

# High Performance Eco-friendly Nanofillers from Palm Fibers

Balasubramanian K.<sup>1</sup>, Navdeep Manhas<sup>2</sup> and Sunil Nimje<sup>3</sup>

<sup>1,2,3</sup>Dept. of Materials Engg DIAT (DU), MoD Pune-411 025  
E-mail: <sup>1</sup>meetkbs@gmail.com, <sup>2</sup>navdeepmanhas@gmail.com, <sup>3</sup>sunil.nimje@diat.ac.in

---

**Abstract**—The surface functionalized cellulose nanofibrils have found commodious applications in various fields such as bio-nanocomposite, tissue engineering scaffolds and nanodevices owing to their excellent mechanical properties, sustainability and renewable nature. Therefore, the present study aspires towards fabrication of competent reinforcing nanofibrils from palm fibers, which have a greater surface area with respect to volume that leads to a superior interaction with matrix system of composite. We have demonstrated an economically viable model for isolation of nanofibrils from palm fibres employing an inexpensive chemical pre-treatment via bleaching powder. The design involves chemi-mechanical techniques which comprises of alkali treatment, bleaching and ultrasonication and are favorable for the cellulose purification and nano fibrillation through delignification and defibrillation. The alkaline treatment of leaves of palm tree with caustic soda partially removed lignin, hemicellulose, wax and oil shielding the peripheral surface of the fibre cell wall and depolymerised the native cellulose. Mercerized fibre was then subjected to 3%, 5%, 7% and 10% of bleaching solution for eradication of the remnant lignin. The optimum concentration of bleaching powder was ascertained at 5% by highest intensity characteristic peak at  $1010\text{cm}^{-1}$  in FTIR spectra which corresponds to pyranose ring skeletal vibration of cellulose. The structural and morphological characteristics of raw fibre, chemically treated fibre and isolated nanofibres were investigated through FE-SEM, which revealed substantial reduction in diameter of palm fibre to 30nm by a greener method of ultrasonication for 60 min. These fibres find extensive applications as nanofillers in structural composites for automobiles and medical fields.

**Keywords:** Paml fibers, cellulose nanofibers, chemical pretreatment, ultrasonication, delignification.

## 1. INTRODUCTION

In the recent years, there is a growing interest in the development of biodegradable and plant derived composite materials, referred to as “green” composites, because of strong global demand for creating a resource circulating society. Sustainability, industrial ecology, eco-efficiency, and green chemistry are the impetus for development of next generation materials, products, and processes [1]. The development of low-cost, sustainable, and renewable resources is critical to meet the growing environmental concerns and sky-high global energy demands [2].

In this regard, the application of renewable and biodegradable biomass fibers reinforced composite materials have been developed to get subsequent generation of sustainable and green materials in this field [3]. Cellulose being the world’s most abundant natural renewable biodegradable polymer is a classical example where the reinforcing elements exist as whisker-like microfibrils that are biosynthesized and deposited in a continuous manner [4]. Cellulose is a biodegradable, biocompatible, long chain polysaccharide with the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  composed of several hundred to over ten thousand  $\beta(1\rightarrow4)$  linked D-glucose units [5]. In nature, the cellulose chains are packed in an ordered manner to form compact nanocrystals (whiskers), which are stabilized by inter and intra-molecular hydrogen bonding [6]. In the cell wall structures of vegetable plants, cellulose nanocrystals (whiskers) are bonded together by amorphous hemicellulose segments to form micro/nanofibrils that constitute the individual cellulose fibres [7,8].

Surface functionalised Nano Cellulose Fibrils (NCFs) can be used as reinforcement in nanocomposites which are generally defined as multiphase products wherein at least one phase has a dimension of 1–100 nm [9]. Composites with nano scale reinforcements have larger surface area and lower defects in reinforcing part compared to micro size reinforced composites [10,11]. Recently, many researchers have employed cellulosic fibers as a filler or reinforcement phase instead of synthetic fibers to keep our environment safe and also because of their biodegradability, lower weight, renewability, lower cost, higher stiffness and strength [12-15].

Cellulose fibers can be fibrillated to micro/nanofibers employing mechanical as well as chemical techniques and contemporary research is targeting a combination of two to achieve optimised results. Mechanical treatments include refining and homogenizing, microfluidization, grinding, cryocrushing and high intensity ultrasonication [16-19]. Other treatments are chemical treatment of acid hydrolysis, biological treatment of enzyme-assisted hydrolysis, steam explosion, TEMPO-mediated oxidation and electrospinning. All these methods lead to cellulose nanostructures with

different morphologies and crystallinities, depending on the cellulose raw material, its pretreatment and more importantly, on the disintegration process itself [20-24]. Recently, High intensity ultrasonication (HIUS) has emerged as a greener method to isolate cellulose nanofibers wherein oscillating power is used to isolate cellulose fibrils by hydrodynamic forces of ultrasound [25]. During the process, cavitation leads to a powerful mechanical oscillating power and therefore, high intensive waves, which consists of formation, expansion, and implosion of microscopic gas bubbles when molecules absorb ultrasonic energy [26].

In the present study, an effort has been made to extract cellulose nanofibrils from palm fibers which is one of the copious natural source of cellulose implementing novel techniques. Currently, we have demonstrated an economically viable model for the isolation of nanofibre from palm fibre employing inexpensive chemical pretreatment followed by a green defibrillation process. The technique involves alkali treatment, bleaching with domestically available bleaching powder and finally ultrasonication. Alkali treatment is responsible for depolymerisation of cellulose structure and bleaching process renders delignification of the raw fibre. In our work the isolation of nanocellulose has been undertaken via facile and non-toxic method of ultrasonication which is profoundly effective in retaining the crystalline regions of pure cellulose compared to commonly used acid-hydrolysis technique. Concurrently, the presented technique of ultrasonication avoids costly setup of HIUS equipment and employs conventional and versatile Vibracell ultrasonicator making the process effortless as well as cost effective.

## 2. RAW MATERIALS

The palm fibers (PFs) as raw material for the experiment were obtained from Palm trees within the institute. The material was air dried in sunlight for 48 hrs initially and subsequently dried in oven for 24 hrs at 40°C to get rid of any moisture. HCOOH and NaOH pellets (for making 5 wt% NaOH solution in de-ionized water) were obtained from Merck (India). De-ionized water was used for all the experiments and was obtained from a Millipore Milli-Q system. The commercially available bleaching powder has been used as bleaching agent.

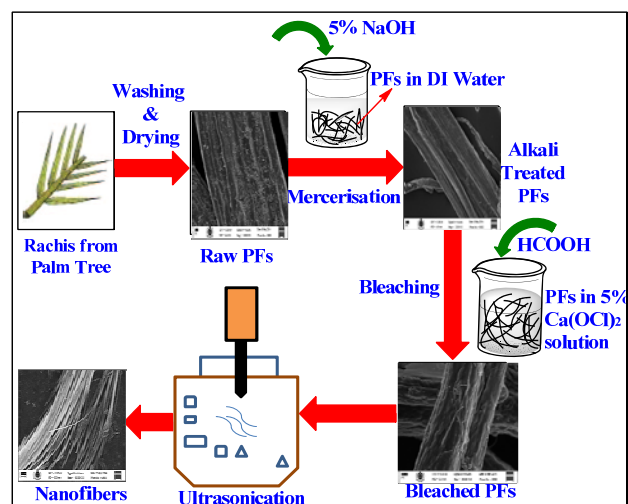
## 3. EXPERIMENTAL WORK

Fig. 1 shows the extraction process of micro/nano sized palm fibrils from raw palm. Raw PFs were extracted from rachis of Palm tree which was followed by washing with DI water and oven drying process. In alkali treatment or mercerization, fibers were immersed in 5% NaOH solution for 24 hrs at room temperature followed by heating at 60°C for 5 hrs and washing with deionised water recurrently until neutral pH was obtained. For bleaching mercerised fibers were then immersed in 3%, 5%, 7% and 10% bleaching solution. Formic acid was added drop by drop to achieve a pH of 3-4 and solution was

heated on a magnetic stirrer for 4 hrs at 60°C followed by washing with deionised water. Chemically treated fibers were then soaked in distilled water (concentration: ~0.5% in mass) and ultrasonicated using Vibracell ultrasonicator (Model VCX 750) for time intervals of 20, 40 and 60 min each. The ultrasonic treatment was carried out in an ice/water bath and energy consumption was monitored which is illustrated in table 1. Post ultrasonication the suspension was centrifuged at 12000 rpm in a high speed centrifuge (Model REMI CPR-30 Plus).

**Table 1: Parameters of ultrasonication process**

Sample No	Ultrasonication time (min)	Energy consumed per cycle (J)	Total energy consumed (kJ)	Power (W)
S1	20	2786	167.9	142
S2	40	2850	346.4	145
S3	60	2864	512.1	145



**Fig. 1: Procedure for individualizing cellulose nanofibers from PFs**

## 4. CHARACTERISATION

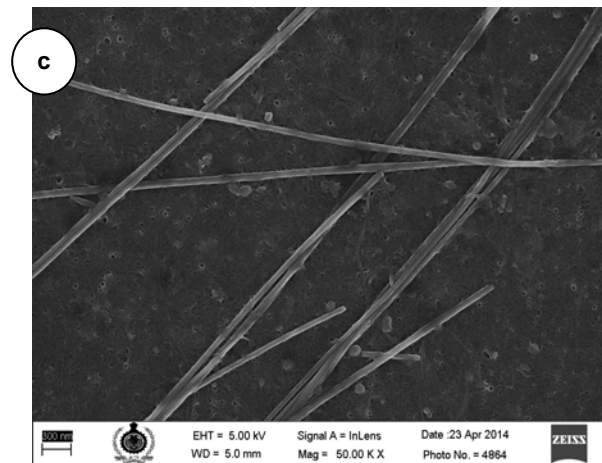
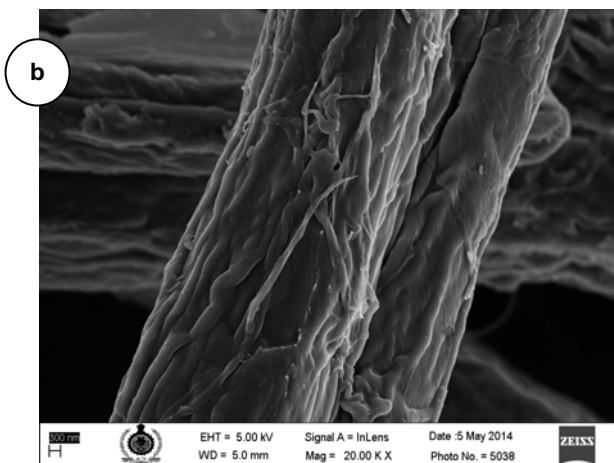
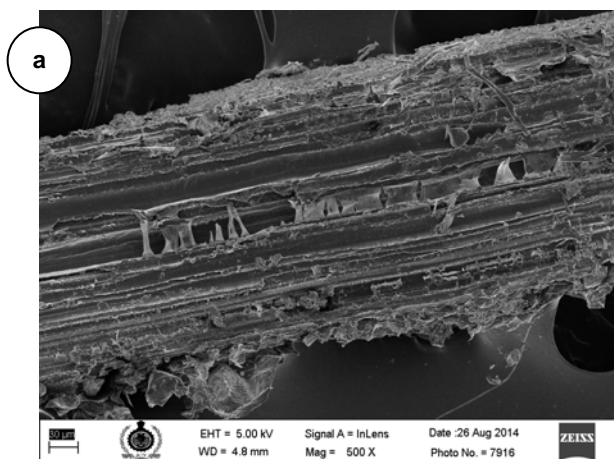
In order to analyse morphology of the suspension of palm nanofibrils, FESEM imaging (Carl Zeiss) was performed on sample prepared by drop casting. The samples were sputtered using Au-Pd for 75 seconds in 10 mA under the pressure of  $0.6 \times 10^{-2}$  Pa and analysed under the microscope at 5 kV.

Functional groups and fingerprints for the chemical modification of PFs were identified using FT-IR spectroscopy. The FT-IR spectra were recorded between 500 and 4000  $\text{cm}^{-1}$  using KBr pellets at room temperature on a PerkinElmer Spectrum BX FTIR system.

## 5. RESULTS AND DISCUSSION

### 5.1 FESEM analysis

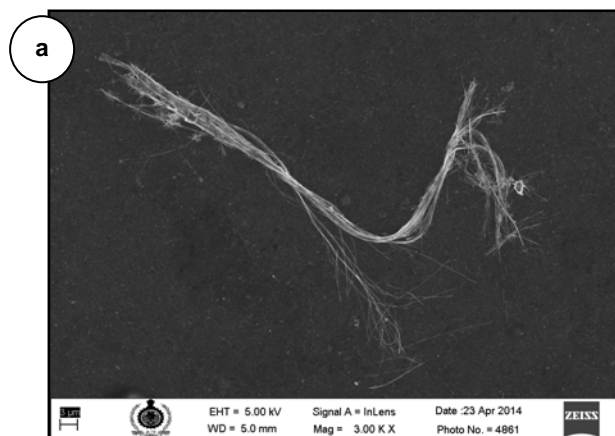
Fig. 2 shows the microscopic images of raw, bleached and ultrasonicated PFs. Each raw PFs Fig. 2(a) fibre is composed of several microfibrils with diameters in the range of 10-15  $\mu\text{m}$ . Each elementary fibre shows a compact structure exhibiting alignment in the fibre axis direction with non-fibrous components on the fibre surface [27]. The fine structure of cellulose materials is composed of crystalline and amorphous regions. The amorphous regions easily absorb chemicals such as dyes and resins, whereas the compactness of the crystalline regions makes it difficult for chemical penetration. The percentage of crystalline cellulose increases when treated with NaOH [28]. Hemicellulose, lignin, pectin and wax which act as cementing materials were eliminated post alkali treatment and bleaching which was also confirmed by FTIR results [29]. The chemical treatments also lead to defibrillation and depolymerisation of raw PFs. The fiber dia was reduced to 5-15  $\mu\text{m}$ . Fiber diameter was again reduced during mechanical treatment of ultrasonication and finally pure cellulose fibre with average diameter of 30 nm was obtained [2].

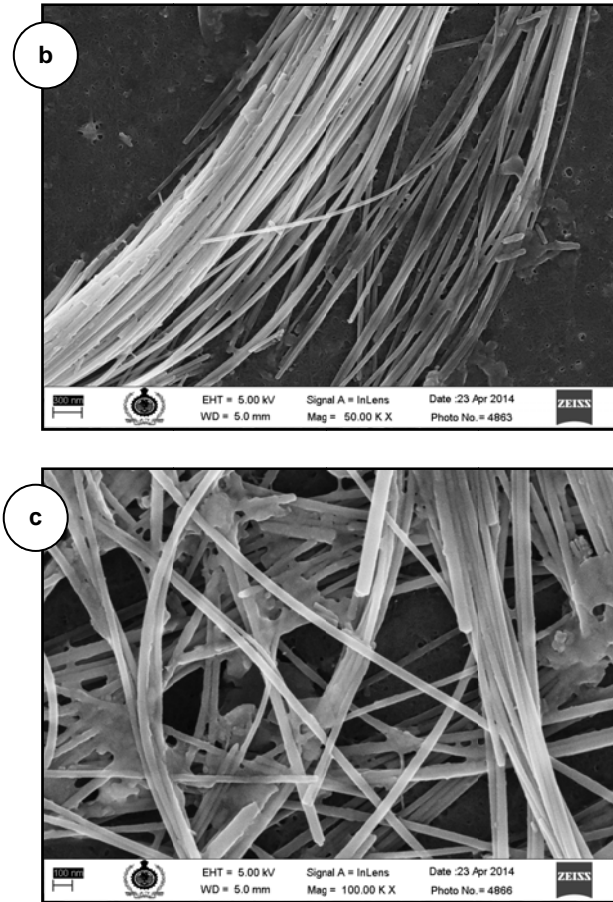


**Fig. 2: FESEM micrographs of (a) raw PFs (b) bleached PFs (c) nano fibers**

Fig 3 shows the FESEM images of NFCs, generated by ultrasonication of bleached PFs for 60 min duration. These images pertain to nanofibrils suspension in distilled water obtained by high speed centrifuging (12000 rpm) post ultrasonication. High speed centrifugation separates the nanofibres from microfibrils resulting in nanofiber suspension in supernatant and mixture of micro and nanofibers in the residue of centrifuge. In ultrasonication, defibrillation occurs due to effect of acoustic cavitation of high frequency (20 kHz) ultrasound. The sonification impact can break the relatively weak interfaces among the nanofibers, which are bonded to each other mainly by nonbonding interactions such as the van der Waals forces [30]. The slurry obtained after the sonication exhibited a remarkably high viscosity. It suggested that the synthesis of homogeneous dispersion of hydrophilic cellulose nano fibrils in water from natural fibres has been accomplished [31].

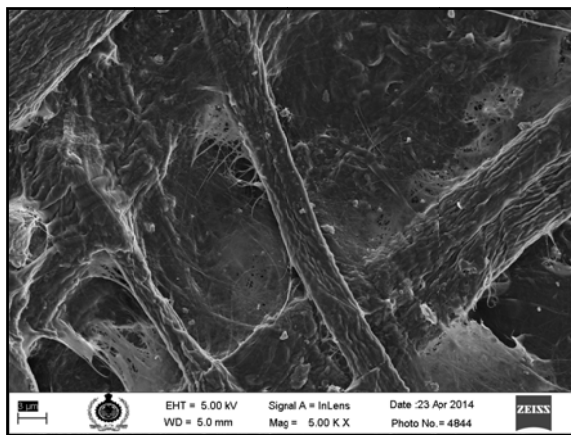
The results reveal that the ultrasonication time strongly affects the defibrillation of nanofibres from microfibrils as 20 min and 40 min of sonication were insufficient for nanofiber individualization.





**Fig. 3: FESEM images of mercerized and bleached PFs post ultrasonication for 60 min with magnifications (a) 3 kX (b) 50 kX (c) 100kX**

60 min of ultrasonication resulted in production of nanofibers with high aspect ratio (Fig. 3(a)) and wirelike meshed network structure with diameter in range of 20-40 nm (Fig. 3(b,c)).

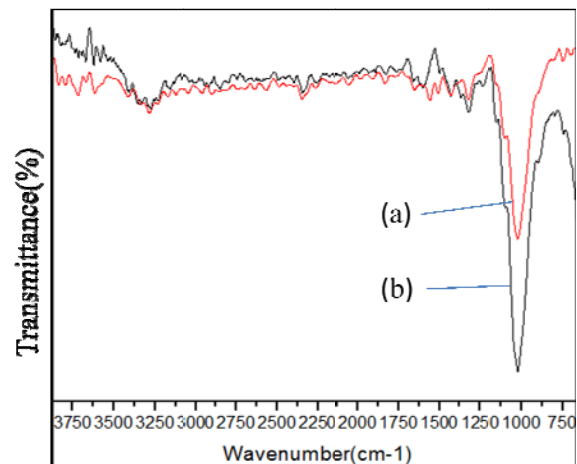


**Fig. 4: FESEM image for residue of centrifugation post 60 min ultrasonication.**

Fig. 4 shows the FESEM image for residue of centrifugation post ultrasonication wherein nanofibers can be seen partially cleaved along the longitudinal axis of microfibrils. These nanofibers are relatively bigger in diameter than the nanofibers obtained in suspension. If additional energy is imparted by longer duration of ultrasonication, these partially detached nanofibers will be free from the parent microfibril and will remain suspended in distilled water indicating, that a higher concentration of nanofibers in suspension is obtained with higher time interval of ultrasonication [32].

## 5.2 FTIR analysis

Changes in chemical composition of PFs due to bleaching treatment of mercerized PFs can be perceived in Fig. 5. The dominant peaks at  $3200\text{--}3400\text{ cm}^{-1}$  is related to the  $\text{--OH}$  groups present in the repeating units of cellulose [33]. This also imparts the hydrophilic nature to cellulose. The  $1645\text{ cm}^{-1}$  peak is associated with the  $\text{H-O-H}$  stretching vibration of absorbed water in carbohydrates. This peak was also observed in bleached cellulose but with diminished intensity which indicates presence of small amount of hemicelluloses in purified cellulose fibers [34,35]. In the spectrum of unbleached PFs, the peak at  $1505\text{ cm}^{-1}$  represents aromatic rings of lignin [36,37]. The absence of this peak in bleached PFs indicates delignification by treatment with  $\text{Ca}(\text{OCl})_2$ . The prominent peak at  $1020\text{ cm}^{-1}$  is related to  $\text{--C-O-C--}$  pyranose ring skeletal vibration. The intensity of this peak sharply rises, indicating increase in cellulose content in the bleached sample [6].



**Fig. 5: FTIR spectra of PFs before bleaching treatment (a) and after bleaching treatment (b)**

Bleaching treatment leads to effective elimination of lignin, pectin and hemicelluloses in the raw fiber. The common trend from observation is the gradual decrease of amorphous components like lignin and hemicellulose from raw fibre to bleached fibre [2]. The lignin will react with  $\text{Ca}(\text{OCl})_2$  and dissolve out as lignin chloride. In order to achieve



optimization of concentration of bleaching powder IR spectra was obtained for 3%, 5%, 7% and 10% respectively. In Fig. 6 broad peaks were obtained at  $3260\text{ cm}^{-1}$  for all four concentrations, signifying the OH-stretching [33]. Apart from delignification, prominent peaks were obtained at  $1010\text{ cm}^{-1}$  in all spectra but with varying intensities. The highest intensity was exhibited by 5% bleached PFs and lowest by 10% bleached PFs. The results have indicated that cellulose content increased as bleaching concentration was augmented from 3% to 5% [38,39]. But a further increase to 7% and 10% exhibited lower spectral intensity suggesting initiation of deterioration of crystalline regions, leading to reduced cellulose content. Consequently 5% bleaching concentration is optimum value for delignification of PFs whilst conserving the cellulose content and same was used further in the experiments.

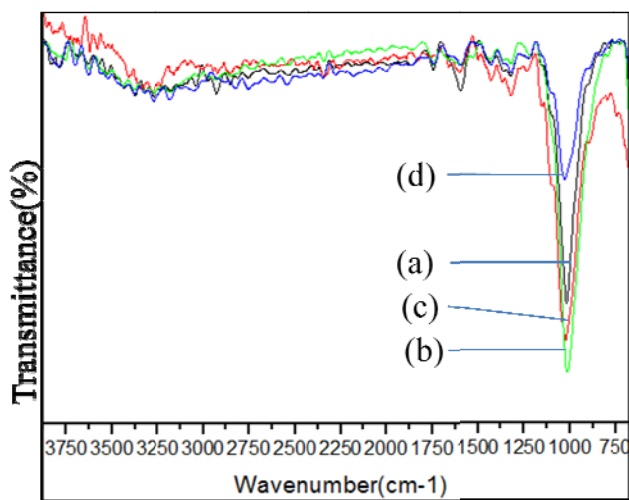


Fig. 6: FTIR spectra of PFs with various concentration of bleaching powder (a) 3% (b) 5% (c) 7% and (d) 10%

## 6. CONCLUSIONS

The present study was focused on cellulose nanofibrils fibrillation from palm fibers using inexpensive chemical pretreatment followed by greener method of ultrasonication. Alkali treatment was employed for depolymerisation and delignification was achieved via treatment with bleaching powder. Increase in cellulose content post bleaching treatment has been supported by FTIR spectra wherein an optimized bleaching concentration of 5% was ascertained. Results have demonstrated that extent of defibrillation of nanofibers from surface of microfibers depends on time interval for which ultrasonication is carried out. Results were obtained for 60 min ultrasonication time wherein FESEM images have shown fiber diameter in the range of 20-30 nm with high aspect ratio. The inexpensiveness and abundance of PFs in nature make them a desirable raw material for production of nano-fillers for the polymeric composites which bear tremendous potential in field of automobile, aerospace, bio-nanocomposites and structural applications.

## 7. ACKNOWLEDGMENTS

Authors thank Vice Chancellor Dr. Surender K Pal for the encouragement and support. The authors also thank Ms Aneesa, CBST (CIPET) for her help and technical support.

## REFERENCES

- [1] H.P.S. Abdul Khalil, A.H. Bhat, A.F. Ireana Yusra *Carbohydrate Polymers* 2012, **87**, 96.
- [2] E. Abrahama, B. Deepaa, L.A. Pothana, M. Jacobc, S. Thomasb, U. Cvelbard, R. Anandjiwalac *Carbohydrate Polymers* 2011, **86**, 1468.
- [3] H.P.S. Abdul Khalil, Y. Davoudpoura, Md. Nazrul Islama,c, Asniza Mustaphaa, K. Sudeshd, Rudi Dunganiana,e, M. Jawaidd *Carbohydrate Polymers* 2014, **99**, 649.
- [4] Itoh, T., & Brown, R. M., Jr. *Planta* 1984, **160**, 372.
- [5] Klemm, D., Heublein, B., Fink, H.-P. & Bohn, A. *Chemie International Edition* 2005, **44**, 3358.
- [6] Alemdar, A., & Sain, M. *Bioresource Technology* 2008, **99**, 1664.
- [7] Kamel, S. *Express Polymer Letters* 2007, **1**, 546.
- [8] Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R., Rowan, S.J., et al. *Materials Science* 2008, **45**, 1.
- [9] Manocha, L. M., Valand, J., Patel, N., Warriar, A., & Manocha, S. *Indian Journal of Pure and Applied Physics* 2006, **44**, 135.
- [10] Ramazanov, M. A., Ali-Zade, R. A., & Agakishieva, P. B. *Journal of Nanomaterials and Biostructures* 2010 **5(3)**, 727.
- [11] Seydibeyoglu, M. O., & Oksman, K. *Composite Science and Technology*, 2008, **68**, 908.
- [12] Joshi, S. V., Drzal, L. T., Mohanty, A. K., & Arora, S. *Composite Part A* 2004, **35**, 371.
- [13] Dufresne, A. *Macromolecules* 2010, **15**, 4111.
- [14] George, J., Sreekala, M. S., & Thomas, S. *Polymer Engineering and Science* 2001, **41(9)**, 1471.
- [15] Li, X., Tabil, L. G., & Panigrahi, S. D. *Journal of Polymer Environment* 2007, **15**, 25.
- [16] Dufresne, A., Dupeyre, D., & Vignon, M. R. *Journal of Applied Polymer Science* 2000, **76**, 2080.
- [17] Ferrer, A., Filpponen, I., Rodriguez, A., Laine, J., & Rojas, O. J. *Bioresource Technology* 2012, **125**, 249.
- [18] Chakraborty, A., Sain, M., & Kortschot, M. *Holzforchung* 2005, **59**, 102.
- [19] Frone, A. N., Panaitescu, D. M., Donescu, D., Spataru, C. I., Radovici, C., Trusca, A., et al. *BioResources* 2011, **6(1)**, 487.
- [20] Szczesna-Antczak, M., Kazimierzczak, J., & Antczak, T. *Fiber and Textile in Eastern Europe* 2012, **20(2(91))**, 8.
- [21] Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J.-L., Heux, L., Dubreuil, F., & Rochas, C. *Biomacromolecules* 2007 **9(1)**, 57.
- [22] Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. *Biomacromolecules* 2006, **7**, 1687.
- [23] Frenot, A., Henriksson, M.W., & Walkenstrom, P. *Journal of Applied Polymer Science* 2007, **103(3)**, 1473.
- [24] Kim, C. W., Kim, D. S., Kang, S. Y., Marquez, M., & Joo, Y. L. *Polymer* 2006, **47(14)**, 5097.
- [25] Cheng, Q., Wang, S., & Rials, T. G. *Composites:Part A* 2009, **40**, 218.
- [26] Chen, P., Yu, H., Liu, Y., Chen, W., Wang, X., & Ouyang, M. *Cellulose* 2013, **20**, 149

- 
- [27] Garcia, C., Jaldon, G., Dupeyre, D., & Vignon, M. R. (1998). *Biomass & Bioenergy*, **14**, 251.
- [28] Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. *Comprehensive cellulose chemistry Wiley-VCH Verlag GmbH* 2004, **2.4-2.4.3**, 130.
- [29] Huu Dat Nguyen, Thi Thanh Thuy Mai, Ngoc Bich Nguyen, Thanh Duy Dang1, My Loan Phung Le, Tan Tai Dang and Van Man Tran *Advances In Natural Sciences: Nanoscience And Nanotechnology* 2013 **4** 015016 (9pp).
- [30] Hong-Ping Zhao and Xi-Qiao Feng *Applied Physics Letters* 2007, **90**, 073112.
- [31] Wenshuai Chen, Haipeng Yu, Yixing Liu *Carbohydrate Polymers* 2011, **86**, 453.
- [32] Adriana N. Frone, Denis M. Panaitescu, Dan Donescu, Captalin I. Spataru, Constantin Radovici, Roxana Trusca and Raluca Somoghi *Bioresources* 2011, **6(1)**, 487.
- [33] Lojewska, J., Miskowiec, P., Lojewski, T., & Pronienwicz, L. M. (2005). *Polymer Degradation and Stability* 2005, **88**, 512.
- [34] Herrick, F. W., Casebier, R. L., & Hamilton, J. K. *Journal of Applied Polymer Science: Applied Polymer Symposium* 1983, **37**, 797.
- [35] Turbak, A. F., Snyder, F. W., & Sandberg, K. R. *Journal of Applied Polymer Science: Applied Polymer Symposium* 1983, **37**, 815.
- [36] Sain, M., & Panthapulakkal, S. *Industrial Crops and Products* 2006, **23(1)**, 1.
- [37] Sun, R. C., Tomkinson, J., Wang, Y. X., & Xiao, B. *Polymer* 2000, **41(7)**, 2647.
- [38] Elanthikkal S, Gopalakrishnapanicker U, Varghese S and Guthrie J T *Carbohydrate Polymers* 2010, **80**, 852.
- [39] Kaushik A and Singh M *Carbohydrate Resources* 2011, **346**, 76.