



Received:  
24 June 2015  
Revised:  
24 September 2015  
Accepted:  
15 October 2015

Heliyon (2015) e00038



# High strength paper production based on esterification of thermomechanical pulp fibers in the presence of poly(vinyl alcohol)

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## Abstract

Thermomechanical pulp (TMP) fibers, generally used to produce newspapers and carton materials, have poor inter- and intra-fiber bonding contributing to low strength properties. Poly(vinyl alcohol) (PVOH) was applied as a co-additive of 1,2,3,4-butanetetracarboxylic acid (BTCA), in the presence of sodium hypophosphite (SHP) as a catalyst, to esterify paper sheets based on TMP fibers. Fourier transform infrared (FTIR) spectroscopy technique was used to confirm the formation of the ester bond. The effects of curing temperature, molar mass and mass amount of the PVOH on the tensile index were investigated. The increasing of the curing temperature improved further the wet tensile index. The presence of PVOH increased both the dry and the wet tensile index of the paper sheets. The rise of both the molar mass and the mass amount of PVOH improved the tensile index.

Keywords: Materials chemistry, Materials science, Polymers, Biomaterials

## 1. Introduction

In pulp and paper industry, thermomechanical pulp (TMP) fibers are generally used to produce newspapers and packaging materials. While the use of newspapers has shown a decrease due to the trend in the use of new technology (computer, smart phone, tablet . . . ), the use of packaging materials has shown a continuous increase. Nevertheless, packaging industry used petroleum-derived as raw material which can involve some environmental problem due to the non-degradability of the final product. Therefore, packaging based on TMP fiber offers an environmental advantage. In addition, the high yield and significant energy reductions, regarding the kraft fibers, offer environmental and economic reasons to use these fibers. However, the presence of lignin, decreases the inter- and intra-fiber bonding leading to low strength properties (Paszner and Behera, 1985; Toth et al., 2007; Awada et al., 2012; Montplaisir et al., 2008). Past research showed the possibilities to improve the strength properties, of paper sheets based on TMP fibers, by chemical modification (Sang and Xiao, 2009), by physical adsorption of cationic component (Gandini and Pasquini, 2012) or by oxidation (Ma and Zhai, 2013).

In our previous work, polycarboxylic acids such as 1,2,3,4- butanetetracarboxylic acid (BTCA) and citric acid (CA), were used to chemically cross-linked paper sheets prepared from TMP fibers in the presence of SHP as catalyst (Awada et al., 2014). This esterification improved the wet tensile index of paper sheets. Nevertheless, the dry properties of treated paper sheets were slightly increased or decreased after esterification. In addition, BTCA was found to be more effective than CA. The use of polycarboxylic acid to esterify cellulose and the esterification mechanism were shown by others in the literature (Zhou et al., 1995; Peng et al., 2012).

It was demonstrated that poly(vinyl alcohol) (PVOH) can improve the dry tensile index of paper based on kraft pulp (Xu et al., 2001). Polyvinyl alcohol is the largest synthetic biodegradable and water soluble polymer produced in the world (Ding et al., 2002; Shi et al., 2008). Moreover, PVOH was also used as reinforcing agent of paper.

The main objective of this study is to use BTCA in combination with PVOH to improve both the dry and the wet tensile index of paper based on TMP fibers. Because PVOH and TMP fibers are both containing hydroxyl groups, BTCA can be expected to cross-link them, and further improve the interfibers bonds. Depending on the experimental conditions, in the presence of SHP, BTCA should cross-link cellulose fibers and PVOH chain through ester linkages.

The influence of curing temperature, molar mass of the PVOH and mass amount of PVOH, on the mechanical properties of paper sheets based on TMP fibers,

will be studied. In particular the value of both the dry and the wet tensile index properties of paper sheets after each treatment will be reported and compared.

## 2. Materials and methods

### 2.1. Materials

Unbleached TMP was collected from Kruger (Trois-Rivières, Québec). Pulp consistency was approximately 32–38%. 1,2,3,4-butanetetracarboxylic acid (BTCA, purity = 99%), was purchased from Sigma-Aldrich. Sodium hypophosphite monohydrate ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , purity > 99%) was supplied by American Chemicals Ltd. Poly(vinyl alcohol) (99% hydrolysed, 10,000 g/mol (PVOH 10k) and 77,000 g/mol (PVOH 77k)) was acquired from Avantor. All of these products were used as received.

### 2.2. Methods

#### 2.2.1. Paper sheets process

Paper sheets with a grammage of 60 g/m<sup>2</sup> each were made in a British sheet-mould according to TAPPI Standard T 205 (1995). Then, the paper sheets were conditioned overnight in a conditioning room at 23 °C and 50% relative humidity (according to TAPPI Standard T 402 (2003)) prior to testing or treatment.

#### 2.2.2. Paper sheets treatment and esterification

The esterification reactions of the paper sheets and the preparation of control paper sheets are described in our previous work (Awada et al., 2014). Briefly, solutions containing PVOH (10k or 77k), BTCA and SHP were prepared. The mass amount of BTCA and SHP was fixed to 10% of the paper weight. The mass amount (wt%) of PVOH was modified (1, 3 and 5%) for a given temperature (200 °C). The influence of temperature was investigated by testing three curing temperature (150 °C, 180 °C and 200 °C) for a given amount of PVOH (5%). The pH of all the solution was adjusted to 2.4 (Pantze et al., 2008; Yang, 1993). For each experimental condition five paper sheets are treated and analyzed. In addition, each condition was replicated three times.

#### 2.2.3. Fourier transform infrared spectrometry (FTIR)

Transmittance infrared spectra were performed using a Perkin Elmer 2000 Fourier transform infrared (FTIR) spectrometer. The FTIR analysis was used to verify the formation of ester bond after esterification. All samples were treated with a 0.1 M NaOH solution for 5 minutes before FTIR analysis as described in our past work (Awada et al., 2014).

### 2.2.4. Paper sheets characterization

Wet and dry tensile index were performed using an Instron 4201 according to the TAPPI T494os70 method (2001) as described in our previous work (Awada et al., 2014).

### 2.2.5. Scanning electron microscopy characterization

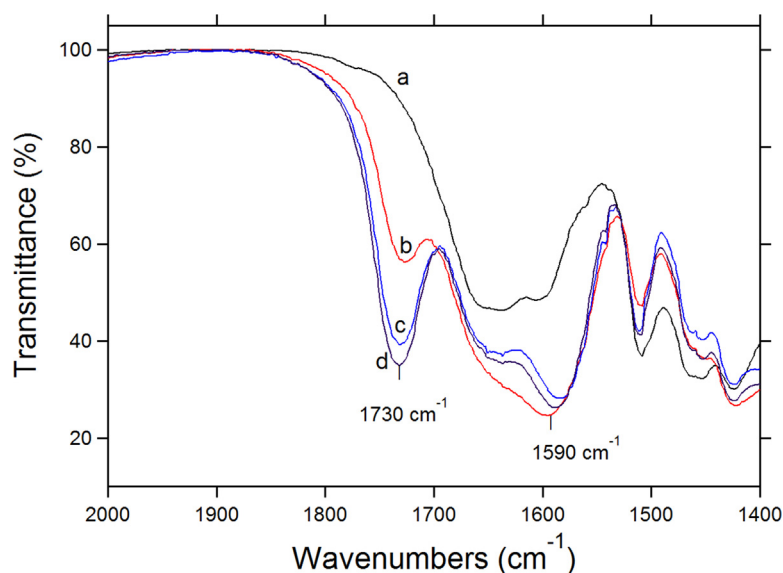
Scanning electron microscope (SEM) analysis was performed using a JEOL JSM-5500 with a voltage of 15.0 kV. Three different locations on top side of the paper sheet surface were analyzed.

## 3. Results and discussion

### 3.1. FTIR analysis

FTIR spectra of paper sheet treated with a 10% BTCA/10% SHP/5% PVOH 77k and cured at different temperature [(b) 150 °C, (c) 180 °C and (d) 200 °C] are shown in Fig. 1. FTIR spectra of an untreated paper sheet is also shown in Fig.1a, for comparison.

From the spectra, the formation of the ester bond was clearly detected. In addition, it is evident that, the intensity of both peaks ( $1730\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$ ) was increased with the augmentation of the temperature (Fig. 1, spectra b, c, d). These results showed that the increasing of the temperature (from 150 to 200 °C) improved the formation of the ester function, as expected. The carboxylic function



**Fig. 1.** Partial FTIR spectrum of (a) control paper sheet and of paper sheets treated with BTCA (10%)/SHP(10%)/PVOH 77k(5%) and cured during 5 min: (b) 150 °C, (c) 180 °C and (d) 200 °C.

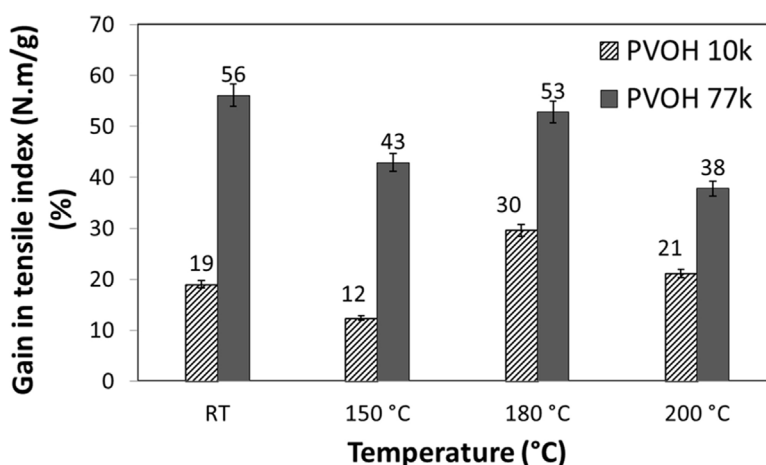
was also increased after treatment. Further, for the paper sheets treated with the PVOH 10k g/mol, the same results were observed (spectra not presented here). When the temperature was increased the intensity of the ester function peaks was increased. On the other hand, FTIR spectra (not presented here) of paper sheets treated with different percentage of PVOH (10k or 77k) showed that the intensity of the peaks at  $1730\text{ cm}^{-1}$  was close.

## 3.2. Tensile index measurement of the paper sheets

### 3.2.1. Influence of the curing temperature and the PVOH molar mass

The values of the dry tensile index are presented as a gain (%) to the control paper sheet. Fig. 2 shows the variation of these gains as function of the cured temperature for the two molar mass of the PVOH (10k and 77k). The dry tensile index of the control paper sheet was  $36 \pm 2\text{ N.m/g}$ .

We observed that the dry tensile index was depended on the presence of PVOH, molar mass of PVOH and curing temperature. It is evident that the presence of PVOH improves the dry strength of the paper before and after crosslinking. Indeed, it is proposed that PVOH can lead to overall better strength properties for two reasons. Firstly, before the curing, PVOH enhances fiber to fiber bonding through hydrogen bonding. Furthermore, after curing, PVOH reacts with part of the carboxylic acid groups of BTCA, thus forming long-range fiber to fiber crosslinkages. Secondly, before and after curing, the presence of PVOH contributes to the stress dissipation of the fiber network. To further support the



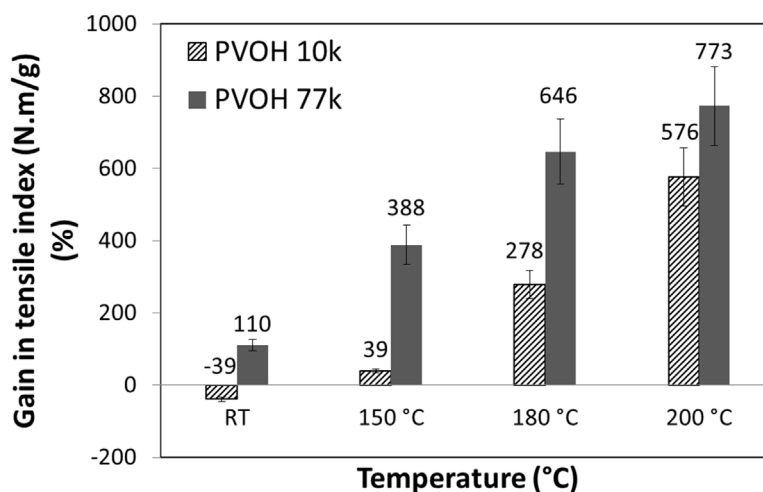
**Fig. 2.** Gain in dry tensile index (presented as percentage compared to the control paper sheet) of the paper sheets as a function of the temperature. The paper sheets were treated with a 10% of BTCA, in the presence of SHP (10%) and PVOH (5%). The dry tensile index of the control paper sheet was  $36 \pm 2\text{ N.m/g}$ .

above hypothesis on the influence of PVOH, esterification was done at 180 °C, without the presence of PVOH for comparison. The dry tensile index was slowly decreased by 7%. This result supported that the presence of PVOH is necessary to improve the dry tensile index of paper sheets. On the other hand, high molar mass leads to better results as expected. Indeed, the length of the polymer chain and the increasing of PVOH viscosity can be at the origin of this difference. Actually, a polymer chain with a high length may increase the hydrogen bond between the fibers. In addition, a high length of polymer chain may improve the stress dissipation (Brogly et al., 2006). Also, the viscosity plays a role in the diffusion of polymer chain between the fibers. While the low molar mass can easily diffuse into the network, the high molar mass tends to stay on the fiber surface.

Moreover, the modification of curing temperature showed a modification in the variation of the dry tensile index. Two reasons may explain this variation. Firstly, the amount of the ester bond after curing. Secondly, the retention amount of PVOH in the paper. While the ester bond may contribute to a slow decreasing of the dry tensile index (as demonstrated with the sample esterified without the presence of PVOH) the amount of PVOH should increase the dry tensile index. For a curing temperature of 150 °C, the dry tensile index is slowly decreased. This is due to the high melting point of BTCA (195 °C) (Yang and Wang, 1998). This can be contributing to a low degree of esterification and then a high quantity of PVOH can be removed with the water after curing (the gain in paper sheet mass was 3.7% and 5.7% for PVOH 10k and PVOH 77k, respectively). When the temperature was increased to 180 °C, the amount of the ester bond and the PVOH retention was increased (the gain in paper sheet mass was 9.7% and 13.2% for PVOH 10k and PVOH 77k, respectively). When the temperature increased further to 200 °C, the amount of the ester increased and the network became brittle. The gain in paper sheet mass was also increased (13% for PVOH 10k and 15.4% for PVOH 77k).

The values of the measured wet tensile index are presented as a gain (%) to the control paper sheet. Fig. 3 shows the variation of these gains with the variation of the cured temperature. The PVOH amount was 5%.

We can clearly observe that the wet tensile index depends on the presence of PVOH, the molar mass of PVOH and curing temperature. For the uncured samples, a difference was observed between PVOH 10k and PVOH 77k. This difference could be related to the high viscosity of PVOH 77k. Moreover, for the cured sample, we can also observe a relation between the temperature applied during curing and the wet tensile index. One can observe that the wet tensile index increases remarkably as the curing temperature increases. A meaningful raise was observed when the temperature was increased from 150 °C



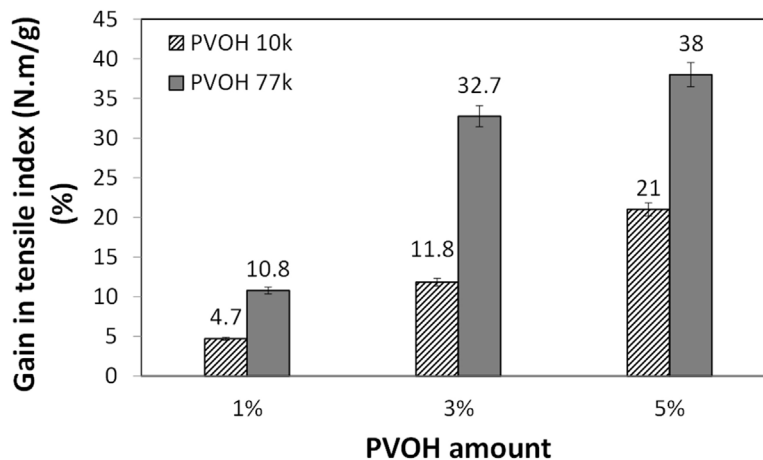
**Fig. 3.** Gain in wet tensile index (presented as percentage compared to the control paper sheet) of the paper sheets as a function of temperature. The paper sheets were treated with a 10% of BTCA, in the presence of SHP (10%) and PVOH (5%). The wet tensile index of the control paper sheets was  $3.74 \pm 0.5$  N.m/g.

(39% for PVOH 10k and 388% for PVOH 77k) to 180 °C (278% for PVOH 10k and 646% for PVOH 77k) and further to 200 °C (576% for PVOH 10k and 773% for PVOH 77k). At 180 °C we started to be close to the melting point of the BTCA. The main reason for this improvement was related to the raise of the ester function and the PVOH amount. These results are in good agreement with those observed in FTIR. These results are not surprising while the presence of water decreases the influence of hydrogen bonds; (Awada et al., 2011) the physical properties of the paper sheets are governed by the chemical bonds (fibers–fibers, fibers–PVOH–fibers, fibers–PVOH) and the presence of PVOH. For comparison, the esterification of the paper sheet, using a curing temperature of 180 °C, without the presence of PVOH led to a gain in the tensile index equal to 140% (the presence of PVOH 77k increased this gain to 646%).

### 3.2.2. Influence of the PVOH amount

The influence of mass amount (1%, 3% and 5%) of both PVOH 10k and PVOH 77k, during the esterification, on both the dry and the wet tensile index of the paper sheets was also investigated. Fig. 4 shows the variation of gain in dry tensile index in function of the variation of PVOH amount. The curing temperature was 200 °C.

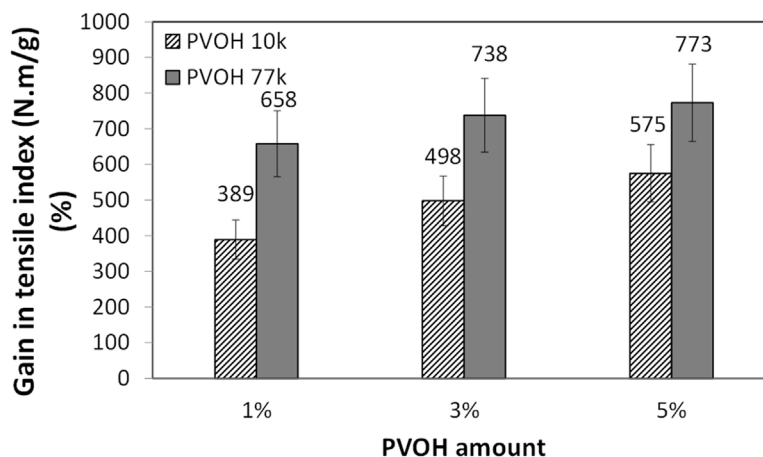
Whatever the molar mass of PVOH, we can clearly observe that, the rise of the percentage of the polymer increased the dry tensile index. It is evident that, this improvement is related to the presence of PVOH.



**Fig. 4.** Gain in dry tensile index (presented as percentage compared to the control paper sheet) of the paper sheets as a function of PVOH amount. The paper sheets were treated with a 10% of BTCA, in the presence of SHP (10%) at 200 °C.

The values of the gain in the wet tensile index with the variation of PVOH amount are shown in Fig. 5.

One can observe that the wet tensile index increased slightly when PVOH amount increased from 1% to 3% and to 5%. The results are in good agreement with those obtained in the literature. Xu et al. (2001) used PMA in the presence of PVOH to crosslink kraft fibers. The author claimed a competition between cellulose fibers and PVOH during the esterification with the carboxylic function of the polycarboxylic acid. Herein, PVOH should react with BTCA to participate in the crosslinking of the cellulose fibers, thus contributing to the increasing of the interfiber bonding. However, not all of PVOH molecules can



**Fig. 5.** Variation of wet tensile index (presented as percentage of the controls paper sheets) of the paper sheets as a function of PVOH amount. The paper sheets were treated with a 10% of BTCA, in the presence of SHP (10%) at 200 °C.

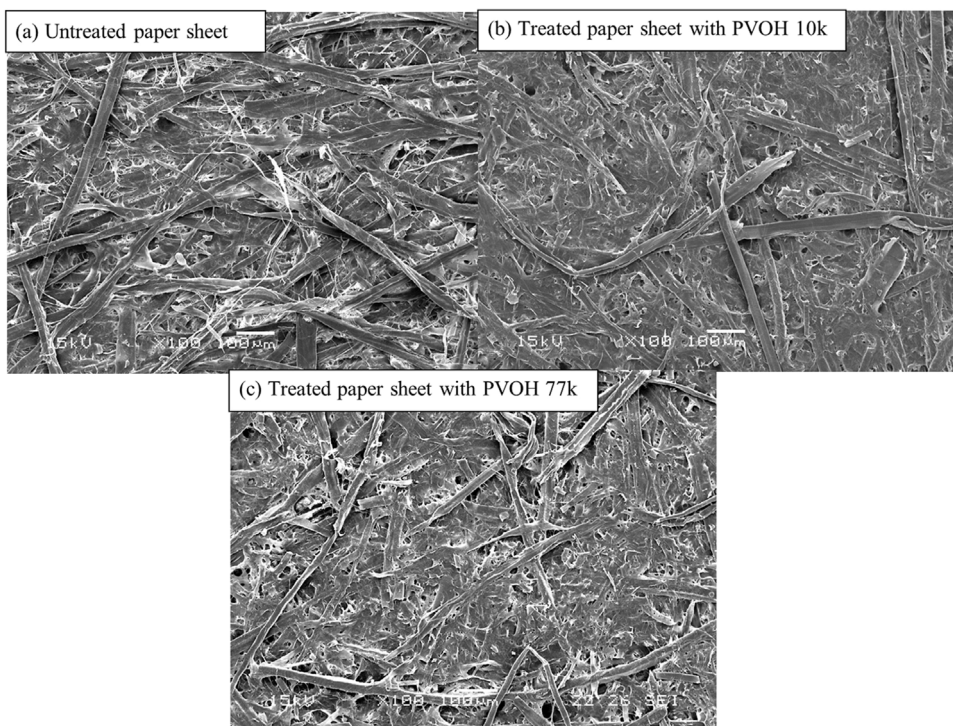


participate in a crosslinking reaction. In fact, a part can only esterify with one cellulose fiber, contributing to the increase of the dry tensile index instead of the increasing of wet properties. On the other hand, it is evident that the presence of a high amount of PVOH on the fibers surfaces increased the ability of PVOH to participate to crosslinking between the fibers. Due to the high viscosity of PVOH 77k, the latest should be present more on the fibers surface than the PVOH 10k, consequently the PVOH 77k, should participate further to the crosslink between the fibers.

### 3.3. Scanning electron microscopy characterization

To further support the hypothesis of PVOH diffusion, untreated and treated samples were analyzed by SEM. Fig. 6 shows a comparison between three kinds of paper sheets [(a) untreated, (b) treated with PVOH 10k and (c) treated with PVOH 77k; (b) and (c) are both treated in the presence of BTCA and SHP, and cured at 200 °C].

From the SEM images we observed the presence of PVOH on fibers surfaces after esterification. A difference between PVOH 10k and PVOH 77k was also observed. The PVOH with a high molar mass seems to be adsorbed further



**Fig. 6.** SEM images of (a) untreated paper sheet, (b) treated paper sheet with PVOH 10k in the presence of BTCA and SHP (10%/10%) and cured at 200 °C and (c) treated paper sheet with PVOH 77k in the presence of BTCA and SHP (10%/10%) and cured at 200 °C.

on the surface of cellulose fibers. The PVOH 10k seems to be incorporated in the hole between the fibers matrix. This difference can be attributed to the viscosity of each polymer. The manner of the absorption of the polymer and the difference between the mechanical properties due to the molar mass explain the difference between the mechanical properties of the paper sheets.

#### 4. Conclusions

Paper sheets based on TMP fibers are cross-linked using BTCA in the presence of SHP and PVOH. Two molar masses of PVOH were used. Temperature curing and mass amount of PVOH were modified. FTIR analysis confirmed the formation of ester bonds in the network of the fibers and the PVOH, after curing, in the presence of BTCA. The degree of esterification was found to be related to temperature during the curing. The dry and the wet tensile index of paper sheets were measured after each treatment. We observed that the presence of PVOH allows the improvement of both the dry and the wet tensile index of the paper sheets. Moreover, a difference between low and high molar mass of the PVOH was observed. The increasing of PVOH molar mass increased further the dry and wet tensile index. In addition, the increasing of temperature and PVOH amount improved also the wet and the dry tensile index of the paper sheets. Finally, SEM analysis showed a difference between PVOH 10k and the PVOH 77k. While PVOH 10k may penetrate further into the matrix, PVOH 77k seems to be more adsorbed on the surface of the fibers. The increasing of both the wet and dry tensile index offer the possibility to elaborate a high strength paper packaging based on biodegradable material. We can also use the final product to decrease the weight of existing paper packaging for the same tensile strength properties.

#### Declarations

##### Author contribution statement

Houssein Awada: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mohamed Bouatmane: Performed the experiments.

Claude Daneault: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

##### Funding statement

The authors gratefully acknowledge the support of the Green Fibre Network and the Natural Science and Engineering Research Council of Canada (NSERC).

## Competing interest statement

The authors declare no conflict of interest.

## Additional information

No additional information is available for this paper.

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