1 Introduction

Currently great attention is being paid to composites made from biobased polymeric matrix reinforced with natural fibers to address the sustainability issues and satisfy the market expectation for green materials. Biocomposites are favored for their environmentally friendly attributes such as ease of removal after end use and reduced dependence on petroleum based raw materials. Natural fiber reinforced composite materials offers weight and cost savings to automotive industries while increasing the fuel efficiency of the automobile. Blends of two different bioplastics are being used as a matrix system for composite applications to take advantage of the combinatory properties of blended polymers. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) from the family of polyhydroxyalkanoates is one of the widely studied biopolymer. PHBV is known to have mechanical properties similar to petroleum based traditional plastics such as polypropylene. The drawback of PHBV is its brittleness and high cost; therefore blending it with other suitable polymers could help in overcoming those disadvantages that are hindering its commercial applications.

Poly (butylene adipate-co-terephthalate) (PBAT), an aliphatic aromatic co polyester is derived from petrochemicals but a biodegradable. PBAT is an ideal choice of blending partner for PHBV because of its high toughness. Properties of PHBV/PBAT blends at different weight ratios have been studied [1] and it is established as a matrix that possesses an optimal balance of stiffness and toughness. Therefore, commercially available PHBV-PBAT blend was used as a matrix polymer in this study.

Natural fibers like jute, sisal, hemp, flax, and kenaf have been explored adequately as reinforcing agents for composite applications. Agricultural residues like corn stalk, wheat straw, oat hulls, soy stalk, other seed hulls, and perennial grasses such as miscanthus and switchgrass are emerging as promising alternatives due to their cost advantages and low density values compared to bast fibers and traditional glass fibers. Apart from cost and weight savings, using these perennial grasses and agricultural residues as a source of reinforcements could possibly extend the entire value chain of a crop and bring in substantial economic benefits to the farmers. One of the studies in this area looked at hybridizing the agricultural residues for composite application as a solution to supply chain issues that might arise if a composite containing one type of such fiber is commercialized for industrial applications [2]. Results of this study proved that the properties of hybrid agricultural residue based composite compared well with that of individual fiber types. Our recent study on comparing the reinforcing effects of different perennial grasses and agricultural residues [3] also added substantial knowledge to this aspect of natural fiber composites.

Current work focused on exploring the properties of composites with switchgrass and soy stalk, chosen from perennial grass and agricultural residues category and added to PHBV-PBAT matrix at 30 wt% fiber loading. Natural fibers are susceptible to
moisture uptake as they are hydrophilic while most of the polymers are hydrophobic. This naturally leads to a low level of interaction between these two phases in a composite system. Therefore, presence of a compatibilizing agent that can react with both fibers and the matrix becomes important to achieve a desired level of performance. For this purpose, polymeric diphenyl methane diisocyanate (pMDI) was added as a compatibilizer at a concentration of 0.75 phr (parts per hundred by weight).

2 Materials, Methods and Characterization

2.1 Materials

Enmat 5010 P, a commercially available PHBV-PBAT blend was purchased from Tianan Biologic Materials Co. Ltd, China. This pre-blend contains 45 % PHBV and 55% PBAT (Ecoflex®). The valerate content in PHBV is mentioned to be 3%. Switchgrass was provided by Nott Farms Ltd, Clinton, ON, Canada. Soy stalk was supplied by Elora Research Station, Elora, ON, Canada.

2.2 Fabrication Method

PHBV/PBAT matrix and biocomposites with 30 wt% natural fibers were fabricated by extrusion and injection molding technique. Micro twin screw extruder (co-rotating, 15 cc) and a 12 cc micro injection molding machine (DSM Research, Netherlands) were used for compounding and molding. All the composite formulations were processed at a processing temperature of 180 °C and screw rpm of 100. The melt comin out of the extruder (extrudate) was collected and transferred to the micro injection molding machine with the help of a preheated collector having a piston cylinder assembly. The collector temperature was also set to 180 °C and the molding was accomplished at a mold temperature of 45 °C for all the formulations. Test samples needed for assessment of mechanical and thermal properties were prepared and conditioned in ambient laboratory conditions as per ASTM D 618.

2.3 Testing and Characterization

Mechanical properties like tensile and flexural properties were measured in Instron (Model 3382) by adopting the corresponding ASTM standards (D 638 and D 790). Notched Izod impact strength of the matrix and composites were tested using the impact tester, TMI 43-02 according to the ASTM S 256. Heat deflection temperature (HDT) was measured in Dynamic mechanical analyzer (TA Instruments) and the values are reported at a deflection of 250 μm.

Qualitext melt flow indexer 2000A was used to measure the melt flow index (MFI) of the neat polymer matrix and fabricated biocomposite samples as per ASTM standard D 1238-10 (procedure A 190/2.16). Prior to testing, it was mandatory to dry the samples for 6 hours at 80 °C to avoid the degradation due to the presence of moisture. Testing conditions for bioplastic blends and biocomposites are not established and these materials degrade at a temperature higher than 200 °C therefore the test was accomplished at 190 °C under a load of 2.16 kg. Fracture surface morphology of the composites was observed under scanning electronmicroscope (SEM) developed by FEI, Netherlands (Inspect S 50).

3 Results and Discussion

3.1 Density

Density of switchgrass and soy stalk was back calculated from the density of neat polymer and composites using the following equation.

\[
\frac{1}{\rho_c} = \left(\frac{W_f}{\rho_f}\right) + \left(\frac{1 - W_f}{\rho_p}\right)
\]

Where, \(W_f\) is the weight fraction of fiber, \(\rho_c\), \(\rho_f\) and \(\rho_p\) are the densities of composite, fiber and polymer respectively.

Density of switchgrass was calculated to be 1.323 g/cc while that of soy stalk was 1.392 g/cc. It is important to mention that as the composites were fabricated based on weight percentages, this difference in density values contribute to the difference in actual volume occupied by switchgrass and soy stalk in the matrix and hence difference in their mechanical performance. This will be explained further in discussion on mechanical properties of the composites.

3.2 Tensile and Flexural Properties

Matrix and fabricated composite formulations were tested for tensile and flexural properties to evaluate their mechanical performance. From Fig. 1 it can be noticed that the tensile strength of soy stalk and
switchgrass based composites was almost same as that of the matrix, considering the standard deviation. Such same value of strength maintained even after the addition of these agricultural fibers indicates an acceptable level of interaction that is present between the matrix phase and the fiber. The average aspect ratio ($l/t$) of switchgrass and soy stalk used in this work reduced from approximately 18 to 11 as the fibers were subjected to high shear forces during extrusion in the processing equipment. Reduction in aspect ratio could have affected the reinforcing efficiency of the fiber and thereby failed to increase the strength. Systematic investigation on increasing the loading levels of switchgrass have been conducted previously and reported elsewhere [4]. Tensile strength and other properties were beginning to decline at a loading level of 30 wt% according to that study as aggregation of the fibers occurred at higher loading levels.

 Addition of fibers showed a definitive effect on the Young’s modulus of these green composites. Generally, incorporation of lignocellulosic fibers into the polymer matrix material is expected to increase the modulus due to the relatively high stiffness of the fibers and the restricted mobility of the polymer chains. Composite with switchgrass showed lower modulus compared to the composites containing soy stalk. This could be attributed to the difference in composition of the individual fibers.

 Flexural strength and modulus of composites are shown in Fig. 2. Similar to tensile properties, higher level of increase in flexural strength and modulus was notice with soy stalk composites, again due to difference in fiber composition.

 Early studies on natural fiber composites have established the fact that drastic improvements in the performance of the composites can be achieved by enhancing the level of adhesion that exists between the two phases; fiber and matrix. Therefore, effect of introducing a compatibilizer to promote higher level of interactions between the PHBV/PBAT matrix and the lignocellulosic fibers were evaluated. Many studies have reported that the performance of the composite system was improved with the addition of pMDI which acted as a compatibilizer [5-7]. In our work, it was hypothesized that pMDI facilitated compatibility as its reactive end groups (-NCO) chemically bonded with the OH groups present in the matrix and the added lignocellulosic fibers.

 As hypothesized, the tensile properties of composites compatibilized with pMDI showed good level of improvement. The compatibilizer added to the composite certainly increased the interfacial adhesion that originally existed between the fiber and PHBV/PBAT which in turn improved the tensile strength of compatibilized switchgrass composites by 40% and soy stalk composites by 20%. The mechanism of compatibilization of switchgrass and PHBV/PBAT matrix was proposed in a previous study and was supported by Fourier transform infrared spectroscopy [4]. Critical concentration of pMDI was thought to exist for effective compatibilization and for switchgrass composites, this was 0.75 phr. In this study, it is obvious that the pMDI had certainly helped in improving the properties of the composites with soy stalk but the level of increase achieved is considerably lesser compared to the drastic improvements noticed in switchgrass composites. This signifies that the critical concentration of pMDI in soy stalk composites might be higher than 0.75 phr and that it needs further investigation.

 Oever et al [8] studied the effect of incorporation of 30 % switchgrass (pulped and untreated) as a reinforcing agent into polypropylene (PP) matrix with and without maleic anhydride grafted PP (MAPP) as a compatibilizer. PP matrix had a flexural strength of 42±1.5 MPa and the incorporation of either pulped or untreated switchgrass fibres into the PP matrix had only slightly contributed to the strength. However, they found that the use of MAPP as a compatibilizer increased the strength by 20 and 50% for untreated and pulped fibers respectively. Ahankari et al [9] investigated the reinforcing effect of agricultural residues such as soy stalk, corn stalk and wheat straw on PHBV matrix and compared with PP matrix. In case of PP/soy stalk composites, they achieved a tensile and flexural strength of 30 MPa and 50 MPa respectively. Comparing these literature values to the results achieved in our work, we can say that with the help of pMDI we were successfully able to obtain the same level of properties with PHBV/PBAT matrix.


The stress-strain curves obtained for the matrix and composites with and without compatibilizer are provided in Fig. 3. Stress-strain curve of neat PHBV/PBAT shown in the inset is different from the uncompatibilized and compatibilized composites. This reveals that the addition of lignocellulosic fiber reduces the % elongation at break. Neat PHBV/PBAT is a ductile polymer with elongation value of about 130%. With the incorporation of 30 wt% fiber, % elongation at break for composites significantly reduced to ca. 4%, immaterial of the fiber type. Strain at break for composite materials decreased with fiber incorporation and improved for composites compatibilized with pMDI.

The area under the curve signifies the amount of energy a material can absorb before fracture and is referred to as toughness of the material. It is apparent that compatibilization has increased the toughness of the composites and the effect is higher in case of soy stalk. This indicates that the pMDI could have plasticized the PBAT part of the matrix, rather than compatibilizing the fiber and the matrix in soy stalk composites. In addition to this, modulus improvement in case of soy stalk was mainly due to the incorporation of fibers. Addition of pMDI did not have any significant effect in increasing the modulus which also supports the claim that pMDI could possibly plasticize the composites. Similar behavior in PLA natural fiber composites containing pMDI as compatibilizer has been reported by other researchers [5]. However, in the case of compatibilized switchgrass composites, addition of fiber and the compatibilizer both had a pronounced effect on increasing the modulus.

This difference in behavior noticed between switchgrass and soy stalk composites can be due to the difference in the density values of these fiber types. As switchgrass fibers were found to have lesser density compared to soy stalk, the composites will naturally have more fibers in case of switchgrass for the same level (30 wt%) of loading. When pMDI was added as a compatibilizer, the possibility of pMDI in plasticizing the matrix is higher in case of soy stalk composites due to relatively less volume occupied by the fiber.

3.3 Impact Strength

The impact strength of uncompatibilized and compatibilized composites is presented in Fig. 4. Impact strength denotes the ability of a material to withstand or resist damage when subjected to high rate stress applied suddenly at high speed. Load transfer efficiency, fiber-matrix bonding strength, volume fraction and distribution of the reinforcements in the matrix, resistance to crack propagation, are few of the major factors that cast their influence on the impact strength of composites.

Impact strength of green composites had significantly increased with the addition of compatibilizer. This could be directly correlated to the observed increase in area under the stress strain graph shown in Fig. 3. Interfacial adhesion between PHBV/PBAT and fibers such as switchgrass and soy stalk was believed to be improved due to competing reactions such as formation of secondary bonds and urethane linkages, and plasticization occurring in composites containing pMDI [10]. Impact strength was found to increase by 95% and 77% in case of compatibilized switchgrass and soy stalk composites compared to their uncompatibilized counterparts. Similar trend in impact properties of PBS and lignin composites were reported by Sahoo et al [10].

3.4 Heat Deflection Temperature (HDT)

Maximum temperature a polymer can withstand before deforming is referred as heat deflection temperature (HDT). In other words, it can be referred as a maximum service temperature of a polymeric material and it is an important parameter to be considered in composite material selection for any particular application. It can be noticed from Fig. 5 that HDT of composites increased considerably with incorporation of switchgrass and soy stalk, and compatibilization helped in further improvement.

The modulus enhancement due to the addition of stiff lignocellulosic fibers played a substantial role in increasing the HDT of the composite and the values obtained here corresponds well with the flexural modulus data. Switchgrass based composites compatibilized with pMDI exhibited the highest...
HDT of about 123 °C while that of soy stalk composites was 118 °C.

3.5 Melt Flow Index (MFI)
MFI denotes the “output rate/flow of a 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 (ASTM D1238-10).” [3]. MFI generally gives an indication of ease of processing of a material and based on the range of MFI value of a material, suitable processing method can be adopted. For industrial scale injection molding, the MFI is mostly expected to be higher than 4 gm/ 10 min.

MFI values obtained for the PHBV/PBAT matrix and composites with different fiber types are presented in Fig. 6. With the incorporation of 30 wt% fiber, flow of the polymer matrix is hindered therefore viscosity of the composite material is subjected to increase which is reflected as the reduction in MFI [11]. There was a difference in MFI values observed for composites with switchgrass and soy stalk. This strongly indicates that fiber surface characteristics and type of fiber play a critical role in regulating the restriction offered to the polymer chain mobility [12].

In addition to the above mentioned effects, compatibilization reactions leading to secondary bonds and urethane linkage formations are known to affect the molecular weight thereby reducing the MFI to a further low value. In such situations, processability of these compatibilized composites can be improved by the addition of flow additives.

3.5 Morphology of Fractured Surface
Morphology of composites (uncompatibilized and compatibilized) that were impact fractured were observed under SEM and the micrographs are shown in Fig. 7 and 8.

In case of uncompatibilized composites containing switchgrass and soy stalk, voids and fiber pullouts were visible, at some places fiber clustering were also noticed (not shown in the figure). These observations indicated poor adherence of the fiber to PHBV/PBAT blend. In the compatibilized composites, the fibers were noticed to be well embedded in the matrix and fiber fracture, a less energy dissipating fracture mechanism was most prevalent. In addition, the increased interfacial adhesion with the addition of pMDI had offered to hinder the crack propagation. These observations further support the results obtained for mechanical properties of these composites.

Conclusion
Results obtained from this study indicate that the compatibilized composite materials could be a promising option for variety of applications. Renewably sourced fibers, their high modulus, low density could favor the production of light weight and less expensive composite materials with acceptable performance. Tensile and impact strength achieved for these composites are comparable to that of polypropylene based natural fiber composites. Heat deflection temperature of around 120 °C in compatibilized composites makes it ideal for applications that require service temperature of about 30- 120 °C. The slight difference noticed among the performance of the switchgrass and soy stalk based composites could possibly be due to their differences in density values and individual chemical composition. Investigation on composites containing same volume fraction of these fibers might provide further insight on possibilities of hybridization of these fibers for composite applications.

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References


BIOMASS BASED GREEN COMPOSITES: FABRICATION AND PERFORMANCE EVALUATION

Fig. 1. Tensile strength and modulus of neat polymer, uncompatibilized and compatibilized composites

Fig. 2. Flexural strength and modulus of neat polymer, uncompatibilized and compatibilized composites

Fig. 3. Stress-strain graph of uncompatibilized and compatibilized composites

Fig. 4. Impact strength of uncompatibilized and compatibilized composites
Fig. 5. HDT of matrix, uncompatibilized and compatibilized composites

A- PHB/V/PBAT
B- PHB/V/PBAT + 30 wt% Switchgrass
C- PHB/V/PBAT + 30 wt% Switchgrass + 0.75 Phr pMDI
D- PHB/V/PBAT + 30 wt% Soy stalk
E- PHB/V/PBAT + 30 wt% Soy stalk + 0.75 Phr pMDI

Fig. 6. MFI of matrix, uncompatibilized and compatibilized composites

A- PHB/V/PBAT
B- PHB/V/PBAT + 30 wt% Switchgrass
C- PHB/V/PBAT + 30 wt% Switchgrass + 0.75 Phr pMDI
D- PHB/V/PBAT + 30 wt% Soy stalk
E- PHB/V/PBAT + 30 wt% Soy stalk + 0.75 Phr pMDI

Fig. 7. SEM images of (a) uncompatibilized and (b) compatibilized switchgrass composites
Fig. 8. SEM images of (a) uncompatibilized and (b) compatibilized soy stalk composites