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Properties of ball milled thermally treated hemp fibers in an inert atmosphere for potential composite reinforcement

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Hemp (*Cannabis Sativ L.*) is an important lignocellulosic raw material for the manufacture of cost-effective environmentally friendly composite materials. From an earlier experiment it was found that when hemp bast fibers were heated between 160°C and 260°C, there was softening of lignin leading to opening of fibers and the preliminary observations showed that heat treatment at 220°C in an inert environment seemed to provide enough fiber without affecting the associated tissues of the fibers. However, these heat treated fibers need to be separated by mechanical action. For this experiment, hemp fibers were given heat treatment in an enclosed vessel in a nitrogen environment at 220°C for 30 min and then they were ball milled. It was found that there was further opening of fibers upon ball milling of the heated fibers and the total number of fibers increased for the equal weight of fibers. It was not possible to find strength properties of shorter length fibers; however, the results from shorter clamping length indirectly indicated that these fibers were of higher strength. The ball milled fibers also contained copious amount of fines which must be removed before using the fibers for composite manufacturing.

1. Introduction
1.1. General
Ecological concerns have given fresh impetus to the use of natural fibers. Natural fibers are cheap, renewable, biodegradable and nonabrasive. They have a high aspect ratio, a high strength to weight ratio, low density, and good tensile strength and modulus. These properties make them attractive alternatives to glass fibers for reinforcement in engineering composites. However, natural fibers have high low-dimensional stability, poor microbial resistance, and low compressive strength. The challenge in promoting their widespread industrial use lies in overcoming those deficits without compromising their inherent merits.

Natural fibers are bundles of individual strands of fibers. Most of the research has focused on fiber bundles consisting of secondarily thickened, highly elongated fiber cells [1]. However, within the walls of plant cells, there is a second level of fiber structure on a much smaller scale, held together by bonds of pectin and lignin, which is a weak bond whose strength is far less than that of the individual fibers. This is the limiting factor because, when these bonds fail on application of force, the whole fiber bundle fails. If these binding materials are removed and individual fibers are released without damaging them, they can potentially produce composites of high strength. Current processes for removing lignin include chemical or chemo-mechanical treatment. The major drawbacks of such treatments are that they are costly and use wet processes and that they change the chemical nature of the fibers. This makes them undesirable for composite manufacture. Thermomechanical processes can also be used to release individual fibers from fiber bundles. When fibers are subjected to heat treatment much above the glass transition temperature of lignin, it is postulated that lignin will be softened and released. During heat treatment, the lignin and to some extent the hemicellulose are depolymerized into smaller molecules with aldehyde- and phenolic functionalities, leaving cellulosic microfibrils [2].

There are some more advantages of these processes. During the heat treatment, lignin and/or extractives migrate to the fiber surface increasing the hydrophobicity of the surface [3, 4] and are likely to improve the capability with the matrix such as polypropylene [5]. Also during processing of composites particularly based on thermoplastics, the moisture content can

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lead to poor processability giving undesirable porous products [6].

In the first phase of the experiments, a natural fiber (hemp) was used. Heat treatment was performed in an air as well as in an inert atmosphere. The strength parameters were determined by fiber pullout tests. There were large standard deviations for each strength parameter due to various uncertainties in the experiments. It was not possible to conclude that the difference between any two samples was statistically significant at the 90% confidence level. However, the goal was to obtain a qualitative idea of the performance of the treated fibers. Based on the results, the treatment protocol for several minutes at a high temperature in an inert atmosphere seemed to give the maximum strength and stiffness. Also heat treatment led to defibrillation of the raw fibers. Further experiments are being carried out to arrive at more precise values and to study the surface topology.

1.2. Size reduction of fibers by ball milling

After heating the fibers in a nitrogen environment in order to soften the lignin, the next step is to defibrillate the fibers or open up the fiber bundles into individual strands of fibers. While heating results in softening the lignin, which binds the microfibrils, it still needs some shear forces in order to break the bonds.

Size reduction is a process in which particles are broken into smaller pieces. Generally there are four processes involved: (1) cutting, (2) attrition or rubbing, (3) impact, and (4) compression [7]. Compression is coarse reduction of hard solids; impact yields medium and fine products; attrition gives fine products while cutting is employed to obtain materials of definite size. For our purposes where the aim is to open up the fiber bundles, mostly along the diameter, keeping the length intact as far as possible and without damaging the opened up fibers, the choice would be a process of impact and attrition. The mills where such fibers can be defibrillated by impact and shear forces are called tumbling mills. A cylindrical shell rotates about a horizontal axis filled part by solid grinding media and part by the feed. Tumbling mills could be (a) rod mills (b) ball or pebble mills (c) tube or compartment mills.

For this study, ball milling is chosen to defibrillate the inert atmosphere heated fiber bundles. The ball milling process used for fiber opening processes has a number of potential advantages.

- the reduction is carried out mostly by shear, hence, the possibilities of fiber bundles opening into fibers along the diameter is high; at the same time the reduction in length will be minimal;
- the process operates at room temperatures thus increasing the safety and reducing energy the consumption;
- the process uses well established mineral processing equipment and principles;
- the process results in a high degree of agitation helping in breakage of any agglomerated material;
- no gaseous emissions or liquid effluents are produced.

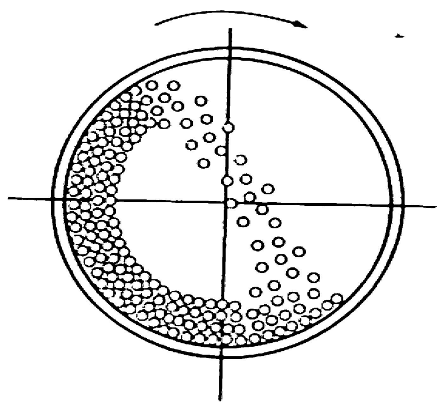

Figure 1 Impact action of free falling balls.

1.3. Principles in ball milling

The ball milling process is a mechanical process which relies on the energy released at the point of collision between balls as well as on the high grinding energy obtained due to centrifugal action in a ball mill. In a ball mill most of the reduction is carried out by impact as the balls drop from near the top of the shell. The loads of balls in a ball mill is kept in such a way that when the mill in a rest position, the balls occupy about one-half the volume of the mill and the total void fraction in the mass of balls, when at stationary is typically, 0.40 [7].

When the mill rotates, the balls are picked up by the mill wall and are taken to the top, where they loose contact with the wall and fall down by gravity to the bottom of the mill to be picked up again. During the upward motion, the balls remain in contact with the walls and with each other due to centrifugal forces. While in contact with the walls, the balls do some grinding by slipping and rolling over each other, but most of the grinding takes at the bottom of the mill which is hit by the free-falling balls (Fig. 1).

The faster the mill is rotated, the farther the balls are carried up inside the mill. The higher the ball lifted, greater is the impact of the ball at the bottom. When the rotation of the mill is too high, the balls inside the mills are carried over all along the walls and do not drop down. At this stage, the mill is centrifuging. The rotation speed at which centrifuging occurs is called the critical speed. At a speed equal to or greater than the critical speed, there is no free fall of balls and there is little or no grinding taking place. Therefore, the operating rotation speeds must be less than the critical speed for any meaningful size reduction.

Thus the ball in rotation experiences two kinds of forces—gravitational and centrifugal forces and the relationship between the critical speed over which the balls will not lose contact with the mill with respect to the radius of the mill (R) and the radius of ball (r) is given by:

$$n_c = \frac{1}{2\pi}\sqrt{\frac{g}{R-r}}$$

Ball mills typically run at 65 to 80 percent of critical speed, the higher figure is meant for dry grinding while the lower one for wet grinding [8].

The overall aim of the work is to explore the possibilities of improving effective mechanical properties of hemp fibers by thermo-mechanical means so that when they are used for manufacture of composites, the composites can compare well with currently used fiber glass composites. In the earlier studies, weight changes and the morphological consequences of heating hemp (*Cannabis Sativ L.*) stem and fibers were studied to establish the optimum temperature and time of treatment [9]. The aim of this study is to investigate the ball milled treated hemp fibers, such as length and diameter distributions and their tensile strength and Young's modulus.

2. Materials and methods

2.1. Natural fiber

For this experiment, the natural fiber—hemp (*Cannabis Sativ L.*) was used which was procured from Hempline Inc. industry. Hempline contracts the work of hemp plantation and harvesting in the southwestern Ontario, near the city of London, Canada. Harvested on maturation, they are processed in the Hempline mills to make ultra fine hemp fibers. The fibers then were chopped to different sizes.

2.2. Heat treatment

The earlier experiment [9] had indicated that heat treatment of hemp fiber above the glass transition temperature of lignin leads to enough softening of lignin without effecting the associated tissues of the fibers. It was therefore envisaged to give heat treatment at 220°C to the hemp fibers in an air as well as in an inert atmosphere. Duration of heating was kept constant at 30 min for both the cases. The process used in this experiment for the thermal treatment was followed as used earlier in our laboratory for pulping processes [10].

2.3. Fiber diameter measurement

Both untreated and treated fibers were used to determine their diameter and length. A total of 0.2 gm of fibers was weighed in each case and one fiber was pulled out at a time till all the fibers were exhausted. The samples prepared for strength measurements were used for diameter measurements as described by Prasad and Sain [14]. The gauge length of fiber was taken as 20 mm for testing because it was easier to find large numbers of fibers of such a length from the samples and also because this is the average critical fiber length of the hemp fiber [11]. The diameter was measured using a calibrated graticule eyepiece on reflectance light microscope. The overall diameter of a fiber was assessed according to the features of a fiber. For example, in some fibers, there is just one strand of the fiber, for which the diameters were measured at various intervals and averaged out. In some other case, there were many strands at one end but only few were running all the way to the other end, in such case, the average diameters of only those portions were taken which were running all through. In some cases, the minimum diameter was taken as the only one strand of the fiber seems to be running all though the length.

2.4. Strength measurements

After measuring the diameter of the fibers, they were left in a humid atmosphere for 24 h so that the fibers reach equilibrium moisture. The strength measurements were carried out on a Sintech 1 tensile tester [14].

2.5. Optical micrographs

A Reichert-Jung made Polyvar microscope was used with 40×, 100× and 400× magnification. The fibers were observed at various intervals to its entire length.

2.6. Scanning electron micrographs

SEM micrographs of fiber surface and cross sections of stems and fibers, before and after treatment, were taken using a scanning electron microscope (model Hitachi S-2500). Prior to SEM evaluation, the samples were coated with gold by means of a plasma sputtering apparatus (Cresingtor sputter coater 108).

2.7. Ball milling

The fiber samples were placed in a cylindrical porcelain jar which can be tightly covered. Two kind of porcelain jars were used, the bigger one has a length of 22 cm and diameter of 21 cm while the smaller had length of 11 cm and diameter of 7.2 cm. The balls were in solid cylindrical shape with length of 1.3 cm and diameter of 1.2 cm. The jar was rotated on the US stoneware 755 RMV jar roller machine. The jar was filled up half its volume by the balls of same size.

3. Results and discussion

A principle aim of this work was to explore the possibilities of opening up the hemp fiber bundles by means of thermo-mechanical treatment into individual strands. There opened up fibers are supposed to be having of greater strength characteristics which can compete with the strength properties of glass fibers. As the fibers are heated to a temperature higher than the glass transition temperature of lignin, it is expected that there will be flow of lignin leading to opening up of the fiber bundles. Earlier studies pointed towards fiber treatment temperature of around 220°C for about 30 min to affect lignin softening in the bast hemp fibers without charring [9]. However, at higher temperature, although softening of lignin takes place, the fibers would get oxidized in the air atmosphere leading to lowering of the overall strength of the fiber. Thus, all the advantages of opening up fibers get off-set by their oxidation. This problem of oxidation can be overcome when the fibers are heated in an inert atmosphere. However for this experiment, the heat treatment was carried out in both air and inert environments to compare strength properties in these two situations.

TABLE I Rotational parameters of jars.

Jar	Small	Big
Diameter, mm	72	210
Critical rotational speed per sec	1.94	1.1
Critical rotational speed per min	116	66
80% of critical speed per min	93	52

The fibers were placed in a robust steel digester lowered in a heated oil bath. The idea behind using oil bath for heating the digester as against other kind of heating was (i) to have a uniform heating and (ii) it was easy to maintain the desired temperature with the help of a thermocouple.

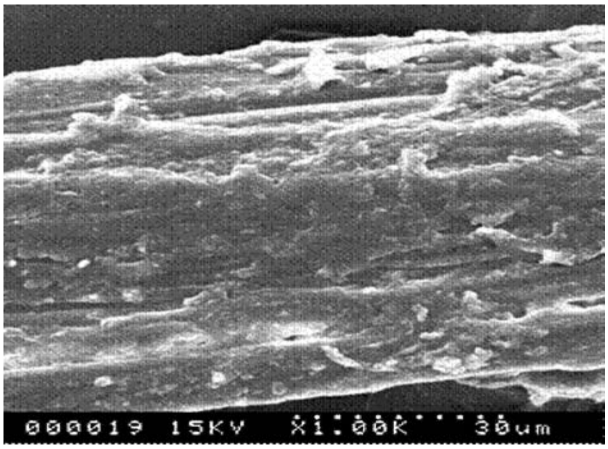

Figure 2 Scanning micrographs of untreated hemp fiber.

3.1. Calculation of rotational speed

In our laboratory, two jars, one big and another smaller were used for ball milling purposes while balls for the same diameters were used for both the jars. The radii of the balls used in our experiment were 6 mm. As the grinding was carried out dry, the rotational speed was taken 80% of the critical speed. The rotational speeds for two set-ups have been calculated and shown in the Table I.

3.2. Mass of fibers used for ball milling

In order to decide upon the optimum mass of fibers for ball milling, different amounts of heat treated fibers in the nitrogen environment were taken for ball milling. For this purpose fibers were ball milled for two hours, after an hour the fibers were taken out, redistributed and again placed in the jar and milled for another hour. It was found that for the bigger jar mass between 15–20 g of fibers works well and for smaller about 2 g.

3.3. Optical microscopy

For microscopy, it would have been better if the same sample had been used for observations before and after heat treatment. However, it was not possible to treat the same sample twice or more times. Further, it was still more difficult in case of fiber, where one strand of fiber was impossible to heat treat. Nevertheless, care was taken to select similar kinds of fibers from each treatment for each set of observations to maintain the uniformity.

The optical microscopy of the fibers did not reveal much as the fiber thickness was too high for transmission light to be effective in observing the fiber morphology

3.4. Scanning electron microscopy

SEM micrographs of surface of untreated and heat treated hemp fibers in an inert atmosphere at 220°C are shown in Figs 2 and 3 respectively. There is an evidence of physical microstructure changes occurring to the fiber surface due to heat treatment. The structure of hemp is made up of cellulose microfibrils bound together by a matrix of lignin and hemicellulose, which

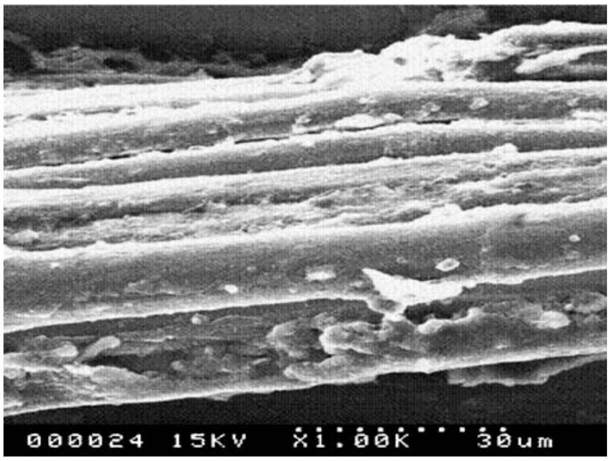

Figure 3 Scanning micrograph of hemp fiber after heat treated in inert atmosphere.

are then subsequently bond together to form larger fiber bundles. The individual fibers are well connected with the pectin matrix. The opening up of the fiber bundles can be seen. The individual fibers appear to have a smooth surface. Some fiber damage can also be seen, however, it is not clear whether the damage was present before treatment or was induced due to heat treatment. In Fig. 3, although the individual fibers are still intact, the fiber bundle is separated and the matrix in between the individual fibers has disappeared. At this stage, the treated fibers require a mechanical action so that the fiber bundles opening process is completed. This mechanical process should be such that it does not damage the fiber during the process. The process adopted is ball milling.

The purpose of ball milling is not only to open up the fiber bundles but also to make fibers with more uniform properties.

3.5. Number of fiber

An equal quantity of 0.2 gm of fibers each of raw hemp fibers, hemp fibers heat treated in inert environment and ball milled after heat treatment in an inert environment were taken. The numbers of fibers for untreated and treated in inert atmosphere were taken from earlier study [14], while the numbers of ball milled fibers were taken in this study. In earlier study, the fiber length

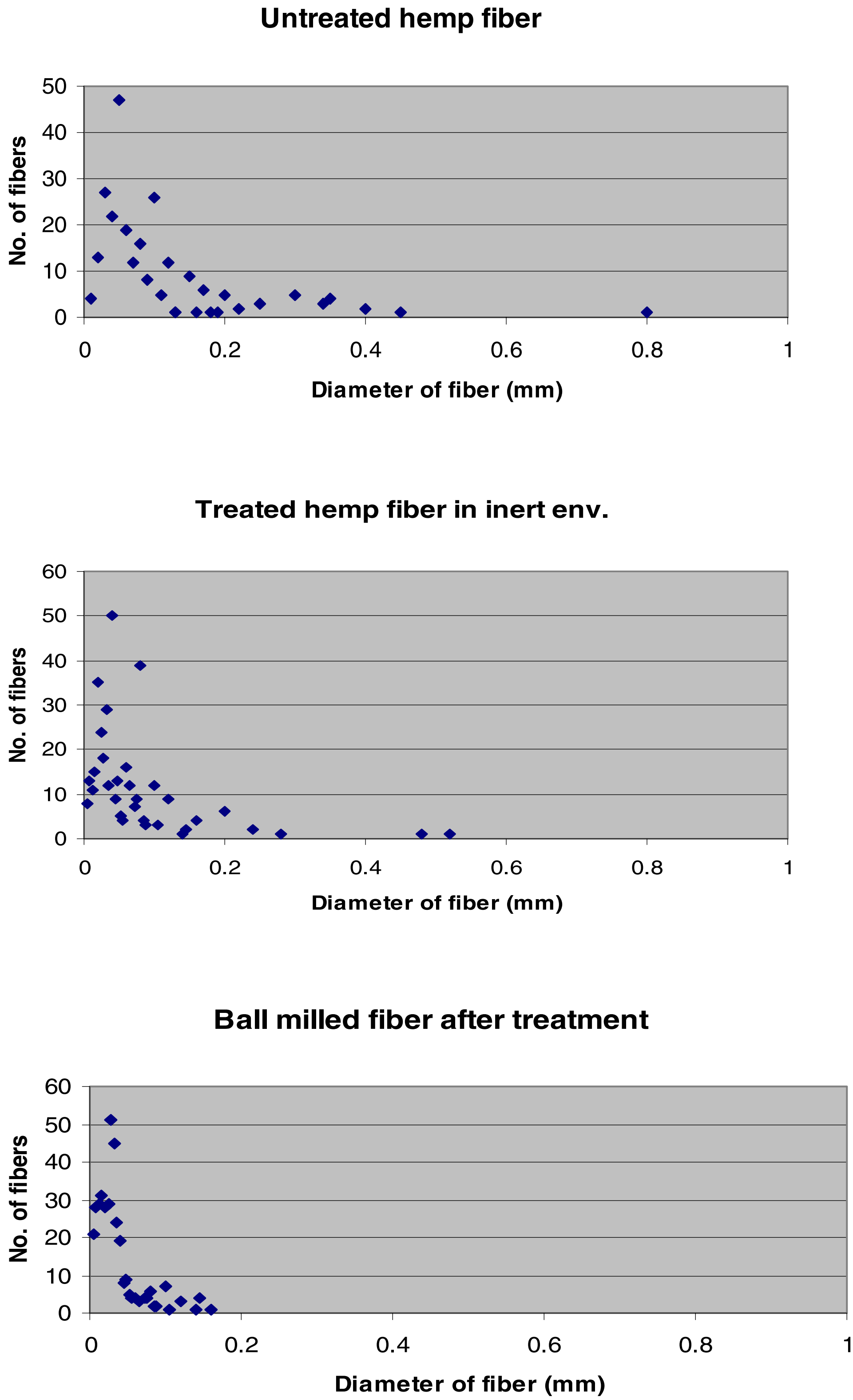

Figure 4 No. of fibers versus diameter fibers for hemp fiber (a) untreated (b) treated in inert atmosphere (c) ball milled after treatment in inert atmosphere.

were 3 inches but such a high length of fiber tend to conglomerate upon ball milling, therefore, the fibers were chopped to half an inch length for ball milling. In each case, individual fibers were taken out for measurement of length, diameter and strength properties and their numbers were counted. The total numbers of fibers in each case for 0.2 gm of weight of fiber (except in case of ball milled where .33 gm of fiber was taken to make it equivalent as the fibers have been chopped to 6 times) are shown in Table II.

Although the fibers collected in each case were different nevertheless they came from the same mass of fibers and weighed the same and hence their numbers can be compared. The total number of heat treated fibers in an inert environment was about 1.4 times more than the untreated fiber (or 32% increment) and this figure is

TABLE II Number of fibers for different treatment protocol.

Treatment protocol	No. of fibers	% increase
Untreated fiber	257	–
Fiber treated in inert environment	378	32
Fiber treated in inert environment & ball milled	318	19

1.2 times for ball milled fibers treated in inert (or 19% increment).

This was due to splitting of the fibers at the length points as well as along the diameter since the fibers experience high pressure inside the heating chamber and also sudden change of pressure during quenching of the chamber. The numbers of ball milled fibers, however, showed lesser increments because during ball milling, while fiber bundles got opened up, some of the fibers together with the interfaces become powder. An increase in number of fibers can also be attributed to the loss of moisture which resulted in picking up larger quantum of fibers for the same weight. However, the weight loss in case of an inert heated fiber was only 7.1% [14], therefore, the increase in numbers of fibers are obviously not merely due to this fact. Taking these two factors into account, nevertheless, the higher numbers of treated fibers were results of opening up of the fibers both along the length as well as along the width or diameter.

3.6. Diameter distribution

The diameter distributions of the fibers for untreated as well treated in an inert environment, taken from earlier report [14] and those ball milled are shown in Fig. 4. The diameters lie between 4 and 800 μm and have been distributed in different classes, the selected width is shorter for lesser diameter and bigger for larger diameter. Henceforth, whenever diameter is meant, it would really mean the diameter interval. It can be seen that in case of untreated fibers (Fig. 4a), there are more fibers of larger diameters compared to treated fibers both in inert environment (Fig. 4b) as well as in ball milled ones (Fig. 4c). In treated fibers, a greater number of smaller diameter fibers can be seen. Assuming that the length and diameter distribution of fibers is same in all cases, this observation shows that many raw hemp fibers opened up along diameter directions as well, apart from opening along the length direction as discussed above. However, it is not possible to indicate the proportion of opened up fibers along the diameter to the opened up fibers along the length. In a way, it is not necessary to distinguish the two processes of opening of fibers since both the processes take place simultaneously. Again for ball milled fibers, more fibers can be seen for lesser diameter clusters.

3.7. Strength properties

More than 90% of fibers as mentioned in Table II were used for testing. The rest of the fibers could not be taken for the testing because their length was less than the gluing length and hence it was difficult to glue them on the paper. Of the useful length fibers again, not all of them were valid as some of the fibers broke during diameter measurement; some of the fibers broke when the fibers were being gripped, while some of them were pulled out from the grip itself soon after loading. For each diameter, again the numbers of fibers were different for the testing, more fibers for the diameters falling around the mean and lesser on the extremities. The strength properties for natural fibers are greatly influenced by the diameter of the fiber. For the first phase of study, the clamping length was constant for each case so as to compare the strength properties for different diameter for different experimental conditions.

The tensile strength and modulus for ball milled fibers after treated in an inert environment are shown in Figs. 5 and 6.

From the above figures, it can be seen that the strength and modulus for ball milled fibers with clamping length 20 mm showed the usual trend, that is, these strength parameters decrease as the fiber diameters increase. However, contrary to expectations, strength properties have decreased when compared with the strength parameters unball-milled hemp fibers which has been treated in an inert atmosphere [14]. However, this was not altogether unexpected as the fibers of the size length used in this experiment was such that they were found to have been entangled during the ball milling process which would have led to fiber damage. So whatever fiber opening process has been facilitated by ball milling was off-set by the fiber damage due to entanglement of the fibers. The entanglement of fibers occurred during the initial period of ball milling and the milling had continued in this state itself causing copious

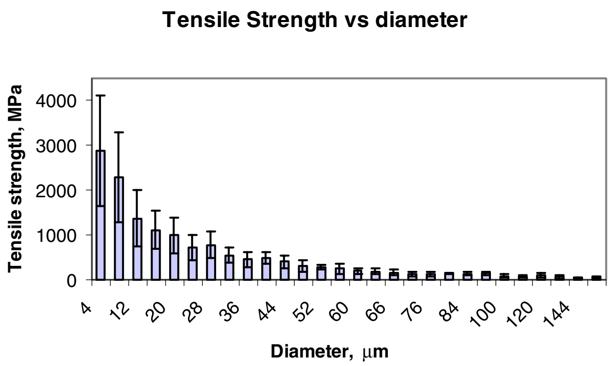

Figure 5 Tensile strength versus diameter for ball milled inert atmosphere treated hemp fibers.

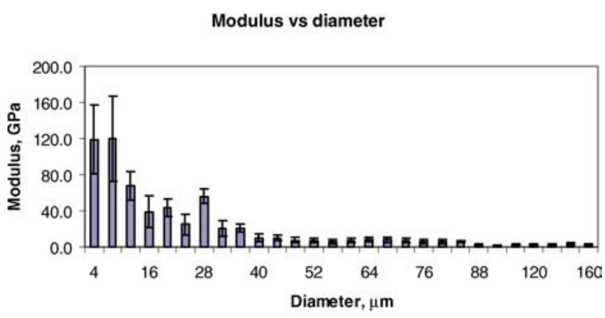

Figure 6 Modulus versus diameter for ball milled inert atmosphere treated hemp fibers.

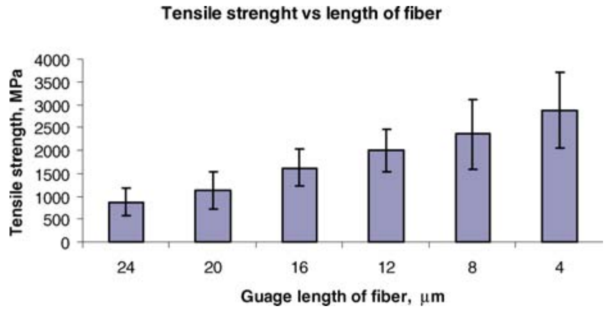

Figure 7 Tensile strength versus gauge length for ball milled inert atmosphere treated hemp fibers for 20 μm diameter fiber.

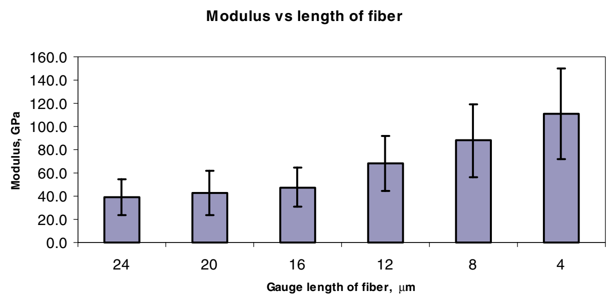

Figure 8 Modulus versus gauge length for ball milled inert atmosphere treated hemp fibers for 20 μm diameter fiber.

amount of fiber damage. Also, the strength values of the hemp fibers treated in an inert environment was really the values of the opened up fibers as the each individual fiber was picked up by hand. Such fibers are just like the fibers which can be obtained by any mechanical process including ball milling. Therefore, expected values of strength parameters of ball milled fibers were about the same as the fibers which were heat treated in an inert environment.

After this, strength properties were found out for the fibers of same set of diameter with different clamping lengths. One set of experiments was tried with the diameter of 20 μm with clamping length of 4, 8, 12, 16, 20 and 24 mm. The tensile strength and modulus for different clamping lengths are shown in Figs. 7 and 8.

As can be seen from the above figures, the strength and modulus increases as the clamping lengths decreases for the same diameter of the fibers. Clearly the fiber damage is lesser for a smaller length fiber. It indicated that for ball milling it is better to use fibers with shorter length. Next, different fibers were used for ball milling and at the end, they were observed for entanglement of the fibers.

3.8. Critical length of fibers suitable for ball milling

Different lengths of fibers were used for ball milling to see which length combinations of fibers give untangled fibers. It was seen that if the fibers are of greater length, they tend to clump together which is not good for any beneficial usage, greater the length, more is clumping. As the length is decreased, the clumping will be lesser and lesser; however, we cannot decrease the aspect ratio of fiber too low or around 1. Therefore, investigation was carried out with different lengths of fibers and the following results were obtained:

Length of fiber (inch)	2	1	1/2	1/4
Clumping of fibers	high clumping	clumping	less clumping	little or no clumping

Fibers with 1/4 inches showed very less clamping are good for ball milling.

The standard deviations in case of strength parameters were quite high. Apart from the smaller numbers of samples, very high standard deviations are due to the in-homogeneous form of naturally occurring fibers and the predominance of defects with their structures. As mentioned earlier, because of difficulties encountered during measurement of fiber diameter, assumptions were made about the cross-section area, which may also have contributed to the apparent variability of the properties.

These problems may possibly be dealt with if a very large sample were taken for the experiments in order to produce a statistically significant result. However, the goal here was to obtain a qualitative idea of the performance of the treated fibers.

4. Conclusions

In this study, hemp, a natural fiber was given heat treatment in an inert atmosphere and then ball milled in order to open up fiber bundles into fiber of lesser diameters and thereby improve their strength characteristics. During the heat treatment process hemp bundles are mechanically defiberated. In course of heat treatment, the lignin softens leading to opening up of the fibers. The fibers, thus obtained, are not separated individually and require mechanical intervention to make them apart. As the fibers are loosely bonded, very little energy is required to separate them. Also, little mechanical intervention means, the fibers will not undergo much damage which may be the case when high energy mechanical intervention is applied which also have increases the cost of operation further. By ball milling process, an inert environment heated treated fibers are further defibrilled which can be used for composite making. The tensile strength and modulus of these ball milled decreased for 3 inches fibers. This was due to severe entanglement of the fibers leading to fiber damage. However, it was found that as the clamping length was decreased, the strength properties increased and finally for fibers with quarter inches length, there was very little or no entanglements and they were suitable for ball milling. It was not possible to find strength properties of these shorter length fibers by the pull out testing methods, however, the results from shorter clamping length indirectly indicated that these fibers were of higher strength. These fibers should further be used to manufacture composites and the results should then be validated. However, the ball milled fibers contains lot of fines which should be removed before making composites. Fines are an issue because they decrease the overall aspect ratio.

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