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ORIGINAL PAPER

Water resistant nanopapers prepared by lactic acid modified cellulose nanofibers

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Abstract The current work reports a novel, completely water based approach to prepare the water resistant modified cellulose nanopapers. Lactic acid in aqueous medium was attached on cellulose nanofibers surface with the aid of ultra-sonication and later oligomerized (polymerized) by compression molding under high temperature and pressure, to obtain the modified nanopapers with enhanced mechanical properties. The modified nanopapers showed an increase of 32% in the elastic modulus and 30% in the yield strength over reference nanopapers. Additionally, the modified nanopaper was hydrophobic in nature and had superior storage modulus under moist conditions. The storage modulus of wet modified nanopaper was three times (2.4 GPa) compared to the reference nanopapers (0.8 GPa) after 1 h immersion in water. Finally, the thermal stability of the modified nanopaper was also higher than reference nanopaper. The material reported is 100% bio-based.

Keywords Cellulose nanofibers · Lactic acid · Water resistant nanopaper · Mechanical properties

Introduction

The growing human population and increasing consumption has resulted in excessive use of our non-renewable natural resources. This demands the development of new and more sustainable materials from renewable resources. Cellulose, the most abundant renewable biomaterial in the world, has been widely studied as a raw material for new biomaterials, especially as a form of nano-sized cellulose crystals (CNCs) and fibers (CNFs). Nanocellulose has astonishing mechanical properties: an elastic modulus of around 150 GPa (Lee et al. 2014) and for that reason it has widely been studied as reinforcements for polymers (Lee et al. 2014), or as a sheet-like material termed as nanopaper (Sehaqui et al. 2012).

Nanopapers are prepared by removing water from nanocellulose suspensions, usually by vacuum filtration or evaporation. The morphology of the nanopapers indicate an intricate network of cellulose nanofibers, which high amount of interfibrillar bonding due to

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presence of hydroxyl groups on cellulose molecules. This bonding results in excellent mechanical properties; it has been demonstrated that nanopapers can have modulus of 9.4–14 GPa and strength of 103–449 MPa (Lee et al. 2014; Sehaqui et al. 2012). With such excellent properties and renewable nature, nanopapers have raised themselves as potential replacement for non-renewable materials applications such as food packaging and electronic displays (Sehaqui et al. 2014).

Despite high strength of the nanopapers, there exists a fundamental weakness: they lose their strength in damp conditions. Sehaqui et al. portrays this problem in their work, they found that in wet state tensile modulus of nanopapers was only 5% of the value in dry state (Sehaqui et al. 2014). Even in high humidity of 95%, the storage modulus was 25% of storage modulus in dry conditions. The reason behind this was explained by the fact that in presence of water molecules, the interfibrillar bonds between fibers are heavily weakened (Sehaqui et al. 2014). Due to absence of interfibrilar bonds the fibers easily slides under external stress resulting in diminished strength of the nanopaper. Additionally, water molecules plasticizes the amorphous regions of cellulose (Benítez et al. 2013). This inability to combat moisture negates the positive advantages of high strength nanopaper. Hence, it is of interest to prepare the water resistant nanopapers. In fact, it has been proposed that commercial viability of nanopapers can only be ensured if they have enhanced mechanical properties in the presence of water (absorbed moisture or liquid) (Benítez et al. 2013).

The hydrophilicity of cellulose surface and its ability to absorb water can be altered by chemically modifying the surface of nanocellulose. The functionalization of cellulose has been reported by using two mechanisms: covalent grafting of chemical entities and physical adsorption on the cellulose surface (Tingaut et al. 2012). Covalent grafting is a common approach to improve hydrophobicity of cellulose nanofibrils. Sehaqui et al. prepared hydrophobic nanopapers by modifying cellulose by mild esterification by alkyl chains, which showed decreased moisture intake (Sehaqui et al. 2014). Additionally, the wet strength was improved as much as 24 times when compared to reference. However, the esterification is usually done in organic solvent or monomer medium (Habibi 2014; Sehaqui et al. 2014), which are hazardous and costly. Therefore, use of water as medium is of great practical value.

This work uses esterification of CNF surface with lactic acid in water medium. Although, the esterification of CNFs is not a vastly studied topic, few researchers have published relevant results in solvent medium (Lönnberg et al. 2006; Peltzer et al. 2014; Teramoto et al. 2002). Esterification is a dehydration reaction which is often is not feasible in water medium, as the reaction product itself is a water molecule. The product water is in equilibrium with medium water and reaction is not preferred due to law of mass action (Kobayashi et al. 1997). However, esterification in water medium has been done with the help of catalysts. Kobayashi et al. (1997) used lipase based enzyme for polycondensation, and Tanaka and Kurihashi (2003) used dodecylbenzenesulfonic acid as catalyst and surfactant.

This work attempts a novel approach to prepare esterified CNF nanopapers, which includes the ultrasonication of CNFs in presence of lactic acid in water medium. Chemical reactions with the aid of acoustic energy relates to the field of sonochemistry. During sonication, cavities (vacuum pockets) are formed which have short life time. The cavities implode at an extremely high speed to form hotspots which have high temperatures and pressures, (5000 K and pressure of 1000 atmospheres). The process is known as cavitation. Such extreme conditions can produce chemical reactions that may otherwise not happen (Suslick 2000). After ultrasonication, modified nanopapers were made by removal of water under vacuum filtration and further processing at high temperature (150 °C) and pressure (10 MPa). The samples were characterized by tensile testing, swelling studies, dynamic mechanical analysis (DMA) under varying moisture and thermogravimetric analysis (TGA).

Experimental

Materials

L-(+)-Lactic acid (80%) was purchased from Sigma-Aldrich. Stannous chloride (Merck Millipore) was purchased from VWR. Bleached soft wood sulfite fibers were kindly supplied by Stora Enso (Oulu, Finland). The pulp (1.6 wt%) was grinded in Masuko grinder. The pulp was repeated fed in contact mode from 0-point, and distance was gradually decreased from − 20 (3 passes), − 40 (4 passes), − 60 (5 passes) and − 90 (7 passes). The chemical composition of the reference pulp was 95.0 wt% cellulose, 4.2 wt% hemicellulose, 0.3 wt% lignin and 0.5 wt% inorganics.

Modification of nanofibers and processing of nanopapers

After the fibrillation, cellulose nanofibers were diluted to the concentration of 0.4 wt% and LA was added according to formulation given in Table 1. It is worth mentioning that tests were conducted with different level of LA, it was found that there is no significant effect on the properties of modified nanopapers (especially modulus), perhaps due to the amount of LA attached to the surface of nanocellulose was not different; therefore for the purpose of simplicity, only a relevant formulation is reported in this study. Stannous chloride was added in trace amounts as catalyst for esterification (Yoo et al. 2006). The suspensions were stirred at 9000 rpm in Ultra-turrax homogenizer for 5 min, and further sonicated with the help of probe type sonicator (Heilscher UP 400 s). The sonication was stopped when the sonication energy reached 1100 J/ml. After the sonification the suspensions were kept in the oven at 100 °C for 36 h. The schematics are presented in Fig. 1. These suspensions, henceforth mentioned as LA modified CNFs, were used to make nanopapers.

Nanopapers (reference and modified) were prepared by diluting LA modified CNFs and reference CNF suspension to 0.2 wt% by vacuum filtering through a Durapore PVDF membrane filter (Fisher Scientific, Pittsburgh, USA) with a pore size of 0.65 µm (Fig. 1). The suspensions were degassed under the vacuum of 70 kPa for half an hour before the filtering. After the vacuum filtration, the wet cellulosic sheet was carefully peeled from the membrane and kept between two steel mesh cloths (mesh size 70 µm), which were further stacked in paper carrier board. The CNF sheet-steel mesh-paper board was kept under compression molding plates at temperature of 100 °C at the pressure of 10 MPa for 30 min to remove water. The LA-grafted nanopapers were further compression molded at 150 °C for 5 min, to increase the yield of esterification. In order to take account the effect of the sonication, two type of references were prepared, one sonicated suspension and one without sonication. All the nanopapers were stored in ambient conditions for 72 h before testing. The grammage (weight in grams per square meters) of nanopapers was between 27 and 30 gsm.

Table 1 Formulations of CNF suspensions with lactic acid before sonication

	Sample name	
Materials	Reference nanopaper	Modified nanopaper
CNF	0.4	0.4
L-Lactic acid	0	7.6
$SnCl_2$	0	0.0002
Water	99.6	92
Total	100 wt%	100 wt%

Characterization

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to confirm the esterification of CNFs. The filtered wet cake from nanopaper preparation was rolled into a spherical shape and kept in oven at 90–95 °C overnight to remove water. The modified CNFs were further kept at 150 °C for half an hour. It was done as because the restriction from the equipment that FTIR data from thin nanopapers was not feasible. The hardened reference and modified CNFs were grinded into powder, and the spectra were collected from dried samples with Bruker Vertex 80 V spectrometer (USA), in the 400–4000 cm^{-1} range, and 40 scans were taken at a resolution of 4 cm^{-1} for each sample.

Wide angle X-ray diffraction (WAXRD) was used to determine the crystalline structure of the reference and the modified nanopaper. Rigaku SmartLab 9 kW rotating anode diffractometer (Japan) using a Co Kα radiation (40 kV, 135 mA; $\lambda = 1.79030$ Å) was used for measurements. Bragg's angle (2θ) was varied from 10° to 50°, with a step width of 0.02°. The scanning speed was kept at 2° min^{-1}. The degree of crystallinity (CrI) was calculated from the peak intensity of the main crystalline plane (200) diffraction (I_{200}) which was at 26.2° and from peak intensity at 22° C, which is associated to amorphous fraction of cellulose (I_{am}) (French 2014), according to the Eq. 1:

$$CrI = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) \quad (1)$$

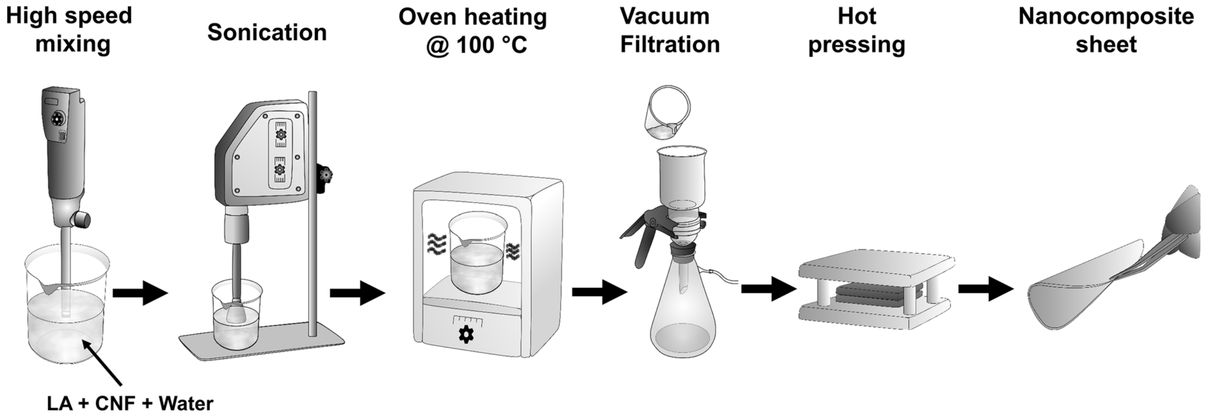

Fig. 1 Schematic diagram of process used for preparation of nanopapers

We would like to mention that due to the Co Kα radiation source, the peak of cellulose have different diffraction angles compared to the peaks obtained for Cu Kα radiation source.

The average size of crystallite (L) was calculated from the Scherrer equation (Ahtee et al. 1983):

$$L = \frac{K \times \lambda}{\beta \times \cos\theta} \tag{2}$$

where K is a constant value 0.74, λ is the X-ray wavelength (0.17903 nm), β is the half-height width of the diffraction band (200); and θ is the Bragg angle corresponding to the (200) plane.

Mechanical testing was done to evaluate tensile properties of the CNF networks using Instron 5544 universal material testing machine (Norwood, USA). Strips with a length of 50 mm and a width of 5 mm were conditioned at 23 °C and relative humidity (RH) of 50% for 72 h prior to the testing. A load cell of 100 N was used, the crosshead speed was 2 mm/min and the gauge length of 30 mm. The tests were conducted in special chamber maintained at a RH 50% and in the temperature of 23 °C. The elastic modulus (E) was determined from slope in linear region and yield strength $\sigma_{0.2}$ was determined by intersection of 0.2% offset line and stress strain curve. The results are reported as average of minimum 5 samples.

Zeiss Ultra Plus (Oberkochen, Germany) field emission scanning electron microscopy (FE-SEM) was used for analysis of fiber-polymer network morphology of the samples. The acceleration voltage of 3 kV was used. The samples were coated with platinum to avoid charging. Inlens detector was used to collect the signals for imaging.

Dynamic mechanical analysis (DMA) under variable humidity was conducted in order to determine the effect of humidity on storage modulus of reference and modified nanopaper using DMA Q800, TA Instruments (New Castle, USA) (equipped with RH accessory) along with strain mode with amplitude of 10 μm and frequency of 1 Hz. The samples were equilibrated at 30 °C and 0% relative humidity for 2 h to remove the absorbed moisture. Subsequently, relative humidity was raised from 0 to 95% at the rate of 1%/min and the storage modulus was recorded. The mechanical properties in wet condition were studied using same equipment and the isothermal tests were conducted in tension mode at an amplitude of 20 μm and using a frequency of 1 Hz.

Thermogravimetric analysis (TGA) of the nanopapers (reference and modified) was conducted in order to determine the thermal stability of samples using TA-TGA Q500 (New Castle, USA). Sample weighing around 10 mg was kept on a hanging platinum pan and heated till the temperature of 900 °C under the nitrogen atmosphere, with the heating rate of 10 °C/min. The moisture content of samples was determined by weight loss between 0 and 200 °C.

Results and discussion

Modification of CNFs

The esterification reaction between hydroxyl groups of CNF and carboxylic groups of LA was confirmed by

FTIR is shown in Fig. 2. A peak around 1750 cm^{-1} (indicated by dotted line in Fig. 2) can be seen in modified nanopaper sample, which indicates the presence of ester bond (Tjeerdsma and Militz 2005). A small peak can already be observed in FTIR spectra after sonication treatment of CNFs with lactic acid (see Figure 1 supplementary information). High temperature and pressure on nanopapers (after water removal) was used to shift the reaction towards higher conversion.

Crystal structure

The effect of LA modification on crystal structure of nanopaper was studied using WAXRD and the patterns of reference and modified nanopaper are shown in Fig. 3. Both samples exhibited typical cellulose I crystalline structure (French 2014). CrI calculated by Segal equation (Eq. 1) indicated different amount of crystallinity between samples (79.5 and 47.8% for modified nanopaper and reference, respectively). However, from the Fig. 3 it can be seen that relative heights between 1 and 10/110 doublet and the 200 main peak varies significantly between samples. This might indicate that there is substantial preferred orientation of the samples, caused be sample fabrication. The presence of preferred orientation can have significant effect on the CrI calculation (Park et al. 2010). To verify this, we attempted to grind the samples; however, the preferred orientation remained. Our mill also apparently substantially reduced the crystallinity of the samples. However, based on the Scherrer equation (Eq. 2), both samples exhibited similar crystallite size (around 3 nm), indicating that no significant amount damage on the cellulose crystals was caused by ultrasonic treatment.

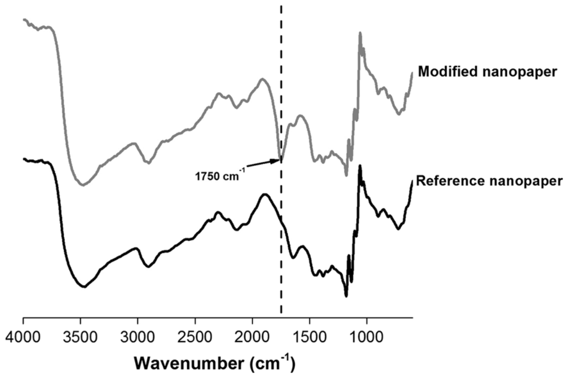

Fig. 2 FTIR spectra of reference and modified nanopapers. The esterification peak is marked with dotted line around 1750 cm^{-1}

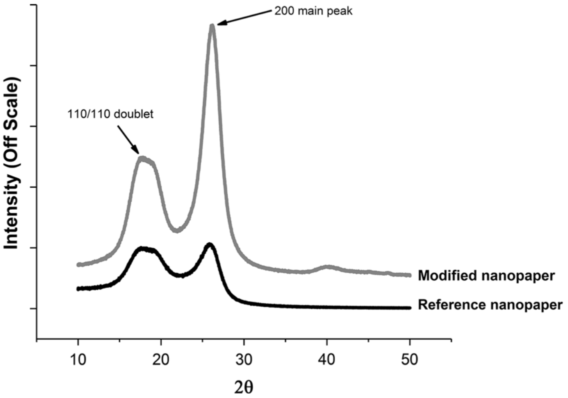

Fig. 3 XRD diffraction patterns of reference and modified nanopapers

Mechanical properties

Compared to reference nanopaper, modified nanopaper had higher modulus (Fig. 4). The increase is around 32% (quantitative results are presented in Table 2). It can be speculated that the LA under the high temperature of 150 °C and pressure of 10 MPa is polymerizing (or oligomerizing), as it has been reported that high temperature and pressure advances the esterification reaction (Ballard et al. 1961). The hydroxyl group from cellulose are also likely to participate in the reaction and forming a strong covalent bond and entire structure can be considered

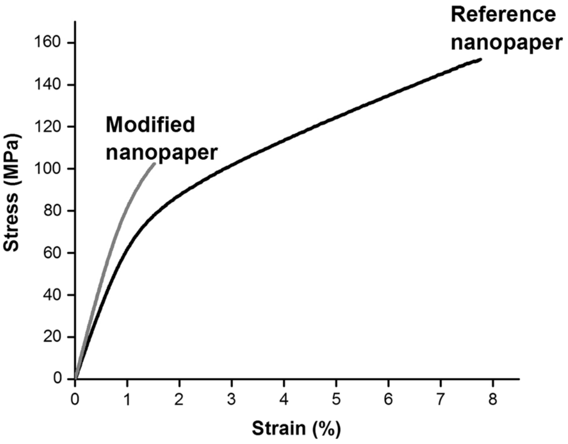

Fig. 4 Stress-strain curve of reference and modified nanopaper. Modified nanopaper has higher modulus and yield strength, and lower elongation

Table 2 Quantitative results from stress strain analysis enlisting values (along with standard deviation) elastic modulus, elongation to break, tensile strength, toughness and yield strength of reference and modified nanopapers

Materials	E-modulus* (GPa)	Elongation to break* (%)	Tensile strength* (MPa)	Toughness*	Yield strength (MPa)	Density (gm/cm^3)
Reference (unsonicated)	6.8 (0.6)^a	8.7 (1.1)^a	170 (18)^a	985 (219)^a	80 (5)^a	1.34
Reference (sonicated)	6.4 (0.3)^a	11 (2.5)^b	177 (19)^a	1234 (360)^a	77 (5)^a	1.4
Modified nanopaper	9 (0.4)^c	1.7 (0.2)^c	111 (7)^c	101 (24)^c	104 (3)^c	1.28

* Means that are marked by different superscript letters within the same column are significantly different at 5% level based on the one-way ANOVA

as one rigid hybrid network where hydrogen bonding of CNFs is replaced by covalent bonds, which is restricting movement of CNFs in external load and hence the elastic modulus is increasing. The reaction scheme is provided in Fig. 5.

It should also be observed that the yield strength is improved in modified nanopaper by 30% (Table 2). The strength, determined by interfibrillar sliding (Benítez et al. 2013), implies that the modified nanopapers are more resistant to permanent deformation. This restricting of chains is clearly observed in tensile testing fractured samples in Fig. 7, where the reference nanopaper has separated fibrils at fractured cross-section, on the other hand, in modified nanopapers the fibers are heavily bonded to each other. The results implies that modifying the surface of CNFs can be beneficial in making stiffer nanopapers.

The effect of sonication on cellulose was also studied. As mentioned before, sonication is an intensive technique and provides energy of 10–100 kJ/mol (Suslick 2000; Tischer et al. 2010), which is of order of hydrogen bonding (Tischer et al. 2010; Przybysz et al. 2016). Wang et al. concluded that sonication can cause structural change in cellulose fibril by causing defibrillation (Wang and Cheng 2009). Therefore, our first step was to analyze the effect of sonication by preparing a nanopaper with same amount of sonication as modified samples. The results is presented in Table 2: the elastic modulus (E) of sonicated nanopaper is approximately 5% less than non-sonicated one. However, it is worth mentioning that the sonicated

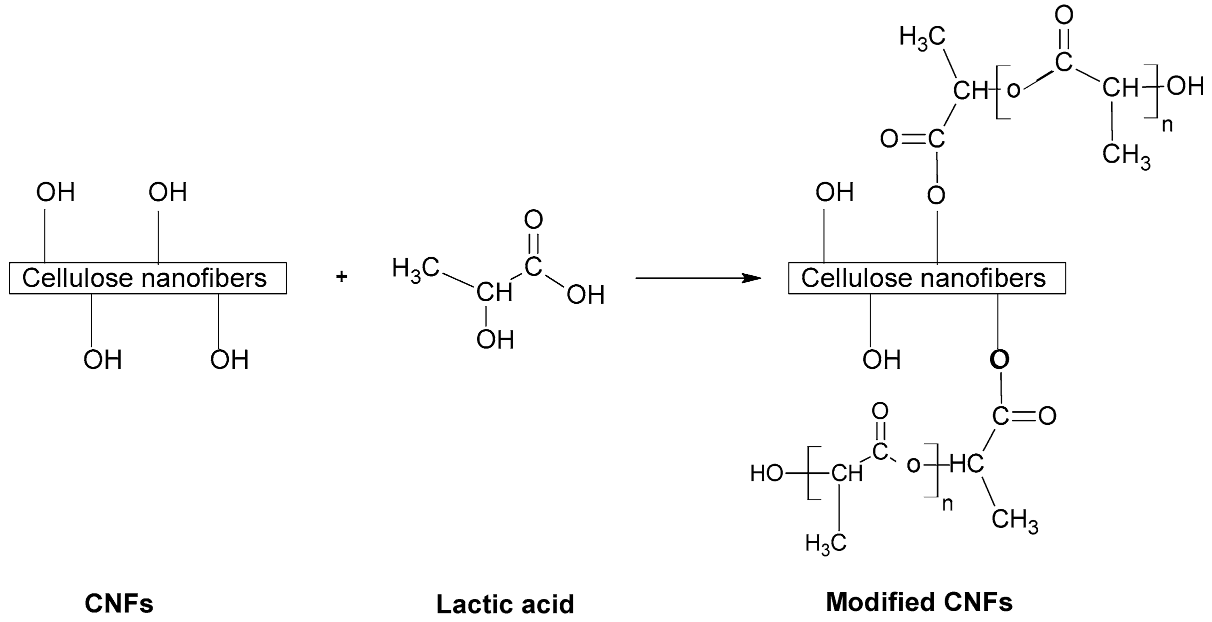

Fig. 5 Reaction scheme of CNF with LA under high pressure and temperature

reference nanopaper has higher density (5%) so loss in modulus is more marked when density is considered.

Finally, the results of this study are particularly outstanding as modified nanopaper reported is 100% bio-based, offer diverse opportunities as applications such as packaging.

Morphology

The reference was transparent but modified nanopaper was translucent (Fig. 6); which might indicate the presence of separate phases of lactic acid and nanocellulose (Yang et al. 1996). Another possible reason can be that the modified nanopaper is porous and trapped air. The difference in density indicate the slight porosity. The reference nanopaper had density of 1.34 gm/cm^3 and modified nanopaper had 1.28 gm/cm^3.

Both reference and modified nanopaper had layered structure Fig. 7a, b, which is due to “concentration induced aggregation and floc formation” during filtration (Benítez et al. 2013). The reference has loosely adhered layers, indicating the debonding between the layers under the tensile load, which is likely due to breaking of inter layer hydrogen bonds. Additionally, the fracture mechanism is debonding of layers along with pull out of fibers. Small fibrils can be seen protruding from inset image of reference, no such fibrils are present in modified nanopaper. In modified nanopapers, fibrils appears to be tightly glued which indicates lack of slipping. This slipping can be attributed to high elongation of around 8% (Fig. 7), which is missing in modified nanopaper. The modified nanopaper, on the other hand, has compact structure in which layers are tightly adhered to each other (Fig. 7b). The esterification of surface, and LA moieties are binding the layers to each other which is the reason for enhanced mechanical properties (Fig. 4). Additionally, the fracture mechanism seems to more brittle as no fibrils are bulging from the surface (compared to reference) and nanofibers are in a way glued to each other. This might be the reason for brittle fracture, as they are unable to slide and fracture from cross-section instead of pull out.

Fig. 6 Photographic images of the reference nanopaper, and modified nanopaper

Effect of moisture and water content

The modified nanopaper was more resistant to moisture absorption from atmospheric humidity as compared to nanopaper (Fig. 8a). It absorbed 43% less moisture compared to reference nanopaper, indicating the hydrophobicity of samples. It has been mentioned that fewer hydroxyl group on the surface of CNFs are accessible in the presence of polymer (oligomer) leading to lower moisture absorption (Henriksson and Berglund 2007). Additionally, Fig. 8b presents the graph depicting amount of water absorbed by samples when soaked in water. The trend is corresponding to moisture content results; modified nanopaper are considerably hydrophobic than reference. The modified nanopaper has 35% less water after 18 h of absorption.

The modified nanopaper has better mechanical performance under humidity (Fig. 9a), when compared to reference nanopaper. It can be observed that humidity has devastating effect on stiffness of nanocellulose paper, which has been reported in literature (Benítez et al. 2013); however, reference nanopaper showed an interesting behavior that at relative humidity of around 75%, it has a sharp drop in storage modulus which indicates the sample loses its stiffness suddenly. A reason might be that the water molecules are penetrating inside the material destroying the structure and acting as plasticizer, resulting in loss in storage modulus (Sehaqui et al. 2014). The results are in agreement with (Benítez et al. 2013), who also reported a steep drop in mechanical properties of nanopaper from 80% RH to 95% RH. The modified nanopaper has higher storage modulus than reference over the entire range of humidity.

Figure 9b presents the evolution of wet storage modulus of water soaked modified nanopaper and reference after various time intervals. It can be observed that there is a huge drop in modulus in both reference and modified nanopaper; however, the modified nanopaper have superior properties in wet state as the storage modulus is three times that of reference nanopaper even when samples are soaked in water for 21 days. The water affects the mechanical properties in two ways, by plasticizing the amorphous

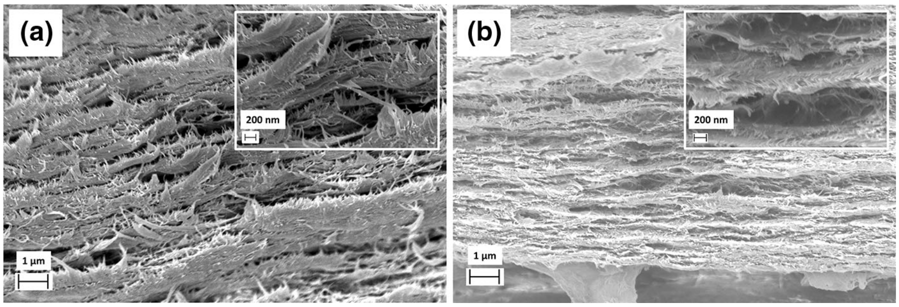

Fig. 7 FESEM micrographs of fractured surface from tensile samples of **a** Reference nanopaper and **b** Modified nanopaper. Two different scales are shown: the bigger image represents the coarser scale (1 µm) and inset image represents finer scale (200 nm). The reference material with typical layered structure of the nanopaper with the individual fibers. In contrast, modified nanopapers have the individual fibers and layers tightly glued to each other due to esterification

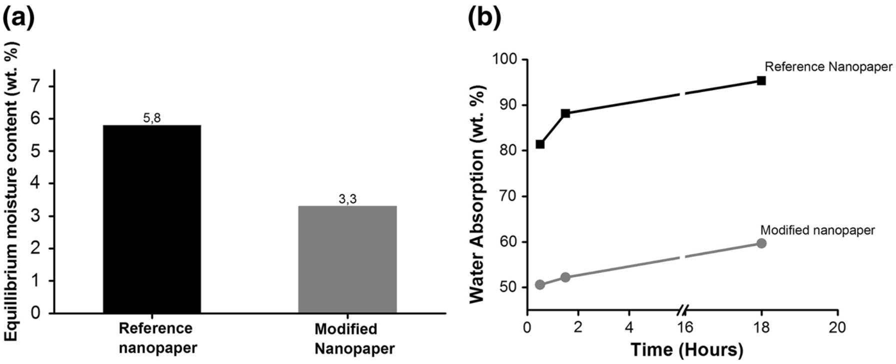

Fig. 8 **a** Moisture content of reference nanopaper and modified nanopapers after storing at 20 °C temperature and RH 50% for 96 h; reference has considerably high amount of moisture uptake than the modified nanopaper indicating the hydrophobic nature and, **b** Amount of water absorption as a function of time by reference nanopaper and modified nanopaper when soaked under water

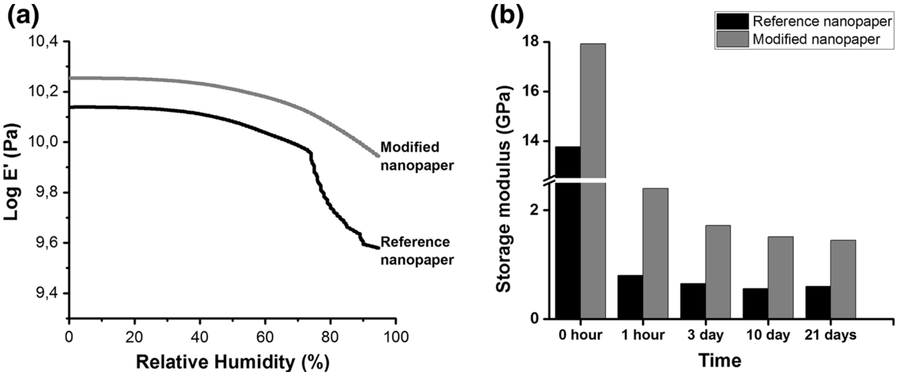

Fig. 9 **a** Variation of storage modulus with respect to relative humidity of modified nanopaper and reference nanopaper. **b** Evolution of wet storage modulus from of modified nanopaper and reference nanopaper, when kept in water for extended period of time

regions and by affecting hydrogen bonding among the nanofibrils (Benítez et al. 2013). This gives an understanding about our results. In modified nanopapers, the humidity was able to plasticize the amorphous region of cellulosic domains; however, due to presence of LA moieties at interface, it did not alleviate the bonding between fibril as it does in reference. Hence, the modified nanopaper was able to maintain higher stiffness when compared to reference. The results indicate that modified nanopaper has far better performance than reference under the influence of water.

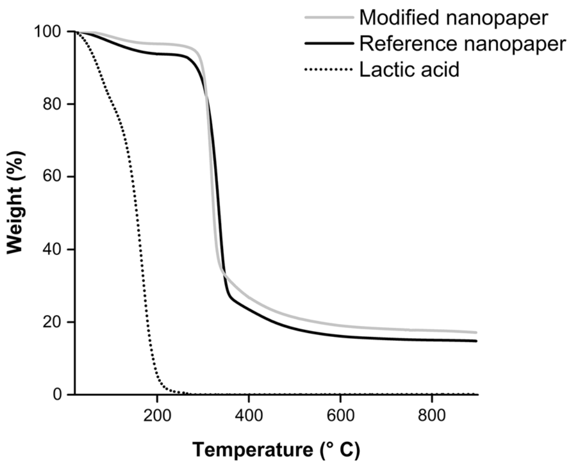

Fig. 10 Thermogravimetry results indicating thermal stability of modified nanopaper along with reference nanopaper and lactic acid; the results have been normalized after removing moisture content. Modified nanopaper has higher stability than reference nanopape. Lactic acid thermogram is also included

Thermal stability

Figure 10 shows that modified nanopapers are more thermally stable than the reference nanopaper. The reference nanopaper lost 5 wt% of weight at 147 °C. On the other hand, modified nanopaper took 279 °C, almost twice the temperature taken by reference (90% higher) to lose 5% of weight. It is worth mentioning that the results have been normalized after removing the amount of moisture in the samples. Esterified nanocellulose has been reported to have better thermal stability than reference (Agustin et al. 2016). It is worth noticing that at temperatures higher than 310 °C, reference has slower degradation than modified samples which can be as a result from steeper degradation of LA phase.

Conclusion

This study presents a novel approach to prepare modified nanopapers with enhanced properties. Lactic acid monomer in aqueous medium was used, along with aid of ultrasonication and compression molding. The modified nanopaper has higher modulus and yield strength, however, it lost the tensile strength. Additionally, the modified nanopaper performed superiorly under humid environment and presence of water. At 95% RH the storage modulus of modified nanopaper was three times that of reference. Similar results were obtained for water soaked samples. Finally, the modified nanopaper was thermally stable than when compared to reference nanopaper. The effect of parameters such as sonication, temperature and catalyst is currently being pursued.

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