MICRO- CELLULOSE PREPARATION METHOD BASED ON UREA/NaOH DISSOLVED SYSTEM

Zhong-Jin NI[1*], Xu LI[2], Ya-Nan ZHANG[3], Bai-Yang LOU[4], Sheng PAN[5], Yan LV[6], Da-Lie LIU[7]

Urea/NaOH solution has been used for swelling pretreatment of the pulp fibers and a mechanical method is proposed for the preparation of cellulose. The cellulose was treated with different concentrations of urea/NaOH solutions. The chemical structure, crystalline state, and micro morphology of cellulose were characterized by FTIR, SEM, and XRD. After these experiments, the optimum procedure of preparation could be established. The result shows the most stable cellulose suspension can be obtained at -10℃, 7.5% NaOH/10% urea. -cellulose has a loose networked structure, with the diameter among 0.05-0.6μm while the average is about 0.25μm. After the pretreatment, the degree of crystallinity of the -cellulose decreases. The hydrogen absorption peak in FTIR spectra moved and the characteristic peak of cellulose II appeared. Some crystalline cellulose changed from type I to type II indicating that NaOH/urea solution has destructive effect on the cellulose crystalline regions; under mechanical forces, the hydrogen bonds in cellulose are broken and restructured, causing the scale cellulose and the change of crystalline type.

Keywords: cellulose fibers; urea/NaOH solution, pretreatment; grinding; characterization

1. Introduction

The environmental protection draws great attention as the growing scarcity of resource. The use of biomass resources is of great significance. There are a lot of cellulose fibers (CNFs) in the plant cell wall [1], which has strong mechanical properties and high length-diameter ratio. CNF's surface is very rich in hydroxyl groups, and is a kind of reinforced materials with great potential for development. CNFs have the characteristics of renewable raw materials, low cost, low density, high strength and good biocompatibility. CNFs have wide applications in areas

[1]School of Mechanical Engineering, Zhejiang University of Technology, Hangzhou, and School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China, e-mail: neezj@163.com
[2] School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China
[3] School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China
[4] School of Mechanical Engineering, Zhejiang University of Technology, Hangzhou
[5] School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China
[6] School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China
[7] School of Engineering, Zhejiang A&F University, Lin'an, Zhejiang, China

such as tissue engineering [2], wound dressing [3], and filtration media [4], electronics devices [5], carbon fiber production [6] and hydrophobic coating [7].

Compared with low length-diameter ratio of crystal cellulose and cellulose whiskers, CNFs not only have the advantages of scale and abundant source, but also have high length -diameter ratio, high specific surface area and other advantages, with the fibers interwoven into mesh winding structure. Using the structural properties of CNFs, the preparation of high performance and functional composite materials becomes a hot research topic in the field.

In the last decade, many methods of manufacturing cellulose fibers have been developed. These methods include mechanical, chemical, electro spinning, biosynthesis, mechanical and so on [8-10]. Some articles have compared these methods [11-13]. Khalil et al [14] proposed a mechanical method of preparation. In this method, cellulose fibers were first swelled in water and then added to a high-shear homogenizer at high pressure (up to 1500 bar) [15]. This method can produce fibers but the energy wasted is high. In order to reduce energy consumption and improve efficiency, pretreatment technology has always been applied in mechanical method.

In the process of preparing celluloses, because cellulose has large molecular weight and contains a crystalline region with a tight structure, it is necessary to be pretreated to make its structure fluffy. There are some common pretreatment methods, such as alkali pretreatment, biological pretreatment, oxidation pretreatment and so on.

Other researchers [16-18] showed that NaOH and urea can be used to form a special complex which can quickly destroy the hydrogen bonds between cellulose intermolecular and intramolecular, and prevents the recombination of cellulose molecule. Using shearing force and other physical methods, the pretreated cellulose could be separated into cellulose fibrils. Alkali solution can promote separation of lignin and polysaccharides from cellulose, and can dissolve the residual fructose and hemicellulose, but the concentration of alkali solution is too high and this could produce the fiber breakup. Oxidation pretreatment method is necessary to upload the surface of cellulose with electric charge and then to generate mutual exclusion between fibers before preparing the microfibers. The peeling reaction may occur in the process of preparation and the degree of degradation cannot be well controlled [19, 20]. Miao [19] took about 4% of the pre-hydrolyzed wood pulp as raw material, and used mechanical milling method to prepare cellulose with good performance.

Zhang et al. [16] used a PFI refiner to beat the pulp after chemical pretreatment of bleached pulp, and then used a high-pressure homogenization process to prepare cellulose. The diameter obtained was about 1nm.

In order to improve preparation efficiency and reduce energy consumption of the cellulose preparation, urea / NaOH pretreatment combined with mechanical

grinding are discussed in this paper. Through the characterized results of -cellulose, the best concentration and temperature of pretreatment solution are also proposed.

2. Experimental Part

Cork pulp: Zhejiang Paper Research Institute; NaOH, AR，Qingdao Jacob Chemical Reagent Sales Co., Ltd.；urea，AR，Yutai County Haina Environmental Protection Technology Co. Ltd. The experimental instruments used in this work are shown in Table 1.

Table 1

The main equipment and characterization instruments

Name	Model	Company
Electronic balance	JM2003Max	Ji Ming weighing equipment Co., Ltd.
Electric Thermostatic Drying Oven	XMTA-6000	Ye Tuo instrument and Meter Co., Ltd.
Haier refrigerator	BCD-256WDGH	Qingdao Haier Co., Ltd.
Ultrafine pulverize	MKCA6-2	Fortune Industrial Co., Ltd.
Ultrasonic cleaner	YJ5120-B	Yongjie Experimental Instrument Co. Ltd.
Scanning electron microscope	SS-550	Shimadzu Corporation
Transmission electron microscope	Tecnai F30	Holland Philips-FEI company
X-ray diffractometer	XRD6000	Shimadzu Corporation
FTIR spectrometer	IR Prestige-21	Shimadzu Corporation

Determination of pretreatment conditions

Using different proportions of NaOH and urea, the experiments were carried out at different temperatures: 20 ℃, 0 ℃, -5 ℃, -10 ℃ and -15 ℃, respectively. The conditions of the pulp fiber in the pretreatment solution at different temperatures are shown in Fig. 2. The solution is transparent with pretreatment temperatures at 20 ℃, 0 ℃ and -5 ℃. When the temperature is reduced to -10℃, there is a little white crystal precipitation in the solution. When the temperature continues to decrease, the crystals are precipitated and the solution becomes solid. In the process of swelling and dissolving the cellulose in NaOH / urea, the effect of alkali is an exothermic process and the low temperature is conducive to the reaction. If the temperature is too low, the solute in the solution slows down the swelling of the cellulose. So, when the temperature reaches -10℃, the pretreatment solution just shows a small amount of crystallization and dissolves the cellulose quickly. Thus, we conclude that -10 ℃

is the best temperature for cellulose pretreatment.

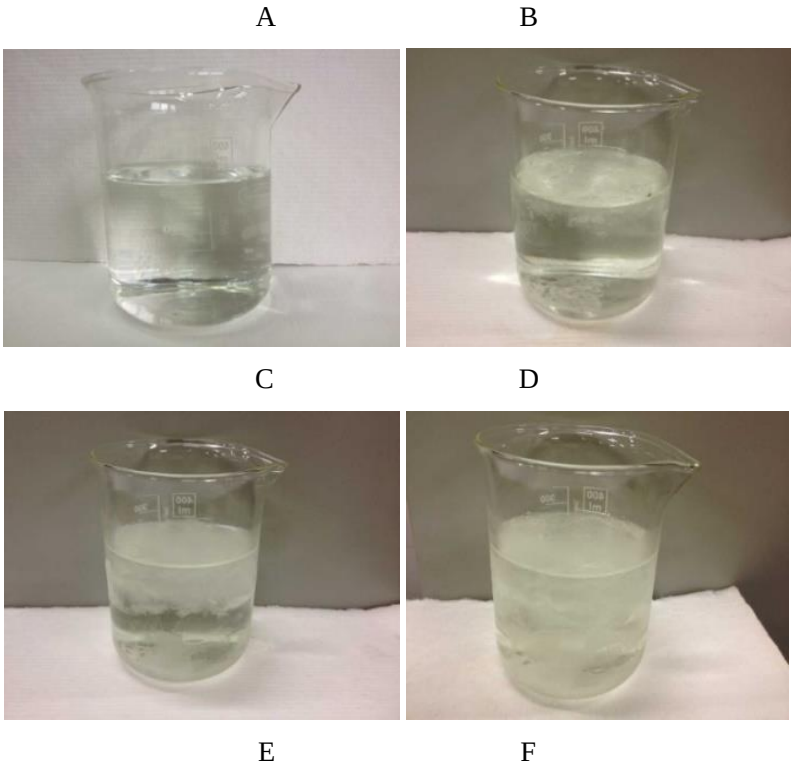

Fig. 1. Pretreated solutions at different temperatures: A - pretreated solutions at 20 ℃; B - pretreated solutions at 0 ℃; C - pretreated solutions at 20 ℃; D - pretreated solutions at 0 ℃; E - pretreated solutions at 20 ℃; F - pretreated solutions at 0 ℃

Micro preparation of cellulose

Under the conditions of -10 ℃, the softwood pulp is dissolved in urea / NaOH solution of different concentration, mixed rapidly, and then standed for 15 mins. The different samples of the cellulose pulp are prepared with a solid content of 1%. Then an ultrafine pulverizer is used for mechanical grinding at the speed of 1600 rpm, meanwhile adjusting the grinding plate gap. After grinding by 35 times, the slurry is repeatedly washed to neutral, and the fiber water suspension is obtained.

3. Results and Discussions

Settling of cellulose suspension

Ten kinds of cellulose suspension samples were obtained by different urea / NaOH concentration solutions. They were filled severally in the same size bottles. The initial level height of samples in all bottles was 55 mm. Then, these

sample bottles were placed on a horizontal table and observed the sedimentation height in different days: 0 days, 3 days, 7 days, 14 days and 21 days, respectively. The level height of different number of days is recorded. The results are summarized in Table 2.

Table 2

Settlement records of cellulose suspension

Sample	C_{NaOH}	C_{Urea}	0 days	3 days	7 days	14 days	21 days
C0	0	0	55.0	41.2	38.7	37.6	36.7
C1	5%	10%	55.0	40.3	38.1	36.7	36.2
C2	5%	12.5%	55.0	46.8	40.3	33.2	31.7
C3	5%	15%	55.0	36.9	34.6	28.5	27.6
C4	7.5%	10%	55.0	51.2	50.6	48.2	48.1
C5	7.5%	12.5%	55.0	50.3	43.5	39.1	38.0
C6	7.5%	15%	55.0	48.6	42.8	35.7	33.1
C7	10%	10%	55.0	50.3	39.5	37.9	37.5
C8	10%	12.5%	55.0	40.1	35.2	24.1	22.4
C9	10%	15%	55.0	26.5	23.4	23.2	20.3

Note: C0 is the sample that was not pretreated

From Table 2, after settling for 21 days, with the same concentration of NaOH, the level of cellulose suspension decreased when the concentration of urea increased. The liquid level of cellulose suspension was the highest when the concentration of NaOH was 7.5% with the same concentration of urea. With the increase of alkali concentration, the stability of cellulose suspension was improved. However, the increase of urea concentration would cause large settlement of the solution, which would decrease the system stability. According to the 10 sets of data shown in Table 2, the curves of settlement height change, when the solution settled were obtained; these findings are shown in Fig. 2

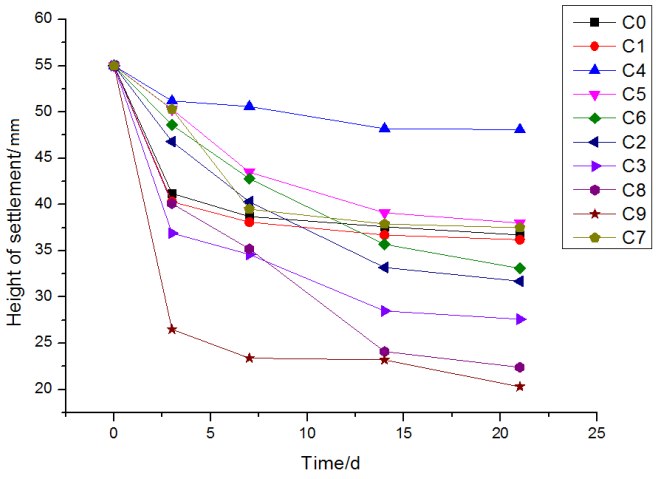

Fig. 2. Fibers solution liquid surface height changes versus time

It can be seen that the cellulose solution has the highest stability after

pretreatment with 7.5% NaOH / 10% urea.

SEM and TEM images of -cellulose

Fig. 3 shows the scanning electron micrographs of the -cellulose. As can be seen from this figure, the pulp fibers were broken down into -filaments after pretreatment and mechanical grinding for 35 times. Using the size distribution calculation software Measure, the particle size distribution of -cellulose was analyzed and the obtained results are shown in Fig. 4. The particle size is well distributed and the -cellulose particle size distribution is between 0.05-0.6 μm, with an average diameter of about 0.25 μm.

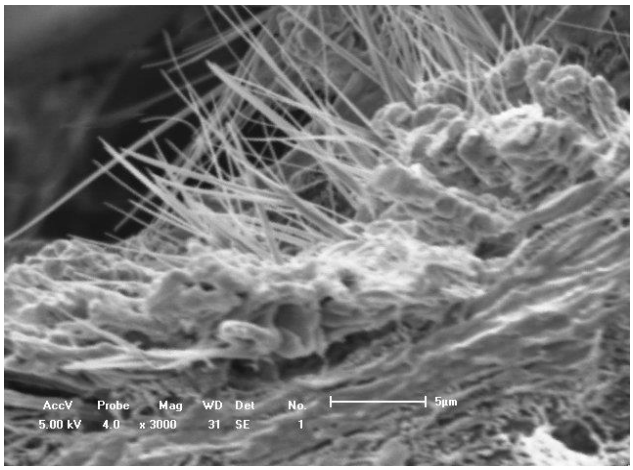

Fig. 3. SEM image of -cellulose after pretreated and 35th mechanical grinding

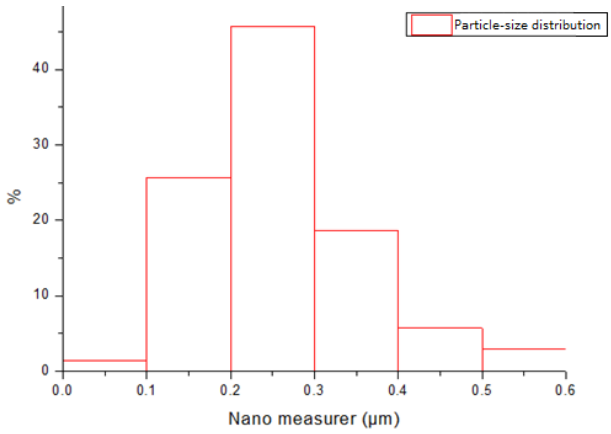

Fig. 4. Diameter distribution of -cellulose after grinding for 35 times

The TEM images presented in Fig. 5 and Fig. 6 show that there are no angle and no filaments around the hole, which is formed by the effect of pretreatment solution. There is a certain angle between the aperture of other

fibers, indicating that these filaments were extruded and sheared under mechanical forces. After repeated mechanical forces under double disc, large cellulose fibers were sheared and broken at scale level and finally the fibers were formed.

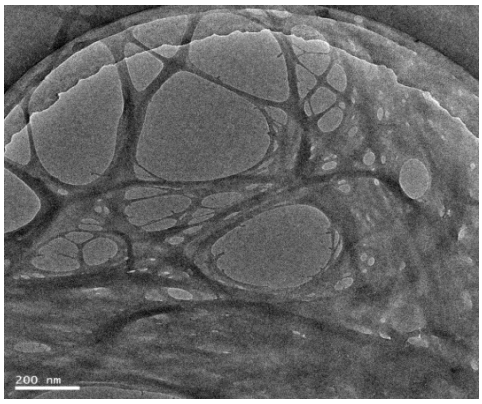

Fig. 5. -cellulose TEM image

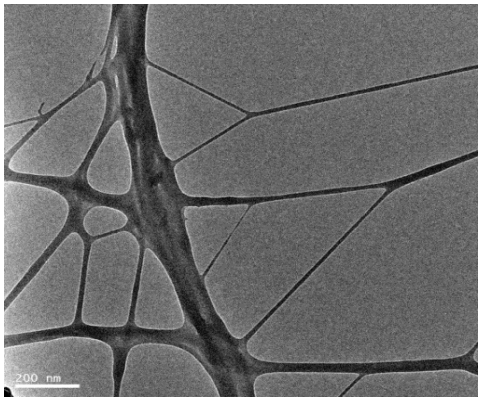

Fig. 6. -cellulose TEM detailed image

XRD patterns of cellulose

As can be seen from the XRD pattern presented in Fig. 7, the characteristic peaks are consistent with the crystallization peaks of cellulose I, indicating that the cellulose obtained without pretreatments are still cellulose I. As shown in Fig. 8, the -cellulose prepared after 7.5% NaOH /10% urea pretreatment belongs to the mixture of cellulose I and cellulose II.

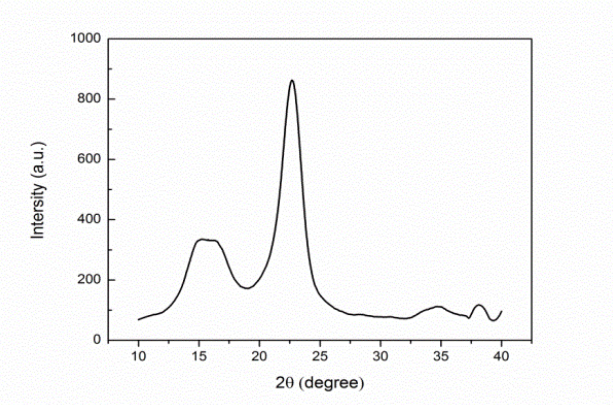

Fig. 7. XRD pattern of cellulose without pretreatment

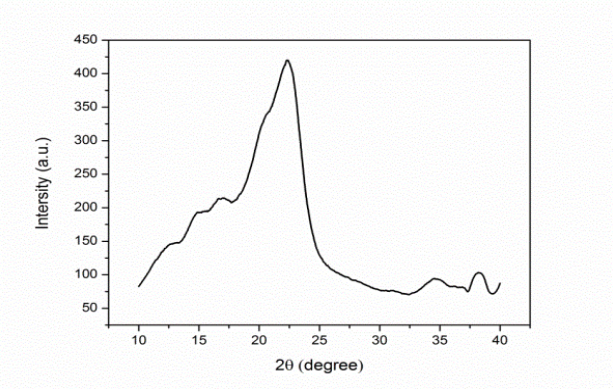

Fig. 8. XRD pattern of cellulose after preatreatment

By using Segal method, the crystallinity percentage of -cellulose without the pretreatment preparation is 71.43%. Moreover, the relative degree of crystallinity is 51.77% after 7.5% NaOH/ 10% urea pretreatment. This value is lower than that of the -cellulose obtained with mechanical polishing at -10℃ conditions. NaOH/urea solution can effectively damage cellulose structure in the crystalline region.

FTIR spectra of -cellulose

In Fig. 9 are presented the FTIR spectra of cellulose. FTIR spectrum (a) in Fig. 9 is for the cellulose after pretreatment, and the spectrum (b) in Fig. 9 is for the cellulose without pretreatment.

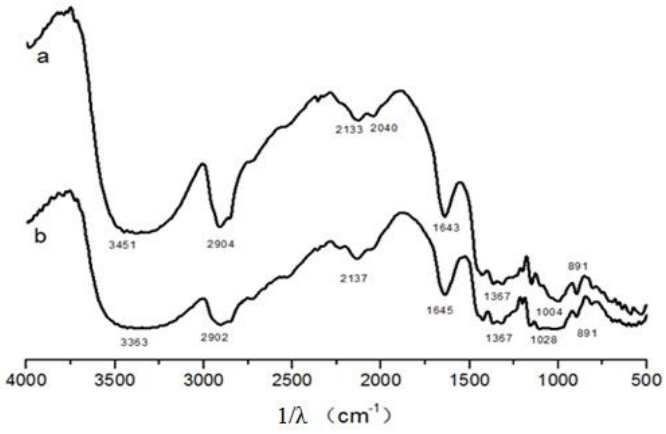

Fig. 9. FTIR spectra of two different cellulose types: (a) cellulose after pretreatment and (b) cellulose before pretreatment

In the FTIR spectrum (b) a strong stretching vibration of the hydroxyl appears wide in the vicinity of 3363 cm^{-1}. This is attributed to -OH stretching, because the signals of -OH groups are superimposed and form a strong absorption

peak. In the spectrum (a), the absorption peak belonging to -OH stretching vibration appears in the vicinity of 3451 cm^{-1}, and it corresponds to the hydrogen absorption peak produced by the inner cellulose II molecules. It indicates that cellulose crystalline transition may occur after NaOH / urea pretreatment preparation. The symmetric stretching vibration of C-H near 2900 cm^{-1} belongs to the -CH_2. The peaks near 1643 cm^{-1} is due to the water absorption by the cellulose samples, indicating that the cellulose samples are highly water absorbent. The absorption peak appeared in the region of 1367 cm^{-1} is partially due to the symmetric vibration caused by a CH_2 group, and also due to the polysaccharide aromatic ring C-H and C-O group bending vibration. The absorption peak in the vicinity of 891 cm^{-1} is due to the C-O-C stretching vibration at β-(1→4)-glycosidic linkages.

4. Conclusions

Cellulose pulp was used to prepare the -cellulose after NaOH /urea solution pretreatment. When a solution of 7.5% NaOH /10% urea is used, the -cellulose suspension is stable. The -cellulose particle size distribution measured is between 0.05-0.6 μm, with an average diameter of about 0.25 μm. After the pretreatment, the degree of crystallinity of -cellulose was decreasing. The -OH absorption peak in IR spectrum is shifted and appeared a characteristic peak of cellulose II. We presume that a part of cellulose was converted from type I to type II. This indicates that NaOH /urea solution has a destructive effect on the cellulose crystalline regions. Under mechanical forces, the hydrogen bonds in cellulose are broken and restructured, causing scale effects of the cellulose structure and the changing its crystalline type.

We consider that, with the decline of the crude oil and other fossil energy resources, and with the growing interest in pollution reduction, the use of green chemistry and of materials obtained from biomass are the key to environmental protection. Due to the strong surface adsorption and other interesting properties at scale level, cellulose can be manufactured into functional aerogels and green composite materials, which can reduce the plastic pollution and which could be helpful to treat the oil spills on the sea surface.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 51605446 and 21404092) and the Natural Science Foundation of Zhejiang Province (Grant No. Y3110284).

R E F E R E N C E S

[1]. *Lu J., Drzal L. T.,* "Microfibrillated cellulose/cellulose acetate composites: Effect of surface

Treatment", J. Polymer Sci. B, vol. 48, no.2, 2010, pp. 153-161.
[2]. *Bodin A., Backdahl H., Fink H., Brumer H., Risberg B., Gatenholm P.,* "Modification of Cellulose with a xylogucan–RGD conjugate enhances adhesion and proliferation of endothelial cells: implications for tissue engineering", Biomacromolec., vol. 8, no. 12, 2007, pp. 3697-3704.
[3]. *Brown Jr., Malcolm R., Czaja, W., Jeschke, M., et al.,* "Multiribboncellulose as a matrix for wound healing", US, WO 2007027849 A3. 2007.
[4]. *Wertz J., Schneiders I.*, "Filtration media: Advantages of fibre coating technology", Filtration Separ., vol. 46, no.4, 2009, pp.18-20.
[5]. *Masaya N., Hiroyuki Y.*, "Transparent composites based on cellulose produced by bacteria offer potential innovation in the electronics device industry", Adv. Mater., vol. 20, no.10, 2008, pp.1849-1852.
[6]. *Jazaeri E., Zhang L., Wang X., Tsuzuki T.,* "Fabrication of carbon fiber by pyrolysis of freeze-dried cellulose fiber", Cellulose, vol. 18, no.6, 2011, pp.1481-1485.
[7]. *Arbatan T., Zhang L., Fang X.-Y., Shen W.,* "Cellulose fibers as binder for fabrication of superhydrophobic paper", Chem. Eng. J., vol. 210, no.6, 2012, pp.74-79.
[8]. *Kim C.W., Kim D.S., Kang S.Y., Marquez M., Joo Y.L.*, "Structural studies of electrospun cellulose fibers", Polymer, vol. 47, no. 14, 2006, pp. 5097–5107.
[9]. *Recouvreux D.O.S., Rambo C.R., Berti F.V., Carminatti C.A., Antonio R.V., Porto L.M.,* "Novel three-dimensional cocoon-like hydrogels for soft tissue regeneration", Mater. Sci. Engineering C, vol. 31, no.2, 2011, pp.151-157
[10]. *Frey M.W.,* "Electrospinning cellulose and cellulose derivatives", Polymer Rev., vol. 48, no.2, 2008, pp.378-391.
[11]. *Khalil H.P.S.A., Bhat A.H., Yusra A.F.I.*, "Green composites from sustainable cellulose fibrils: A review", Carbohydrate Polym., vol. 87, no.2, 2012, pp.963-979.
[12]. *Siro I., Plackett D.*, "Microfibrillated cellulose and new composite materials: a review", Cellulose, vol. 17, no.3, 2010, pp. 459-494.
[13]. *Lavoine N., Desloges I., Dufresne A., Bras J.,* "Microfibrillated cellulose - its barrier properties and applications in cellulosic materials: a review", Carbohydrate Polym., vol. 90, no.2, 2012, pp.735-64.
[14]. *Khalil H.P.S.A., Davoudpour Y., Islam M.N., Mustapha A., Sudesh K., Dungani R., Jawaid M.,* "Production and modification of fibrillated cellulose using various mechanical processes: A review", Carbohydrate Polym., vol. 99, no.1, 2014, pp.649-665.
[15]. *Zimmermann T., Bordeanu N., Strub E*., "Properties of fibrillated cellulose from different raw materials and its reinforcement potential", Carbohydrate Polym., vol. 79, no.4, 2010, pp.1086-1093.
[16]. *Zhang S., Li F., Yu J., Gu L.,* "Novel fibers prepared from cellulose in NaOH/thiourea/urea aqueous solution", Fibers Polym., vol. 10, no.1, 2009, pp.34-39.
[17]. *Jin H., Zha C., Gu L.*, "Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution", Carbohydrate Res., vol. 342, no.6, 2007, pp.851-8.
[18]. *Zhang L., Dong R., Gao S.,* "Dissolution and regeneration of cellulose in NaOH/thiourea aqueous solution", J. Polym. Sci. B, vol. 40, no.14, 2002, pp.1521-1529
[19]. *Miao C., Hamad W.Y.*, "Cellulose reinforced polymer composites and composites: a critical review", Cellulose, vol. 20, no.5, 2013, pp.2221-2262.
[20]. *Zhang J.H., Song H.N., Lin L., et al.*, "Effects of high-pressure homogenization treatment on the preparation of microfibrillated cellulose", J. Cellulose Sci. Technol., vol. 17, no.3, 2009, pp.7-8.