

Improvement of paper properties of Rice Straw Pulps by/ Microcrystalline Cellulose / Calcium Carbonate

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ABSTRACT: Rice straw is a locally available lignocellulosic material. In this study, it is rice straw was pretreated by soaking it in water for 48 hours at room temperature. The pretreated straw was cooked by in 5% NaOH at 100 °C and in atmospheric pressure. The structure and mechanical properties of paper made from cooked pulp was investigated. Hydrogen peroxide as a bleaching agent was applied to the high yield pulp to enhance its brightness level in a single stage process in the presence of sodium hydroxide and magnisium sulphate. Microcrystalline cellulose (MCC) was prepared from alpha cellulose of rice straw pulp bleached using 2% hydrogen peroxide solution. so that it is The MCC was characterized by 45.5% crystallinity and nano in size vide XRD and TEM respectively. Microcrystalline cellulose and/ calcium carbonate were added to unbleached pulp as fillers. Air permeability of filled paper was improved in the presence of MCC filler more than in the presence of calcium carbonate alone. Optical properties and water permeability resistance of filled pulp showed improvements in the presence of microcrystalline cellulose filler compared to unfilled pulp.

Key words: (Rice straw, microcrystalline cellulose, water permeability, air permeability)

1. INTRODUCTION

Many cereal straws, particularly rice straw, have been used as raw materials for paper production. Non-wood raw materials account for 5-7% of the total pulp and paper production worldwide [1]. Sarwar Jahan [2] studied the effect of hot-water and alkaline pre-extraction treatment of rice straw on soda-anthraquinone pulping. His results showed that rice straw after with alkaline pre-extraction treatment had showed better pulp yield and strength properties compared with the pulp from hot-water pre-extraction treatment. In another work, the potential of using bleached wheat straw pulp (BWSP) was explored to improve the tensile strength of the high-yield pulp (HYP) while preserving its high bulk property. The explanation was that micro fines from refined BWSP can act as binders to improve the HYP inter-fiber bonding, as a result, the HYP tensile strength can be improved by using a small amount of BWSP, while the HYP bulk is not significantly affected [3]. Bleaching of pulp with alkaline hydrogen peroxide resulted in conversion of

34 conjugated chromophoric groups associated with lignin structure to carboxylic acids and
35 other degradation products [4]. Previous studies also reported that the number of charged
36 groups increases in peroxide bleaching and/or alkaline treatment of mechanical pulps due
37 to alkaline hydrolysis of ester groups in the pulps [5]. Cellulose is a classical example of
38 a renewable and biodegradable structural plant polymer which can be processed into
39 whisker-like micro fibrils [6,7]. Recently, researchers reported the extraction of cellulose
40 fibers from rice husk by alkali and bleaching treatments, which were subsequently
41 converted to nanocrystals using a sulfuric acid (H_2SO_4) hydrolysis treatment [8]. Isolation
42 of microcrystalline cellulose has been carried out from jute cellulose by using the same
43 acid hydrolysis (H_2SO_4) approach [9] The hydrolysis of cellulose to obtain MCC can be
44 accomplished using enzymes or microorganisms. Although enzymatic methods are
45 desirable because glucose, a useful by-product, is created, these methods are more
46 expensive and create MCC products having a lower crystallinity. Thus, acid hydrolysis is
47 the conventional method of choice for manufacturing MCC [10].

48 Microcrystalline cellulose could be produced from alpha cellulose obtained from wood
49 pulp by hydrolysis with hydrochloric or sulphuric acid. Microcrystalline cellulose could
50 be also produced in an autoclave from ground lignocellulosic materials by heating with
51 steam at 205- 250 °C for 15 minutes, followed by bleaching of cellulose with hydrogen
52 peroxide and finally hydrolyzing cellulose with mineral acids [11].

53 Microcrystalline cellulose (MCC) is widely used as a filler and a binder for wet
54 granulation, direct compression tableting and as a filler for hard gelatin capsules. It has
55 low chemical reactivity combined with excellent compatibility at low pressures. [12].

56 The choice of fillers usually takes into consideration primarily the desired performance in
57 a specific paper grade, the mill internal situation, logistical possibilities and
58 consequences, the general availability of the product, and the costs, including the external
59 and internal logistics. Optimizing one type of filler for a specific paper grade usually
60 results in a compromise between the obtainable properties with this filler. In cases where
61 one single pigment does not meet all the requirements, filler combinations are applied.
62 There is a continuous trend towards fully or partially replacing specialty pigments by
63 regular or modified regular fillers [13]. The brightness of the regular filler, kaolin is
64 distinctly lower than most $CaCO_3$ based fillers. For this reason, in recent decades, kaolin
65 has been largely globally replaced by $CaCO_3$ fillers in wood-free uncoated papers [13].
66 Rice straw is an available, local fibrous material produced in large quantities every year.
67 Recently, it is used for paper making or as filler in wood plastic composites industry. In
68 the present investigation, it is used for the production of micro crystalline cellulose by
69 hydrolysis using hydrochloric acid. The aim of the present work is to produce height high
70 yield pulp from rice straw at low temperature and at atmospheric pressure. Improving the
71 properties of paper made from this pulp was achieved by adding microcrystalline
72 cellulose and calcium carbonate as fillers to the pulp

74 2. EXPERIMENTAL

2.1 Pulping

Rice straw was used as a raw material in this research. It was cut into pieces of approximately 3 cm length. Rice straw was pretreated through soaking in water at room temperature for two days [2]. After the soaking water was peeled decanted, the thus pretreated straw was cooked using 5% sodium hydroxide (obtained from El Nasr Pharmaceutical Chemicals Co, Egypt, as analytical grade) based on oven dry weight of raw material. The condition of pulping was as follows:

Solid to Liquor ratio: 1:8, pulping time: 2 hours, pulping temperature: 100 °C at atmospheric pressure. After the required time, pulp was allowed to cool, filtered, and washed by water till neutrality. Pulp yield was calculated using oven dry weight. This ambiguous, what is oven dry weight? Rather, dried to a constant weight at X°C in an oven

2.2 Bleaching

Hydrogen peroxide: 40 wt% (supplied by FMC Co.,Spain) aqueous solution of commercially available purity grade. All experiments on pulp bleaching were made in plastic bags placed in a thermostatic shaker water bath.

The conditions of bleaching were as follows: pulp concentration – 10%, NaOH 2% on o.d. pulp, H₂O₂ charges were 1, 2, 4%, temperature 80°C, treatment time 90 mins., and MgSO₄·7H₂O (0.6% on o.d. pulp) (obtained from Mallinckrodt Co,Germany) stabilizer was dosed into an alkaline medium (pH 9). After bleaching, the pulps were washed with water to neutral condition and dried at room temperature. Magnesium sulfate was used in the peroxide stage in order to prevent radical degradation reactions of carbohydrates since this salt is reported as extremely efficient at reducing the rate of peroxide decomposition [14,15]. The optical properties of unbleached control, bleached and unbleached filled pulp presented in brightness and opacity were measured using Hunterlab color difference meter D25-2. Calcium carbonate assay 99. 5% obtained from SRL. CO.,Japan and the prepared MCC were added to unbleached rice straw pulp as fillers at 10% by weight based on o.d pulp before paper making by 1 hour.

2.3 Tests

Alpha cellulose of unbleached and bleached pulp was estimated using 17.5% sodium hydroxide solution. Hand-made paper sheets of basis weight 80g/m² were prepared using Tappi Standard Method 414, while T-211 method was used for ash estimation. Water permeability, air permeability, bursting resistances were measured using BS 6906, ASTM D 737, and ASTM D 3786 (Tayousiki Japan methods) respectively.

2.4 Microcrystalline cellulose preparation and characterization

2.5 g alpha cellulose of pulp (bleached using 2% H₂O₂) was added to 50 ml 2.5 N hydrochloric acid (34% purchased from El Nasr Pharmaceutical Chemicals Co.,Egypt) This mixture was heated at 80°C for 15 minutes. It was allowed to cool at 50°C and centrifuged using magnetic stirrer for 10 minutes. The product was filtered and washed by water until it became free from acid, and then air dried then, followed by thermal treatment in the oven dried at 50°C and weighed to calculate the yield. Microcrystalline cellulose was disintegrated by mortar. Crystallinity of MCC was obtained using a Bruker D8 Advance X-ray diffractometer (Germany). The size of MCC was elucidated by JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the MCC particles were prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air. Recast, the underlined is very clumsy.

3. DISCUSSION

3.1 Structural and strength properties of rice straw pulp

The solid pulp yield of from rice straw pretreated with water for 48 hours and pulped using 5% NaOH solution for 2 hour at atmospheric pressure was 74%. Water soaking pretreatment was adopted in this study as against the popular dilute acid pretreatment process to avoid the commonly encountered reactor corrosion problem. Neutral pretreatment is necessary since neutral pH can help to avoid the reactor corrosion problem, which is a major problem of the diluted acid pretreatment process. More so, pretreatment with water improved pulping efficiency of non-wood material and produced pulp containing 68.33% alpha-cellulose. This percent was suitable to prepare microcrystalline cellulose. The oxidative treatment of lignocellulosics by hydrogen peroxide in presence of magnesium sulphate as a stabilizer in an alkaline medium was established. Table 1 indicates the effect of H₂O₂ charge on bleached rice straw pulp properties. Pulp obtained using 2% H₂O₂ had 72.727% alpha- cellulose content and 61.5 pulp yield. Yield of bleached pulp using 1 and 4% H₂O₂ was 67.85 and 62.9% respectively with corresponding and had 69.33%, 69.556 alpha- cellulose content of 69.33% and 69.556 respectively at the same conditions. H₂O₂ charge had no effect on burst strength but tensile strength was improved on using 4% H₂O₂ in bleaching. Air permeability of paper sheets made from bleached pulp was greater than the unbleached one. This may be due to increasing the porosity of bleached pulp as a result of partial loss part of lignin content.

Table 1 physical properties of unbleached and bleached rice straw pulp

pulp	Air permeability, $\text{Cm}^3/\text{cm}^2.\text{sec.}$	Burst, Kg/cm^2	Tensile strength, Kg/mm
Unbleached pulp	1.3	1.1	2.2
1% H_2O_2 bleached pulp	2.4	1.1	2.2
2% H_2O_2 bleached pulp	2.2	1	2.3
4% H_2O_2 bleached pulp	1.8	1.2	3

3.2 X-ray diffraction (XRD) of microcrystalline cellulose

It is widely recognized that cellulose contains both crystalline and amorphous region [16]. The X-ray diffraction (XRD) patterns of MCC obtained from alpha cellulose of 5% hydrogen peroxide bleached rice straw pulp cooked in this study was illustrated in Figure no. 1. The crystallinity of MCC was 45.5 %, with the remainder being the amorphous fraction. so the samples had to include cellulose in an amorphous form, which indicates that the cellulose microfibrilles did not become single crystals. Kindly note that you gave no information on the XRD quantitative analysis of the cellulose crystallinity nor was any comparison of the diffractogram made with an existing one, Why?

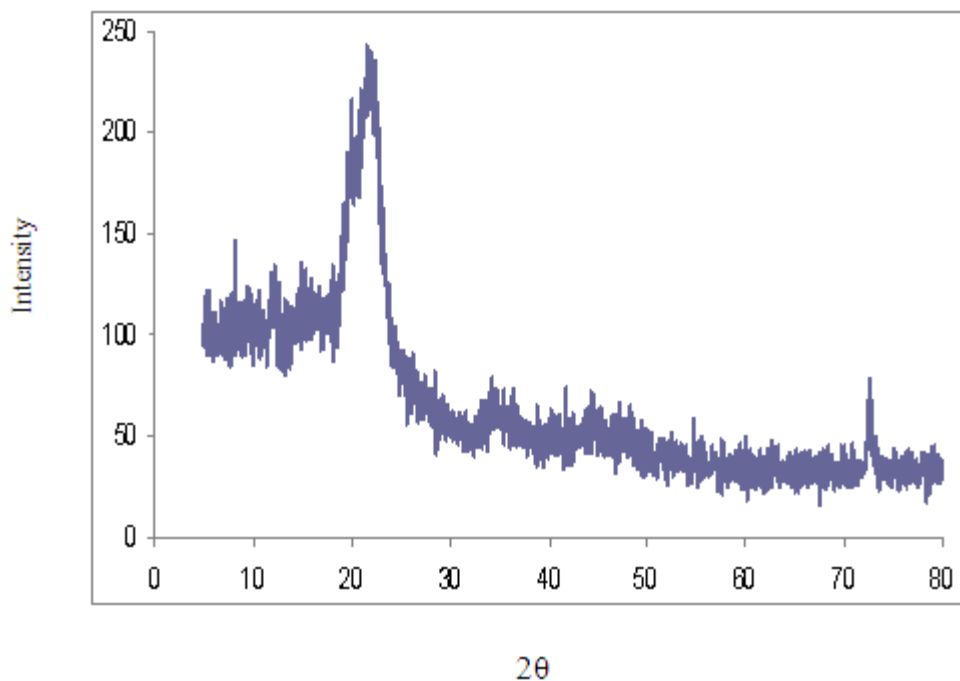
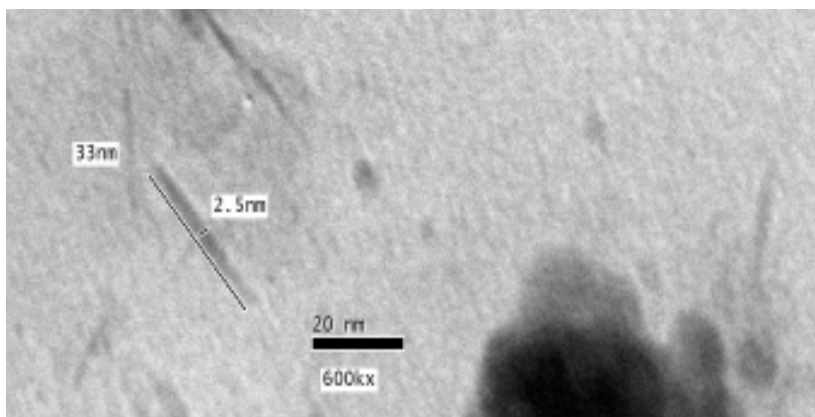


Fig.1 XRD profiles of microcrystalline cellulose

3.3 Transmission electron microscopy of MCC

TEM of the MCC prepared from the rice straw's alpha- cellulose of H_2O_2 bleached low temperature soda rice straw pulp was illustrated in Figure no. 2. The actual yield of MCC related to alpha cellulose content of rice straw pulp was 77.32%. MCC having nanoscale was obtained. The length of this microfibrill was 33 nm and its width was 2.5 nm which were in agreement with other studies [17]



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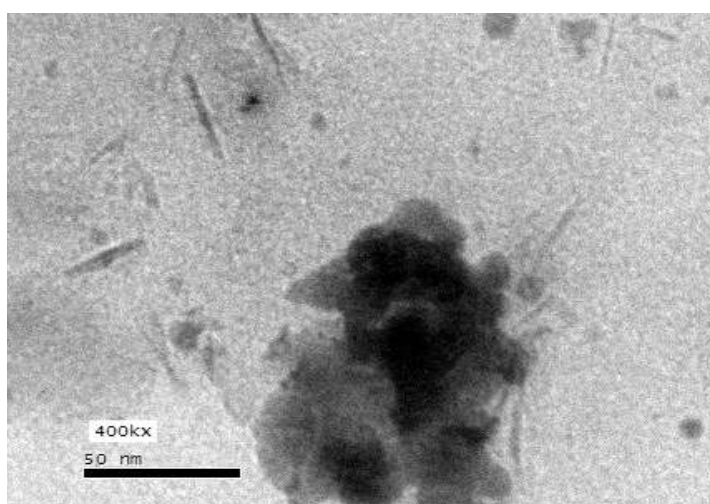


Fig.2: TEM graphs of MCC from alpha- cellulose of bleached (2% hydrogen peroxide) rice straw pulp.

194 3.4 Filler effect on paper properties

195 CaCO_3 is soluble under acid conditions, and therefore requires a near-neutral or slightly
 196 alkaline pH papermaking environment [18]. To be able to use CaCO_3 as a filler and/or as
 197 a coating pigment, numerous paper and board mills around the globe have converted their
 198 wet end systems from acid to neutral and slightly alkaline pH. Since calcium carbonate is
 199 binder-less and MCC was used as a binder and filler in many studies [19], the effect of
 200 these two substances on hand-made paper sheets properties was investigated. Table 2
 201 illustrates this investigation. Binder-less character of CaCO_3 was shown from the
 202 approximately unchanging ash content of the unfilled pulp in comparison to the filled
 203 pulps (paper sheets). 15.1% ash of paper sheets prepared by adding 10% calcium
 204 carbonate to beaten pulp before sheet making by one hour indicated that it is not a binder
 205 to the pulp compared to 14.4% ash content of unfilled pulp. 15.1% was reduced to 14.72
 206 and 14.52% at 5%, 2.5% calcium carbonate. Regarding tensile strength of the paper
 207 sheets, there was a registrable improvement attributable to the it is improved in presence

of all percents of calcium carbonate and MCC which prepared in this study in nano scale. MCC forms hydrogen bonds with cellulose, therefore strengthening the fibers. Air permeability is a typical structural property reflecting pores distribution and type and in some way, pores dimension, representing pigment particle packing ability [20] OP

Air permeability of filled paper was improved to $1.5 \text{ cm}^3/\text{cm}^2.\text{sec.}$ in the presence of MCC as a filler, more than in while the presence of calcium carbonate alone showed no improvement on this parameter when compared to the unbleached pulp $1.32 \text{ cm}^3/\text{cm}^2.\text{sec.}$ Water permeability resistance of the paper sheets was improved upon in the presence of the two fillers; it is the water permeability reduced from 1.4 (for unfilled paper) to 0.82 litre/sec on adding 7.5% MCC as filler. Paper sheets filled by MCC and calcium carbonate blend have higher water permeability than paper sheets filled with calcium carbonate alone. This is attributed to hydrophilic nature of amorphous cellulose included in MCC.

Differences in particle size and particle morphology of the two fillers affect paper sheet properties. Moreover, on several occasions, quite significant discrepancies were found which were attributed to differences in molecular weight, percentage crystallinity and polymorphism [21,22] How is this related to your results? No connection established.

Table 2 physical and mechanical properties of unbleached filled pulp

Treated pulp	Air permeability, $\text{Cm}^3/\text{cm}^2.\text{sec.}$	Burst, Kg/cm^2	Tensile strength, Kg/mm	Ash%	Water permeability, litre/ sec.
Unbleached pulp(control)	1.3	1.1	2.1	14.4	1.4
10%calcium carbonate	1.3	1	4.8	15.1	0.6
5%calcium carbonate+5%MCC	1.5	1	4	14.7	0.6
2.5%calcium carbonate+7.5% MCC	1.5	1	3.8	14.5	0.8

3.5 Optical properties of unbleached, bleached and unbleached filled pulp

All chemicals used in bleaching rice straw are environmentally friendly substances because they contain hydrogen, oxygen, sodium and magnesium. The bleaching is achieved using a single stage. NaOH is used to bring the pH up to 9 because H₂O₂ becomes active at this pH or oxidation starts at this pH. Table 3 indicates higher brightness of bleached pulp compared to unbleached pulp one 26.1% (control sample). Adding calcium carbonate alone or mixed with MCC filler to unbleached pulp improves brightness of paper by a small percent, approximately 10.34%. Opacity is a measure of a material's ability to obstruct the passage of light. Sufficient opacity is important to prevent showing printed text or figures on the reverse side of paper sheet. MCC and calcium carbonate are efficient in terms of opacity for unbleached paper because small internal voids do scatter the light. It is clear from Table 3 that paper made from unbleached pulp filled by 10% calcium carbonate or 5% calcium carbonate+5% MCC or 2.5% calcium carbonate+7.5% MCC has higher opacity (99.3%, 99.5%, 99.1%) more than unbleached sample (control, 77.7%)

Enhancement in brightness and opacity of unbleached filled paper sheets reflect improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be economically neglected.

Table 3 Optical properties of unbleached, bleached and unbleached filled pulp

Sample	Brightness,%	Opacity%
Unbleached pulp (control sample)	26.1	77.7
1% H ₂ O ₂ bleached pulp	48.4	96.4
2% H ₂ O ₂ bleached pulp	48.4	97.5
4% H ₂ O ₂ bleached pulp	38.4	97.95
unbleached pulp +10% calcium carbonate	28.4	99.3
unbleached pulp +(5% calcium carbonate+5% MCC)	28.9	99.5
unbleached pulp +(2.5% calcium carbonate+7.5% MCC)	28.8	99.1

4. CONCLUSION

Rice straw is a locally available waste lignocellulosic non wood material and can be converted into pulp at atmospheric pressure. This pulp can be employed in paper making industry and in preparing a valuable product like microcrystalline cellulose. Paper sheets filled by MCC and calcium carbonate blend have higher water permeability than paper sheets filled with calcium carbonate alone. The effect of moisture on packaged products depends on the product. For some, it is necessary to maintain the moisture content at a high level to prevent the product from drying out. For others the reverse may be the case, as by absorbing moisture the product may lose texture. Compared with the unfilled paper, MCC and calcium carbonate fillers gave slightly more increase in air permeability. Burst strength was not affected by fillers. Adding calcium carbonate alone or mixed with MCC filler to unbleached pulp improves brightness of paper by a small percent approximately; 10.34%. Calcium carbonate and MCC are efficient in terms of opacity for unbleached paper because small internal voids do scatter light. Enhancement in brightness and opacity of filled paper sheets reflect improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be economically neglected.

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REFERENCES

- [1] Navaee-Ardeh S, Mohammadi-Rovshandeh J, Pourjoozi M, Influence of rice straw cooking conditions in the sodaethanol- water pulping on the mechanical properties of produced paper sheets, [Bioresour Technol.](#), 2004, 92: 65-69
- [2] Sarwar Jahan M, Shamsuzzaman M, Mostafizur Rahman M, Iqbal Moeiz S M, Nic Y. Effect of pre-extraction on soda-anthraquinone (AQ) pulping of rice straw Ind.Crop Prod, 2012 , 37:164– 169.
- [3] Zhang H, He Z, Ni Y. Improvement of high-yield pulp properties by using a small amount of bleached wheat straw pulp. [Bioresour Technol.](#) 2011, 102(3): 2829-2833
- [4] Gierer J, The chemistry of delignification, Wood Sci. Technol., 1985, 19:289-312
- [5] Sundberg A, Pranovich A.V, Holmbom B, Proceedings of the 10th International Symposium on Wood and Pulping Chemistry, Seoul, Korea, 1999 , p. 254.
- [6] Abraham, E, Deepa, B, Pothan, L A, Jacob M, Thomas S, Cvelbar U. Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. Carbohydr. Polym, 2011, 86: 1468–1475.

288 [7] Eichhorn, S. J. Cellulose nanowhiskers: Promising materials for advanced
289 applications. *Soft Matter*, 2011 , 7: 303–315.

290 [8] Johar N, Ahmad I, Dufresne, A. Extraction, preparation and characteri-zation of
291 cellulose fibres and nanocrystals from rice husk. *Ind.Crop Prod*, 2012 , 37: 93–99.

292 [9] Jahan M. S, Saeed, A, He Z, Ni Y. Jute as raw material for the preparation of
293 microcrystalline cellulose. *Cellulose*, 2011, 18: 451–459.

294 [10] Hanna M., Blby G, Miladinove V. Production of microcrystalline of rice straw
295 cooking conditions in the sodaethanol- water pulping on the mechanical properties of
296 produced paper sheets, [Bioresour Technol.](#), 2001, 92: 65-69

297 [11] Ilindra A. , Dhake J D. Microcrystalline cellulose from bagasse and rice straw *Indian*
298 *J. Chem. Technol* , 2008 , 15: 497-499

299 [12] Michael J T, Gerard P M., John N S, Edge S. Physicochemical comparison between
300 microcrystalline cellulose and silicified microcrystalline cellulose *Int. J. Pharm* 1998,
301 169: 183–194

302 [13] Holik H., *Handbook of paper and board WILEY –VCH ISBN, 3-527-30997-*
303 *7,35,47,2006*

304 [14]Lapierre, L., Berry, R., Bouchard, J., The effect of magnesium ions and chelants on
305 peroxide bleaching. *Holzforschung* 2003 ,57 (6):627–633.

306 [15] Ashori A., Raverty W D, Harun J. Effect of totally chlorine free and elemental
307 chlorine free sequences on whole stem kenaf (*Hibiscus cannabinus*) pulp characteristics.
308 *Polym. Plast. Technol. Eng.* , 2006, 45: 205–211.

309 [16] Klemm D., Heublein B., Fink, H. P., Bohn, A. Cellulose: Fascinating biopolymer
310 and sustainable raw material. *Angew. Chem., Int. Ed*, 2005. 44: 3358–3393.

311 [17] Lepanen K., Andersson S., Torkkeli M. Knaapila M., Kotlnkova N., Serimaa R.
312 Structure of cellulose and microcrystalline cellulose from various wood species, cotton
313 and flax studied by x-ray scattering. *Cellulose* 2009 , 16:999-1015

314 [18] Laufmann M., Hummel W. Neutral Groundwood Containing Papermaking,
315 Overview-Anion. Trash-Conversion, *WOCHENBL PAPIERFABR.*, 1991, 119 (6):
316 269–293

317 [19] Dogan N, McHugh T H. Effects of Microcrystalline Cellulose on Functional
318 Properties of Hydroxy Propyl Methyl Cellulose Microcomposite Films. *J. Food Sci* 2007
319 [72](#): E016–E022

320 [20] Santos N F, Velho J, Gomes C. Influence of calcium carbonate coating blends upon
321 paper properties. Congreso Iberoamericano de investigation en celulosa Y Papel 2000

322 [21] Psomiadou E. , Arvanitoyannis I. , Yamamoto N. Edible films made from natural
323 resources; microcrystalline cellulose (MCC), methylcellulose (MC) and corn starch and
324 polyols—Part 2, Carbohydr. Polym 1996 ,[31](#): 193–204

325 [22] Petersson L. , Oksman K. Biopolymer based nanocomposites: Comparing layered
326 silicates and microcrystalline cellulose as nanoreinforcement, Compos. Sci. Technol.,
327 2006, 66: 2187–2196

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330 Key: Blue means add; Red means delete, while purple
331 stands for comments.