Carbohydrate Polymers 96 (2013) 549–559

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Chemical modification of cellulosic fibers for better convertibility in packaging applications

Sauli Vuoti[a,*], Elina Laatikainen[b], Harri Heikkinen[c], Leena-Sisko Johansson[d], Erkki Saharinen[c], Elias Retulainen[b]

[a] VTT, Valta-akseli PL 21, 05201 Rajamäki, Finland
[b] VTT Technical Research Centre of Finland, Koivurannantie 1, FI-40101 Jyväskylä, Finland
[c] VTT, Biologinkuja 7, FI-02044 VTT, Finland
[d] Aalto University, School of Chemical Technology, Department of Forest Products Technology, P.O. Box 16100, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 26 April 2012
Received in revised form 27 June 2012
Accepted 1 July 2012
Available online 27 July 2012

Keywords:
Cellulose modification
Transparent paper
Cellulose esterification
Paper elongation
Hydrophobicity

ABSTRACT

Cellulose fiber has been modified by mechanical and chemical means in order to improve paper properties, which respond to moisture and temperature. When the cellulose is first refined and then etherified using hydroxypropylation under dry conditions, the paper sheets prepared from the hydroxypropylated cellulose show improved elongation. When the level of hydroxypropylation is high enough, the paper sheets also become transparent. Additionally, the effect of cellulose activation using different mechanical methods has been compared by esterification reactions. It is shown that removal of water is the most crucial step for the esterification reactions while other methods have a lesser impact. The paper sheets prepared from the esterified cellulose fibers show an increase in contact angles and high hydrophobicity.

1. Introduction

Cellulose fibers offer a large renewable raw material base for several kinds of products, from paper and board to various composite materials ranging from packaging applications to building materials. In addition to paper applications, cellulose fibers are a potential alternative in various multi-component polymer systems: their low cost and density, high stiffness, and biodegradability are characteristics that would establish their sustainable use in various materials. Cellulose fibers are composed of an assembly of microfibrils, which consist of several cellulose molecules. The modification of the surface of the cellulose microfibrils to make them more compatible with non-polar polymers has been established, for example, by introducing hydrophobicity into the structure. The most common way to do this has been to create hydrophobic ester or ether derivatives of cellulose (Bledzki & Gassan, 1999; Boldizar, Klason, Kubat, Näslund, & Saha, 1987; Mark, 1980; Pasquini, Teixeira, Da Silva Curvelo, Belgacem, & Dufresne, 2008; Thielemans, Dufresne, Chaussy, & Belgacem, 2008; Woodhams, Thomas, & Rodgers, 1984; Zadorecki & Michell, 1989). Chemical modification of cellulose fibers has gained attention in the case of composite applications, but very little with paper applications.

Preparation of cellulose esters and ethers has created material with extensive processing qualities: three-dimensional structures and various new types of fibers have been used to prepare composites, films and membranes. Physical properties such as viscosity, charge and solubility can also be altered using chemical modification. It is important to understand the new properties and the reasons causing them in order to completely unveil the potential use of derivatized cellulose fibers in various applications. The ultimate goal would be an understanding of the property changes and the means to fulfill application requirements (Bledzki & Gassan, 1999; Dalvåg, Klason, & Strömvall, 1985; Edgar et al., 2001; Felix & Gatenholm, 1991; Heinze & Liebert, 2001; Raj, Kokta, Maldas, & Daneault, 1989).

The modified properties of these cellulose derivatives give entry into a range of applications greatly expanded from those available to the parent polysaccharide. It is important to gain a fundamental understanding of how structural changes are effected by cellulose modification, the ability to predict how those changes will impact properties, and an understanding of how those property changes translate into performance versus application requirements, in some case in cooperation with other materials or ingredients (Edgar et al., 2001; Heinze & Liebert, 2001).

---

* Corresponding author. Tel.: +358 404820303.
E-mail address: sauli.vuoti@vtt.fi (S. Vuoti).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.07.053

Paperboard materials have a few weaknesses when compared with plastic materials, when aiming at packaging applications. Their deformability and mouldability are low and thus deep-drawing is not a suitable conversion method. The materials are not transparent or heat-sealable. The use of renewable fiber raw materials in packaging applications could be essentially improved if one or several of these weaknesses could be overcome. Chemical modification of cellulose as a means to improve strength-related properties in paper applications was started decades ago. Studies were published already during the 1960s, for example Didwania (1968), Ward (1960), and Ward, Morak, Murray, and Thomas (1965). Some more recent studies include fiber modification by grafting (Rezai & Warner, 1997), carboxymethylation (Alince, 1976; Laine, Lindstrom, Bremberg, & Glad-Nordmark, 2003) or by introduction of functional groups by irreversible polymer absorption (Mitikka-Eklund, Halttunen, Melander, Ruuttunen, & Vuorinen, 1999). The main approach in improving paper strength has been the use of polymeric additives (Lindstrom, Wågberg, & Larsson, 2005). There are also several studies and reviews concerning the strength of cellulosic fibers from the point of view of composite applications (de Menezes, Pasquini, Curvelo, & Gandini, 2009; Pasquini et al., 2008; Thielemans et al., 2008 and the reviews of Bledzki & Gassan, 1999; Edgar et al., 2001). Much less attention has been directed toward the possibility of improving other properties of paper, such as extensibility and rupture elongation, which can be considered one of main requisites for better formability and mouldability of paper and paperboard.

The objective of this research was to modify cellulose fibers with mechanical pre-treatments and chemical modifications to study the potential of the modified fibers in paper and packaging applications. The target of mechanical pre-treatments and drying procedures was to control the openness and porosity of the fiber cell wall. This target is important, because anhydrous conditions are often a prerequisite for high reaction yields. On the other hand, rough water removal results in the closure of fiber cell walls and even the collapse of the fiber structure. This could prevent the accessibility of hydroxyl groups and affect the physical properties of the end products. The role of the external and internal surface area of fibers, as well as the way in which water removal has taken place, can therefore have a notable impact on the results. When hydrophobicity is introduced to the structure, the water sensitivity of the fibers is reduced, but the interfiber bonding and the strength of the fiber network are also somewhat decreased. Good convertibility and formability of the materials therefore require suitable properties that improve their use under elevated temperatures and high moisture content, but do not weaken the fiber strength notably.

In this work, we have prepared hydroxypropyl cellulose ethers and cellulose hexanoate esters and evaluated their properties as potential new paper application materials. The chemical modifications were conducted heterogeneously in order to preserve the fibrillar structure of cellulose (Belgacem & Gandini, 2008, chap. 8).

2. Materials and methods

2.1. Materials

All commercial reagents (hexanoyl chloride, pyridine, ethylene oxide) were purchased from Sigma–Aldrich and were used as received. Other reagents were of analytical grade. The cellulose material in this study was dried commercial ECF-bleached sulfate pulp from first thinning pine (*Pinus sylvestris*) produced at the UPM Kymmene Pietarsaari mill. Never-dried pine kraft was also used in some of the experiments.

2.2. Methods

2.2.1. Refining and pre-treatment of cellulose

Never-dried kraft pulp was used for the preparation of hexanoyl esters of cellulose. Samples of different porosity were produced using mechanical treatments and drying. In some cases the drying was done only after solvent exchange. The pre-treatment procedures have been presented in detail in Table 1. The pulp was refined with a PFI-refiner using 0–10,000 revolutions. Fines were removed through a 200 mesh wire. Water was solvent exchanged to acetone (continuous extraction) and then further to toluene. The fibers were dried in an oven after the solvent exchange. The fiber treatments in each experiment are listed in Table 1. All the remainder of the previous solvent was removed by filtration before proceeding to the next step. The temperature of the toluene was elevated to 110 °C to remove all residual acetone and water.

The results of the mechanical treatments and drying after solvent exchange were evaluated by measuring a BET-specific surface (TriStar 3000) of samples, using Simons' stain (Yu, Minor, & Atalla, 1995) and with microscopy. Even small amounts of moisture can disturb the BET-measurements. Moisture adsorption from air could occur during storage of the samples and when transferring the samples into the measuring device. Therefore the samples were kept at 90 °C overnight in a helium flow to ensure complete dryness of the samples before each BET-measurement.

The pine pulp used in the hydroxypropylation was dried commercial pulp beaten using a Valley laboratory beater (SCAN C25-76 standard) to SR 70. The fines fraction of the beaten pulp was removed using a modified large-size DDJ type of device and a 200 mesh screen.

2.2.2. Preparation of hydroxypropyl cellulose

Hydroxypropyl cellulose (HPC1) was prepared according to a modified procedure published by de Menezes, Pasquini, et al. (2009). The cellulose is first filtered over fritted glass and then rinsed with ethanol. The cellulose is then stirred twice in 500 mL of ethanol and filtered each time. The cellulose is finally mixed with ethanol to form a 10% suspension and then activated with 1 mol equivalent of KOH/Cell OH overnight. The ethanol is then removed

Table 1
Pre-treatment of individual samples in processing order from left to right.

Exp. point	Removal of fines	Oven drying 105 °C	Dispersed into water again	PFI refining revolutions if any	Removal of fines	Solvent exchange to acetone (continuous extraction)	Fibers mixing in toluene	Drying-temperature (°C)
1	X	X						
2		X	X	1500	X			105
3	X					X		60
4				1500	X	X		60
5				10,000	X	X		60
6	X					X	X	115
7				10,000	X	X	X	115

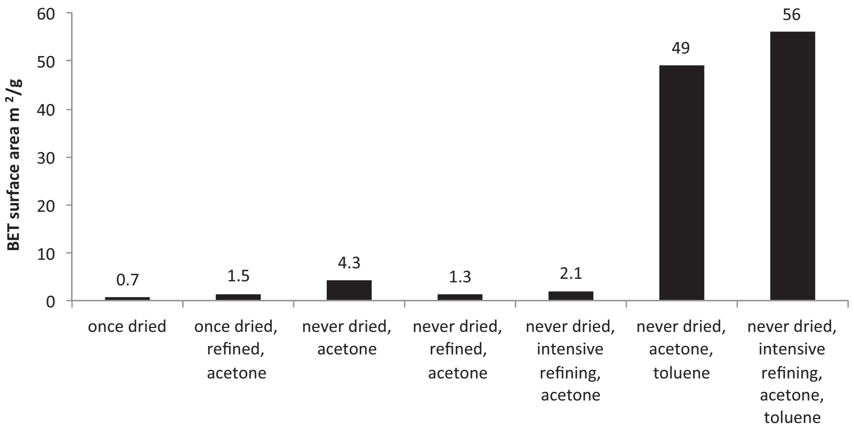


Fig. 1. The effects of different treatments on specific surfaces of fibers.

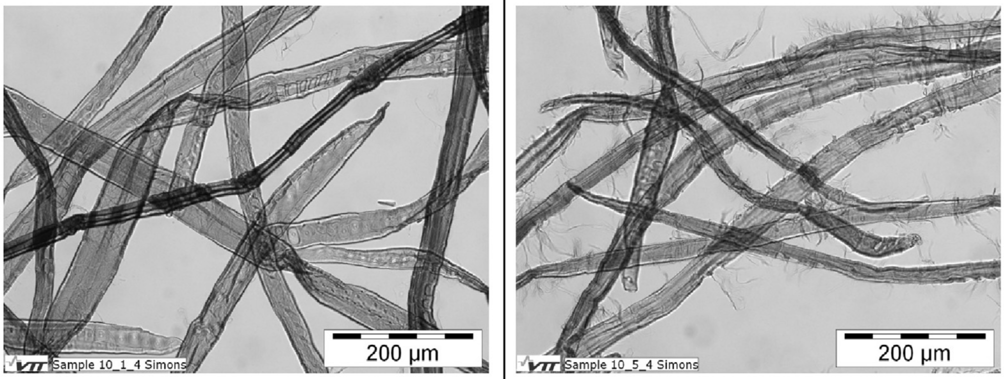
in a vacuum, and a 10 mol equivalent of propylene oxide/Cell OH is pressed into a reactor, and the mixture warmed to 130 °C. After the system returns to atmospheric pressure, the cellulose is then washed thoroughly with acetone, ethanol and water. The same reaction was repeated (HPC2) using only a 3 mol equivalent of propylene oxide. A sample was dried in a vacuum overnight for NMR/XPS analysis.

2.2.3. Preparation of cellulose hexanoates

Cellulose hexanoates were prepared according to a modified procedure published by Matsumura, Sugiyama, and Glasser (2000). Cellulose and 2.0 mol of hexanoyl chloride equivalent to Cell OH are mixed thoroughly in 8.0 mol of pyridine equivalent to Cell OH, and the mixture is then warmed to 70 °C. The mixing is continued for 16 h at a constant temperature. The product is then filtered and

Low BET-specific surface (0.67 m²/g), no fibrillation

Low BET-specific surface (2.1 m²/g), fibrillation



High BET-specific surface (49 m²/g), no fibrillation

High BET-specific surface (56 m²/g), fibrillation

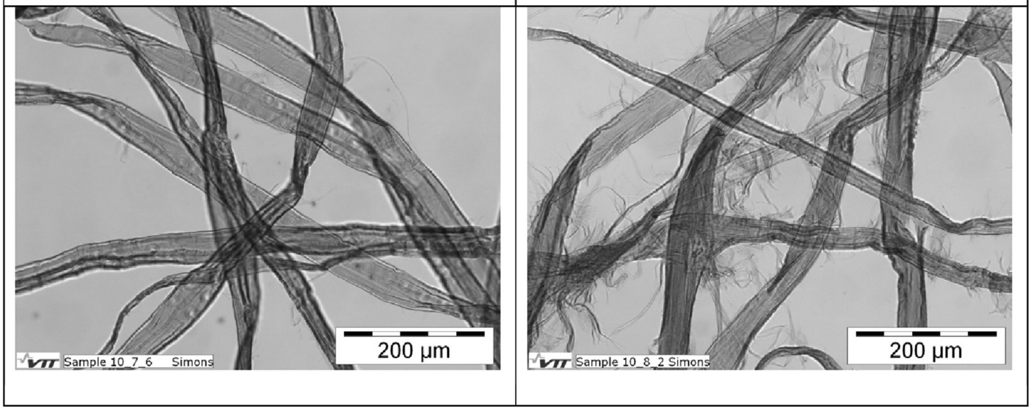


Fig. 2. Microscopy images of the fibers with different specific surface area and external fibrillation combinations.

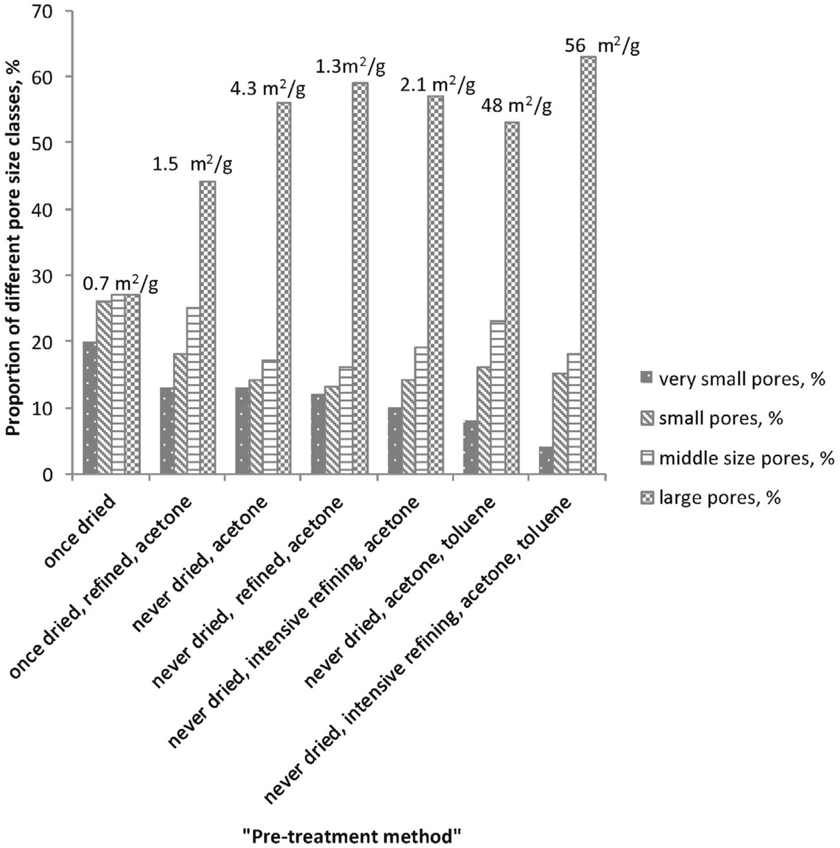


Fig. 3. Simons' staining deviations for different samples. BET-specific surface values are marked above the bars.

thoroughly washed with acetone and then finally with water. A sample is dried in a vacuum overnight for NMR/XPS analysis.

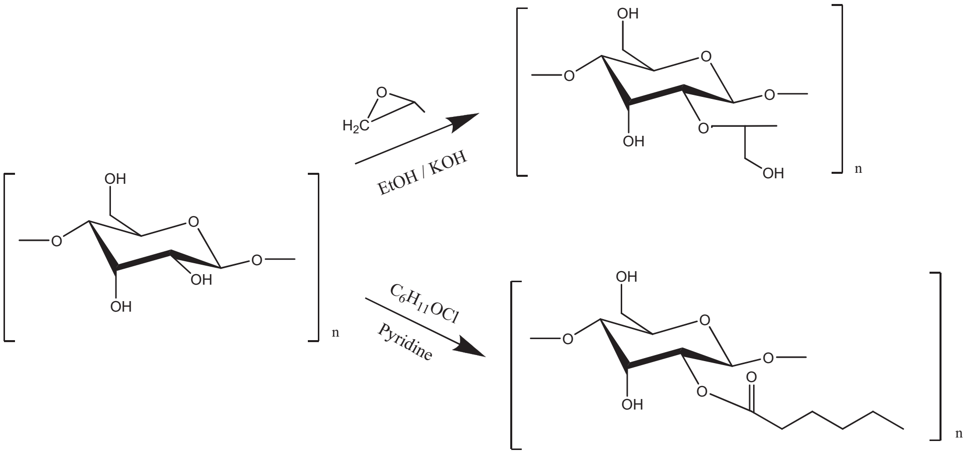
2.3. Measurements and characterization

2.3.1. ^{13}C CP/MAS NMR analysis

The prepared cellulose esters were characterized using ^{13}C NMR. The ^{13}C CP/MAS NMR measurements were performed with a Chemagnetics CMX 270 MHz Infinity NMR spectrometer, using a 6.0 mm double-resonance MAS NMR probe operating at 68.01 MHz. For all the samples, 20,000 transients were accumulated using a 3 ms contact time, a 3 s recycle time, and a spinning speed of 5 kHz. The chemical shifts were referenced to hexamethylbenzene (HMB) using the methyl signal (+17.35 ppm) as an external reference. For comparison, a solution state ^{13}C NMR experiment was carried out for the free hexanoyl acid chloride in $CDCl_3$ with a Bruker 500 MHz Avance III NMR spectrometer, using a 5.0 mm BBO probe operating at 125.8 MHz.

2.3.2. X-ray photoelectron spectroscopy

The surface compositions of samples were investigated with X-ray photoelectron spectroscopy (XPS). The monochromatic XPS measurements were performed using a Kratos Analytical AXIS 165 electron spectrometer and A1 Kα X-ray irradiation at 100 W. Prior



Scheme 1. Chemical modification of cellulose fiber.

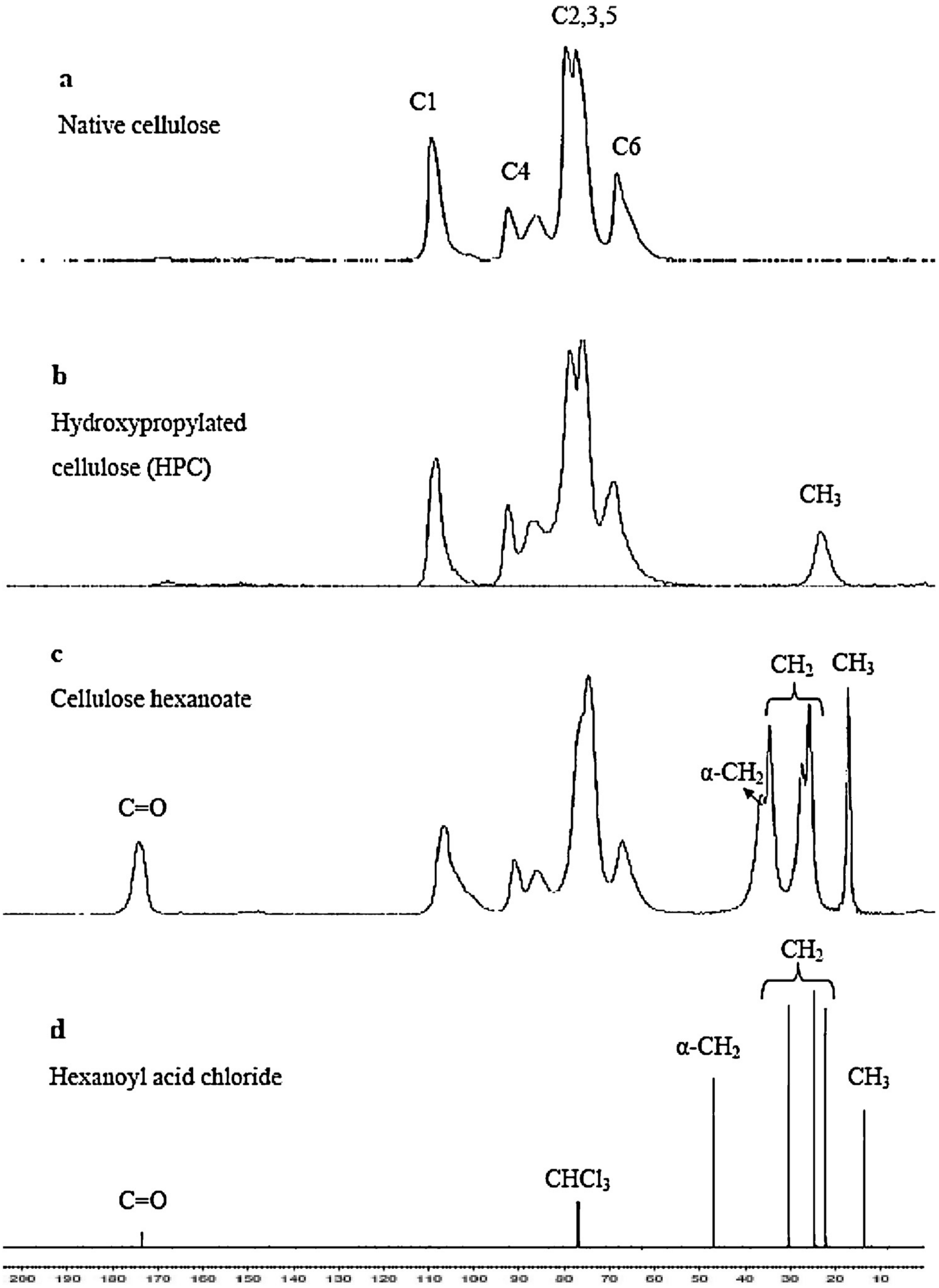


Fig. 4. ^{13}C NMR spectra with signal assignment of (a) native cellulose, (b) hydroxypropylated cellulose (HPC1), (c) cellulose hexanoate and (d) hexanoyl acid chloride.

to the experiments, the samples were attached to the sample holder with UHV-compatible carbon tape and evacuated in the prechamber overnight, in order to stabilize the vacuum conditions. All spectra were collected at an electron take-off angle of 90°, from sample areas of less than 1 mm in diameter. Both low resolution survey data from 0 to 1100 eV and sets of high resolution spectra of carbon (C 1s) and oxygen (O 1s) regions were collected. Spectra from all samples were recorded at three different locations. As a standard procedure of the lab, an in situ reference sample of 100% cellulose filter paper was measured with each sample batch, in order to confirm satisfactory vacuum conditions during the analysis (Johansson, Campbell, Koljonen, & Stenius, 1999). No sample degradation (due to an ultra-high vacuum or X rays) was observed during the measurements.

In the data analysis, elemental surface compositions and atomic O/C ratios were determined from the survey spectra while the degree of substitution was evaluated using the high resolution carbon C 1s signal fitted into four Gaussian components (Johansson & Campbell, 2004). The four components refer to carbon atoms with 0, 1, 2 or 3 bonds to neighboring oxygen and are named as CC, C—O, O—C—O and O—C=O.

2.4. Forming and testing of handsheets

Laboratory handsheets of 60 g/m^2 were formed from the treated fibers according to the SCAN CM 26:99 standard. In the case of hydroxypropylated fibers, the handsheets were dried against a drying plate (using a standard method SCAN CM 26:99 that prevented

Table 2
The degrees of substitution acquired using NMR and XPS analysis for the prepared cellulose derivatives.

Sample number	Degree of substitution (NMR)	Degree of substitution (XPS)	Pre-treatment method
1	0.60	1.4	Removal of fines and oven drying
2	0.61	1.3	Drying, re-dispergation to water and then refining (PFI 1500 rounds), removal of fines, solvent exchange to acetone and oven drying
3	0.61	1.3	Removal of fines, solvent exchange to acetone and oven drying
4	0.70	1.8	Refining (PFI 1500 rounds), removal of fines, solvent exchange to acetone and oven drying
5	0.65	1.5	Refining (PFI 10,000 rounds), removal of fines, solvent exchange to acetone and oven drying
6	0.71	1.9	Removal of fines, solvent exchange to acetone and then to toluene, followed by oven drying
7	0.67	1.6	Refining (PFI 10,000 rounds), removal of fines, solvent exchange to acetone and then to toluene, followed by oven drying
HPC1	0.51	0.5	Beaten using a Valley laboratory beater (SCAN C25-76 standard) to SR 70, followed by KOH/EtOH activation
HPC2	0.15	0.15	Beaten using a Valley laboratory beater (SCAN C25-76 standard) to SR 70, followed by KOH/EtOH activation

shrinkage) but also between two wires that have a gap of 1 mm, which allows free shrinkage of the sheets.

Testing of the handsheets was done using a special C-Impact device. The device is principally a tensile tester measuring the strength and strain at break. The straining speed was 1 mm/s. The device is equipped with a water spray and an ultrasound atomizer, which makes it possible to spray small amounts of water evenly on the sample. The length of the test strip was 124 mm and the re-wetted area was 70 mm. Re-wetting of the paper strip was done to three dryness levels: 50%, 65% and 80%. Re-wetting was followed by a tensile test after a 7 s wetting period.

2.5. Dynamic mechanical analysis test

Dynamic mechanical analysis (DMA) was used to measure the viscoelastic properties of materials as a function of temperature, time and frequency when the strip of paper was subjected to a periodic tensile stress. The paper strips were tested using a Mettler Toledo DMA/SDTA861^e device. The size of the sample was 9 mm (span length) × 3.8 mm (width), the applied static load was 0.4 N, the amplitude was 0.2 N, and the frequency used in this analysis was 1 Hz. Before testing, the paper strips were kept for 24 h in an air-conditioned room (23 °C and 50% RH). The temperature range in the test was between 100 °C and 250 °C. During the testing, the relative humidity of the test room varied from 5.7 to 11% RH.

3. Results and discussion

3.1. Mechanical pre-treatment and drying of cellulose fiber

The specific surface properties depend greatly on the drying procedure. The BET-specific surface area varied from 0.7 m^2/g to 56 m^2/g (Fig. 1). The highest density was found in the sample dried directly from the water. The highest BET-specific surface was in the sample that was first refined and then solvent exchanged through acetone to toluene. Acetone-dried samples clearly had a higher BET-specific surface area than the samples dried from water, but much lower than the samples dried from toluene.

Microscopic studies and BET measurements showed that the significance of external fibrillation is low compared to the significance of cell wall internal pores in the formation of a specific surface area. Highly fibrillated fibers can have a low specific surface area and, accordingly, the non-fibrillated samples can have a large specific surface area (Fig. 2).

In Simons' staining, two stains of different molecular sizes and affinities for fiber behave differently. Larger yellow stain molecules with a higher affinity for the fiber wall stain the fiber if the pore size in the fiber wall is large enough. A blue stain consists of smaller molecules than a yellow stain, but if the pores are large enough for the yellow stain to penetrate into the fiber wall, it will replace the blue stain due to its higher affinity. Simons' staining was done in water suspension and therefore it also measures the pores that were possibly reopened during rewetting.

Surface porosity measured using Simons' staining did not correlate with a specific surface area (Fig. 3). The results show that solvent exchange treatment, as well as the use of never-dried pulp, had a tendency to increase the surface porosity and surface openness (as illustrated by the increase in the yellow proportion in Fig. 3).

The results show that dry fiber cell wall openness, porosity and external fibrillation can be controlled by mechanical treatments and the removal of water. Drying the never-dried pulp fibers in an oven after solvent exchange was an efficient method of producing fibers with a high dry surface area for anhydrous chemical modifications. Efficient water removal from a fiber before the solvent

Table 3
Carbon HiRes components (% total C) from XPS measurements for the cellulose derivatives.

Sample	C—C (%)	C—O (%)	C=O (%)	COO (%)	O/C
Cellulose reference	9.5	72.7	17.1	0.8	0.69
1	45.7	35.5	9.1	9.9	0.39
2	45.6	35.3	9.0	9.8	0.38
3	45.7	35.3	9.0	9.9	0.38
4	53.0	29.0	7.6	10.5	0.35
5	46.3	33.6	9.9	10.3	0.39
6	52.6	28.6	8.0	10.8	0.34
7	50.2	30.0	9.1	9.9	0.37
Cellulose reference for hydroxypropyl derivatives	5.1	75.3	17.3	0.7	0.74
HPC1	15.1	71.7	12.9	0.3	0.62
HPC2	6.5	70.6	20.7	2.3	0.67

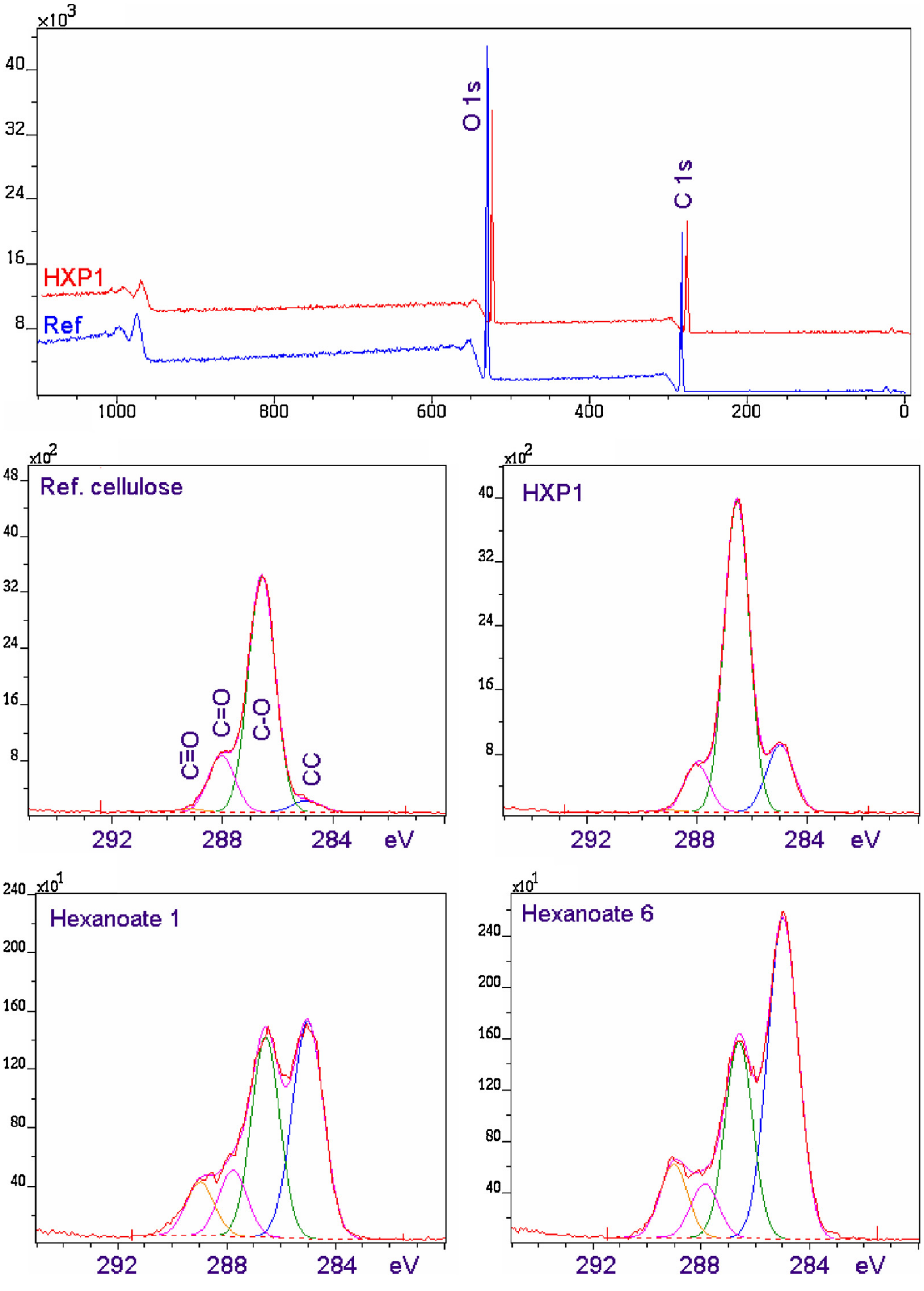


Fig. 5. XPS wide scans and curve-fitted XPS high-resolution carbon 1s regions of hydroxypropyl cellulose (HXP1) and cellulose hexanoates 1 and 6.

exchange to a less-polar solvent was the most critical step. When water was removed completely, the final exchange to a non-polar solvent increased the specific surface area of the fiber. The solvent exchange was carried out by continuous acetone extraction. Never-dried pulp is a prerequisite for a high surface area, because in bale pulps, the pores of the cell wall collapse irreversibly during drying. External fibrillation had only a minor effect on the BET-specific surface area of fibers with high surface areas. Most of the surface area originates from the open, laminated structure of the cell wall.

3.2. Preparation and characterization of the cellulose derivatives

The reactions for preparation of hydroxypropyl cellulose and the cellulose hexanoates are presented in Scheme 1. The derivatives can be prepared conveniently using these procedures. Propylene oxide reacts with refined and solvent-exchanged cellulose under elevated pressure without an additional solvent, to form hydroxypropyl cellulose with a moderate degree of substitution. The acquired degrees of substitution were 0.15 for HPC1 and 0.51 for HPC2 according to ^{13}C CP/MAS spectroscopy.

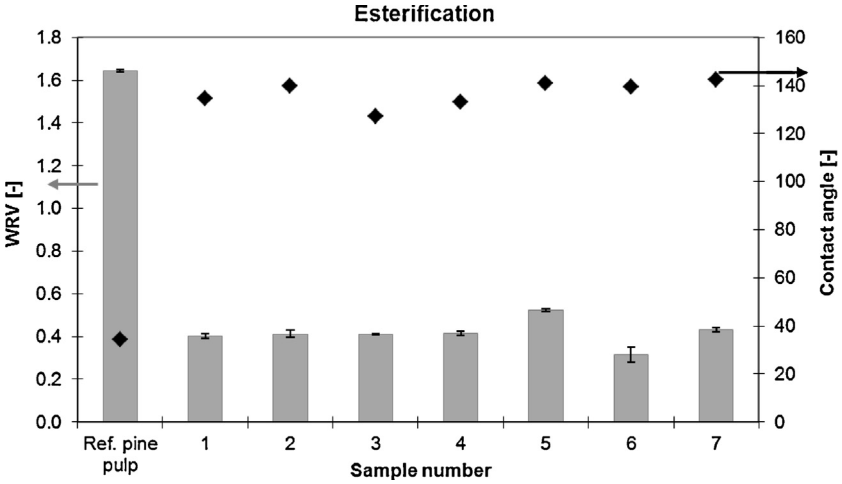


Fig. 6. Water retention values and contact angles of sheets using different pre-treatment methods followed by esterification.

The synthesis of cellulose hexanoate was initially attempted for cellulose material without any pre-treatment or drying, but the synthesis provided only very low levels of substitution (~0.1). This is understandable when the fiber contains some water and the hexanoyl acid chloride reacts violently with it. However, pre-treatments of the fiber material, and especially the removal of moisture by oven drying, rendered the fiber highly reactive for esterification. A higher specific surface area gained by refining could potentially increase the number of active reaction sites on the fiber surface. However, no clear differences in the amount of degree of substitution were seen, regardless of the pre-treatment method. Removal of water seems to be the most essential treatment to improve reactivity.

The degrees of substitution of the samples can be determined using solid state NMR by integrating the ester carbonyl signal and comparing that with the C1 integral of cellulose (Karrasch et al., 2009; Sievers et al., 2009; Torri, Cosentino, Delben, Simonutti, & Sozzani, 1999). Fig. 4 shows the ^{13}C CP/MAS solid state NMR spectra of native cellulose, hydroxypropylated cellulose (HPC1) and hexanoate cellulose 1. For reference, a solution state ^{13}C NMR spectrum of hexanoyl acid chloride was measured (Fig. 4d). The solid state ^{13}C CP/MAS NMR technique is a very informative characterization tool for cellulose and its derivatives, due to their solubility issues, respectively. The solid state NMR technique in general gives information regarding all the bulk material, not just from the surface. In theory, signal integrals in the ^{13}C NMR spectrum indicate populations of different carbon moieties. However, absolute integral values from ^{13}C CP/MAS NMR experiments are rarely achieved because the CP method in general emphasizes ^{13}C close to protons. In contrast to solution state NMR, quantitative ^{13}C NMR is usually achieved using an inverse-gated decoupling sequence and reasonably long pulse delays (5*T1) to provide complete relaxation of all nuclei (Zhang & Gellerstedt, 2007). For these reasons, solid state ^{13}C CP/MAS NMR provides detailed information on the cellulose derivative structure and a rough estimation of the total degree of substitution throughout the fiber.

For HPC1 (Fig. 4b), a new signal resonating at 21 ppm can be assigned to arise from the methyl group of the hydroxypropyl moiety, and for the hexanoate cellulose 1, new signals corresponding to methyl (δ 13.6 ppm), methylene (δ 22.1, 24.7, 30.5 ppm), α-methylene (δ 47.0 ppm) and carbonyl (δ 173.6 ppm) moieties could be identified. The measured cellulose ester spectrum show rather broad carbonyl resonance, most likely indicating congregation from different bond lengths, bond angles and chemical shift anisotropy associated to ester bonds in the modified cellulose fibers. Therefore, the success of the esterification was confirmed based on the change seen for the α-methylene signal resonance. It was also observed that the crystallinity degree (I_{cr}) of the cellulose derivatives remained somewhat the same after the modifications, and hence the fibrillar structure is well preserved. The degrees of substitution were determined by comparing integrals from the methyl (CH_3) and C1 signals of cellulose, with the aid of signal deconvolution using Gaussian line shapes (Jandura, Kokta, & Riedl, 2000; Tezuka, Tsuchiya, & Shiomi, 1996).

XPS also gives a good estimate of the degree of substitution of the surface (de Menezes, Siquiera, Curvelo, & Dufresne, 2009;

Fig. 7. Handsheets prepared using hydroxypropylated cellulose. The reference is on the left, HPC2 in the middle, and HPC1 on the right.

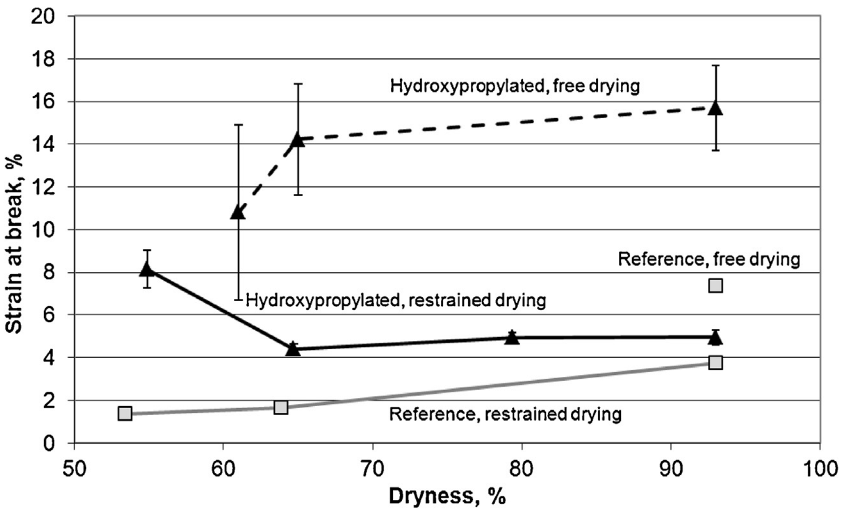


Fig. 8. Effect of hydroxypropylation (HPC2) on the elongation potential of remoistened and dry paper.

Uschanov, Johansson, Maunu, & Laine, 2011). XPS wide scans and curve-fitted XPS high-resolution carbon 1 s regions of hydroxypropyl cellulose (HXP1) and cellulose hexanoates 1 and 6 are presented in detail in Fig. 5. The DS based on XPS data for the hexanoate samples was calculated as a ratio of carboxylic carbon to C—O carbon, which is the major component in cellulose C 1s spectra, while CC, C—O and O—C—O-carbons were used in the case of hydroxypropylated samples. In the wide spectra, the major components in the samples were carbon and oxygen. The O/C ratio of modified cellulose decreases after modification. This further confirms successful derivatization and follows trends observed elsewhere (de Menezes, Siquiera, et al., 2009; Uschanov et al., 2011). The degree of substitution on the surface was calculated from the high resolution carbon spectra.

In the case of the hexanoate esters of cellulose, the proportions of CC carbon atoms (carbon without oxygen neighbors) and O—C=O carbons (carboxyl carbon atoms) were found to increase significantly after the modification was performed. This would be expected, because pure cellulose is composed of C—O and O—C—O carbons only, while acid chlorides consist of carbon chains without oxygen neighbors (C—C), which are then linked to the cellulose with a carboxyl bond in the esterification reaction. In the case of hydroxypropylation, the ratio of C—O and O—C—O carbons changed, together with the increasing C—C carbon, indicating successful derivatization. The degrees of substitution acquired using different methods are presented in detail in Table 2 and the XPS measurement parameters for each individual sample in Table 3.

In the case of hexanoate derivatives, the degrees of substitution received by XPS provided a higher estimate than those acquired by NMR, while both estimates for the hydroxypropylated derivatives follow similar trend lines. This can be explained by the different analysis volumes of the methods: XPS probes only few nanometers at the topmost surface while NMR is a bulk method covering the whole sample. So, significantly higher SDs calculated from XPS data suggest that the reaction happened mainly at the fiber surface, and also that the derivative layer was effectively screening out the cellulose signal. However, in the case of hydroxypropylated derivatives, the degrees of substitution acquired by both methods are similar. This suggests that the hydroxypropyl groups are spread evenly throughout the fiber. This could also be the result of the beating done for the fiber used in hydroxypropylation, which is expected to increase the surface area more than refining.

In the case of the hexanoyl esters of cellulose, the degrees of substitution acquired using NMR change only slightly with the pretreatment method, but using XPS, we can see some differences in the reactivity of the fiber surface. The degree of substitution at the surface is highest in the process where fines are removed from the fiber and the fiber is then solvent-exchanged to toluene through acetone and then dried. This is in unison with the highest BET-specific surface area value acquired by the same pre-treatment method, and consequently there is the largest number of active reaction sites available on the surface. Refining itself had only a minor influence on the reactivity of the surface, and longer-term refining seems to render the surface less reactive (Table 2).

3.3. Preparation of sheets

Preparation of paper sheets from the cellulose hexanoate esters was challenging because the fibers were very hydrophobic and the sheets consequently were weak. Therefore, the sheets were drained and dried on a wire fabric. After wet pressing, the dry matter content in the sheets was unusually high, even 88%. The dry sheets were also very brittle. Sheets made from pre-treated and esterificated fibers showed low density (~300 kg/m^3) and very low strength (tensile index 0.1–1.8 Nm/g). The water retention values and contact angles of the sheets are presented in Fig. 6.

The esterificated fibers show only low water retention values. The sheets made from these fibers also have a very high contact angle with water even if the porosity is high, which implies

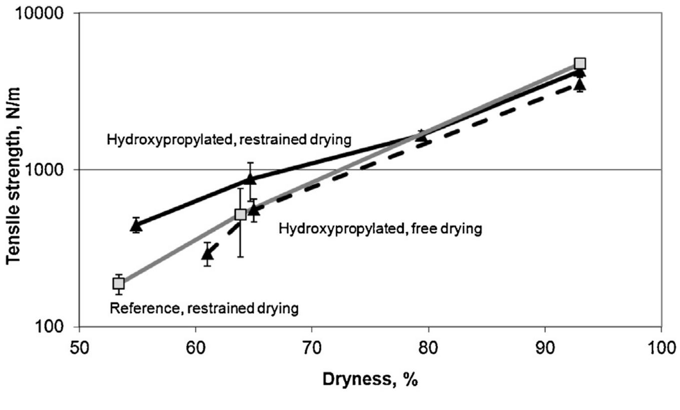


Fig. 9. Effect of hydroxypropylation (HPC2) on the tensile strength of remoistened and dry paper (basis weight 60 g/m^2).

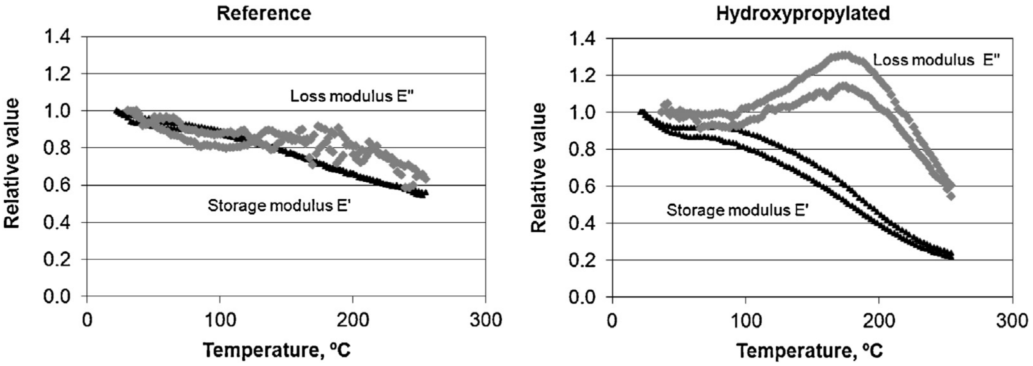


Fig. 10. Results of dynamic mechanical analysis of the reference sample and the hydroxypropylated sheet (HPC1). The curves are for two parallel measurements.

increased hydrophobicity. The degree of substitution at the surface had only a minor effect on the contact angles.

Fig. 7 shows that the sheets made from hydroxypropylated cellulose were comparatively transparent. The hydroxypropylated cellulose 1 with the higher degree of substitution also showed higher transparency than the sheet prepared from the hydroxypropylated cellulose 2, which had a lower degree of substitution. The high transparency of the sheets was an indication of a scarce air–fiber interface area, which is normally capable of scattering light. The low light-scattering surface area is also related to the high density and low-porosity of the sheets, which have similar properties to films. The sheet densities were 840 kg/m^3 for HPC1, and 970 kg/m^3 for HPC2. Additionally, the sheets showed a slightly increased hydrophobicity. Hydroxypropylation increased the contact angle of the sheets from 30° to 65°.

The hydroxypropylated fiber also revealed other interesting properties compared with the reference pine pulp. The fiber length after hydroxypropylation was 1.38 mm, whereas for the reference fibers the length was 1.9 mm. There was also a clear difference in drainage times of the sheets: 13 s for the reference sheet and 325 s for the hydroxypropylated sheet. The shrinkage potential was high (11.1%) with the hydroxypropylated sheets when they were allowed to shrink freely, while the reference sheets shrunk only 3.8%. Hydroxypropylation also increased the elongation potential of the paper, as can be seen in Fig. 8.

The sheets made from hydroxypropylated cellulose also showed good elongation when the paper was remoistened. When using free shrinkage drying, the highest elongation of paper achieved was 15.7%. Above a dryness level of 65%, the strain at break was not very sensitive to the moisture content of the samples.

In Fig. 9, it can be seen that the tensile strength of the hydroxypropylated sample when dried under restraint was better or about the same as the strength of the untreated reference. Higher drying shrinkage was probably the main reason for the somewhat lower strength of the free-shrinkage hydroxypropylated sheets.

Dynamic mechanical analysis (DMA) is used to measure the viscoelastic properties of materials as a function of temperature, time and frequency when the material is subjected to a periodic stress variation.

DMA results (Fig. 10) show the difference in softening behavior between the reference pulp and the hydroxypropylated fiber (HPC1). The loss factor of the hydroxypropylated sheets reached a maximum at 170 °C, which is an indication of thermal softening. Compared to that, the reference pulp did not indicate any specific softening point. This also indicates that the effect of hydroxypropylation is more distinct at elevated temperatures than at room temperature.

4. Conclusion

In this study, we have shown that by combining suitable mechanical and chemical methods, the properties of fibers and the fiber network can be modified, and the extensibility of the fiber network can be increased notably for paper applications.

Hydroxypropylation of cellulose fiber was found to be a promising method for increasing elongation and modifying paper properties, which respond to moisture and temperature. Paper sheets made from hydroxypropylated cellulose were transparent, nearly poreless, and showed good elongation (8.5%) when the paper was rewetted. Even 15.7% elongation of paper was achieved when free-shrinkage drying was used. Additionally, when the degree of substitution for the hydroxypropylation becomes high enough, the sheets become transparent. The increased fiber wall modification enhances the swelling and conformability of fibers, boosting the inter-fiber interaction in a wet state and resulting in a highly compacted sheet structure.

Preparation of cellulose hexanoate esters can be done conveniently, if the water is removed thoroughly before modification. Hexanoyl chloride reacts with cellulose under anhydrous conditions to produce hexanoate esters with high hydrophobicity, confirmed by an increase in the contact angle. Because of the increased hydrophobicity of fibers, pulps showed very low water retention values as well as poor bondability in paper sheets. Poorly bonding fibers have fewer applications in conventional papermaking, but in composites and other special applications, their hydrophobicity and low water sensitivity can be utilized.

Acknowledgements

This study was conducted in the FuBio (Future Biorefinery) programme under Forestcluster LTD. Additional thanks to Sanna Virtanen, Eija Silvast, Marketta Hiltunen and Minna Kalliosaari.

References

Alince, B. (1976). Partial carboxymethylation of rayon and its effect on interfibre bonding. *Svensk Papperstidning*, *79*, 259–262.

Belgacem, M. N., & Gandini, A. (2008). Surface modification of cellulose fibers. In M. N. Belgacem, & A. Gandini (Eds.), *Monomers, polymers and composites from renewable resources* (pp. 385–400). Amsterdam: Elsevier.

Bledzki, A., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, *24*, 221–274.

Boldizar, A., Klason, C., Kubat, J., Näslund, P., & Saha, P. (1987). Prehydrolyzed cellulose as reinforcing filler for thermoplastics. *International Journal of Polymeric Materials*, *11*, 229–262.

Dalvåg, H., Klason, C., & Strömvall, H. (1985). The efficiency of cellulosic fillers in common thermoplastics. Part II. Filling with processing aids and coupling agents. *International Journal of Polymeric Materials*, *11*, 9–38.

de Menezes, A. J., Pasquini, D., Curvelo, A. A. d. S., & Gandini, A. (2009). Self-reinforced composites obtained by the partial oxypropylation of cellulose fibers. 1. Characterization of the materials obtained with different types of fibers. *Carbohydrate Polymers*, *76*, 437–442.

de Menezes, A. J., Siquiera, G., Curvelo, A., & Dufresne, A. (2009). Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. *Polymer*, *50*, 4552–4563.

Didwania, H. (1968). *A study of the effects of hydroxyethylation on bonding of paper*. Doctoral Dissertation. Institute of Paper Chemistry, Wisconsin (89 p.).

Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C., et al. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science*, *26*, 1605–1688.

Felix, J. M., & Gatenholm, P. (1991). The nature of adhesion in composites of modified cellulose fibers and polypropylene. *Journal of Applied Polymer Science*, *42*, 609–620.

Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, *26*, 1689–1762.

Jandura, P., Kokta, B. V., & Riedl, B. (2000). Fibrous long-chain organic acid cellulose esters and their characterization by diffuse reflectance FTIR spectroscopy, solid-state CP/MAS ^{13}C-NMR, and X-ray diffraction. *Journal of Applied Polymer Science*, *78*, 1354–1365.

Johansson, L., & Campbell, J. M. (2004). Reproducible XPS on biopolymers: Cellulose studies. *Surface and Interface Analysis*, *36*, 1018–1022.

Johansson, L., Campbell, J. M., Koljonen, K., & Stenius, P. (1999). Evaluation of surface lignin on cellulose fibers with XPS. *Applied Surface Science*, *144–145*, 92–95.

Karrasch, A., Jäger, C., Karakawa, M., Nakatsubo, F., Potthast, A., & Rosenau, T. (2009). Solid-state NMR studies of methyl celluloses. Part 1: regioselectively substituted celluloses as standards for establishing an NMR data basis. *Cellulose*, *16*, 129–137.

Laine, J., Lindstrom, T., Bremberg, C., & Glad-Nordmark, G. (2003). Studies on topochemical modification of cellulosic fibres. Part 4: toposelectivity of carboxymethylation and its effects on the swelling of fibres. *Nordic Pulp & Paper Research Journal*, *18*, 316–325.

Lindstrom, T., Wågberg, L., & Larsson, T. (2005). On the nature of joint strength in paper: A review of dry and wet strength resins used in paper manufacturing. In *Advances in Paper Science and Technology: 13th fundamental research symposium* Cambridge, Pulp and Paper Fundamental Research Society, (pp. 457–562).

Mark, H. (1980). Fifty years of cellulose research. *Cellulose Chemical Technology*, *14*, 569–581.

Pasquini, D., Teixeira, E., Da Silva Curvelo, A., Belgacem, M., & Dufresne, A. (2008). Surface esterification of cellulose fibres: Processing and characterisation of low-density polyethylene/cellulose fibres composites. *Composites Science and Technology*, *68*, 193–201.

Matsumura, H., Sugiyama, J., & Glasser, W. (2000). Cellulosic nanocomposites. I. Thermally deformable cellulose hexanoates from heterogeneous reaction. *Journal of Applied Polymer Science*, *78*, 2242–2253.

Mitikka-Eklund, M., Halttunen, M., Melander, M., Ruuttunen, K., & Vuorinen, T. (1999). Fibre engineering. In *10th international symposium on wood and pulping chemistry – 10th Biennial ISWPC* Yokohama, Japan, Vol. 1, oral presentations, (pp. 432–439).

Raj, R. G., Kokta, B. V., Maldas, D., & Daneault, C. (1989). Use of wood fibers in thermoplastics. VII. The effect of coupling agents in polyethylene–wood fiber composites. *Journal of Applied Polymer Science*, *37*, 1089–1103.

Rezai, E., & Warner, R. (1997). Polymer-grafted cellulose fibers. I. Enhanced water absorbency and tensile strength. *Journal of Applied Polymer Science*, *65*, 1463–1469.

Sievers, C., Marzialetti, T., Hoskins, T. J. C., Valenzuela Olarte, M. B., Agrawal, P. K., & Jones, C. W. (2009). Quantitative solid state NMR analysis of residues from acid hydrolysis of loblolly pine wood. *Bioresource Technology*, *100*, 4758–4765.

Tezuka, Y., Tsuchiya, Y., & Shiomi, T. (1996). ^{13}C NMR determination of substituent distribution in carboxymethylcellulose by use of its peresterified derivatives. *Carbohydrate Research*, *291*, 99–108.

Thielemans, B., Dufresne, A., Chaussy, D., & Belgacem, M. (2008). Surface functionalization of cellulose fibres and their incorporation in renewable polymeric matrices. *Composites Science and Technology*, *68*, 3193–3201.

Torri, G., Cosentino, C., Delben, F., Simonutti, R., & Sozzani, P. (1999). Novel cellulosic ethers with low degrees of substitution—II. Magic angle spinning NMR study. *Carbohydrate Polymers*, *40*, 125–135.

Uschanov, P., Johansson, L., Maunu, S., & Laine, J. (2011). Heterogeneous modification of various celluloses with fatty acids. *Cellulose*, *18*, 393–404.

Ward, K. (1960). Chemical modification of papermaking pulps. *Tappi*, *43*, 54–59.

Ward, K., Morak, A., Murray, M., & Thomas, W. (1965). The improvement of bonding in paper sheets by chemical modification of the fibers: Some screening tests with cotton linters. *Tappi*, *48*, 207–210.

Woodhams, R. T., Thomas, G., & Rodgers, D. K. (1984). Wood fibers as reinforcing fillers for polyolefins. *Polymer Engineering & Science*, *24*, 1166–1171.

Yu, X., Minor, J., & Atalla, R. (1995). Mechanism of action of Simons' stain. *Tappi*, *78*, 175–180.

Zadorecki, P., & Michell, A. J. (1989). Future prospects for wood cellulose as reinforcement in organic polymer composites. *Polymer Composites*, *10*, 69–77.

Zhang, L., & Gellerstedt, G. (2007). Quantitative 2D HSQC NMR determination of polymer structures by selecting suitable internal standard references. *Magnetic Resonance in Chemistry*, *45*.