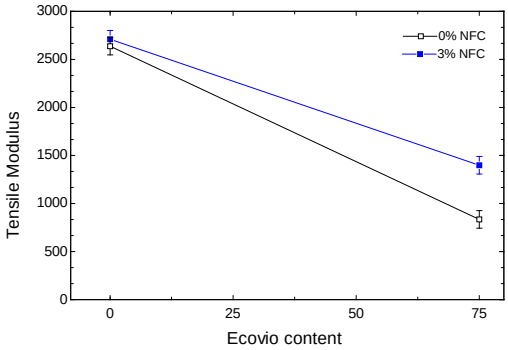


Figure 4: Ecovio content × NFC content interaction for the tensile modulus. Symbols represent the averages of the different levels of Ecovio and NFC content. Error bars show plus and minus one standard deviation.

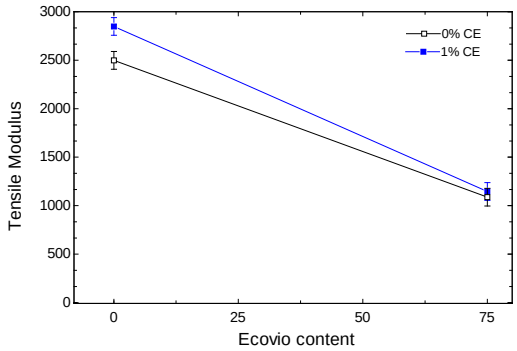


Figure 5: Ecovio content × CE content interaction for the tensile modulus. Symbols represent the averages of the different levels of Ecovio and CE content. Error bars show plus and minus one standard deviation.

Morphology of the Fracture Surfaces

Figure 6 shows the SEM images of the tensile fracture surfaces of the PHBV blends. The tensile fracture surfaces of PHBV + 75% Ecovio (Fig 6 (c)) and PHBV + 75% Ecovio + 3% NFC (Fig. 6 (d)) exhibited ductile fractures. This observation was supported by the values of strain-at-break obtained from the tensile tests. Furthermore, Figure 6 (b) shows that NFC aggregates were visible on the fracture surface and a few fibril aggregates were pulled-out.

Conclusions

A two-level, full-factorial DOE was performed to determine how NFC, Ecovio, CE, and their interactions affected the mechanical properties of PHBV blends and composites. The average tensile modulus of PHBV was 12% higher when 1% CE was added, which was due to the increase of PHBV's molecular weight. The Ecovio, because of its large content level, had the largest influence on the properties studied. Increasing Ecovio content increased the strain-at-break and reduced the tensile modulus and strength. These results were not surprising since Ecovio contains 55% PBAT, which is commonly used as a toughening agent. NFC, which tended to aggregate in PHBV composites, was found to reinforce PHBV + 75% Ecovio. To summarize, adding NFC, Ecovio, and/or CE to PHBV was found to be an effective way of modifying the mechanical properties of biobased PHBV.

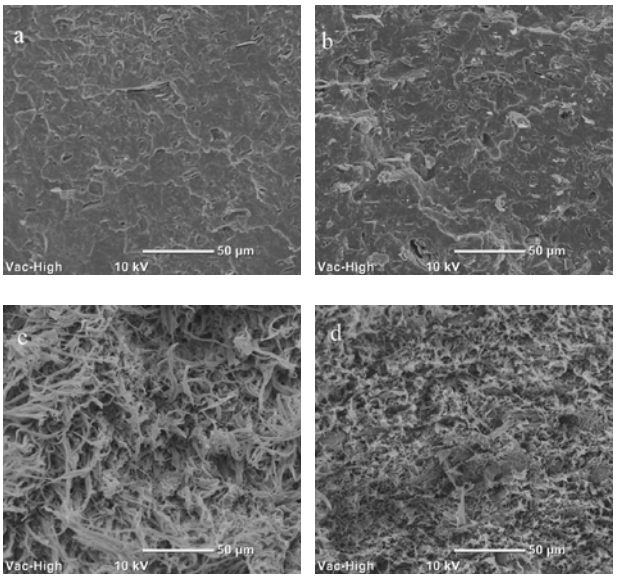


Figure 6: Tensile fractured surfaces of (a) PHBV, (b) PHBV + 3% NFC, (c) PHBV + 75% Ecovio, and (d) PHBV + 75% Ecovio + 3% NFC.

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