Carbohydrate Polymers 94 (2013) 843–849

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Polymorphic transformation of cellulose I to cellulose II by alkali pretreatment and urea as an additive

P.K. Gupta [a,*,1], Vanshi Uniyal [a], Sanjay Naithani [b]

[a] Centre for Advanced Studies in Chemistry of Forest Products, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India
[b] Cellulose and Paper Division, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India

ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form 15 January 2013
Accepted 9 February 2013
Available online 18 February 2013

Keywords:
Cotton linter
Cellulose I
Cellulose II
NaOH
Urea

ABSTRACT

The effect on crystalline structure transformation from cellulose I to cellulose II polymorph was studied of the cotton linter treated with NaOH with and without urea as an additive, analyzed by wide-angle X-ray diffraction analysis. Cotton linter treated with increasing NaOH concentration showed at 15 wt% sudden transformation from cellulose I to cellulose II polymorph. But when urea 5 wt% was used as additive along with 15 wt% NaOH concentration the magnitude of the transformation reduced largely. The crystallinity index showed a gradual decrease with increasing concentration of NaOH. The crystallinity index showed a gradual decrease with increasing concentration of NaOH with or without addition of urea, nevertheless with addition of urea a further slight more transformation was also observed.

1. Introduction

The most abundant biopolymer on earth is cellulose which is of particular interest in providing renewable, sustainable, biodegradable biopolymer for industrial applications (Klemm, Heublein, Fink, & Bohn, 2005). Its cellular structure is organized into fibrils, which are further surrounded by a matrix of lignin and hemicelluloses (Hult, Larsson, & Iversen, 2000; Krassig, 1993). Cellulose is a linear 1,4-β-glucan polymer, where the monomer units are able to form highly ordered structures, which is due to the result of extensive interaction through intra- and intermolecular hydrogen bonding of the three hydroxyl groups present in each cellulose unit. Cellulose when treated with aqueous sodium hydroxide (NaOH) solutions has a considerable impact on morphology, molecular and supramolecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure of fibrils in cellulosic fibres (Goswami, Blackburn, El-Dessouky, Taylor, & White, 2009). The use of cellulose is limited because of its insoluble nature in solvents and does not melt without thermal degradation. Hydrogen bonds present in the cellulose substrates are modified by some physical and/or chemical transformations for various applications. (Dinand, Vignon, Chanzy, & Heux, 2002; Jähn, Schroder, Futing, Schenzel, & Diepenbrock, 2002; Zugenmaier, 2001). Common methods for the characterization of crystalline cellulose structure are based on X-ray (Dinand et al., 2002; Gert et al., 2001; Gumuskaya, Usta, & Kirci, 2003; Nishiyama, Langan, & Chanzy, 2002; Nishiyama, Sugiyama, Chanzy, & Langan, 2003) or electron diffraction (Atalla & VanderHart, 1999; Sugiyama, Vuong, & Chanzy, 1991), FT Raman (Atalla & VanderHart, 1999; Cael, Gardner, Koenig, & Blackwell, 1975; Jähn et al., 2002; Proniewicz et al., 2001) density determinations, infrared (IR) absorption (Akerholm, Hinterstoisser, & Salmen, 2004; Colom & Carrillo, 2002; Gert et al., 2001; Gumuskaya et al., 2003; Ruan, Zhang, Mao, Zeng, & Li, 2004; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004) and nuclear magnetic resonance (NMR) (Atalla & VanderHart, 1999; Newman & Davidson, 2004). Amongst them, wide-angle X-ray diffraction gives the most direct results and quantitative information. The polymorphic transformation of cellulose I to cellulose II has been studied with X-ray diffraction in many cellulosic fibres (Beg & Pickering, 2004; Bledzki, Fink, & Specht, 2004; Gassan & Bledzki, 1999a, 1999b; Mirjana, Biljana, & Petar, 2008; Mwaikambo & Ansell, 2003; Ouajai & Shanks, 2005; Prasad & Sain, 2003; Zhou, Yeung, Yuen, & Zhou, 2004). The hydrogen bonding in cellulose II is complex than cellulose I. The anti-parallel chain model enables the formation of not only inter-chain but also of inter-plane hydrogen bonds. From technical and commercial point of view, diverse cellulose polymorphs are favored as special requirement by different industries. For example the paper industry needs high crystallinity with more of cellulose II polymorph content, whereas the establishments dealing with preparation of cellulose derivatives look for alpha cellulose with

* Corresponding author. Tel.: +91 9358126046; fax: +91 662 2154459.
E-mail addresses: guptapk@icfre.org, nidhipraveen@yahoo.co.uk (P.K. Gupta).
[1] Tel.: +91 1352224211.

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.02.012

low crystallinity and more of cellulose I polymorph content. High concentrations of NaOH is used to prepare alpha cellulose from lignocellulosic biomass. The objective of the present study is evaluate effect on the structural transformation of cellulose I to cellulose II polymorphs of cotton linter when treated with different NaOH concentrations and the influence of urea when used as an additive.

2. Experimental

2.1. Materials

The cellulose used in this study was a fibrous medium from cotton linter, was shredded in the form of powder in an ultra centrifugal mill and oven-dried. Analytical grade reagents were used as received.

2.2. Alkali pretreatment

The alkalization of cellulose was performed in Erlenmeyer flasks (250 ml) and the solution was mixed with a magnetic stirrer. The sodium hydroxide was first dissolved in different NaOH concentrations of 5 wt%, 10 wt%, and 15 wt% in the flasks. The mixture was homogenized and the cotton linter was added to the flasks. The temperature was regulated at room temperature for all the reactions for 24 h. After the treatments, all mercerized samples were washed to neutral (pH 7.0) with distilled water. Samples were centrifuged to remove unhydrolysed residue. The residues were air-dried, stored and kept in desiccators.

2.3. Alkali treatment with urea as an additive

The cellulose was treated with alkali and urea in Erlenmeyer flasks (250 ml) and the solution was mixed with a magnetic stirrer. With pure water systems, the sodium hydroxide was first dissolved in water of different concentrations 5 wt%, 10 wt%, and 15 wt% and with constant concentration of urea 5 wt% as an additive in the flasks. After the mixture was homogenized, cotton linter was added to the flasks. The temperature was regulated at room temperature for all the reactions for 24 h. After the treatments, all mercerized samples were washed to neutral (pH 7.0) with distilled water. Samples were centrifuged to remove unhydrolysed residue. The residues were air-dried, stored and kept in desiccators.

2.4. Crystal structure measurements

The crystallinity of untreated cotton linter cellulose fibers was examined by wide-angle X-ray diffraction (WAXD) technique, using Ni-filtered Cu K_α radiation ($\lambda = 1.5406$ Å), equipped with computerized data collection and analytical tools. XRD measurements were performed on a Philips PANalytical X'Pert PRO system in order to estimate the crystalline – amorphous ratio of the initial cellulose samples and of the residues. The X-ray source was operated at a voltage of 45 kV and a filament current of 40 mA. Samples were scanned from $2\theta = 5^\circ$ to $2\theta = 45^\circ$ with a step size of 0.016°.

2.5. Crystallinity index

Crystallinity for the X-ray diffractograms of all samples was analyzed using the empirical procedure of Segal, Creely, Martin, and Conrad (1959). The calculation of the crystallinity index (Cr. I.) followed the Eq. (1):

$$\text{Cr.I.}\ (\%) = \frac{I_{(002)} - I_{(\text{am})}}{I_{(002)}} \times 100 \quad (1)$$

where I_{002} is the maximum intensity of diffraction of the (002) lattice peak at a 2θ angle of between 22° and 23°, and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 18° and 19° where the intensity is at the minimum (Roncero, Torres, Colom, & Vidal, 2005). Taking the Lorentzian distribution function as the shape of the resolved bands, cellulose I and cellulose II components were resolved into four and three reflections, respectively (Oh et al., 2005).

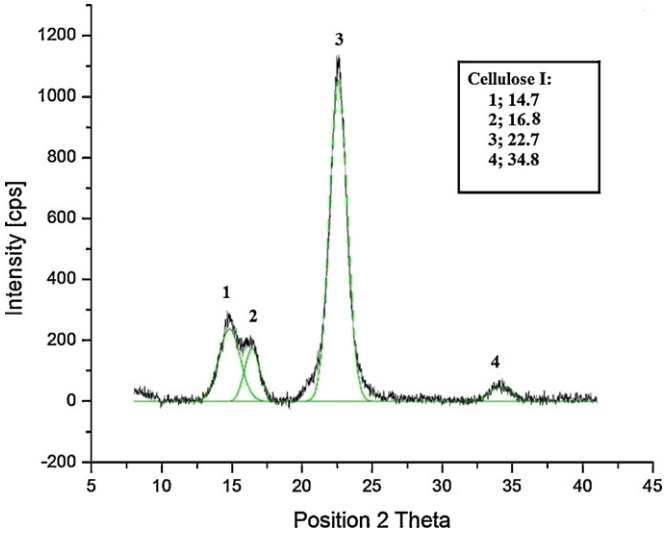

Fig. 1. WAXD of control cotton linter.

3. Results and discussion

3.1. Wide-angle X-ray diffraction (WAXD) analysis

The X-ray diffraction pattern of control cotton linters is presented in Fig. 1 shows a pattern which is quite similar to the native cellulose (cellulose I). The characteristic peaks of the untreated cotton linters are approximately located at $2\theta = 14.7^\circ$, 16.8°, 22.7°, and 34.8°, which are the positions of the (1 0 1), (1 0 −1), (0 0 2) and (0 4 0) crystallographic plane reflections, respectively. The diffractogram revealed a relatively ordered structure with narrow peak at 22.7° (0 0 2) and a diffuse peak between 14.7 and 16.8° (1 0 1 and 1 0 −1). The sharper diffraction peak at 22.7° (0 0 2) indicates region of higher crystallinity. The linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure. Individual fibrillar units consist of long periods of ordered crystalline regions interrupted by completely disordered amorphous regions. The findings are in agreement with observations reported by earlier researchers (Alemdar & Sain, 2008; Berlant & Khalifa, 1991; Chen, Yu, Zhang, & Lu, 2011; Davidson, Newman, & Ryan, 2004; Ouajai & Shanks, 2005; Quddiani, Chaabouni, Msahli, & Sakli, 2011; Sotton, Arniaud, & Rabourdin, 1978).

3.2. X-ray diffraction and polymorphic transformation of cotton linters treated with alkali

The cotton linter was treated with different concentrations of NaOH (Table 1). The alkali infiltrate the cellulose fiber and causes a rearrangement of the crystal packing of chains from native cellulose I (chains aligned in parallel) to cellulose II (anti-parallel). The peaks for cellulose II polymorph are located at $2\theta = 12.1^\circ$, 20.1° and 21.9° which correspond to the diffraction of (1 0 1), (1 0 −1) and (0 0 2) crystallographic plane reflections, respectively (Beatriz, Assa, & Belgacemb, 2006; Chen, Nattakan, Ni, & Ton, 2008; Oh et al., 2005; Ouajai & Shanks, 2005; Raymond, Kvick, & Chanzy, 1995). This change is irreversible and normally accompanied by

Table 1
NaOH and urea treatment of cotton linter.

Sample	NaOH			Urea 5 wt%	Combination attained during the reaction
	5 wt%	10 wt%	15 wt%		
Cotton linter	√	x	x	x	5 wt%NaOH
	√	x	x	√	5 wt%NaOH + urea
Cotton linter	x	√	x	x	10 wt%NaOH
	x	√	x	√	10 wt%NaOH + urea
Cotton linter	x	x	√	x	15 wt%NaOH
	x	x	√	√	15 wt%NaOH + urea

√, treated; x, untreated.

a decrease in the crystallinity. The NaOH treatment loosens the hydrogen bonding within the fiber bundles causing the fibers to move apart, where it provokes the observed changes (Buschle-Diller & Zeronian, 1992; Nishimura & Sarko, 1987; Quddiani et al., 2011).

The X-ray diffractogram of NaOH treated cotton linters at different concentrations control, 5 wt%, 10 wt%, and 15 wt%, are presented in Fig. 4. The diffractogram show change in peak intensity pattern at different crystallographic plane reflections and polymorphic transformation from cellulose I to cellulose II with increase in NaOH concentration. The peak intensities at different 2θ angle plane reflections for cellulose I and cellulose II for NaOH treated cotton linters at different concentrations is given in Table 2. The change in different peak intensity and peak intensity percent at different 2θ plane reflections for cotton linters treated with low alkali concentration to high alkali concentration is shown in Figs. 6 and 7 respectively.

There is almost no effect on the structure of cellulose I polymorph of cotton linter treated with water (control) and was same as untreated cotton linter. There is a decreasing trend in all the characteristic peaks intensity at $2\theta = 14.7^\circ$, 16.8°, 22.7°, and 34.8° for cellulose I polymorph from control to alkali treated cotton linters.

The peaks intensity at $2\theta = 14.7^\circ$ for cellulose I polymorph decreased gradually from 309 for control to 278 (90%) for cotton linter treated with 10 wt% NaOH and a sharp decline to 46 (15%) was observed on further treatment with 15 wt% NaOH. However the peak intensity percent at $2\theta = 14.7^\circ$ of total peak intensity remained around 18% from control to 10 wt% NaOH with sharp fall to 3% at 15 wt% NaOH.

Similar trend was observed for peaks intensity at $2\theta = 16.8^\circ$ for cellulose I polymorph from control to alkali treated cotton linters. The peaks intensity decreased gradually from 208 for control to 172 (83%) for cotton linter treated with 10 wt% NaOH and a sharp decline to 9 (4%) was observed on further treatment with 15 wt% NaOH. The peak intensity percent remained around 12% from control to 10 wt% NaOH with sharp fall to 1% at 15 wt% NaOH.

The peak intensity at $2\theta = 22.7^\circ$ is the most dominant for cellulose I polymorph constituting 66% of the total peak intensity for control cotton linter. A major decline was observed in it from control to alkali treated cotton linters. The peaks intensity decreased with increase in NaOH concentration from 1142 for control to 860 (75%) for cotton linter treated with 10 wt% NaOH and a sharp fall to 112 (10%) was observed on further treatment with 15 wt% NaOH. The peak intensity percent remained around 66–59% from control to 10 wt% NaOH with sharp drop to 8% at 15 wt% NaOH.

The peak intensity at $2\theta = 34.8^\circ$ is the smallest for cellulose I polymorph constituting 4% of the total peak intensity for control cotton linter. No major fall was observed in it with increase in NaOH concentration, though a increase by 28% was recorded at 10 wt% NaOH concentration.

The peak intensity located at $2\theta = 12.1^\circ$, 20.1° and 21.9° for cellulose II polymorph were absent in the control cotton linter however they appeared and increased gradually on treating with increasing concentration of NaOH.

The peaks intensity at $2\theta = 20.1^\circ$ for cellulose II polymorph appeared on treatment of low NaOH concentration at 5 wt%. It increased gradually up to 10 wt% NaOH forming 5% of the total peak intensity percent. On further treatment with 15 wt% NaOH it increased sharply making 42% of the total peak intensity percent. This increase was associated with sharp appearance of peak at $2\theta = 21.9^\circ$ making 39% of the total peak intensity percent and another peak at $2\theta = 12.1^\circ$ for 4% total peak intensity percent for cellulose II polymorph. The peaks at $2\theta = 12.1^\circ$ and 21.9° did not show its appearance on treatment with NaOH concentration <10 wt%, indifferent to the peak at $2\theta = 20.1^\circ$ for cellulose II polymorph that appeared even on treatment of cotton linter with low NaOH concentrations. The X-ray diffraction of cotton linters treated with 15 wt% NaOH is presented in Fig. 2.

The overall transformation in peak intensity and peak intensity percent from cellulose I polymorph to cellulose II polymorph for cotton linter on treatment with increasing concentration of NaOH is shown in Fig. 8. The results show there was little transformation maximum by 5% of cellulose I polymorph to cellulose II polymorph on treatment up to 10 wt% NaOH concentration. On further treatment with 15 wt% NaOH a major transformation by 84% was observed from cellulose I polymorph to cellulose II polymorph. Though no definite reason could be assigned to this sudden transformation at 15 wt% NaOH but it appears that a defined swelling and spacing is required for transformation from cellulose I polymorph to cellulose II polymorph where a rearrangement of the crystal packing of chains aligned in parallel for native cellulose I to antiparallel for cellulose II takes place in cellulose fiber (Figs. 3 and 4).

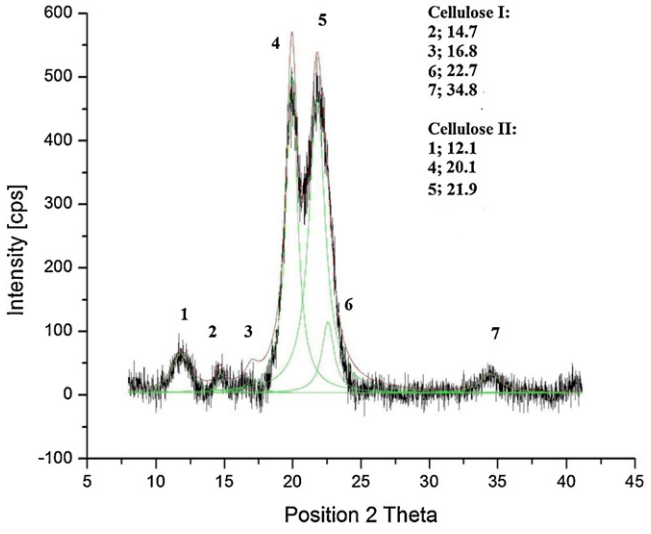

Fig. 2. WAXD of NaOH (15 wt%) treated cotton linter.

Table 2
WAXD peak intensity (I) and peak intensity percent (%) at different 2θ angle for control and treated cotton linters samples – C = cotton linters; N = NaOH; U = 5 wt% urea; Cell-I = cellulose I; Cell-II = cellulose II.

WAXD 2θ angle		Control		C + U		5% N		5% N + U		10% N		10% N + U		15 N		15 N + U	
Cell-I	Cell-II	I	%	I	%	I	%	I	%	I	%	I	%	I	%	I	%
	12.1													51	4	31	2
14.7		309	18	302	18	289	17	287	17	278	19	256	18	46	3	155	11
16.8		208	12	205	12	176	10	174	10	172	12	168	12	9	1	141	10
	20.1			32	2	78	5	76	5	71	5	53	4	572	42	252	18
	21.9													540	39		
22.7		1142	66	1114	65	1102	65	1092	65	860	59	851	60	112	8	748	55
34.8		67	4	61	4	59	3	59	3	86	6	94	7	48	3	41	3
	Total	1726	100	1714	100	1704	100	1688	100	1467	100	1422	100	1378	100	1368	100
Cell-I		1726	100	1682	98	1626	95	1612	95	1396	95	1369	96	215	16	1085	79
	Cell-II	0	0	32	2	78	5	76	5	71	5	53	4	1163	84	283	21

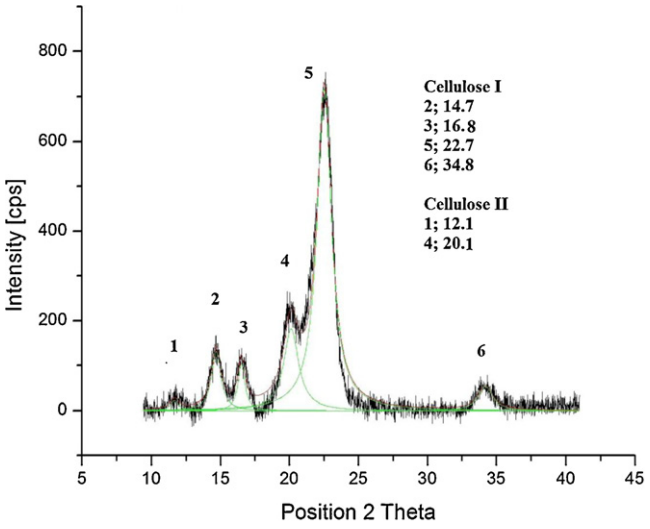

Fig. 3. WAXD of NaOH (15 wt%) and urea (5 wt%) treated cotton linter.

3.3. X-ray diffraction and polymorphic transformation of cellulose treated with alkali and urea

The cotton linter was treated with different concentrations of NaOH and urea as additive (Table 1). The X-ray diffractogram of NaOH treated cotton linters at different concentrations control, 5 wt%, 10 wt%, and 15 wt% with urea 5 wt% as an additive are presented in Fig. 5. The diffractogram showed change in peak intensity pattern at different crystallographic plane reflections and polymorphic transformation from cellulose I to cellulose II with increase in NaOH concentration with urea as an additive. The peak intensities at different 2θ angle plane reflections for cellulose I and cellulose II are given in Table 2. The change in different peak intensity and peak intensity percent at different 2θ plane reflections for cotton linters treated with low alkali concentration to high alkali concentration is shown in Figs. 6 and 7 respectively.

There is very little effect on the polymorphic structure of cellulose I of cotton linter treated with 5 wt% urea alone and most of the peak intensities remain almost constant equivalent for untreated cotton linter. In addition only one peak at $2\theta = 20.1^\circ$ for cellulose II polymorph showed it presence making 2% of total peak intensity.

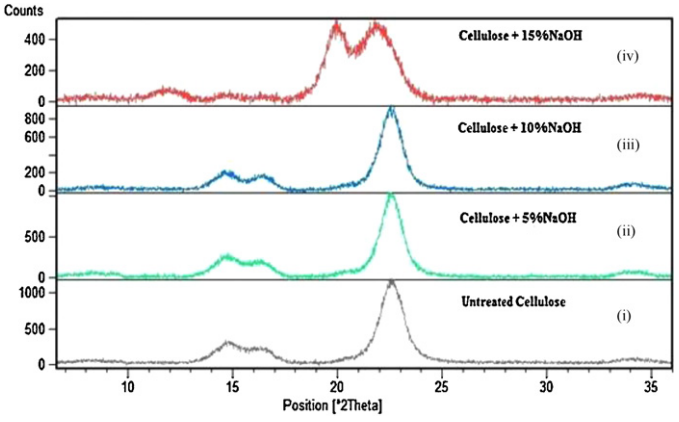

Fig. 4. WAXD of cotton linter treated with different concentrations of NaOH.

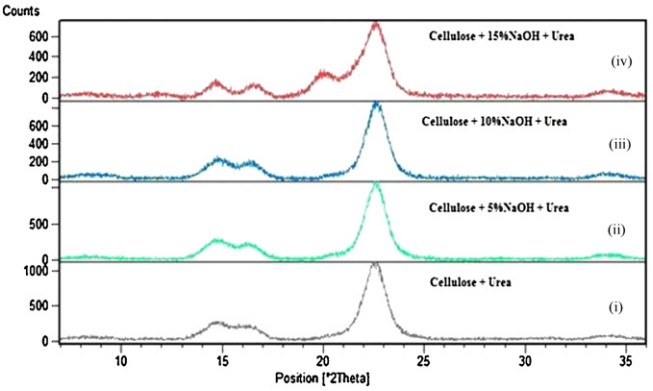

Fig. 5. WAXD of cotton linter treated with different concentrations of NaOH with urea (5 wt%) as additive.

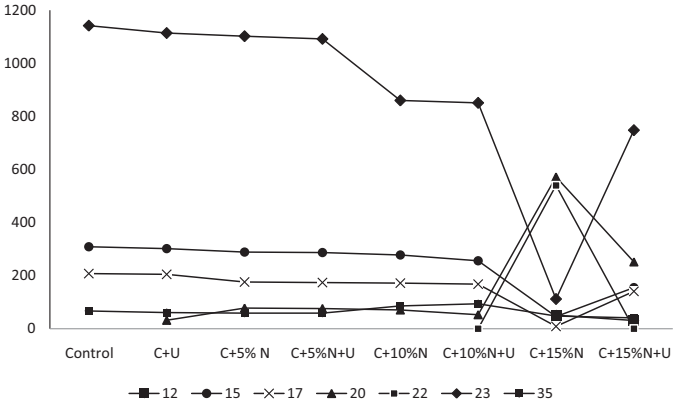

Fig. 6. WAXD peak intensity at different 2θ angle [cellulose I ~15, 17, 23, 35; cellulose II ~12, 20, 22] for control and treated cotton linters samples [C = cotton linters; N = NaOH; U = 5 wt% urea].

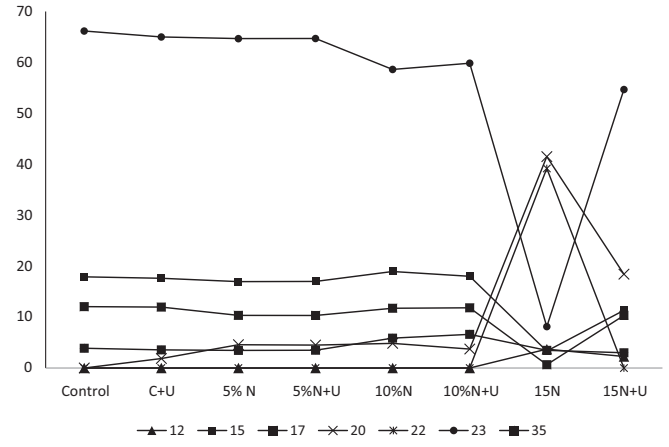

Fig. 7. WAXD peak intensity percent (%) at different 2θ angle [cellulose I ~15, 17, 23, 35; cellulose II ~12, 20, 22] for control and treated cotton linters samples [C = cotton linters; *N* = NaOH; U = 5 wt% urea].

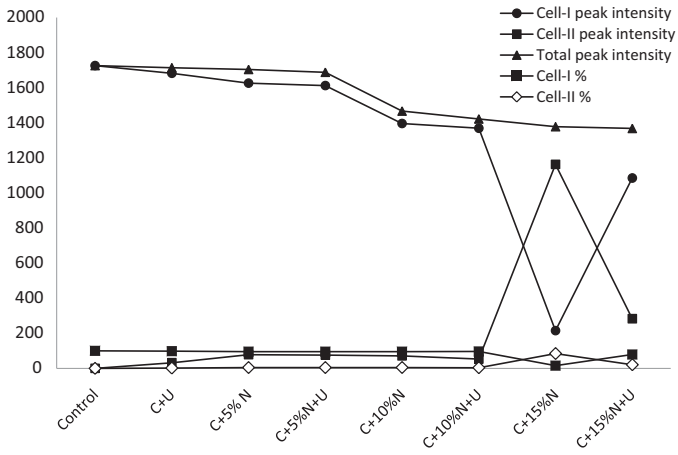

Fig. 8. WAXD total peak intensities and total peak percent (%) for cellulose I (Cell-I) and Cellulose-II (Cell-II) for control and treated cotton linters samples [C = cotton linters; *N* = NaOH; U = 5 wt% urea].

As was in the case of NaOH treated cotton linter there is a decreasing trend in all the characteristic peaks intensity at $2\theta = 14.7^\circ$, 16.8°, 22.7°, and 34.8° for cellulose I polymorph from control to alkali treated cotton linters with 5 wt% urea as additive. The peak intensity at $2\theta = 14.7^\circ$, 16.8°, 22.7° showed minor decrease on treatment with 5 wt% urea and NaOH up to <10 wt% compared to when treated with NaOH alone. Peak intensity at $2\theta = 34.8^\circ$ also showed similar trend by first decreasing up to 5% and then a slight increase at 10 wt% NaOH + 5 wt% urea.

The extent of decreasing trend for 15 wt% NaOH alone for $2\theta = 14.7^\circ$, 16.8° and 22.7° for cellulose I polymorph did not follow the same when the cotton linter was treated with 15 wt% NaOH with 5 wt% urea as an additive. The peak intensity percent for $2\theta = 14.7^\circ$, 16.8° and 22.7° for cellulose I polymorph was observed much higher as 11%, 10% and 55% for 15 wt% NaOH with 5 wt% urea as an additive, against a low of 3%, 1%, and 8% respectively when treated alone with 15 wt% NaOH. The peak intensity at $2\theta = 34.8^\circ$ for cellulose I polymorph however, showed decreasing trend in both the cases when treated with 15 wt% NaOH alone and with 5 wt% urea as an additive.

The peak intensity located at $2\theta = 12.1^\circ$ and 21.9° for cellulose II polymorph were absent in the cotton linter treated with NaOH concentration <10 wt% with 5 wt% urea. The peak intensity located at $2\theta = 20.1^\circ$ for cellulose II polymorph increased gradually up to NaOH concentration <10 wt% with 5 wt% urea. Differently the cotton linter treated with 15 wt% NaOH and 5 wt% urea showed peak intensity percent for $2\theta = 12.1^\circ$, 20.1° and 21.9° as 2%, 18% and nil against 4%, 42% and 39% for 15 wt% NaOH alone respectively. The X-ray diffraction of cotton linters treated with 15 wt% NaOH and 5 wt% urea is presented in Fig. 3.

The overall transformation in peak intensity and peak intensity percent from cellulose I polymorph to cellulose II polymorph for cotton linter on treatment with increasing concentration of NaOH with 5 wt% urea is shown in Fig. 8. The result show there was little transformation of cellulose I polymorph to cellulose II polymorph by maximum of 5% on treatment up to 10 wt% NaOH with 5 wt% urea as was in the case when treated with 10 wt% NaOH alone. On further treatment with 15 wt% NaOH with 5 wt% urea a transformation by only 21% was observed from cellulose I polymorph to cellulose II polymorph against of 84% when cotton linter was treated with 15 wt% NaOH alone although the total peak intensity decreased and remained almost same 1368 and 1378 respectively. No definite reason could be assigned to this decline in transformation from cellulose I to cellulose II polymorphs at 15 wt% NaOH concentration with 5 wt% urea used as an additive, however it appears urea opposed requisite swelling and spacing needed for transformation from cellulose I polymorph to cellulose II polymorph through urea–$NH_3^+\cdots O^-$–cellulose interaction.

Table 3
Crystallinity index of cotton linter with different concentrations of NaOH and urea (5 wt%) as additive.

S. no	Treatment	Type of cellulose	Crystallinity index Cr.I. (%)
1	Cotton linter with water	I	90.8
2	Cotton linter with urea	I	90.0
3	Cotton linter with 5 wt% NaOH	I	89.9
4	Cotton linter with 5 wt% NaOH + urea	I	89.7
5	Cotton linter with 10 wt% NaOH	I	88.9
6	Cotton linter with 10 wt% NaOH + urea	I	88.5
7	Cotton linter with15 wt% NaOH	I & II	80.8
8	Cotton linter with 15 wt% NaOH + urea	I & II	80.3

3.4. Change in crystallinity index by polymorphic transformation

The crystallinity index of the control cotton linters, cotton linter treated with different NaOH concentrations with and without urea as an additive was calculated according to the method developed by Segal et al. (1959) and the results are depicted in Table 3. The crystallinity index for control cotton linter was observed as 90.8% and when treated with 5 wt% urea alone was 90.0%. There was little and gradual fall in crystallinity index when treated upto <10 wt% NaOH but on treatment with 15 wt% NaOH the value of crystallinity index reduced to 80.8%, and when the sample was treated with addition of 5 wt% urea it fell further to 80.3%. This reduction is supported from data in Table 2 and Fig. 8, where cotton linter when treated with 15 wt% NaOH showed major transformation from cellulose I to II polymorph, suggesting that at this concentration there was enough swelling of the cellulose microfibril and dissociation of hydrogen bonds in cellulose I polymorph, and a portion of this during transformation to cellulose II misaligned leading to significant loss in cellulose crystallinity. There was no significant effect of urea on crystallinity index when treated alone or in addition with different concentrations of NaOH. This is because the urea does not contribute towards dissociation of hydrogen bonds and swelling of cellulose microfibrils.

4. Conclusions

The effect on crystalline structure transformation from cellulose I to cellulose II polymorph was studied of the cotton linter treated

with NaOH with and without urea as an additive was analyzed by wide-angle X-ray diffraction analysis. No structural transformation from cellulose I to cellulose II polymorph was observed on treatment with water alone. There was a gradual decrease in all the peak intensities at $2\theta = 14.7^\circ$, 16.8°, 22.7°, and 34.8° for cellulose I polymorph on increasing the NaOH concentration up to <10 wt%, except at peak intensity $2\theta = 34.8^\circ$ showed first decrease and then increase at 10 wt% NaOH concentration, but on further increasing the NaOH concentration to 15 wt% all the peak intensities fall sharply. The peak at $2\theta = 20.1^\circ$ for cellulose II polymorphs showed it presence at 5 wt% NaOH concentration and increased gradually up to 10 wt% NaOH concentration and on further treating it with 15 wt% NaOH it increased sharply and also two more peaks at $2\theta = 12.1^\circ$ and 21.9° emerged for cellulose II polymorph. The total peak intensity showed moderate transformation by 5% from cellulose I to cellulose II polymorph up to <10 wt% NaOH concentration but at 15 wt% NaOH concentration there was sudden significant transformation from cellulose I to II polymorph transformation by 84%.

The addition of 5 wt% urea to different concentration of <10 wt% NaOH showed added effect on peak intensities for cellulose I and cellulose II polymorphs, but when treated with 15 wt% NaOH concentration indifferently there was no sharp fall of peak intensities for cellulose I polymorph and no enormous increase of peak intensities for cellulose II polymorph as observed when the cotton linter was treated with 15 wt% NaOH alone, though the total peak intensity decreased constantly. The total peak intensity showed gradual transformation from cellulose I to cellulose II polymorph by 4% up to <10 wt% NaOH concentration with 5 wt% urea as additive, but at 15 wt% NaOH concentration with 5 wt% urea as additive it showed transformation by only 21% against 84% when treated with 15 wt% NaOH alone. The crystallinity index showed a gradual decrease with increasing concentration of NaOH, and on treatment with 15 wt% NaOH the crystallinity index reduced significantly; however, the addition of urea showed an additional minor decrease only.

Acknowledgement

The authors are thankful to Dr. P. P. Bhojwaid, Director, Forest Research Institute, Dehradun, India for encouragement and funding the research project.

References

Akerholm, M., Hinterstoisser, B., & Salmen, L. (2004). Characterization of the crystalline structure of cellulose using static and dynamic FT-IR spectroscopy. *Carbohydrate Research*, *339*, 569–578.

Alemdar, A., & Sain, M. (2008). Isolation and characterization of nanofibers from agricultural residues: Wheat straw and soy hulls. *Bioresource Technology*, *99*, 1664–1671.

Atalla, R. H., & VanderHart, D. L. (1999). The role of solid state 13C NMR spectroscopy in studies of the nature of native celluloses. *Solid State Nuclear Magnetic Resonance*, *15*, 1–19.

Beatriz, A. P., Assa, M. N., & Belgacemb, E. F. (2006). Mercerized linters cellulose: Characterization and acetylation in *N*,*N*-dimethylacetamide/lithium chloride. *Carbohydrate Polymers*, *63*, 19–29.

Beg, M. D. H., & Pickering, K. L. (2004). Effect of fibre pre-treatment on the mechanical properties of wood/polypropylene composites. In *Proceedings of the 2nd International Conference on Structure, Processing and Properties of Materials* February, Dhaka, Bangladesh, (pp. 240–247).

Berlant, A., & Khalifa. (1991). Crystalline character of native and chemically treated Saudi Arabian cotton fibers. *Textile Research Journal*, *61*(10), 602–608.

Bledzki, A. K., Fink, H. P., & Specht, K. (2004). Unidirectional hemp and flax EP and PP-composites: Influence of defined fiber treatments. *Journal of Applied Polymer Science*, *93*, 2150–2156.

Buschle-Diller, G., & Zeronian, S. H. (1992). Enhancing the reactivity and strength of cotton fibers. *Journal of Applied Polymer Science*, *45*, 967–979.

Cael, J. J., Gardner, K. H., Koenig, J. L., & Blackwell, J. J. (1975). Infrared and Raman spectroscopy of carbohydrates. Normal coordinate analysis of cellulose I. *Journal of Chemical Physics*, *62*, 1145–1153.

Chen, C., Yu, J., Zhang, Z., & Lu, C. (2011). Study on structure and thermal stability properties of cellulose fibers from rice straw. *Carbohydrate Polymers*, *85*, 245–250.

Chen, Q., Nattakan, S., Ni, X., & Ton, P. (2008). The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydrate Polymers*, *71*, 458–467.

Colom, X., & Carrillo, F. (2002). Crystallinity changes in lyocell & viscose-type fibres by caustic treatment. *European Polymer Journal*, *38*, 2225–2230.

Davidson, T. C., Newman, R. H., & Ryan, M. J. (2004). Variations in the fiber repeat between samples of cellulose I from different sources. *Carbohydrate Research*, *339*, 2889–2893.

Dinand, E., Vignon, M., Chanzy, H., & Heux, L. (2002). Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II. *Cellulose*, *9*, 7–18.

Gassan, J., & Bledzki, A. K. (1999a). Alkali treatment of jute fibers: Relationship between structure and mechanical properties. *Journal of Applied Polymer Science*, *71*, 623–629.

Gassan, J., & Bledzki, A. K. (1999b). Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres. *Composites Science and Technology*, *59*(9), 1303–1309.

Gert, E. V., Socarras-Morales, A., Zubets, O. V., Shishonok, M. V., Torgashov, V. I., Matyulko, A. V., et al. (2001). New methods for the preparation of cellulose II powder forms of various morphology. *Cellulose Chemistry and Technology*, *35*, 417–427.

Goswami, P., Blackburn, R. S., El-Dessouky, H. M., Taylor, J., & White, P. (2009). Effect of sodium hydroxide pre-treatment on the optical and structural properties of lyocell. *European Polymer Journal*, *45*, 455–465.

Gumuskaya, E., Usta, M., & Kirci, H. (2003). The effects of various pulping conditions on crystalline structure of cellulose in cotton linters. *Polymer Degradation Stability*, *81*, 559–564.

Hult, E.-L., Larsson, P. T., & Iversen, T. (2000). A comparative CP/MAS ^{13}C-NMR study of cellulose structure in spruce wood and Kraft pulp. *Cellulose*, *7*, 35–55.

Jähn, A., Schroder, M. W., Futing, M., Schenzel, K., & Diepenbrock, W. (2002). Characterization of alkali treated flax fibres by means of FT Raman spectroscopy and environmental scanning electron microscopy. *Spectrochimica Acta*, *58*, 2271–2279.

Klemm, D., Heublein, B., Fink, H.-P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, *44*, 3358–3393.

Krassig, H. A. (1993). *Cellulose: Structure, accessibility and reactivity*. Gordon and Breach Science Publishers.

Mirjana, K., Biljana, P., & Petar, S. (2008). Quality of chemically modified hemp fibers. *Bioresource Technology*, *99*, 94–99.

Mwaikambo, L. Y., & Ansell, A. P. (2003). Hemp fibre reinforced cashew nut shell liquid composites. *Composite Science and Technology*, *6*, 1297–1305.

Newman, R. H., & Davidson, T. C. (2004). Molecular conformations at the cellulose–water interface. *Cellulose*, *11*, 23–32.

Nishimura, H., & Sarko, A. (1987). Mercerization of cellulose. III. Changes in crystallite sizes. *Journal of Applied Polymer Science*, *33*, 855–866.

Nishiyama, Y., Langan, P., & Chanzy, H. J. (2002). Crystal structure and hydrogen bonding system in cellulose Iβ from synchrotron X-ray and neutron fiber diffraction. *Journal of the American Chemical Society*, *124*, 9074–9082.

Nishiyama, Y., Sugiyama, J., Chanzy, H., & Langan, P. (2003). Crystal structure and hydrogen bonding system in cellulose Ia from synchrotron X-ray and neutron fiber diffraction. *Journal of the American Chemical Society*, *125*, 14300–14306.

Oh, Y. S., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y., Chung, Y. S., Park, W. H., & Youk, J. H. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research*, *340*, 2376–2391.

Ouajai, S., & Shanks, R. A. (2005). Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polymer Degradation and Stability*, 327–335.

Prasad, B. M., & Sain, M. M. (2003). Mechanical properties of thermally treated hemp fibers in inert atmosphere for potential composite reinforcement. *Material Research and Innovation*, *7*(231), 231–238.

Proniewicz, L. M., Paluszkiewicz, C., Weselucha-Birczynïska, A., Majcherczyk, H., Baraňıski, A., & Konieczna, A. (2001). FT-IR and FT-Raman study of hydrothermally degradated cellulose. *Journal of Molecular Structure*, *596*, 163–169.

Quddiani, A. El., Chaabouni, Y., Msahli, S., & Sakli, F. (2011). Crystal transition from cellulose I to cellulose II in NaOH treated Agave Americana L. fibre. *Carbohydrate Polymers*, *86*, 1221–1229.

Raymond, S., Kvick, A., & Chanzy, H. (1995). The structure of cellulose II: A revisit. *Macromolecules*, *28*, 8422–8425.

Roncero, M. B., Torres, A. L., Colom, J. F., & Vidal, T. (2005). The effect of xylanase on lignocellulosic components during the bleaching of wood pulps. *Bioresource Technology*, *96*(1), 21–30.

Ruan, D., Zhang, L., Mao, Y., Zeng, M., & Li, X. (2004). Microporous membranes prepared from cellulose in NaOH/thiourea aqueous solution. *Journal of Membrane Science*, *241*, 265–274.

Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoisser, B. (2004). Effects of short-time vibratory ball milling on the shape of FTIR spectra of wood and cellulose. *Vibrational Spectroscopy*, *36*, 23–40.

Segal, L., Creely, J. J., Martin, A. E., & Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal*, *29*, 764–786.

Sotton, M., Arniaud, A. M., & Rabourdin, C. (1978). Etude par diffractomérie des rayons X des paramètres de cristallinité et de désordre dans les fibres textiles. *Bulletin Scientifique ITF*, *7*(27), 265–290.

Sugiyama, J., Vuong, R., & Chanzy, H. (1991). Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall. *Macromolecules*, *24*, 4168–4175.

Zhou, L. M., Yeung, K. W., Yuen, C. W. M., & Zhou, X. (2004). Characterization of ramie yarn treated with sodium hydroxide and crosslinked by 1. 2,3,4-butanetetracarboxylic acid. *Journal of Applied Polymer Science*, *91*, 1857–1864.

Zugenmaier, P. (2001). Conformation and packing of various crystalline cellulose fibers. *Progress Polymer Science*, *26*, 1341–1417.