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CELLULOSE MICRO PARTICLES FROM JUTE

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SUMMARY OF THE THESIS

Title of the thesis:	Cellulose Micro Particles from Jute
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Abstract

Jute is an important natural fiber which has a great potential to produce multipurpose products in daily routine life. Unprocessed raw fiber is being utilized as an input source to textile sector for products with high mechanical properties. Jute is one of the longest and most commonly used natural fibers for various technical applications. It is obtained from the inner bark of the plant's stem. Jute is being known as Golden Fiber due to its golden and silky shine. These fibers are composed of the plant materials like cellulose (major component of plant fiber) and lignin (major components of wood). In this specific study, inexpensive jute fibrous waste has been utilized to extract the cellulose particles.

Oxidation of cellulosic materials is required in many fields like textile processing, natural fiber reinforced composites and medical utilization etc. In present study, jute fibers were treated with ozone gas to remove lignin for further utilization of these oxidized fibers.

This study was designed to explore the possibility of ozone treatment as a greener oxidation process of jute fibers. Ozone gas was being used for the treatment of jute fibers for different time periods in a humid atmosphere.

Several characterization techniques, namely physical appearance, fiber mechanical properties, copper number, Fourier Transform Infrared (FTIR) spectroscopy, Wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), moisture regain percentage and lightness values (L) were used to assess the effect of ozone treatment on jute fibres. Results showed that fiber tensile properties weaken gradually as a function of ozone treatment time and surface functional groups alter accordingly. Physically the fiber bundles were split into brittle single fibers and the lightness value increased from brownish shade to lighter colour.

It was clear that physical properties of jute fibers were degraded drastically after certain time of treatment and chemical properties were changed with the change in functional groups present in the fiber morphology. Ozone degrades lignin and slightly solubilizes the hemicellulose fraction, improving resultant fiber morphology for further use. It was concluded in this research that ozonation is a very good and greener substituent of chemical oxidation of cellulose fibers especially jute.

In subsequent step, untreated, chemical (alkali) and ozone pre-treated jute fibers were hydrolyzed by cellulase enzymes for separation of longer jute micro crystals (JMC). The influence of non-cellulosic contents on the enzyme hydrolysis and morphology of obtained micro crystals was presented.

Later, jute micro crystals were incorporated into poly (lactic acid) matrix to prepare composite films by solvent casting. The reinforcement behavior

was evaluated from tensile tests, dynamic mechanical analysis, and differential scanning calorimetry.
In the end, a good level of agreement for maximum reinforcement was confirmed at certain percentage of loading of JMC when compared with predicted values from different mechanical models.
Quadratic regression was applied to the actual values of tensile modulus of composites corresponding to volume fraction of reinforcement and the obtained prediction model was developed using generalized rule of mixture. This model can be used for the prediction of the system properties.

Key words: Cellulose; Enzymatic Hydrolysis; Jute; Ozone; Oxidation

Summary

1. Introduction

In the context of environment protection and current disposal of the textile wastes, it becomes essential to recover useful products from the wastes for economic reasons. Traditionally, textile wastes are converted to individual fiber stage through cutting, shredding, carding, and other mechanical processes [1], [2]. The fibers are then rearranged into products for applications in garment linings, household items, furniture upholstery, automotive carpeting, automobile sound absorption materials, carpet underlays, building materials for insulation and roofing felt, and low-end blankets. In this way, textile waste industries were emerged typically as shredders, shoddy producer, laundry and wiping rag producer. However, due to recent increase in competition and reduced profit margins in these industries, it has become important to search for new recycling techniques of waste textiles in order to utilize them for high end applications. One such interesting way is to separate the nanofibrils or Nano crystals from the textile wastes and subsequently incorporate them as fillers into high performance composite materials [3]–[5]. In this way, the exploration of these inexpensive industrial fiber wastes as bio resource for making industrial products will open new avenues for the utilization and at the same time add value to the creation of economy.

Among various raw materials, cellulose fibers are popularly used in the textile industry due to their high aspect ratio, acceptable density, good tensile strength and modulus [5]. These properties make them attractive class of textile materials traditionally used in manufacture of yarn by spinning process. But, due to certain limitations of the spinning process, shorter fibers (i.e. below 10 mm) generated during mechanical processing are not suitable to reuse in yarn manufacture and consequently result into the waste [5]. Generally fibers have been used for variety of applications depending on their length [6]. Here the idea of separation of nanostructures from waste fibers and subsequently incorporating them as fillers in nanocomposite films could provide cost-effective solutions to the struggling textile industries.

The micro/nanostructures of cellulose have gained significant amount of importance due to its higher mechanical properties. The crystalline segments in cellulose have a greater axial elastic modulus than the synthetic fiber Kevlar, and their mechanical properties are within the same range as those of other reinforcement materials such as carbon fibers, steel wires and carbon nanotubes [3], [4]. The nanostructures of cellulose are considered as bundles of molecules which are elongated and stabilized through hydrogen bonding. The remarkable improvements in mechanical properties of cellulose nanostructures, in range of 130-170 GPa, are considered due to this parallel arrangement of molecular chains which are present without folding [4]. Previous work on composites made from cellulose nanostructures showed improved strength and stiffness with a little sacrifice of toughness, reduced gas/water vapor permeability, lower coefficient of thermal expansion, and increased heat deflection temperature [3], [7]. These properties thus could promise in replacement of conventional petroleum based composites by new, high performance, and lightweight green nanocomposite materials.

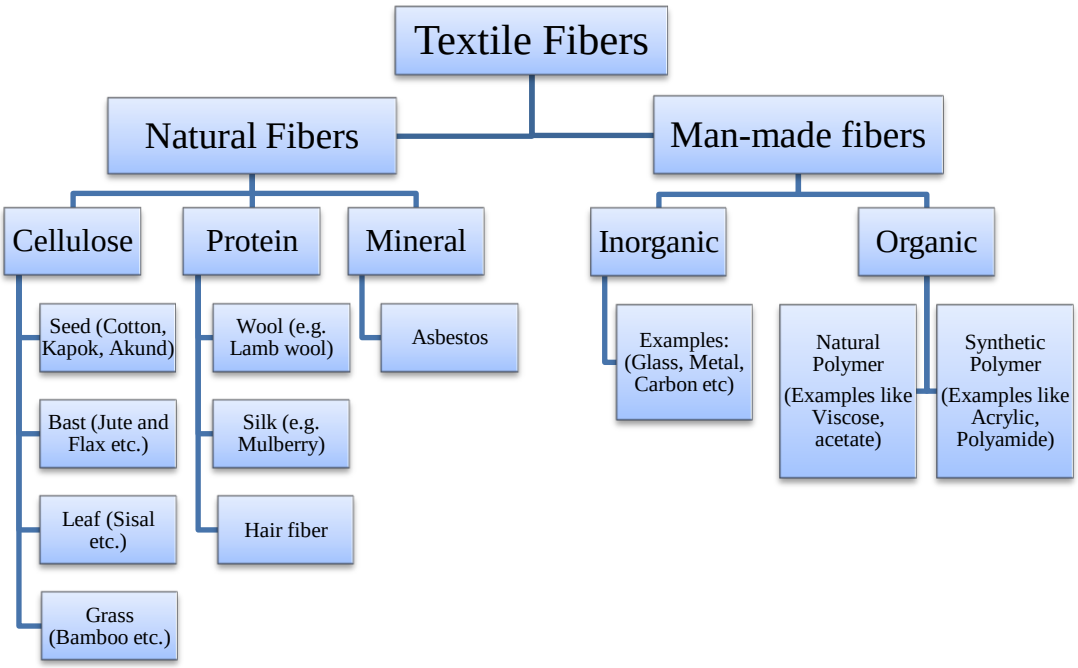


Figure 1. Classification of Different Textile Fibers

Nanocomposites are a relatively new generation of composite materials where at least one of the constituent phases has one dimension of less than 100 nm [4]. This new family of composites is reported to exhibit remarkable improvements in material properties when compared to conventional composite materials. The small size of the reinforcement leads to an enormous surface area and thereby to increased interaction with the matrix polymer on molecular level, leading to materials with new properties. Well dispersed nano particles can improve tensile properties and even improve the ductility because their small size does not create large stress concentrations in the matrix. The small size also increases the probability of structural perfection and will in this way be a more efficient reinforcement compared to micro sized reinforcements [7].

Although the cellulose nanostructures have a great potential for reinforcement into biopolymers, the major challenge in order to use them is the extraction. The variety of techniques like acid hydrolysis [8], enzymatic hydrolysis [9], ultrasonication [10], high pressure homogenization [11], etc. have been employed. However, most of these techniques used in the extraction are time consuming, expensive in nature and low in yields [4]. The commonly used strong acid hydrolysis method has a number of important drawbacks such as potential degradation of the cellulose, corrosivity and environmental incompatibility [12]. In order to promote the commercialization of cellulose nanofibrils, the development of more flexible and industrially viable processing technique is needed. The core part of thesis describes the enzymatic hydrolysis of jute fibers pretreated with ozone gas in a controlled atmosphere as a practical and greener method to disintegrate the jute fibrous waste to obtain longer micro crystals of cellulose in bulk quantity.

Table 1. Mechanical properties of textile fibers [13]

Fiber	Density (g cm^{-3})	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
Flax	1.5	40–600	345–1500	27.6	2.7–3.2
Hemp	1.47	25–500	690	70	1.6
Jute	1.3–1.49	25–200	393–800	13–26.5	1.16–1.5
Kenaf			930	53	1.6
Ramie	1.55	—	400–938	61.4–128	1.2–3.8
Nettle			650	38	1.7
Sisal	1.45	50–200	468–700	9.4–22	3–7
Henequen					
PALF		20–80	413–1627	34.5–82.5	1.6
Abaca			430–760		
Oil palm EFB	0.7–1.55	150–500	248	3.2	25
Oil palm mesocarp			80	0.5	17
Cotton	1.5–1.6	12–38	287–800	5.5–12.6	7–8
Coir	1.15–1.46	100–460	131–220	4–6	15–40
E-glass	2.55	<17	3400	73	2.5
Kevlar	1.44		3000	60	2.5–3.7
Carbon	1.78	5–7	3400[a]–4800[b]	240[b]–425[a]	1.4–1.8

A single lignocellulose fiber consists of several cells (except in cotton). These cells are formed out of cellulose-based crystalline micro fibrils, which are connected to a complete layer by amorphous lignin and hemicellulose (Fig. 2 & 3). To form a multiple layer composite lignocellulosic fiber, multiples of such cellulose–lignin–hemicellulose layers in one primary and three secondary cell walls stick together. About several hundred to 10 million of glucose units condense to form a straight chain of a polysaccharide unit in the form of cellulose nanofibrils. The free OH groups in one polysaccharide thread have higher possibilities to form hydrogen bonds with another thread. Therefore a number of nanofibrils bind through intermolecular hydrogen-bonding with each other to form microfibers and then to microscopic cellulose fibers.

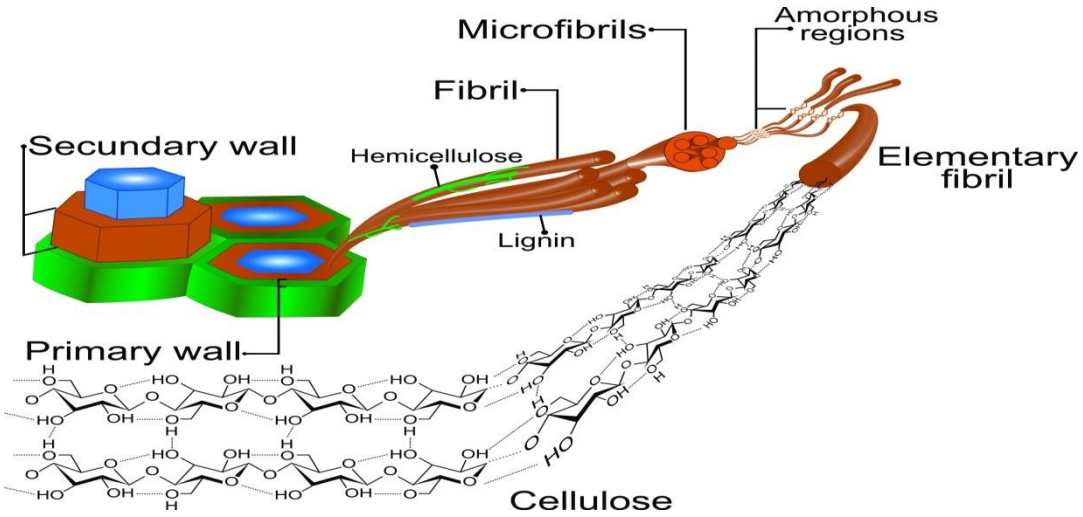


Figure 2. Hierarchical structure of cellulose extracted from plants [14]

The study [15] regarded the micro fibril itself as being made up of a number of crystallites, each of which separated by a para crystalline region and later termed it as elementary fibril. According to this concept, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites is held together by parts of the long molecules reaching from one crystallite to the next, through less ordered inter-linking regions (Fig. 3). Their structure consists of a predominantly crystalline cellulosic core which is covered with a sheath of para crystalline polyglucosan material surrounded by hemicelluloses. As they are almost defect free, the modulus of these sub entities is close to the theoretical limit for cellulose.

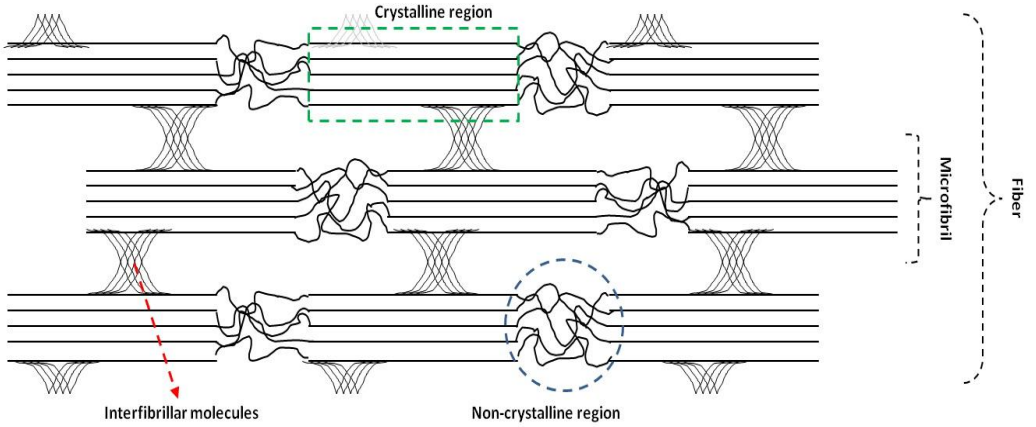


Figure 3. Arrangement of cellulose molecules in fiber [16]

Jute fibers consist of lignin (12~14 %), cellulose (58–63 %), hemicellulose (21~24 %), nitrogenous matter (0.8~1.5 %), traces of pigments, inorganic matter (0.6~1.2 %) and fats and waxes (0.4~0.8 %) [17], [18]. However, the presence of non-cellulosic substances found to hinder the reaction between hydroxyl groups of fibers and polymer matrices, which consequently deteriorated the mechanical properties of composites [19]. In order to have better bonding between fibers and matrix, the non-cellulosic contents should be removed. The various surface treatments such as sodium hydroxide, peroxide, organic and inorganic acids, silane, anhydrides and acrylic monomers have been attempted by researchers in previous works to improve the compatibility between fibers and matrix [19]. However, such chemical treatments are not environment friendly and require more energy, time and water. The motivation of present work was to search for alternative and relatively greener techniques for surface modification of jute fibers.

The oxidation of jute fibers using ozone gas is one of the alternatives over chemical treatments for removal of lignin. Ozone is an oxidizing agent with a strong oxidation potential of 2.07 eV [20]. It is an unstable allotrope of oxygen containing three atoms. Ozone is highly reactive towards compounds incorporated with conjugated double bonds and functional groups of high electron densities [21]. Due to high content of C=C bonds in lignin, ozone treatment of jute fibers is likely to remove lignin by release of soluble compounds of less molecular weight such as organic acids. Therefore, the ozone treatment is environment friendly, causes minimal degradation of cellulose and hemicelluloses, and requires less

energy, time and water [22]. The effectiveness of ozone treatments in the textile wet processing has already been demonstrated. The ozone treatment was found suitable for bleaching of cotton [21]. In another study, the effect of ozone was found to improve the whiteness degree and dye ability of Angora rabbit fibers [23]. The study of ozone treatment on silk reported it to turn into yellowish, harsh and without luster [20].

More recently, separation of individual cellulose fibrils or crystals is reported in many research works for achieving extremely higher mechanical properties suitable in high performance composites [24]. In order to disintegrate fibers to the level of mechanically strong cellulose elementary fibrils without complete dissolution, it is necessary to work on chemically less aggressive hydrolysis concepts. The ozone pre-treatment of jute fibers before the action of enzyme hydrolysis is considered to be advantageous in this aspect. Due to removal of lignin by ozone pre-treatment, the jute fibers are expected to have less strength and more open structure. In this way, even a less concentration of cellulase enzyme or less hydrolysis time is likely to provide extensively entangled networks, higher strength and higher aspect ratio of the cellulose elementary fibrils. Cellulases are a group of multi component enzyme systems produced by microorganisms that help in the degradation of cellulose. The filamentous fungus Trichodermareesei is one of the most efficient producers of extra cellular cellulase enzyme [25]. There are further two sub-groups of cellulase that affect crystalline and amorphous regions of cellulose separately. Cellobiohydrolase attacks the crystalline structure of cellulose, whereas endogluconase catalyzes the hydrolysis of amorphous cellulose [9].

In present study, jute fibers were pre-treated with ozone gas for removal of lignin. The change in single fiber strength, fiber surface morphology, whiteness, moisture absorbency, etc. of jute fibers due to ozone pre-treatment is discussed in detail. For comparison purpose, chemical pre-treatment of jute fibers was also carried out. In subsequent step, untreated, chemical and ozone pre-treated jute fibers were hydrolyzed by cellulase enzymes for separation of longer jute micro crystals. The influence of non-cellulosic contents on the enzyme hydrolysis and morphology of obtained micro crystals was investigated. Later, 3 wt. % of jute micro crystals were incorporated into poly(lactic acid) (PLA) matrix to prepare composite films by solvent casting. The reinforcement behavior was evaluated from tensile tests, dynamic mechanical analysis, and differential scanning calorimetry.

Ozone is an advanced oxidizing agent having a powerful oxidation potential of 2.07 eV [20]. This gas has been used for the oxidation of cellulose to improve the functionality of fluoromonomer. The combination of ozone and fluorocarbon treatments on cotton can increase the contact angle due to higher efficiency of the water repellent polymer on the surface of the ozone-gas treated fibers [26]. Ozone gas treatment has the great potential of savings the precious utilities of our daily life like time, energy and water. This treatment also reduces the hazardous impact on environment, especially chemical oxygen demand (COD) values, of the processes [27].

Besides the surface treatments for the oxidation of cellulose, many other surface treatments including physical, chemical, physicochemical and biological methods are being tried for other purposes applicable on natural as well as synthetic fibers [28]. For example, atmospheric air-plasma has been tried on polyester fiber to improve the performance of nano-emulsion silicone. This pretreatment modifies the surface of polyester fibers and increases the

reactivity of substrate toward nano-emulsion silicone resulting in the decreased moisture absorption due to uniform coating of the silicone emulsion on the surface of fibers [29]. Thin film plasma functionalization of polyethylene terephthalate has been suggested to induce Bone-like hydroxyapatite Nano crystals for the its utilization in the field of tissue engineering [30].

Corona discharge ionization is another physical surface treatment for polyester to be anionized which will have an increased reactivity of the fibers towards cationic dyes [31]. Ozone gas treatment has the great potential of savings the precious utilities of our daily life like time, energy and water. This treatment also reduces the hazardous impact on environment, especially chemical oxygen demand (COD) values of the processes [27]. As Ozone gas is used in water treatment and fabric finishing processes, etc., it is interesting to use this gas to treat/oxidize the cellulosic fibers. Keeping in view this idea the present study was designed to explore the possibility of using ozone for the advanced oxidation of jute fiber. The aim of this study was to investigate low cost and energy efficient fiber treatment method with low environmental impact. This oxidized jute may then be utilized for different applications such as medical field or for the production of cellulose Nano fibrils or Micro/Nano crystals.

2. Purpose and aim of the thesis

2.1 Extraction and characterization of jute micro/nano particles

The main objective of the work is to obtain jute based cellulose micro/nano particles on large scale quantity from waste jute fibers using environment friendly method of extraction. The enzymatic hydrolysis method was utilized for the extraction of cellulose particles from oxidized jute. The fibers used for the enzymatic hydrolysis were pretreated with Ozone gas for the environment friendly oxidation. These oxidized fibers were then used as a substrate for the enzymatic hydrolysis.

In this work, enzymatic hydrolysis of untreated, chemically pretreated and the jute fibers pretreated by Ozone gas was carried out to check the effect of pretreatment on the hydrolysis process as well as on the quality of the obtained microcrystals.

Particle size distribution of untreated jute micro crystals (UTJMC), chemical treated jute micro crystals (CTJMC) and ozone treated jute micro crystals (OTJMC) obtained after enzyme hydrolysis was studied on Malvern zetasizer nano series. In addition, morphology of enzyme hydrolyzed crystals was observed on (SEM).

For Ozone pretreatment, three parameters affecting the oxidation of jute fibers by ozonation i.e. oxygen flow rate, ozonation power and time of treatment were also optimized before enzymatic hydrolysis.

2.2 Reinforcement of biopolymer by cellulose particles.

The obtained enzymatically hydrolyzed cellulose particles were then incorporated into a biodegradable polymer matrix as reinforcement. Poly lactic acid (PLA) biopolymer was used as a matrix for preparation of composite films which can be used in the applications of biodegradable food packaging, agriculture mulch covers, etc. The incorporation of JMC is expected to improve the mechanical and thermal properties of semi-crystalline polymeric films. The improvements in mechanical properties were investigated from the morphology and crystallization behavior of composite films using differential scanning calorimetry, tensile

tests, dynamic mechanical analysis tests etc. In order to have the basic understanding of the stiffening, strengthening and toughening properties of JMC in polymeric matrix, the critical evaluation of experimental results with theoretical models is also performed. In the end, a prediction model was developed using generalized rule of mixture to predict the system property corresponding to volume fraction of reinforcement along with interaction effect of volume fractions of reinforcement (JMC) and matrix i.e. PLA.

3. Overview of the current state of the problem

3.1 Extraction of cellulose Micro/Nanostructures

Isolation, characterization, and search for applications of novel forms of cellulose (i.e. crystallites, nano crystals, whiskers and nano fibrils) are generating much activity these days [3], [4]. Such isolated cellulosic materials with one dimension in the nanometer range are referred to generically as nanocelluloses. Novel methods for their production range from top-down methods involving enzymatic, chemical, physical methodologies (Fig. 4) to the bottom-up production from glucose by bacteria. Depending on the source and extraction method, the size and shape of the nanocellulose structures are different. In a unique manner, these nanocelluloses combine important cellulose properties such as hydrophilicity, broad chemical-modification capacity, and the formation of versatile semi crystalline fiber morphologies due to the large surface area of these materials. On the basis of their dimensions, functions, and preparation methods, nanocelluloses are classified in three main subcategories as nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC) and bacterial nanocellulose (BNC) [4].

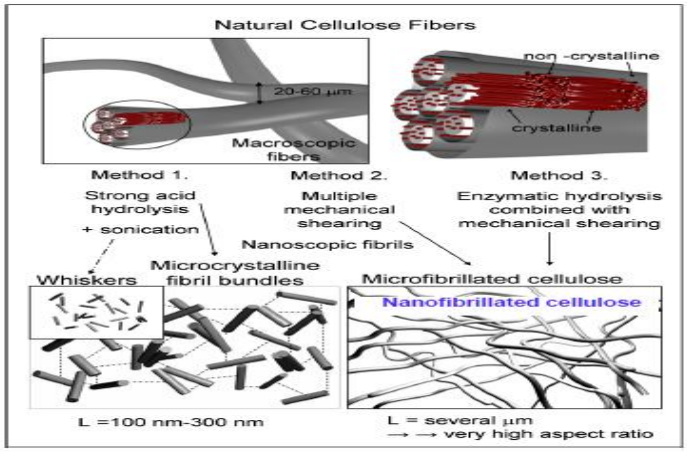


Figure 4. Types of cellulose nanostructures [32]

3.2 Applications in biodegradable composites

The replacement of long cellulosic fibers by cellulosic material of smaller axial ratios is an interesting option for composite preparation. With their better dispersibility and lower susceptibility to bulk moisture absorption, a theoretical elastic modulus of 138 GPa (comparable to that of steel), and a large surface area of several hundreds of square meters per gram [3], [4], cellulose micro/nanofibrils are more efficient filler candidates. The small dimensions of cellulose micro/nanofibrils enable direct contact between cellulose and matrix polymers, allowing for a large contact surface and thus excellent adhesion. Favier et al. [33] were the first to demonstrate the reinforcing properties of cellulose Nano crystals. They

prepared PBA latex composite which showed a significant improvement in the matrix modulus in the rubbery state. Following this advance, the incorporation of cellulose nanostructures from different sources into composite materials with enhanced properties has been investigated thoroughly and summarized in several review articles [34]. Apart from applications of cellulose nanofibrils in composites, their use in health care areas are also promising due to their high strength and stiffness combined with low weight, biocompatibility and renewability [35]. Cellulose nanofibrils can also be used as a rheology modifier in foods, paints, cosmetics and pharmaceuticals [36]. In cosmetics, nanocellulose is suitable as an additive in skin-cleansing cloths and as part of disposal diapers, sanitary napkins, and incontinence pads [37].

3.3 Investigation of mechanical properties of composites

The important properties which contribute to the mechanical properties of composites are interaction between matrix and reinforcement, matrix crystallinity, trans crystallization phenomenon and moisture uptake [38]. The increase in matrix crystallinity due to addition of cellulose nanostructures is studied by Dufresne [39]. They reported an increase in the crystallinity of their plasticized starch matrix as the whisker content was increased. Trans crystallization is the phenomenon whereby a highly oriented layer of a semi crystalline polymer forms at the matrix/filler interface [39]. Such layers only develop under specific conditions and affect the quality of interactions between the matrix components. Dufresne et al. [39] Scientists invoked trans crystallization of PHA latex by cellulose whisker surfaces to explain the enhanced performance of the composite. The quality of cellulose-matrix adhesion was found to diminish especially in case of hydrophobic matrices due to moisture on the surfaces of hydrophilic cellulose reinforcements [40].

In addition, the effectiveness of reinforcement is often addressed by percolation theory, which can predict long-range connectivity in the matrix during film formation [41]. It was reported from previous studies that percolated network of nanofibrils could slow down the propagation of cracks during the fracture and consequently improve the mechanical properties of composites [42]. This extended network is presumably generated through hydrogen-bond formation between the cellulose Nano crystals, whose packing structure depends on the distribution and orientation of the rods as well as their aspect ratios.

4. Method used and studied material

4.1 Materials

Short waste jute fibers were measured to have a density of 1.58 g/cm^3, tensile strength of 440 MPa, elongation at break of 3 % and modulus of 20 GPa. PLA was purchased from Nature Works LLC, USA through local supplier Resinex, Czech Republic. The PLA had a density of 1.25 g/cm^3 and the average molecular weight (Mw) of 200,000. The chloroform, which was used as solvent, purchased from Thermofisher Czech Republic. The TEXAZYM AP cellulase enzyme was provided by the company INOTEX in Czech Republic. The optimal pH in range of 4.5-5.5 and temperature in range of 50-60 °C was selected for enzyme activity.

In this work, Ozone Generator with identification name plate as “TRIOTECH GO 5LAB-K, made in Czech Republic” was used and the power setting was kept constant at 50 % for all treated samples. An Oxygen Concentrator “Krober MEDIZINTECHNIK, Germany” with a

controllable output Oxygen flow rate was used as an oxygen supplier/feeder to the Ozone Generator.

4.2 Ozone Treatment of Jute fibers

The substrate fibers of Jute waste were placed in a humid ozonized atmosphere for different times. The outlet gases of the system were analyzed and measured the mass flow of ozone as 4.5 mg/L. The output concentrated oxygen flow rate from Oxygen Concentrator was adjusted at 5.0 L/minute and this oxygen was being fed to the Ozone Generator. As humid atmosphere is more effective for the reaction of Ozone with lignocellulosic material, so this treatment was done in humid atmosphere [43].

As the Oxygen provided by Oxygen Concentrator and Ozone produced by Ozone Generator in series are dry in nature. So a humidification system was developed in the way of Ozone to the jute samples. Due to this system the dry nature of Ozone was changed to humid one as shown in figure 5. The jute samples were removed from the container after each one hour. The ozone treated fibers were immediately pounded in nonionic surfactant solution for one hour to remove the residual ozone. A concentration of 1 g/L of nonionic surfactant in distilled water was used for this solution. After that distilled water was used for rinsing the treated fibers and then dried in an oven at 105 °C for 3 hours. So according to plan there were six samples.

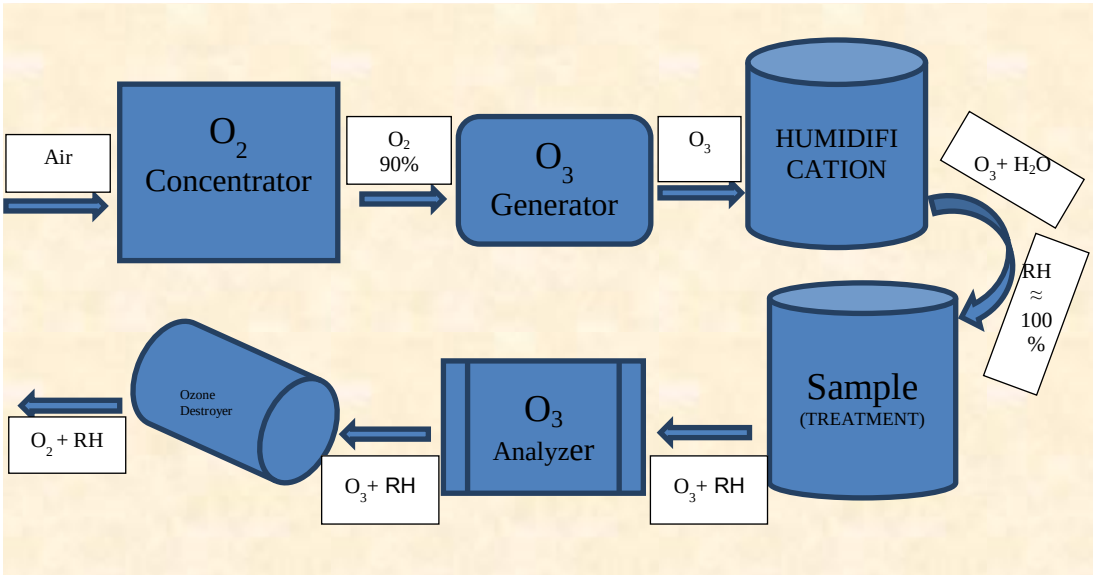


Figure 5. Schematic diagram of the Ozone Treatment Setup.

4.2.1 Optimised parameters for tenacity and weigth loss after oxidation

Using software of DESIGN EXPERT, independent variable parameters including oxygen flow rate, ozone power and time for ozone treatment was optimized keeping in view minimum tenacity value and target for weight loss of fibers at 7 %. Following optimum values were derived from the software after processing the data of design of experiment and the values of responses in the runs designed by the same software.

Oxygen flow rate	=	5.160 Liters per minute
Ozone power of generator	=	50.271 % and
Time for ozone treatment	=	4.024 hours

4.3 Characterization of Ozonized waste jute fibers

4.3.1 Fiber Topography:

The surface topography of jute fibers (untreated and ozone treated) was observed by scanning electron microscope. An accelerated voltage of 20 kV was selected for SEM images on TS5130-Tescan Scanning Electron Microscope.

4.3.2 FTIR analysis:

Fourier Transform Infrared Spectroscopy (FTIR) analysis was utilized for the quantitative study about the removal of lignin and modification of internal physical microstructure of the jute fibers after ozone treatment. It was done on Nicolet 6700 reflection ATR technique on an adapter with a diamond crystal.

4.3.3 Wide Angle X-Ray Diffraction for evaluation of crystalline structure:

The crystalline structure of the jute substrate, before and after the action of ozone gas, was investigated using Wide-angle X-ray Scattering by means of an X'Pert Pro System (PANalytical, Netherlands) with Cu Kα (λ=0.154 nm) source and operating at 40 kV and 30 mA. Prior to the measurements, jute fibers were ground to obtain powder specimens. The diffraction profiles were obtained in the 2θ range 10 – 35° with 0.02° step.

4.3.4 Fiber tensile properties:

VIBRODYNE Lenzing Instruments was used for measuring the tensile properties including fiber Tenacity and Elongation at Break Percentage of untreated and ozone treated jute fibers. A crosshead speed of 10 mm/min, pre-tension of 2000 mg and a gauge length of 10 mm was used for the tensile properties measurement. Average and standard deviation of 50 observed values for each sample were calculated.

4.3.5 Degree of Reflectance and Lightness Value:

Spectraflash 600 was being used to measure the degree of reflectance corresponding to the wavelength in the visible light range. *L, a & b* values were also found out on the same equipment. The change in the shade of the jute samples after Ozone treatment was described by graphical representation of the *L* (Lightness) values of the samples.

4.3.6 Moisture absorption:

The moisture absorption behavior of untreated and Ozone a treated jute fiber was also assessed by measuring moisture regain percentage values of the samples. For this purpose preconditioned samples in a standard atmospheric conditions (relative humidity = 65 ± 4 % and temperature = 20 ± 2 °C) for 24 hours were placed in an oven at 105 °C for drying up to the point where there was no further loss in mass (Oven Dry mass).

4.3.7 Copper number:

Copper number is the weight of Copper from Cu^{2+} to Cu^{+} state reduced by 100 gm of dry cellulose and is a measure of its inter and intra chain breakdown. It is an expression of the reducing power of degraded celluloses. Oxidation of cellulose can produce ring fission of the

glucose residues, resulting in the formation of aldehyde groups at carbon atoms 2 and 3. The copper number was measured using a standard Czech test method (CSN 80 0600) for the determination of the weight of copper in cellulose materials [44].

5. Summary of the results achieved

5.1 Oxidation of Jute fibers by Ozone

The usage of Ozone gas was increased greatly over the last two decades and have been used for the treatment of ground and industrial wastewaters [45]. Ozone affects lignin and hemicellulose giving water soluble products without damaging cellulose. Following results obtained by the treatment of jute fibers with Ozone gas in humid atmosphere for different times.

5.1.1 Apparent changes in jute fibers after ozone treatment

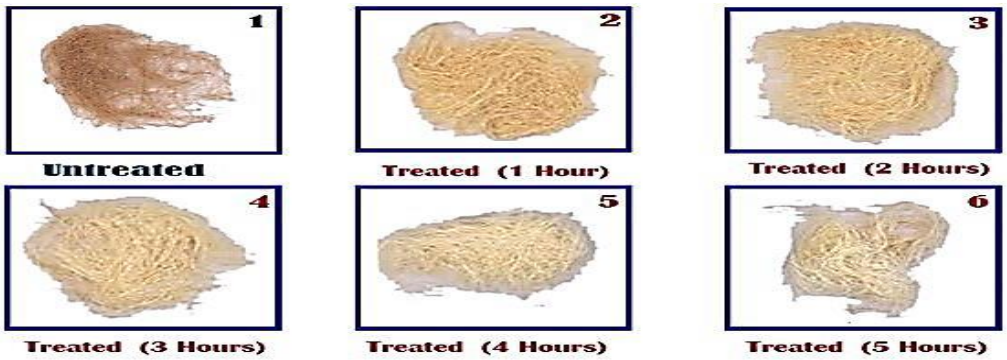


Figure 6. Apparent change in color of untreated and Ozone treated samples of jute

5.1.2 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared (FTIR) Spectroscopy results were taken for the untreated and treated Jute samples to check the non-cellulosic contents in the substrate before and after the action of ozone. Functional groups assignments and their respective interactions of Jute fiber can be deduced using FTIR Spectra (Fig. 7). Natural fibrous specific bands and their corresponding bonding interactions have been studied by numerous researchers [46], [47]. There is some variation in the reported bands from one researcher to another; however the difference is not too significant because most natural fibrous materials are made up of celluloses, hemicelluloses and lignin.

Peaks at 1370, 1316, 1238, 1157 and 1103 cm^{-1} raw jute fiber samples are due to cellulose related group were changed to variable extent after treatment indicated successful interaction of ozone with jute fiber that may result in removal of impurities from fiber surface. The absorption band at 1316 cm^{-1} can be attributed to the symmetrical deformation of NO_2 in the cellulose azo compound [48].

Absorption peaks at 1048 cm^{-1} and 897 cm^{-1} are associated with C -- O stretching and β-glycosidic linkages of the glucose ring of cellulose were shifted to high wave number [49].

These absorptions are consistent with those of a typical cellulose backbone [50] and showed that the structure of cellulose had not been smashed after the ozonation. It could be summarized that ozone treatments removed most of the lignin and cellulose contents and changed nature of fiber.

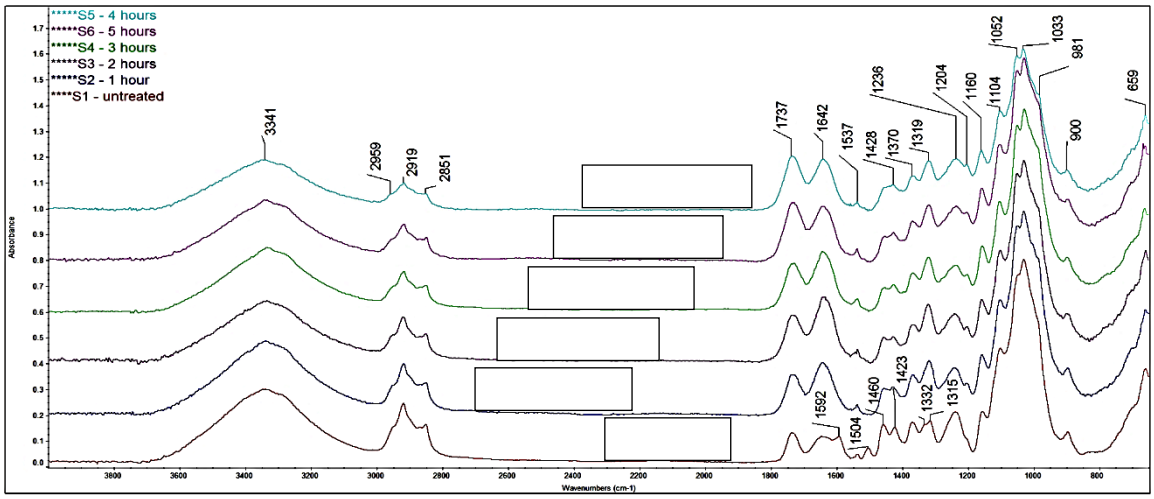


Figure 7. FTIR Spectra of Untreated and Ozone treated Jute samples

5.1.3 Mechanical Properties of Ozone treated Jute Fibers

5.1.3.1 Tenacity:

For the comparative study of the tensile properties of untreated and treated fibers, Standard Test Method for Tensile Strength and Young's Modulus of Fibers (ASTM C1557-14) was followed and the tenacity measured for the untreated jute fiber was found to be 44.16 cN/Tex. Ozone treated fibers showed declined values of tenacity with the increasing of treatment time (Fig. 8). The treated sample with time 1, 2, 3, 4 and 5 hours exhibited the value of tenacity as 31.61, 23.12, 19.75, 16.01 and 8.12 cN/Tex respectively. This decrease may be attributed to significant delignification and destruction of cellulosic chains through the ozone treatment [44].

5.1.3.2 Elongation at Break (%):

The elongation at break examined according to the Standard Test Method for the untreated jute fiber [43] and it was observed to be 3.28 %. Ozone treated samples showed declined values with the increasing of treatment time as shown in figure 9. The treated samples corresponding to treatment time 1, 2, 3, 4 and 5 hours revealed 2.32, 2.14, 1.89, 1.80 and 1.04 % of Elongation Percentage at Break correspondingly. The elongation at break in these fibers also decreased very much with the increment of treatment time. The fall in elongation at break from 3.28 % to 1.04 % could be correlated to disbanding of amorphous region after ozonation of jute fibers.

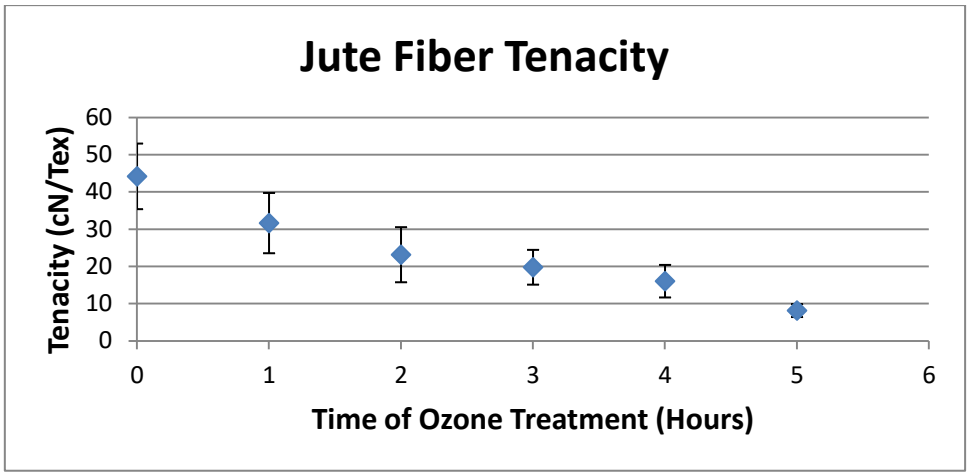


Figure 8. Decreasing trend of Tenacity with ozone treatment time (Error Bars = ± 2δ)

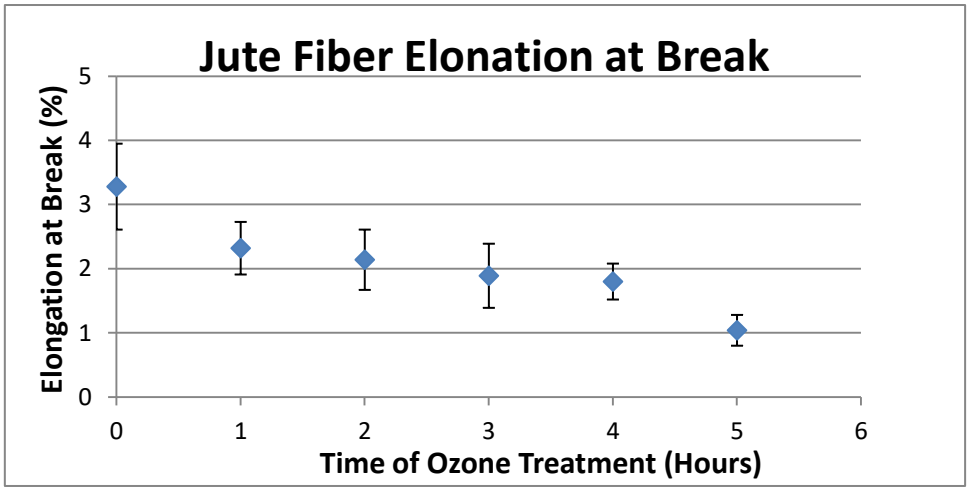


Figure 9. Elongation at Break (%) with Ozone treatment time (Error Bars = ± 2δ)

5.1.4 Copper number:

It was measured to assess the degradation of cellulose by ozonation and the formation of aldehyde groups in this experiment. Results show that the copper number increased with the increase in treatment time gradually i.e., 2.26 after two hours and 2.35, 2.44, 2.43 after three to five hours respectively (Table 2). The value of the copper number at 4 hour of ozone treatment is high and at this point oxidation is enough for the some useful purposes like production of micro/Nano crystals of cellulose. After five hours of treatment copper number has a slight decrease looking abnormal which may be due to some noise or human error.

Table 2. Copper number of the samples

Jute Fiber	Sample Number	Copper number
Untreated	01	1.2
Treated with O_3	02	2.26
	03	2.26
	04	2.35
	05	2.44
	06	2.43

5.1.5 Moisture absorption:

The moisture absorption tendency of ozonized jute fiber was increased as compared to untreated jute fibers. The moisture regain percentage value of 5 hours ozonized jute fibers was enhanced up to 22.3 %, whereas untreated jute fibers had only 10.5 % moisture regain.

5.1.6 Evaluation of crystalline structure by XRD:

WAXD results were taken for the untreated and ozonized Jute samples to analyze the influence of ozone treatment on crystalline structure of studied material. In figure 10, the comparison of X-ray profiles recorded for all studied Jute samples are presented.

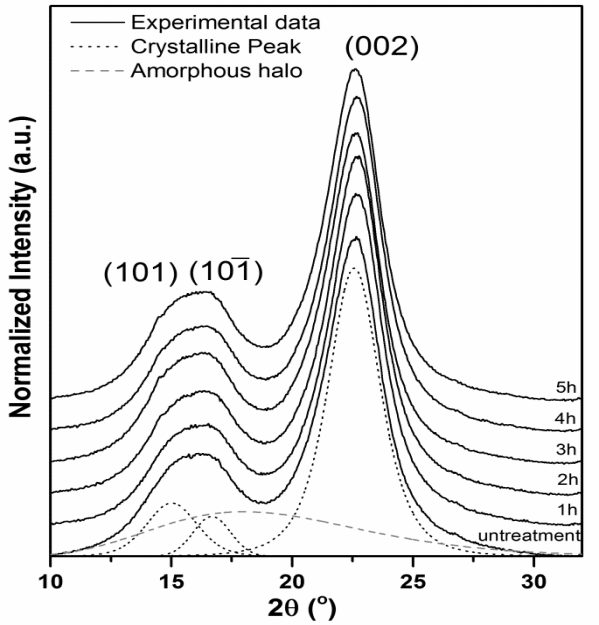


Figure 10. X-ray Diffraction Profiles of Untreated and Ozone Treated Samples of Jute Fiber

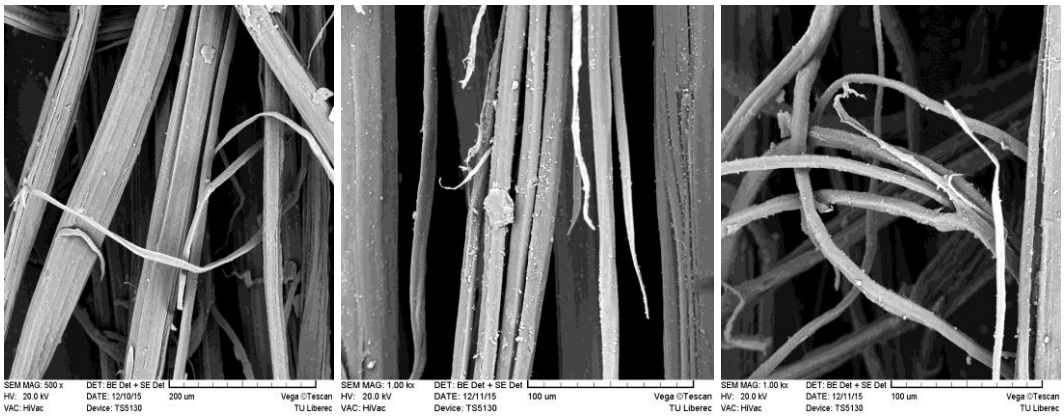
Table 3. Crystalline parameters of studied samples.

Sample	$L_{(101)}$ (nm)	$L_{(10\bar{1})}$ (nm)	$L_{(002)}$ (nm)	χ_c (%)
Untreated	3.63	4.92	3.54	68.5
1h	3.81	4.97	3.60	69.1
2h	3.81	5.18	3.64	69.8
3h	3.82	5.36	3.65	70.1
4h	3.82	5.31	3.68	70.0
5h	3.87	5.32	3.68	70.4

5.1.7 Fiber Topography/SEM Images:

Samples were analyzed under the scanning electron microscope (SEM) to check the changes in fiber surface appearance due to the Ozone treatment (Fig. 11).Clear changes in surface morphologies were observed after ozone treatment. SEM images showed a comparatively smooth surface for untreated fibers; however, after ozonation, all the fibers exhibited uneven

surfaces [51]. Figure 11(a) was taken at grid of 200 micrometer to view the surface of untreated jute fiber in spite of 100 micrometer grid as the fibers were in bundles. SEM images of treated samples at 4 hours and 5 hours shown in figure 11 (b) and (c) were taken at 100 micrometer grid as these fibers were no more in bundle form. Untreated sample viewed with SEM revealed that the fibers were closely packed with each other in bundles. In case of untreated jute fibers, there were many substances like lignin, hemicellulose, pectin and waxy elements etc. on the surface of jute fibers. On the other hand, the ozone gas created many modifications on the surface of the fiber. With Ozone treatment the bond between individual fibers damaged considerably along with increased rough surface. Results clearly exhibited that with the increase in treatment time of ozone the roughness in fiber surface is also increasing.



a) Untreated b) 4 hour treatment c) 5 hour treatment

Figure 11. SEM Images of Untreated and Ozone Treated Samples of Jute Fiber

5.2 Preparation of jute fibers for enzymatic hydrolysis

5.2.1 Pre-treatment of short jute fibers

In order to remove the non-cellulosic contents in jute fibers, chemical and ozone pre-treatment was carried out before the enzyme hydrolysis.

5.2.1.1 Chemical pre-treatment.

It was carried out sequentially with 4 % sodium hydroxide (NaOH) at 80 ^{o}C for 1 hour and with 7 g/l sodium hypochlorite (NaOCl) at room temperature for 2 hours under a pH of 10-11. Subsequently, the fibers were antichlor treated with 0.1 % sodium sulphite at 50 ^{o}C for 20 min.

5.2.1.2 Ozone pre-treatment.

Jute fibers were treated with ozone gas for the duration of four hours. For effective ozone treatment, one humidification system was introduced between Oxygen Concentrator Krober MEDIZINTECHNIK and Ozone Generator TRIOTECH GO 5LAB-K as shown in figure 26. The jute fibers were pre-humidified by spraying 50 % water (w/w) and then vertically hung inside the container for ozone treatment of 4 hours. The ozone concentration 4.5 mg/L with

charging time of 1.5 min was used. The oxygen production setting of 5.0 L/minute was used as an input source for the Ozone Generator. After ozone treatment, the jute fibers were washed with 1 g/L nonionic surfactant for 1 hour in order to remove residual ozone. The fibers were then rinsed by distilled water and dried at 105 ^{o}C in an oven for 3 hours.

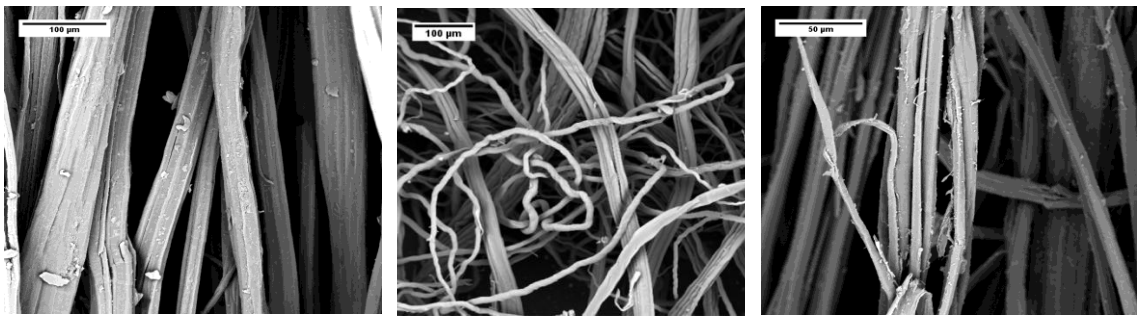
5.2.2 Characterization of pre-treated jute fibers

5.2.2.1 Single fiber strength.

The single fiber strength of untreated, chemical and ozone treated jute fiber was evaluated from VIBRODYNE Lenzing Instruments in order to know the change in mechanical properties. The single fiber strength was performed with a gauge length of 10 mm at a crosshead speed of 10 mm/min and at a pre-tension of 2000 mg. Total 50 readings were taken and then average was calculated. In the end, the additional properties like moisture absorption, whiteness index, etc. were also determined.

5.2.2.2 Surface morphology of fibers used for enzyme hydrolysis.

The removal of non-cellulosic contents after the action of chemical and ozone pre-treatment was studied from the morphology of jute fibers. According to the SEM photographs shown in figure 12(a), it can be clearly seen that untreated jute fibers have a smooth surface and the individual fibers are closely packed together in bundle form. However, when jute fibers were subjected to chemical and ozone pre-treatment, the bond between individual fibers weakened significantly. From figure 12(b), the chemically treated jute fiber revealed significant reduction in fiber diameter and higher fibrillation tendency, which indicated removal of non-cellulosic contents to the greater extent including lignin, hemicelluloses and pectin [19].
Nevertheless, ozone treated jute fibers in figure 12(c) exhibited uneven rough surfaces, peeling and breaking, which indicated only partial removal of non-cellulosic contents such as lignin but not hemicelluloses or pectin.



a) UTJF b) CTJF c) OJTF

Figure 12. SEM image of Different Jute fibers used for Enzymatic Hydrolysis

5.2.2.3 FTIR spectroscopy.

FTIR analysis was carried out to confirm the presence of non-cellulosic contents in jute fibers after the action of ozone pre-treatment. Figure 13 shows the FTIR spectra of UTJF and OTJF. A broad absorption band in the range of 3300 - 3500 cm^{-1} represented OH stretching vibrations of cellulose and hemicelluloses. The peak at 1738 cm^{-1} is attributed to acetyl and uronic ester groups of hemicellulose or the ester linkage of carboxylic group of ferulic and p-coumaric acids of lignin and hemicelluloses [19]. This peak was found to decrease in the spectrum of OTJF to explain the partial removal of lignin after ozone pre-treatment. The peak

at 1642 cm^{-1} represents aromatic vibration of benzene ring in lignin. The absorption band at 1537 cm^{-1} is due to CH_2 bending in lignin, whereas the peak at 1423 - 1460 cm^{-1} is due to OH in-plane bending [52]. The band at 1236 cm^{-1} corresponds to C-O stretching of acetyl group of lignin [53]. The reduced height of these peaks in OTJF confirmed removal of lignin after ozone treatment. The peaks at 1030 cm^{-1} and 995 cm^{-1} are associated with C-O stretching and C-H rock vibrations of cellulose[53]. The growth of these peaks in spectra of OTJF over UTJF showed increase in the percentage of cellulosic components after ozone treatment.

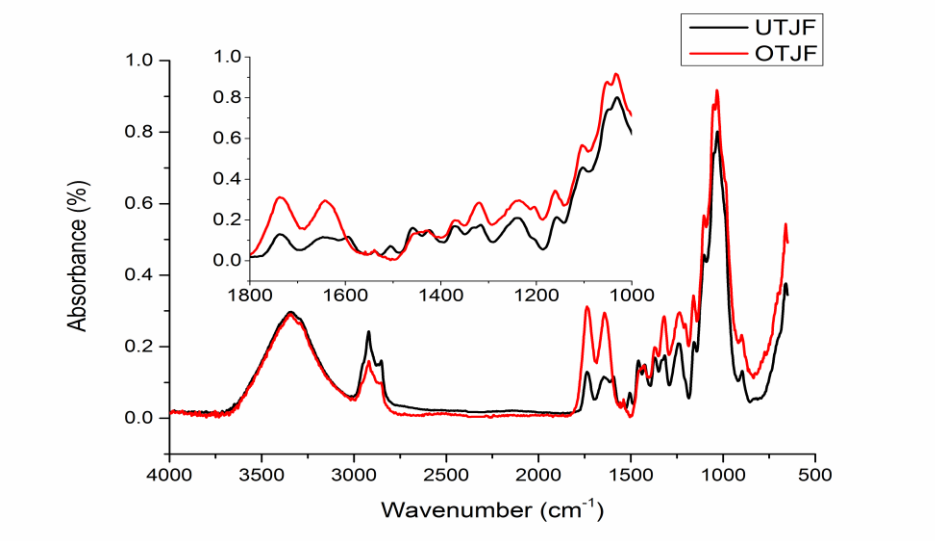


Figure 13. FTIR spectra of untreated and ozone treated jute fibers

5.2.2.4 Mechanical properties.

From figure 14 and table 4, the tenacity and breaking elongation of jute fibers was found to reduce after chemical and ozone treatment. The maximum reduction in tenacity was observed in case of OTJF, where it dropped from 44.16 cN/tex to 16.01 cN/tex after four hours of ozone treatment. This behavior is attributed to non-uniform removal of lignin and subsequent formation of more uneven rough surfaces, peeling, breaking and fibrillation of jute fibers after the ozone treatment shown in figure 12(c). The drop in breaking elongation from 3.28 % to 1.80 % could be related to dissolution of amorphous region after ozone treatment of jute fibers. This clearly showed that crystalline structure of jute fibers could not be disintegrated and rupture of cellulose macromolecules could be avoided by proper control over ozone induced surface modification of fibers. In spite of more fibrillation, CTJF was found to have higher mechanical properties than OTJF. This was due to more uniform removal of non-cellulosic substances from jute fibers after chemical pre-treatment shown in figure 12(b). Maximum fiber strength of untreated jute fiber is attributed to presence of lignin, which holds the number of fibrils together in bundle form shown in figure 12(a). The pattern of mechanical properties of UTJF, CTJF and OTJF was also evident from SEM images and FTIR analysis discussed in the previous sections.

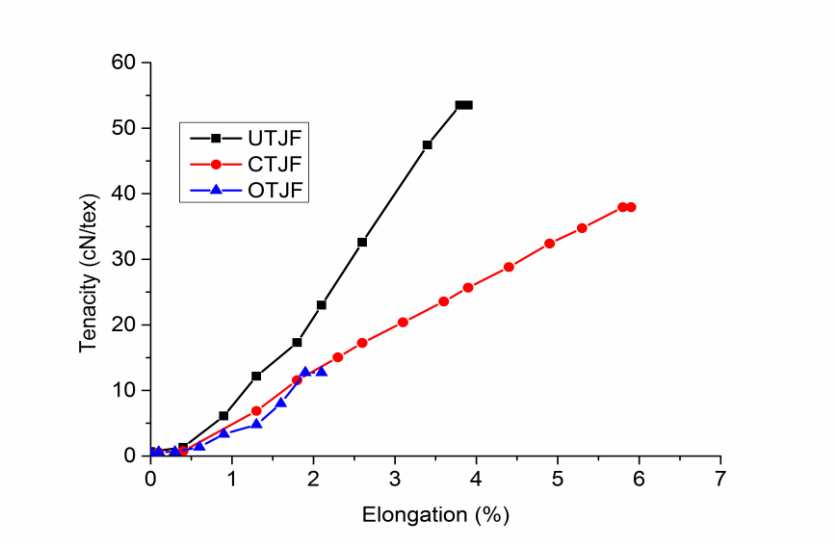


Figure 14. Single fiber strength of untreated and pre-treated jute fibers

Table 4. Mechanical properties of untreated and pre-treated jute fibers

Sample name	Initial modulus YM1 (cN/tex)	Tenacity (cN/tex)	Elongation (%)
UTJF	898.64±140.48	44.16±8.81	3.28±0.67
CTJF	266.28±73.78	28.39±6.34	6.98±1.10
OTJF	201.32±84.74	16.01±4.37	1.80±0.28

5.2.2.5 Moisture absorption.

The ozone treated jute fiber was found to have maximum moisture absorption tendency than untreated jute fibers. The moisture regain of ozone treated jute fibers was found near 22.3 %, whereas 10.5 % for untreated jute fibers. This behavior is attributed to the increased uneven rougher surfaces of ozone treated jute fibers, which provided additional specific surface area and pores for moisture absorption. Another reason for more moisture absorbency could be weakening of amorphous region after the ozone treatment.

5.3 Influence of enzyme hydrolysis on pre-treated jute fibers

The separated jute micro crystals after 6 days of enzyme hydrolysis are shown in figure 16. The particle size distribution of jute crystals obtained from UTJF, CTJF and OTJF are depicted in figure 15 respectively. The pre-treatment of jute fibers was found to have significant effect on particle size reduction and particle size distribution of obtained jute micro crystals. The average particle size of UTJMC, CTJMC and OTJMC was observed as 5392 nm, 3743 nm and 4238 nm respectively from dynamic light scattering measurements. This clearly indicated easier separation of individual micro crystals after pre-treatment of jute fibers. On the other hand, the maximum resistance for enzyme hydrolysis was found in case of UTJF due to presence of non-cellulosic contents which hold the fiber bundle together [32].

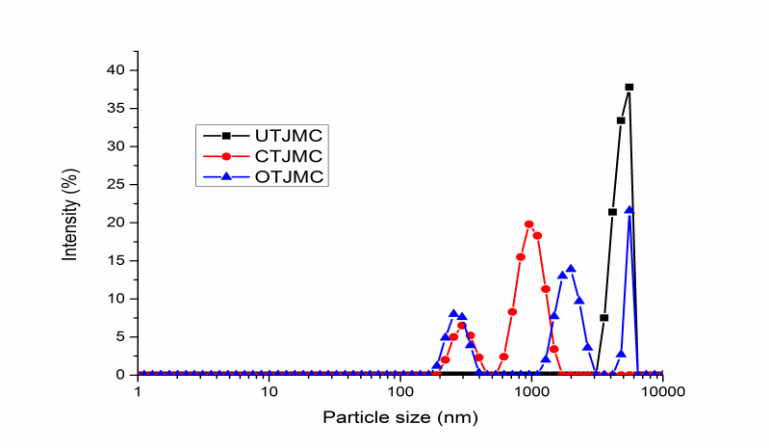
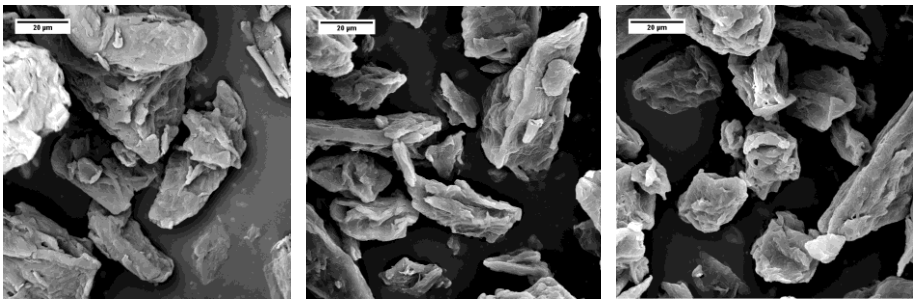


Figure 15. Particle size distribution of jute micro crystals

The enzyme hydrolysis of OTJF was found to result into bigger crystals having wider size distribution than CTJF. This behavior is attributed to non-uniform and partial removal of non-cellulosic contents by ozone treatment, which further offered relatively higher resistance for diffusion of cellulase enzyme into the jute fibrous structure [9]. This resulted into uneven dissociation of glucosidic bonds from surface to core of the cellulose in ozone treated jute fibers and consequent non-uniform separation of micro crystals having wider size distribution. The similar results were also evident from SEM images shown in figure 16(a), figure 16(b) and figure 16(c). The micro crystals obtained after ozone pre-treatment found to exhibit both cylindrical and spherical morphology as shown in figure 16(c), whereas those obtained after chemical pre-treatment revealed only cylindrical morphology with higher aspect ratio shown in figure 16(b).



a) UTJMC b) CTJMC c) OJTMC

Figure 16. SEM images of Jute Micro Crystals obtained by Enzyme Hydrolysis

The yield of obtained crystals was calculated from the percentage of ratio of dry mass of micro crystals to the initial dry mass of jute [54]. The obtained lower yield of less than 10 % in all cases indicated significant amount of conversion of cellulose into glucose, cellobiose, cellotriose, and cellotetraose by the action of enzymes [55].

5.4 Utilization of cellulose particles in composites

These cellulose particles obtained after the enzymatic hydrolysis of different treated jute fibers were then utilized in composites as reinforcement.

5.4.1 Preparation of PLA composite films

The composite films of 3 wt. % filler content were prepared by mixing the calculated amount of UTJMC, CTJMC and OTJMC into chloroform solution of 5 wt. % PLA using a magnetic stirrer. One neat PLA film was also prepared without addition of jute micro crystals for comparison purpose.

Neat PLA film and the film reinforced with cellulose micro crystals were prepared by solvent casting technique and different functional properties of these composite films were measured. The descriptions of the measured properties are described below.

5.4.2 Characterization of composites

5.4.2.1 Thermal behavior of PLA composite films.

DSC analysis was carried out to study the thermal behavior of PLA after addition of UTJMC, CTJMC and OTJMC. Table 5 shows the results of glass transition (T_g), followed by cold crystallization (T_{cc}), and melting point (T_m). It was observed from figure 17 that T_g value of PLA increased only marginally after incorporation of CTJMC and OTJMC, and reduced after addition of UTJMC. This indicated lesser flexibility of PLA chains due to some improvements in intermolecular interactions, steric effects, and the cross linking density between pre-treated jute micro crystals and PLA [56]. As compared to T_g, the melting temperature T_m of PLA was found to increase significantly after addition of CTJMC and OTJMC. This behavior is attributed to increase of PLA crystallinity after addition of CTJMC and OTJMC as reported in table 5 [57]. The lower cold crystallization peak observed in case of composite films of CTJMC and OTJMC further indicated nucleating behavior of pre-treated jute micro crystals for development of crystallinity through trans crystallization phenomena [7]. The absence of cold crystallization peak in UTJMC/PLA sample showed inability of UTJMC to develop PLA crystallinity. This behavior is attributed to the non-cellulosic substances (i.e. wax) present on the surface of UTJMC, which reduced the interaction between PLA and UTJMC.

Table 5. Behavior of neat and composite PLA films on application of heat

Sample	T_g (^oC)	T_{cc} (^oC)	T_m (^oC)	ΔH (J/g)	Crystallinity (%)
Neat PLA	42.35±0.30	98.85±1.10	147.49±0.10	17.33±2.80	18.63
3% UTJMC+PLA	40.01±0.43	-	153.00±0.18	19.26±3.21	21.35
3% CTJMC+PLA	44.84±0.34	96.88±1.39	155.47±0.14	24.53±2.34	27.19
3% OTJMC+PLA	45.01±0.47	96.52±1.22	154.32±0.13	23.09±2.03	25.59

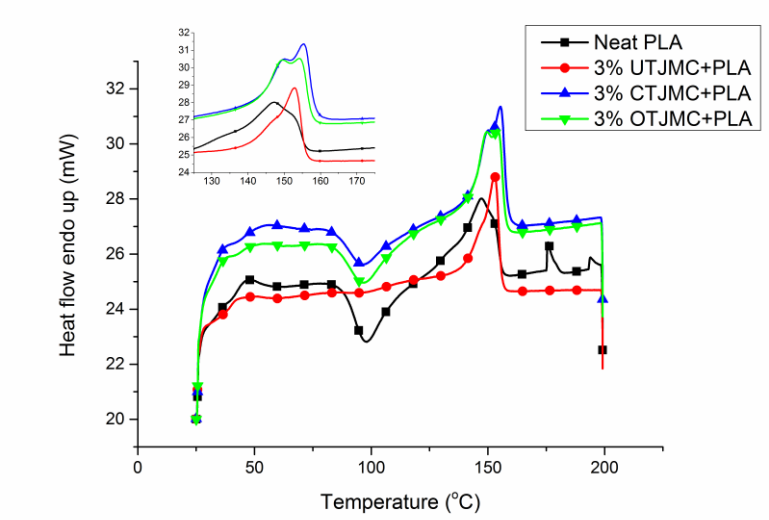


Figure 17. Differential scanning calorimetry of neat and composite PLA films

5.4.2.2 Thermo-mechanical properties of PLA composite films

The dynamic mechanical analysis was performed to get an idea about reinforcement potentials of jute micro crystals obtained before and after pre-treatments of jute fibers. The load bearing capacity of neat and composite PLA films is shown in figures 18 & 19 along with table 6. From evaluation of figure 18, all samples of PLA composite films were found to exhibit higher storage modulus results at 35 ^{o}C as compared to neat PLA film. This behavior is attributed to the efficient stress transfer from PLA to stiff jute micro crystals at 35 ^{o}C [58]. The maximum reinforcement was provided by jute micro crystals (JMC) obtained after pre-treatment (i.e. CTJMC and OTJMC) than those obtained from raw untreated jute fibers (i.e. UTJMC). The storage modulus of PLA composites at 35 ^{o}C increased from 3.09 GPa to the level of 4.11 GPa, 5.16 GPa and 5.13 GPa after the addition of UTJMC, CTJMC and OTJMC, respectively. This trend is attributed to rough surface of OTJMC and less non-cellulosic substances in CTJMC, which dispersed them uniformly within PLA matrix and consequently resulted into maximum surface area of micro crystals interacting with PLA. The least improvement in case of PLA/UTJMC can be attributed to the poor bonding of UTJMC with PLA due to presence of non-cellulosic contents like wax on the surface of UTJMC.

Table 6. Storage modulus of neat and composite PLA films at different temperature

Sample name	*E'* (35 ^{o}C) (GPa)	*E'* (60 ^{o}C) (GPa)
Neat PLA	3.09±0.20	0.48±0.02
3 % UTJMC+PLA	4.11±0.72	0.16±0.01
3 % CTJMC+PLA	5.16±0.58	0.24±0.01
3 % OTJMC+PLA	5.13±0.51	0.17±0.01

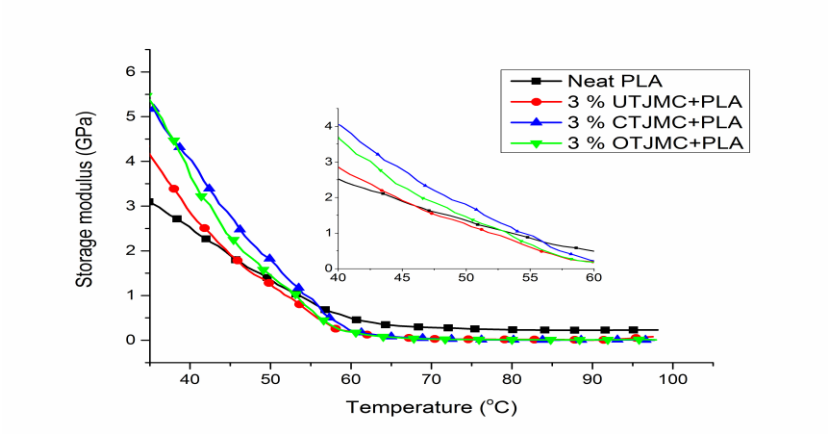


Figure 18. Storage modulus of neat and composite PLA films

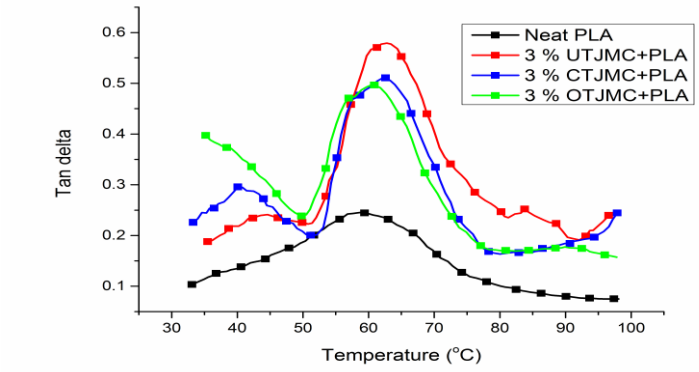


Figure 19. Damping factor of neat and composite PLA films

The concept of addition of jute micro crystals for improvement of load bearing capacity of PLA was found negative at higher temperature of 60 °C. With the increase in temperature from 35 to 60 °C, the storage modulus of PLA composite films was dropped at faster rate than neat PLA film. This showed inability of jute micro crystals to restrict the motion of PLA chains at higher temperature and thus poor transfer of stress from matrix to micro crystals. This behavior was found not in agreement with previous results [57]. The reasons could be micro scale dimensions of jute crystals, which were unable to penetrate between the PLA chains.

The ratio of loss modulus to storage modulus is defined as mechanical loss factor or tan delta. The damping properties of the material give the balance between the elastic phase and viscous phase in a polymeric structure [59]. Figure 19 showed that the tan delta peak of PLA was positively shifted after the addition of all different types of jute micro crystals. The maximum shift of 5 ^{o}C was reported in case of CTJMC/PLA composites due to their clean surfaces for maximum interaction with PLA. This subsequently restricted segmental mobility of the PLA chains around them and improved the damping factor of composites.

5.4.2.3 Tensile properties of PLA composite films

The stress–strain curve of neat PLA and its composite films is shown in figure 20, whereas average values and standard deviations of mechanical properties are reported in table 7. It is clear from results that PLA composite films of pre-treated jute micro crystals show higher mechanical properties than those jute micro crystals obtained from untreated jute fibers. The

maximum increase in tensile strength and initial modulus was found in case of CTJMC/PLA, which is an indication of better stress transfer across the interphase due to good interfacial bonding between CTJMC and PLA matrix[60]. This behavior is attributed to less non-cellulosic contents in CTJMC, which consequently improved their compatibility with PLA matrix as compared to other jute micro crystals. The higher mechanical properties of OTJMC/PLA over UTJMC/PLA composite films are attributed to rough uneven surfaces of OTJMC, which provided increased surface area of interaction than UTJMC.

Table 7. Tensile properties of neat and composite PLA films

Sample name	Initial modulus (GPa)	Tensile strength (MPa)	Yield point elongation (%)
Neat PLA	1.04±0.03	25.98±0.13	4.84±0.72
3 % UTJMC+PLA	1.41±0.07	22.72±0.47	1.60±0.50
3 % CTJMC+PLA	1.63±0.04	34.92±0.39	2.14±0.41
3 % OTJMC+PLA	1.55±0.03	30.40±0.41	1.96±0.47

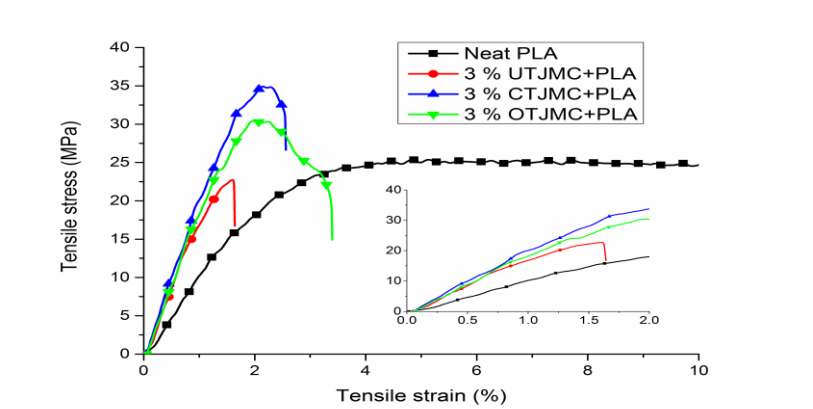


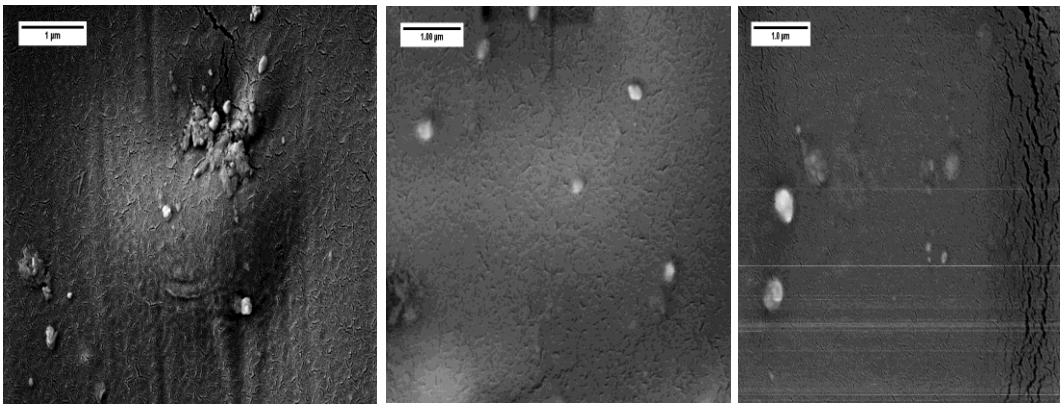
Figure 20. Stress-strain curve of neat and composite PLA films

Moreover, the increase in crystallinity of PLA discussed in section 5.4.2.1 was also found to have significant effect on mechanical properties. With increase in crystallinity, the brittleness of PLA also increased. This subsequently resulted into reduction in yield point elongation and increase in initial modulus of all PLA composites. In addition, the tendency of stress concentrations due to stiff nature of jute micro crystals could also be considered for reduction in yield point elongation.

5.4.2.4 Microscopic evaluation of different composite films

In order to get clear idea of interaction between PLA and different jute micro crystals, the morphology of composite films was investigated under FESEM microscopy. The absence of voids, intact position of fillers, interfacial bonding between fillers and matrix, and absence of agglomerations of fillers decide the intensity of filler–polymer adhesion [61]. It is clear from figure 21(a), 21(b) and 21(c) that the presence of non-cellulosic contents and roughness of jute crystals affect the homogeneous dispersion and tendency of agglomerations in composites. From figure 21(b) and figure 21(c), the composite films of CTJMC and OTJMC

revealed uniform dispersion with minimum agglomerations due to their respective clean and rough surfaces having minimum percentage of non-cellulosic contents. The intact position of CTJMC and OTJMC confirmed stronger interaction between them and PLA due to their uniform wetting. On the other hand, figure 21(a) for composites films of UTJMC showed significant agglomerations as a result of poor bonding caused by their smooth surfaces having more non-cellulosic substances. The gap around the surface of UTJMC in PLA confirmed their poor interfacial adhesion.



a) UTJMC/PLA b) CTJMC/PLA c) OJTMC/PLA

Figure 21. Morphology of different composite films

6. Evaluation of results and new findings

6.1 Prediction Model using Generalized Rule of Mixtures

When we consider simple rule of mixtures, it is often utilized in the prediction of various material properties such as modulus, electrical, thermal conductivity etc. However, in most cases, the prediction models underperform and don't predict the system properties accurately. It is due to the fact that there are various interactions present in the system.

The values of tensile modulus of the composites were plotted against the volume fraction of jute micro crystals and multiple linear regressions are applied.

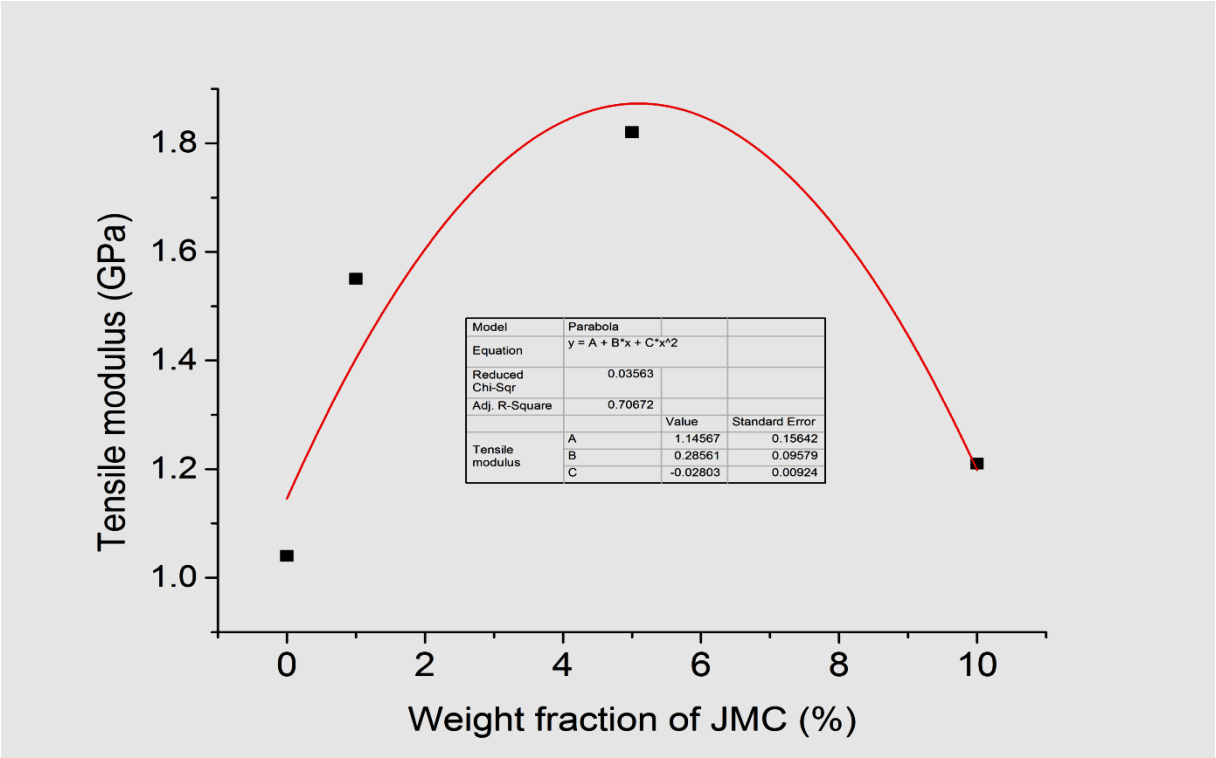


Figure 22. Prediction model using multiple linear regressions

Corresponding to figure 22, multiple linear regressions equation of the composite system as described below:

$$E = 1.146 + 0.286X_r - 0.028{X_r}^2$$

where $1.146 = E_m$; $0.286 = (E_r - E_m + I)$ and $(-0.028) = (-I)$ or

$$E_m = 1.146$$

$$E_r - E_m + I = 0.286$$

$$I = 0.028$$

(E = Composite or system modulus, E_m = Matrix modulus, E_r = Reinforcement modulus and I = Coefficient representing the intensity of interactions)

It is evident that interaction between the volume fractions of reinforcement (JMC) and matrix (PLA) in this particular system of composite films preparation enhances the overall composite system property (Tensile modulus) by at least 2.8%.

It is worth mentioning that the accuracy of generalized rule of mixtures predicts the component system up to 70.67% as shown by R^2 value.

6.2 CONCLUSIONS

The present study was focused on the development of environment friendly approach for surface treatment of jute fibers and subsequent separation of individual cellulose micro crystals. The sequential action of ozone pre-treatment followed by enzyme hydrolysis was selected for this purpose. At first, jute fibers were pre-treated with ozone gas for the duration of four hours. For comparison purpose, one sample with chemical treatment of jute fibers was also prepared. The effect of pre-treatments on mechanical properties and surface morphology of jute fibers was investigated. The maximum deterioration in mechanical properties was found in case of ozone treated jute fibers than chemically treated jute fibers. The tenacity was

dropped from 44.16 cN/tex to 16.01 cN/tex after four hours of ozone treatment. Under SEM, more uneven rough surfaces, peeling, breaking and fibrillation of jute fibers were observed due to partial removal of non-cellulosic contents after ozone treatment. On the other hand, chemical treatment revealed significant reduction in fiber diameter and higher fibrillation due to maximum removal of non-cellulosic contents. In addition, the moisture absorbency of ozone treated fibers was found higher than untreated and chemical treated jute fibers.

Later, enzyme hydrolysis was carried out to separate longer cellulose micro crystals from jute fibers. The pre-treatment of jute fibers was found to have significant effect on particle size reduction and particle size distribution of obtained jute micro crystals. The rate of refinement of untreated fibers having non-cellulosic contents was found slower than treated jute fibers due to strong holding of fiber bundles by non-cellulosic contents. The average particle size of 5392 nm, 3743 nm and 4238 nm was found for crystals obtained from untreated, chemically treated and ozone treated fibers respectively. This indicated easier separation of individual micro crystals after ozone pre-treatment. The enzyme hydrolysis of ozone treated fibers was found to result into bigger crystals of both cylindrical and spherical morphology having wider size distribution.

When jute micro crystals were incorporated in PLA matrix, the maximum reinforcement was provided by crystals obtained after pre-treatment than those obtained from raw untreated jute fibers. These improvements in mechanical properties are attributed to their rough uneven surface, higher percentage of cellulosic contents and smaller particle size. The SEM morphology of fractured surfaces also confirmed homogeneous dispersion and fewer tendencies of agglomerations due to fewer amounts of non-cellulosic contents and roughness of jute crystals. Nevertheless, the role of jute micro crystals as reinforcement of PLA was found negative at higher temperature of 60 °C. This showed inability of larger jute micro crystals to restrict the motion of PLA chains at higher temperature and thus poor transfer of stress from matrix to micro crystals. In this way, the present study showed a green process for reusing of waste jute fibers and converting them into useful cellulose powder for reinforcement in composite materials. Moreover, the ozone treatment was found attractive in terms of less energy, time and water with additional advantage of minimum degradation of cellulose.

Finally, experimental results of Initial modulus were compared with predicted modulus of mechanical models. A good level of agreement was observed from 1 to 3wt % loading of jute micro crystals and close fit with Cox-Krenchel theory indicated random orientation of micro crystals in PLA matrix. In this way, this study showed a green process for reusing of waste jute fibers and converting them into useful cellulose powder for reinforcement in composite materials.

By applying quadratic regression to the plotted actual values of obtained tensile modulus of composite corresponding to different volume fraction of jute micro crystals in the system, we got a quadratic equation using generalized rule of mixture explaining interaction of the volume fraction of jute micro crystals and PLA as well. Using this generalized rule of mixture the predicted model can be utilized for the prediction of tensile modulus corresponding to volume fraction of reinforcement and the interaction between volume fractions of reinforcement and matrix.

6.3 Future Scope of Work

Fungal treatment on cellulose fibers responsible for its degradation should be tried for degradation of fibers to obtain micro/nano particles using top down approach.

As poly(lactic acid) is an anionic matrix, cationization of the cellulose reinforcement should be tried to get better properties of the composites. In this case, ionic bonds can replace van der Waals forces and resultant composite might exhibit better properties.

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8. List of papers published by the author

8.1 Publications in journals

1. Ozonation: a Green Source for Oxidized Cotton.
Fibers and Textiles in Eastern Europe ***(Published)***

2. Reinforcement of Enzyme Hydrolyzed Longer Jute Micro Crystals in Poly(lactic acid).
Polymer Composites ***(Published)***

3. Reinforcement of ozone pre-treated and enzyme hydrolyzed longer jute micro crystals in poly lactic acid composite films.
Composites Part B ***(Published)***

4. Ozone Treatment of Jute Fibers. ***Cellulose*** ***(Published)***

5. Development and characterization of solution cast cellulose reinforced poly(lactic acid) thin film. ***Bulletin of Material Science*** ***(Under Review)***

6. Cationization of Cellulose fibers for composites.
The Journal of Textile Institute ***(Published)***

7. Effect of Cellulose Coating on Properties of Cotton Fabric.
Materials Science Forum ***(Published)***

8. Impact of Filling Yarns on the woven fabrics performance.
Fibers and Textiles in Eastern Europe ***(Accepted)***

9. Optimization of parameters for Oxidation of Jute by Ozone Treatment. ***(In Process)***

8.2 Contribution/presentations in international conferences

1. Surface treatment /cationization of cellulose fibers for composites. ***ICCMME 2016***

2. Stress Strain Curves for PES Fiber and Yarns. ***STRUTex 2014***

3. Effect of cellulose coating on properties of cotton fabric. ***ICCMME 2016***

4. Ozonation: a Green Source for Oxidized Cotton. ***Svetlanka Workshop 2014***

5. Thermal Properties of Yarn. ***Svetlanka Workshop 2015***

6. Reinforcement of cationized cellulose in anionic matrix. ***Bila Voda Workshop 2016***

7. Enzyme hydrolysis of ozone pre-treated jute fibrous wastes. ***44th TRS IIT Delhi 2016***

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Publications in journals

1. Ozonation: a Green Source for Oxidized Cotton.
Fibers and Textiles in Eastern Europe (Published)

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Contribution/presentations in international conferences

1.	Surface treatment /cationization of cellulose fibers for composites.	***ICCMME 2016***
2.	Stress Strain Curves for PES Fiber and Yarns.	***STRUTex 2014***
3.	Effect of cellulose coating on properties of cotton fabric.	***ICCMME 2016***
4.	Ozonation: a Green Source for Oxidized Cotton.	***Svetlanka Workshop 2014***
5.	Thermal Properties of Yarn.	***Svetlanka Workshop 2015***
6.	Reinforcement of cationized cellulose in anionic matrix.	***Bila Voda Workshop 2016***
7.	Enzyme hydrolysis of ozone pre-treated jute fibrous wastes.	***44th TRS IIT Delhi 2016***

Brief description of the current expertise, research and scientific activities

Doctoral studies

Studies	Textile Engineering
Field	Textile Techniques and Material Engineering
Specialization	Material Engineering
Research projects	SGS 21030, Surface treatment of natural fiber reinforcements in textile composites, project leader, 2014 SGS project, Thermal Properties of yarn, project participant, 2015

Alongwith my PhD research, I am also involved in research regarding "strong acid hydrolysis of Viscose and its applications" with Prof. Jakub Wiener.
Also participating in areas like "Experimental Tensile Force Utilization Coefficient (TFUC) of Staple Spun Yarns" with Muhammad Zubair (PhD Scholar in KTT. FT. TUL). These research works are related to SGS project.

Record of the state doctoral exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

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prospěl **~~neprospěl~~**

Komise pro SDZ:

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Místopředseda:	prof. Ing. Jakub Wiener, Ph.D.	
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	Ing. Blanka Tomková, Ph.D.	Tomková

V Liberci dne 3. 2. 2016

O průběhu SDZ je veden protokol.

Recommendation of the supervisor

Supervisor's opinion on PhD thesis of Hafiz Shahzad Maqsood

Topic: Cellulose Micro Particles from Jute

Jute is one of the longest natural fibers used for various textile applications. Jute fibers are mainly composed of cellulose and lignin. Extracting the cellulose particles from inexpensive fibrous waste is very important step in the field of greener composites.

The main goal of this PhD thesis was to explore the possibility of ozone treatment as a greener oxidation process for jute fibers. Physical appearance, fiber mechanical properties, copper number, Fourier Transform Infrared spectroscopy, Wide-angle X-aray diffraction, scanning electron microscopy, moisture regain percentage and lightness values were used to assess the effect of ozone treatment. Further, ozone degrades lignin and slightly solubilizes the hemicellulose fraction, hence changing fiber morphology. Chemical and ozone pre-treated jute fibers were hydrolyzed by cellulase enzymes for separation of longer jute micro particles. In the end, PLA composites with jute micro crystals as reinforcement were prepared and were tested for tensile properties, dynamic mechanical analysis and differential scanning calorimetry to check the effect of reinforcement. Good agreement of measured values was visible with predicted values of different mechanical models. Prediction model was developed using generalized rule of mixture applying quadratic regression on the obtained tensile modulus values of composites.

The thesis is quite systematic, all experimental procedures are written clearly and language level is quite high.

The PhD candidate has followed objective measurements for cellulose particles' evaluation. Author was studying fluently, step by step, and with care.

His publication activities are in very good level. He has 6 (six) papers in impact factor journal, 1 (one) in scopus-indexed journal and 7 (seven) presentations in international conferences.

I can say that in this work, novel ways for oxidation of jute fibres and its characterization were used. Results of this work are very good and indispensable for the use of jute fibers for the extraction of cellulose micro/nano particles.

I therefore recommend the PhD thesis for defence.

Liberec, 14.10.2016

Ing. Jana Salačová, Phd.

Supervisor

Reviews of the opponents

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-16/4814/042019, dated 10. 11. 2016) of **Hafiz Shahzad Maqsood, MSc.** entitled **"Cellulose Micro/Nano Particles from Jute"**. Tutor of the PhD. student was Ing. Jana Salačová, Ph.D. Above mentioned Ph.D. dissertation thesis deals with the topic of jute fibers application as a filler material in polymer composites. Several pretreatment techniques were used for fiber surface treatment, such as ozone and enzymatic. As a comparison an original jute fibers were used as well. There was found and described mechanism of the disintegration of the natural composite structure of the jute, its chemical modification and surface structure and topology changes. Obtained results were confirming earlier knowledge of the matter on similar products e.g. of the wood fibers bases etc. Author used many characterization techniques as well as the theoretical modeling. Majority of the results was already published in the highly respected scientific journals. The aims of the thesis were fulfilled and completed. I have found some formal errors in the text of the thesis, e.g. in quality of the figures (too small digits at the axes (e.g. Fig. 20, etc.)), text structuring etc. as well as have some questions on the applicant related to the topic studied.

1. It should be beneficial to characterize the fibers color change e.g. by Datacolor instrument and represent the results e.g. in CIE L*a*b scale or other method (page 42, Fig. 18). Can you explain why you have not done so?

2. There is missing formal kinetic modelling of the obtained dependences e.g. Fig. 19. Can you provide these data at the thesis defense and describe their statistical parameters?

3. Similar as in the point 2), there is missing a numerical as well as a statistical evaluation of data dependences in Figs. 22 and 23. Please deliver at the defense results of the ANOVA analysis.

4. With respect to all experiments performed, can you characterize the reproducibility of your measurements?

5. How do you explain negative effect of the jute filler on loading bearing capacity as shown in page 64? Please explain.

6. Explain differences obtained between applied theoretical models and experimental data of modulus vs concentration in Fig. 39?

Based on the thesis, I would like to hear answers from the applicant on the above questions.

Author has published majority of the data obtained during the PhD. studies in relatively high number of scientific papers in well-established journals (4 items published, 2 accepted, and 3 under review). Mr. Hafiz Shahzad Maqsood is the author of 7 conference proceedings.

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Hafiz Shahzad Maqsood, M.Sc. for defense.

In Zlín, December 2, 2016

prof. Ing. Ľubomír Lapčík, Ph.D.

Professor for materials science and engineering
Tomas Bata University in Zlín

Referee´s report on PhD. thesis of

Hafiz Shahzad Maqsood

„ Cellulose Micro Particles From Jute“

Professor Miroslav Černík

The presented thesis consists of 86 pages divided into 6 major chapters plus conclusions and 2 appendixes (research articles published). The thesis deals with jute fibres and their treatment for production of cellulose fibres and micro crystals. Many various techniques were investigated for jute fibres characterization after oxidation with ozone. Their properties are significantly changed after oxidation.

Chapter 1 (Introduction) is about morphology of lignocellulose fibres, techniques for separation of individual cellulose crystals and fibrils, including oxidation by ozone.

Chapter 2 (Aim and objectives) deals with extraction and characterization of jute micro/nano particles and reinforcement of biopolymers by cellulose particles.

Chapter 3 (Overview of the current state of the problem) shows different techniques for extraction of cellulose micro and nano structures.

Chapter 4 (Methods used and studied materials) deals with ozone treatment of jute fibres, and different views to changes the fibres after the oxidation process.

Chapter 5 (Summary of results achieved) is one of two main chapters of the thesis, where result are present. The jute fibres after oxidation change their colour (lightness value), FTIR spectrum and tenacity. The fibres were additionally treated by enzymatic hydrolysis to produce jute micro crystals. Three types of crystals were obtained (untreated jute micro crystals, chemical treated jute micro crystals and ozone treated jute micro crystals).

Chapter 6 (Evaluation of results and new findings) summarizes the determined results of the thesis. Untreated and ozone treated fibres were compared by SEM pictures, FTIR spectroscopy, mechanical properties, moisture absorption and whiteness index. Similarly jute micro crystals were compared. Their particle size distribution is significantly different, where after treatment significantly smaller particles (submicrone) were produced. The last part evaluates PLA composite films produced by addition of jute micro crystals.

Conclusions highlight results described in the previous chapter. Ozone treatment of jute fibres has significant influence to fibre properties. Tenacity drops significantly and dropping with increasing of oxidation time. Removal of non-cellulosic content (by oxidation) has influence to fibre diameter, fibres after treatment have smaller size. This treatment also leads to easier separation of crystals.

At the end, the author presents the paper on Reinforcement of Enzyme Hydrolyzed Longer Jute Micro Crystals in Polylactic Acid and Reinforcement of ozone pre-treated and enzyme hydrolyzed longer jute crystals in poly lactic acid composite films.

Referee remarks, question and conclusions

The thesis is logically divided into chapter, the content is explained illustratively, and all determined results are simply described. The author shows a story consists of three steps – material oxidation for production of fibres, enzymatic crystal separation and their incorporation into PLA matrix. In all steps the produced material is characterized by all available techniques and different types of treatment is compared.

QUESTIONS

1. Why ozone was selected for fibre oxidation? Have you information on various oxidation techniques for non-cellulose material removal from the fibres?
2. The three dimensional surface plots (p.36-39) are not illustrative enough for me. Could you summarize the results of these plots in more clear way?

Imperfections and recommendations

Language of the thesis is very good. I did not find many errors and mistypes. Only sometimes capital letters are used within the sentence without need.

Referee´s conclusion

The presented thesis is logic, has all necessary parts and show the author understand his work and he is able to put results logically into appropriate parts. The thesis shows one topic with different steps (oxidation enzymatic reaction, PLA matrix, characterization). The work significantly contributes to knowledge in the subject. There are no significant recommendations for next author´s work. The language is good and fully understandable.

The thesis is good and meets all criteria to be taken to the defence.

Miroslav Černík

In Liberec (Czech R.) on February 6, 2017 **Professor Miroslav Černík**