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Time-triggered calcium ion bridging in preparation of films of oxidized microfibrillated cellulose and pulp

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ABSTRACT

One of the main trends in developing bio-based materials is to improve their mechanical and physical properties using MFC derived from sustainable natural sources and compatible low-cost chemicals. The strength of anionic MFC-based materials can be increased with addition of multivalent cations. However, direct mixing of solutions of multivalent cations with oxidized MFC may result in immediate, uncontrollable fibril aggregation and flock formation. The aim of this study was to design a method where Ca 2+ ions liberate from solid CaCO3 particles on bleached hardwood (birch) kraft pulp, which was mixed with oxidized MFC and crosslink it to tailor the mechanical properties of the dried structure. In few minutes after adding acetic anhydride, pH of the wet film dropped from 7.3–4.8 through liberation of acetic acid and CaCO3 particles solubilized releasing Ca 2+. The novel method could be applied on industrial scale for improving the performance of packaging materials.

1. Introduction

Increased environmental awareness has raised interest in renewable and sustainable packaging materials. Cellulose, besides some hemi-celluloses and lignin, is the main chemical component in various products of the forest industry (Spence, Venditti, Rojas, Habibi, & Pawlak, 2010). Together, these biopolymers form the pulp fibers, the dimensions and mechanical properties of which vary depending on the wood species. Mechanical refining, also called beating, of the pulps can significantly improve conformability of the fibers and, consequently, interfiber contact area in fiber networks (Carvalho, Ferreira, & Figueiredo, 2000; Subramanian, Maloney, Kang, & Paulapuro, 2006). Depending on the mechanical load applied, the refining process may e.g. delaminate, fibrillate or cut the fibers. Although these changes make the pulp more difficult to dewater, the mechanical strength of the resulting dry fiber web increases while its porosity decreases.

In comparison with pulp fibers, microfibrillated cellulose (MFC) can often provide cellulosic materials with impressive mechanical properties (Subramanian, Fordsmand, & Paulapuro, 2007). Several mechanical treatments, such as homogenization, microfluidization, micro-grinding and cryocrushing, can be applied in manufacture of MFC for various applications (Spence, Venditti, Rojas, Habibi, & Pawlak, 2011; Spence, Venditti, Rojas, Pawlak, & Hubbe, 2011). Compared to pulp refining, MFC production consumes huge amounts of energy (Spence, Venditti, Rojas, Habibi et al., 2011). As a result, the original fiber wall is completely destroyed and the degree of polymerization of cellulose and its crystallinity can be lowered (Henriksson, Henriksson, Berglund, & Lindström, 2007; Siró & Plackett, 2010; Svan & Samir, & Berglund, 2008). The high energy consumption of MFC production can be significantly reduced by enzymatic or chemical pretreatments of the pulp (Dufresne, Cavaille, & Vignon, 1997; Pääkkö et al., 2007; Wang & Sain, 2007a, 2007b, 2007c). The most promising chemical pretreatment for producing MFC is 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation of the pulp (Saito & Isogai, 2006). This catalytic treatment introduces carboxylate and aldehyde groups on cellulose microfibril surfaces under relatively mild aqueous conditions (Habibi & Vignon, 2008; Lasseguette, Roux, & Nishiyama, 2008; Saito & Isogai, 2005, 2006; Saito, Kimura, Nishiyama, & Isogai, 2007, 2009). The oxidized pulp is easy to fibrillate to form a thick aqueous gel that is difficult to dewater. Films prepared by drying the oxidized MFC gel are highly transparent and stiff. The fibrils may increase the dry strength of fiber-fiber joints by mechanical entanglement (Weber, Koller, Schennach, Bernt, & Eckhart, 2013). Additionally, the dry strength can be improved by using additives like carboxymethyl cellulose which

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results in increased charge density in the fiber network (Duker & Lindström, 2008).

It was recently shown that diffusion aided bridging of the carboxylate groups in wet, oxidized cellulose nanofibril films with multivalent cation salts may positively affect the strength of the films after drying them (Shimizu, Saito, & Isogai, 2016). However, this phenomenon is difficult to implement industrially because the diffusion times are relatively long over distances of > 1 mm (Bender et al., 1973). To overcome this practical limitation, we introduce here an alternative time-triggered bridging where the multivalent cations dissolve with time from insoluble salts that are originally mixed with MFC/pulp gel prior to the film formation. We demonstrate the principle of the method by using precipitated calcium carbonate (PCC) as the insoluble multivalent cation salt and acetic anhydride (Ac₂O) as an additive that lowers pH with time due to liberation of acetic acid and solubilizes PCC. To guarantee its even mixing in the MFC/pulp, we precipitated PCC on the pulp.

The paper industry uses PCC widely as a pigment in coating colors and as a filler. By adding the filler, many benefits can be achieved, including cost and energy savings and improvements in optical properties, printability, and the appearance of the paper product (e.g. brightness and smoothness) (Giovanu, Bobu, & Cioclașcu, 2010; Song, Dong, Ragauskas, & Deng, 2009). However, the use of such a filler, especially at high loading levels, has certain disadvantages, e.g. causing poor filler retention, decreased sizing efficiency and bending stiffness (Shen, Song, Qian, & Yang, 2010). Some of the drawbacks have been overcome by methods reported in various industrial practices (Lourenço, Gámelas, Sequeira, Ferreira, & Velho, 2015; Shen et al., 2010). As an example, PCC can be coated with silica to improve the strength of the paper (Lourenço, Gámelas, & Ferreira, 2014). Another method to precipitate the filler particle on the fines/fibrils fraction of pulp (2006; Silenius, 2000; Subramanian et al., 2007). Indeed, intensive efforts have recently been made to control the nucleation and subsequent aggregation, growth and crystallization of CaCO₃ as a filler (Palmqvist, Nedelec, Seisenbäeva, & Kessler, 2017). Depending on the technique, the size of the precipitated CaCO₃ particles on the cellulose surface can be controlled. CaCO₃ remains poorly soluble in neutral and basic media, while it rapidly solubilizes in acidic conditions through liberation of Ca²⁺ and HCO₃⁻ ions.

2. Experimental

2.1. Materials

Bleached hardwood (birch) kraft pulp and TEMPO-oxidized MFC (Na⁺ form) were obtained from a Finnish pulp mill and were used without any further treatment. The pulp had the following fiber characteristics: average fiber length 0.91 mm, curl index 41.3%, kinks 4160 m⁻¹ and carboxylic acid content of 0.02 mmol/g. The consistency of the MFC dispersion was 2.5%, its carboxylate content was 0.8 mmol/g and pH 5.5. The average width of the fibrils was ca. 7 nm measured by transmission electron microscopy. Calcium oxide (CaO) from Lhoist, Ltd. (France) and acetic anhydride from VWR were used without further purification. Pure CO₂ gas was from AGA (Finland).

2.2. CaCO₃ co-precipitation onto pulp fibers

Calcium carbonate (CaCO₃) can be produced by carbonation of CaO in two steps. First, water is added to CaO to obtain calcium hydroxide (Ca(OH)_2). Then, CO₂ is added which dissolves in the aqueous phase and forms carbonic acid, which reacts with the Ca(OH)_2 to form precipitated calcium carbonate (PCC).

For this study, the pulp was first adjusted to 25 ± 2% solid content and then mixed for 5 min at moderate rotational speed in a KM098 Kenwood mixer, suitable for materials at high solid contents. Ca(OH)_2 was produced by adding CaO (Lhoist, Ltd.) to deionized water at 50 °C in a ratio of 1–5. The slurry was mixed with a high-shear mixer for 10 min. Ca(OH)_2 was added to the pulp and newly mixed at room temperature and moderate speed. The pulp:Ca(OH)_2 ratio was calculated to produce 7% PCC after carbonization. After 10 min mixing, the homogeneity of the suspension was tested by measuring the pH of 4 different samples. An acceptable homogeneity was achieved at pH 12.6 ± 0.2. PCC co-precipitation was accomplished by feeding CO₂ gas into the covered mixing chamber at a flow rate of 0.3 L/min (NTP). The reaction was considered completed after ca. 7 min, when the pH measured 7.7 ± 0.1. After this pH was reached, the gas flow was stopped and mixing continued for another 30 min. The final pH was 8.3 ± 0.1. The PCC content determined by standard ISO 2144:1997(E) was 7.6 ± 0.1 wt%.

2.3. Preparation of MFC/pulp films

A mixture of MFC, pulp (containing PCC) and water (2.3% dry matter content) was homogenized using an Ultra Turrax mixer (IKA, D125 Basic) for 20 min to obtain a uniform hydrogel. After adding Ac₂O (0.54–2.15%) the hydrogel was mixed for additional few seconds. Then 35 g of the cellulose hydrogel was applied over a Teflon mold (60 mm x 140 mm) by a rod coating setup, K101 Control Coater, RK Print Coat Instruments Ltd, Herts, UK. The hydrogel was dried in the mold without any further treatment at 23 °C and 50% RH for 24 h. The films were made by varying the ratio of the pulp and MFC (30:70, 50:50, 60:40, 70:30). Reference samples were prepared similarly without the addition of Ac₂O.

2.4. Analyses

Tensile testing of the cellulose films was carried out at 23 °C and 50% RH using an Instron 4204 Universal Tensile Tester equipped with a 50 N load cell, a gauge length of 20 mm and a cross-head speed of 1 mm/min. The film specimens were 10 mm wide and 50 mm long and they were equilibrated for ≥3 h at RH 50% before the mechanical testing. For film imaging, scanning electron microscopy (SEM) was used with magnifications 10,300x and 35,490x (Zeiss Sigma VP Field-Emission Scanning Electron Microscope (FE-SEM)). The operating voltage was 3 kV and the working distance approximately 2.5 mm. Prior to the imaging, the samples were sputtered with gold-palladium.

A relative humidity (RH) of 50% and a temperature of 23 °C were maintained during the mechanical testing measurements. The film thickness was estimated by a thickness gauge under a low and constant pressure, according to the international standard regarding thickness of paper and board (ISO 534). The film density was calculated from the weight and volume (thickness times area) of the dry film. This apparent density measurement was repeated at least three times for each sample. The moisture contents of conditioned films were calculated from the weight before and after heating at 100 °C for 3 h.

3. Results and discussion

Fig. 1 illustrates the principle of the time-triggered bridging of oxidized MFC/pulp with Ca²⁺ ion. CaCO₃ is first precipitated on the pulp. The pulp is then mixed with the oxidized MFC after which Ac₂O is directly mixed with the hydrogel in a short time. The hydrogel is then spread on a support as a 2–3 mm thick layer in this case. Ac₂O releases two equivalents of acetic acid (AcOH) with time, which lowers the pH and allows CaCO₃ to solubilize as Ca²⁺ and HCO₃⁻ ions (Eqs. (1) and (2)). Due to Donnan phenomenon (Donnan & Harris, 1911; Procter & Wilson, 1916), the liberated Ca²⁺ replaces Na⁺ as the counter ion of the hydrogel, forms ionic bridges between the carboxylate groups in MFC and pulp and solidifies the gel.

\[ \text{Ac}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{AcOH} \]  
(1)
CaCO₃(s) + AcOH ⇌ Ca²⁺ + HCO₃⁻ + AcO⁻  

(2)

The dosage of the added Ac₂O was varied depending on the dry content of cellulose fibers that contained CaCO₃. Adding Ac₂O into the MFC/pulp suspension lowered its pH from 7.3–4.8 in 15 min due to the formation of AcOH. SEM images of the prepared MFC/pulp films showed that the addition of Ac₂O solubilized the precipitated CaCO₃ particles (< 1 μm) on the fiber surfaces in part or completely depending on the amount of added Ac₂O (Fig. 2). Too large dosages of Ac₂O (> 4%) led to fast flocculation of the MFC/pulp suspension, probably because of too fast liberation of Ca²⁺, and prevented even film formation with the rod coating setup. Similarly, direct addition of aqueous CaCl₂ to the MFC/pulp mixture resulted in immediate floc formation.

MFC/pulp films were prepared by mixing MFC and pulp (containing PCC) in different ratios (Table 1). It was noted that films containing more than 70% of MFC shrank remarkably during drying and became very brittle (the mechanical properties of these low quality films were not measured). In contrast, the films formed with ≤70% MFC kept their lateral dimensions during drying. Thus, the hydrogels shrank only in the vertical direction. The film density was, in average, 16% lower when Ac₂O was added. Although the observed surface roughness of the films may have led to some systematic error in their thickness measurement, the effect of adding Ac₂O on the density was obvious in all cases. The change in density might indicate that the electrostatic bridging partially prevented consolidation of the films. The SEM images of freeze-fractured cross sections showed a layered structure of the films independent of how the films were prepared (Fig. 3).

Even though the Ac₂O treatment lowered the film density, the tensile index and breaking strain seemed to increase by the treatment (Fig. 4, Table 1). The film with the highest MFC content (70%) was very brittle, i.e. the strain at break was very low, when Ac₂O was not added. The increase in tensile strength was especially high in the case of the film with the highest pulp content. It is very evident from these changes that the bridging by Ca²⁺ occurred and that affected positively the internal strength of the films. The bridges were most probably formed between the negatively charged fibrils of MFC which then increased bonding in the fiber network similar to carboxymethyl cellulose (Duker

![Fig. 1. The principle of preparing MFC/pulp films. (a) CaCO₃ is precipitated on pulp, which is then mixed with oxidized MFC and Ac₂O under neutral pH and the hydrogel is spread on a support. (b) Ac₂O hydrolyzes with time to form AcOH which releases Ca²⁺ that forms ionic bridges between the carboxylate groups in the hydrogel.](image)

![Fig. 2. SEM images of MFC/pulp films (30% MFC, 70% pulp with 7.6% PCC on it) prepared without (a, b) and with addition of 1.1% Ac₂O (c, d). CaCO₃ particles (< 1 μm) were initially present (b) but the addition of Ac₂O mostly removed them.](image)
The bridging seemed to increase the specific bond strength but not the relative bond area that tends to increase the web density. Thus, it is likely that mechanism of strength improvement in fiber-fiber bonds is indeed entanglement of external fibrils rather than increased contact area (Hirn & Schennach, 2018).

Overall, the results show that adding Ac₂O solubilized the insoluble CaCO₃ with time and liberated Ca²⁺ ions which bonded then with the carboxylate groups present in MFC, especially. Thus, the delay in the release of Ca²⁺ prevented fibril aggregation during the initial mixing of the components and facilitated crosslinking of the structure in the already formed film. In the future, the delay time could be adjusted with the selection of the ester component, temperature and initial pH. In our experiments the effect of the time-triggered Ca²⁺ ion bridging was largest with the lowest MFC/pulp mixing ratio (30:70). In theory, a molar ratio of 1:2 between Ca²⁺ and carboxylates would be needed for complete bridging between the ionic sites of MFC (the carboxylate groups were in the calcium form after the precipitation of CaCO₃). However, comparable results were obtained also with lower molar ratios between the calcium and carboxylate ions (30:30 MFC/pulp ratio, 0.54 vs. 2.15% Ac₂O) (Table 1).

### 4. Conclusion

Crosslinks between the ionic sites of cellulose fibrils and fibers and multivalent cations can significantly contribute to the properties of the fibril-fiber network. In general, such homogeneous network structures are difficult to build from the ionic components due to the rapid ionic flocculation during their mixing. The novel time-triggered bridging, exemplified here with PCC on pulp and acetic anhydride, overcomes the initial flocculation and enables building of homogeneous structures that crosslink with time when the ester additive releases acid with time, and subsequently the multivalent cation. The insoluble salt, for example PCC, can be added into the system also directly, without the need to precipitate it on the pulp beforehand. Industrial processes use elevated temperatures and short mixing times under which relatively fast acid releasing esters, like acetic anhydride, are optimal additives. In laboratory, the use of less reactive esters might be advantageous to give enough time for mixing of the components and forming the structure. We believe that our novel concept will open a spectrum of different approaches to tailor the properties of cellulose fiber/fibril based materials for different applications, such as packaging, in the future.

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### Table 1

Mechanical properties of the cellulose films, their moisture contents and densities at 23 °C and 50 RH. The actual grammage varied significantly between the experiments, which explains part of the variation in thickness.

| MFC/pulp Ac₂O (%) | RCO₂⁻ (mol/kg) | Ca²⁺ (mol/kg) | Tensile index (Nm/g) | Strain (%) | Young’s modulus (GPa) | Moisture content, % | Thickness (μm) | Density (g/cm³) |
|-------------------|---------------|--------------|---------------------|------------|----------------------|-------------------|----------------|---------------|
| 70:30             | 0.58          | –            | 43.3 ± 4.5          | 1.2 ± 0.1  | 5.8 ± 0.7            | 7.1 ± 0.7         | 100 ± 8.5      | 1.02 ± 0.0    |
| 70:30             | 0.58          | 0.11         | 54.7 ± 6.4          | 3.2 ± 0.1  | 5.5 ± 1.2            | 9.1 ± 0.6         | 89 ± 9.5       | 0.79 ± 0.1    |
| 70:30             | 2.15          | 0.44         | 52.1 ± 5.2          | 3.2 ± 0.6  | 5.1 ± 2.2            | 7.1 ± 1.7         | 100 ± 22       | 0.79 ± 0.1    |
| 50:50             | 0.42          | –            | 51.1 ± 1.3          | 3.5 ± 0.1  | 5.2 ± 0.4            | 7.6 ± 0.5         | 113 ± 4.5      | 1.04 ± 0.1    |
| 50:50             | 0.80          | 0.16         | 55.6 ± 6.9          | 3.8 ± 0.5  | 3.4 ± 0.9            | 8.1 ± 1.1         | 145 ± 4.4      | 0.88 ± 0.0    |
| 40:60             | 0.34          | –            | 50.3 ± 4.5          | 3.2 ± 0.1  | 3.4 ± 0.9            | 7.9 ± 0.8         | 107 ± 8        | 1.02 ± 0.1    |
| 40:60             | 0.94          | 0.19         | 59.2 ± 2.0          | 4.4 ± 0.2  | 3.9 ± 0.6            | 7.5 ± 1.1         | 133 ± 1        | 0.88 ± 0.1    |
| 30:70             | 0.26          | –            | 44.7 ± 6.0          | 3.5 ± 0.8  | 2.5 ± 0.0            | 6.7 ± 1.3         | 137 ± 8        | 0.99 ± 0.23   |
| 30:70             | 1.07          | 0.26         | 72.9 ± 11.0         | 4.3 ± 0.5  | 3.5 ± 1.7            | 7.8 ± 2.5         | 145 ± 9        | 0.85 ± 0.1    |

* Amount of released Ca²⁺ ions calculated from the stoichiometry of Eqs. (1) and (2).
Fig. 4. Tensile index against strain at break (a) and density (b) for cellulose films, prepared by different molar ratio of PCC-on-pulp and MFC at 23 °C and 50% RH.

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