Wood Science and Technology (2019) 53:1035–1050
https://doi.org/10.1007/s00226-019-01115-x

ORIGINAL

Direct esterification of reinforced papers by immersion method and evaluation of their properties

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Received: 5 February 2019 / Published online: 17 July 2019

Abstract

Today, the use of biodegradable packaging materials is very noteworthy. They are one of the most used materials in the packaging industries. These materials require proper barrier and mechanical strength properties. Cellulose nanofibril (CNF) can improve the mechanical strength and air resistance of paper, but it is not able to improve its water barrier property. In this study, modification of the water barrier property of CNF-reinforced papers was evaluated using the esterification process. Handsheets were made by adding CNF to the pulp fibers. After drying, the handsheets were esterified using the liquid-phase acetylation process without any catalyst for different reaction times (0.5, 1, and 3 h). Infrared spectroscopy confirmed a successful chemical modification. The mechanical properties and air resistance of the paper sheet were significantly increased by adding CNF to the pulp. The esterification led to a decrease in the water absorption of the unmixed and mixed papers of about 24.5 and 48%, respectively. Therefore, the addition of CNF to the pulp and surface esterification of the mixed paper caused simultaneous improvement in the barrier and mechanical strength properties of paper.

Introduction

The different types of paper represent various required properties, including biodegradability, renewability, affordability, and mechanical flexibility (Samyn et al. 2018). They also require specific properties depending on their applications. Nowadays, the packaging industry is one of the most important consumers of paper, so that about one-third of the materials used in this industry are cellulose fibrous materials

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(Missoum et al. 2013). Considering the type of application, these papers commonly need to have acceptable mechanical strength and barrier properties. The most important barrier properties of packaging papers are barrier against water, gases, greases, and flavors. These properties are usually obtained by adding petroleum-based chemicals to the paper-making wet-end chemistry, impregnation, and coating (Missoum et al. 2013). In recent years, environmental concerns are driving the need for using eco-friendly materials and methods in industries. One of the suitable methods recently used to improve the barrier properties of paper products, especially water barrier properties, is chemical surface modification of cellulose and its related lignocellulosics. Among the modification reactions, esterification is broadly applied. Acetylation is one of the most important methods of esterification (Ernest-Saunders et al. 2014; Habibi 2014). This reaction also is an inexpensive and eco-friendly method that has been broadly used in wood modification (Rowell et al. 1986; Zhang et al. 2013). During the acetylation process, hydroxyl groups (−OH) of cellulose are substituted with acetyl (CH_3CO) groups; thus, hydrophilicity of cellulose materials decreases (Celen et al. 2008; Halip et al. 2019; Sain and Fortier 2002; Zhou et al. 2016). This process was also used to improve the barrier properties of paper (Sain and Fortier 2002; Soltani et al. 2013).

Two methods can be used to improve the water barrier properties of paper by the acetylation process. They include acetylation of pulp fibers before paper-sheet making, and surface acetylation of paper sheets. It was reported that surface acetylation of paper sheets is a better method compared to the acetylation of pulp fibers, as the mechanical properties of the acetylated paper remain constant or slightly reduced (Soltani et al. 2013). In fact, during the acetylation of pulp fibers, hydrogen bonding sites of polysaccharides (the free hydroxyl groups of cellulose and hemicellulose in fiber structure) will be partially replaced by acetyl groups, which can lead to a decrease in the relative bonding area (RBA) of paper sheet, and consequently, decrease its mechanical properties (Wang and Li 2018). On the other hand, after the paper-making and during the acetylation process, free hydroxyl groups (generally on the paper surface) can be reacted and blocked by acetyl groups. Therefore, water absorption of paper will be reduced, while the mechanical properties of paper will be preserved. Surface acetylation of paper only leads to a decrease in interactions that occur between the paper surface and the water due to the replacement of the free hydroxyl groups by acetyl groups. As water absorption of paper is also performed through capillary flow due to the paper web pores, it seems that cellulose nanofibril (CNF) can be a good choice to further improve the barrier properties of paper due to partial change of paper network pore size from micro- to nanoscale. The CNF refers to the cellulose fibers that have been fibrillated to reach agglomerates of cellulose microfibril units (Nechyporchuk et al. 2015; Žepič et al. 2014). The CNF fibers have nanoscale diameter with micron-scale length (Ho et al. 2011; Kekäläinen et al. 2015; Su et al. 2013). The CNF also has unique properties such as high specific surface area, plenty of surface hydroxyl groups and potential reinforcing properties (Abdul Khalil et al. 2012; González et al. 2012; Khalil et al. 2013; Wang et al. 2016). In fact, adding CNF to the paper leads to an increase in mechanical entanglement of fibrils, number of inter-fiber hydrogen bonds, minimization of paper structure pores, and finally improvement of paper physical properties and

mechanical strength (González et al. 2013; Hii et al. 2012; Xiao et al. 2009). In a previous research work, the effect of adding acetylated NFC to pulp fiber suspension on improvement of paper properties was investigated (Mashkour et al. 2015).

In this study, for the first time, surface acetylation was applied to CNF-reinforced papers. In this way, cellulose nanofibril-reinforced paper was esterified directly by liquid-phase acetylation process without any catalyst to simultaneously improve barrier and strength properties of paper.

Materials and methods

Commercial long fiber pulp (American southern pine pulp) was provided by Linter Pak Company (Behshahr, Iran). Cationic polyacrylamide (C-PAM) with medium cationic charge and high molecular weight (Farinret K325, Degussa Co., Frankfurt, Germany) was applied as a retention aid. Acetic anhydride was prepared in analytical grade from Merck Chemical Company (Darmstadt, Germany) and applied without further purification.

Preparation of pulp

The water freeness of the as-received softwood pulp was assessed as 770 mL CSF (Canadian Standard Freeness) according to the TAPPI T 277 om-04 standard. Based on the TAPPI T 248 sp-00 standard, the freeness of pulp was adjusted to 350 mL CSF using PFI refiner (VI Hamar Co., Hamar, Norway). This pulp was used to make handsheets.

Manufacture of CNF

In order to manufacture CNF, first the provided softwood pulp was washed to remove the pollutions. Then, the water slurry with 1 wt% purified softwood fibers was passed three times through a disk grinder (MKCA6-3; Masuko Sangyo Co., Ltd., Kawaguchi-city, Japan) at 1500 rpm to produce CNF (Afra et al. 2013; Ghaderi et al. 2014; Yousefi et al. 2011).

Handsheet preparation

The laboratory handsheets (60 g m^{-2}) were made according to the TAPPI T 205 sp-02 standard. During the CNF-reinforced handsheets making, C-PAM was used as a retention aid. Before, C-PAM was diluted to a concentration of 0.05% (w/w). The NFC and pulp dry content in the systems were kept constant at 0.3% (w/w), while the relative composition of the component was constant (10% CNF to 90% pulp). The amount of the added C-PAM was also constant (0.3% (w/w)). The retention of fines and CNF was measured at about 79 ± 4% using a Britt Dynamic Drainage Jar, based on the TAPPI standard method (T 261cmp-00). The C-PAM was added to the fiber suspension, and 10% CNF was added after 15-min mixing at 500 rpm

(Mashkour et al. 2015; Taipale et al. 2010). The pH of the resulting suspension (pulp + CNF + C-PAM) was between 7.5 and 8. Handsheets were formed using a laboratory handsheet maker according to the method described in the TAPPI standard (T 205 sp-02) after further mixing for 15 min. The handsheets were conditioned for 24 h at 23 °C and 50% relative humidity (RH) according to the TAPPI standard prior to the esterification process.

Esterification process

The handsheets were esterified using acetylation (liquid phase, without any catalyst). The reaction vessel containing acetic anhydride was placed in an oil bath on a magnetic shaker and heated to 70 °C. Then, the preconditioned handsheets were immersed in acetic anhydride. Every time, two preconditioned handsheets were immersed in about 800 ml of acetic anhydride. A water condenser system was used to prevent evaporation of the acetic anhydride. The esterification process was performed for different reaction times (0.5, 1, and 3 h) to obtain different degrees of esterification. After the reaction time was completed, the handsheets were soaked in water to discontinue the esterification reaction. Then, the esterified papers were completely washed with water to eliminate residual chemicals and afterward pressed at 400 kPa for 5 min. The wet-treated handsheets were dried on the press plates for 24 h and then stored at 23 °C and 50% RH for at least 3 days prior to the analysis. The produced handsheets are shown in Table 1.

Measurements

Measurement of fiber dimensions

The fiber dimension measurement, including length, diameter, and wall thickness, was taken using an optical microscope (Olympus Co., Tokyo, Japan).

Table 1 Series of handsheets produced in this study

Handsheet	Esterification time (h)	Abbreviation
Unmixed paper (100% pulp)	0	UMP
	0.5	EUMP-0.5h
	1	EUMP-1h
	3	EUMP-3h
Mixed paper (90% pulp + 10% CNF + C-PAM)	0	MP
	0.5	EMP-0.5h
	1	EMP-1h
	3	EMP-3h

CNF characterization

CNF morphology was characterized by scanning electron microscope model VEGA\\TESCAN-LMU instrument (Brno-Kohoutovice, Czech Republic) with an accelerating voltage of 3 kV. Image processing and analysis were performed with ImageJ (version 1.44) software.

Chemical characterization of handsheets

Fourier transform infrared (FTIR) spectroscopy In order to characterize the changes in the functional groups that may have been caused by the treatments, Fourier transform infrared (FTIR) spectroscopy studies were done using a PerkinElmer Spectrum RXI (Lambda, USA). Prior to the analysis of handsheets, 1.0 mg of paper fibers was milled and mixed with 100 mg potassium bromide (KBr). The obtained powder was pressed into transparent pellets and analyzed. The FTIR analysis was carried out using 64 scans with a resolution of 4 cm^{-1}, in absorbance mode within the range of 4000–400 cm^{-1}. To compare the resultant FTIR spectra, all spectra were normalized to absorption peak at 1059 cm^{-1} wavenumber associated with C–O stretching.

Hydrophobicity was examined by evaluation of the surface properties of handsheets with dynamic contact angle (DCA) measurements at different check times (0.2, 10, and 60 s.). The measurements were taken at 23 °C and 50% RH with a contact angle goniometer (Dataphysics OCA 15 plus, Filderstadt, Germany).

Structural analysis of handsheets

In order to analyze the structure of the handsheets, SEM micrographs were acquired with a Pemtron PS-230 (Seoul, Korea) scanning electron microscope at 10 kV accelerating voltage. The samples were coated with gold and observed in the secondary electron mode to avoid sample charging. Image processing and analysis were performed with ImageJ (version 1.44) software.

Measurement of physical and mechanical properties of papers

The thickness of the handsheets was measured with a PTA thickness tester N1101 (Birkenau, Germany). The density was calculated by dividing the handsheet base weight by its thickness. The bursting strength of the handsheets was measured with a digital burst-tester (FRANK PTI GmbH, Birkenau, Germany), according to the TAPPI standard method (T 403 om-02). The tensile strength measurement of the handsheets was taken according to the TAPPI standard method (T 494 om-01) using a horizontal tensile tester (L & W Tensile Strength Tester, Stockholm, Sweden). All measurements were taken at 23 °C and 50% RH.

The air resistance test was performed according to the TAPPI standard method (T 460 om-02) with a Gurley tester 4110 (genuine Gurley™, Troy, NY, USA).

The water absorption was measured according to the TAPPI standard method (T 441 om-04) by a ring of 10 cm diameter, and to avoid errors associated with the capillarity, all samples were cut around the ring. Deionized water (100 ml) was added into the ring for 60 s, and then wet samples were pressed once between two absorbent papers with a roll of 10 kg in order to remove residual water, and then weighed by using a digital balance four digit. The Cobb index represents the ratio between mass of water absorbed and the wet area (g m^{-2}).

The statistical analysis of experiments was performed by a completely randomized design with three replications. Some data were analyzed by one-way analysis of variance (ANOVA). Mean separation was conducted using Duncan's multiple comparison test at $p < 0.05$. All statistical analyses were carried out with SPSS 18.0 software (IBM Corporation).

Results and discussion

Fiber and CNF characterization

SEM image of the CNF is presented in Fig. 1. The nanofibers showed a fibrillar structure with a diameter of about 33 ± 5.6 nm. The diameter of nanofibers was obtained by digital image processing (ImageJ) of SEM picture (minimum of 50 measurements were taken). Further, the averages of length and diameter of softwood

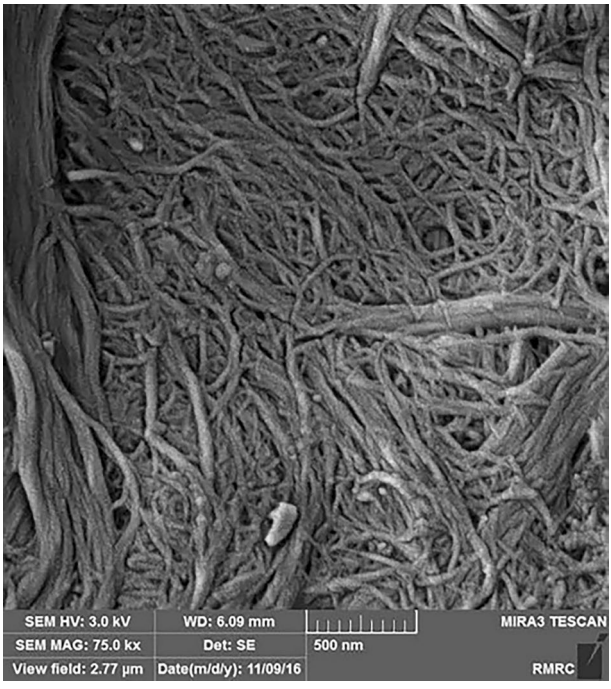

Fig. 1 Scanning electron microscopy image of the extracted CNF from the bleached softwood pulp

fibers were around 3374 ± 456 µm and 34 ± 8 µm, respectively, which were measured by an optical microscope. These data show that the softwood fibers with a diameter of 34 ± 8 µm were downsized to CNF with a diameter of 32 ± 10 nm via a fast and simple grinding process. As network-like highly entangled CNF, it seems that the individual nanofibers do not have any clear ends, so an exact length of CNF cannot be given, neither in the present investigation nor in the literature. With regard to transmission electron microscope (TEM) and FE-SEM micrographs, the length of CNF was appraised to be longer than 10 µm (Afra et al. 2013; Ghaderi et al. 2014; Hassan et al. 2012; Yousefi et al. 2011).

Chemical characterization

In order to assess the chemical characteristics of the handsheets before and after esterification, FTIR spectroscopy was performed. The FTIR spectra of esterified and unesterified samples of unmixed and mixed papers are shown in Fig. 2a and b, respectively. As compared to the FTIR spectrum of unesterified paper, those of esterified paper showed specific acetyl bands appearing at 1735–1744 cm^{-1} (carbonyl C=O stretching of ester) (Adebajo et al. 2006; Chen et al. 2016; Jonoobi et al. 2010), 1375–1377 cm^{-1} [C–H in –O(C=O)–CH_3] (Li et al. 2009; Peredo et al. 2015; Rodionova et al. 2013), and 1256–1260 cm^{-1} (C–O stretching of acetyl group) (Cetin et al. 2011). In addition, esterification caused a decrease in the absorption intensity of the band located at around 3427 cm^{-1}, assigned to the stretching of the hydroxyl group. Partial substitution of the hydroxyl groups with acetyl groups in unmixed and mixed papers results in decreasing absorption intensity of hydroxyl group bond. The lack of absorption peak at 1700 cm^{-1} referred to carboxylic group and showed that the product was also free of any acetic acid by-product (Ashori et al. 2014).

The degree of esterification was estimated from the IR spectra by computing a ratio, called R_1, which is defined as the ratio between the intensity of the acetyl C=O stretching band of ester at 1735–1744 cm^{-1} (Jonoobi et al. 2010; Rodríguez et al. 2015; Wang et al. 2019) and the intensity of C-O stretching vibration of the cellulose backbone at about 1059 cm^{-1}, that is, $R_1 = I_{1740}/I_{1059}$. The peak ratios (I_{1740}/I_{1059}) for esterified unmixed and mixed papers are indicated in Table 2. The results show that the degree of esterification was increased by increasing of esterification time.

In addition, the contact angle measurements were taken to compare the hydrophobic behavior of the esterified unmixed and mixed papers with unesterified ones (Table 2). As expected, the obtained contact angle values of a water drop deposited on the surface of the esterified papers were higher than those found for the unesterified papers. This proved indirectly the successful chemical surface modification. In addition, the contact angle values increased by increasing reaction time at different check times (0.2, 10, and 60 s.). The highest contact angle for the esterified unmixed papers and esterified mixed papers was registered after a 3-h treatment, 59.35° and 66.60°, respectively (Fig. 3). The longer wetting time of paper led to a decrease in the contact angle (Table 2). In addition, the decrease in the contact angle of the unmixed papers was more than that of the mixed papers. A possible explanation for

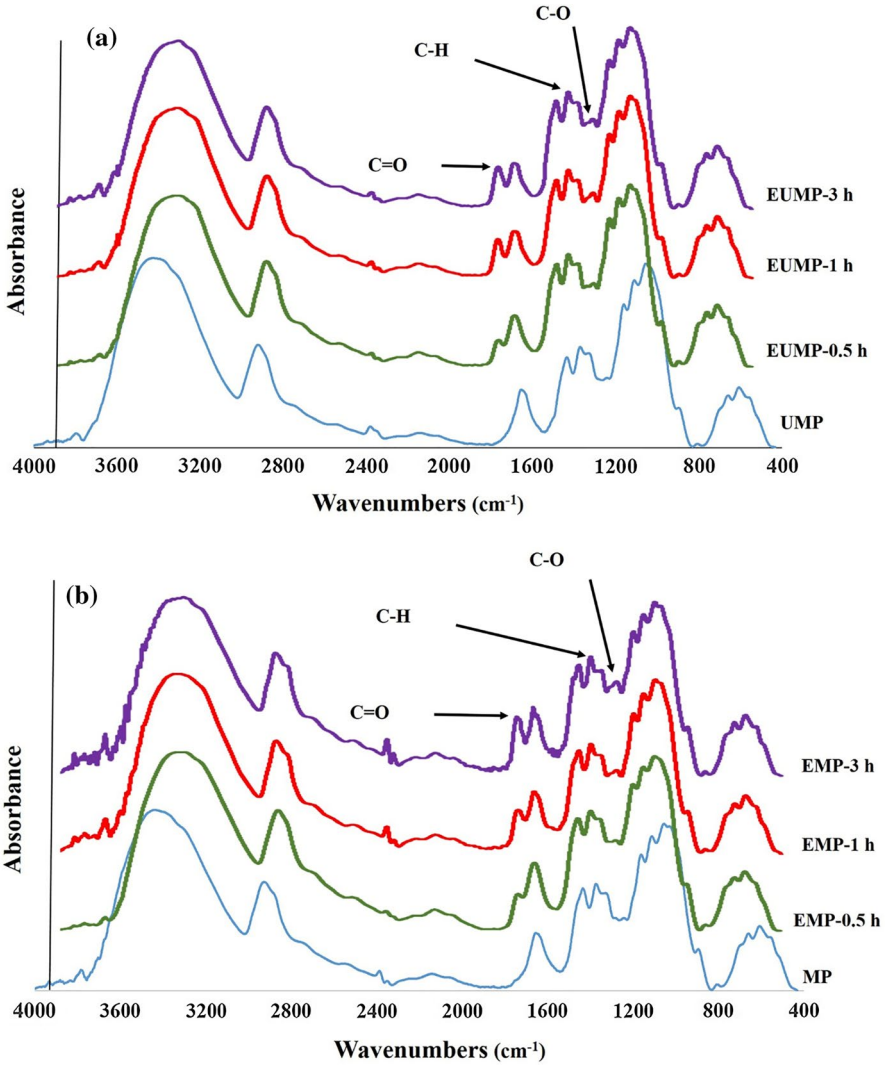

Fig. 2 Normalized FTIR spectra of unesterified and esterified samples of **a** unmixed and **b** mixed papers

higher contact angle of the mixed papers could be the filling of the voids between the fibers in the paper network by CNFs, which leads to an increase in paper density; therefore, CNFs can act as a physical barrier against water.

Handsheet structural characterization

The SEM micrographs of papers (UMP, EUMP-3h, MP, and EMP-3h) are shown in Fig. 4. The visual evaluation reveals that adding CNF/C-PAM to the paper structure resulted in minimization and closure of pores since the nanofibrils were acting as

Table 2 Degree of esterification (determined by studying the FTIR spectra) and contact angle for unmodified and esterified unmixed and mixed papers

Paper specimen	I_{1740}/I_{1059}	Contact angle		
		0.2 s	10 s	60 s
UMP	–	39.57 ± 4	0	0
EUMP-0.5h	0.15	45.28 ± 3.1	0	0
EUMP-1h	0.21	55.4 ± 3.3	20.46 ± 1	0
EUMP-3h	0.24	59.35 ± 1.5	30.08 ± 3	4.75 ± 0.2
MP	–	41.42 ± 4.1	26.57 ± 1.1	13.2 ± 1.2
EMP-0.5h	0.2	50.20 ± 5	44.82 ± 1.6	32.86 ± 1
EMP-1h	0.23	62.4 ± 3.4	56.66 ± 1.2	43.66 ± 1.4
EMP-3h	0.33	66.6 ± 1.2	59.23 ± 1.1	45.92 ± 1.5

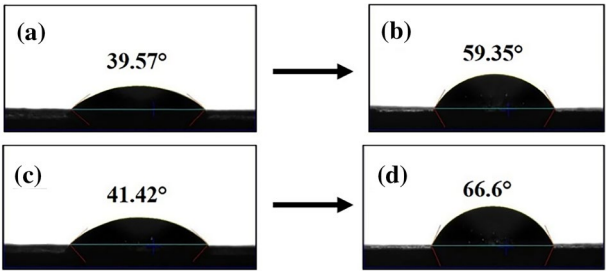

Fig. 3 Contact angles of water droplet on the surface of **a** unmodified unmixed paper, **b** esterified unmixed paper for 3 h, **c** unmodified mixed paper, and **d** esterified mixed paper for 3 h, after 0.2 s

an agent for improving relative bonding area of the paper (Mashkour et al. 2015) (Fig. 4c, d). It should be mentioned that such a structural development, which is a result of CNF addition, has already been studied previously (Charani et al. 2013; Hassan et al. 2012; Sehaqui et al. 2013). ImageJ analysis also showed that the percent of porous area was not significantly changed by esterification of unmixed and mixed papers ($p > 0.05$). This result can be used in explaining the barrier and strength properties of paper sheets in this research.

Handsheets physical and mechanical properties

The density of papers was increased by adding CNF to the pulp by about 15% compared to the density of the control sheet (UMP) (Fig. 5a). Esterification had no significant effect on the density of both unmixed and mixed papers ($p > 0.05$).

CNF is a nanosized cellulosic fraction with high specific surface area and plenty of hydroxyl groups (Chandra et al. 2016). This is why it can increase the amount of bonds between the fibers, and it is also able to fill the gaps between fibers in wet-pressed sheets. This phenomenon causes the increase in paper density. The same results have been reported previously (Eriksen et al. 2008; Hassan et al. 2015; Vallejos et al. 2016).

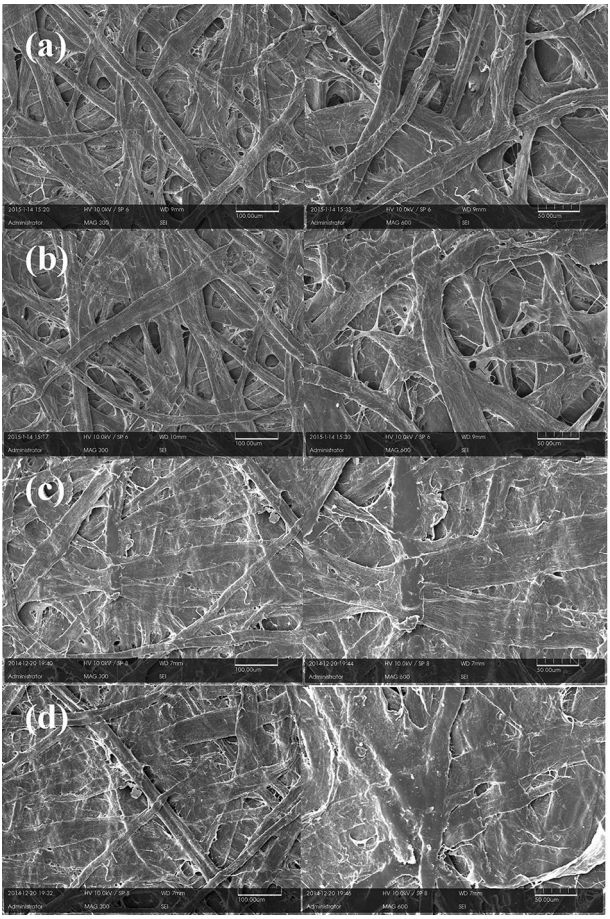

Fig. 4 SEM micrographs of the surface of **a** UMP, **b** EUMP-3h, **c** MP, and **d** EMP-3h. The surface images were acquired at 300 (left) and 600× (right) magnification

The effects of CNF addition and surface esterification on bursting and tensile strength of the produced papers are demonstrated in Fig. 5b, c, respectively. By adding CNF to the pulp, the bursting and tensile strengths increased by about 33% and 24.5%, respectively. In addition, esterification treatment had no significant effect on the bursting and tensile strengths of produced papers ($p > 0.05$).

Paper strength can be regarded as a result of the strengths of individual fibers, plus the number and strengths of bonds between those fibers. Adding CNFs to the paper leads to an increase in physical entanglements of fibrils, number of inter-fiber bonds, and finally improvement of the mechanical strengths of paper (Adel et al. 2016; Boufi et al. 2016; Hassan et al. 2012). The same results have been reported previously (Espinosa et al. 2016; Guan et al. 2019; Liu et al. 2015; Taipale et al. 2010). The density and strength properties of paper after the esterification process did not have significant changes. Therefore, it can be concluded that only the free

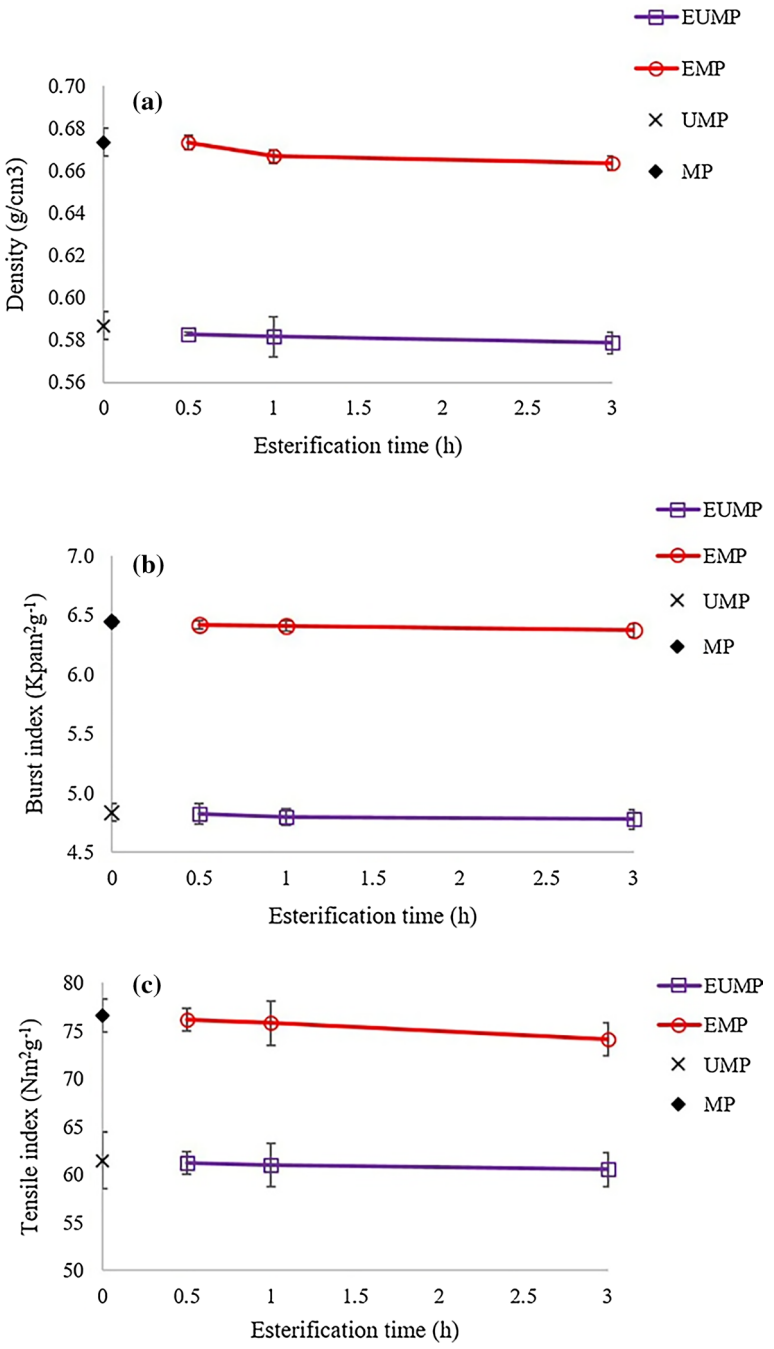

Fig. 5 Effect of esterification treatment on the **a** density, **b** bursting strength, and **c** tensile strength of the handmade papers

bonding sites reacted and were blocked by acetyl groups. The same porosity on the surface of untreated and treated paper sheets shown in Fig. 4 also proves it. Therefore, the fiber-to-fiber joint strength (bonding strength) was not affected by esterification (Soltani et al. 2013). The same results have been reported previously (Sain and Fortier 2002; Soltani et al. 2013).

Handsheets barrier properties

The air resistance of the handsheets is indicated in Fig. 6a. As can be seen, the highest and lowest air resistance values were acquired for MP and UMP, respectively. The air resistance was increased by about 1208% by adding CNF to the pulp. Esterification had no significant effect on the air resistance of the papers ($p > 0.05$).

The paper porosity, defined as the ratio of pore volume to total volume, is an effective main factor of the air resistance of paper. According to Syverud and Stenius (2009), CNF is a good choice to improve the gas barrier properties of paper because

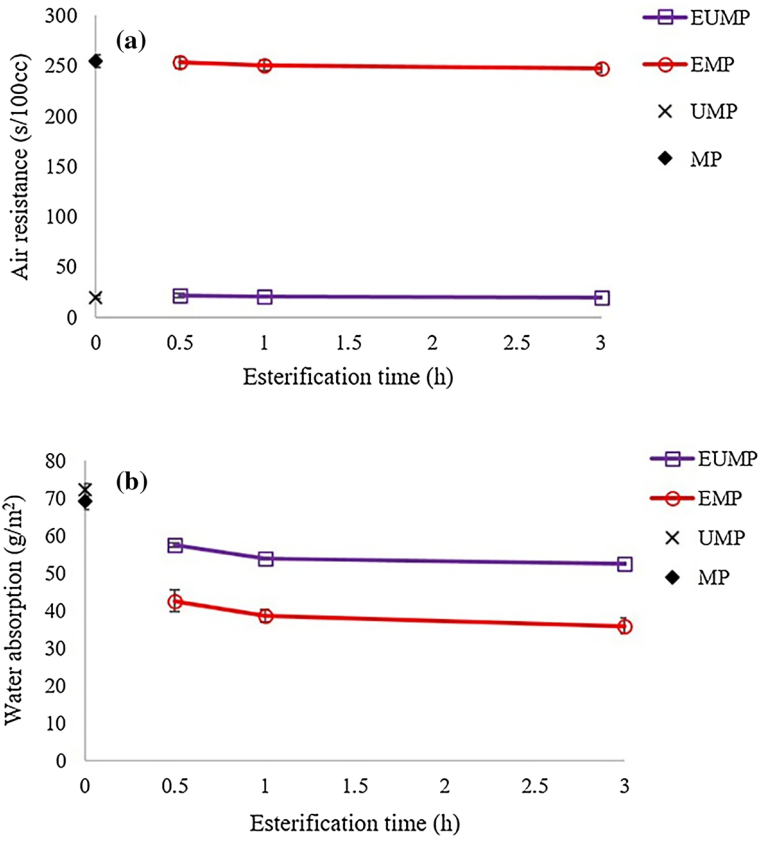

Fig. 6 Effect of esterification treatment on **a** air resistance and **b** water absorption of the handmade papers

of a partial change from microporous to nanoporous in the paper network. In fact, the CNF causes the better bonding between fibers by creating entanglements among them (Syverud and Stenius 2009), thus causing a decrease in the paper porosity and increase in the paper air resistance (Guan et al. 2019).

The water absorption of papers was measured using the Cobb test method. The results are shown in Fig. 6b. UMP and EMP-3h had the highest and lowest water absorption values, respectively. As previously mentioned, the water barrier properties of paper are limited due to the free hydroxyl groups of cellulose and hemicellulose in the fibers structure, along with the porous structure of the paper fiber network (Scott and Trosset 1989). Esterification decreased water absorption of UMP and MP by about 27% and 50%, respectively, after a 3-h treatment. In fact, esterification decreased the paper water absorption due to the substitution of free hydrophilic groups (hydroxyl) on the paper-sheet surface with hydrophobic groups (acetyl) (Huang et al. 2018; Sain and Fortier 2002; Soltani et al. 2013), which was also confirmed by the results of water contact angle test.

In this study, using CNF as a reinforcing agent did not show a significantly desirable effect on the improvement of the water barrier property of paper. The same results have been reported previously (Hassan et al. 2015; Missoum et al. 2013).

Adding CNF to the paper sheet decreased the number and size of paper pores (Fig. 4a, c), leading to a decrease in the water entering into the paper network structure. However, because of the high hydrophilicity of CNF due to its specific surface area and plenty of OH groups, adding CNF to the paper sheet did not totally lead to significant changes in water absorption of MP compared with UMP ($p > 0.05$). On the other hand, water absorption of MP was decreased by significantly increasing the esterification time ($p < 0.05$).

Conclusion

According to the results, addition of 10 wt% CNF to the pulp led to significant improvement in the paper mechanical strengths such as tensile strength (about 24.5%) and the paper air resistance (about 1208%), while it had no significant effect on the water barrier property of the paper. Treatment of the CNF-reinforced paper by surface esterification process led to a significant improvement in the water barrier property of the paper (about 48%) with no significant effect on the paper mechanical strength and the paper air resistance. In addition, the water absorption of the paper sheet decreased by increasing the esterification time significantly.

With regard to simultaneous access to the strength and barrier properties through surface esterification of the CNF-reinforced paper, it seems that the cellulose nanofibril-reinforced esterified paper, as a promising product, has application potential for many types of paper, in particular packaging papers.

Acknowledgements We would like to acknowledge the Iran Nanotechnology Initiative Council for its financial support. We also thank Nano Novin Polymer Co. (Iran) for their help in producing cellulose nanofibers.

References

Abdul Khalil H, Bhat A, Ireana Yusra A (2012) Green composites from sustainable cellulose nanofibrils: a review. Carbohyd Polym 87:963–979. https://doi.org/10.1016/j.carbpol.2011.08.078

Adebajo MO, Frost RL, Kloprogge JT, Kokot S (2006) Raman spectroscopic investigation of acetylation of raw cotton. Spectrochim Acta Mol Biomol Spectrosc 64:448–453. https://doi.org/10.1016/j.saa.2005.07.045

Adel AM, El-Gendy AA, Diab MA, Abou-Zeid RE, El-Zawawy WK, Dufresne A (2016) Microfibrillated cellulose from agricultural residues. Part I: papermaking application. Ind Crops Prod 93:161–174. https://doi.org/10.1016/j.indcrop.2016.04.043

Afra E, Yousefi H, Hadilam MM, Nishino T (2013) Comparative effect of mechanical beating and nanofibrillation of cellulose on paper properties made from bagasse and softwood pulps. Carbohyd Polym 97:725–730. https://doi.org/10.1016/j.carbpol.2013.05.032

Ashori A, Babaee M, Jonoobi M, Hamzeh Y (2014) Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion. Carbohyd Polym 102:369–375. https://doi.org/10.1016/j.carbpol.2013.11.067

Boufi S, González I, Delgado-Aguilar M, Tarrès Q, Pèlach MÀ, Mutjé P (2016) Nanofibrillated cellulose as an additive in papermaking process: a review. Carbohyd Polym 154:151–166. https://doi.org/10.1016/j.carbpol.2016.07.117

Celen I, Harper D, Labbe N (2008) A multivariate approach to the acetylated poplar wood samples by near infrared spectroscopy. Holzforschung 62:189–196. https://doi.org/10.1515/HF.2008.048

Cetin NS, Özmen N, Birinci E (2011) Acetylation of wood with various catalysts. J Wood Chem Technol 31:142–153

Chandra J, George N, Narayanankutty SK (2016) Isolation and characterization of cellulose nanofibrils from arecanut husk fibre. Carbohyd Polym 142:158–166. https://doi.org/10.1016/j.carbpol.2016.01.015

Charani PR, Dehghani-Firouzabadi M, Afra E, Blademo Å, Naderi A, Lindström T (2013) Production of microfibrillated cellulose from unbleached kraft pulp of Kenaf and Scotch Pine and its effect on the properties of hardwood kraft: microfibrillated cellulose paper. Cellulose 20:2559–2567. https://doi.org/10.1007/s10570-013-9998-z

Chen J, Xu J, Wang K, Cao X, Sun R (2016) Cellulose acetate fibers prepared from different raw materials with rapid synthesis method. Carbohyd Polym 137:685–692. https://doi.org/10.1016/j.carbpol.2015.11.034

Eriksen O, Syverud K, Gregersen O (2008) The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. Nord Pulp Pap Res J 23:299–304. https://doi.org/10.3183/npprj-2008-23-03-p299-304

Ernest-Saunders R, Pawlak JJ, Lee JM (2014) Properties of surface acetylated microfibrillated cellulose relative to intra-and inter-fibril bonding. Cellulose 21:1541–1552. https://doi.org/10.1007/s10570-014-0177-7

Espinosa E, Tarrés Q, Delgado-Aguilar M, González I, Mutjé P, Rodríguez A (2016) Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application to papermaking slurries. Cellulose 23:837–852. https://doi.org/10.1007/s10570-015-0807-8

Ghaderi M, Mousavi M, Yousefi H, Labbafi M (2014) All-cellulose nanocomposite film made from bagasse cellulose nanofibers for food packaging application. Carbohyd Polym 104:59–65. https://doi.org/10.1016/j.carbpol.2014.01.013

González I, Boufi S, Pèlach MA, Alcalà M, Vilaseca F, Mutjé P (2012) Nanofibrillated cellulose as paper additive in eucalyptus pulps. BioResources 7:5167–5180

González I, Vilaseca F, Alcalá M, Pèlach M, Boufi S, Mutjé P (2013) Effect of the combination of biobeating and NFC on the physico-mechanical properties of paper. Cellulose 20:1425–1435. https://doi.org/10.1007/s10570-013-9927-1

Guan M, An X, Liu H (2019) Cellulose nanofiber (CNF) as a versatile filler for the preparation of bamboo pulp based tissue paper handsheets. Cellulose. https://doi.org/10.1007/s10570-018-2212-6

Habibi Y (2014) Key advances in the chemical modification of nanocelluloses. Chem Soc Rev 43:1519–1542. https://doi.org/10.1039/C3CS60204D

Halip JA, Hua LS, Ashaari Z, Tahir PM, Chen LW, Uyup MKA (2019) Effect of treatment on water absorption behavior of natural. In: Jawaid M, Thariq M, Saba N (eds) Mechanical and physical

testing of biocomposites, fibre-reinforced composites, 1st edn. Woodhead Publishing, Kepong, pp 141–156

Hassan ML, Mathew AP, Hassan EA, El-Wakil NA, Oksman K (2012) Nanofibers from bagasse and rice straw: process optimization and properties. Wood Sci Technol 46:193–205. https://doi.org/10.1007/s00226-010-0373-z

Hassan ML, Bras J, Mauret E, Fadel SM, Hassan EA, El-Wakil NA (2015) Palm rachis microfibrillated cellulose and oxidized-microfibrillated cellulose for improving paper sheets properties of unbeaten softwood and bagasse pulps. Ind Crops Prod 64:9–15. https://doi.org/10.1016/j.indcrop.2014.11.004

Hii C, Gregersen ØW, Chinga-Carrasco G, Eriksen Ø (2012) The effect of MFC on the pressability and paper properties of TMP and GCC based sheets. Nord Pulp Pap Res J 27:388–396

Ho T, Zimmermann T, Hauert R, Caseri W (2011) Preparation and characterization of cationic nanofibrillated cellulose from etherification and high-shear disintegration processes. Cellulose 18:1391–1406. https://doi.org/10.1007/s10570-011-9591-2

Huang X, Kocaefe D, Kocaefe Y, Pichette A (2018) Combined effect of acetylation and heat treatment on the physical, mechanical and biological behavior of jack pine (*Pinus banksiana*) wood. Eur J Wood Prod 76:525–540. https://doi.org/10.1007/s00107-017-1232-5

Jonoobi M, Harun J, Mathew AP, Hussein MZB, Oksman K (2010) Preparation of cellulose nanofibers with hydrophobic surface characteristics. Cellulose 17:299–307. https://doi.org/10.1007/s10570-009-9387-9

Kekäläinen K, Liimatainen H, Biale F, Niinimäki J (2015) Nanofibrillation of TEMPO-oxidized bleached hardwood kraft cellulose at high solids content. Holzforschung 69:1077–1088. https://doi.org/10.1515/hf-2014-0269

Khalil H, Aprilia N, Bhat A, Jawaid M, Paridah M, Rudi D (2013) A Jatropha biomass as renewable materials for biocomposites and its applications. Renew Sustain Energy Rev 22:667–685. https://doi.org/10.1016/j.rser.2012.12.036

Li J, Zhang L-P, Peng F, Bian J, Yuan T-Q, Xu F, Sun R-C (2009) Microwave-assisted solvent-free acetylation of cellulose with acetic anhydride in the presence of iodine as a catalyst. Molecules 14:3551–3566. https://doi.org/10.3390/molecules14093551

Liu K, Chen L, Huang L, Ni Y, Sun B (2015) Enhancing antibacterium and strength of cellulosic paper by coating triclosan-loaded nanofibrillated cellulose (NFC). Carbohyd Polym 117:996–1001. https://doi.org/10.1016/j.carbpol.2014.10.014

Mashkour M, Afra E, Resalati H, Mashkour M (2015) Moderate surface acetylation of nanofibrillated cellulose for the improvement of paper strength and barrier properties. RSC Adv 5:60179–60187. https://doi.org/10.1039/C5RA08161K

Missoum K, Martoïa F, Belgacem MN, Bras J (2013) Effect of chemically modified nanofibrillated cellulose addition on the properties of fiber-based materials. Ind Crops Prod 48:98–105. https://doi.org/10.1016/j.indcrop.2013.04.013

Nechyporchuk O, Pignon F, Belgacem MN (2015) Morphological properties of nanofibrillated cellulose produced using wet grinding as an ultimate fibrillation process. J Mater Sci 50:531–541. https://doi.org/10.1007/s10853-014-8609-1

Peredo K, Reyes H, Escobar D, Vega-Lara J, Berg A, Pereira M (2015) Acetylation of bleached Kraft pulp: effect of xylan content on properties of acetylated compounds. Carbohyd Polym 117:1014–1020. https://doi.org/10.1016/j.carbpol.2014.10.004

Rodionova G, Hoff B, Lenes M, Eriksen Ø, Gregersen Ø (2013) Gas-phase esterification of microfibrillated cellulose (MFC) films. Cellulose 20:1167–1174. https://doi.org/10.1007/s10570-013-9887-5

Rodríguez F, Cortés L, Guarda A, Galotto M, Bruna J (2015) Characterization of cetylpyridinium bromide-modified montmorillonite incorporated cellulose acetate nanocomposite films. J Mater Sci 50:3772–3780. https://doi.org/10.1007/s10853-015-8942-z

Rowell RM, Tillman A-M, Simonson R (1986) A simplified procedure for the acetylation of hardwood and softwood flaxes for flakeboard production. J Wood Chem Technol 6:427–448

Sain M, Fortier D (2002) Flax shives refining, chemical modification and hydrophobisation for paper production. Ind Crops Prod 15:1–13. https://doi.org/10.1016/S0926-6690(01)00090-5

Samyn P, Barhoum A, Öhlund T, Dufresne A (2018) nanoparticles and nanostructured materials in papermaking. J Mater Sci 53:146–184. https://doi.org/10.1007/s10853-017-1525-4

Scott WE, Trosset S (1989) The barrier and resistance properties of paper. In: Scott WE, Abbott JC, Trosset S (eds) Properties of paper: an introduction, 2nd edn. TAPPI Press, Atlanta, pp 101–108

Sehaqui H, Zhou Q, Berglund LA (2013) Nanofibrillated cellulose for enhancement of strength in high-density paper structures. Nord Pulp Pap Res J 28:182–189. https://doi.org/10.3183/NPPRJ-2013-28-02-p182-189

Soltani M, Andalib M, Ravanbakhsh M (2013) Some physical and mechanical properties of uncatalysed acetylated paper. BioResources 8:1274–1282

Su J, Mosse WK, Sharman S, Batchelor WJ, Garnier G (2013) Effect of tethered and free microfibrillated cellulose (MFC) on the properties of paper composites. Cellulose 20:1925–1935. https://doi.org/10.1007/s10570-013-9955-x

Syverud K, Stenius P (2009) Strength and barrier properties of MFC films. Cellulose 16:75–85. https://doi.org/10.1007/s10570-008-9244-2

Taipale T, Österberg M, Nykänen A, Ruokolainen J, Laine J (2010) Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. Cellulose 17:1005–1020. https://doi.org/10.1007/s10570-010-9431-9

Vallejos ME, Felissia FE, Area MC, Ehman NV, Tarrés Q, Mutjé P (2016) Nanofibrillated cellulose (CNF) from eucalyptus sawdust as a dry strength agent of unrefined eucalyptus handsheets. Carbohyd Polym 139:99–105. https://doi.org/10.1016/j.carbpol.2015.12.004

Wang B, Li R (2018) Inhibition of hornification of eucalyptus kraft pulp by acetylation. In: IOP conference series: earth and environmental science, vol 170, p 4. Chemical science and biochemical engineering

Wang H, Zhang X, Jiang Z, Yu Z, Yu Y (2016) Isolating nanocellulose fibrills from bamboo parenchymal cells with high intensity ultrasonication. Holzforschung 70:401–409. https://doi.org/10.1515/hf-2015-0114

Wang Z-W, Zhu M-Q, Li M-F, Wei Q, Sun R-C (2019) Effects of hydrothermal treatment on enhancing enzymatic hydrolysis of rapeseed straw. Renew Energy 134:446–452. https://doi.org/10.1016/j.renene.2018.11.019

Xiao L, Salmi J, Laine J, Stenius P (2009) The effects of polyelectrolyte complexes on dewatering of cellulose suspension. Nord Pulp Pap Res J 24:148–157. https://doi.org/10.1016/j.renene.2018.11.019

Yousefi H, Faezipour M, Nishino T, Shakeri A, Ebrahimi G (2011) All-cellulose composite and nanocomposite made from partially dissolved micro- and nanofibers of canola straw. Polym J 43:559–564. https://doi.org/10.1038/pj.2011.31

Žepič V, Fabjan ES, Kasunic M et al (2014) Morphological, thermal, and structural aspects of dried and redispersed nanofibrillated cellulose (NFC). Holzforschung 68:657–667. https://doi.org/10.1515/hf-2013-0132

Zhang G, Huang K, Jiang X, Huang D, Yang Y (2013) Acetylation of rice straw for thermoplastic applications. Carbohyd Polym 96:218–226. https://doi.org/10.1016/j.carbpol.2013.03.069

Zhou X, Lin X, White KL et al (2016) Effect of the degree of substitution on the hydrophobicity of acetylated cellulose for production of liquid marbles. Cellulose 23:811–821. https://doi.org/10.1007/s10570-015-0856-z