Effects of Pre-Treatments on Pigeon Pea Stalk Fibers

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ABSTRACT

India being an agricultural country has great potential to utilize fiber derived from agricultural waste. Pigeon pea stalk (PS) is an agricultural waste. The pre-treatments of PS fibers enhance their compatibility with polymer in the area of polymer composites. This work deals with three different types of pre-treatments of PS fiber. The treatments were studied with the help of SEM, XRD, FTIR, TGA and XPS. The PS fibers have undergone laccase enzyme treatment, alkaline treatment with sodium hydroxide and potassium permanganate treatment. The results confirmed the reduction of lignin and hemicellulose after the chemical modification of fibers. The increase in % crystallinity and thermal stability in treated fibers has been observed. The morphological evaluation showed the increase in surface area and roughness of the fiber surface which is useful for efficient bonding with the polymer matrix.

INTRODUCTION

Fibers are long thread like material that are used as a source of reinforcement in various kinds of polymer composites (Mohammed et al. 2015). They are either synthetic like carbon, aramid, glass etc or natural like leaf fiber, bast fiber/skin fiber, fruit fiber, stalk fiber, seed fiber etc.

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Synthetic fibers have several advantages like being strong and provide high reinforcement to the composites but also suffer from various disadvantages like posing a threat to the environment for being non-biodegradable and non-renewable. Natural fibers have shown advantages over synthetic fibers mainly with respect to environment and applications towards new polymer composite preparations (Braga et al. 2014).

The natural fiber consists of cellulose, hemicelluloses, lignin and others which include pectin, waxes and extractives. The fibers are used in various studies as a source of reinforcement in polymer composites where the matrix used is either a thermoplastic or thermoset polymeric material. For thermoset, epoxy used as a matrix having good adhesion with natural materials like banana, coconut, bagasse, pineapple leaf etc (Biswas et al. 2011; Maleque et al. 2007; Baranitharan and Mahesh 2014; Acharya et al. 2011; Naidu et al. 2013; Payae and Lopattananon 2009). High-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene (PP) and polyester are some of the thermoplastic polymers which have been used as a matrix in preparation of natural fiber filled composites (Roe and Ansell 1985; Kalaprasad et al. 1997; Bahra et al. 2015; Joseph et al. 1999).

The natural fibers have shown disadvantages of high moisture uptake that weakens the interfacial bonding between the polymer matrix and the fiber. This leads to the deterioration in the mechanical properties of composites and dimensional instability. In order to overcome these issues and to improve the fiber matrix adhesion, a pretreatment of the fiber surface have been done for the modification of the surface of the fiber. Some of the common

chemical treatment practiced includes alkali treatment (Ramadevi et al. 2012; Benyahia and Merrouche 2014; William et al. 2011), potassium permanganate treatment (Khan et al. 2006) and enzyme treatment. Some of the enzymes studied in the reported literature are pectinase (Saleem et al. 2008), cellulose, xylanase (Jayapriya and Vigneswaran 2010), laccase (Islam et al. 2013; Nasir et al. 2013, Cao et al. 2012, Peng et al. 2010).

The utility of agricultural waste as a natural fiber is a step towards sustainable development. India being an agricultural country has great potential to utilize agricultural waste as natural fibers. The pigeon pea (Cajanus cajan) is a perennial legume belongs to the family Fabaceae and is the sixth most important legume crop in the world (Ayenan et al. 2017). India is one of the major pigeon peas producing countries of the world where this plant is more popularly known as Arhar or red gram (Ayenan et al. 2017; Samanta et.al 2013). The stalks are the waste after harvesting the food grain and hence its value addition is vital for sustainability. The pigeon pea stalk has been studied in the preparation of cement bonded composite boards (Aggarwal et al. 2008). We herein report the pretreatment studies of Pigeon pea stalk (PS) fibers using chemical and enzymatic treatments to understand their potential for composite preparations.

RESULTS AND DISCUSSION
Morphological study
The morphological changes in the untreated and treated fiber due to the treatment was studied through SEM (Figure 2). From the SEM images, it is observed that the untreated fibers have been covered with a layer of waxes, oils and extractives which agrees with the literature (Carvalho et al. 2010). The SEM of treated fibers reveals that the fiber become porous and have been partially disintegrated which could be due to extraction of residual lignin that holds the fibrils together. The removal of lignin and presence of depressions leads to increase in the

surface area and roughness of the fiber surface which promotes better interaction and formation of mechanical bond more efficiently with the polymer matrix (Pietak et al. 2007).

Crystallinity Index (CI) study
The X-ray diffraction patterns of untreated and treated PS fibers have been depicted in figure 3. The diffractogram showed that the treatment has led to the increase in the fiber crystallinity index. The major and intense peaks have been observed at values $2\theta = 16°$ and $2\theta = 22º$, which represents the cellulose crystallographic planes I101 and I002 respectively (Yuan et al. 2013). This is same for all the fibers untreated and treated with only variation in intensity. The X-ray apparent crystallinity (%) of cellulose was calculated using peak height method (Segal et al 1959) by the following equation:

$$C = 100 \text{ x } \frac{I_{200} - I_{\text{non-cryst}}}{I_{200}} [\%]$$

where: C is the apparent crystallinity [%], I_{200} gives the maximum intensity of the peak corresponding to the plane in the sample with the Miller indices 200 at a 2θ angle of between $22\text{-}24º$.

The *non cryst I* represent the intensity of diffraction of the non-crystalline material, which is taken at an angle of about $18º$ 2θ in the valley between the peaks (Terinte et al. 2011). The PS-ALT fiber peak intensity is the sharpest in comparison to the untreated fiber among all the treatments which confirms that the removal of amorphous portion thus increasing the crystalline portion of the fiber. The diffraction peaks at the 2θ angles and the % crystallinity index (calculated as per equation) for all the fibers have been given in table 1. The increase in % crystallinity index was observed *vis-a-vis* comparison of untreated fiber with treated fibers. Alkali treated (PS-ALT) and Potassium permanganate treated (PS-KMT) showed highest increase in crystallinity index than the enzyme treatments. The increase in crystallinity is also reported for the treated fibers in the study by
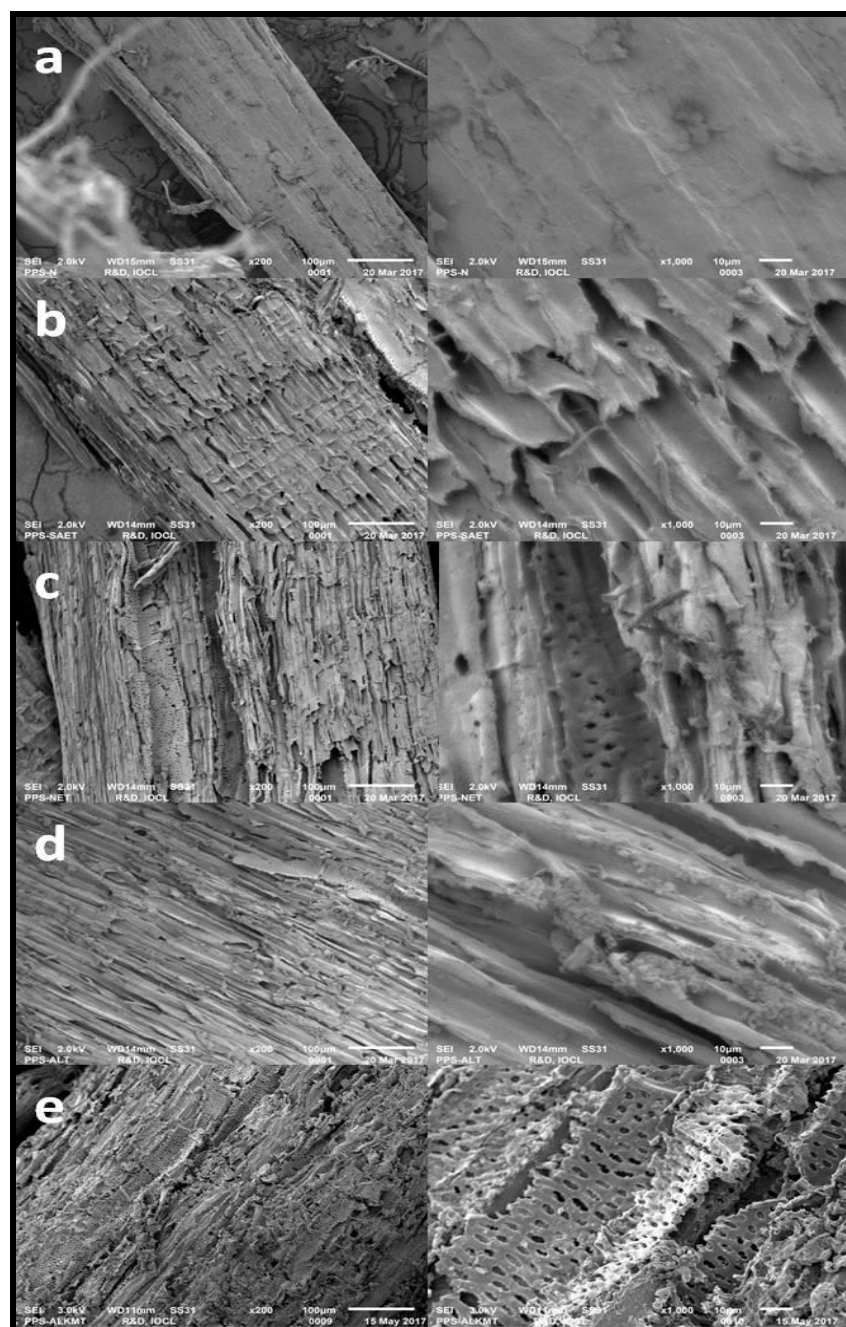
200 X   1000

Figure 2. SEM images of (a) PS-raw and untreated (b) PS-SAET (c) PS-NET (d) PS-ALT (e) PS-KMT   fiber at 200X and 1000X magnification

Duchemin and Staiger 2009. The increase in %CI may be due to the removal of hemicelluloses, which normally separates the cellulose chains (Sinha et al 2007). This resulted in the formation of new hydrogen bonds between some part of the cellulose chains.

Sample Detail	I_{002}	I_{101}	% Crystallinity Index
PS	1233 (16.31)	2720 (22.41)	66
PS-SAET	1025 (16.29)	2494 (22.44)	68
PS-NET	977 (16.29)	2191 (22.28)	73
PS-ALT	1100 (16.25)	2998 (22.61)	79
PS-KMT	834 (16.41)	2315 (22.71)	81

Table 1. Intensity and Crystallinity index of untreated and treated PS fiber

FTIR study

Untreated and treated PS fibers were studied by FTIR spectroscopy. Difference in the spectra was observed due to treatments on the fiber (Figure 4). The band at 3100-3600 cm^{-1} for fibers is due to the –OH vibration of cellulose structure. The peak observed at 1735 cm^{-1} for the untreated fibers, associated with the carbonyl group C=O, proved the presence of pectins, which disappeared after the alkaline extraction with NaOH. The band observed at 1464 cm^{-1}, corresponding to the bending vibration mode of the CH$_2$ group, and at 1530 cm^{-1}, corresponding to the vibration of the C-H bond in the aromatic ring which is present in the lignin, have decreased considerably. The peak at 1735 cm^{-1} which corresponds to carbonyl (Sgriccia et al. 2008) is seen in untreated and enzyme treated (PS-SAET and PS-NET) fibers. However, the intensity has decreased in enzyme treated fibers in comparison to untreated fiber. This peak is not present in PS-ALT and PS-KMT treated fibers which corresponds to C=O stretching of acetyl groups of hemicelluloses. The removal of hemicellulose leads to exposure of OH group of cellulose. The band at 1247 cm^{-1} is due to COO stretching in lignin, band intensity has decreased after treatment in comparison to untreated fibers which could be due to degradation or modification of lignin (Islam et al. 2013) that is more pronounced in PS-ALT and PS-KMT treated fibers. is more pronounced in PS-ALT and PS-KMT treated fibers.
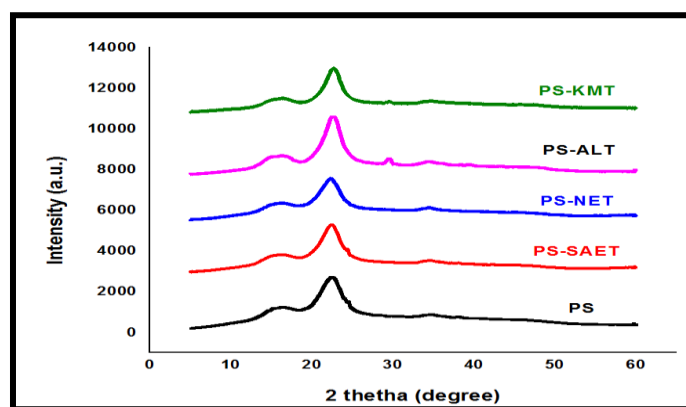
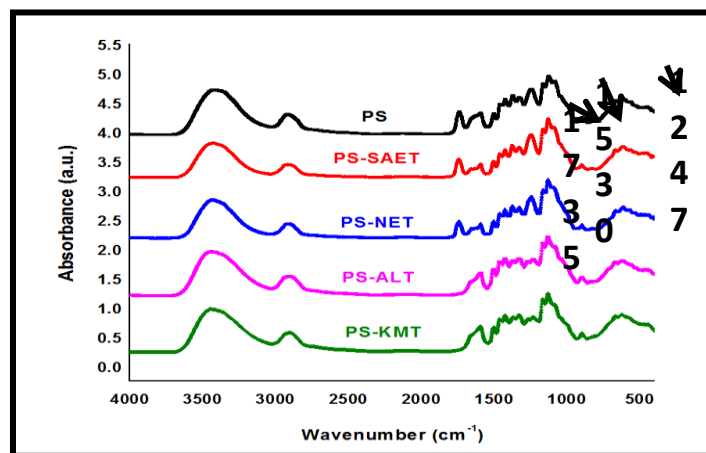

Figure 3. XRD spectrum of untreated and treated PS fiber

Figure 4. FTIR spectra of untreated and treated PS fibers

Thermal study

Two-step degradation is observed in PS untreated and the enzyme treated fiber whereas in the case of alkali and potassium permanganate treated fibers, single step degradation is observed (Figure 5a). In the first step, a weight loss is observed due to desorption of water. Though the fibers have been analyzed after drying but due to hydrophilic nature of the natural fibers, total elimination of water may not be possible (Guimarães et al 2009). The mass loss of natural fiber is due to the cellulose, hemicelluloses and lignin degradation. Hemicellulose decomposes mainly between 220-315ºC, cellulose decomposes between 315-400ºC and degradation of lignin after that (Yang et al. 2007). T_{max} is the temperature at which rate of mass loss is maximum (obtained from DTG trace). The T_{max}, % weight loss and % residue left is given in table 2. The weight loss below 250ºC is negligible. Maximum weight loss occurs in the temperature zone of 250-400ºC. The initial weight loss peak which is due to the loss of moisture is in the temperature region ~70-85ºC for untreated and treated fiber. The % weight loss (due to moisture) of treated fiber is more than the untreated one which could be due to more pores in the treated ones. This result is in agreement with the reported study (Khan et al. 2012). Above the main degradation peak i.e. T_{max} all the volatile material is taken off from the sample which further results in the final leftover called the residual char.

In DTG scans (Figure 5b) which is studied as a function of rate of weight loss (mg/min) *versus* temperature, in case of untreated fibers two peaks are observed i.e at ~294ºC and the other at 348ºC. The first peak is for the degradation of hemicellulose and the second is of cellulose and lignin approximately. The 12-15ºC and 5-6ºC increase in degradation peak temperature of enzyme treated and alkali and potassium permanganate treated fiber respectively have been observed. This indicates better thermal stability of treated fibers in comparison to untreated one. It is also reported that the alkali treatment reduces the hemicelluloses in the fiber, which makes it the fiber more stable (Saha

Sample Detail	~Temperature range (C)	% Weight loss	Residue char (%)	T_{max} (ºC)
PS	RT-150	5.21	19.07	348.6
	150-250	3.75		
	250-400	66.28		
	400-800	5.77		
PS-SAET	RT-150	6.01	15.82	363.7
	150-250	1.47		
	250-400	71.54		
	400-800	5.42		
PS-NET	RT-150	6.91	16.59	360.8
	150-250	1.53		
	250-400	74.66		
	400-800	8.75		
PS-ALT	RT-150	7.22	18.01	354.4
	150-250	1.19		
	250-400	66.65		
	400-800	6.9		
PS-KMT	RT-150	7.01	23.49	353.6
	150-250	2.42		
	250-400	56.7		
	400-800	10.43		

et al. 1991, Khan et al. 2012).

Table 2. Results of Thermogravimetric Analysis (TGA) for untreated and treated fiber

X-ray Photon Spectroscopic study

XPS spectra (Figures 6a and 6b) were obtained for untreated and treated PS fibers. Cellulose and lignin have an O/C ratio of 0.83 and 0.35

respectively (Zhong et al. 2010). Increase in O/C ratio indicates lower lignin concentration (Dorris et al. 1978a and 1978b). The changes in carbon (C) and oxygen (O) regions have been shown in figures 6a and 6b respectively. Elemental composition in the untreated and different treated fibers obtained from survey spectra have been given in table 3. The spectra of all the fibers contained carbon and oxygen primarily which form the structure of these fibers while calcium, phosphorous, magnesium, aluminium and potassium were detected but present in small quantities.
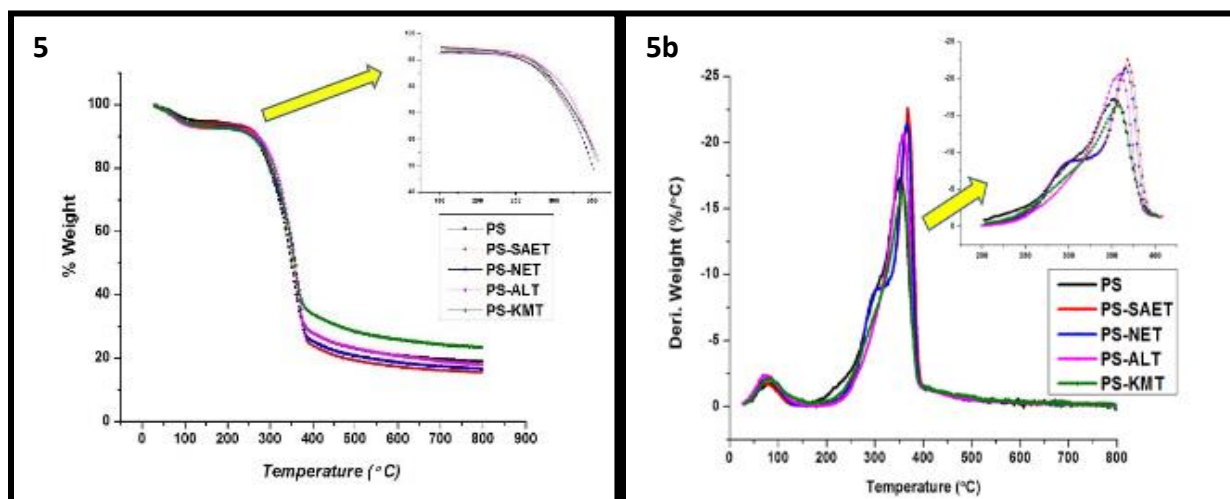

Figure 5a & b: TG and DTG traces of PS untreated and treated fiber respectively in nitrogen atmosphere (heating rate 10°C /min)

As observed through the evaluation and the results tabulated, it is observed that the treated and untreated fibers have less O/C than 0.83 which confirms that the surface has a greater proportion of lignin and waxes on it (Sgriccia et al 2008). It has been found that the O/C ratio increase on the treatment of fibers vis-a-vis comparison of untreated fiber. This took place due to increase of the oxygen exposure on fiber surface after the removal of soluble extractives. A decrease in N/C ratio after treatment of fiber also suggested that the surface was affected by the treatment procedure.
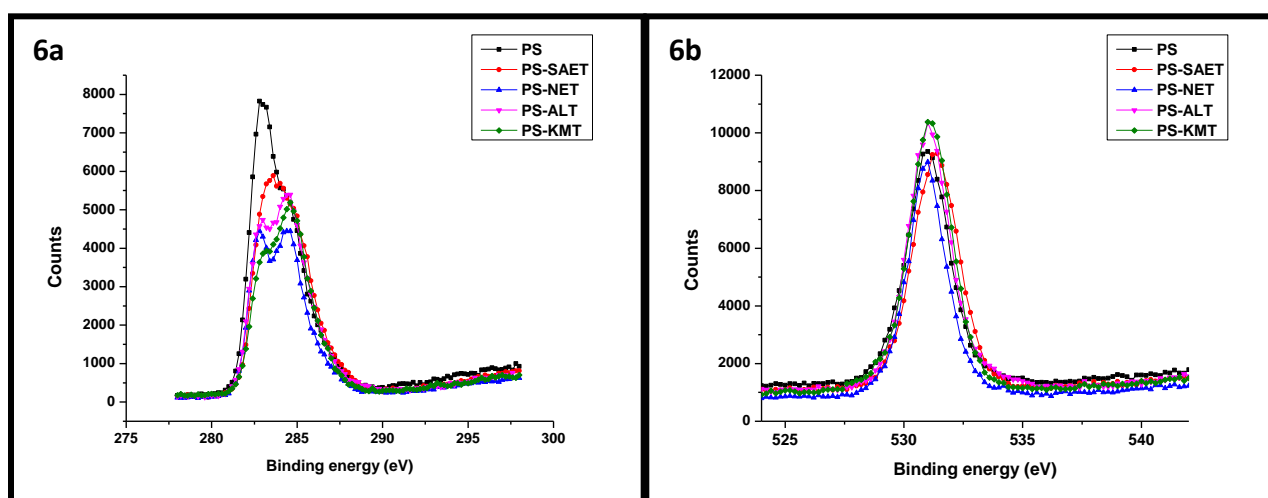

Figure 6a & b: Carbon and Oxygen region respectively of XPS spectra in untreated and treated PS fibers

	PS	PS-SAET	PS-NET	PS-ALT	PS-KMT
C	70.6	70.0	68.1	67.4	64.1
N	27.1	28.1	30.8	31.4	34.2
O	1.5	1.6	0.8	0.6	0.7
Ca	0.3	0.3	0.3	0.6	0.7
P	0.2	0.1	-	0.1	-
Mg	0.2	-	-	-	0.3
Al	0.2	-	-	-	-
K	0.1	-	-	-	-
C-C	18	18	20	14	11
C-O	42	42	22	27	28
C=O	30	31	45	42	49
Carbonate	2	1	2	3	1
O/C	0.38	0.40	0.43	0.44	0.48
N/C	0.021	0.022	0.011	0.008	0.009

Table 3: Elemental Composition of Untreated and Treated PS fiber obtained from Survey Spectra

Bulk Density

Bulk density is an intrinsic property. This is the ratio of the mass of the material and the volume they occupy. The particle volume, internal pore volume and inter void volume constitutes the total volume.

Sample Detail	Bulk Density (g/cm^3)
PS	199 ± 5.0
PS-SAET	152± 1.8
PS-NET	134 ± 0.7
PS-ALT	156 ± 2.8
PS-KMT	172± 1.4

Table 4. Bulk density of untreated and treated fiber

Bulk density of untreated fiber is more than the treated fiber (Table 4). Bulk density of PS-NET fiber is the lowest of all the treatments given to the fiber.

CONCLUSIONS

Chemical surface modification or treatment of natural fibers helps in increasing the adhesion between the fibers which are hydrophilic in nature and the matrix being hydrophobic in nature. Modification of surface of fiber has been explored using different treatments like enzymes, alkali and potassium permanganate. SEM observation confirmed that the all the treatments were capable in removing waxes and the unwanted impurities and thus making the surface of the fiber porous. FTIR spectra showed the removal of hemicelluloses and lignin in all the treatments provided to the PS fiber. An

increase in crystallinity index was observed by XRD in comparison to the untreated fiber. The crystallanity index was maximum for potassium permanganate treatment. The crystallanity index increased ~2-23% for treated PS fibers in comparison to untreated fiber. Thermal studies carried out using TGA also confirmed an increase in the thermal stability of fiber which is confirmed by the increase in T_{max} which has been increased by ~5-15°C for different kind of treatment done on the fiber. XPS studies confirmed the increase in O/C ratio which shows decrease in lignin content and the soluble extractives thus increasing the oxygen exposure on fiber surface.

From the study conducted, it was observed that the chemical treatment takes an edge over the enzyme treatment of fibers in terms of increase in thermal stability, % crystallinity and removal of lignin. The enzyme treatment is equally suitable considering the environmental benefits. The study showed that the agricultural waste, PS has potential to be utilized as a source of reinforcement. The pre-treated PS fiber may further be used to prepare polymer (PE/PP) composites.

EXPERIMENTAL
Materials
Pigeon pea stalk (PS) was collected from Agra, India. The stalk was cut manually into 10-15 cm small pieces and grinded in a Retsch cutting mill, SM 200 with maximum particle size up to 2 mm (Figure 1). Chemicals used for the treatment of PS fiber like sodium hydroxide (analytical grade with 97% purity), potassium permanganate (analytical grade with ≥98.5 % purity) and acetic acid (analytical grade with ≥98.8 % purity) are purchased from reputed company and used without further purification. Laccase enzyme obtained from two sources i.e. L2157 (Rhus Vernicifera) from Sigma and Novozyme-51003 (Aspergillus oryzea) from Novozyme, Denmark. The ash content of PS fiber powder was measured using quartz crucible. The crucible containing known weight of PS fiber was heated at 800°C in microwave furnace for four hours. The ash content was calculated to be 1.5%

approximately using weight difference method. The chemical composition of Pigeon Pea stalk from Indian origin consists of Cellulose (46%), holocellulose (77%), acid insoluble lignin (22%), cellulose to lignin ratio (2:1), pentosan (18%) (Elzaki et al. 2012).
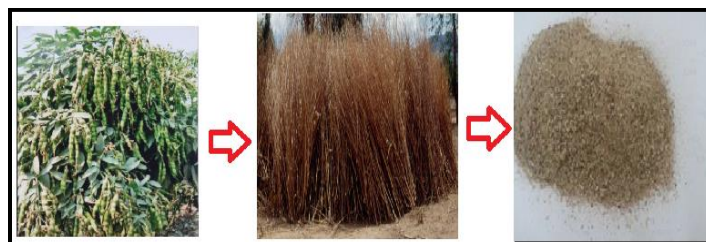

Figure 1. Pigeon Pea Stalk used in grinded (fibers) form

Methods of treatment
The fiber has been studied for three types of pretreatments i.e. alkaline, potassium permanganate and laccase enzyme treatment.

Alkaline treatment of fiber:
PS fibers were soaked in 5% (w/v) sodium hydroxide solution at 23°C maintaining a solution: fiber ratio of 20:1 (ml/g) for 24 h under continuous stirring. The sodium hydroxide solution was prepared in distilled water. After treatment, fibers were thoroughly washed with distilled water to remove any traces of alkali on the fiber surface and to further attain 7.0 pH. The treated fibers (PS-ALT) were then dried.

Potassium permanganate treatment of fiber:
Alkali treated PS fibers were soaked in 0.5% concentrated $KMnO_4$/acetone for 10 minutes with continuous stirring (Khan et al. 2015), maintaining a solution to fiber ratio of 15:1 (ml/g). After treatment fibers were thoroughly washed with distilled water. The treated fibers (PS-KMT) were then dried.

Lacasse treatment of fiber:
Novozyme 51003: Enzyme treatment of PS fiber was carried out at pH 5.5 with enzyme dosage of 1.5 wt% for 4 h under continuous stirring at 23°C (Islam et al. 2013). The pH of the solution was

maintained to 5.5 using acetic acid. A solution to fiber ratio of 30:1 (ml/g) was taken for the experiment. Air flow was maintained for the better treatment of fibers in the vessel containing solution of fiber and enzymatic solution throughout the treatment time. Then the fibers were washed with distilled water until a pH of 7.0 was reached for avoiding any acidic effect on them. The treated fibers (PS-NET) were then dried.

Sigma L2157: Enzyme treatment of 30 u/g was used to treat a PS fiber for 2 h under continuous stirring at 23°C at pH 5.5 maintained with acetic acid (Cao et al. 2012). A solution to fiber ratio of 30:1 (ml/g) was maintained for the experiment. Air flow was taken for the better treatment of fibers in the vessel containing solution of fiber and enzymatic solution throughout the treatment time. Then the fibers were washed with distilled water until a pH of 7.0 was reached for avoiding any acidic effect on them. The treated fibers (PS-SAET) were then dried.

Characterization
Scanning Electron Microscopy (SEM): Morphology of PS fibers was performed using EVO-50 scanning electron microscope (SEM) at the conditions of accelerating voltage of 2.0 kV. Before being examined, the fibers being non-conducting were coated with a thin layer of gold prior to conduction and the final morphologies of the samples were studied (Kaushik et al. 2012).

Fourier Transform Infrared Spectroscopy (FTIR): The FTIR spectra at room temperature were measured in the spectral range of 4000 to 400 cm^{-1} using an FTIR spectrometer (Shimadzu IR Prestige 21). A total of 100 scans were taken for each sample with a resolution of 4 cm^{-1}. The dried PS fibers were pulverized by ball milling before performing spectroscopic measurements, which were obtained of dried PS fibers.

Crystallinity Index: PS fibers were placed in a WAXD analysis using a Rigaku Rint 2000 PC,

Rotating anode–18 KW X-ray diffractometer at room temperature. The XRD patterns of untreated and treated fibers were obtained in the 2θ range of 5–60º at a scan rate of 0.3º/min. *Thermogravimetric analysis (TGA)*: In order to study the change in thermal stability after treatment of PS fibers, TGA was performed using a TA Instrument TGA Q 500. Sample weighing 8-10 mg were taken for the analysis. Thermogravimetric (TG)/derivative thermogravimetric (DTG) traces were recorded at a heating rate of 10ºC/min in N$_2$ atmosphere in the temperature ranging from room temperature to 800ºC.

X-ray photoelectron Spectroscopy (XPS): XPS analysis was performed with a PHI Versa Probe III using a micro-focusing monochromatic Al Kα X-ray source at an operating pressure of not more than 10^{-8} mbar. The spectrophotometer was equipped with a monochromator Al Kα X-ray source (hν = 1486.6 eV) of 200W operating at 15kV. The kinetic energy of the photoelectrons was determined with a hemispherical analyze set to pass energy of 187.0 eV for the survey spectra and of 20.0 eV for high resolution spectra respectively. During all measurements, electrostatic charging of the sample was over compensated by means of a low energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were corrected for electrostatic charging by setting the component peak of the saturated hydrocarbons in the C1s spectrum to 284.8 eV. In all experiments the base pressure in the analysis chamber was less than 10^{-8} m bar.

Bulk Density: Bulk density of PS fibers was obtained by adding a known mass of powder to a graduated cylinder. The density is calculated as mass/volume.

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