

Effect of Compatibilizer and Fillers on the Properties of Injection Molded Lignin-Based Hybrid Green Composites

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ABSTRACT: Composites were prepared from poly(butylene succinate) (PBS), lignin, and switchgrass using extrusion followed by injection molding techniques. The effects of the fillers (lignin and switchgrass) and polymeric methylene diphenyl diisocyanate (PMDI) compatibilizer on the physicomechanical and thermal properties of the composites were investigated. Use of hybrid filler (1 : 1 lignin : switchgrass) resulted in slight improvement in the flexural strength of the composites. Incorporation of 1% PMDI into the hybrid filler reinforced composites significantly enhanced properties compared with the neat PBS which accounts for improvements in the flexural strength, flexural modulus, and heat deflection temperature (HDT) by nearly 165%, 375%, and by 24°C respectively. Lignin exhibited some effects on the thermal properties of composites. However, switchgrass demonstrated a minor effect on the thermal behavior of the composites compared with the lignin. An improved interface was observed from the scanning electron microscopy (SEM) of the compatibilized hybrid composites. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

In recent years, green composite materials based on lignin and natural fibers as reinforcements, or as blending partners, have received a significant scientific attention. Many researchers have focused their attention to find out novel combinations of biodegradable polymer and comparatively inexpensive natural fillers in order to promote new classes of eco-friendly products. Investigations have targeted to use plant biomass including agricultural residues and industrial co-products not only to develop low cost composite materials, but also to add value to those downstream products. Also, utilization of these biomass residues and co-products in high value applications resolves most of the waste disposal issues owing to its large-scale generation.

Lignin is a biomass constituent and one of the most abundant natural biopolymers next to cellulose. Most of the industrial lignins are obtained as co-products during paper pulping processes. Currently, lignin is also generated as a co-product from the lignocellulosic bioethanol industries. Despite its widespread potential availability, industrial applications of lignin are not well explored until now. A major fraction of generated lignin is used as an energy source¹, i.e., burned in an energy recovery

step of the pulping process. A large amount of lignin production is expected from the emerging cellulosic bioethanol and paper industries in near future which demands for an extensive scientific approach towards the novel use of this biomass co-product.

A number of studies on lignin that focused on finding new uses for it, other than fuel, have been reported in the literature. Recently, an extensive review on the utilization of lignin in polymeric materials is reported by Kumar et al.² It states that lignin is an amorphous polyphenolic material that contains a large number of chemical functionalities in its molecular structure.² These chemical functionalities make lignin a suitable component for the polymeric applications. Important functional groups, chemical units and inter unit linkages present in lignin are phenolic —OH, aliphatic —OH, biphenyl, carbonyl, diaryl ether, alkyl aryl ether, phenyl propane, syringyl, guaiacyl, etc.² The details of the chemical functionalities and inter unit linkages are reported in the literature.² The presence of the phenolic groups imparts antioxidant properties to lignin which provides stability to the polymers against thermo- and photooxidations.^{1,3} Lignin is a low cost, light weight, and low abrasive¹

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material and has the potential to be used as a flame retardant additive.^{1,3} Despite all these attractive properties, lignin has been used very rarely for industrial applications.

Lignin has already been used in asphalts, adhesives, polyurethanes, polymer blends, and composites^{2,4-7} although its applications in these fields are very limited. Lignin is not very compatible with the nonpolar polyolefins and its incorporation into polyolefin reduces the tensile strength and the elongation of the blends.² However, the addition of coupling agents improves the properties of the blends.² Lignin also acts as a β -nucleation agent, fire retardant, and toughening agent for the neat polypropylene (PP), and as a compatibilizer in the jute-PP composites.⁵ A very limited study on the lignin-based biodegradable polymer composites has been reported in the literature until now. Few reports on the lignin-based starch, polyhydroxyalkanoates, polylactide, and all biodegradable biopolymer composites can be found in the literature. Lignin acts as a plasticizing agent for the starch polymer,⁶ as a nucleating agent for the polyhydroxybutyrate polymer,⁷ and as an adhesion promoter between the natural fiber and the polymer.⁸ Lignin reduces the tensile strength and the elongation when added to the polylactides (PLA).⁹

Poly(butylene succinate) (PBS) is a tough polymer compared with the known biopolymers like PLA and polyhydroxyalkanoates (PHAs). PBS can be made from both fossil and renewable resources and considered as a new biopolymer. PBS has already been used as the matrix polymer in the natural fiber reinforced composites.¹⁰⁻¹⁴ A higher percentage (50 wt %) of natural fiber incorporation into PBS matrix resulted in great improvements in some of the material properties.¹⁰ Again, surface treatments of natural fibers further improve the properties of composites.^{12,13} These reports enforced researchers to choose PBS as a potential matrix polymer for the lignin reinforcement.

The natural fibers and the plant biomass, such as hemp, jute, kenaf, flax, wheat straw, soy stalk, various grass fibers, etc. have been used as reinforcing fillers in the polymer composites. Switchgrass is a perennial grass biomass that shows a strong promise for the composite applications because of its low cost, low maturation time, high yield, low input requirement, underground carbon sequestration, and soil remediation potential.¹⁵ Switchgrass has been used as filler in the polyolefin composites.^{16,17} Like other hydrophilic biofibers, switchgrass also requires the use of compatibilizers in order to improve the mechanical properties of the polyolefin composites. The compatibilizers/coupling agents such as maleic anhydride grafted polymers, silanes, titanates, and isocyanates are often used to improve the properties of composites. Recently, polymeric methylene diphenyl diisocyanate (PMDI) and methylene diphenyl diisocyanate (MDI), two isocyanate compatibilizers, have been used in the lignin filled PBS composites to improve some of the properties of the investigated composites.^{18,4} PMDI also improves the mechanical performance of the natural fiber composites.¹⁹ Another innovative technique in order to improve the material properties is the use of hybrid fillers (mixture of two or more fillers) in the composites.²⁰ In the current investigation, lignin and switchgrass have been used as hybrid fillers in the

PBS matrix. The effect of PMDI on the mechanical, thermal, and thermomechanical properties of the hybrid filler based composites have been investigated. The objectives of the study were to compare the reinforcing effects of the fillers and to study the compatibilization effect of PMDI on the properties of the lignin and grass based hybrid composites.

The lignin used in the study was a compounded product which is commercially available with a trade name "Arboform[®] F 45." It is a melt processable thermoplastic material having modified alkali lignin, natural additives, and 45% ground plant fibers, such as hemp, flax, and wood particles in it.^{21,22} The objective of our research project was to investigate the effect of various types of commercially available lignin on the processing and properties of lignin-based composite materials. We have used compounded lignin (Arboform[®] F 45) as well as sulfur free raw lignin powder without any additives in our investigations. In this article (as well as in our published literature i.e. Ref. 18) we have reported the properties of compounded lignin (Arboform[®] F 45) based composite materials. The properties of sulfur free raw lignin powder based composite materials will be reported shortly.

Lignin is a brittle amorphous material and its incorporation into the polymer system drastically reduces the impact performance of the material. Although, Arboform[®] F 45 is a compounded thermoplastic material, its processing alone (without blending it with polymer) was not achievable in the current study. Arboform[®] F 45 acted as a better blending partner with thermoplastic polymer. Compared with raw lignin, Arboform[®] F 45 offered processing suitability and better properties when added to PBS. Hence, properties of compounded lignin (Arboform[®] F 45) based composites have been reported in this article.

EXPERIMENTAL

Materials

Bionolle[®] 1020 (PBS), a product of Showa Highpolymers, Japan, was procured from Toyo Plastics Co. Osaka, Japan. Polymeric methylene diphenyl diisocyanate (PMDI) "Rubinate[®] M" was a product of Huntsman polyurethanes, NJ. Compounded lignin (Arboform[®] F 45) pellets were received from Tecnar GMBH, Germany. Chopped switchgrass fibers were used as reinforcing filler and were collected from Nott Farms, Ontario, Canada. The scanning electron microscopy (SEM) pictures of Arboform[®] F 45 and switchgrass are presented in Figure 1(i, ii). Figure 1(i) depicts the presence of lignin particles (~5–10 μm) as well as ground fibers (~20–150 μm) in Arboform[®] F 45. It can be observed from Figure 1(i) that fibers are associated with different aspect ratios with smooth or rough surfaces, which indicates the presence of various types of fibers (i.e. hemp, flax, wood, etc.) in the lignin compound (Arboform[®] F 45). Figure 1(ii) shows the size of switchgrass used in the study. It can be observed that a major fraction of the switchgrass fibers were approximately 0.2–2mm in length. However, a very small fraction of fibers of micrometer scale are also observed in the SEM picture of switchgrass [Figure 1(ii)]. Unlike jute, kenaf, hemp like bast fibers, grass fibers consist of nonuniform fiber morphology as it contains both leaf and stem fibers. Again the stem

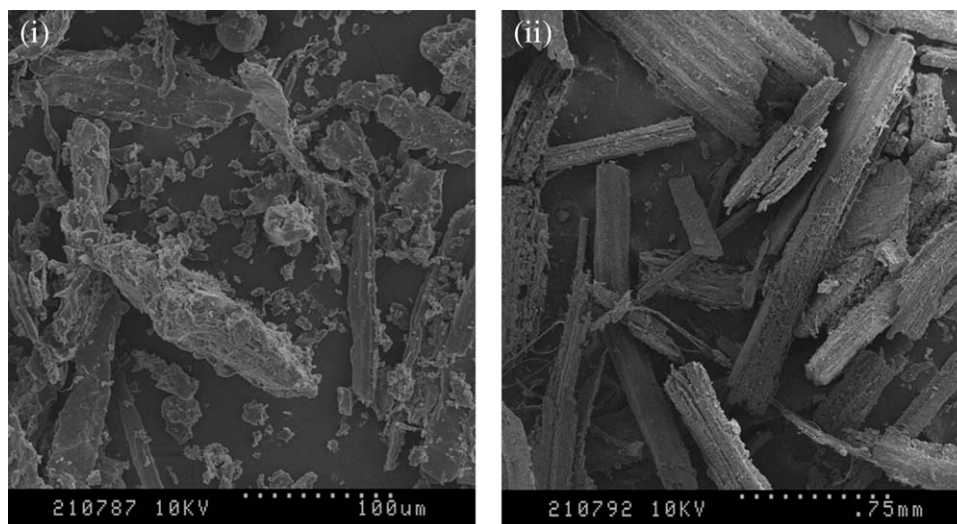


Figure 1. (i) Morphology of lignin (Arboform® F 45). (ii) Morphology of switchgrass.

of the grass consists of many layers i.e. a smooth skin layer, a woody inner layer and a spongy core layer. Arboform® F 45 has been described as lignin in this article.

Composites Fabrication

PBS, lignin, and switchgrass were dried for 3 to 4 h at 80°C before the composite fabrication. Specimens from PBS and 50 wt% filler based composites were prepared using a microextruder followed by a microinjection molder (DSM Explore, the Netherlands). Processing parameters were 160°C barrel temperature, 150 rpm screw rotation, 6 min compounding time, and 30°C mould temperature. Composites were also prepared by adding 1 wt % PMDI to 50% hybrid filler (1 : 1, lignin:switchgrass)-PBS composites. PBS, filler, and PMDI were added together in the microextruder. The following acronyms are used for the composites in this manuscript i.e. lignin composite, switchgrass composite, hybrid composite, and compatibilized hybrid composites. The polymer, filler, and compatibilizer composition of the specimens are presented in Table I.

Characterization

The effect of fillers i.e. lignin, switchgrass and hybrid filler (1 : 1 lignin : switchgrass) on the PBS matrix was studied and the properties of the resulting composites were compared with the neat PBS polymer (control). The composites with hybrid filler were selected for the PMDI (1%) incorporation (Table I). The properties of the compatibilized composites were compared with the properties of the hybrid composites as well as the neat PBS. All results presented were the average values of five replica-

tions for the tensile and flexural properties, six replications for the impact strength, and three replications for the physical and thermal properties. The following characterizations were carried out during the investigation.

Mechanical Testing. The tensile and flexural properties of the composites were measured by a Universal testing machine Instron 3382 according to ASTM standards D 638 and D 790, respectively. The notched Izod impact strength was measured with TMI Monitor impact tester (model no. 43-02-01) according to ASTM D 256 with a 5 ft lb pendulum. Type IV specimens with length of 115 mm, width of 6.02 ± 0.05 mm and thickness of 3.22 ± 0.05 mm were used for the tensile tests. The tensile test was carried out at a span length of 50 mm and a crosshead speed of 50 mm/min for PBS and 5 mm/min for composites at room temperature. Flexural tests were carried out at a gauge length of 52 mm with a crosshead speed of 14 mm/min using rectangular specimens with 127 mm length, 12.7 ± 0.1 mm width and 3.23 ± 0.05 mm thickness. Rectangular specimens with 63.5 mm length, 12.7 ± 0.1 mm width and 3.23 ± 0.05 mm thickness were used for the impact tests.

Fourier Transform Infrared Spectroscopy. The Fourier Transform Infrared Spectroscopy (FTIR) spectrographs were taken in a Thermo Scientific Nicolet™ 6700 FTIR spectrometer in an attenuated total reflection infrared (ATR-IR) mode with a resolution of 4 cm^{-1} and a number of 32 scans per sample. About 30 to 50 mg of each material was used for each test. The

Table I. Composition of Composites

Types of specimen	PBS (%)	Filler (%)	PMDI (%)	Filler type
Neat PBS	100	0	0	-
Lignin composite	50	50	0	Lignin
Switchgrass composite	50	50	0	Switchgrass
Hybrid composite	50	50	0	Lignin:switchgrass (1 : 1)
Compatibilized hybrid composites	49.5	49.5	1	Lignin:switchgrass (1 : 1)

composites and the PBS specimens were cut into slices (30–50 mg) to make samples for the FTIR test.

Dynamic Mechanical Analysis. The viscoelastic properties of the composites were measured in a Dynamic mechanical analyzer (DMA Q 800, TA Instrument Inc.) with a three-point bending clamp (50 mm span length). The test was carried out by heating the samples from -50 to 70°C at a heating rate of $3^{\circ}\text{C}/\text{min}$, oscillating amplitude of $20\ \mu\text{m}$ and $1\ \text{Hz}$ frequency. The heat deflection temperature (HDT) was investigated by heating the specimens from room temperature to 110°C with a ramp rate of $2^{\circ}\text{C}/\text{min}$ and at a load of $0.455\ \text{MPa}$ (ASTM D 648) using the same clamp with $50\ \text{mm}$ span length. Dimension of specimens for the dynamic mechanical analysis (DMA) and HDT tests was the same as used for the impact tests.

Differential Scanning Calorimeter. The differential scanning calorimeter (DSC) studies of the polymer and the composites were carried out using a DSC Q 200 differential scanning calorimeter (TA Instruments Inc.). The tests were carried out by heating the specimens (6–10 mg) from -50 to 200°C at a heating and cooling rate of 10°C per minute under a heat-cool-heat mode. The records of the second heating cycle were considered for the analysis. Nitrogen purge gas was used for the study. The data was analyzed using TA instrument's Universal analysis software.

Thermo Gravimetric Analysis. The thermal stability of the specimens was studied by using a Thermo gravimetric analyzer (TGA Q500, TA Instrument Inc.) by heating the specimens (4–7 mg) from room temperature to 600°C at a heating rate of $20^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere.

Density Measurement. The density of the composites was measured by an Electronic densimeter MD-300S (Alfa Mirage) that operates according to the Archimedes principle. Specimen dimension for the density measurements was the same as used for the impact tests.

Scanning Electron Microscopy. The morphology of the tensile fractured surfaces of the composites was observed through Hitachi S-570 scanning electron microscope (Hitachi High Technologies, Tokyo, Japan) at an accelerating voltage of $10\ \text{kV}$. The samples were gold sputtered to $21\ \text{nm}$ thickness (at $7\ \text{nm}$ per minute) using an Emitech K-550 sputter coater (Ashford, Kent, UK).

RESULTS AND DISCUSSION

Based upon our previous investigation,¹⁸ the composites with 50 wt % filler content and incorporation of 1 wt % PMDI were selected in order to study the effect of compatibilizer and fillers (lignin and switchgrass individually and together in hybrid form) on the performance of the composites. A detailed characterization of lignin (Arboform[®] F 45) for elemental composition, functional groups, and thermal properties has been reported in our previous study.¹⁸ Switchgrass has been used in this study as biomass filler and used as received without further modification and investigation. Switchgrass contains about 37% cellulose, 29% hemicellulose, and 19% lignin on a dry matter basis.²³ However, the thermal degradation behavior of switch-

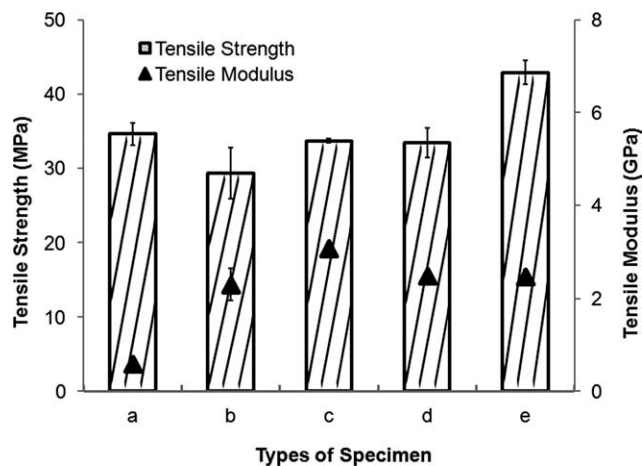


Figure 2. Tensile properties of composites. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

grass has been discussed in the Thermogravimetric analysis section.

Mechanical Properties

The tensile properties of the composites are shown in Figure 2. It is observed that the tensile strength of the composites was decreased with the filler incorporation. While the decrease in the tensile strength of the composites with lignin incorporation was significant, the decrease in the tensile strength with switchgrass and hybrid filler (1 : 1 ratio of lignin and switchgrass) incorporation was very insignificant i.e. the values were nearly same as the values obtained for the base polymer. Although the exact cause of the decrease in the tensile strength of lignin composites cannot be predicted under the scope of the current investigation, we may make a conjecture that the presence of natural additives, modified alkali lignin (possibly plasticized lignin), inadequate crosslinking due to insufficient amount of lignin in that filler content (50%) and presence of very small size of fiber (ground fiber) could be the cause for the decrease in the tensile strength of lignin composites. It is known that fibers smaller than critical fiber length do not offer reinforcement to the polymer and plasticization affects the mechanical performance of a material. Length or aspect ratio of filler plays a significant role against the stretching force. It is worth to note that, fiber length in switchgrass composites was significantly longer compared with the fiber length in lignin composite even after injection molding. It is also reported that the tensile strength of composites also decreases with agro-filler incorporation due to the weaker interfacial adhesion.^{24,25} Although lignin is a natural filler, considering the nature of this thermoplastic lignin (Arboform[®] F 45), its composition and fractured surface morphology, we cannot consider that lignin composites obtained a weaker interface than switchgrass composites. It is also evident from our previous study,¹⁸ where tensile strength of composites increased with increasing lignin (Arboform[®] F 45) content from 30% to 65%. Although the tensile strength of the composites at 30% and 50% lignin (Arboform[®] F 45) content were lower than that of the base polymer, a higher tensile strength compared to

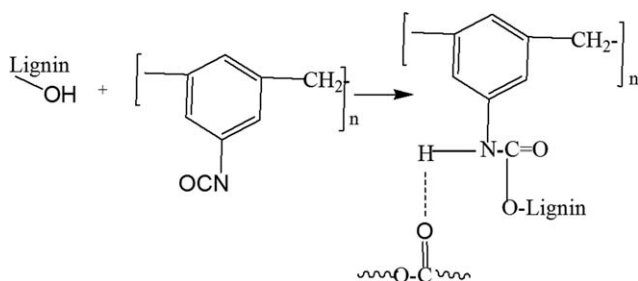


Figure 3. Scheme of reactions.

the base polymer was achieved at 65% lignin incorporation.¹⁸ This improvement was attributed to the crosslinking ability of lignin, matching of solubility parameters, and adhesive nature of lignin.¹⁸ Further, there exists a polar-polar interaction possibly due to hydrogen bonding between ester group of polymer and hydroxyl groups of lignin.^{26,9} Hence, it can be concluded that lower tensile strength obtained by 50% lignin (Arboform[®] F 45) filled composites was not due to the existence of weaker interface. Rather, it could be due to the nature and constituents of compounded lignin (Arboform[®] F 45), and inadequate lignin content which fails to offer its full potential as a crosslinking agent in order to overcome the limitations imparted by modified lignin and presence of ground fiber in it. Incorporation of 1% compatibilizer (PMDI) to hybrid composites improved the tensile strength by 24% compared with the neat polymer and 28% compared with the uncompatibilized hybrid composites. It is reported that PMDI improves the tensile strength and strain at break of composites possibly due to the mechanical interlocking between the polymer and filler.^{18,19} The compatibilization reaction between the filler and PMDI can be attributed to the formation of urethane linkages formed by the reaction of the -NCO group of PMDI and the -OH group of the biofiller as represented in the reaction scheme (Figure 3).

Incorporation of fillers into the matrix improved the modulus by 283% to 418% compared with the polymer. The highest modulus value was obtained with the switchgrass addition and the lowest was observed with lignin incorporation. The tensile modulus of composites remained almost unchanged due to the PMDI (compatibilizer) incorporation. A drastic reduction in the strain at break due to filler incorporation can be observed from the stress-strain curve of the composites (Figure 4). A very high strain percentage for the neat PBS can be seen from Figure 4(i). In order to get a clear picture of the stress-strain curve and fracture behavior of the composite materials, a magnified view of the graph up to 3% strain percentage has been shown in Figure 4(ii). In biocomposites, the percentage elongation reduces significantly with the biofiller incorporation.¹⁰ The addition of PMDI to the hybrid filler based blend slightly improved the strain at break. Although urethane linkages are formed between the PMDI and -OH group of the biofiller that offer compatibilization between polymer and filler (Figure 3), the moisture present in the biofiller also produces urea as a secondary product that plasticizes the composites and results in a slight lowering of modulus and increase in the elongation.¹⁹ In our case the lowering of the modulus was negligible

(i.e. a factor of 0.02 GPa) as we have used only 1% PMDI and dried biomass filler.

It is observed from Figure 5 that the flexural strength and the modulus of the composites increased with the filler incorporation. The hybrid composites achieved a modulus value in between the values of two individual filler reinforced composites. The addition of compatibilizer increased the flexural strength significantly which was about 46% higher than the uncompatibilized hybrid composites and 165% higher than the neat polymer. Greater stress transfer from the matrix to filler through a compatibilizer modified strong interface could be attributed to this significant improvement. The flexural modulus of the composites remained almost unchanged by the addition of PMDI.

Incorporation of fillers into the polymer resulted in significant reduction in the impact strength of the material (Figure 6). Similar effects were also noticed for the agrofiber reinforced composites.^{24,25} It is also reported that lignin is a brittle polymer and its incorporation reduces the impact strength of polymers.²⁷ The composites with switchgrass achieved a 68% higher impact strength compared with lignin composites. However, impact strength of the hybrid composites was a little lower than the switchgrass filled composites. Incorporation of PMDI resulted in an improvement in the impact strength accounting nearly 23% higher impact strength than the hybrid composites without any compatibilizer. This improvement may be attributed to the possible plasticization mechanism¹⁹ as well as the secondary bonding (chemical interlinking between N-H group of urethane linkage and carbonyl group of matrix)²⁸ that might have occurred in the compatibilized composites.

FTIR Analysis

Figure 7(i, ii) shows the FTIR spectra of the neat PBS and all the composites. Characteristic carbonyl (C=O) stretching at 1715 cm^{-1} , C-H stretching at $2850\text{ to }2950\text{ cm}^{-1}$, C-O stretching at $1145\text{ to }1155\text{ cm}^{-1}$ and 1044 cm^{-1} appear in the spectra of PBS and all the composites. Broad peaks for hydrogen bonded OH groups at $3400\text{ to }3100\text{ cm}^{-1}$ appear in

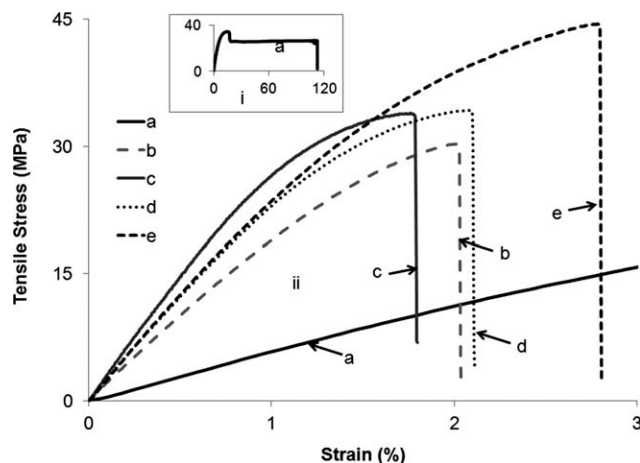


Figure 4. Stress-strain curve of the composites. (i) Full strain (%) of PBS, (ii) 3% strain. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

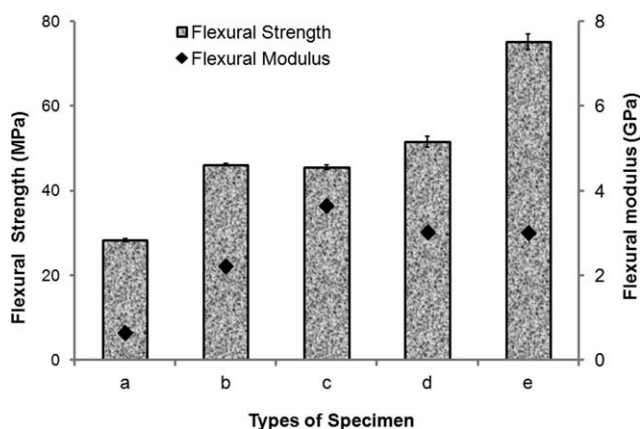


Figure 5. Flexural properties of composites. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

the spectra of all the composites, where a small shoulder appears in this region in the spectra of PBS, which might be due to the presence of terminal —OH groups in the polymer. Characteristic peaks due to aromatic $\text{C}=\text{C}$ stretching appear near 1601 cm^{-1} and 1512 cm^{-1} in the spectra of the composites having lignin. Lignin contains an ether group which appears in the range of 1300 to 1000 cm^{-1} overlapping with the ester and alcohol C—O— stretching region. Comparatively broader spectra in the composites can be believed as the overlapping of ester, ether and alcohol C—O stretching from lignin as well as grass fiber. No characteristic peak for NCO (isocyanate group of PMDI) appears at 2270 cm^{-1} in the spectra of compatibilized composites which indicates a complete reaction of isocyanate in the composite system. As per the reaction (Figure 3), N—H bond formation is expected during the reaction. As N—H stretching appears at 3350 to 3180 cm^{-1} (overlapping with hydrogen bonded —OH stretching), C—N stretching appears in 1350 to 1000 cm^{-1} overlapping with many C—O and O—H

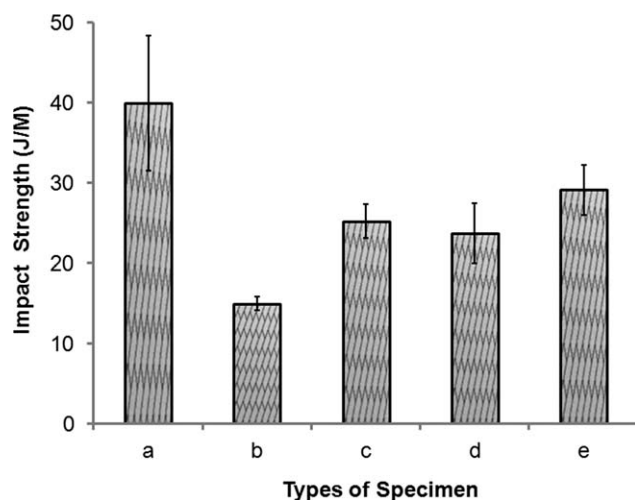


Figure 6. Impact strength of composites. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

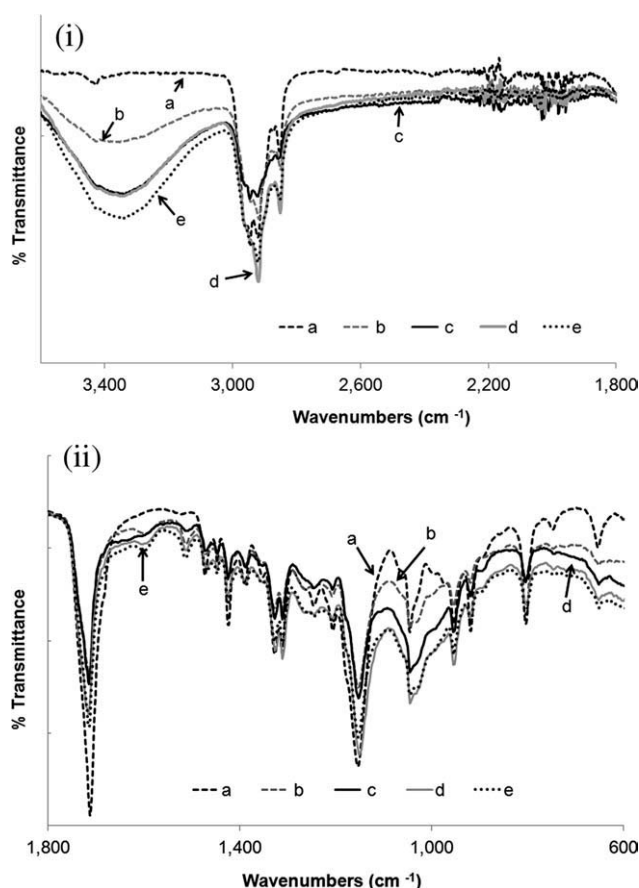


Figure 7. FTIR of composites. (i) Spectra in the region of 3600 to 1800 cm^{-1} . (ii) Spectra in the region of 1800 to 600 cm^{-1} . a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

peaks, and N—H bending overlaps with aromatic $\text{C}=\text{C}$ in 1640 to 1560 cm^{-1} , disappearance of peak at 2270 cm^{-1} and increased intensity of the peak at 3350 to 3180 cm^{-1} can be considered as a confirmation of urethane formation in the compatibilized composites.

Dynamic Mechanical Analysis of Composites

Dynamic mechanical analysis is widely used for the study of viscoelastic behavior of composite materials. The storage modulus gives information about the stiffness and the peak of damping measurement ($\tan \delta$) gives information about the glass transition temperature (T_g). The storage modulus accounts for the elastic component of the complex modulus of material. The storage modulus and $\tan \delta$ of PBS and its reinforced composites are shown in Figure 8. It is observed that the storage modulus of the polymer and composites decreased with increasing temperature [Figure 8(i)] which may attribute to the increase in the chain mobility of the polymer matrix at high temperature. The storage modulus of the materials increased with the filler incorporation. Similar results were observed in the agro flour filled composites.²⁹ The storage moduli of specimens at room temperature were considered to study the effect of filler and compatibilizer. The switchgrass filled composites resulted in higher modulus value and lignin-filled composites showed the lower

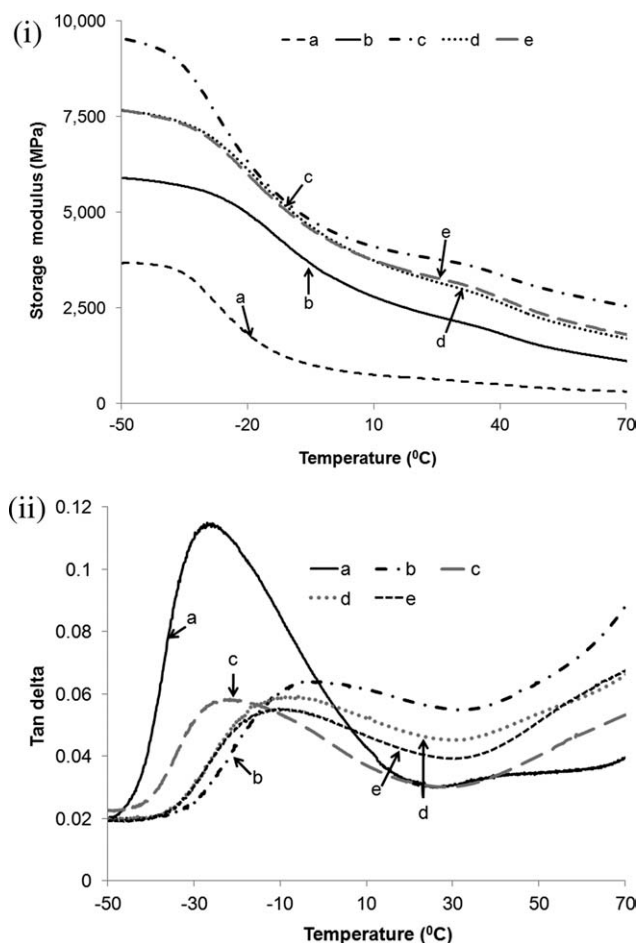


Figure 8. Dynamic mechanical analysis of composites. (i) Storage modulus of composites. (ii) Tan δ of composites. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

modulus value among all the composites, which may attribute to the composition and nature of fillers. The storage modulus of the hybrid composites was intermediate between the two individual filler based composites. As expected, no significant change in the storage modulus value of composites was observed due to PMDI addition. This observation may be attributed to various competitive reactions caused by the addition of PMDI. However, compared with the neat polymer, the increment in the storage modulus of compatibilized hybrid composites was nearly 400%.

An increase in the $\tan \delta$ peak temperature (referred as glass transition temperature, T_g) and broadening of the $\tan \delta$ thermograms in the lignin-filled composites can be observed in Figure 8(ii). The increased T_g of the composites may be attributed to two possible effects that might have taken place in the lignin-based composite structures. The first effect may be the creation of an amorphous component in the composite structure where both the polymer and the filler coexist in a closely associated state reducing free volume in the composites and hence increasing T_g . The second may be the formation of sec-

ondary bonds that act as quasi-crosslinks and restricted the Brownian motion of long chain molecules.³⁰ Increase in the T_g of composites indicates an interaction between polymer and filler. Although a decrease in the tensile strength of composites, particularly lignin composites, was noticed that may depict a weaker interaction, the crosslinking ability of lignin owing to its amount, its constituents and reaction condition believed to have played a major role in the thermomechanical behavior of lignin-based composites. Also, lignin is also used as a coupling agent in the composites for improving interfacial adhesion.^{8,31} The coupling action of lignin further validates its crosslinking ability and intermolecular interactions. A very insignificant improvement or almost no improvement was observed for the T_g of the switchgrass filled composites which suggests a weaker interaction between the grass fiber and matrix. A similar result was also observed in the flax fiber filled PLA composites.³² The hybrid composites showed a T_g which is intermediate between two individual filler-based composites. No significant effect on the T_g of composites was observed with PMDI addition. This may be attributed to the effects such as improved interaction and plasticization due to PMDI addition. Improved interaction between polymer and filler improves the T_g and plasticization lowers the T_g of a material. Hence, no change in the T_g value with PMDI incorporation is an expected observation as PMDI promotes polymer-filler interaction and plasticization of the polymer.

The damping behavior of the material is measured by the magnitude of $\tan \delta$ since it is a ratio of the energy dissipated to the energy stored during a dynamic loading cycle.¹⁰ The $\tan \delta$ peak value of PBS and all the composites located at the subambient temperature region (α -peak) corresponds to the relaxation effect at the glass transition temperature range and increased $\tan \delta$ values after 50°C could be associated with the slippage of the crystallites [Figure 8(ii)]. The $\tan \delta$ value decreased with the filler incorporation irrespective of the filler type. A similar observation due to the incorporation of biofiber into biodegradable polymer was also reported by many researchers.^{10,11,32,33} A slight reduction in the $\tan \delta$ value owing to the PMDI incorporation can be noticed from the thermogram. It can be attributed to the decrease in the molecular mobility in the composite structure as well as the reduction of mechanical loss that occurs to overcome the interfriction between molecular chains of the composite materials.

Heat deflection temperature (HDT) is a measure of the dimensional stability of the material. The HDT values of neat PBS and all the composites are shown in Table II. Filler incorporation resulted in the increase in the HDT of the materials by 9 to 28°C. The highest HDT value was obtained for switchgrass reinforcement and the lowest value obtained with lignin reinforcement. As usual, an intermediate HDT value between the values for the two individual filler composites was obtained for the hybrid composites. The addition of compatibilizer further enhanced the HDT of the material. This effect might be due to the improved interfacial chemistry in the compatibilized composites. The improvements in the HDT values owing to biofiber reinforcement as well as due to the improved interface were reported in the literature.³⁴

Table II. HDT and Density Analysis of Composites and Neat PBS Specimens

Types of specimen	HDT (°C)	ρ (g/cm ³)
Neat PBS	78 ± 1.4	1.26 ± 0.00
Lignin composite	87 ± 2.7	1.30 ± 0.00
Switchgrass composite	106 ± 0.2	1.35 ± 0.00
Hybrid composite	98 ± 0.6	1.31 ± 0.01
Compatibilized hybrid composites	102 ± 1.2	1.31 ± 0.00

Differential Scanning Calorimetry

DSC is usually used to measure the melting temperature (T_m), crystallization temperature (T_c), and the glass transition temperature (T_g) of the neat polymer and composites. It is extensively used to investigate the miscibility of components in the polymer blends or composites. The results of the nonisothermal DSC experiments of the neat PBS and all the composites are shown in Figure 9(i–iii). A single composition-dependent T_g between the pure components is usually taken as evidence for miscibility of components. At the same time, changes in T_m and the nature of melt endotherm provides collateral evidence on the miscibility of components.⁹ As lignin material used in the study is not only complex in composition and chemical functionalities, but also itself does not show any melting temperature, it is not quite appropriate to explain the miscibility of components. However, the changes in the T_m and T_g of the polymer domain of the composites can be considered as a confirmation for the existence of an intermolecular interaction between the components. It is quite difficult to locate T_g from the melt thermogram [Figure 9(i)]. Hence, a magnified view of the scan is shown in Figure 9(ii). Although a single point T_g from the thermogram is usually obtained by the software, glass transition temperature is a range of temperature where material undergoes a gradual transition. A sharp change in the thermogram of the polymer starting from -34°C can be observed from Figure 9(ii) which can be considered as the T_g of the polymer. The T_g of polymer (PBS) shifted towards a higher temperature (10–14°C higher) with the addition of lignin which indicates the existence of intermolecular interaction between the polymer and filler. A transition in the temperature range of 43 to 53°C can also be observed in the same thermogram (lignin composites) which is believed as the T_g of the lignin component owing to the presence of additives or due to any secondary transition related to lignin. It has to be noted that, amorphous lignin obtains a T_g around 100°C. As it is mentioned earlier that it is a thermoplastic lignin, the T_g at 43 to 53°C due to possible plasticization or presence of additives is not surprising. Melt endotherm of this composite [Figure 9(i)] shows a slightly lower T_m compared with the T_m of the polymer that provides further evidence on its miscibility or intermolecular interactions. The effect of switchgrass on the T_g of the polymer was not very significant although a slight lowering effect was observed. The hybrid composite obtained a T_g for the polymer domain in between the T_g values of the individual filler based composites and a T_g for the lignin domain at 43 to 53°C. Unlike hybrid composites, no sharp transition at 43 to 53°C was noticed for the compatibilized composites that indicates a reaction between lignin and

PMDI compatibilizer in that composite. From Figure 9(ii) it appears that PMDI does not have significant effect on the T_g of PBS domain, rather it has certain interaction with lignin component. Figure 9(i) depicts that filler incorporation does not have significant effect on the melt temperature T_m . However, composites having lignin in the composition showed slightly lower T_m than others. A chemical change due to PMDI incorporation can be observed by comparing the nature of endotherms for the hybrid (broad) and compatibilized hybrid (narrow) composites.

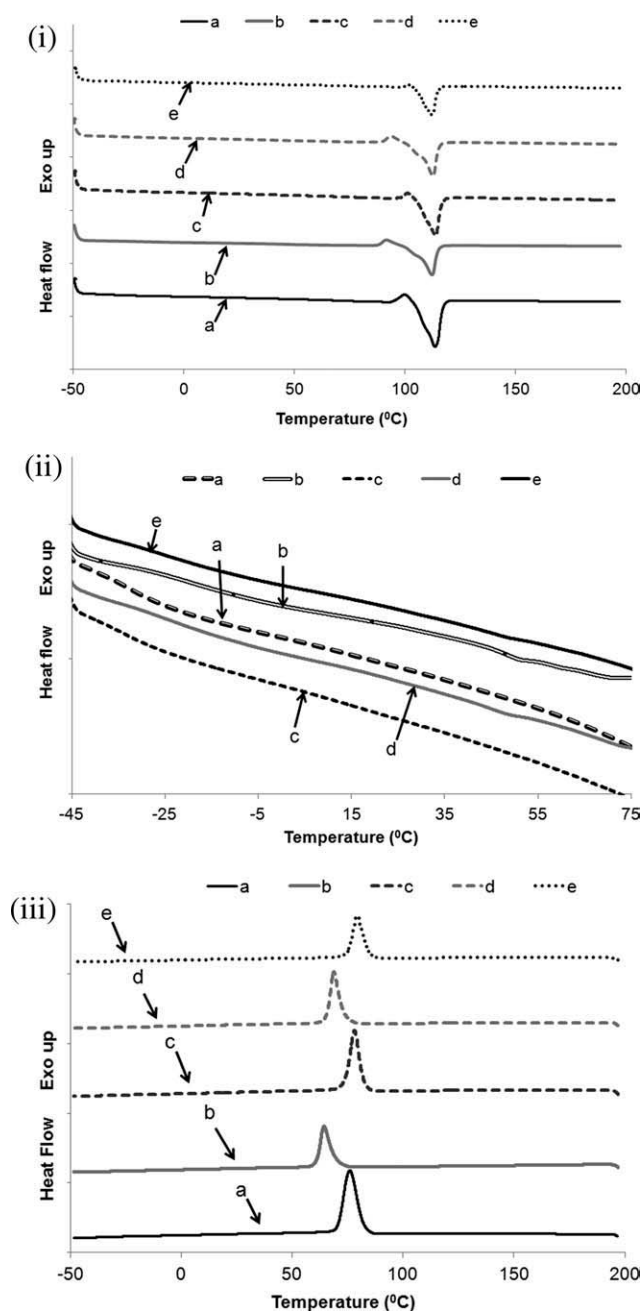


Figure 9. DSC analysis of composites. (i) Melt endotherm. (ii) T_g of samples. (iii) Crystallization exotherm of samples. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

Typical nonisothermal crystallization thermograms of the investigated materials are presented in Figure 9(iii). It can be observed from the figure that the crystallization peak temperature (T_c) shifted to lower temperature with the lignin and hybrid filler addition. However, T_c remained almost unaffected with the addition of switchgrass to PBS. The T_c of composites was further increased by the addition of PMDI to the hybrid blend and achieved a value almost equal to the T_c of the polymer. Although, the effect of PMDI on the thermal properties of natural filler based composites is not very clear,¹⁹ the resultant effect of improved interfacial adhesion and possible plasticization effect may be attributed as the cause of the observed effects.

Thermogravimetric Analysis

The thermal degradation properties of lignin, switchgrass, neat polymer and all composites are shown in Figure 10. The percentage mass loss as a function of temperature (TG curves) is shown in Figure 10(i) and the derivative of mass loss percentage as a function of temperature (DTG curves) is shown in Figure 10(ii). The degradation onset [Figure 10(i)] and the maximum degradation temperature [deg_{max} , Figure 10(ii)] of the polymer decreased with the filler incorporation. The lignin composites showed the lowest degradation onset temperature (238°C). However, almost the same degradation onset temperature (245–246°C) was observed for all other composites. The mass loss at the degradation onset temperature can be attributed to the loss of moisture and volatile components from the materials. Major degradations of the composites occurred at three different temperature ranges owing to various competitive thermochemical reactions in the filler that released many chemical components at various temperature ranges. Usually, the degradation of switchgrass occurs in three different temperature ranges due to the degradation of cellulose (main peak), hemicelluloses (a shoulder left of the main peak) and lignin³⁵ that produces carbon monoxide, acetic acid, and ethanol with the low concentrations of methane, carbonyl sulfide, methyl isocyanate, and isocyanic acid. Lignin degrades at a very broad range of temperatures between 150 and 800°C and releases gases like CO, CO₂, H₂O, and CH₄.^{35,36} The major degradation temperature of the composites at higher temperature corresponds to the degradation of polymer which is believed to have overlapped with the degradation of cellulose and lignin in the composites. It can be observed that the deg_{max} of the switchgrass is about 15°C higher than lignin. However, the deg_{max} for the lignin composites is only about 7 degrees lower than the switchgrass composite (395°C). This result may indicate a better compatibility of lignin with PBS matrix than the switchgrass. The maximum degradation temperature of hybrid composites has obtained an intermediate value in between the two individual filler based composites. The incorporation of PMDI has not shown any significant effect on the degradation behavior of the composites. The mass loss at 400°C was higher in the case of switchgrass and its composites (74–75%) compared with lignin and the composites having lignin in the composition (64–69%). This result can be attributed to the higher degradation rate of cellulose (and hemicelluloses) at that temperature. The lowest mass loss was observed for the neat PBS. As mentioned earlier, lignin degradation continues until a comparatively higher temper-

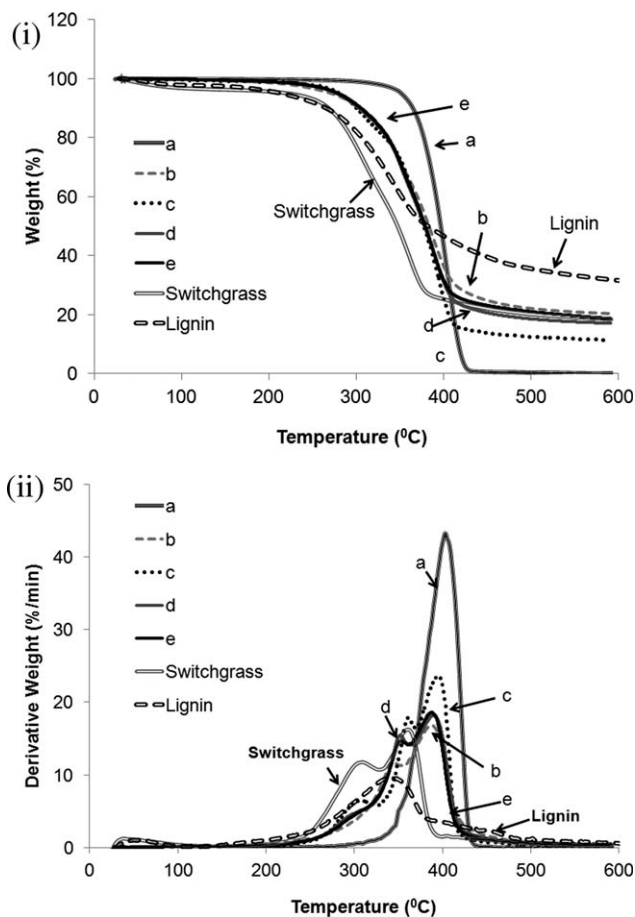


Figure 10. TG analysis of lignin, switchgrass, and composites. (i) TG curves. (ii) DTG curves of composites. a. Neat PBS. b. Lignin composite. c. Switchgrass composite. d. Hybrid composite. e. Compatibilized hybrid composites.

ature around 800°C. Hence a quite significant fraction of lignin does not degrade within 400°C. The percentage of charred residue left at 600°C was the lowest for neat PBS and highest for lignin owing to the presence of high ratio of highly condensed aromatic structures in lignin. Charred residue slightly increased with the use of compatibilizer. Char yield is directly related to the flame retardant potential of a material.¹² The flame retardant ability of lignin can be understood from the results.

Density of Composites

The density (ρ) of the neat polymer and the composites were measured by a densimeter and presented in Table II. The neat polymer showed densities of 1.26 g/cm³. ρ values obtained for the composites were between 1.30 and 1.35 g/cm³. Density of the lignin composites was lower than the density of switchgrass composites. The tensile strength and Young's modulus of materials are almost linear function of their densities. The mechanical properties of material improve as the amount of porosity reduced or density increased. However, composites impart better mechanical properties even at lower density level or for a slight increase in the density compared with the neat polymer which was observed from our study. While no change in the density was observed owing to PMDI incorporation, the tensile

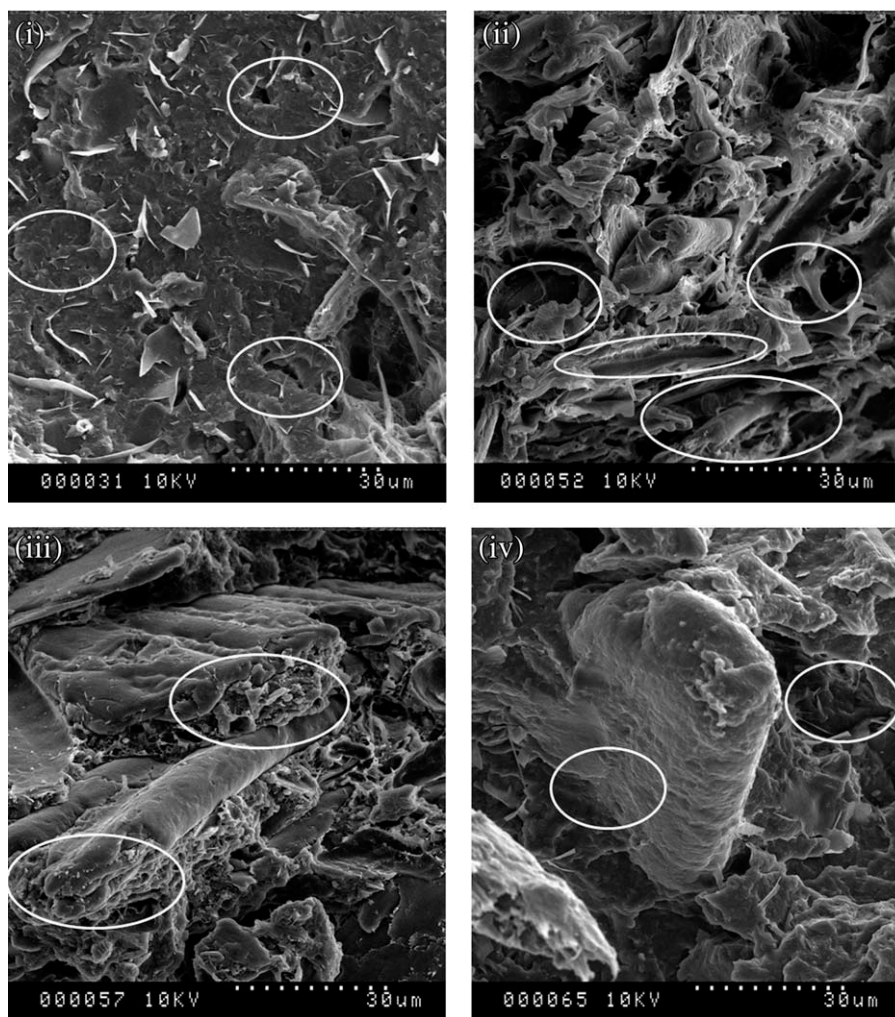


Figure 11. SEM micrograph of composites at 30 μm scale and 10 kV operating voltage. (i) Lignin composite. (ii) Switchgrass composite. (iii) Hybrid composite. (iv) Compatibilized hybrid composites.

strength of composites was improved with the compatibilizer. Addition of compatibilizer synergizes the mechanical performance of composites without affecting density of the material significantly. However, modulus of PMDI compatibilized composites remained almost unchanged as the density remained almost the same. It is believed that the moduli of the PMDI compatibilized composites are more dependent on the plasticization mechanism as discussed before. Compared with glass fibers, incorporation of biofibers into polymer was effective in reducing density of composites and can offer an acceptable specific strength to the materials. The current study indicates that lignin could also be considered as a potential filler for reducing density of composites.

Surface Morphology of Composites

The SEM photographs of the composites are shown in Figure 11. The micrograph of the tensile fractured surface of the lignin composite is shown in Figure 11(i). A comparatively smooth and homogeneous phase can be observed from the micrograph that may suggest a better compatibility of lignin (compared with switchgrass) in the PBS matrix. The matching of solubility parameters and possible polar-polar interaction could be the

causes of this compatibility. The lignin-PBS compatibility corroborates the increase in the glass transition temperature of the lignin composites. Further, matrix cracking, voids with irregular shapes were observed in the micrograph of the fractured surface which further indicate a stronger polymer-filler interface in the composites. These voids indicate fiber pullouts with adhered resin matrix. Again, pulled out fibers can be clearly observed in the micrograph of lignin composites. It was already mentioned that the fibers present in the lignin (Arboform[®] F 45) were finely ground. By observing the length of pulled out fibers from lignin composites it may be inferred that the presence of ground fibers (short fiber) in the lignin promoted easy fracture failure through a short fiber pull out mechanism which might have contributed to the lower mechanical performance of the composites. Fiber breakages, pulled out fibers as well as voids were present in the micrograph of switchgrass composites [Figure 11(ii)]. It also gives evidence of the better fiber dispersion in the polymer matrix which contributes positively to the mechanical performance of the composites. It was also observed that fibers present in the switchgrass composites were sufficiently thicker than the fibers present in the lignin composites which

probably contributed to the higher modulus of the switchgrass composites. However, fiber debonding, voids due to fiber pullouts, and gaps between fiber and matrix observed from the micrograph [Figure 11(ii)] depicts insufficient adhesion between the hydrophobic polymer and hydrophilic grass fiber. Fiber breakage contributes much lesser to energy than the fiber pullouts in the net fractured energy. In general, better dispersion, fiber breakage mechanism, and insufficient adhesion worked together in a fracture failure process of the switchgrass composite which resulted in tensile strength nearly same as that of the virgin polymer. Figure 11(iii) depicts the micrograph of tensile fractured surface of the hybrid composites. Although fiber debonding can be observed in the micrograph of the hybrid composites which indicates a weaker interface due to the presence of switchgrass, by carefully observing the micrograph [Figure 11(iii)] one can see that the fibers have obtained a well-packed stacked arrangement with lignin-polymer mixture adhered between the stacks. This arrangement provides a compact structure to the hybrid composites and probably the cause of the improved flexural strength of this composite. Unlike switchgrass composites, no gap between fiber and matrix phase can be observed in the micrograph of hybrid composites which reflects a better interfacial chemistry in this composite. It validates the compatibilizing ability of lignin in the fiber reinforced composites. As hybrid composite contains a 1 : 1 ratio of lignin and switchgrass, an intermediate tensile strength between the two individual filler based composites were expected for the hybrid composites. However, the tensile strength of the hybrid composite was very close to the switchgrass composite which further depicts the compatibilization effect of lignin in the hybrid composites. The micrograph of hybrid composites reflects a good agreement between the discussed hypothesis and the resulted properties of the composites. The fractured surface morphology of compatibilized hybrid composite can be observed from Figure 11(iv). It was observed from the micrograph that the pulled out fiber was strongly adhered with the polymer matrix which indicates a strong interfacial adhesion between the filler and polymer matrix in the compatibilized hybrid composites. No gap between fiber and polymer matrix can be observed in the micrograph. Large holes were observed in the micrograph which was possibly caused by the pulling out of the fibers with significant amount of adhered resin matrix. The polymer-lignin phase also appeared very homogeneous in the micrograph. All these observations offer good evidences in support of the compatibilization effect of PMDI in the composites and are in good agreement with the mechanical properties of the compatibilized composites.

CONCLUSIONS

Lignin and switchgrass were used as the reinforcing filler in the PBS matrix which synergistically improved many properties of the composites. Hybrid filler proved more beneficial over single filler in the composites that obtained a better flexural strength than the individual filler based composites. The addition of PMDI compatibilizer improved the mechanical and thermomechanical properties of the composites reflecting a key improvement in the flexural strength and toughness of the composites. Incorporation of biofillers as well as PMDI compatibilizer improved the heat deflection temperature of the polymer. A maximum improvement in the

storage modulus and HDT values was obtained by the switchgrass composites. Incorporation of lignin to the PBS polymer improved the glass transition temperature significantly. PMDI did not have significant effect on the glass transition temperature of the material. As usual, thermal degradation onset temperature reduced on biofiller incorporation. However, the high amount of char content indicates that lignin could act as a flame retardant in the composites. The surface morphology and interface chemistry was greatly improved by the addition of PMDI compatibilizer to the hybrid composites.

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