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Improving accessibility and reactivity of celluloses of annual plants for the synthesis of methylcellulose

Daiyong Ye and Xavier Farriol*
*Chemical Engineering Department, Rovira i Virgili University, 26 Avinguda dels Països Catalans, 43007 Tarragona, Spain; *Author for correspondence (e-mail: xavier.farriol@urv.net)*

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Abstract

Pretreatments (water-soaking, pre-mercerization, mercerization under a pressure of 15 bars and steam explosion) were used to improve the accessibilities and reactivities of celluloses of bleached flax, hemp, sisal, abaca and jute pulps for the synthesis of methylcellulose. Degrees of crystallinity were determined by X-ray Diffraction (XRD) spectra. The iodine adsorption accessibilities of pulps were low and accessible fractions ranged from 1.3 to 5.2%. Accessible fractions in amorphous cellulose were calculated in the 5–18% range. The accessibilities of these pulps were hemp pulp > flax pulp > sisal pulp > jute pulp > abaca pulp. Fourier Transform Infrared (FTIR) spectra showed that mean hydrogen bond strengths were weakened and relative crystallinity indexes were decreased by pretreatments. The accessibility and reactivity of the abaca pulp were improved by water soaking, mercerization under 15 bars pressure, steam explosion and preliminary mercerization, of which steam explosion and pre-mercerization were the best treatments. Species was the main factor for the accessibility and reactivity.

Introduction

Annual plants have received increasing attention in recent years because they have a high annual yield of cellulose and may be a substitution for wood as a resource for paper, paperboard and cellulose derivatives (Pierce 1991; Pande 1998). The annual plant pulp is impure cellulose and its main chemical components are cellulose, hemicellulose, trace lignin and ash. Cellulose is an unbranched bio-homopolymer consisting of b-D-glucopyranose units linked by (1 → 4) glycosidic bonds (Purves 1954). The degree of polymerization is about 10,000 glucopyranose units in wood cellulose and 15,000 in cotton cellulose (Sjoström 1981).

Cellulose structurally comprises three hierarchical levels (Krässig 1993; Osullivan 1997): (1) The molecular level of a single molecule; (2) the supermolecular level of the assembling of the molecules as crystals in elementary fibrils; and (3) the morphological level, i.e., the arrangement and aggregation of fibrils and interstitial voids in a pulp. Because of the existence of a complex structure, i.e., fibril aggregation, crystalline regions and intermolecular and intramolecular hydrogen bonds, the cellulose of dissolving pulp usually has a low accessibility and low reactivity. To synthesize methylcellulose, the cellulose needs to be activated in order to improve its accessibility and reactivity (Krässig 1993). Some physical and chemical methods have been invented to

Table 1. Properties of ECF bleached pulps.

	Flax	Hemp	Sisal	Abaca	Jute
Degree of polymerization	1165	948	998	1928	1413
Brightness (%)	83.3	85.4	89.3	88.1	73.9
Fiber length (mm)	1.8–6.2	2.1–6.3	1.8–4.5	3.3–6.8	1.5–3.7
Humidity (%)	5.32	5.53	8.53	7.04	7.72
Alpha cellulose (%)	89.77	88.59	88.77	89.43	87.52
Kappa number	0.82	0.55	1.33	0.78	1.21
Lignin (%)	0.12	0.08	0.20	0.12	0.18
Ash (%)	1.51	0.83	1.04	0.97	1.30
Pentosans (%)	5.32	5.22	17.68	11.67	12.59
Accessibility (mg I_2/mg pulp)	16.59	21.24	14.88	5.38	14.51
Degree of crystallinity (%)	75	71	75	71	70
Accessible fraction[a](%)	4.0	5.2	3.6	1.3	3.5
Amorphous fraction[b](%)	25	29	25	29	30
Ratio of accessible and amorphous fraction (%)	16	18	14	5	12

[a] Estimation by the ratio of accessibility divided by 412 (the accessibility of amorphous cellulose)

[b] The amorphous fraction was the value that 100% subtracted the degree of crystallinity.

activate cellulose (Tanichev 1972; Su et al. 1989). Conventional physical activation methods include dry or wet milling (Kelsey and Shafizadeh 1980), steam explosion (Yamashiki et al. 1990a, b, c), ammonia explosion (Jung et al. 1975; Su et al. 1998), and solvent exchange (Robertson 1964; Mantanis et al. 1995) or impregnation (with or without pressure, water soaking, in an aqueous or organic solution etc.). Conventional chemical activating methods include hydrolysis (Skachkov and Sharkov 1966), oxidation (Glegg 1951; Pekarovicova 1986), thermal activation (Lewin et al. 1981), radiation (Dilli et al. 1967), mercerization (Ant-Wuorinen et al. 1958; Warwicker et al. 1966), and regeneration (Roffael 1970).

During physical pretreatments, morphological structural changes, such as the disintegration of aggregated fibers, swelling, separation of assembled fibrils, and increase of accessible surface and voids, are most important (Krässig 1993). During chemical pretreatments, the most significant changes are decrystallinity, depolymerization, the modification of cellulose polymorph, the weakening of the hydrogen bond strength and the transformation of crystalline cellulose to amorphous cellulose (Krässig 1993).

During the pulp preparation process (i.e. pulping and bleaching), heating and drying influence the accessibility of cellulose (Ant-Wuorinen et al. 1960; Hult et al. 2003). Some pretreatments of cellulose hinder the penetration of the methylation reagent into the interior of the fiber (Tanichev 1972).

In this study, we have characterized and compared the accessibilities and reactivities of five annual plant pulps for the synthesis of methylcellulose. Pre-mercerization was used to improve the accessibilities and reactivities of five pulps. Several pretreatments (water-soaking, pre-mercerization, mercerization under a pressure of 15 bars and steam explosion) were used to improve the accessibility and reactivity of the abaca pulp, which had the lowest accessibility and reactivity of these five pulps.

Experimental

Pulps and chemical reagents

A Spanish company, Celulosa de Levante, S. A., kindly supplied bleached flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), sisal (*Agave sisalana*), abaca (*Musa textilis*) and jute (*Corchorus capsuloris*) pulps, which were produced by a soda/AQ pulping process with elemental chlorine free (ECF) bleaching. The main properties of these pulps are listed in Table 1. All chemicals were bought as reagent grade from Sigma-Aldrich Company and used without pretreatments.

Pretreatments

Water soaking

About 10 g pulp (oven dry weight) was soaked in 500 g distilled water for one hour at room temperature (about 20 °C). The pulp was collected by filtration and dried in the air.

Mercerization

About 10 g pulp (oven dry weight) was mercerized in 200 g 50% sodium hydroxide solution for 1 h at room temperature (about 20 °C) under ambient pressure. The mercerized pulp was collected by filtration and washed with distilled water until the pH value was close to 7. The mercerized pulp was dried in the air.

Preliminary mercerization

About 10 g pulp (oven dry weight) was mercerized in 200 g 15% sodium hydroxide solution for 15 min at room temperature (about 20 °C) under ambient pressure. The mercerized pulp was collected by filtration and pressed to a press weight ratio for the solution and pulp of 3. The mercerized pulp was kept in the air at room temperature for 4 h. The pulp was washed with distilled water until the pH value was close to 7. The mercerized pulp was dried in the air.

Mercerization under pressure

About 10 g pulp (oven dry weight) was mercerized in 200 g 50% sodium hydroxide solution for 1 h at room temperature (about 20 °C) under 15 bars nitrogen pressure. The mercerized pulp was collected by filtration and washed with distilled water until the pH value was close to 7. The mercerized pulp was dried in the air.

Steam explosion

The saturated steam directly heated about 10 g pulp (oven dry weight) in steam explosion equipment. The temperature was quickly raised to 140 °C and maintained at 140 °C for 4 min by adding a little steam at intervals. The pressure was suddenly decompressed. The pulp was exploded into a vessel, and then was collected by filtration and dried in the air.

Methylation of pulps

About 5 g pulp (oven dry weight) was mercerized in 50% NaOH solution of about 120 g at ambient temperature for 1 h. The mercerized pulp was filtered and pressed to a weight ratio of the NaOH solution and the pulp of 3. The mercerized pulp and isopropanol of 300 ml were added to a flask of 500 ml. The suspended solution was stirred for 1 h at room temperature (about 20 °C). The flask was installed with a condenser and placed in a water bath. Fifty-milliliter of Iodomethane was added. The suspended solution was stirred for another 1 h at room temperature (about 20 °C). The temperature of the reactants was raised to 60 °C and maintained for 22 h. After this first methylation, a second mercerization and methylation were carried out to obtain a higher degree of substitution. The synthesized methylcellulose was collected by filtration, neutralized with glacial acetic acid and washed with ethanol and acetone three times respectively. The methylcellulose was dried in an oven at 60 °C and stored in a cooler at 4 °C.

Fractionation of methylcellulose

About 1 g methylcellulose (oven dry weight) was added to 20 g distilled water in a glass sample bottle and stirred for 2 h. The bottle was placed in a cooler at 4 ° for 24 h to improve the solubility of water-soluble methylcellulose. The bottle was taken out and the suspended solution was stirred for 2 h. The bottle was placed into a centrifuge and centrifuged at 4000 rpm for 30 min. The solid was collected by filtration and washed three times with distilled water. The solution of methylcellulose and the washed solution were collected for further dialysis. The solid comprised alkali soluble methylcellulose and unreacted pulp. The aqueous solutes mainly comprised water-soluble methylcellulose and by-products. The solid was dried first in the air and then in a desiccator under vacuum. The dried solid, which did not dissolve in water, was extracted by 4% NaOH solution. The 4% NaOH solution extracted solid was neutralized with glacial acetic acid, washed with distilled water until the pH value was close to 7, and dried first in the air and then in a desiccator under vacuum. The solid, which did not dissolve in the 4% NaOH solution, was assumed to be unreacted pulp, which may comprise of methylcellulose of a very low degree of substitution.

The solution of methylcellulose and the solution washed in water were collected, mixed and placed in several dialysis membrane bags. Each dialysis bag was suspended in distilled water for 3 weeks. For dialysis purification we used the Spectrum® dialysis tubing cellulose membrane bag with an average flat width of 76 mm (3.0 in.), which was supplied by Spectrum Laboratories Inc., via the Sigma-Aldrich Company. Each dialysis tube bag was clamped with two 110 mm dialysis-tubing closures. The cellulose membrane was able to separate salts and methylcellulose with an Mw of less than 12,000. The diffusion velocity of dialysis was improved by continuous stirring of the distilled water. The dialysis methylcellulose was dried first in the air and then in a desiccator under vacuum.

Characterization

Determination of the properties of the pulps

The ash content was determined according to TAPPI T 211 om-02. The viscosity of pulp was determined according to TAPPI T 230 om-99. The intrinsic viscosity of pulp was determined according to ISO 5351/1-1981. The kappa number was determined according to TAPPI T 236 om-99. The alpha cellulose was determined according to TAPPI T 203 cm-99. The pentosan content was determined according to T 223 cm-01. The accessibility of the pulps was determined by an iodine absorption method (Hon and Yan 2000).

Determination of the degree of crystallinity

The XRD spectra of the pulps showed a very intense peak at 22.6°, which corresponded to the crystalline region (plane 002), and other intense peaks before 18.0° (Segal 1959). The XRD measurements were obtained using a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical $\theta - \theta$ goniometer) fitted with a curved praphite diffracted beam monochromator, a diffracted beam Soller slit, a 0.06° receiving slit and a scintillation counter as a detector. The angular 2θ-diffraction range was between 5 and 70°. The data were collected with an angular step of 0.05° at 3 s per step and sample rotation. $\mathrm{Cu_{ka}}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

The crystallinity index (CrI) was calculated using the intensities of diffraction of the crystalline structure (plane 002, $2\theta = 22.6°$) and of the amorphous fraction ($2\theta = 18.0°$):

$$\mathrm{CrI} = 100 \times \left(\frac{I_{002} - I_{\mathrm{amorphous}}}{I_{002}}\right)$$

FTIR spectra

FTIR spectra were obtained using a JASCO FT/IR-6300 spectrometer with attenuated total reflectance (ATR). A total of 64 scans with a resolution of 2 cm^{-1} were recorded. The wave number region ranged from 4000 to 400 cm^{-1}. Each sample was measured twice and its average value was calculated and used. The absorbance band area, which was calculated from a local baseline between adjacent peaks, were automatically calculated at the maximum absorbance found by a noise level of 0.1 using the Spectra Manager for windows 95/NT from the JASCO Corporation. The baseline was corrected automatically by the peak find tool using the Spectra Manager software.

The area ratio of band 1375 and 2900 was assigned to be the relative CrI (O'Connor et al. 1958; Nelson and O'Conner 1964; Selim et al. 1994). The area ratio of band 3300 and 2900 was assigned to be the mean hydrogen bond strength (O'Connor et al. 1958; Selim et al. 1994).

Results and discussion

Properties of celluloses of pulps

Pulps used for cellulose ethers are well bleached and have high levels of purity, low lignin contents and high *a*-cellulose contents (over 86%). The *a*-cellulose contents of the flax, hemp, sisal, abaca and jute pulps in our study were over 87% (Table 1). Their lignin contents were under 0.20% (Table 1). These ECF-bleached pulps satisfied the requirements for raw materials of methylcellulose (Brandt 1986). Flax, hemp, sisal, abaca and jute therefore have another application as raw materials of methylcellulose, thus upgrading them from low-value to high-value products.

Celluloses from non-wood plants have different chemical composition and structures (Han and Rowell 1997; Focher et al. 2001). The most different properties of celluloses from these pulps are the pentosan content and the degree of polymerization (see Table 1). The flax and hemp pulps in our study had lower pentosan contents than other pulps. The abaca pulp had the highest degree of polymerization, which indicates that the abaca pulp could be used to produce methylcellulose of higher molecular weight. The hemp, sisal and flax pulp could be used to produce methylcelluloses of lower molecular weight. The jute pulp was a better raw material for methylcellulose of intermediate molecular weight.

Accessibility

The accessibility of the cellulose pulp mainly depends on the amorphous cellulose because the inaccessible crystalline region has little influence (Timell and Purves 1951; Krässig 1993). After soda/AQ pulping, ECF bleaching and drying, pulps usually have different chemical compositions, chemical distributions of components in their pulps (Treimanis 1996) and morphological fibrous structures, such as cellulose fibril aggregation and cellulose structure (Evans et al. 1995; Hult et al. 2003) which strongly influence their accessibilities and reactivities (Krässig 1993). During the pulping and bleaching of annual plants, pores (capillaries) increase due to the dissolution of solid and to swelling (Sjoström 1981; Treimanis 1996). The chemical reagents are known to diffuse more easily along the fibrils and reach the surface of cellulose crystals in more fibrous pulps with more porous voids. More fibrous pulps therefore have higher accessibilities and reactivities.

The accessibilities of these pulps were hemp pulp > flax pulp > sisal pulp > jute pulp > abaca pulp (Table 1). All these five pulps need to improve their accessibilities in order to increase their reactivities.

The sequence of the degree of crystallinity of these pulps, from high to low, was flax pulp = sisal pulp > hemp pulp = abaca pulp > jute pulp (see Table 1). A lower degree of crystallinity did not mean higher accessibility. For example, the abaca pulp had the lowest accessibility and a low degree of crystallinity (Table 1), which indicated that other factors as well as cellulose crystals, such as fibril aggregation (Hult et al. 2003), pores (Treimanis 1996) and other morphological cellulose structures (Krässig 1993), were also important.

The sisal pulp had a higher degree of crystallinity than the abaca pulp but also higher accessibility (Table 1). The hemp pulp had a low degree of crystallinity but the highest accessibility (Table 1). This indicates that the species is a major factor for accessibility and reactivity.

Accessible fraction in the amorphous cellulose

The amorphous cellulose of dried pulps is not completely accessible (Timell and Purves 1951). Drying or irreversible hornification causes the fibrous amorphous cellulose to be partially inaccessible because some of the swollen cellulose aggregates into amorphous fibrils of a higher density, which are kept together by strong hydrogen bonds and weak van de Waals forces (Timell and Purves 1951). These aggregated celluloses are therefore inaccessible to iodine during the determination of the accessibility of cellulose. The morphology of the amorphous cellulose is one of the main factors influencing the accessibility. Disintegration, increasing the voids and accessible surfaces of pulps, weakening the hydrogen bond strength, depolymerization and decrystallinity are therefore essential to improving accessibility and reactivity (Krässig 1993). The species, however, is the deciding factor.

The sequence of the accessible fraction in the amorphous cellulose was hemp pulp > flax pulp > sisal pulp > jute pulp > abaca pulp (Table 1). The accessible fraction of the abaca pulp in the amorphous cellulose was 5% (Table 1), which indicates that about 95% of the amorphous cellulose was inaccessible. The low accessibility in amorphous cellulose is reasonable because dipole and van de Waals interactions, and intermolecular and intramolecular hydrogen bonds bind the cellulose molecules into inaccessible regions, in which hydrophobic and hydrophilic reagents cannot penetrate such well-ordered areas (Krässig 1993). This small accessible fraction shows that most microfibrils were aggregated and few voids were available in the abaca pulp. Most of the amorphous cellulose of the other four pulps was also inaccessible. The hemp pulp had a little more accessible amorphous cellulose than the other four pulps. This hemp pulp therefore had the highest reactivity and the greatest accessibility of the five pulps.

It is essential to activate these pulps in order to improve their reactivities and accessibilities before subsequent methylations. Otherwise, synthesized methylcelluloses will have partially unreacted celluloses and lower properties, such as a lower degree of substitution and a lower molecular weight of water-soluble methylcellulose (Krässig 1993).

Effect of pretreatments

The relative CrI of each pulp was significantly decreased by mercerization and preliminary mercerization (Table 2). The mean hydrogen bond strength of each pulp (Table 2), which relates to assemblies of cellulose and elementary fibrils together (Krässig 1993), is weakened also by pretreatments (Krässig 1993). During the mercerization and preliminary mercerization, strong swelling action and forces rupture inter-fibrils, thus increasing the accessible internal surface (Krässig 1993). The strong swelling action and forces open intra- and inter-hydrogen bonds, thus causing the lattice transformation and the penetration of sodium hydrate ions into the widened space between the 101 lattice sheets (Krässig 1993).

After mercerization and preliminary mercerization, the sisal and abaca pulps had a higher CrI than the others (Table 2), which indicates that they were more difficult to mercerize.

Flax had the highest initial CrI but, after mercerization, it was among the lowest of the five pulps (Table 2). Thus, flax was easily treated to improve its accessibility and reactivity by mercerization.

The abaca pulp was the most difficult to be activated in order to improve accessibility and reactivity (Table 2). All pretreatments of the abaca pulp had a positive influence on its properties. Water soaking did not change crystallinity very much but it greatly decreased the mean hydrogen bond strength (Table 2) by swelling and solvent penetration (Krässig 1993). Mercerization under 15 bars decreased the relative CrI (Table 2) and the degree of polymerization (Table 4). Steam explosion did not change the CrI much either. However, it did decrease the mean hydrogen bond strength (Table 2) and the degree of polymerization (Table 4). When both the CrI and the mean hydrogen bond strength decreased, the accessibility of reactivity of the treated abaca pulps increased (Table 7).

The intrinsic viscosities of the treated pulps decreased after mercerization and after preliminary mercerization (Tables 3, 4). Mercerization reduced the degree of polymerization and increased the accessibility and reactivity of the pulps (Table 6). Water soaking did not change the intrinsic viscosity or degree of polymerization (Table 4). Mercerization and mercerization under 15 bars pressure seemed to have a similar effect on the intrinsic viscosities (Table 4). Neutral steam

Table 2. Properties measured by FTIR.

Pulp	Treatment	Relative crystallinity index[a]	Mean hydrogen bond strength[b]
Flax	Original	5.2	11.4
Flax	Mercerization	0.3	9.3
Flax	Preliminary mercerization	0.3	10.8
Hemp	Original	5.0	10.4
Hemp	Mercerization	0.3	10.3
Hemp	Preliminary mercerization	0.2	10.0
Sisal	Original	2.6	11.4
Sisal	Mercerization	0.6	10.9
Sisal	Preliminary mercerization	0.5	10.8
Abaca	Original	2.3	11.2
Abaca	Mercerization	0.5	9.3
Abaca	Preliminary mercerization	0.5	9.4
Abaca	Water, 1 h	2.2	7.3
Abaca	Pressure mercerization	0.6	9.9
Abaca	Steam explosion	1.8	9.2
Jute	Original	2.6	10.6
Jute	Mercerization	0.3	9.6
Jute	Preliminary mercerization	0.3	10.2

[a] Calculated by A_{1375}/A_{2900}.

[b] Calculated by A_{3300}/A_{2900}.

Table 3. Intrinsic viscosities of pretreated pulps.

Pulp	Flax	Hemp	Sisal	Abaca	Jute
Original intrinsic viscosity (ml/g)	747	659	640	1253	946
Mercerized intrinsic viscosity (ml/g)	707	589	626	1032	564
Preliminarily mercerized intrinsic viscosity (ml/g)	547	588	614	917	540

Table 4. Intrinsic viscosities of pretreated abaca pulps.

Pretreatment	Intrinsic viscosity (ml/g)
Original abaca pulp	1253
Water soaking	1199
Mercerization	1032
Mercerization under pressure	1004
Steam explosion	995
Preliminary mercerization	917

explosion decreased the intrinsic viscosity of the abaca pulp (Table 4). Preliminary mercerization decreased the intrinsic viscosity considerably because the pulps were kept in an alkaline environment for a long time (Table 4).

Reactivity of pulps

The unreacted pulp content was related to the accessibility and reactivity of the pulp (Tables 1, 5). The abaca pulp had the lowest accessibility (Table 1), so it had the highest unreacted pulp content (Table 5). The hemp pulp had the highest accessibility (Table 1), so it had the lowest unreacted pulp content (Table 5). For the methylation of pulps without pretreatments, the unreacted pulp content was related to the inaccessibility of the pulps. In other words, the methylcellulose content was proportional to the accessibility. When pulps were not pretreated, the main component of methylcellulose was alkali-soluble methylcellulose.

After preliminary mercerization, the unreacted pulp content decreased considerably (Table 6). The flax and abaca methylcellulose had no unreacted pulp (Table 6). The hemp, sisal and jute methylcellulose had little unreacted pulp (Table 6). The water-soluble methylcellulose content increased after preliminary mercerization, while the alkali soluble methylcellulose content decreased. These data indicate that preliminary mercerization increased the reactivity of the pulps. The final effect of preliminary pretreatment depended on the characteristics of the pulps: pore content and distribution, content and distribution of lignin and hemicellulose, and fibril aggregations (Krässig 1993). Pulps of low accessibility and low degrees of crystallinity, such as the abaca pulp, could use preliminary mercerization to improve accessibility and reactivity. However, pulps of high accessibility and high degrees of crystallinity, such as the hemp pulp, had less effect.

Several pretreatments were carried out with the abaca pulp (Table 4). Water soaking reduced the unreacted pulp content considerably (Table 7). During the one-hour of water soaking, water diffused and penetrated the capillary and voids, and the pulp swelled. Water weakened the hydrogen bond strength (Table 2) and separated the aggregate fibrils (Krässig 1993), which was confirmed by the FTIR spectrum. Mercerization under 15 bars of pressure reduced the unreacted abaca pulp content to 0% (Table 7). The pressure of 15 bars helped the alkaline solution to penetrate the capillaries, increased the velocity of penetration and therefore improved the swelling effect. The distribution of the alkali solution in the pulp was therefore more uniform, which helped the iodom-

Table 5. Fractionation of methylcellulose of conventionally mercerized pulps.

Sample	MD45	MD41	MD44	MD55	MD42
Pulp	Flax	Hemp	Sisal	Abaca	Jute
Water-soluble methylcellulose (%)	11.03	16.67	18.82	12.50	18.48
Alkali-soluble methylcellulose (%)	72.47	68.41	43.53	48.56	62.46
Unreacted pulp (%)	16.51	14.93	37.66	38.94	19.06

Table 6. Fractionation of methylcellulose of preliminarily mercerized pulps.

Sample	MD52	MD59	MD46	MD47	MD57
Pulp	Flax	Hemp	Sisal	Abaca	Jute
Water-soluble methylcellulose (%)	56.52	33.73	27.41	51.72	30.64
Alkali-soluble methylcellulose (%)	43.48	62.23	64.45	48.28	66.74
Unreacted pulp (%)	0.00	4.04	8.14	0.00	2.62

Table 7. Fractionation of methylcellulose of preliminarily treated abaca pulp.

Sample	MD55	MD48	MD54	MD53	MD47
Pretreatment	Non	Water soaking	Mercerization with pressure	Steam explosion	Preliminary mercerization
Water-soluble methylcellulose (%)	12.50	18.75	14.63	49.23	51.72
Alkali-soluble methylcellulose (%)	48.56	77.27	85.37	50.77	48.28
Unreacted pulp (%)	38.94	3.98	0.00	0.00	0.00

ethane to diffuse and react with alkali cellulose. Steam explosion and preliminary mercerization significantly improved the water-soluble methylcellulose content (Table 7). The methylcellulose samples of the abaca pulp had a water-soluble methylcellulose content of almost 50% (MD53 and MD47, Table 7). Steam explosion could reduce the degree of polymerization by oxidation at high temperature and disintegrate the aggregated fibrils by a sudden evaporation of the liquid in the voids when the pressure is suddenly decompressed (Yamashiki et al. 1990a, b, c). The abaca pulp treated by steam explosion therefore had considerable accessibility.

Conclusions

Flax, hemp, abaca, jute and sisal pulps had low accessibilities. Most of the amorphous celluloses in the pulps were inaccessible before pretreatment. After preliminary mercerization, the intrinsic viscosity, mean hydrogen strength and relative CrI of the pulps decreased, which improved their accessibilities and reactivities. Water soaking, pre-mercerization, mercerization under 15 bars of pressure, and steam explosion increased the accessibility and reactivity of the abaca pulp. These pretreatments have different effects on different celluloses of annual plants, which indicates that species is the main influencing factor.

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References

Ant-Wuorinen O. and Visapaa A. 1958. Studies on the accessibility of cellulose. III. The effect of alkaline treatment on cellulose. Paperi ja Puu 40: 313–321.

Ant-Wuorinen O. and Visapaa A. 1960. The accessibility of cellulose. V. The effect of heating and drying on cellulose. Paperi ja Puu 42: 317–326.

Dilli S., Ernst I.T. and Garnett J.L. 1967. Radiation-induced reactions with cellulose. IV. Electron paramagnetic resonance studies of radical formation. Aust. J. Chem. 20: 911–27.

Evans R., Newman R.H., Roick U.C., Suckling I.D. and Wallis A.F.A. 1995. Changes in cellulose crystallinity during kraft pulping. Comparison of infrared, x-ray diffraction and solid state NMR results. Holzforschung 49: 498–504.

Focher B., Palma M.T., Ganetti M., Torri G., Osentino C. and Gastadi G. 2001. Structural differences between non-wood plant celluloses: evidence from solid state NMR, vibrational spectroscopy and X-ray diffractometry. Ind. crop. prod. 13: 193–208.

Glegg R.E. 1951. The oxidation of cellulose by chromium trioxide – a new method for determining accessibility. Text. Res. J. 21: 143–8.

Han J.S. and Rowell J.S. 1997. Chemical composition of fibers. In: Rowell R.M., Young R.A. and Rowell J.K. (comp., eds), Paper and Composites from Agro-Based Resources. Boca Raton, FL, CRC Lewis Publishers, pp. 83–134.

Hon D.N.S. and Yan H. 2000. Cellulose furoate. I. Synthesis in homogeneous and heterogeneous systems. J. App. Polym. Sci. 81: 2649–2655.

Jung H.Z., Berni R.J., Benerito R.R. and Carra J.H. 1975. Liquid ammonia versus sodium hydroxide mercerization as pretreatment for the cotton-butadienediepoxide reactions. Spectral and microscopical studies. Text. Res. J. 45: 681–691.

Kelsey R.G. and Shafizadeh F. 1980. Enhancement of cellulose accessibility and enzymic hydrolysis by simultaneous wet milling. Biotechnol. Bioeng. 22: 1025–1026.

Krässig H.A. 1993. Cellulose: Structure, Accessibility and Reactivity. Gordon and Breach Science Publishers,Polymer Monographs, Vol. 11 pp. 167–323

Lewin M., Guttmann H. and Derfler D. 1981. Modification of the fine structure of cellulose by halogen and by heat treatments. Ekman-Days 1981, Int. Symp. Wood Pulp. Chem. 4: 84–90.

Mantanis G.I., Young R.A. and Rowell R.M. 1995. Swelling of compressed cellulose fiber webs in organic liquids. Cellulose 2: 1–22.

O'Connor R.T., DuPre E.F. and Mitcham D. 1958. Application of infrared absorption spectroscopy to investigations of cotton and modified cottons. I. Physical and crystalline modifications and oxidation. Text. Res. J. 28: 382–392.

Osullivan A.C. 1997. Cellulose: the structure slowly unravels. Cellulose 4: 173–207.

Pande H. 1998. Non-wood fibre and global fibre supply. Unasylva 193: 44–50.

Pekarovicova A., Zemanovic J., Luzakova V. and Kosik M. 1986. Enhancement of accessibility of wood polysaccharides for hydrolytic processes. 4. Effect of oxidative changes of cellulose on its enzymic hydrolyzability. Drevarsky Vyskum 108: 51–56.

Pierce B. 1991. Recycled how many times? Timber Prod., (April): 18–21.

Purves C.B. 1954. Chemical nature of cellulose and its derivatives. In: Spurlin H.M. and Grafflin M.W. (eds), Cellulose and Cellulose Derivatives, Part 1. Interscience, New York, pp. 29–98.

Robertson A.A. 1964. Cellulose-liquid interactions. Pulp and Paper Magazine of Canada 65: 171–177.

Roffael E. 1970. Chemical reactivity of viscose pulps. Holzforschung 24: 128–132.

Segal L., Creely J.J., Martín A.E. and Conrad C.M. 1959. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Text. Head. J. 29: 786–794.

Selim I.Z., Basta A.H., Mansour O.Y. and Atwa A.I. 1994. Hydroxyethyl cellulose. 2. IR spectra and their relation with the dielectric properties of hydroxyethyl celluloses. Polymer-Plastics Technology and Engineering 33: 161–74.

Sjoström E. 1981. Wood Chemistry Fundamentals and Applications. Academic Press, New York, p. 49

Skachkov V.M. and Sharkov V.I. 1966. Study of changes in accessibility of cotton cellulose during hydrolysis by the method of deuterium exchange. Mater. Nauch.-Tekh. Konf. Leningr. Lesotekh. Akad. 7: 197–201.

Su M.Y., Gao G. and Lin S. 1989. Study on the effects of pretreatment by chemical activation on the fine structure and reactivity of cellulose fiber. Huanan Ligong Daxue Xuebao, Ziran Kexueban 17: 94–102.

Su M.Y., You L.L., Gao G. and Yang S. 1998. Effect of liquid ammonia pretreatment on the accessibility and carboxymethylation reactivity of cotton linter cellulose. Xianweisu Kexue Yu Jishu 6: 44–51.

Tanichev V.A. 1972. Effect of the origin and pretreatment of cellulose on its reactivity in methylation with dimethyl sulfate. Nauch. Tr., Leningrad. Lesotekh. Akad. 152: 81–86.

Timell T.E. and Purves C.B. 1951. A study of the initial stages of the methylation of cellulose. Svensk Papperstidning, arg 54: 303–332.

Treimanis A. 1996. Wood pulp fiber structure and chemical composition, their influence on technological processes. Nordic Pulp. Paper Res. j. 3: 146–151.

Warwicker R.L., Jeffries R.L. and Colbran P.N.R. 1966. A Review of the Literature on the Effect of Caustic Soda and Other Swelling Agents on the Fine Structure of Cotton. St. Ann's Press, Altrincham.

Yamashiki T., Matsui T., Saitoh M., Matsuda Y., Okajima K., Kamide K. and Sawada T. 1990c. Characterization of cellulose treated by the steam explosion method. Part 3: Effect of crystal forms (cellulose I, II and III) of original cellulose on changes in morphology, degree of polymerization, solubility and supermolecular structure by steam explosion. Brit. Polym. J 22: 201–212.

Yamashiki T., Matsui T., Saitoh M., Okajima K., Kamide K. and Sawada T. 1990a. Characterization of cellulose treated by the steam explosion method. Part 1. Influence of cellulose resources on changes in morphology, degree of polymerization, solubility and solid structure. Brit. Polym. J 22: 73–83.

Yamashiki T., Matsui T., Saitoh M., Okajima K., Kamide K. and Sawada T. 1990b. Characterization of cellulose treated by the steam explosion method. Part 2: Effect of treatment conditions on changes in morphology, degree of polymerization, solubility in aqueous sodium hydroxide, and supermolecular structure of soft wood pulp during steam explosion. Brit. Polym. J. 22: 121–128.