

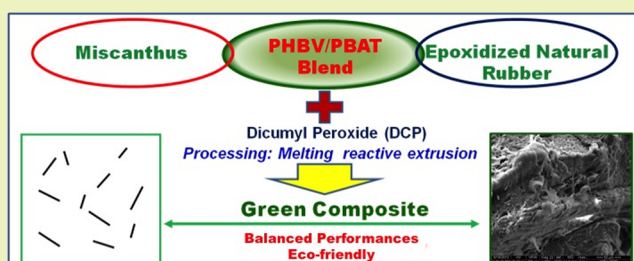
Toughened Sustainable Green Composites from Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) Based Ternary Blends and Miscanthus Biofiber

Kunyu Zhang,[†] Manjusri Misra,^{†,‡} and Amar K. Mohanty^{*,†,‡}

[†]Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, and [‡]School of Engineering, Thornborough Building, University of Guelph, Guelph, N1G2W1, ON, Canada

ABSTRACT: Novel green composites with an excellent balance of properties were successfully fabricated from poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) based renewable ternary blends and miscanthus through a cost-efficient reactive extrusion process. The ternary blend of PHBV with poly(butylene adipate-co-terephthalate) (PBAT) and epoxidized natural rubber (ENR) was engineered as a high toughening matrix for the natural fiber composites using dicumyl peroxide (DCP) as the reactive compatibilizer. The addition of miscanthus fibers into the matrix significantly enhanced its stiffness and thermal resistance while still keeping a good toughness. A high value of impact strength up to 240.5 J/m was still achieved even with 20 wt % miscanthus added. The mechanical modulus of the composites were also analyzed using mathematical models including rule of mixtures (ROM), inverse rule of mixtures (IROM), and the Tsai–Pagano equations. In the multiphase blends and composites, ENR played unique dual roles as an effective coupling agent and impact modifier in the presence of DCP. Scanning electron microscopy (SEM) results indicated good interfacial adhesion among the different phases in the composites, which played a vital role in improving the strength and toughness of the materials. At the same time, balanced melt viscosity and density were also achieved for the composites, which are important for wide application.

KEYWORDS: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), Ternary blend, Green composites, Toughness, Natural fiber



INTRODUCTION

In recent years, growing concern over environmental problems and depleting fossil oil reserves has stimulated academia and industry to pursue eco-friendly materials from renewable resources.^{1–9} In this context, green composites from sustainable biomass-based polymers and natural fibers are envisioned as one of the most promising options thanks to attractive benefits such as renewability, biodegradability, low cost, and comparable properties.^{2–5,10–22} Wide use of these green composites as alternatives to petroleum-based materials will significantly reduce dependence on petroleum resources and benefit the environment and the bioeconomy.^{1,3–5} Consequently, over the years, a lot of effort has been made to develop biocomposites from natural fibers and biobased polymers.^{2–5,10–22}

Among the biopolymers used in biocomposites, polyhydroxyalkanoates (PHAs), a renewable aliphatic polyester, have attracted lots of attention because of their excellent biocompatibility, biodegradability, and vast array of properties.^{2–5,9} PHAs are intracellularly synthesized by various microorganisms as an energy reserve.⁶ They can be efficiently and fully degraded into water and carbon dioxide by microorganisms in most biologically active environments.^{6–8} Consequently, PHAs have been considered to be the most fascinating alternative for petroleum-based synthetic polymers used in commercial applications.^{7,8} In the family of PHAs, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) has

been intensely studied because of its commercial availability, excellent thermal resistance, and comparable mechanical properties.^{9–13,15–22} However, the industrial and commercial applications of PHBV are limited by its high cost, brittleness, and narrow processing windows.^{9,19–22} Natural fibers, which are inexpensive and abundantly available, offer a wide variety of advantages to PHBV such as significantly lowering the cost of PHBV based materials, improving the biodegradability, stiffness, and thermal resistance.^{4,5,10–13,15–22} A lot of studies have been performed on incorporating various types of natural fibers into the PHBV-based matrix to fabricate green composites in recent years.^{10–13,15–22} However, the poor toughness and tensile strength of the material resulting from the poor adhesion between the PHBV-based matrix and hydrophilic fibers are still grand challenges in creating PHBV/natural fibers composites.^{10,18–20} Especially, the poor toughness of the PHBV/natural fiber biocomposites significantly hinders wide commercial applications such as in the automotive industry and packaging materials.

To improve the toughness of the polymer composites, many strategies can be adopted including increasing the matrix toughness, optimizing the filler-related properties such as size

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and distribution, adding compatibilizer or reactive blending to improve the interfacial adhesion, and fiber surface modification.^{23,24} It is well-established that the toughness of the matrix and fiber–matrix interfacial adhesion play very important roles in modification of mechanical performance of the polymer/fiber composites.^{23,24} Many methods have been adopted in enhancing the interfacial adhesion between the PHBV matrix and the natural fibers such as using fiber surface modification, adding coupling agents, and introduction of reactive functional groups on PHBV segments.^{2–5} These methods effectively modify the mechanical strength and stiffness of the composites. However, without the toughening of the PHBV matrix, the effects on the toughness of the composites were far from satisfactory. Blending with plasticizers or other flexible biodegradable polymers is a widely used strategy to enhance the toughness and flexibility of the PHBV matrix for the composites. As a commercially available biodegradable polyester with super high toughness, poly(butylene adipate-co-terephthalate) (PBAT) is a very good candidate for combining with PHBV in view of its superior toughness and good compatibility with other biopolyesters.^{25,26} To obtain a stiffness–toughness balance and appropriate thermal properties, recently, our group has performed a series of studies on the sustainable green composites from natural fibers and PHBV/PBAT (45/55) blends.^{20–22} The studies showed that combining matrix toughening and polymer/fiber interfacial modification in a collaborative way is a very promising method in effectively modifying the performance of the composites. Although using compatibilizers such as polymeric methylene diphenyl diisocyanate (PMDI) helped to improve the mechanical strength of the PHBV/PBAT/natural fiber composites, the toughness of the composites is still far from satisfactory. Moreover, the toxicity of PMDI was also a concern for the processing and application of the green composites.

The most attractive attributes of PHBV are that it is produced from renewable feedstocks and demonstrates excellent biodegradability. Resolving the weakness of the PHBV biocomposite without sacrificing its eco-friendly attributes is a great challenge for both industry and academia. In the present study, epoxidized natural rubber, a commercial elastomer derived from renewable resources, is employed as a novel toughening agent and a compatibilizer for the PHBV/PBAT/natural fiber composites through a reactive blending method with a small amount of dicumyl peroxide present. The thermal behavior, compatibility, mechanical properties, density, and thermal resistance of the composites were thoroughly studied. The native reactive compatibilization and toughening mechanisms were also discussed based on the thermal–mechanical and scanning electron microscopy (SEM) results. At the same time, the processing properties and density of the composites were also investigated for potential commercial applications.

MATERIALS AND METHODS

Materials. The PHBV (Mirel P1004, $\bar{M}_w = 2.9 \times 10^5$ g/mol, and PI = 1.62) is a product from Telles Inc. The Mirel P1004 grade consists of a small amount of additives and mineral fillers. It was donated to us by Competitive Green Technologies, ON, Canada. The commercially available PBAT (Biocosafe 2003F) was purchased from Xinfu Pharmaceutical Co. Ltd., China. Miscanthus (MS) with an average fiber length of 4–8 mm was kindly provided by New Energy Farms Ltd., ON, Canada. Epoxidized natural rubber (ENR) with the trade name Epoxyrene was procured from Sanyo Corporation of America. Molecular weights of 3.9×10^4 g/mol were reported by the

manufacturer for the ENR. Dicumyl peroxide (DCP) was purchased from Sigma-Aldrich.

Biocomposite Fabrication. Prior to processing, the PHBV, PBAT pellets, and miscanthus were dried using a conventional oven at 80 °C for 6 h. The ENR was used directly without further treatment. A micro 15 cm³ corotating twin screw compounder and micro 12 cm³ injection molding machine (manufactured by DSM Research, Netherlands) were used to fabricate the blends and composites. The processing was conducted at 175 °C with a screw speed of 100 rpm for 2.5 min (including feeding time). Then, a DSM micro 12 cm³ injection molding machine was used to prepare the samples for measurements. A filling pressure of 3 bar, packing pressure of 4 bar, and molding temperature of 45 °C was used for the optimized injection molding conditions.

Characterization and Testing. The tensile and flexural properties of the samples were tested on an Instron (Model-3382) mechanical testing machine. The crosshead speeds were selected at 50 mm/min for tensile test and 14 mm/min for flexural test respectively according to ASTM standards D 638 and D 790.

Notched and unnotched Izod impact strength of the composites were accomplished by a TMI 43-02 (Testing Machine Inc.) impact tester according to ASTM standard D 256 and ASTM standard D 4812. A pendulum with an impact energy of 5 ft-lb was used, and the notches were cut using a TMI notching cutter. The values reported for the above-mentioned mechanical tests are the average values of 5 samples with standard deviation.

The fractured surface morphology was observed using scanning electron microscopy (SEM), Inspect S 50, FEI Netherlands. A Cressington sputter coater 108 auto was used to sputter coat the samples with gold under an argon atmosphere.

The heat deflection temperature (HDT) was evaluated in a dynamic mechanical analyzer (DMA Q 800, TA, USA). The test was conducted at a temperature range of 23–120 °C with a ramp rate of 2 °C/min in 3-point bending mode of deformation and the applied stress of 0.455 MPa. The HDT was reported as the temperature at which a deflection of 0.25 mm occurred. Three samples of each formulation were tested for the HDT measurements to ensure the repeatability of the results. The storage modulus and the $\tan \delta$ of the samples were also characterized by DMA Q 800. Samples were heated from –70 to 100 °C with a cooling rate of 3 °C/min.

Differential scanning calorimetry (DSC) measurements were performed on a TA Q 200 DSC instrument to study the thermal behavior of the components in the blend and composites. First, the samples were heated to 190 °C with heating rate of 10 °C/min, maintained at that temperature for 2 min under N₂ atmosphere before cooling to –70 °C at a rate of 20 °C/min. After then, the second heating scans were monitored between –100 to 190 °C at a heating rate of 10 °C/min.

The melt flow index (MFI) of the blends and composites were measured in a Qualitest melt flow indexer 2000A according to ASTM standard D1230-10. The test was performed at 190 °C, 2.16 kg load.

Density was measured using an Alfa Mirage electronic densimeter model MD-300S based on the Archimedes principle. Three samples of each formulation were tested for the measurements to ensure the repeatability of the results.

RESULTS AND DISCUSSION

Thermomechanical Properties. The compatibility of the different phases in the blends and composites can be analyzed on the basis of the thermomechanical properties.¹⁷ In addition, the interaction of natural fibers and the matrix could also be evaluated based on the $\tan \delta$ peak intensity and position. Figure 1 presents the storage modulus and $\tan \delta$ of the neat polymers, the blend matrix, and selected composites. As shown in Figure 1a, as a stiff and brittle thermoplastic, the neat PHBV shows the highest modulus. In contrast, the flexible PBAT possesses the lowest modulus in the samples. The modulus of the blends decreases drastically when the soft ENR and PBAT are added

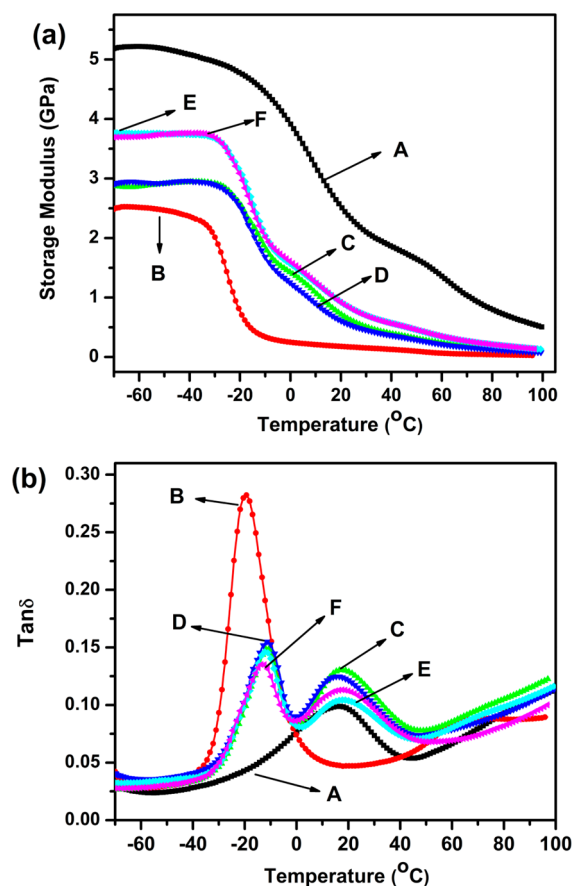


Figure 1. Storage modulus (a) and $\tan \delta$ (b) of the neat polymers, blends matrix, and selected composites: (A) PHBV, (B) PBAT, (C) PHBV/PBAT/ENR50 (50/35/15), (D) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP, (E) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS, (F) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS.

to the PHBV. The incorporation of natural fibers effectively improved the storage modulus of the composites, which results from the reinforcement of the rigid miscanthus. Figure 2 shows

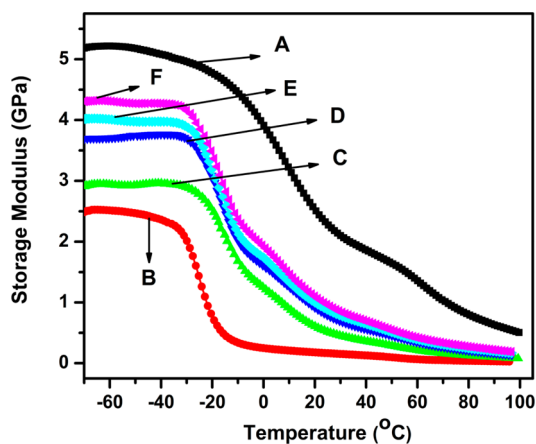


Figure 2. Effect of the miscanthus fiber content on the storage modulus of the composites: (A) PHBV, (B) PBAT, (C) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP, (D) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS, (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS, (F) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS.

the influence of the content of miscanthus fibers on the storage modulus of the composites. It is found that the storage modulus increases with the increasing natural fiber content. These results are inconsistent with the following flexural and tensile modulus trend.

The compatibility and interaction of different phases can also be evaluated based on the $\tan \delta$ peak position and intensity. Figure 1b presents the $\tan \delta$ curves of the blends and composites. As shown in Figure 1b, the neat PHBV has a $\tan \delta$ peak at about 16.5 °C, which is attributed to its glass transition. An intensive peak at -20 °C is observed for neat PBAT. It is clearly found that the peaks attributed to the PBAT and PHBV shifted to each other in the blends compared to neat counterpart polymer. Moreover, compared to the original PHBV/PBAT/ENR (50/30/15) blend, the peaks show a greater shift in the blends with addition of DCP. A similar phenomenon is also found for the composites with the presence of DCP. These results indicate the compatibility of the PHBV with the PBAT and ENR phases is further improved by the DCP. In the literature reports, either ENR or DCP has been used as single modifier for the biodegradable polyesters and their blends, respectively.^{27–36} For the biodegradable polyesters/ENR blends, it was reported that complex reactions between ENR and polyesters at high processing temperature enhanced the compatibility of components. Two main reaction mechanisms have been proposed for the biodegradable polyesters/ENR blends: (1) reaction between the end carboxyl group of the polyesters and the epoxide group of ENR and (2) interchain cross-linking between allylic radical of ENR and the alkyl radicals of polyesters. All these reaction mechanisms having been confirmed in aliphatic biopolyesters/ENR blends including PHAs/ENR, PCL/ENR, and PLA/ENR blend.^{27–32} As an effective free radical initiator, DCP itself was also widely used as reactive compatibilizer for biopolyesters blends recently. Recently, Ma et al. successfully enhanced the compatibility of PHBV/PBS and PHB/PLA blends using DCP.^{33,34} A similar method was also studied in PBAT based blend.^{35–37} The role of DCP and the compatibilizing mechanism was well established for these biopolyesters blends. As a reaction initiator, the DCP initiated free-radical reaction between the different phases to form grafting copolymer and a partially cross-linked network between the different phases, which significantly improved the compatibility of the polyesters blends.^{33–37}

Consequently, based on the above-mentioned mechanism, a good synergistic compatibilizing effect can be anticipated during the melt processing in the present multiphase system in the presence of both the ENR and DCP. With the aid of the DCP, the ENR could play dual positive roles in the present blend and composites: those of an effective toughening agent and compatibilizer. First, thanks to DCPs initiation, interchain cross-linking or grafting copolymer formation between the allylic radical of ENR and the alkyl radicals of polyesters (PHBV and PBAT) at high processing temperature will improve the compatibility of the different phases. During the melt blending, the RO· radicals from DCP abstracted hydrogen from PHBV, PBAT, and ENR50 backbone to yield free radicals.²⁸ The primary alkyl radicals from PBAT and tertiary radicals of PHBV readily accessed the allylic radical of ENR 50 to form interchain cross-linking/grafting via heterogeneous radical coupling reaction.³⁵ Second, in the presence of DCP, shorter chains with end carboxyl groups could also be formed by PHBV and PBAT due to chain scission. These shorter

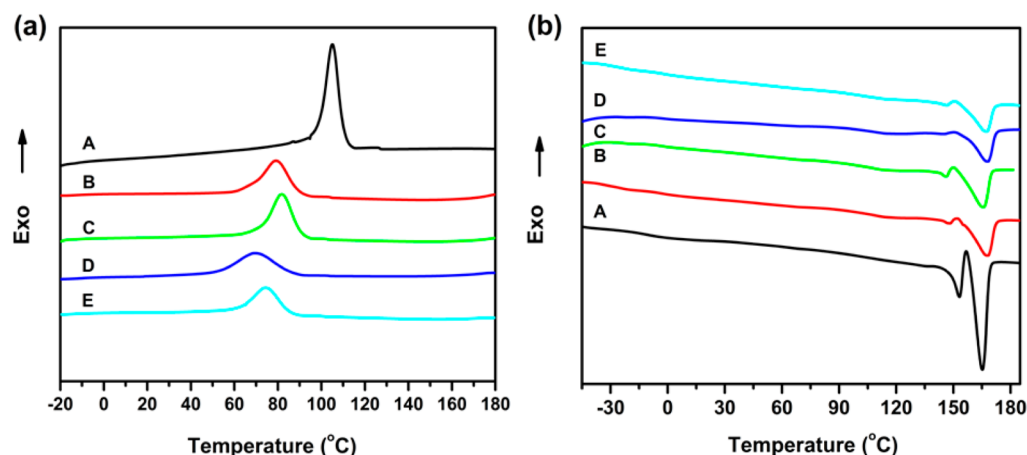


Figure 3. DSC curve of neat PHBV, blends, and selected composites. (a) Cooling curves. (b) Heating curves: (A) PHBV, (B) PHBV/PBAT/ENR50 (50/35/15), (C) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP, (D) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS, (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS.

Table 1. Thermal Properties of Neat PHBV, Blends, and Selected Composites

samples	$T_{c(\text{PHBV})}$ (°C)	ΔH_c (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_c (%)
PHBV	105	36.3	153.2	10.3	165.1	30.4	27.8
PHBV/PBAT/ENR50 (50/35/15)	79.3	24.7	148.1	1.4	166.3	16.2	24.0
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP	81.9	24.9	146.4	2.2	165.8	16.1	25.5
PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS	69.5	23.9	144.9	0.4	168.1	13.2	20.7
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS	74.5	21.4	146.6	1.3	167.2	12.0	20.3

chains with carboxyl end groups may trigger a reaction with the epoxidized group of ENR. At the same time, it is well-known that ENR itself is a very effective toughening agent for the PHAs.^{27,30–32} Consequently, with the help of the improved compatibility, a highly toughened biobased matrix was achieved for the natural fiber composites. In the composites, DCP was also reported to play a positive role on improving the interfacial adhesion between the fiber and matrix by initiating reaction.³⁸ Moreover, the epoxy of ENR can also show better interfacial interaction with the cellulose fiber containing polar hydroxyl group compared to hydrophobic natural rubber and the polymer matrix.^{39,40} These mutual promotions of DCP and ENR significantly improved the compatibility of the phases in the matrix system, which significantly enhanced the mechanical performance of the matrix and composites.

Thermal and Crystallization Behaviors. As a semicrystalline polymer, the crystal morphology and crystallinity of the PHBV have great influence on its physical properties such as mechanical, heat resistance and barrier properties. Consequently, it is very important to investigate the thermal behaviors of the PHBV in the blends and composites. Figure 3 gives the DSC cooling and heating curves of the neat PHBV, the blends, and selected composites. As shown in Figure 3a, it was found that the exothermal crystallization peak shifted toward lower temperature in the blends and selected composites compared to that of the neat PHBV. At the same time, the peaks with the decreasing intensity became wide in the blends and composites. Table 1 summarizes the corresponding thermal parameters from the DSC measurements. It was found that the crystallinity of the PHBV decreased in the blends and composites. These results indicated that the crystallization ability of the PHBV in the blends and composites was confined. Moreover, it was noticed that the crystallization temperature of the PHBV in the blend with presence of DCP (formulation C) was at high

temperature compared the counterpart blend without addition of DCP. This result implied that the DCP played a positive role in improving the nucleation of the PHBV in the blend, which may be attributed to the improved miscibility of the blend components. Similar results were also found in PHBV/PBS/DCP blends.^{33,34} The confined crystallization behaviors of PHBV in the blends and composites could also cause the reduction in strength and modulus. At the same time, it was also reported by Fei et al.³⁷ that the tensile toughness of the PHBV was improved by curing with DCP. Consequently, the thermal behavior of the PHBV in the blends and composites was significantly influenced by the addition of DCP, which then influences the mechanical properties of the blend and composites.

Tensile and Flexural Properties. The tensile test results are summarized and presented in Figures 4 and 5. The PHBV shows a typical behavior of a stiff and brittle plastic: high modulus and strength, with very low elongation below 5%. The poor flexibility of the PHBV significantly hinders its wide application in materials such as those for packaging. When the flexible PBAT and ENR 50 added into the PHBV, the strength and modulus were drastically reduced in the blends due to the low modulus of the PBAT and ENR. However, the elongation of the PHBV was significantly enhanced due to the enhancement of the ductile phases of the PBAT and ENR. Interestingly, one can note that for the PHBV/PBAT/ENR ternary blend with 0.3 wt % DCP added, the tensile strength was significantly improved compared to the original PHBV/PBAT/ENR50 ternary blend. This result implied that the interfacial adhesion of the different phases in the blend was improved by the DCP, which was beneficial for the stress transfer during the tensile test. In formulation D, when 10 wt % miscanthus fibers were added into the original PHBV/PBAT/ENR50 ternary blends, the stiffness and modulus of the blend were improved, which is

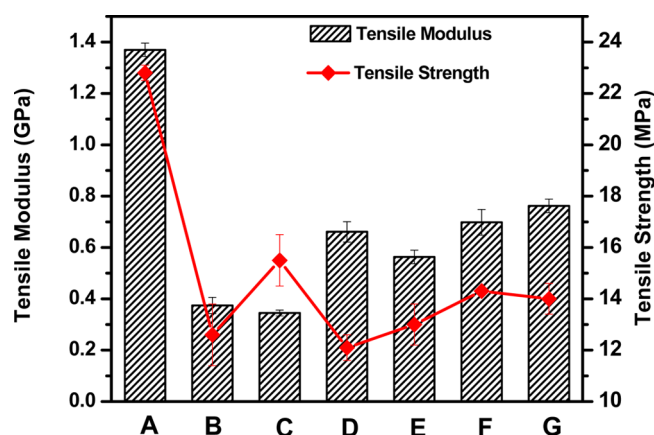


Figure 4. Tensile modulus and strength of the PHBV based ternary blends and composites: (A) neat PHBV; (B) PHBV/PBAT/ENR50 (50/35/15); (C) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP; (D) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS; (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS; (F) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS; (G) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS.

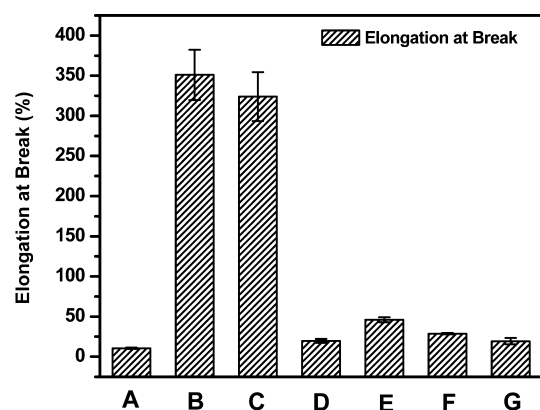


Figure 5. Elongation of the PHBV based ternary blends and composites: (A) neat PHBV; (B) PHBV/PBAT/ENR50 (50/35/15); (C) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP; (D) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS; (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS; (F) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS; (G) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS.

in common when fibers are used as reinforcements for plastics. However, the tensile strength was found to decrease, which may be attributed to the limited interfacial adhesion of the fiber and the matrix in this formulation. It is well-known that the tensile strength is greatly determined by the interfacial stress transfer in the blend and composites, which is significantly influenced by the interfacial adhesion of the different phases. Without enough interfacial adhesion between the phases, the untreated fibers easily resulted in crack initiation, which caused material failure.^{20,22} In the present formulation D, although the addition of ENR50 played positive role in enhancing the interaction of the fiber and matrix, it still not strong enough to efficiently improve the stress transfer between the phases. In addition, the limited interfacial adhesion among PHBV, PBAT, and ENR50 also limited the stress transfer under the tensile stress. On the contrary, the composites with DCP and 10 wt % miscanthus added showed higher strength and elongation

compared the properties of formulation D without DCP additive. More amazingly, with the presence of DCP in the composites, it was also found that both the strength and modulus increased with the content of fiber increasing. It is totally different than the normal results for fiber composites in the past research, where the strength usually decreased with higher content incorporation. Moreover, it is worth mentioning that the elongation of the samples was still maintained with a high value up to 20% even with 20 wt % fibers added. This result further suggested that there is a more effective transfer of stress from the matrix to the fibers during the tensile stress due to the good interfacial adhesion. As discussed previously, the presence of DCP helped the interchain cross-linking/grafting among the PHBV, PBAT, and ENR50, which played a positive role in enhancing the stress transfer among the phases in the blends and composites. Similar results have also been observed for the PHBV/PBAT/switchgrass composites with presence of PMDI compatibilizer.^{20,22} These results were very impressive for the natural fiber composites.

The modulus of the short fiber composites can be predicted by a variety of mathematical models including rule of mixtures (ROM), inverse rule of mixtures (IROM), and the semi-empirical equations proposed by Tsai–Pagano.^{41,42} The rule of mixtures and inverse rule of mixtures are the simplest models to be used for predicting the elastic properties of a composites. The ROM and IROM equations are shown as follows:⁴¹

ROM

$$E = E_f V_f + E_m V_m \quad (1)$$

IROM

$$E = \frac{E_f E_m}{V_m E_f + V_f E_m} \quad (2)$$

As a semiempirical equation, the Tsai–Pagano model is also widely used to predict the Young's modulus of the randomly oriented short fiber composites. The equations for the Tsai–Pagano model are as shown below:⁴²

$$E_{\text{random}} = \frac{3}{8} E_{11} + \frac{5}{8} E_{22} \quad (3)$$

Where E_{random} is the elastic modulus of the composites with randomly oriented fibers. E_{11} and E_{22} represent the longitudinal and transverse modulus which can be derived from Halpin–Tsai model as shown below:

$$E_{11} = \frac{1 + \xi \eta_L V_f}{1 - \eta_L V_f} E_m$$

$$E_{22} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} E_m$$

Parameters η_L and η_T are given by

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \xi}$$

$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2}$$

Where E_f and E_m are the elastic modulus of the fiber and matrix, respectively, and V_f is the fiber volume fraction. ξ is a measure of the geometry of reinforcement. If the fiber is rectangular in cross-section, then ξ is 2 (l/d). Here l/d is the aspect ratio of

the reinforcement. In present work, the Tsai–Pagano model is employed to predict the tensile modulus of the prepared composites and was compared with the experimental results. The modulus value of the miscanthus fiber is 9.5 GPa.⁴³ The density of the matrix PHBV/PBAT/ENR 50 (50/35/15) + 0.3 wt % DCP is 1.22 g/cm³, and the density of the miscanthus fiber is 1.36 g/cm³. The volume fraction of the fiber was calculated using these density values. The comparison of experimental and theoretical tensile modulus of the selected composites as a function of miscanthus fiber volume fraction is shown in Figure 6. As shown Figure 6, both the theoretical and

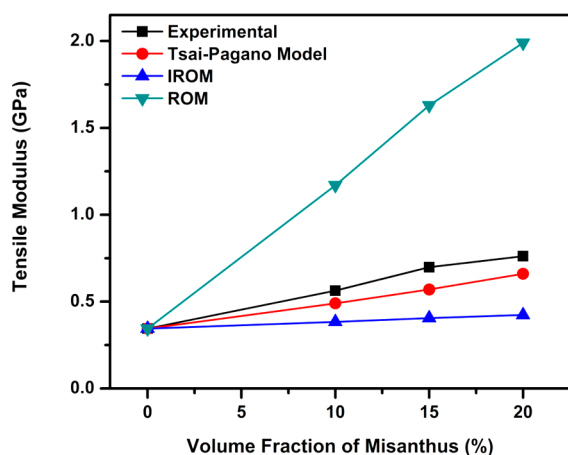


Figure 6. Comparison of experimental and theoretical tensile modulus of the composites as a function of miscanthus fiber volume fraction.

experimental data showed increased modulus trend. The ROM and IROM equations give the upper and lower bounds for the experimental data. Among the used models, it was found that the Tsai–Pagano model is the most accurate equation in predicting the tensile modulus of the composites. Compared to ROM model, the Tsai–Pagano model and IROM equations resemble the experimental results more closely. Considering that the ROM is assuming the fibers are oriented and fully strained along their length, this result may imply that the fibers are mainly randomly distributed in the composites. At the same time, the slightly higher experimental data may suggest the slightly higher modulus value of miscanthus and good load transfer due to the good interfacial adhesion.¹⁶

A similar trend was observed in flexural properties. Figure 7 presents the flexural data of PHBV, blends, and composites. As a stiff biopolymer, neat PHBV possesses high flexural strength and modulus. As shown in Figure 7, the stiffness of PHBV was significantly sacrificed when flexible PBAT and ENR50 were added. One can note that the flexural strength and modulus decreased greatly for the ternary blends. Adding natural fiber is an effective approach to improve the flexural properties for the ternary blend. When 20 wt % fibers were incorporated into the blend, the flexural properties increased up to two times higher than the blend matrix. At the same time, it was also found that the flexural strength of formulation E with DCP added showed a higher value than that of formulation D without DCP presented. This result again indicated that the fibers and the matrix possess better interfacial adhesion for the reactive blending matrix.

Impact Strength. The impact strength reflects the capability of the materials to withstand fracture under load. The impact strength of the polymer matrix and composites

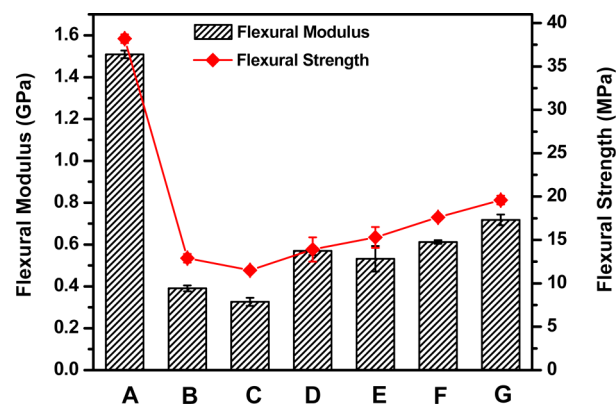


Figure 7. Flexural modulus and strength of PHBV-based ternary blends and composites: (A) neat PHBV; (B) PHBV/PBAT/ENR50 (50/35/15); (C) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP; (D) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS; (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS; (F) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS; (G) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS.

were shown in Table 2. The impact strength of neat PHBV was only at a value of 29.2 J/m. In our previous studies, the blend of

Table 2. Impact Strength of PHBV-Based Ternary Blends and Composites

sample (wt/wt/wt)	impact strength (J/m)
PHBV	29.2 ± 1.2
PHBV/PBAT/ENR50 (50/35/15)	nonbreak
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP	nonbreak
PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS	272.9 ± 30.4
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS	365.0 ± 13.6
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS	289.8 ± 14.6
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS	240.5 ± 20.0

PHBV/PBAT containing 45 wt % PHBV and 55 wt % PBAT only showed 380.0 J/m impact strength.^{20–22} In the present work, high toughness was achieved with nonbroken behavior for the ternary blends based PHBV/PBAT/ENR 50 (50/35/15) under the notched Izod impact test. The superior toughness achieved here suggested that the ENR 50 played a positive role on the toughness of the blends. Nevertheless, as shown in tensile and flexural results, the achieved excellent toughness was also significantly at the expense of strength and modulus.

It is well-known that a stiffness–toughness balance is very important for the structural application of PHBV materials.^{9,19} As mentioned previously, incorporation of the natural fibers into polymer matrix is a very promising method to improve the stiffness of the PHBV materials. Unfortunately, the drastic inevitable reduction in toughness of the material was also observed when directly using natural fibers as fillers. Yet, the excellent toughened PHBV/PBAT/ENR 50 blend obtained here provided us a promising matrix for the natural fiber composites to achieve satisfied stiffness–toughness balanced materials. As shown in Table 2, when 10 wt % fibers were added into the original blend, the impact strength of the composite was about 272.9 J/m. In the composites with same

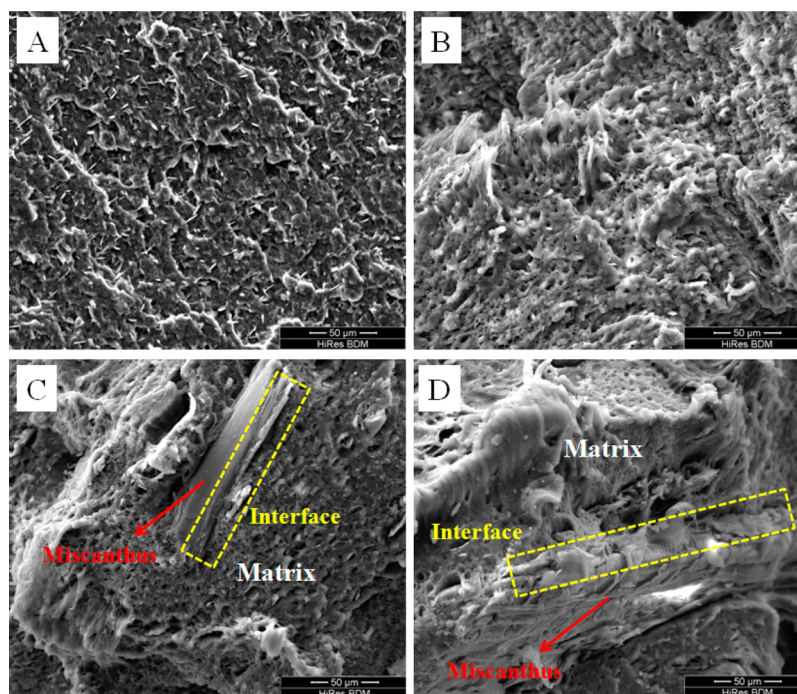


Figure 8. SEM images of the impact–fracture surface of PHBV-based ternary blends and composites: (A) neat PHBV; (B) PHBV/PBAT/ENR50 (50/35/15); (C) PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS; (E) PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS.

content fiber, when DCP was added, the impact strength increased to 365 J/m, which is almost 100 J/m higher than the composites without DCP added. This result indicated that the addition of DCP played a positive role on the impact strength of the composites. More interestingly, even with 20 wt % miscanthus added, the impact strength of the composites still remained at 240.5 J/m in the presence of DCP.

For the polymer–short fiber composites, the impact strength is determined by many factors including fiber–matrix interfacial adhesion, fiber concentration and distribution, load transfer efficiency, etc. Many mechanisms can contribute to the energy absorption of the fiber composites such as fiber pull out or debonding from matrix, crack deflection and fiber bridging mechanism. In general, the fracture of the fiber composites involves several these energy absorption mechanisms simultaneously, which makes it very difficult to figure out the main mechanism.⁸ Among the various factors, the fiber–matrix interfacial adhesion and load transfer efficiency play vital roles on the impact strength. During the melt processing of the composites, the ENR played a very interesting and complex role in the composites with the DCP presence. It is well-known that the ENR has two kinds of functional groups in the chain structure: double bond and the epoxy or oxirane group.^{27–30} The epoxy or oxirane group in ENR can act as a site to react with $-\text{COOH}$ or $-\text{OH}$ of other phases in the composites.^{27–32} In addition, with the initiation of DCP, the reaction of a double bond of ENR with other phases' generated radicals will occur at the interface. Such an interchain reaction will improve the compatibility of the different phases in the blend, which will be beneficial for the stress transfer among the phases. Good interfacial adhesion will improve the energy dissipation occurring through fiber pull-out, debonding, and cavitation. In the present composites, the excellent impact strength may be attributed to the good interfacial interaction of the fibers and matrix. This mechanism is also reflected in the following SEM and thermomechanical results.

SEM Results. The morphologies of the impact fracture surface of selected composites are shown in Figure 8. Pure PHBV showed a smooth and featureless fracture surface without much deformation, indicating a typical brittle fracture behavior. A very rough surface was observed for the PHBV/PBAT/ENR50 blend which coincides with the superior toughness of the material. Figure 8C presents the morphology of composites without the DCP added. Clear evidence of fiber pull out and void can be observed from the graph. The fibers were not completely embedded in the matrix with a clear interfacial gap. This is an indication of low fiber/matrix interfacial adhesion. However, the morphology of composites with the presence of DCP showed good interfacial properties. As shown in Figure 8D, the miscanthus fibers were well trapped by the polymer matrix. A thin deformed matrix layer was found to cover the fibers. At the same time, a rough surface attributed to the matrix deformation can be seen near the fibers. This indicated better stress transfer among the different phases during the fracture processing compared to composites without the added DCP.

HDT. The thermal resistance of the composites is one of the critical factors that greatly determines the application of the materials, especially in such applications as automotive products. The HDT values of the samples were measured and given in Table 3. The virgin PHBV possessed high thermal resistance performance with an HDT value of 115 °C. However, when soft PBAT and ENR were added into PHBV, the HDT decreased drastically from 115 °C to around 63 °C. Similar poor HDT was also observed for the blends with added DCP. These results suggested that, in spite of the fact that the toughness of PHBV was enhanced by soft PBAT and ENR in the blend, the thermal resistance of PHBV was also significantly sacrificed, which undoubtedly limits the application of the material. It has been reported that the addition of fiber usually plays a very positive effect on improving the HDT of the polymer matrix in fiber reinforced polymer composites. In the

Table 3. HDT Values of PHBV-Based Ternary Blends and Composites

sample (wt/wt/wt)	HDT (°C)
PHBV	115 ± 0.5
PHBV/PBAT/ENR50 (50/35/15)	63.4 ± 1.7
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP	63.3 ± 6.2
PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS	70.9 ± 1.9
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS	75.2 ± 1.3
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS	81.9 ± 3.7
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS	98.4 ± 5.0

present studies, when the miscanthus fibers were added into the PHBV-based blends, the HDT values of the composites were found to be improved successfully. As shown in Table 3, the HDT values of the composites increase with the increasing content of fiber. For the composites with 20 wt % fiber added, the HDT increased to 98.4 °C, which is comparable to neat PHBV. In the fiber-filled semicrystalline polymer system, the improved HDT may be attributed to the enhanced flexural modulus and crystallinity.¹⁹ Nielsen pointed out that the increase in the HDT of the polymer–fiber composites is related to the increased modulus due to the reinforcement of the stiff fiber.⁴⁴ The increase in the HDT with increasing fiber content of miscanthus was in agreement with Nielsen's predication. In addition, the fiber surface may also nucleate the crystallization of PHBV in the composites, which will play a positive role in improving the HDT of the composites.^{10,12,19}

Melt Flow Index (MFI) and Density. The melt flow property of the composites determines the processing properties of the composites. Table 4 shows the MFI value of the

Table 4. MFI and Density of PHBV-Based Ternary Blends and Composites

sample (wt/wt/wt)	MFI (190 °C, g/10 min)	density (g/cm ³)
PHBV	13.9 ± 2.0	1.305 ± 0.006
PHBV/PBAT/ENR50 (50/35/15)	15.7 ± 3.6	1.228 ± 0.001
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP	9.1 ± 0.6	1.222 ± 0.001
PHBV/PBAT/ENR50 (50/35/15) + 10 wt % MS	14.3 ± 2.3	1.250 ± 0.006
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 10 wt % MS	8.5 ± 0.5	1.238 ± 0.009
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 15 wt % MS	7.1 ± 0.6	1.243 ± 0.004
PHBV/PBAT/ENR50 (50/35/15) + 0.3 wt % DCP + 20 wt % MS	<3.5	1.243 ± 0.014

blend and composites. As shown in the table, compared to the blend without added DCP, the MFI of the blend in the presence of DCP decreased apparently due to the cross-linking, branching, and M_w increase. Incorporation of the fiber to the blend furthermore reduced the flow index of the composites. This indicated that the fiber confined the mobility of the matrix segment in the melt state. Here, another reason should also be pointed out that the unreacted DCP residue in the composites will also decrease the MFI of the composites during the MFI measurement. Since the measurements were performed at 190 °C, further cross-linking reaction will occur, which will hinder the flow of the polymer matrix.

The density of the composites greatly determines the application of the materials, especially in automotive applications. Consequently, the properties of the density performance were also measured for the samples and the results are summarized in Table 4. Neat PHBV possess high density of 1.305 g/cm³, which may be due to its high crystallinity. The density decreased to 1.228 g/cm³ for the PHBV/PBAT/ENR blend. When DCP is added to the blend, a slight decrease of density was obtained at a value of 1.222 g/cm³, which may due to the confinement of crystallization of PHBV. A slight increase in the density was observed for the composites, which were also reported in our previous research. However, the densities of natural fiber composites are considerably lower than those of the glass fiber composites. It was also found that the composites with DCP added showed lower density compared with the original composites.

CONCLUSION

Green composites from PHBV based multiphase blends and miscanthus fibers with excellent performance balance were successfully fabricated by a simple melt reactive blending method. Toughened blends with low strength and modulus were achieved by melt blending PHBV with PBAT and ENR. DCP was employed as an effective reactive agent to enhance the interfacial reaction of the different phases. The results indicated that DCP and ENR worked in a collaborative way in enhancing the compatibility of the system. The incorporation of miscanthus fibers greatly improved the modulus and strength of the blend matrix without apparent toughness deterioration. It was found that the even with 20 wt % fiber added, the impact strength was still kept at a value of 240 J/m with improved stiffness. Moreover, the composites showed balanced thermal resistance, viscosity, and density performance. The excellent, balanced properties of the composites made these materials suitable for very promising applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mohanty@uoguelph.ca. Tel.: +1-519-824-4120 ext 56664. Fax: +1-519-763-8933.

Notes

The authors declare no competing financial interest.

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