

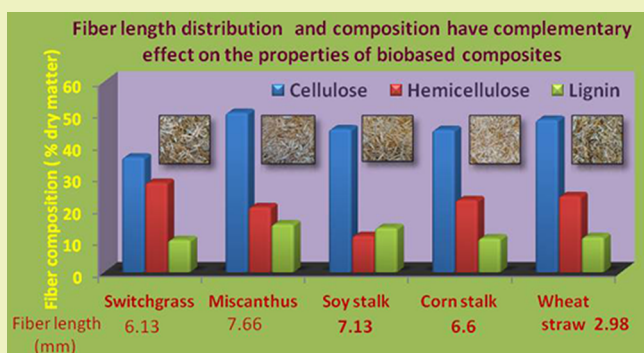
Sustainable Green Composites: Value Addition to Agricultural Residues and Perennial Grasses

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S Supporting Information

ABSTRACT: This work has explored the potential use of lignocellulosic agricultural residues like soy stalk, corn stalk, wheat straw, and perennial grasses, like switchgrass and miscanthus, as reinforcement for engineering value-added biobased composite materials. The effect of incorporating 30 wt % lignocellulosic fibers into a biodegradable polymer matrix comprising a pre-blend of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(butylene adipate-co-terephthalate) (PBAT) has been investigated. Results of this work explain that fiber chemical composition and fiber length distribution provide a complementary effect on the mechanical and thermal properties of the resulting biobased composites. Comparing the effects of all the fiber types, miscanthus (MS)-based composites, showed slightly higher tensile strength, and Young's modulus improved by 104%. The highest heat deflection temperature of 110 °C was obtained with PHBV/PBAT/MS composites. This study has revealed prospects for hybridization of these lignocellulosic fibers to fabricate hybrid composites with enhanced performance.

KEYWORDS: Agricultural residues, Perennial grasses, Biobased composites, Chemical composition, Mechanical properties, Thermal stability



INTRODUCTION

Demand for sustainable materials requires engineers and scientists to think beyond what constitutes the best material for any application. Interest in utilization of renewable resources is increasing because of depleting natural resources, environmental responsiveness, economic considerations, and important technology breakthroughs. Biobased biodegradable polymers and composites derived from renewable biomass feedstock can be a powerful demonstrative case of relevant dimension for sustainable development. They have the potential to compete with petroleum-based products and are currently emerging as alternatives for traditional petroleum-based composite materials. Natural fibers with renewable resource-based polymers benefit the environment, as they can be biodegradable, compostable, and recyclable, and reduce greenhouse gas emissions.¹

Natural fiber composites (biobased composites) have already gained significant attraction from the automotive industry. Fuel economy and service life are some of the major sustainability parameters for automobiles, and choice of materials plays a vital role in deciding the performance. Certain biobased composites are preferred as they can offer weight savings and ease of removal from the environment after end use. They also reduce the dependence on petroleum resources. Natural fibers like kenaf, hemp, sisal, flax, and jute have already been studied

extensively for composite applications.² Therefore, focus of this work is toward perennial grasses and agricultural residues (lignocellulosic fibers), which are inexpensive and abundantly available at present.

Switchgrass and miscanthus are perennial C4 grasses. They are front-runners of energy crops for biomass and biofuel production.³ They yield high quality lignocellulosic material even on marginal lands with low moisture during harvest. Other advantages include efficient use of water and fertilizers.^{4,5} Agricultural residues result from the production stream and subsequent processing operations. Production residues consist mainly of stalk and leaf tissues, whereas the co-products from processing operations are typically straw, hull, or remaining grain components.⁴ Agricultural production residues include soy stalk and corn stalk, while the materials from grain processing operations such as wheat straw belong to the category of processing residues.

Abundance and potential to yield good quality fibers make these perennial grasses and agricultural residue interesting candidates for use as biofibers in composite applications. They can be the principal source of fibers serving as a substitute for

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wood and certain synthetic fibers and fillers. Also, using them as a source of reinforcements will establish an entirely new value chain for that particular crop and add economic benefits to the farmers. However, the market growth of these biobased composites depends on the amounts of grasses and agricultural residues available. About 365 million oven dry tonnes (M ODT) of nonwood fibers are produced in North America per year, and only one-third of the cereal straw produced is utilized for non-agricultural uses.⁶ Canada has the potential to contribute feedstocks for the development of bioproducts as the agricultural activities here produce millions of tons of biomass every year. Sustainably removable residues available from soy stalk, corn stalk, and wheat straw were reported to be 29 M ODT/yr.⁷

Biopolymer blends are receiving increased attention as matrix material for composites as they combine the major properties of both blending components. In that way, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), the prevailing class of polyhydroxyalkanoates blended with an aliphatic-co-aromatic polyester, poly(butylene adipate-co-terephthalate) (PBAT), has good balance of stiffness and toughness properties.^{8,9} To this effect, a pre-blend of PHBV/PBAT is selected as a matrix material for this study.

The performance of agricultural residues when added to high-density polyethylene (HDPE), polylactic acid (PLA), and PHBV has been investigated previously by other researchers.^{10–12} Nanda et al. have studied the effect of incorporating soy hull, switchgrass, miscanthus, and their hybrid at 30 wt % into a PHBV/PLA blend.¹³ Sahoo et al. investigated the composites prepared from poly(butylene succinate) (PBS), lignin, switchgrass, and their hybrid.¹⁴ All these studies were successful in fabricating green composites that exhibited improved modulus but ideally the same or less tensile strength compared to the selected neat polymer. In our previous work, addition of switchgrass at varying weight fraction to a PHBV/PBAT blend was examined, and it was concluded that the strength of the matrix was beginning to decline at fiber concentrations higher than 25 wt %.¹⁵ This work is a step toward exploring the comprehensive use of miscanthus and agricultural residues (lignocellulosic fibers) as reinforcement for the PHBV/PBAT matrix. The effect of incorporating various lignocellulosic fibers at 30 wt % fiber loading into a pre-blended PHBV/PBAT matrix was investigated and compared with composites containing 30 wt % switchgrass.

MATERIALS AND METHODS

Materials and Material Preparation. A pre-blend of PHBV/PBAT containing 45% PHBV and 55% ECOFLEX (PBAT) available in the trade name of ENMAT 5010 P was procured from Tianan Biologic Materials Company, Ltd., China. Switchgrass (SG) was kindly supplied by Nott Farms Ltd., Clinton, ON, Canada. Miscanthus (MS) was supplied by New Energy Farms Ltd., Leamington, ON, Canada. Corn stalk (CS), soy stalk (SS), and wheat straw (WS) were obtained from Elora, ON, Canada. All the fibers were received in chopped form and were sieved to remove the fine particles. Fibers and neat polymers utilized in this work are hygroscopic; therefore, they were dried in an oven at 80 °C for 6 h prior to processing. These are the established drying conditions as the moisture content of the polymer and fiber after drying at the specified conditions was negligible.

Green Composite Fabrication. Fabrication of green composites was achieved through extrusion followed by injection molding. A micro 15 cc corotating twin screw compounder and micro 12 cc injection molding machine, manufactured by DSM Research, Netherlands, was used for this process. The processing temperature was set to 180 °C and was collectively controlled from the feeding end to the

nozzle to avoid degradation of the polymer matrix. The screw RPM was set to 100, and residence time of 2.5 min (including feeding time) was maintained for all composites to facilitate thorough mixing of fibers in the matrix. The molten material from the extruder was collected and transferred through a preheated collector built with piston cylinder assembly to DSM micro 12 cc injection molding machine. After several trial runs, a filling pressure of 5 bar, packing pressure of 6 bar, and mold temperature of 45 °C was found to be suitable as a better finished part with low molded-in stress was achieved at these conditions. These optimized processing conditions were adopted for fabrication of all the composite formulations.

Fiber Dimension Measurement. High resolution photographs of 75 individual fibers spread on a sheet of black paper framed with a ruler for calibration were captured. Fiber length was measured from this photograph using a java image processing program, Image J. To measure the average size of fibers in the processed composite sample, the composites were dissolved in chloroform, and the fibers were recovered by filtering. The average dimension of recovered fibers was measured using Nikon optical microscope (ECLIPSE LV100DA-U) with 5X magnification lens. The fibers were not uniform throughout the length and width; therefore, dimensions were measured at three places to obtain an average. In such a manner, dimensions were measured for 75 individual recovered fibers, and the average of this is reported. The same procedure was followed for all fiber types.

Testing and Characterization. Properties were measured after the test specimens were conditioned in standard laboratory atmosphere for 40h at 23 °C and 50% relative humidity (ASTM D 618-08, Procedure A 40/23/50). The results reported are an average value of five test results for mechanical properties and three test results for thermal properties, density, and water absorption.

Tensile and flexural properties of the neat polymer and composites were measured using Instron Instrument Model 3382 following ASTM standards D 638 and D 790, respectively. Tensile tests for all composite samples were carried out at room temperature with a gauge length of 50 mm and at a crosshead speed of 5 mm/min. A span length of 52 mm and crosshead speed of 14 mm/min were used for flexural tests. Notched Izod impact tests (as per ASTM D 256) at room temperature were accomplished using TMI 43-02 Monitor Impact Tester with a 5 ft-lb pendulum. Mechanical property results were statistically analyzed by a one way ANOVA Tukey method of multiple comparison using MINITAB software. The sample size, “*n*” was 5, and the analysis was conducted at 95% confidence level to determine if the composite properties were significantly different.

Thermal decomposition studies of fibers and composites in nitrogen atmosphere were observed using a TA Instrument TGA Q 500 thermogravimetric analyzer. The experiments were run from room temperature (25 ± 3 °C) to 600 °C with a heating rate of 20 °C/min. Storage modulus and tan δ as a function of temperature were studied using a dynamic mechanical analyzer (DMA Q800) supplied by TA Instruments. Samples were heated from –50 to 130 °C with a ramp rate of 3 °C/min. Heat deflection temperature (HDT) was evaluated in DMA Q 800 with three point bending clamps operated in the DMA controlled force mode. The ramp rate chosen was 2 °C/min, and the deflection was evaluated at 250 μ m while all the samples were heated from room temperature to 130 °C.

Density was measured using Alfa Mirage electronic densimeter model MD-300 S, which works based on Archimedes principle. Melt flow index (MFI) of the polymer matrix and the fabricated composites were measured from Qualitest melt flow indexer 2000 A according to ASTM standard D 1238-10 (procedure A 190/2.16). Samples were dried before testing as the presence of moisture will affect the melt flow rate of the material. Fractured surface morphology was observed by scanning electron microscopy (SEM), Inspect S 50, FEI Netherlands. Cressington sputter coater 108 was used to gold coat the samples for 30 s under an argon atmosphere.

Water absorption test was conducted according to ASTM D 570-98 standard. Three impact test samples for each formulation were dried in an oven for 24 h at 55 ± 2 °C. The dried samples were weighed to precision of 0.001 g and then immersed in distilled water at room temperature for 18 weeks. At periodic time intervals, the samples were

taken out from water and immediately weighed after the surface water was wiped off. The water absorption percentage (M_t %) at a given time can be obtained using the formula

$$M_t(\%) = \frac{W_{(t)} - W_{(0)}}{W_{(0)}} \times 100 \quad (1)$$

$W_{(t)}$ is the weight of the sample at a given time and $W_{(0)}$ is the sample's initial weight.

Fiber composition analysis by wet chemistry was conducted by Agri-Food Laboratories at Guelph, ON, Canada. The content of acid detergent fiber (ADF), neutral detergent fiber (NDF), and lignin in different fiber types were provided. The methods used were based on the AOAC method 973.18 for ADF and lignin and AOAC 2002.04 for NDF. ADF denotes the cell wall portions of the forage containing cellulose and lignin, while NDF refers to ADF fraction plus hemicellulose. Therefore, cellulose content was calculated from ADF and lignin values, and hemicellulose content was calculated from ADF and NDF.

RESULTS AND DISCUSSION

Fiber Architecture and Composition. Fiber architecture includes several factors such as fiber aspect ratio, orientation, and fiber content. All this together controls many composite properties, particularly mechanical properties.¹⁶ Higher aspect ratio (ratio of fiber length to diameter) leads to greater reinforcing efficacy and good stress transfer. The fibers utilized for this work were found to have rectangular geometry rather than perfectly cylindrical structure. Fiber length distribution before processing is given in Figure 1, and the average fiber dimensions after recovery from the composite sample are given in Table 1.

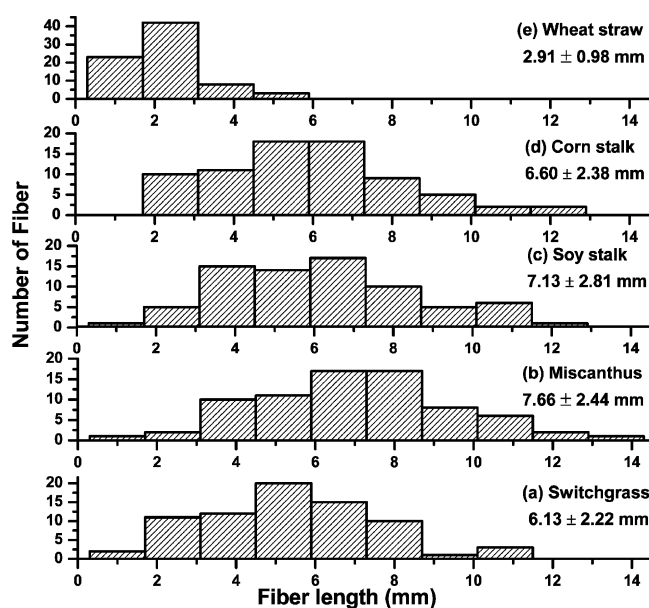


Figure 1. Fiber length distribution of different lignocellulosic fibers.

The average fiber length after processing reduced drastically because of high shear forces involved in the processing operation.¹⁷ Except for wheat straw, the length of all other fiber types recovered from the composites was in the same range considering the standard deviation. The difference in length in the case of wheat straw could be due to the relatively low average fiber length even before subjecting to processing operation. Fiber orientation plays a crucial role in deciding the properties of a composite material and is directly related to the

processing technique by which the composite is produced.¹⁶ In our case, random fiber orientation was predominant from visual observations of the fiber on the composite samples, later supported by SEM images. Percentage of fiber content or loading is also a significant factor in determining the mechanical properties of the composite. Usually the mechanical properties have been observed to increase with increasing fiber content but only to a certain level. On the basis of previous studies conducted on the perennial grass and agricultural residues reinforcement, 30 wt % loading of fibers into the matrix was chosen.^{11,12,15}

Chemical composition of fiber is another important variable that determines the overall properties of the composites. Table 1 shows our findings on fiber dimension and composition. Cellulose and hemicellulose are very hydrophilic, whereas lignin is totally amorphous and hydrophobic in nature. Apart from these three major components, lignocellulosic fibers also contain protein, ash, and other extractives.¹⁸ Miscanthus had the highest cellulose and lignin content, while switchgrass had the lowest of both. However, the hemicellulose content was highest in switchgrass and lowest in corn stalk. These values compare well with the values previously reported for these fibers.¹⁸

Mechanical Properties. The mechanical properties of the matrix and green composites are shown in Table 2 combined with the results from statistical analysis. The tensile strength of composites with switchgrass (SG), soy stalk (SS), corn stalk (CS), and wheat straw (WS) was statistically the same as the tensile strength of the matrix. The retained strength of the PHBV/PBAT matrix even after incorporation of these lignocellulosic fibers suggests a reasonable amount of interaction present between the matrix and fiber. Miscanthus (MS) incorporation resulted in increased tensile strength of the composite. This could be attributed to a relatively higher amount of cellulose present in the miscanthus, which could have led to better interaction with the matrix. The average fiber length of SG, MS, SS, and CS are all statistically the same. However, the strength of these composites has not increased like MS-based composites mainly because of their difference in cellulose content. In the case of WS, the cellulose content is close to MS, but the average fiber length is slightly lower than that of above-mentioned fibers. On the contrary, SG has basically the same average fiber length as MS but very low cellulose content. These observations suggest that fiber length and fiber composition could have a complementary effect in improving the tensile strength of the composites.

The flexural strength of the composites with different fibers has improved significantly, with the exception being switchgrass-based composites that was statistically the same as that of the matrix. Very similar flexural strength values have been reported earlier for PHBV/agricultural residues and PBS/switchgrass composites.¹² The presence of fiber had markedly improved the composite modulus because the molecular chain mobility of the polymer matrix was hindered by the incorporation of fibers.¹⁹ Both tensile and flexural modulus of the green composites showed similar trends. The moduli of the green composites have improved drastically, yet the modulus increase in cases of composites with different fiber types was not significantly different from each other. However, the statistical analysis has grouped the composites based on the improvement in modulus range achieved as shown in Table 2. Correlation of grouping with the composition of fibers indicates that modulus improvement is also dependent on the

Table 1. Fiber Dimension and Composition of Various Lignocellulosics

sample	average fiber dimensions (after recovery)		cellulose (% of dry matter)	hemicellulose (% of dry matter)	lignin (% of dry matter)
	length (mm)	width (mm)			
switchgrass (SG)	1.555 ± 0.375	0.462 ± 0.258	36.12	28.18	10.14
miscanthus (MS)	1.535 ± 0.494	0.446 ± 0.169	50.19	20.47	15.08
soy stalk (SS)	1.455 ± 0.496	0.458 ± 0.267	45.01	11.42	13.93
corn stover (CS)	1.473 ± 0.456	0.433 ± 0.185	44.77	22.68	10.63
wheat straw (WS)	1.101 ± 0.180	0.468 ± 0.167	47.98	23.97	11.04

Table 2. Mechanical Properties of Matrix and Composites^a

material	tensile strength (MPa)	tensile modulus (GPa)	flexural strength (MPa)	flexural modulus (GPa)	elongation at break (%)	impact strength (J/m)
^b PHBV/PBAT	21.60 ± 0.26 (b, c)	1.16 ± 0.01 (c)	37.65 ± 0.2 (b)	1.30 ± 0.11 (d)	106.7 ± 52.49 (a)	369.93 ± 9.55 (a) (non break)
^b PHBV/PBAT/ Switchgrass	20.64 ± 0.7 (c)	1.88 ± 0.06 (b)	35.97 ± 0.71 (b)	1.97 ± 0.18 (c)	3.23 ± 0.28 (b)	35.13 ± 5.09 (b)
PHBV/PBAT/ Miscanthus	23.30 ± 0.34 (a)	2.37 ± 0.03 (a)	44.03 ± 0.26 (a)	2.68 ± 0.10 (a, b)	3.10 ± 0.08 (b)	35.76 ± 3.86 (b)
PHBV/PBAT/Soy stalk	22.44 ± 0.32 (a, b)	1.95 ± 0.04 (b)	45.19 ± 0.59 (a)	2.46 ± 0.04 (b)	3.03 ± 0.31 (b)	45.61 ± 4.8 (b)
PHBV/PBAT/Corn stalk	21.52 ± 0.42 (b, c)	2.25 ± 0.04 (a)	44.73 ± 0.66 (a)	2.72 ± 0.14 (a)	2.82 ± 0.22 (b)	40.17 ± 8.51 (b)
PHBV/PBAT/Wheat straw	21.46 ± 0.25 (b, c)	2.01 ± 0.08 (b)	44.32 ± 0.83 (a)	2.57 ± 0.10 (a, b)	2.75 ± 0.51 (b)	36.41 ± 1.62 (b)

^aLetters in parentheses correspond to groupings of statistically similar results generated by one way ANOVA using the Tukey method of multiple comparison. Mean values that do not share the same letter are significantly different. ^bData for the neat polymer and its composites with 30 wt % switchgrass are from our previous work.¹⁵

composition of the individual fibers. Bourmaud and Pimbert have observed improved modulus performance of PP/miscanthus and PLA/miscanthus composites and attributed it to high cellulose content.²⁰

Incorporation of fibers into the polymer matrix also drastically reduced the composite's elongation at break. The elongation of PHBV/PBAT was greater than 100%, whereas with the composite materials the elongation at break was found to be less than 5% regardless of the biofiber type. As discussed earlier, this occurrence is fairly common because the addition of fibers restricts the molecular mobility of the polymer chains in the composite. In addition, the lignocellulosic filler added to the matrix reduces the ductility of the matrix. Similar behavior has been reported by Habibi et al. in the case of LDPE reinforced with Egyptian agro-residues.²¹

The impact strength is the ability of a material to withstand fracture or the amount of energy required to propagate a crack. It depends on certain factors like fiber and matrix strength, load transfer efficiency, resistance to crack propagation, bonding strength, volume fraction, fiber distribution, and geometry.²² Fibers are known to reduce the impact strength of a composite by two mechanisms: (1) drastic reduction in elongation at break thus reducing the area under stress strain curve, and (2) stress concentration at areas of poor adhesion around fiber ends and fiber–fiber contact.²³ The impact strength of the composites decreased drastically due to the incorporation of fibers (Table 2). In our case, the impact strength behavior can be directly correlated with the observed reduction in percentage elongation at break. The maximum impact strength achieved was 45 J/m with composites containing 30% soy stalk. However, the statistical analysis revealed that the impact strength of composites with different lignocellulosic fiber types did not vary significantly. It should be noted that the achieved impact strength is not quite sufficient for some of the applications but can be increased by the addition of appropriate

impact modifiers. Promoting higher level of compatibility between the fiber and matrix with the use of compatibilizers will also help in increasing the impact strength. It has been demonstrated previously that the properties of the switchgrass-based composites increased significantly with the addition of compatibilizer.¹⁵

All the above observations on mechanical properties indicate that the same trend in property change could be achieved ideally by balancing the fiber length and composition. This realization could be beneficial for commercial injection molding application as the hybridization of these lignocellulosics during composites fabrication could help in achieving the right property balance without compromising mechanical performance in the event of supply chain issues like fiber shortages.

Thermo-Mechanical Properties. Storage modulus (E') is the ratio of the in-phase stress to the applied oscillating strain, measuring the energy stored per cycle of deformation related to the elastic portion, while loss modulus (E'') is out of phase viscous component. The ratio of E'' to E' gives a mechanical damping factor, $\tan \delta$. Figure 2 depicts the temperature dependence of storage modulus (E') and $\tan \delta$ for PHBV/PBAT matrix and composites.

Considerable improvement in the storage moduli of all the green composites was observed, and it can be attributed to the introduction of rigid filler particles into the matrix phase. Throughout the investigated range of temperature, the storage modulus of every green composite was found to be higher than the matrix. At the glass transition zone (primary relaxation of PBAT), there was a sharp decrease in the storage modulus, but the degree of modulus loss in the fiber filled system was reduced markedly compared to the matrix. As the temperature increased, the composites passed through the glass transition zone of PHBV and then softened, which is again observed as a further decrease in the storage modulus. The highest storage

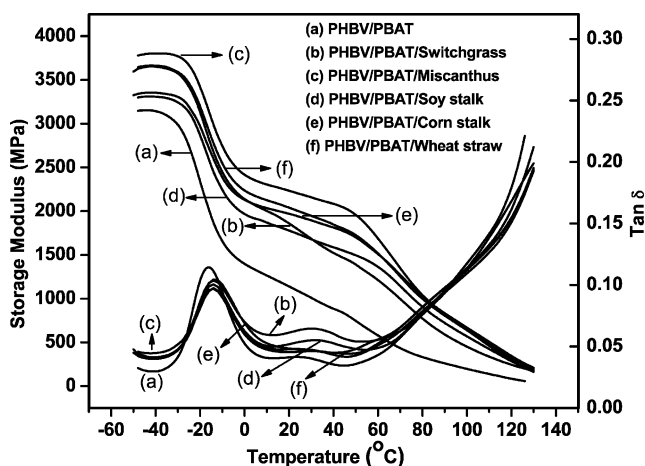


Figure 2. Storage modulus and $\tan \delta$ of the matrix and green composites.

modulus at any given temperature was noticed in PHBV/PBAT with 30 wt % miscanthus.

The damping peak is associated with the partial loosening of the polymer chains facilitating the movement of small groups and chain segments, and it occurs near glass transition (T_g).²³ In the $\tan \delta$ curve, the first peak at a lower temperature corresponds to T_g of PBAT, while the second hump corresponds to T_g of PHBV. It is evident from Figure 2 that the damping peak height of all the composites was reduced, and the peak width was broadened. Interface is believed to be the dissipative component in a composite material. When the composite is under strain, the fiber controls the strain so that the interface is strained to a lesser degree.^{24,25} This could be a possible reason for the above-mentioned behavior noticed in the green composites. Second, the restricted movement of the polymer molecules due to the incorporation of stiff lignocellulosic fillers also accounts for the reduction in peak height. The increase in storage modulus with fiber incorporation, decrease in $\tan \delta$ peak height, and shifting of T_g toward higher temperature are all consistent with the observations of many researchers.^{11,12,24,25}

HDT is defined as the temperature at which a material deflects 0.25 mm under a load of 0.455 or 1.82 MPa. HDT is an important criterion in product design, and higher values are critical for composite application. HDT of composites as given in Table 3 increased considerably with incorporation of different lignocellulosic fibers. It has been reported that modulus enhancement due to the addition of reinforcing fillers has a greater effect in increasing the HDT of the composite, which in turn is dependent on various factors like filler shape,

Table 3. HDT, Density and MFI of Matrix and Green Composites

Sample	Density (g/cm ³)	HDT (°C)	MFI (g/10 min)
PHBV/PBAT ¹⁵	1.234 ± 0.05	91 ± 1.2	19.0 ± 2.02
PHBV/PBAT/Switchgrass ¹⁵	1.261 ± 0.024	107 ± 1.5	7.2 ± 0.63
PHBV/PBAT/Miscanthus	1.296 ± 0.001	110 ± 0.2	11.73 ± 1.18
PHBV/PBAT/Soy stalk	1.278 ± 0.024	107 ± 2.3	8.60 ± 1.38
PHBV/PBAT/Corn fiber	1.286 ± 0.002	108 ± 1.8	9.70 ± 1.80
PHBV/PBAT/Wheat straw	1.276 ± 0.005	108 ± 0.9	8.96 ± 0.82

aspect ratio, size distribution, and orientation.²⁶ The increased storage modulus of composites at higher temperature agrees with HDT values. Also, Nielsen predicted that in a fiber-filled system the heat deflection temperature is related to flexural modulus behavior.²³ Accordingly, HDT values obtained for the green composites were in good agreement with flexural modulus data thereby proving Nielsen's prediction. Composites with 30% miscanthus exhibited higher HDT of 110 °C compared to composites with other fibers.

Thermogravimetric Analysis (TGA). The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for all the fibers are given in Figure 3.

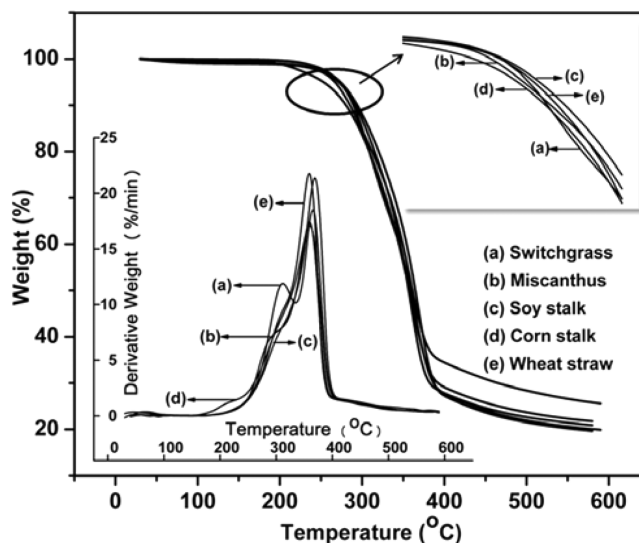


Figure 3. TG and DTG curves of different fibers.

The onset of degradation occurred at around 215 °C for all the fibers except corn stalk, which started showing degradation around 205 °C. The early start of decomposition in corn stalk can be clearly seen from the DTG curve for the fiber in Figure 3. This could be due to the decomposition of pectin and non-structural hemicellulose¹⁰ or loss of light volatiles present in the fiber.²⁷ The decomposition temperature at onset and at 5% weight loss (T_5) is shown in Table S1 of the Supporting Information. Switchgrass and soy stalk have higher thermal stability followed by other fibers. On the basis of a decomposition temperature at 5% weight loss, the order of thermal stability from most to least stability can be given as soy stalk > switchgrass > wheat straw > miscanthus > corn stalk. The DTG curve showed a shoulder peak at the left side of the main peak, and this was attributed to the hemicellulose present in the fiber, while the main peak corresponds to the degradation of cellulose.²⁸ Higher hemicellulose content in switchgrass was reflected in its DTG curve. Lignin is known to degrade over a wide range of temperature, and the flat tailing section of the DTG curve corresponds to the decomposition of lignin.²⁸ All these fibers are suitable to be processed only with polymers having a processing temperature up to 200 °C. However, it is believed that some surface treatment of fibers could improve the onset degradation temperature considerably.

The TG and DTG curves for the matrix and the composites are given in Figure 4. The PHBV/PBAT matrix showed a two-step degradation phenomena. The first step corresponds to the degradation of PHBV, and the second is degradation of PBAT. All the composites followed a three-step degradation

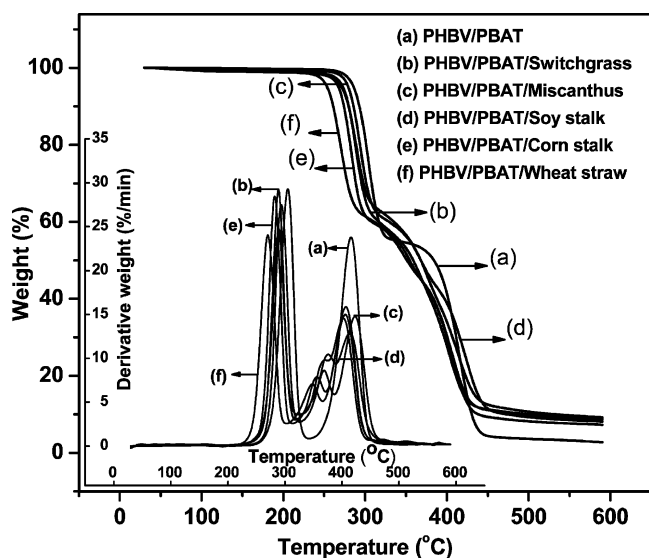


Figure 4. TG and DTG curves of polymer matrix and green composites.

phenomena. The first degradation step corresponds to PHBV, while the second and third step correspond to cellulose and PBAT, respectively.

The thermal degradation onset temperature was lower for the green composite than the polymer matrix mainly due to the lower thermal stability of the fibers. Similar thermal behavior for composites with perennial grasses can be found in the literature.^{13,14} Among all the composites, PHBV/PBAT/WS showed lower thermal stability, while PHBV/PBAT/MS had higher thermal stability. Higher thermal stability in miscanthus composites could be due to better interaction of the fiber with the matrix. Considering the 5% weight loss temperature, the thermal stability of different composites can be ordered as PHBV/PBAT/MS > PHBV/PBAT/SG > PHBV/PBAT/SS > PHBV/PBAT/CS > PHBV/PBAT/WS.

Density. The density of composites plays a vital role in determining the properties, especially for lightweight composite applications. Lightweight composites are preferred by automakers due to potential weight savings. Using lignocellulosic fibers is advantageous for such applications as their density (1.3–1.5 g/cm³) is significantly lower than that of glass fibers (2.6 g/cm³).¹¹ The density of natural fiber composites will be considerably lower than that of glass fiber-reinforced composites provided the matrix material and percentage of the reinforcement are the same. Neat PHBV/PBAT was found to have density of 1.23 g/cm³, while the density of composites with 30 wt % fibers was in the range of 1.26–1.29 g/cm³. This slight increase in density is expected in composites and has been reported earlier.¹¹ The density of PHBV/PBAT/MS was higher compared to all other composites, and this suggests that the density of miscanthus was higher than that of any other fiber type. In that case, for the same weight percentage of fiber added, the volume of miscanthus in the composite is lesser. This signifies that the improved performance in miscanthus-based composites is also due to slightly less amount of fiber present in the matrix.

Melt Flow Index (MFI). MFI is the output rate/flow of the material in gram per 10 min through a die of standard diameter (2.0955 ± 0.0051 mm) and length (8.000 ± 0.025 mm) under prescribed conditions of load and temperature. Incorporation

of fiber into the matrix significantly reduced the melt flow index of all the green composites as shown in Table 3. Lower MFI is associated with higher viscosity, and George et al. have reported that the viscosity of the system is bound to increase with fiber incorporation as it hinders flow of the matrix material.²⁹ Sanadi et al. have also observed the reduction in MFI and mentioned that the restriction offered to the polymer molecules by the fiber will depend upon the type of fiber and fiber surface characteristics.³⁰

Water Absorption. Water uptake behavior of the PHBV/PBAT blend and its composites with different agricultural residues and grasses is shown in Figure 5. The PHBV/PBAT

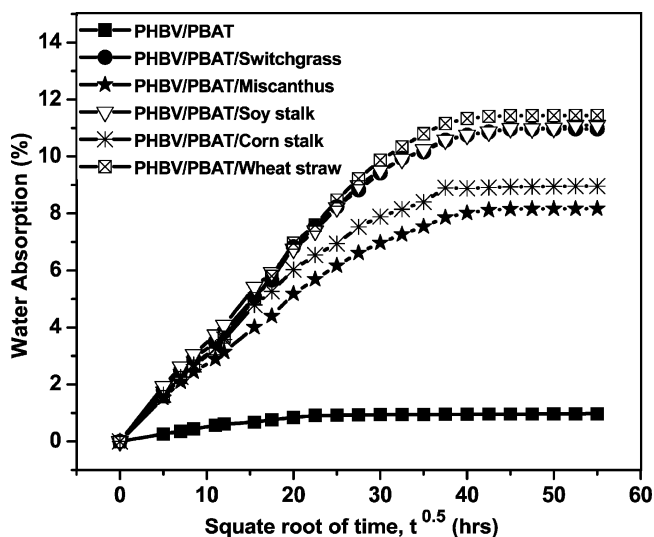


Figure 5. Water absorption behavior of the matrix and green composites.

matrix absorbed much less water due to its hydrophobic nature. Increased water absorption rate was noticed in all the composites mainly due to the hydrophilicity and numerous porous tubular structures associated with lignocellulosic fibers.

Das et al. have mentioned that the three main regions where the water could be observed in a natural fiber composite is through the cell wall, lumen, and voids between the matrix and fiber.³¹ Initially, all the green composite samples showed a very rapid increase in percentage of water absorbed. As the immersion period increased, the absorption curve reached a plateau after 12 weeks, suggesting that the samples attained a saturation point and no more water could be absorbed into the composite system. The test was continued for six more weeks as specified by the standard to confirm the same.

Although the amount of fiber loading was the same in all the green composites, a different percentage of water absorption was observed between the composites. This can be attributed to the variation in chemical composition of each fiber as well as the level of interaction of the fiber with the matrix. The percentage of water absorbed was higher for wheat straw-based composites, while it was relatively low for composites with miscanthus. As mentioned above, the water uptake is dependent on the chemical constituents present in the individual fibers. Out of three major constituents of the lignocellulosic fibers, cellulose and hemicelluloses are hydrophilic, while lignin is hydrophobic in nature. From Table 1, we can say that the holocellulose (cellulose + hemicellulose) content is higher for wheat straw, and the higher percentage of

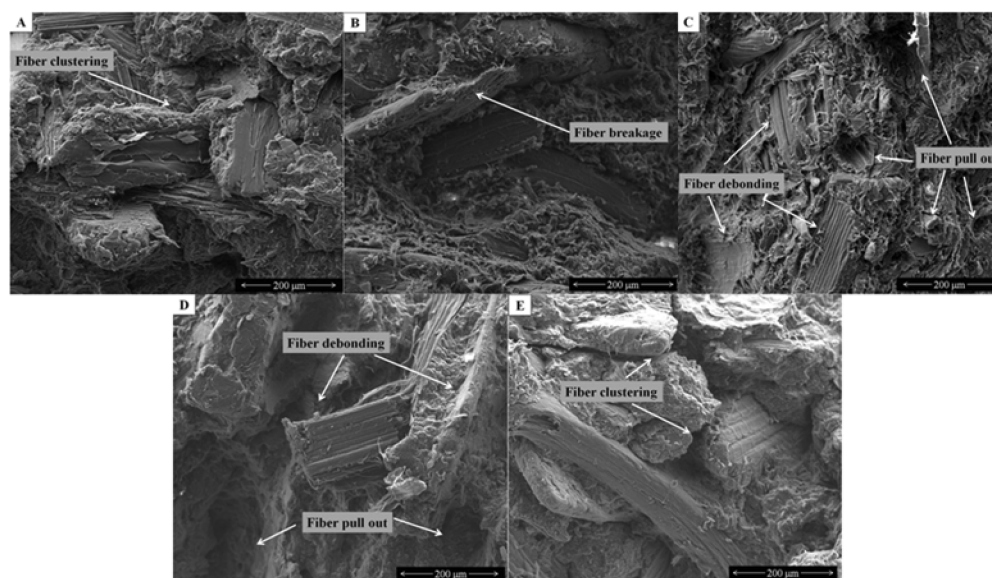


Figure 6. SEM Images of (A) PHBV/PBAT/Switchgrass, (B) PHBV/PBAT/Miscanthus, (C) PHBV/PBAT/Soy stalk, (D) PHBV/PBAT/Corn stalk, and (E) PHBV/PBAT/Wheat straw.

water absorbed in the case of wheat straw composites might be attributed to the comparatively high content of holocellulose and low content of lignin. Similar observations for wheat straw composites have been reported by previous researchers, and they have mentioned that this behavior was due to high amounts of pentosans and low amounts of lignin.³²

Switchgrass, soy stalk, and corn stalk have proportionately less holocellulose compared to wheat straw. This might be the reason for their slightly reduced percentage of water absorption compared to wheat straw composites. Panthapulakkal and Sain have reported that the low water absorption of HDPE/corn stalk composites after initial high water uptake could be due to the presence of low molecular weight leachables in the corn stalk.¹⁰ This was in accordance with our TGA and DTG data obtained for corn stalk. Water in which the samples were immersed was observed to turn light brown in color only in the case of corn stalk composites, which might be due to the above stated reason. Miscanthus composites exhibited relatively low water uptake. As discussed in Mechanical Properties section, a slightly higher content of cellulose in miscanthus would have led to good interaction between the matrix and the fiber, thus preventing water absorption at the interface between the matrix and the fiber. Another point to notice is the relatively high content of lignin in miscanthus that makes the fiber hydrophobic compared to others. The water absorption behavior noticed in all the green composites affirms the fact that the fiber composition and interfacial strength has an effect on the performance of a composite in a moist environment.

Morphology. The scanning electron microscopy (SEM) images of impact fractured surfaces of different composites are shown in Figure 6.

In miscanthus reinforced composites, fiber breakage was apparent. Fractured fiber surface suggested good interfacial adhesion between the matrix and the fiber. Owing to this, energy dissipation could not have occurred effectively through fiber pull-out or debonding, which has resulted in high strength but low impact strength. This is supported by Nielsen's conclusions that fiber pull-out and debonding increase the impact strength, while they reduce the breaking strength of fiber reinforced composites.²³ Mainly pull-outs and debonding

were noticed in soy stalk- and corn stalk-based composites. However, this fracture behavior did not have any apparent significance on increasing the impact strength of these composites. In the case of switchgrass- and wheat straw-reinforced composites, fiber clustering was observed that might be due to high fiber loading, and this may have led to increased stress concentration. Tensile strength of these composites might have not increased as it is critical to this kind of stress concentration.

In some cases, gaps between the fibers and matrix were noticed, which were believed to be quite common due to hydrophobic–hydrophilic disparity. In fact, when fibers are incorporated into a polymer matrix, it is difficult to achieve good bonding between the fiber and matrix. Use of compatibilizer might help in such cases; however, the aim of this study was to find the effectiveness of agriculture residues and grasses as reinforcing fillers without the use of any adhesion-promoting agents.

CONCLUSION

Green composites from a pre-blend of PHBV/PBAT matrix and various lignocellulosic fibers were successfully fabricated through extrusion followed by the injection molding process. The slight difference in strength and modulus values among the green composites was attributed to the difference in individual fiber composition and fiber length distribution. These two factors played a complementary role in deciding the final properties of the composites. Level of interaction between the matrix and fiber was also different in each fiber type. Significant improvement in heat deflection temperature was observed besides the typical increase in stiffness of the composites. PHBV/PBAT/MS showed increased tensile strength, modulus, HDT, and MFI, while exhibiting a relatively low percentage of water absorption. Soy stalk was found to have higher thermal stability compared to other lignocellulosic fibers. When added as a reinforcing fiber into the matrix system, the combination of PHBV/PBAT/MS exhibited higher thermal stability.

The renewable resource-based lignocellulosic fibers are inexpensive and abundantly available. Their potential to impart

high modulus and low density to composites affirms the production of lightweight and eco-friendly composites. Use of these fibers in composite applications will establish an entirely new value chain for the crop. This study has revealed prospects for fabrication of hybrid composites by combining all these lignocellulosics to achieve further performance improvements.

■ ASSOCIATED CONTENT

■ Supporting Information

Table S1: Decomposition temperature of various fibers and green composites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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