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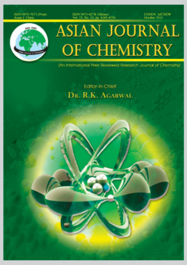

Effect of Applied Different Surface Modification Processes with Cellulose Enzyme on Properties of Luffa Fibres

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Among the natural fibres, luffa cylindrical fibres are the ones that are widely available throughout the world. Luffa fibres are known to have lignocellulosic fibre characteristics.Ligno cellulosic lignin content of fibers and other wastes of various chemicals to clean the surface processes. In this study, cellulase enzyme lignocellulosic-based fibers have the luffa fibers, except with the conventional methods are environmentally friendly and energy, water, power, time-saving microwave, ultrasonic energy surface modifications were made using different methods. The results obtained were examined with %weight loss values, mechanical properties, morphological characteristics (SEM) followed by FT-IR and X-ray powder diffraction. Three different chemical processes, carried out cellulase enzyme were proved to be successful. The reason for the microwave processes to be successful is the strength achieved by sonication. This cellulase enzyme processes were found to adequately modify the fibres surfaces.

Key Words: Luffa cylindrica fiber, Cellulase enzyme, Ultrasonic energy, Microwave energy.

INTRODUCTION

An increasing concern for the environment has given impetus to research on lignocellulosic fibers for total or partial substitution of petroleum-based synthetic fibers, which are neither renewable nor biodegradable[1]. Lignocellulosic fibers are composite materials of lignin, cellulose, hemicellulose and extractives, in which lignin with hemicellulose, is situated as filler between the highly ordered cellulose microfibrilles[2]. The lignocellulosic fiber as well as luffa cylindrica fiber exhibits high hydrophilicity nature due to attraction or interaction between the hydroxyl groups of fibre components and water molecules. The interactions between fibre and water originate from the non-crystalline region and extend to the crystalline region. The uptake of water by hygroscopic substance such as cellulose (non-crystalline, crystalline) and hemicellulose is a hydration process involving accessible hydroxyl groups. Water molecule absorbed by cellulose molecule form cellulose hydrate and the reaction is exothermic, which provide the driving force for further absorption[3,4]. The use of enzyme technology is increasing substantially in the processing of natural fibre. The use of enzyme in the field of textile and natural fibre modification is also rapidly increasing. The major reason for embracing this technology is the fact that application of enzyme is regard as environmental friendly and the reactions catalyzed are very specific with a focussed performance as a consequence. Other potential benefits of enzyme technology include cost reduction, energy and water saving, improved product quality and potential process integration[5]. The application of enzymes to modify the surface of natural fibre, such as hemp, flax, wool, cotton has been widely researched by industry. Most of the industrial applications are aimed to improve surface properties by removing adsorbed components, such as lignin, fats, waxes, proteins and non-crystalline parts.

Today, bio-finishing processes are important for textile finishing. Enzymatic processes applied on cellulosic fabrics are called bio-finishing processes. The enzymes involved in such processes are bio-catalysts formed by metabolic products of living organisms obtained from bacterial derivatives[6]. Amylase is used in desizing, protease for protein fibers such as silk and wool, catalase to remove peroxide following bleaching, lactase to remove indigo dye from denim fabrics, peroxidase in oxidation of the covalent-bonded dye contained in reactive dyestuff, lipase as desizing inducer and degreaser in thread spinning where solid and liquid grease is present, pectinase to bio-clean raw cotton or flax, cellulase in enzymatic stone washing and removal of fibril ends from fiber surfaces of jeans and denim fabrics[7,8]. The fibril ends originating from the fabric surface are the reasons underlying the pilling problem. Purer, softer and denser fabric handling is ensured by performing enzymatic processing prior to dyeing.

Cellulases are highly molecular colloidal proteins obtained from *Aspergillus niger*, *Trichoderma longibrachiatum*, *Fusarium solani* and *Trichoderma viride*. Industrial cellulases, on the other hand, are complex forms, not entirely smooth, of compounds of enzymes such as cellulase and cellobiase. An enzyme-substrate complex is formed in enzyme catalysis (cellulase-cellulose complex). Cellulases are capable of snapping the 1,4 β-glucoside bond of cellulose. Three classes of enzymes display synergetic impact and effect cellulose in a complex way. Endoglucanases affect dissolved and undisclosed glucose chains. Exoglucanase pulls apart the glucose unit on the end of cellulose and cellobiase (glucose dimmers) units on the end of the cellobiohydrolase (CBH) cellulose chain. β-Glucosidase produces D-glucose[8]. In the textiles processing areas, such as desizing, scouring and bleaching of cellulose and woollen fabrics are some examples of successful bio-treatments of textiles[9].

This fiber is quite common in the mid-south of America as well. As for Turkey, it grows well in the areas of the Mediterranean climate. The luffa cylindrical fibers are a subtropical plant of the cucurbitaceous family, which produces a fruit with a fibrous vascular system. Their size varies in relation to the areas they grow in ranging from 15 cm to 1 m or even more than 1 m in certain kinds (Fig. 1)[10]. It has wide use of luffa cylindrical as scouring pads during bathing, for the manufacture of palm sole, inner soler for filters, leather straps for automobiles and other engine etch in the industrial sector[11].

Fig. 1. Luffa fibres

A number of investigatators have explored the capability of additives to enhance adhesion and thereby improve properties, such as tensile, impact and flexural strengths of these composite materials[12,13]. The methods for surface modification can be physical or chemical according to the way they modify the fiber surface frequently used approaches are bleaching, acetylation and alkali treatments. When the chemical characteristics of luffa cylindrical are considered, it can be seen that just in the case of such fibers as manila, sisal, jute, hemp, they consist of cellulosic polymer which are composed of various non-cellulosic impurities that do not affect the hydrophilic characteristic of luffa cylindrical fibers negatively (Table-1)[14].

For this purpose, there are studies carried to improve the hydrophilic characteristic of luffa cylindrical by means of chemical processes. With this aim, mercerization was applied on luffa cylindrical fibers[15], by acetylating and the derivation

TABLE-1
CHEMICAL COMPOSITION OF
LUFFA CYLINDRICA FIBRES [Ref. 14]

Component	Content (%)
Holocellulose	82.4
α-Cellulose	63.0
Hemicellulose	19.4
Lignin	11.2
Extractives	3.2
Ashes	0.4

was achieved[16]. In addition to this, anion exchange capacity of luffa cylindrical fibers and their quaternizated specialties were tested[17]. Luffa cylindrical fibers were coated with different kinds of tip silane agent in order to improve the characteristics of the composite produced from LF/PP[18]. Most of these studies are based on cleaning those impurities affecting the mechanical, chemical, physical and sorption characteristics of luffa cylindrical fibers.

Ultrasonic energy has always been an alternative method. The action of ultrasound energy has become popular in textile sector with positive results in bleaching and dying processes[19-25].

Cavitation is the formation and violent collapse of small bubbles or voids in the liquid as a result of pressure changes. This occurs when longitudinal waves propagate through the liquid. Cavitations cause several chemical and mechanical effects, such as dispersing, degassing, formation of free ions or radicals and intense agitation of the liquid[26].

When the microwaves become 13.56, 27.12 and 40.68 MHz at region of R_f which are industrial frequency, the frequency ranges are between 910-2850 MHz for the MD. Using of microwave technology in textile finishing is related with application, research and development studies which enclose application areas of heating up, drying, condensation, dying and printing[26-35].

In this study, cellulose enzyme was applied on luffa cylindrical fibers with three different kinds of processes which are conventional, ultrasonic energy and microwave energy methods. According to the results of in luffa cylindrical fibres in terms of mechanical, hydrophilic and morphological characteristics.

EXPERIMENTAL

Luffa cylindrica fibres were obtained from the Mediterranean region of Turkey. Its fruit has a fibrous vascular system that forms a natural mat when dried. Their overall lengths are between 400 mm and 600 mm. The luffa fibres were washed with water to remove the adhering dirt. (20 ºC distilled water for 0.5 h). They were dried in an oven at 70 º C for 6 h. After drying, they were conditioned 48 h prior to testing under ± 20 °C and 65 ± 2 RH % condition.

Chemical treatments of luffa fibers treatments: Luffa fibers have been exposed in to three methods in which are given conventional methods, ultrasonic methods and microwave methods in Tables 2-4, respectively. In addition of that, it is applied two kind of chemical processes for each three methods. Ultrasonic method Branson B2200B E4 was carried out at (220 volt and 205 Watt) ultrasonic bath with 20 kHz frequencies.

TABLE-2
CONVENTIONAL METHODS APPLIED TO LUFFA CYLINDRICAL FIBERS

	Solution (chemicals)	Producer/ Supplier	Concentration (g/L)	Temperature (°C)	Time (min)	Rinsed process (25 °C, 10 min, pH 7)	Dry process
Conventional methods	Non-ionic cellulase enzyme activity (800-900IU/G pH 5)	Denepol Bio-Denge Chemistry Turkey	1:100	50 (initial temp.)	30	Distilled water	At room temperature
				70 (final temp.)			

TABLE-3
ULTRASONIC ENERGY METHODS APPLIED TO LUFFA CYLINDRICAL FIBERS

	Solution (chemicals)	Producer/ Supplier	Concentration (g/L)	Temperature (°C)	Time (min)	Rinsed process (25 °C, 10 min, pH 7)	Dry process
Ultrasonic methods	Non-ionic cellulase enzyme activity (800-900IU/G)	Denepol Bio-Denge Chemistry Turkey	1:100	20 (initial temp.)	15	Distilled water	At room temperature
				40 (final temp.)			

TABLE-4
MICROWAVE METHODS APPLIED TO LUFFA CYLINDRICAL FIBERS

	Solution (chemicals)	Producer/ Supplier	Concentration (g/L)	Temperature (°C)	Time (min)	Rinsed process (25 °C, 10 min, pH 7)	Dry process
Microwave methods	Non-ionic cellulase enzyme activity (800-900IU/G)	Denepol Bio-Denge Chemistry Turkey	1:100	20 (initial temp.)	2	Distilled water	At room temperature
				30 (final temp.)			

Microwave method with a Galanz/WP800T was carried out at a frequency of 2.45 GHz. The microwave oven had a maximal power of 800 W with six discrete settings. The mixtures were placed in a sealed glass vessel and treated by the microwave according to the experimental design.

Analytical methods: The weight loss was determined on atmospherically conditioned luffa fibres after different pre-treatment processes, with and without ultrasound. The weight loss percentage (W_i) was calculated from the differences in weight using the following (eqn. 1):

$$W_i = \frac{W_{pre} - W_{after}}{W_{pre}} \times 100\% \quad (1)$$

where W_{pre} is the weight of the conditioned fibres prior to pre-treatment and W_{after} is the weight after performed pre-treatment. Following the conventional ultrasonic method and microwave methods, luffa cylindrica fibre's property is given in Table-1.

Testing and characterization of luffa cylindrica fibres after chemical treatments: Applying the conventional, micro wave and ultrasonic energy methods on luffa cylindrica fibres (single fibres length 10 mm) mechanical characteristic values were performed based on ASTM D 3822 with Instron 4411 (50 N load, speed of 10 mm/min) resistance device. FTIR analysis of the fibres was performed on Shimadzu 8300 FTIR spectrophotometer (between 4000-400 cm^{-1}). Also, morphology properties were investigated by JEOL JSM-5410 LV operated at 20 kV.

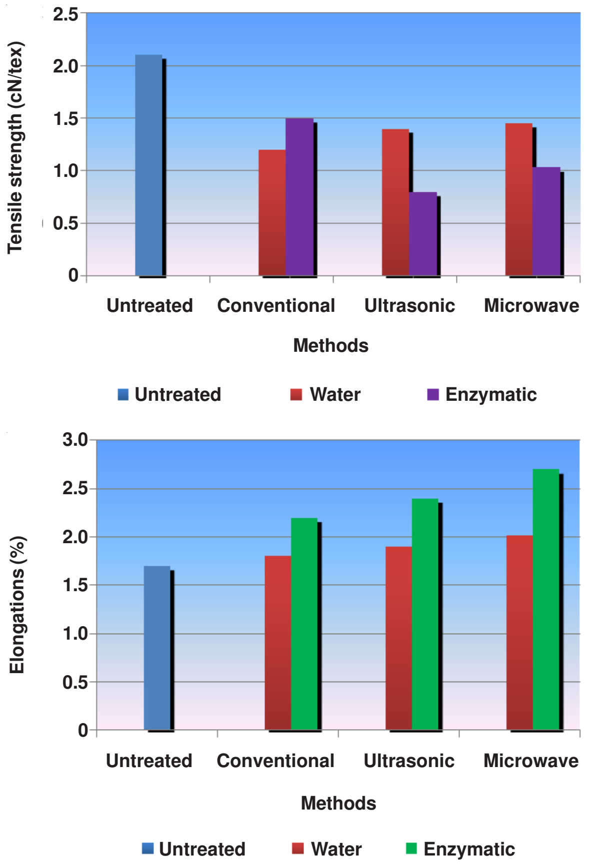

Fig. 2. Mechanical changes in luffa cylindrica fiber following the chemical treatments

RESULTS AND DISCUSSION

Mechanical properties: Fig. 2 shows the mechanical change values of luffa cylindrica fibres after the conventional, microwave and ultrasonic energy method and Table-5 shows % weight loss values. By comparing present results to reference data obtained with luffa fibers, itis observed that the ultrasonic method values given in the literature for the tensile strength and the elongation[23,24]. By comparing the tensile strength,

TABLE-5
LUFFA CYLINDRICAL FIBRES WEIGHT REDUCTION FOR DIFFERENT TREATMENT CONDITIONS (ROOM TEMPERATURE)

Processes	Weight reduction (%)
Conventional water treatment	0.4
Ultrasonic water treatment	0.7
Microwave water treatment	0.8
Conventional cellulase enzyme treatment	1.0
Ultrasonic cellulase enzyme treatment	3.5
Microwave cellulase enzyme treatment	6.3

elongation values of untreated fibers with conventional, ultrasonic and micro wave methods in the determination of these parameters and the data scattering. It appears that the chemical treatments (cellulase enzyme used) reduce the mechanical properties. It can be explained by considering of waxes, gums, *etc*. However acetylation and formylation ultrasonic and microwave methods are made with increases mechanical properties.

The structural changes induced by cellulase enzyme treatment altered the mechanical properties of the fibres as indicated by decreased tensile strength and elongation. When mechanical properties of modified fibres were compared with raw fibres. These decreased with removing of tallow, wax and lignin on the fibres by modifying of surface on three processes. At least differences of mechanical properties were obtained with microwave process. As the reason of this, processing of microwave method is too short and minimizing of mechanical negation. The fibres surface, separated fibre cells, removed lignin, extractive wax and increased the surface area as well as the pore size in the SEM micrographs. The reason for this as demonstrated that microwave irradiation played a positive role in biomass digestion, it has become desirable to investigate the key operating parameters affecting the pre-treatment so as to optimize the conditions for a further efficient hydrolysis of biomass[25].

Pre-treatment processes on the decomposition of impurities and natural pigments are generally characterized by weight loss. It is evident from the result that the acetylation and formylation caused weight lost[23,24]. However, in ultrasonic method and microwave processes weight loss % is higher. In the literature studies carried out, luffa cylindrica fibres loss following the chemical processes is 3-6 %[16]. The reason why such rates are higher within the applied ultrasonic energy processes due to sonication. However, microwave methods are used for weight loss results are better than ultrasonic methods surface fiber energy more quickly due to transmission surface luffa fibre; uniformity of heating, faster throughputs, fast on and off switching, very high power densities developed in the processing zone, superior moisture levelling.

FT-IR analysis properties: The effectiveness of the cellulase enzymes were confirmed by FT-IR analysis. Fig. 3 shows, the spectra of the raw, Fig. 4 shows luffa cylindrica fibres ultrasonic energy cellulase enzyme chemical application results and Fig. 5 shows luffa cylindrica fibres microwave energy cellulase enzyme chemical application results with FTIR. FT-IR (KBr disc, ν_{max}, cm^{-1}): 3560 (-OH), 2920 (aliphatic strength), 1735 (-C-O ester), 1022 (C-O-C), respectively.

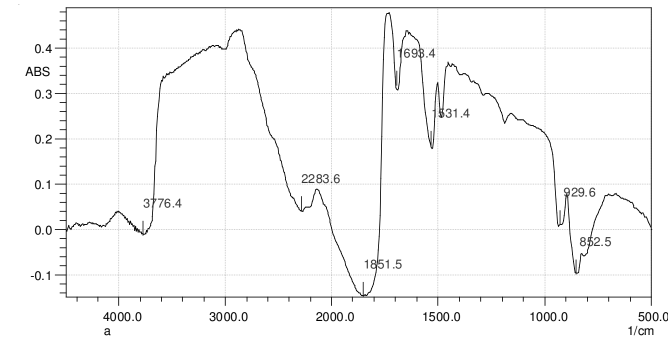

Fig. 3. FTIR spectrum of raw luffa cylindrica fibres

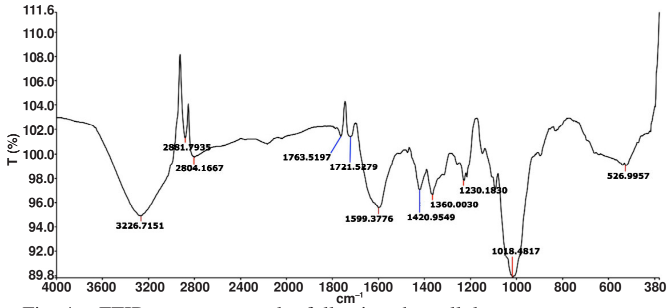

Fig. 4. FTIR spectrum results following the cellulase enzyme treatment with conventional process

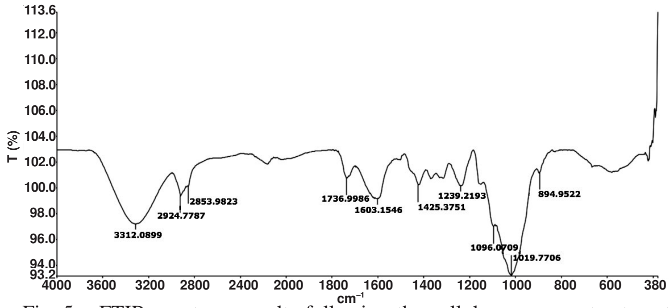

Fig. 5. FTIR spectrum results following the cellulase enzyme treatment with ultrasonic energy

In the FTIR spectrum of the raw fibre, the signals at 3776 and 1647 cm^{-1} can be assigned, Fig. 4 shows that luffa fibres with acidic treatment and ultrasonic energy and Fig. 5 shows FT-IR results with ultrasonic energy and microwave energy on fibres FT-IR with a sharp reduction in the signals assigned to the hydroxyls. However, the remaining signal at 3281-3046 cm^{-1} can be assigned to residual hydroxyl groups. OH group reaction occurred preferentially at the easily accessible hydroxyl group on the cell walls of the fibres. Syndication effect is quite high on accelerating the reactions[16].

The signals at 3568 cm^{-1} correspond to water adsorbed by the fibre. The sharp signals observed at 1714 and 1639 cm^{-1} are assigned to a carbonyl of acetate and formyl group. The presence of these signals in the spectra of the treated fibres confirms that the cellulase enzyme reaction and formyl group reaction were effective. In fact, the partial substitution of the -OH groups on the fibres are interesting, since its hydrophilic character were reduced[17].

SEM observation of luffa cylindrica fibres: SEM micrographs of untreated luffa cylindrica fibres are presented in Fig. 6. Figs. 7-11show SEM photographs of fibres treated with cellulase enzyme by ultrasonic, microwave, conventional

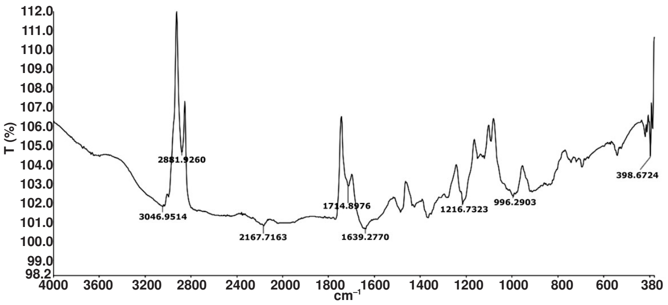

Fig. 6. FTIR spectrum results following the cellulase enzyme treatment with microwave energy

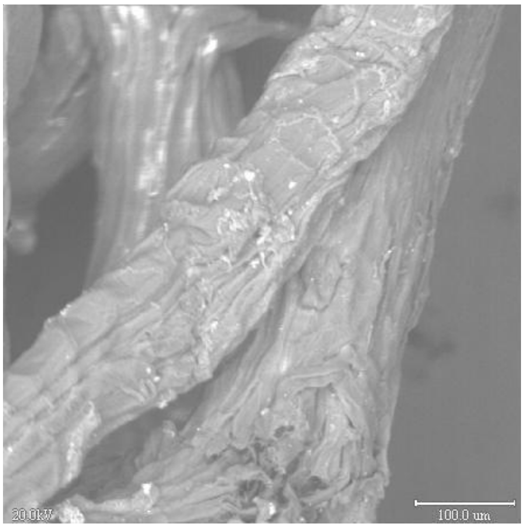

Fig. 7. Untreated luffa cylindrica fibre

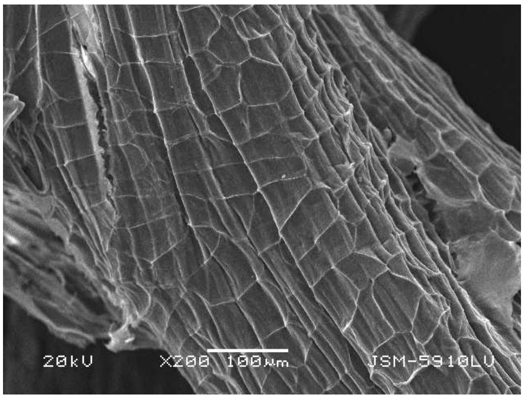

Fig. 8. Treated luffa cylindrica fibre with cellulase enzyme by conventional process

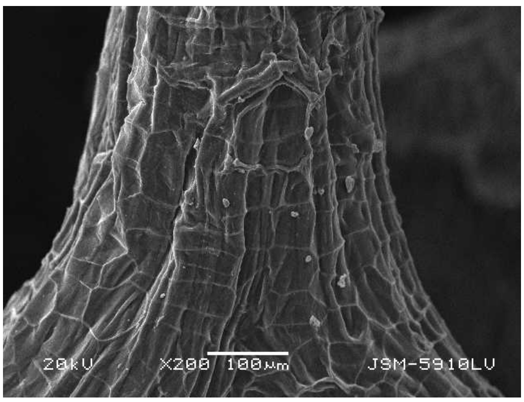

Fig. 9. Treated luffa cylindrica fibre with cellulase enzyme by ultrasonic process

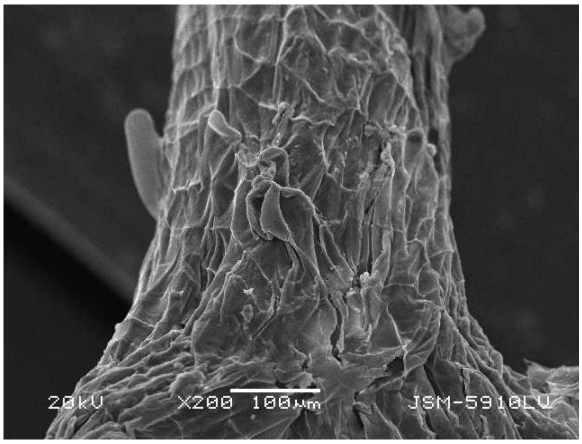

Fig. 10. Treated luffa cylindrica fibre with cellulase enzyme by microwave process

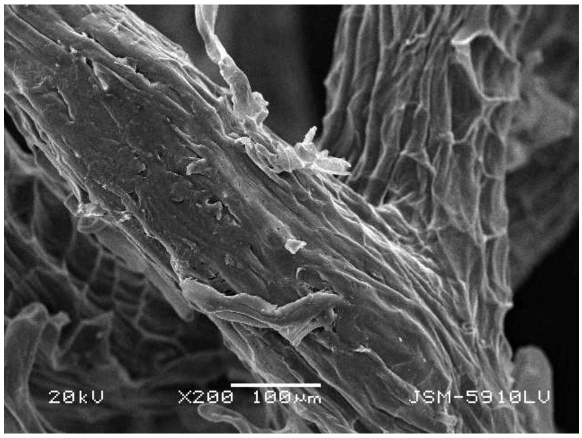

Fig. 11. Treated luffa cylindrica fibre with cellulase enzyme by microwave process

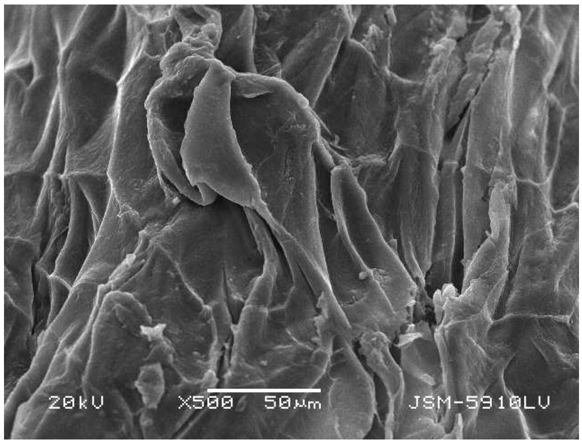

Fig. 12. Treated luffa cylindrica fibre with cellulase enzyme by microwave process

processes. The conventional processes carried out on flax fibres with formic acid, is known to disclose micro fibres better than those treatments achieve with NaOH[28]. It is also known that it reveals the macro fibres on the surface of luffa cylindrica fibres. Following the treatment with cellulase enzyme by means of microwave, the outer layers of parenchyma cells have been removed to expose the inner fibres. The coating of the fibres wore out more as shown in Fig. 8.

Conclusion

Two different processes and four different chemical processes, carried out with cellulase enzyme were proved to be successful. The fibres modification obtained with using of the conventional method has better results than using of both ultrasonic and microwave methods. The best results of reducing of fibres strength and elongation in wet process were obtained by microwave method.

Cellulase enzyme chemical treatment processes were found to adequately modify the fibres surfaces. In this study, % weight loss increase is outstanding with the success of ridding the impurities. Weight loss results can be correlated with mechanical test results, which can be treated as a proof for enhanced interfacial interactions with microwave energy better then ultrasonic energy treatment. Beyond the all results, microwave process is clearly provided to saving of chemical substance, energy, water and time.

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