Influence of Fiber Length and Surface Modification of Wheat Straw Fibers on the Properties of Polypropylene Based Eco Composites

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Abstract— The effects of wheat straw fiber having fiber length (2mm and 6mm) and alkali treatment in polypropylene (PP) matrix were investigated to produce environment friendly composites. Wheat straw fibers were varied at 10%, 20% and 30% wt% in the composite. Wheat straw fibers (treated and untreated) were characterized using Thermo Gravimetric Analysis (TGA), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Crystallinity of treated wheat straw fiber was found to increase by 9.2%. FT-IR showed lignin content decreased from 17.7% to 9.3% whereas cellulose content increased from 35.9 to 45.8% after alkali treatment. Mechanical properties, composite of treated fiber having 2 mm length showed maximum increase in flexural and tensile modulus by 40% and 49% at 30% fiber loading.

Key words: Biocomposites, Wheat Straw Fiber, Biofiller, Alkali Treatment, Polypropylene, Surface Modification

I. Introduction

A growing environmental concern and regulation, alongside depletion of petroleum resources has forced researchers around the globe to seek new fiber reinforced plastics that are environment friendly and abundantly available. Thus, natural fibers are seen as potential alternative to the conventional synthetic fibers. Natural fibers are non toxic, renewable, easily available and their low cost makes them key to industrial and economic interest. In addition, these natural fibers do not abrade processing equipments [1-5]. Therefore, natural fiber reinforced plastics are of significant interest as a replacement for synthetic fiber reinforced plastics in a growing number of industrial sectors including the automotive industry, packaging and furniture production.

Fiber reinforcement may be used in several different forms or arrangements depending on the application and manufacturing route [6]. In terms of length fiber are generally either short (less than 10mm), long (10-20mm) or continuous. Composites prepared from long fibers offer high mechanical properties and the possibility of specific orientations to give the composite directional properties. Recent developments in natural fibers such as jute, sisal, coir, flax, wheat straw etc, have shown that it is feasible to obtain well performing materials using these environment friendly reinforcements [7]. The mechanical properties of natural fiber-reinforced composites can, in fact, be further improved by chemically promoting a good adhesion between the matrix and the fiber [8-9]. Wheat straw is one of the by-products of a large number of food and forestry industries. It is generally treated as waste and is sent to land-fill or is used as a heating medium and/or cattle feed. It is inexpensive and a good renewable source of cellulose-rich fiber, thus having great potential of being used as reinforcement in biocomposites. Typically, wheat straw contains 29-35 wt% cellulose, 16-21 wt% lignin and 26-32 wt% hemicelluloses [10]. Mishra et al. [11] explored the advantages and commercial viability of using wheat straw as fillers for thermoplastic composites. Properties of polyester wheat straw composites were investigated by Halvarsson et al. [12] for manufacturing of medium density fiberboard (MDF). Four weight fractions of wheat straw 2%, 4%, 6% and 8% were chosen in the study. Sultani et al. [13] reported the mechanical characteristics of wheat straw (WS)-high density polyethylene (HDPE) composites.

Mechanical and thermal properties of wheat straw in the form of milled flour in polyolefin and the influence of interfacial interactions has been investigated by Digabel et al. [14]. Study on mechanical properties of wheat straw flour filled high density Polyethylene (HDPE), polypropylene (PP) and their blend (HDPE/PP) has been reported by Mengeloglu et al. [15] Composites with maleic anhydride coupling agents treated matrices showed significant increase in tensile properties, flexural strength, modulus, and impact strength. A study was carried out by Xia et al. [16], Kang et al. [17] and Xia et al. [18] in processing of wheat straw for green composites applications. Wheat straw was per-treated with alkaline solutions and then fractionated with a twin screw extruder at a range of processing conditions to produce straw fiber with various degrees of fractionation. Kang et al. [17] reported that alkali treated wheat straw could be compression molded without addition of any resin. This has provided a feasibility to produce composites from 100% straw, known as self-bonded biocomposites. Reddy et al. [19] prepared polypropylene hybrid composites using wheat straw and clay. The effect of variations in various constituents of a hybrid composite on water absorption and flexural was reported. A study on the flexural properties of wheat straw reinforced polyester composites was reported by Chensong et al. [20]. Wheat straw was varied from 2% to 8% and no increase in flexural properties was found.

In this paper, effect of wheat straw fiber length and alkali treatment on the properties of PP composites was investigated. Composites of PP with wheat straw fibers (a) unmodified (untreated with sodium hydroxide) and (b) modified (treated with sodium hydroxide) having two different lengths were prepared. Morphological, thermal, spectroscopic and mechanical properties of both fibers and composites were studied in detail.

II. Experimental

A. Materials

Commercial isotactic Polypropylene (iPP), impact copolymer (MFI-3g/10min) produced by IndianOil Corporation Limited was used in the study. Wheat straw (WS) used was obtained locally and prior to use, wheat straw was washed with water to remove the dirt. Washed wheat straw was later dried in oven at 70^0C for 24hrs. After thorough washing and drying, wheat straw fibers were cut down to an average length of 2mm and 6mm.

B. Treatment of wheat straw

Cleaned wheat straw fibers were treated with a water solution containing 5wt.% sodium hydroxide at room temperature. The fibers were stirred for 30minutes; later washed repeatedly with water to remove excess sodium hydroxide. These washed fibers were then dried in an oven at 70°C for 24 hrs prior to be used for composite preparation.

C. Composite Preparation

Three different types of composites, polypropylene with unmodified wheat straw fibers with average fibers length of 6mm (PP-WS), untreated wheat straw fibers of 2mm in length (PP-MWS) and wheat straw fibers of length 2mm treated with sodium hydroxide (PP-TWS) were prepared as shown in table 1. The content of wheat straw fibers in the composite i.e. WS, MWS and TWS was varied as 10%, 20% and 30% by weight with iPP. M/s. Labtech Engineering company Ltd (Thailand) twin screw extruder (L/D:40:1) was used for melt mixing of the wheat straw fibers with iPP at 230^0C and 150mm screw speed under N_2. Injection molding of the specimens was done on Toshiba-L&T Aswa 60/320-310 injection molding machine at 230^0C and mold temperature of 60^0C.

Composite name	Fiber type	Fiber proportion (w/wt %)
PP	-	-
PP-WS (90/10)	5mmWheat Straw	10
PP-WS (80/20)	5mmWheat straw	20
PP-WS (70/30)	5mmWheat straw	30
PP-MWS (90/10)	2mmWheat straw	10
PP-MWS (80/20)	2mmWheat straw	20
PP-MWS (70/30)	2mmWheat straw	30
PP-TWS (90/10)	Treated 2 mm Wheat straw	10
PP-TWS (80/20)	Treated 2 mm Wheat straw	20
PP-TWS (70/30)	Treated 2 mm Wheat straw	30

Table 1: PP wheat straw fiber composite: composite name, fiber type and fiber proportion.

Characterization of PP/Wheat Straw Composites

D. Morphological Characterization

Surface topography of interface and fractured surfaces of the composites were scanned with the aid of Zeiss SUPRA™ 55 Field Emission Scanning Electron Microscope. Cryo fractured izod impact specimen were surface-metalized by sputter coating with evaporated gold metal (4nm thickness) before analyzing by FE-SEM at accelerating voltage of 1KV.

E. Thermal Characterization

TA instruments Thermal gravimetry analyzer (TGA) Q500, was used to study thermal stability of the untreated and treated wheat straw fiber. Thermogravimetric traces were recorded at a heating rate of 10^0C/min in N_2 atmosphere in the temperature ranging from 50^0C to 800^0C.

F. Fourier Transform Infrared Spectroscopy

For conducting Fourier transform infrared spectroscopy (FTIR) measurements, Shimadzu IRPrestige-21 instrument was used. FTIR spectras were recorded in a spectral range of 400-4000 cm^{-1} with a resolution of $4cm^{-1}$ and with 32 scans. FOSS FTIR (PROFOSS) installed with WinISI software was used to determine cellulose, hemicelluloses and lignin content in the wheat straw.

G. Wide angle X-ray diffraction (W-XRD)

The crystallinity of untreated and treated wheat straw fiber was evaluated by X-ray diffraction (XRD). X-ray diffraction patterns were obtained with Rigaku X-ray diffractometer model D/max-2500/PC. XRD patterns were recorded at 50 kV and 150 mA at a scanning rate of 2 deg / min with a step size of 0.01 deg in the 2θ range of 5^0 to 40^0.

H. Mechanical properties

Tensile characterization was conducted with injection molded dumb-bell-shaped samples using TIRA 2700 machine. Sample dimensions and testing procedure were in accordance with ASTM 638, the crosshead speed was 100 mm/min. The flexural characterization of PP and PP/wheat straw composites was conducted using three-point loading system in accordance with ASTM 790. For tensile and flexural testing, five samples were tested for each composite and the average value was reported. Izod impact test of the notched specimens was measured using CEAST impact tester as per ASTM 256. The impact strength was expressed in terms of J/m and the results are average of 10 samples tested for each composite.

III. Results and Discussions

A. Spectroscopic analysis

The main components of a natural fiber i.e. wheat straw fiber are lignin, cellulose and hemicelluloses, were demonstrated by FT-IR spectra. Fig.1 shows FT-IR spectra of (a) an untreated wheat straw and (b) chemically treated wheat straw. Stretching vibrations of CH and OH leads to dominant peaks in the region between 3500 and 2900 cm^{-1}. The prominent peak at 1700 cm^{-1} in untreated wheat straw is attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic and p-coumeric acids of lignin and/or hemicelluloses. This peak disappeared completely in the chemically treated wheat straw because of the removal of most of the hemicelluloses and lignin from the wheat straw due to chemical extraction.

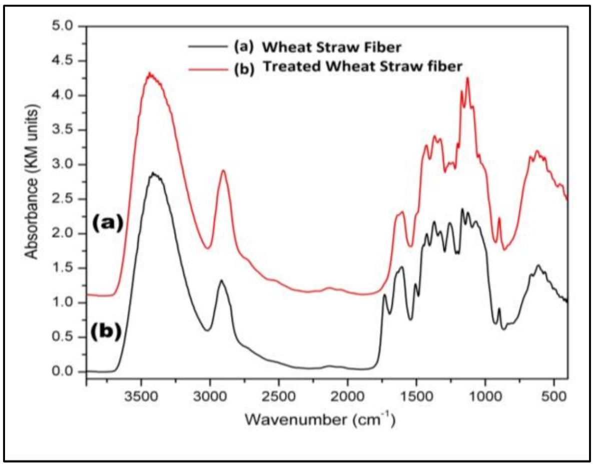

Fig. 1: FT-IR spectra of (a) an untreated wheat straw and (b) chemically treated wheat straw.

The peaks at 1507 and 1380 cm^{-1} in the untreated wheat straw fiber represent the aromatic C=C stretch of aromatic rings of lignin. The intensity of these peaks decreased in the chemically treated wheat straw, which was attributed to the partial removal of lignin. The increase of the band at 896 cm^{-1} in the chemically treated wheat straw indicates the typical structure of cellulose. WinISI software also supports these FT-IR results confirming reduction of lignin by 8.3% and increase in cellulose content by 10% in the treated wheat straw fiber (Table 2).

Wheat Straw	Lignin (%)	Hemi cellulose (%)	Cellulose (%)
Untreated	17.6	19.0	35.9
Treated	9.3	17.8	45.8

Table 2: Cellulose, hemicelluloses and lignin content in treated and untreated wheat straw fiber

B. *Crystallinity of Untreated and Treated Fibers*

Chemical treatments affect the crystallinity of cellulosic fibers. Crystallinity is commonly measured as a ratio between the diffraction portion from the crystalline part of the sample, and the total diffraction from the same sample. Fig.2 shows the XRD patterns of the untreated and treated wheat straw fibers. The peak at $2\theta = 22^{o}$ is sharper for chemically treated wheat straw than untreated cellulose fibers. The sharper diffraction peak is an indication of higher crystallinity degree in the structure of treated fibers. The crystallinity values were estimated at 62.1% and 71.3%, for the untreated and alkali treated wheat straw fibers respectively, indicating that an increase of 9.2%. The increase in the number of crystallinity regions increases the rigidity of cellulose.

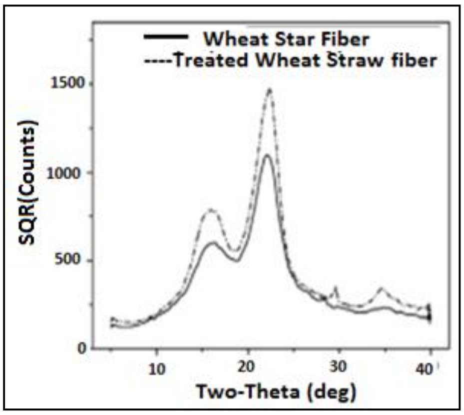

Fig. 2: XRD patterns of the untreated and treated wheat straw fiber.

C. *Thermal properties*

Results represented in figure 3 further indicate that the thermal stability of wheat straw fibers increased after alkali treatment. The degradation temperature of the treated wheat straw fiber increased by 28 ^{0}C (Table 3) which can be attributed to increase in crystallinity of the wheat straw fibers. There was also a distinctive decrease in the residue of treated wheat straw fiber by 3% as compared to untreated wheat straw fiber.

Wheat Straw Fiber	Onset of degradation (^{0}C)	Residue after $500^{0}C$ (%)
Untreated	264.0	14.6
Treated	291.9	11.7

Table 3: Degradation characteristics of wheat straw fibers

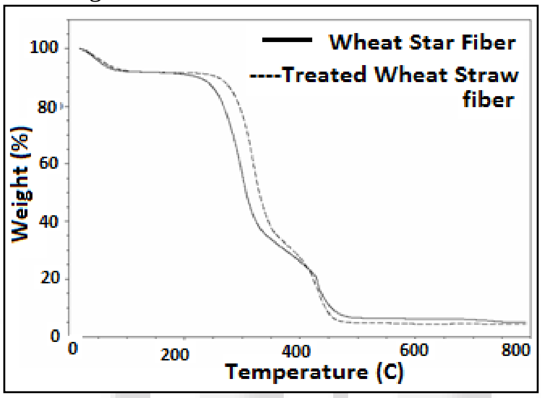

Fig. 3: TGA of the untreated and treated wheat straw fiber

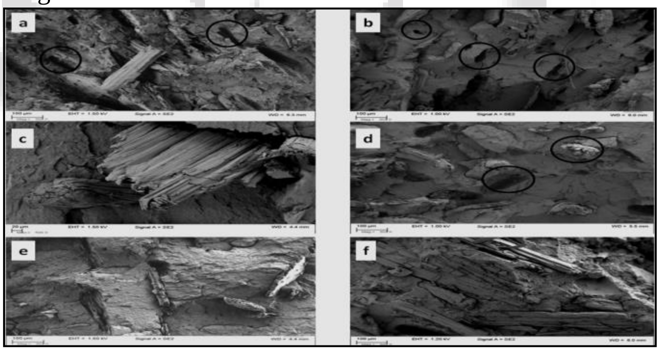

Fig. 4: SEM micrographs of PP/Wheat straw fiber composites

D. *Morphology of composites*

The surface of the freeze broken izod impact specimens were used for SEM analysis. Fig. 4(a) and 4(b) shows micrograph of composite containing 10% and 20 wt.% of wheat straw having 6 mm fiber length (PP-WS). Micrograph 4(a) and 4(b) shows voids created due to fiber pull caused by applying shear during specimen breakage. Fiber pull out indicates poor interaction between the polymer matrix and wheat straw. Fig. 4(c) and 4(d) represent composite micrographs containing 20% and 30 wt.% of wheat straw of 2 mm fiber length (PP-MWS). It was apparent from the micrographs that there was better dispersability of the fibers due to smaller length. Few fibers pull out can be due to the poor adhesion of fibers with polypropylene. Fig. 4(e) and 4(f) shows micrographs of composite containing 20 and 30 wt.% of treated wheat straw. The micrographs shows fibers aligned in direction to the applied stress indicating good interaction between the polymer matrix and the fiber. The good interaction is attributed to the modification of the fiber after chemical treatment. High modulus values observed on these composite samples also corroborates these observations.

E. Mechanical properties of composites

Table 4 shows the tensile strength of PP composite as a function of wheat straw content. It can be seen that with the increase in wheat straw fiber content the tensile strength increased for the three type of composites i.e. PP-WS, PP-MWS and PP-TWS. Higher tensile strength (Fig. 5) in PP-MWS and PP-TWS than PP-WS composites can be attributed to better compatibility of fibers and their distribution within polymer matrix which played a significant role. Tensile strength of PP-TWS composite increased by 26% to 39% whereas for PP-MWS and PP-WS composites tensile strength increased by 8% to 25% and 1% to 10% with increase in fiber content. Due to alkali treatment, fibers had better adhesion with polymer matrix leading to high tensile strength for PP-TWS composites. Increase in the wheat straw (%) resulted in higher stiffness and hardening of composites thus decreasing the percent elongation (Fig. 6) of these composites with increase in fiber loading.

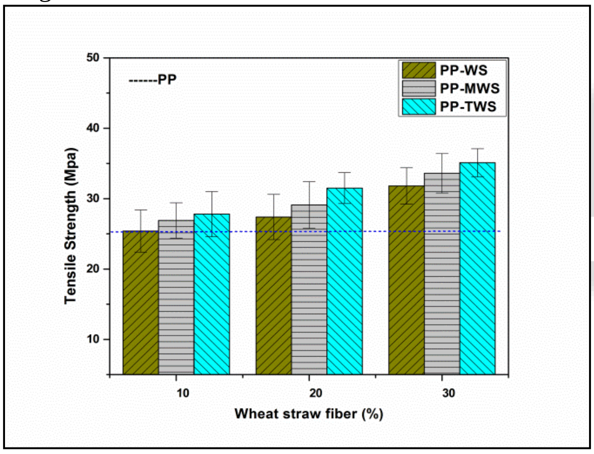

Fig. 5: Tensile Strength of PP/Wheat straw fiber composites

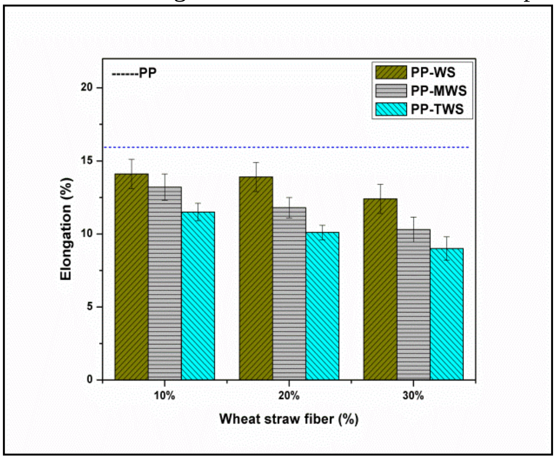

Fig. 6: % Elongation of PP/Wheat straw fiber composites

Tensile and flexural modulus values (Fig. 7 and 8) were found to increase linearly with the increase in wheat straw fiber (%) from 10% to 30%. This behavior is primarily due to the reinforcing effect of the wheat straw fibers leading to a uniform stress distribution from a continuous polymer matrix to the dispersed fiber phase. Lower modulus value in PP-WS composite is possibly attributed to non-compatibility of hydrophilic wheat straw with hydrophobic polypropylene matrix. This resulted into poor interfacial adhesion between the fiber and the polymer matrix. In addition, the presence of voids in PP-WS composite could have contributed to lower modulus values as compared to PP-MWS and PP-TWS composites. This scenario improved when 2 mm fibers were used in the PP-MWS composite. Due to smaller fiber length the fibers were able to get dispersed in a better way thus providing improved stability to the polymer matrix. For PP-TWS composite an increase of 49% in tensile modulus and 40% in flexural modulus was observed at 30% fiber loading.

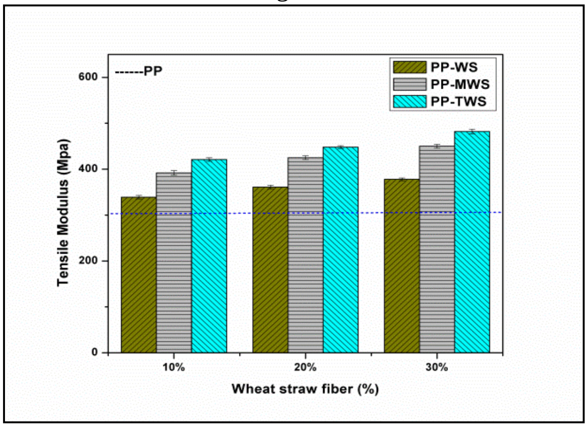

Fig. 7: Tensile Modulus of PP/Wheat straw fiber composites

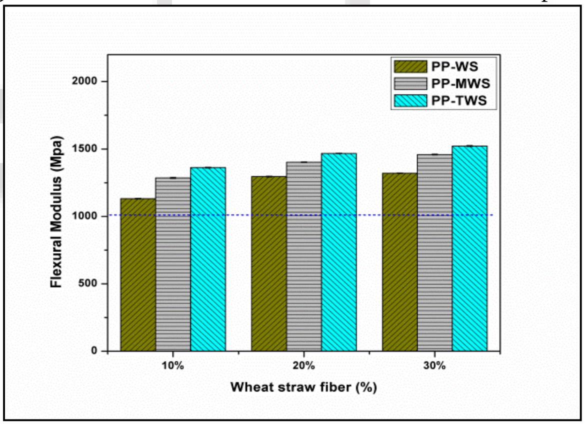

Fig. 8: Flexural Modulus of PP/Wheat straw fiber composites

Higher tensile and flexural modulus values of PP-TWS when compared to PP-WS and PP-MWS composites may be attributed to the fact that the alkaline treatment of wheat straw fibers improved the adhesive characteristics of the fiber surface by removing natural impurities. The alkaline treatment of wheat straw resulted in increase in the effective fiber surface area available for contact with polymer matrix. This leads to better reinforcing and therefore a uniform stress distribution from the continuous polymer matrix to the dispersed fiber phase.

The impact strength of the composites decreased significantly with the increase in fiber percentage. This change may be attributed to the increase in the rigidity of the composite (Fig. 9). Increase in the fiber concentration in the polymer matrix increased the overall rigidity of the composite thus reducing the crack initiation energy and consequently the impact strength of composite. Impact strength decreased by maximum of 33%, 22% and 19% for PP-TWS, PP-MWS and PP-WS composites respectively.

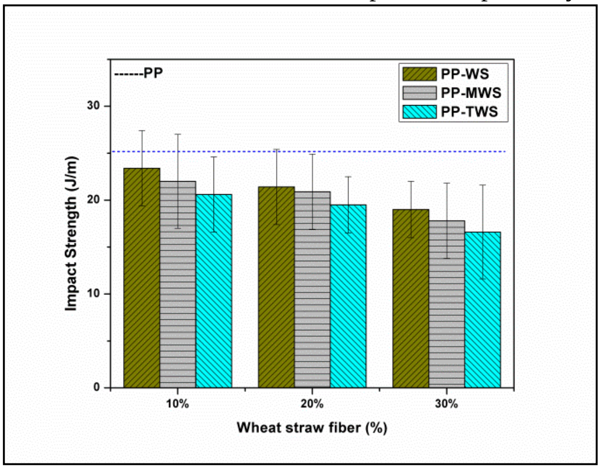

Fig. 9: Impact Strength of PP/Wheat straw fiber composites

IV. Conclusion

In this study, PP composites of wheat straw fibers were prepared. Chemical composition, morphology, thermal and mechanical properties of the fiber and composites were subsequently analyzed. FT-IR. measurements revealed the removal of lignin and increase in cellulose content due to alkali treatment.

The crystallinity of the treated wheat straw fibers increased by 9.2% when compared to untreated fibers. Chemically treated wheat straw fibers showed enhanced thermal properties wherein thermal degradation temperature increased by 28 ^{0}C. Percent elongation and impact strength of PP-wheat straw fibers decreased with increase in fiber loading. However, tensile and flexural modulus of the composites increased with increasing fiber loading. Tensile modulus increased to maximum of 33%, 41% and 49% for PP-WS, PP-MWS and PP-TWS composites respectively. In comparison, flexural modulus increased to maximum by 25%, 35% & 40% for PP-WS, PP-MWS and PP-TWS composites respectively. Reduction in fiber length resulted in better dispersion of the fiber in the polypropylene matrix. Enhanced interfacial bonding of the wheat straw fibers with the polypropylene matrix caused due to chemical treatment resulted in overall superior properties of PP-TWS composite.

Composite name	Tensile Strength (Mpa)	Elongation %	Tensile Modulus (Mpa)	Flexural Modulus (Mpa)	Impact Strength (J/m)
PP	25.2	15.8	316	1085	25.1
PP-WS (90/10)	25.4	14.1	339	1132	23.4
PP-WS (80/10)	26.9	13.2	392	1286	22.0
PP-WS (70/10)	27.8	11.5	421	1362	20.6
PP-MWS (90/10)	27.4	13.9	361	1296	21.4
PP-MWS (80/10)	29.1	11.8	425	1402	20.9
PP-MWS (70/10)	31.5	10.1	448	1467	19.5
PP-TWS (90/10)	31.8	12.4	378	1321	19.0
PP-TWS (80/10)	33.6	10.3	450	1459	17.8
PP-TWS (70/10)	35.1	9.0	472	1522	16.6

Table 4: Mechanical properties of PP wheat straw properties

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