

The Development of a Composite Based on Cellulose Fibres and Polyvinyl Alcohol in the Presence of Boric Acid

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Boric acid was employed to improve the homogeneity and mechanical properties of a composite based on cellulose fibres and polyvinyl alcohol (PVOH). The influence of boric acid, under different pH values, on the mechanical properties cellulose fibres (handsheets) was investigated. The presence of the boric acid, under alkaline conditions, further improved the mechanical properties of the handsheets. A composite based on PVOH and cellulose fibres was prepared in the presence of boric acid and glycerol, a plasticizer. The employment of the boric acid, under alkaline conditions, was necessary to obtain a homogenous composite. The morphology of the final product was analysed by SEM, and their tensile properties were measured.

Keywords: Cellulose fibres; Paper properties; Composite

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INTRODUCTION

Recently, the use of petroleum-based polymer materials has significantly increased. Similarly, an increase in said petroleum-based materials can lead to environmental problems because they are non-recyclable and non-degradable. Therefore, biodegradable polymers are increasingly being used as environmentally friendly composite materials (Bledzki and Gassan 1999; Chai *et al.* 2009; Faruk *et al.* 2012; Huang and Netravali 2009).

The present study explores the possibility of a composite that is based on a biodegradable polymer, *i.e.*, polyvinyl alcohol (PVOH) and cellulose fibres. Cellulose fibres are the most abundant polymer in nature, and its advantageous properties include its large availability, renewability, biodegradability, biocompatibility, and the fact that it can be derivatized to yield various useful products (Awada *et al.* 2012; Mohanty *et al.* 2012).

Despite relatively low cellulose fibre prices, some of their properties, such as a lack of moisture resistance, prevent their use in daily life to replace other commonly used materials. One solution is to create a composite based on cellulose fibres and a biodegradable matrix polymer such as PVOH. Polyvinyl alcohol is the largest synthetic water-soluble polymer produced in the world (Ding *et al.* 2002) with several useful properties, such as excellent chemical resistant, optical, and mechanical properties; good film forming capability; water solubility; and excellent biocompatibility (Shi *et al.* 2008). The wide spectrum of property profiles opens the way of using it in a broad field of

applications, among which is their use as a matrix for biodegradable composites. The stability, homogeneity, and mechanical properties of such a composite are directly linked to the capacity of its components to create strong bonds between the fibres and the matrix. A strong-fibre-matrix interface bond is very critical for composites to have high mechanical properties. Therefore, to improve the interface and adhesion between the fibre and the matrix, a third component, which is called a compatibilizer, must be used for matrix modification or the fibres surface have to be initially modified for the preparation of the composites.

It has been reported that boric acid can form a strong bond interaction between hydroxyl groups. The trivalent B atom in boric acid has an empty p orbital that is very electrophilic in nature, which causes it to rapidly react with various nucleophiles to form complexes (Rietjens and Steenberg 2005). Because PVOH and cellulose fibres are both rich in hydroxyl groups, boric acid can be expected to cross-link them and further improve the adhesion between the fibres and the PVOH matrix. On the other hand, glycerol, a plasticiser, can be used to prevent the composite from becoming brittle after formation. Reddy and Yang (2010) used glycerol to crosslink starch film and found that above 15% glycerol, the plasticising effect was too pronounced. Borate has the special ability to crosslink PVOH through the “di-diol” reaction. Cui *et al.* (2009) reported that under alkaline conditions, boric acid is present as borate ions that can condense onto polymer chains with cis-diol groups. Pelton *et al.* (2009) reported that $B(OH)_4^-$ is more reactive than $B(OH)_3$. Moreover, it was reported that using alkaline solution to treat the cellulose fibres is one of the chemical treatment methods that can improve the mechanical properties of natural fibre reinforced polymer composite and further to produce high quality composites (Siregar *et al.* 2010). Despite the covalent appearance of the borate-oxygen bonds, the binding constants typically range from 10 to 5000 L/mol. These values are more typical of hydrogen bonds than covalent bonds (Chen *et al.* 2009). Notley *et al.* (2009) increased the adhesion between cellulose surfaces by grafting phenylboronic acid groups on a polyvinylamine backbone. Figure 1 shows the crosslinking reaction mechanism between polymer chains containing hydroxyl functional groups in the presence of boric acid as a crosslinking agent.

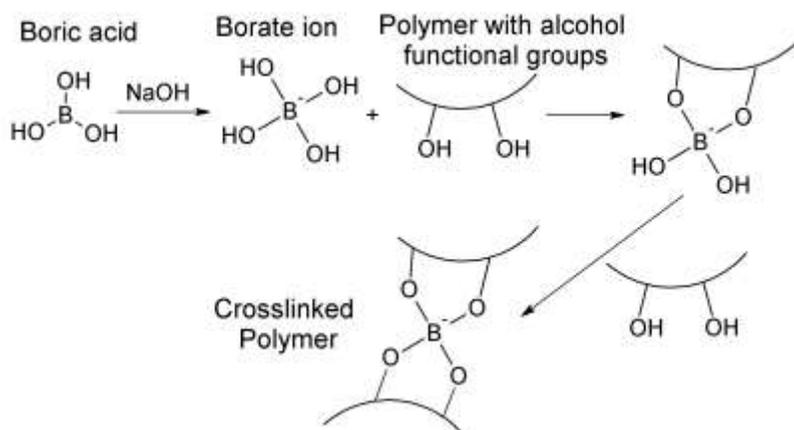


Fig. 1. Crosslinking mechanism of a polymer containing alcohol functional groups in the presence of boric acid

Because the composite prepared in this study is based on cellulose fibres and PVOH, it was important to investigate the ability of the boric acid to crosslink each component alone. Thus, this study had two purposes. The first purpose was to explore the influence of boric acid on the mechanical properties of cellulose fibres or PVOH-based materials. To accomplish this, handsheets made from cellulose fibres and PVOH films were prepared separately, in the presence of boric acid as a crosslinking agent. The second purpose was to investigate the influence of boric acid on the homogeneity and mechanical properties of a composite obtained from cellulose fibres and PVOH. The best results obtained with the handsheets will be applied to elaborate the composite.

EXPERIMENTAL

Materials

Bleached hardwood kraft pulp (cellulose fibres source) was purchased from Windsor/Domtar, Quebec. PVOH (99% hydrolysed, 10,000 g/mol, melting point of 200 °C) was acquired from Kuraray Poval (Japan). Glycerol (92.09 g/mol, ≥ 99% hydrolysed) and boric acid (purity of 98%, melting point of 171 °C) were supplied by Sigma Aldrich. All products were used as received.

Methods

Boric acid treatment of the cellulose fibres

Chemical modification experiments were conducted in a glass reactor that was placed in an oil bath at 80 °C. The cellulose fibres (20 g) were disintegrated in 2 L of deionised water for 10 min and then transferred to the glass reactor. Then, 40 mL of an aqueous solution (25 g/L) containing boric acid (5% based on cellulose fibre weight) were added dropwise to the cellulose fibre suspension.

The pH of the suspension was varied from 5 to 12. The pH was adjusted with 1 M NaOH or 1 M HCl solution, depending on the situation, using a pH controller. The suspension was continuously mixed with a magnetic stirring bar for 2 h. At the end of the predetermined reaction time, the cellulose fibres were dispersed in deionised water at 0.15% consistency, and a set of 5 handsheets was made. Each experimental condition was replicated 3 times.

Handsheet process and characterisation

After the boric acid treatment of the cellulose fibres, handsheets with grammage of 60 g/m² were made in a British sheet-mould according to TAPPI standard methods. All handsheets were pressed respectively for 5 min on one side and 2 min on the other side with 345 kPa pressure. Then, the handsheets were stocked overnight in a conditioning room at 23 °C and 50% of relative humidity (according to the standard TAPPI conditioning), before characterization. Three sets of handsheets, from unmodified cellulose fibres (control handsheets), were prepared for comparison. The tear index and breaking length were measured according to TAPPI standard testing methods T414os65 and T494os70. Two strips (15 mm wide × 150 mm length) from each handsheet were prepared. In total 10 specimens were tested for each handsheet set.

Boric acid treatment of the PVOH

PVOH powder was added to the deionized water at a weight ratio of 1:9 to form PVOH solution kept in a water bath at 80 °C and stirred for 2 h. Because the film of the PVOH was brittle, it was difficult to measure its mechanical properties. Therefore, the control sample was made from PVOH and glycerol to improve the tensile properties of the PVOH.

One hundred millilitres of the PVOH (10 g) was mixed with 3 g of glycerol and heated constantly at 80 °C in a glass reactor. Then, 20 mL of a boric acid solution (25 g/L) was added dropwise to the solution. The pH of the mixture was adjusted to 10. The mixture was stirred with a magnetic stirrer for 2 h.

A solution containing 1 g of the solid material (PVOH, boric acid, and glycerol) was casted on a Petri dish and dried in a forced air drier at room temperature to form a flat PVOH film. A film composed of PVOH and glycerol solution, as a control sample for comparison, was prepared by casting, without the addition of boric acid. Thicknesses of all specimens were about 100 µm.

Composite preparation

A sample consisting of 7 g of the PVOH solution (70 mL) was mixed with 3 g of disintegrated cellulose fibres and glycerol (30% based on the total weight) in a glass reactor. The mixture was heated constantly at 80 °C. Boric acid solution (5% based on the total weight) was added dropwise. The pH of the mixture was adjusted to 10. The mixture was stirred with a magnetic stirrer for 2 h. A 1-g amount of the composite was cast on a Petri dish and dried in a forced air drier at room temperature to form a flat PVOH-Cellulose fibres film. A control sample, for comparison, was also prepared without the use of boric acid. As mentioned previously the specimen thickness were about 100 µm.

Structural analysis

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

Mechanical characterisation of PVOH and composites

The tensile properties (maximum load, extension at maximum load, and Young's modulus) were measured with a universal testing apparatus (INSTRON 4201). The samples were prepared and cut into rectangular specimens of 30 mm in length and 15 mm in width.

As mentioned previously the specimen thickness were about 100 µm. The crosshead speed and the applied load were specified at 500 N and 10 mm/min, respectively, while the support span was 10 mm. In the case of the composites, only the properties of the homogenous samples were measured. Each condition was replicated three times. Five specimens were tested, per experiment, to get the average value.

RESULTS AND DISCUSSION

Mechanical Properties of Paper Influenced by pH

Figure 2 shows the effect of pH variation from 5 to 12 on the tear index and the breaking length. The values are presented as a percentage to the control handsheets. These values are averages calculated from three different handsheet sets. The tear index and the breaking length of the control handsheet were $5.8 \pm 0.2 \text{ mN}\cdot\text{m}^2/\text{g}$ and $2.6 \pm 0.1 \text{ km}$, respectively.

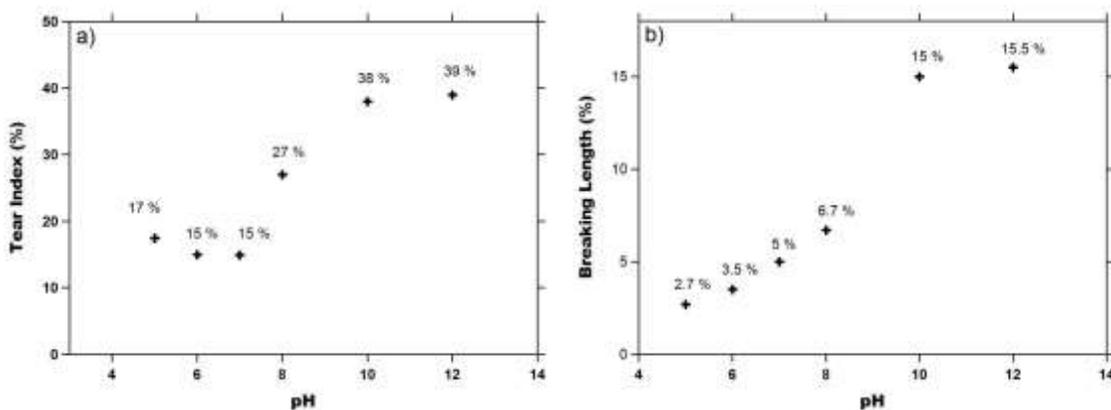


Fig. 2. Variation of (a) tear index and (b) breaking length as a function of pH. The tear index and the breaking length of the control handsheet were $5.8 \pm 0.2 \text{ mN}\cdot\text{m}^2/\text{g}$ and $2.6 \pm 0.1 \text{ km}$, respectively.

Figure 2 shows that at any pH value, an improvement of both the tear index and the breaking length were observed when boric acid was added. Moreover, when the pH was increased above 9, these improvements became more apparent. By increasing the pH from 10 to 12, these properties were quasi-unmodified. Two reasons can explain the enhancement of mechanical properties when the pH was increased – the chemical configuration of the boric acid at high pH and the alkaline conditions. According to the literature (Pelton *et al.* 2009), boric acid is a Lewis acid and has a pKa of approximately 9.2. Therefore, for a pH value below 9.2, the uncharged boric acid dominates, and boron has the possibility to create three bonds with the hydroxyl groups. Alternatively, for a pH above 9.2, $\text{B}(\text{OH})_4^-$ dominates and allows the boron to link to four hydroxyl groups. As interfibre bonding increases, the effort needed to pull-out unbroken fibres from their surrounding networks increases. Therefore, an improvement was observed in the mechanical properties of the handsheets. Likewise, alkali treatment can modify the mechanical properties of handsheets. The alkali treatment improved the adhesive characteristics of fibre surfaces by removing natural and artificial impurities, thereby producing a rough surface topography. In addition, alkali treatment leads to fibre fibrillation, *i.e.* breaking down of the fibre bundles into smaller fibres (Siregar *et al.* 2010). To further understand the origin of the improvement, three sets of handsheets were prepared from fibres treated in alkaline condition (pH = 10, $T = 80 \text{ }^\circ\text{C}$, time = 2 h) without the presence of the boric acid. However, there was up to a 12% increase in the tear index for a pH of 10 without the boric acid, compared to the 38% increase when

boric acid was employed. One can conclude that the presence of boric acid under alkaline condition increased more the mechanical properties of the papers.

For the PVOH films and the composite, a pH of 10 was employed during the treatment with boric acid.

Morphological Observation of Composite Based on PVOH and Cellulose Fibres

Because the use of the boric acid at a pH of 10 yielded better results for the cellulose fibres, thereafter, this condition was used to crosslink the PVOH and to prepare a composite based on the PVOH and on the cellulose fibres (in the presence of glycerol). For comparison, composites of cellulose fibres and PVOH were prepared in the presence of glycerol without the use of boric acid. Figure 3 shows digital images of the composite prepared with and without boric acid.

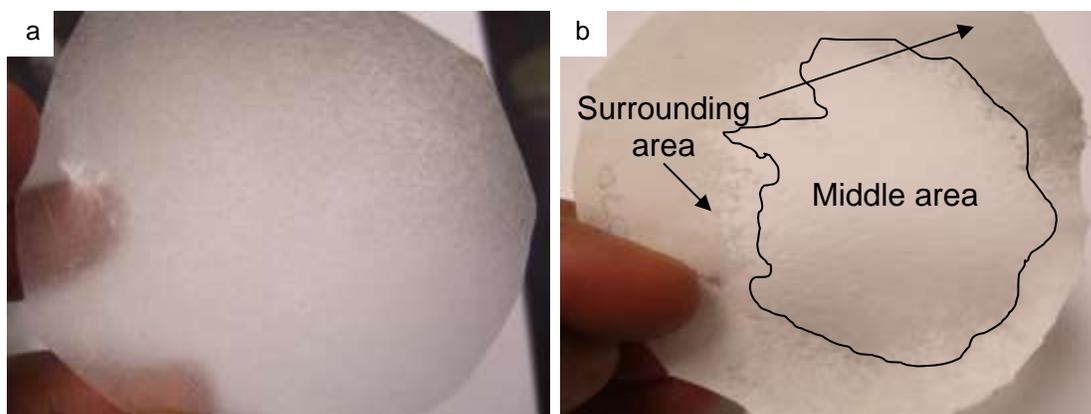


Fig. 3. Typical samples prepared from cellulose fibres and PVOH (a) with boric acid and (b) without boric acid

Figure 3a shows a homogenous material, while Fig. 3b shows a heterogeneous one. In Fig. 3a, the presence of the boric acid increases the interaction between the cellulose fibres and the PVOH.

In addition to favouring the bond between the alcohol function through the boron atom (boric acid is present as borate ions), the alkaline condition generally resulted in a rougher fibre topography, which can further improve the fibre matrix adhesion in a composite by providing additional sites for mechanical interlocking (Gonzalez *et al.* 1999; Mohanty *et al.* 2000). This leads to a good fibre distribution within the PVOH matrix (*i.e.* the formation of a homogenous composite). Also it should be pointed out that the alkaline condition, without the presence of the boric acid, was not enough to obtain an homogenous composite.

Figure 3b is composed of two areas. The surrounding one, composed of high amounts of cellulose fibres, and the middle one, composed of high amounts of PVOH. The two samples presented in Fig. 3 were analysed using SEM to determine the morphology of each material. Figure 4 shows the morphology of cellulose fibres (Fig 4a) and of the homogenous material (Fig 4b).

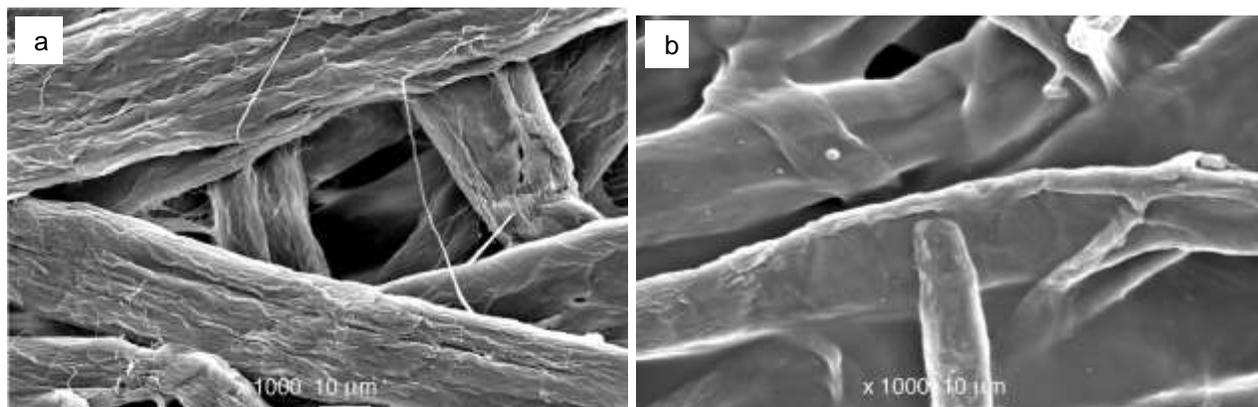


Fig. 4. Typical SEM image of (a) cellulose fibres and (b) homogenous sample

The comparison between Fig. 4a and 4b shows the presence of the cellulose fibres fully surrounded by the polymer matrix of PVOH. The adhesion between the fibres and the matrix of PVOH seem to have been improved by the presence of the boric acid in alkaline condition.

The surrounding and middle areas of the heterogeneous material were analysed separately and are presented in Fig. 5a and b, respectively.

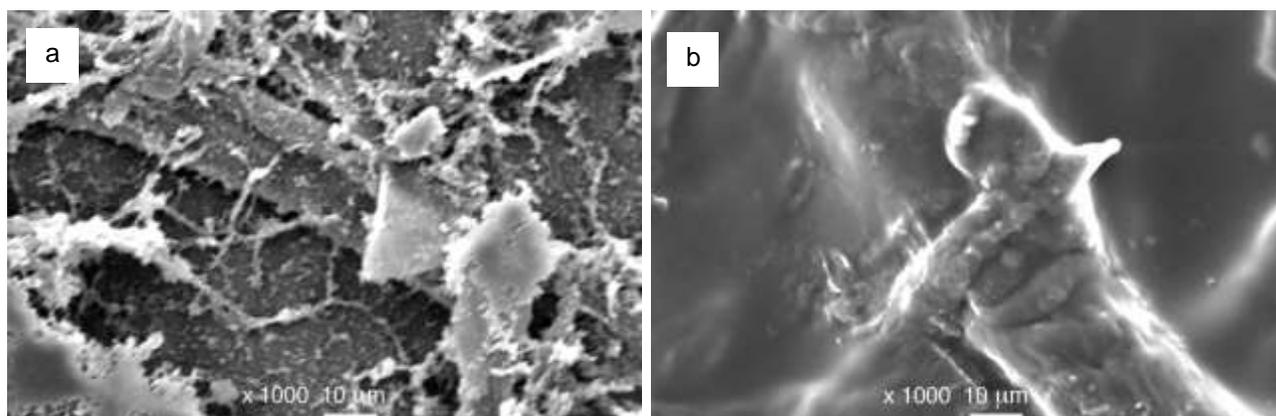


Fig. 5. Typical SEM image of (a) the surrounding area, and (b) the middle area

Figure 5a and b indicate that there is considerable difference between the two areas. SEM analysis confirms the heterogeneity of the composite when the boric acid was not used. In the two areas the cellulose fibres, in different amounts, were observed.

Influence of the Boric Acid on the Mechanical Properties of the Composite

The tensile properties of the crosslinked PVOH were measured and compared to those of the control sample. Table 1 shows the tensile properties for the control sample and the PVOH after crosslinking. On the other hand, the heterogeneous behaviour of the composite made without boric acid prevents a meaningful mechanical analysis. Therefore, the tensile properties of the homogenous composite were measured (Table 1). The data given here are the average of 5 measurements on three different samples.

Table 1. Tensile Properties of the Control PVOH sample, Crosslinked PVOH Sample with the Boric Acid, and the Crosslinked Composite Film Made from PVOH and Cellulose Fibres in the Presence of Boric Acid

	Young's Modulus (MPa)	Maximum Load (N)	Extension at Maximum Load (mm)
Control PVOH sample	62 ± 17	9 ± 4	3 ± 0.3
Crosslinked PVOH sample	192 ± 26	29 ± 4	11 ± 5
Crosslinked composite Film	730 ± 170	115 ± 27	2 ± 0.3

The glycerol was used in all of these samples. The pH was adjusted to 10.

The Young's modulus of the control PVOH was 62 MPa. The Young's modulus of the crosslinked PVOH sample was higher than for PVOH. This increase can be explained by the bond created between the polymer chains of the PVOH by the boron atom. The same comment can be added for the variation of the maximum load and the extension at maximum load.

In the case of the composite, the Young's modulus and the maximum load were significantly increased with the presence of the cellulose fibres. This is expected since the Young's modulus of the cellulose fibres is much higher. The extension at maximum load of the composite was lower than the control PVOH and much lower than the crosslinked PVOH. The decrease of the extension at maximum load is related to the low elastic properties of the cellulose fibres. It should be noted that the Young's modulus of the composite is comparable to the polyethylene (Young's modulus: 800 MPa).

These results show the possibilities replace a part of petroleum-based polymer by an environmentally friendly material. Moreover the employment of the cellulose fibres increased the mechanical properties of the final product.

CONCLUSIONS

1. Boric acid was used to increase the mechanical properties of papers. By the variation of the pH value it was demonstrated that, under alkaline conditions, the treatment of the cellulose fibres with the boric acid had the most significant effect on the mechanical properties of papers.
2. The best conditions obtained with the papers were applied to prepare a composite based on PVOH and cellulose fibres.
3. The presence of the boric acid under alkaline conditions improved the homogeneity of a composite based on cellulose fibres and PVOH.
4. Moreover, the presence of the cellulose fibres in the matrix of the PVOH, with high mechanical properties, shows the possibility of replacing an amount of petroleum-based polymer (PVOH) with an environmentally friendly material (cellulose fibres).

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Article submitted: February 26, 2014; Peer review completed: March 30, 2014; Revised version received and accepted: April 17, 2014; Published: April 25, 2014.