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Effects of Acetylation and Alkylation on the Properties of Wheat Straw Fiber

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ABSTRACT

Wheat straw, a lignocellulosic fiber is an agricultural by-product found abundantly everywhere in Bangladesh. This fiber contains about 35% α-cellulose, 25% hemi-cellulose, 23% lignin. As compared to other natural fibers, it is a low cellulosic fiber. Acetylation and alkylation of this fiber were carried out and modified fibers were characterized by physical, mechanical and thermal methods, such as moisture absorption, tensile properties, thermal properties and surface morphology. The moisture content decreases by increasing extent of acetylation and alkylation. Moisture content of alkylated fibers is lower than that of acetylated fibers. Ultimate tensile strength of alkylated fibers are higher than that of acetylated fibers and about 120 MPa for 20% NaOH treated fiber. The Elongation at break or strain of wheat straw fiber increases by increasing extent of acetylation and alkylation. The Young's Modulus of treated fiber increases upto the 10 wt% (concentration) for both treatments. From the analysis of DTA, DTG and TGA profiles, it is found that the thermal stability of acetylated fibers is higher than that of alkylated fibers.

Key words: Wheat Straw Fiber, Acetylation, Alkylation, Thermal Stability, Chemical Modification

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INTRODUCTION

Natural fibers are the main source of cellulose and may be considered as a composite of hollow cellulose fibrils held together by cementing materials like lignin and hemicelluloses [1-2]. It is biodegradable, biocompatible and obtained from renewable resources. Intensive research is going on lignocellulosic fibers as an alternative to man-made fibers to reduce the environmental impact. They are expected to minimize the use of expensive, pollution causing synthetic fibers of petrochemical and mineral origin. Agricultural by-products such as wheat straw, rice straw, corn cobs and stalks are also sources of cellulose based fibers although they have lower cellulose content as compared to wood and other natural fibers [3]. Wheat straw fiber is a hard fiber extracted from the stems of wheat (Triticum aestivum) plant. However, abundant availability of these inexpensive residues could be used for different purposes directly or indirectly in composites preparation. Large amount of unused wheat straw residues is produced every year, and little amount has been used for applications such as feedstock, energy production, plant mulching and rural road pavement construction. Broadened the applications of these agricultural residues could open new markets for wheat straw and help the rural agricultural based economy in Bangladesh. Wheat straw fiber has high specific properties, low density, less abrasive behaviour to the processing equipment, good dimensional stability and harmlessness. Wheat straw fiber also is a low cost, eco-friendly product, easy to transport, superior drivability as well as moisture retention capacity [4-7]. However, there are some disadvantages and limitations to use natural fibers, e.g. when used as reinforcement for composites, are related to the lack of proper interfacial adhesion, poor resistance to moisture absorption, low processing temperature and low dimensional stability (shrinkage, swelling). The elementary unit of cellulose macromolecules are anhydro-D-glucose, which contains three hydroxyl (OH^-) units. The presence of large amount of hydroxyl groups is responsible for the hydrophilic nature of this fiber. Several natural fiber surface treatment methods have been studied to improve the adhesion properties between fiber and surrounding matrix as well as simultaneously to reduce water absorption. Effective methods include scouring, dewaxing, bleaching, acetic acid treatment, alkali treatment, etc. [8-10]. Acetylation is a rather attractive method of modifying the surface of natural fibers and making it more hydrophobic by the reaction of hydroxyl groups (OH^-) of the fiber with acetyl groups

($CH3CO^-$), therefore rendering the fiber surface more hydrophobic. The hydroxyl groups in the crystalline regions of the fiber are closely packed with strong inter-chain bonding, and are inaccessible to chemical reagents [11]. The acetylation of the OH^- group in cellulose is represented below.

$$\text{Fiber-OH} + CH_3\text{-CO-O-OC-}CH_3 \xrightarrow[\text{Conc. } H_2SO_4]{CH_3COOH} \text{Fiber-O-CO-}CH_3 + CH_3COOH$$

Acetylation has been shown to be beneficial in reducing moisture absorption of natural fibers. Reduction of about 50% of moisture uptake for acetylated jute fibers and of up to 65% for acetylated pine fibers has been reported in the literature [12]. Also alkali treatment leads to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The removal of hydrogen bonding in the network structure takes place by the treatment with sodium hydroxide. The alkali treatment reaction is as follows [13-14]:

$$\text{Fiber-OH} + NaOH \longrightarrow \text{Fiber-O}^-Na^+ + H_2O$$

However, there are little or no research report based on the effects of treatments on the properties of wheat straw fiber. In this research we are investigating the effects of acetylation and alkylation on the properties of wheat straw fiber. Modified fiber could be used for different purposes directly or with other materials as composites.

MATERIALS AND METHODS

The wheat straw fiber was collected from local region of Kushtia district in Bangladesh. The removal of dirty materials was carried out in a solution containing 6.5 gm of soap flake and 3.5 gm of soda per liter at 70-75^{0}C for 30 minutes in a large beaker (fiber and solution was 1:50) and washed with distilled water, dried in an open air [15] and finally dried in an oven at 105^{0}C.

Acetylation of Wheat Straw Fiber

10 gm dried fiber was immersed in distilled water for half an hour, filtered and placed in a stopper bottle and covered with 150 ml of glacial CH_3COOH. After being shaken occasionally for 1 hour, the fiber was pressed out as before, the fiber was given a second dewatering as the manner. The fiber with about 20gm of adhering CH_3COOH was taken in a stoppard bottle containing 180 ml of 10% CH_3COOH and 1 ml of concentrated H_2SO_4 at 25^{0}C. The mixture was shaken vigorously for about 1 minute and then 5-20% of acetic anhydride was added and again shaken. The resultant solution was held 5 minutes at 25^{0}C [16,17]. The fiber was then washed with distilled water. Finally, the fiber was dried at 60^{0}C and then stored in a desiccator.

Alkylation of Wheat Straw Fiber

Fibers were soaked in a 5-20% NaOH solution at 30^0 C maintaining a liquor ratio of 15:1 for 2 hours. For investigating the effects of alkali concentration, the fibers were treated with NaOH solutions at varied concentrations by weight (0, 5, 10, 15, and 20%). The fibers were washed several times with demineralised water to remove any NaOH sticking to the fiber surface, neutralized with 2% CH_3COOH solution and finally rinsed again with distilled water until neutral [18, 19]. The fibers were then dried at room temperature for 48 hours followed by oven drying at 105^0 C for 6 h.

Characterization Techniques

The moisture content of acetylated and alkylated wheat straw fibers were measured by using computerized moisture analyzer (KERN RH NO-3) machine. The fibers were placed in the machine and the amounts of moisture in the fibers were observed. Maximum capacity of this analyzer was 120 g. Hounsfield UTM 10KN (H10KS) was used for tensile strength tests of these fibers. Fibers were cut into equal pieces of length 15 cm and the length of each specimen between the jaws of the machine was maintained 10 cm. One twist per 2 cm was given along the length of the fiber between the jaws of the machine. For measuring breaking strength of wheat straw fiber, 0.5 gm of each specimen was weighted out and then the breaking strength of it was measured. The breaking load was gradually increased after starting the machine and at a particular point the specimen was broken down. The machine was stopped at the point of break. The breaking load was shown on the scale of the tensile tester. In each experiment breaking strength for 5 specimens was taken and the mean of 5 readings gave the breaking strength of the fiber. Tensile strength, elastic modulus and elongation at break were determined by this test. Thermo-gravimetric analysis (TGA) and Differential thermal analysis (DTA) of the fibers were carried out in a TG/DTA (SII-6300 analyzer). The samples (4-10 mg) were heated from 30 to 600 °C at 20 °C min $^{-1}$ under nitrogen, after equilibrating at 50 °C. The change of weight percent and its derivative (DTG) were recorded as a function of temperature [13, 17, 27].

RESULTS AND DISCUSSION

The properties of natural fiber depend on the properties of the individual constituents, the fibrillar structure, and the lamellae matrix [20]. This fiber contains 35 % α-cellulose, 25% hemicellulose and 23% lignin which are similar to

some published report [21-22]. Table-1 shows that α-cellulose in wheat straw fiber is much lower than that of banana fiber, pulque fiber and jute fiber. It also contains large amount of hemicellulose and lignin as compared with other natural fiber [4]. The lower amount of cellulose shows the lower crystallinity which affects its different performances.

Moisture content

Fig.1 shows the moisture content of acetylated (5, 10, 15, 20%) and alkylated (5, 10, 15, 20%) fibers. From fig.1 we can see that the moisture content is higher for raw fiber and decreases with increasing acetic anhydride or sodium hydroxide concentrations. Also moisture content of alkylated fibers is much lower than that of acetylated fibers. Both Acetylation and alkylation modify the surface of the fibers and making it more hydrophobic by reducing hydroxyl groups (OH^-) of the fiber with groups ($CH3CO^-$) and (NaO^-).The hydroxyl groups are mainly responsible for moisture absorption which supports previous reports [11, 23-25]. We may conclude that alkylation could remove more hydroxyl groups than that of acetylation.

Table - 1 Amount of α-Cellulose, Hemicellulose and Lignin in Some Natural Fiber

Constituents	Amounts percentage (dry basis)			
	Wheat straw	Banana fiber[4]	Pulque fiber[4]	Jute fiber[4]
α-Cellulose	35	63-64	66	60
Hemi-cellulose	25	19	12	22
Lignin	23	5	7	12

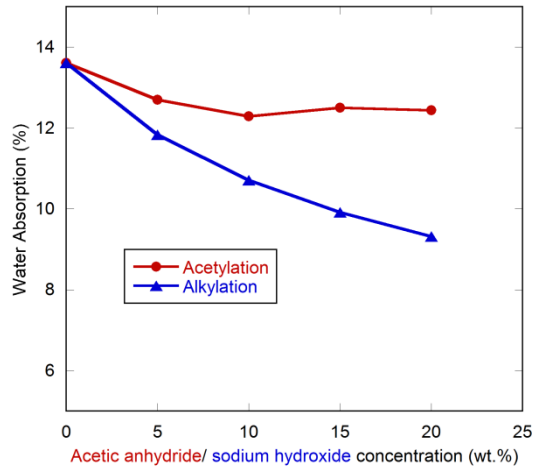


Fig. 1 Effect of acetylation and alkylation on moisture absorption properties of wheat straw fiber

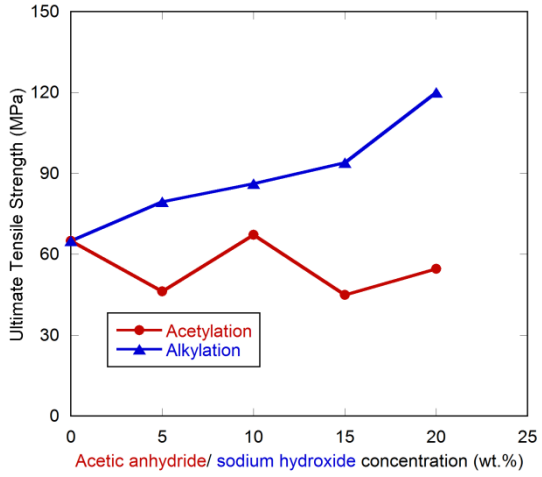


Fig. 2 Effect of acetylation and alkylation on ultimate tensile strength of wheat straw fiber

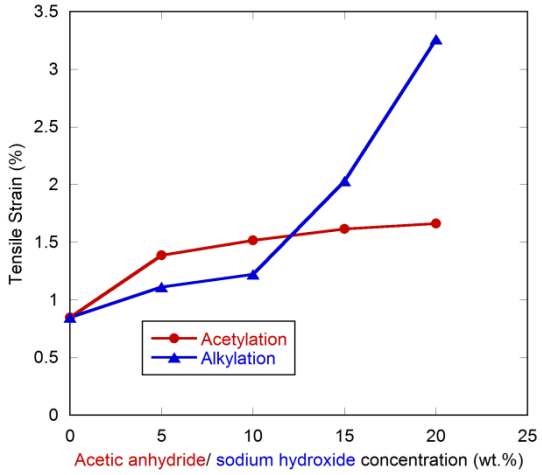


Fig. 3 Effect of acetylation and alkylation on tensile strain of wheat straw fiber

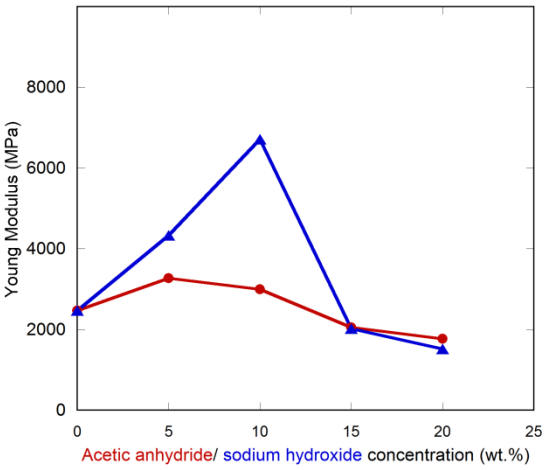


Fig. 4 Effect of acetylation and alkylation on young modulus of wheat straw fiber

Tensile Properties

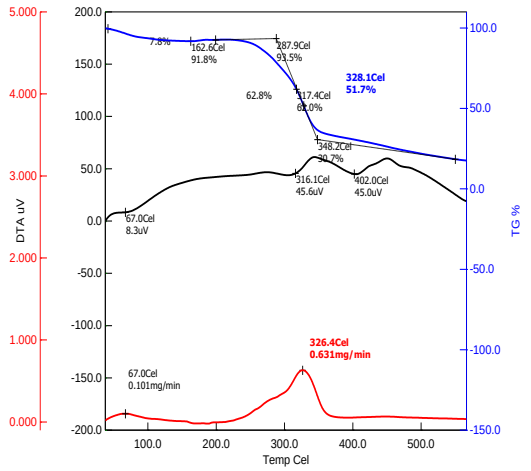
Fig. 2 shows tensile strength of acetylated (0, 5, 10, 15 and 20%) and alkylated (0, 5, 10, 15, 20%) fibers. From Fig. 2 we can conclude that the tensile strength is higher for alkylated wheat straw fiber than that of acetylated and raw fiber. It is because of alkylation wheat straw loses more light materials and replacing more OH^- groups with (NaO^-) [17, 19], which reduces the intermolecular hydrogen bond that present in raw fiber. Another reason of the reduction

of UTS is the loss of more hemicellulose in the fiber during alkylation than that of acetylatioin. Fig. 3 shows tensile strain acetylated and alkylated fiber at different concentrations. Tensile strain is increasing with increasing concentration of acetic anhydride and sodium hydroxide. Fig. 4 shows young modulus of acelytated and alkylated fiber. From fig-4 we can see that young modulus is increasing upto 10% of acetic anhydride and sodium hydroxide concentration and then decreased.

Thermal Properties

Fig. 5 and Fig. 6 show TGA, DTA and DTG profiles of wheat straw fiber at different acetic anhydride and sodium hydroxide concentrations (0%, 5%, 10%, 15%, 20%). Data obtained from these TGA, DTA and DTG profiles are shown in Table 3 and Table 4. It is evident from the TGA curve and data that all fibers contain moisture which is evolved up to about 100ºC and this temperature is called minimum weight loss temperature and about 4-7% minimum weight loss corresponds to the removal of this moisture content. Then the mass is continuous losing having initial slower rate and ending in the faster rate. It's attributed to the start of decomposition of light fractions (pectin, hemicellulose and lignin) slowly. Thermogravimetry revealed that thermal degradation of any fiber depended mainly on the cellulose structure and the content of non-cellulosic components that were present in the fiber. The components of the fibers and the nature of the cellulose contribute significantly to the thermal stability. 50% weight loss occurred at 328-360°C.

Differential thermal analysis (DTA) is a technique by which phase transition or chemical reactions can be followed through observation of heat absorbed or liberated. With constant heating, any transition or thermally induced reaction in the sample will be recorded as a peak or dip in an otherwise straight line. An endothermic process will cause the thermocouple junction in the sample to lag behind the junction in the reference material, and hence develop a voltage, whereas an exothermic event will produce a voltage of opposite sign. It is customary to plot exotherms upward and endotherms downward [26]. Two endothermic DTA peaks at 67-73ºC and 316-360°C were obtained.



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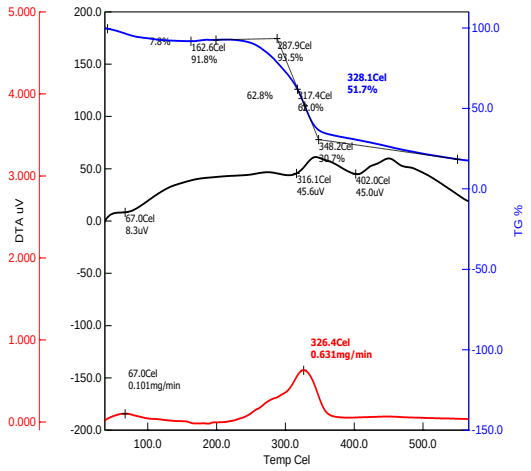

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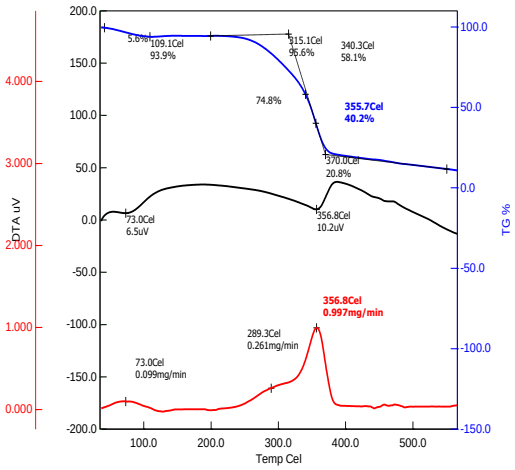

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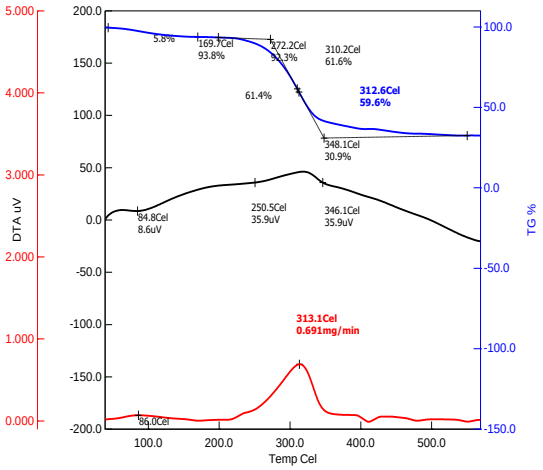

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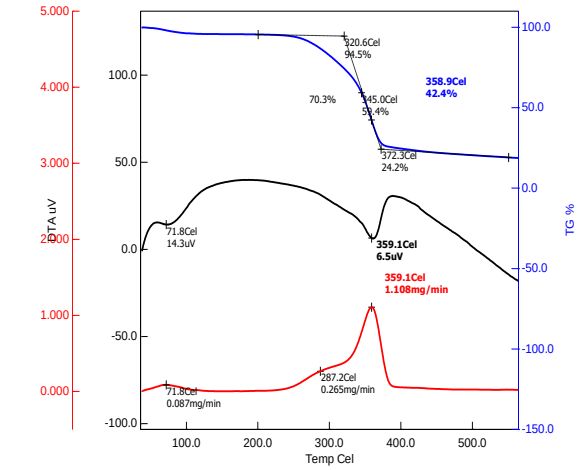

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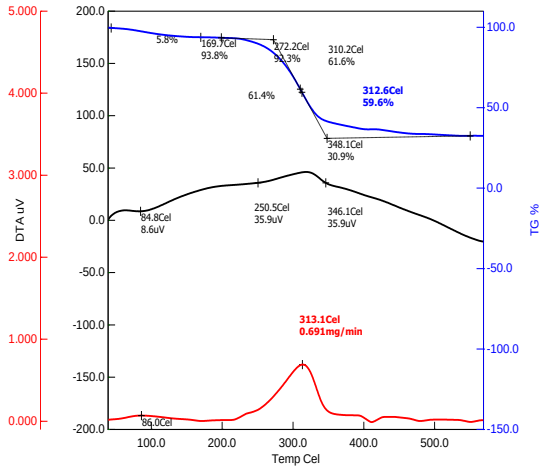

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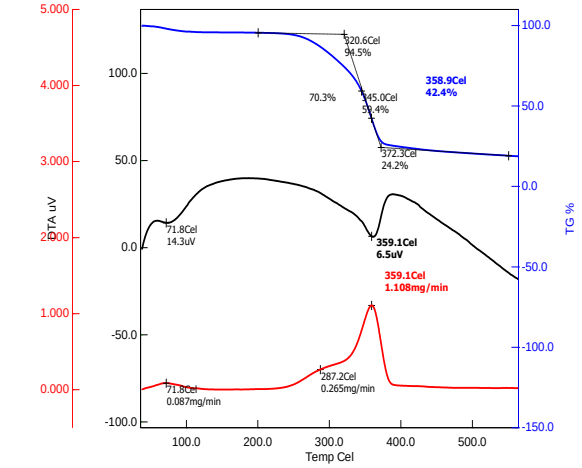

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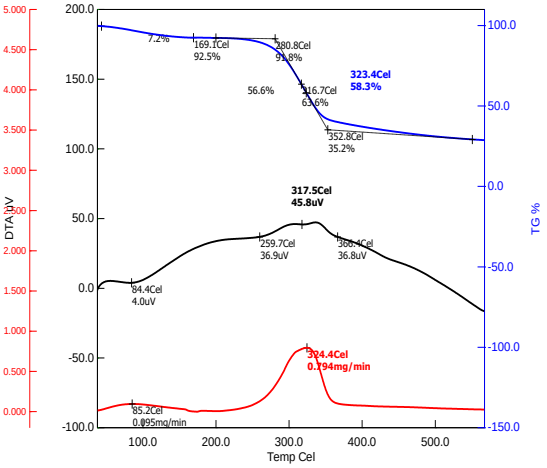

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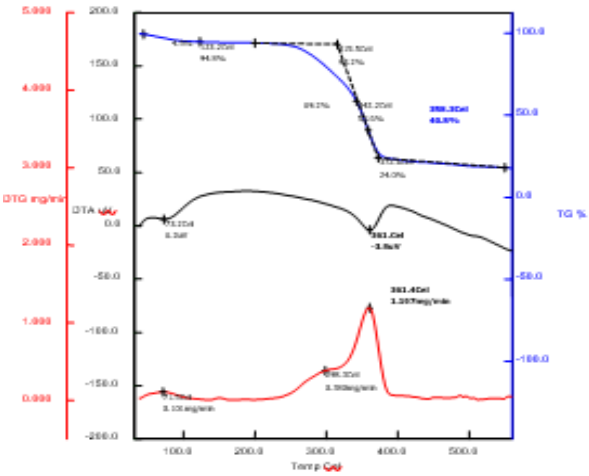
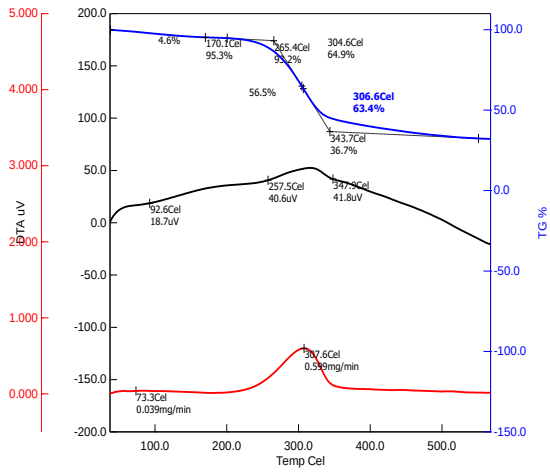


e

Fig.5 TGA, DTA and DTG of acetylated fiber at different acetic anhydride concentrations [(a) 0% , (b) 5%, (c) 10%, (d) 15%, (e) 20%]



e

Fig. 6 TGA, DTA and DTG of alkylated fiber at different sodium hydroxide concentrations [(a) 0%, (b) 5%, (c) 10%, (d) 15% and (e) 20%]

The 1st peak is due to removal of moisture is consistent with TGA data, 2nd peak is for degradation. Two exothermic DTG were also found which are corresponded to lighter material and heavier material. From the analysis of DTA, DTG and TGA profiles data, it is found that the thermal stability of acetylated fibers is higher than that of alkylated fibers. This is consistent with previous results that alkylation removes more hydroxyl groups from the fiber and causes the more degradation than that of acetylation.

Table-3 TGA and DTG Data of Acetylated and Alkylated Wheat Straw Fiber

Samples	Initial loss (%)	Initial degradation (°C)	Initial degradation rate (mg/min)	50% loss at °C	Maximum degradation (°C)	Maximum degradation rate (mg/min)
Raw fiber	7.0	67.0	0.101	328.1	326.4	0.631
Acetylated-05%	5.6	73.0	0.099	355.7	356.8	0.997
Acetylated-10%		71.8	0.087	358.9	359.1	1.108
Acetylated-15%	4.6	71.4	0.107	358.7	360.7	1.191
Acetylated-20%	4.5	71.5	0.101	358.3	361.4	1.197
Alkylated - 05%	52.	81.2	0.070	327.3	326.7	0.845
Alkylated - 10%	5.8	86.0	0.091	312.6	313.1	0.691
Alkylated- 15%	7.2	85.2	0.095	323.4	324.4	0.794
Alkylated - 20%	4.6	73.0	0.039	306.6	307.6	0.599

Table-4 DTA Data of Acetylated and Alkylated Wheat Straw Fiber

Sample	1st peak at °C	2nd peak at °C	3rd peak at °C
Raw fiber	67.0	316.1	402.0
Acetylated-05%	73.0	356.8	.....
Acetylated-10%	71.8	359.1	.....
Acetylated-15%	72.7	360.7	.....
Acetylated-20%	73.2	361.1	
Alkylated - 05%	81.2	265.5	325.7
Alkylated - 10%	84.8	250.5	346.1
Alkylated - 15%	84.4	259.7	368.4
Alkylated - 20%	92.6	257.4	340.9

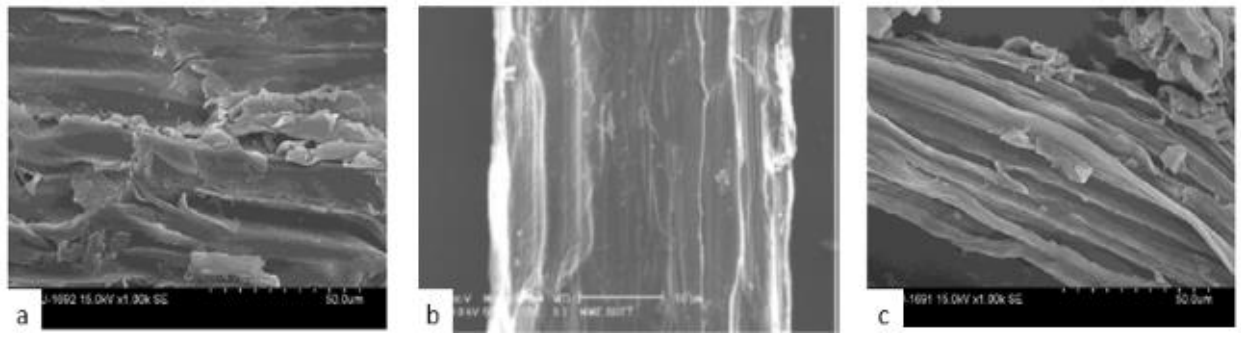


Fig. 7 SEM micrograph of (a) raw, (b) 10% Acetylated and (c) 10% Alkylated wheat straw fiber

From Fig.7 we see that the diameter of the original wheat straw fiber was much bigger and each fiber appears to be composed of several microfibrils [Fig.7 (a)]. Each elementary fiber possesses a compact structure; exhibiting an alignment in the fiber axis direction. The micrograph of non-treated wheat straw fiber also shows a lot of non-fibrous components scattered over the fiber surface and is smooth due to the presence of waxes and oil. On acetylation through complex formation and depolymerisation occurs and fiber gets smoother [Fig.7 (b)]. By the treatment with alkali, the hemicellulose becomes water soluble by hydrolysis. These help in defibrillation of the fibrils and result in micrograph [Fig.7 (c)] whereby the diameter of the fibrils is reduced to a great extent, also possibly because of removal of other constituents. This result is consistent with previous results.

CONCLUSIONS

On the basis of results obtained from our investigation, the following conclusions may be drawn:

- Wheat straw is a low lignocellulosic fiber.
- Water absorption of treated fiber decreases with increasing extent of acetylation and alkylation. Moisture content of alkylated fibers are lower than that of acetylated fibers.
- Tensile strength and tensile strain of wheat straw fibres were found to be affected by acetic anhydride and sodium hydroxide treatment and higher for alkylated fiber than that of acetylated fiber.
- From the TGA and DTG curve, it can be concluded that thermal stability of acetylated fibers are higher than that of alkylated fibers. This is because except scouring all types of chemical treatment affect the cellulose structure of the fiber.
- SEM shows that treated fibers have the relatively rough surfaces than that of raw fiber and fiber diameter reduced by the treatment.

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