

HYDROGEL STATE IMPREGNATION OF CELLULOSE FIBRE-PHENOL COMPOSITES: EFFECTS OF FIBRE SIZE DISTRIBUTION

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Abstract

Whilst it has been well established that cellulose nanofibres (CNF) networks produce films that have high stiffness and strength, they are difficult to impregnate. Investigated in this study is whether by controlling the degree of nanofibrillation of cellulose, composites based on micro- and nano-size cellulose fibres can be made that are more easily manufactured and have better impregnation than solely cellulose nano-fibre based composites. To evaluate this, cellulose at different stages of ultrafine grinding, extracted at time intervals of 30, 60 and 290 mins, were used to make composites. To achieve good impregnation a novel strategy was used based on impregnation with phenol resin whilst the fibrillated cellulose is in a hydrogel state. The composites were subsequently dried and consolidated by hot press. The current results show that this method of impregnation is successful and the phenol matrix greatly improves the properties of the cellulose with a low degree of fibrillation. In general, as the degree of fibrillation and the proportion of nanofibres increases, the mechanical properties of the networks and their composites increase. The addition of the matrix appears to restrict the deformation of CNF network, increasing the modulus and yield strength but decreasing the ultimate strength. The method also appears to restrict the consolidation and voids remain in the composite, which reduces the modulus when compared to theoretical maximum values for this material. More work on the consolidation process is necessary to achieve the full potential of these composites.

1. Introduction

Paper is network of fibres pressed together to form a continuous sheet and the mechanical properties depend on the properties of the individual fibres and the bonding that can be achieved between them. They are also currently used as reinforcement in composites for uses such as in flooring, circuit boards and parchment. These cellulosic fibres can be fibrillated further into nanofibres, the elementary fibres in the plant cell wall and form stronger and stiffer sheets than their micro-sized pulp counterparts [1]. The cellulose nanofibres themselves have stiffness and strength in the region of 140GPa [2] and 10 GPa [3], respectively, and strong hydrogen bond between the fibres. These bonds combined with the high surface area of nano particles, leads to these good mechanical properties of the network. Additionally, Aitomäki et al [4] showed that the properties, in particular the strength, depend heavily on the porosity of these networks, and Berglund [5] suggested that the highest properties come from having consistent size distribution.

From calculation based on a number of different CNF based nanocomposites, Aitomäki and Oksman [6] also suggests that the mechanical properties of high volume fraction nanocomposites depend more on the network properties than on the fibre properties since using a model of embedded fibres (shear lag model) gives such inconsistent results. The results suggested that one of the reason for the discrepancy between theory and model can be the difficulty in have good impregnation and of course because embedded models do not take inter-fibre bonding into account.

A means of achieving good properties from these composite is therefore to get good impregnation without the loss of integrity from strong inter-fibre bonding. To get good impregnation, a water swelling approach was used following that of Qing et al [7] but simplified to avoid first drying and rewetting the network. In the procedure, fibrillated fibres suspensions are filtered but remain in a hydrogel state before being immersed in a solution of polymer. Evaluated is the effectiveness of this nanocomposite processing procedure and whether larger fibres combined with nanofibres improve the degree of impregnation.

2. Method

Suspensions of large fibres combined with smaller fibres were simply produced by fibrillating Birch Kraft pulp to different degrees. This was done by mixing 1.5 wt.% fibre pulps with distilled water for 2 h using a high shear mixer (L4RT, Silverson Machine Ltd., UK) prior to grinding it using an ultrafine grinder (MKZA6-2, Masuko Sangyo Co., Ltd., Japan). 500 ml samples of fibrillated fibre suspension were taken during the fibrillation process at 30, 60 and 290 min. These were used to investigate the effect of fibre size distribution on the impregnation and composite properties. An additional batch of cellulose ground to nanofibres was used to test the influence of the polymer concentration.

The fibre suspensions were diluted to 0.2% with distilled water before being filtered on a hardened filter paper with a pore size of 7µm (Whatman Grade 52, GE Healthcare, UK) in a Büchner funnel. Whilst in its hydrogel state, the cellulose was placed in Propanol-2 (VWR International, USA) for 2 h. It was then transferred to a 5 wt.% of Phenol formaldehyde (PF) in Propanol-2 for 24 hours at room temperature (see Fig. 1). After this, the surface of the impregnated cellulose was rinsed carefully to remove excess PF and left to dry for 1 hour. The cellulose/PF composite was then dried, consolidated and cured by placing it between two metal gauzes and absorbent material for 30 minutes at 110°C under a pressure of 1.1MPa and finally transferred to be pressed between highly polished metal plates with release film for 30 minutes at 110°C under a pressure of 2.5 MPa. Cellulose only sheets from the different samples were made following the same drying and consolidation procedure.

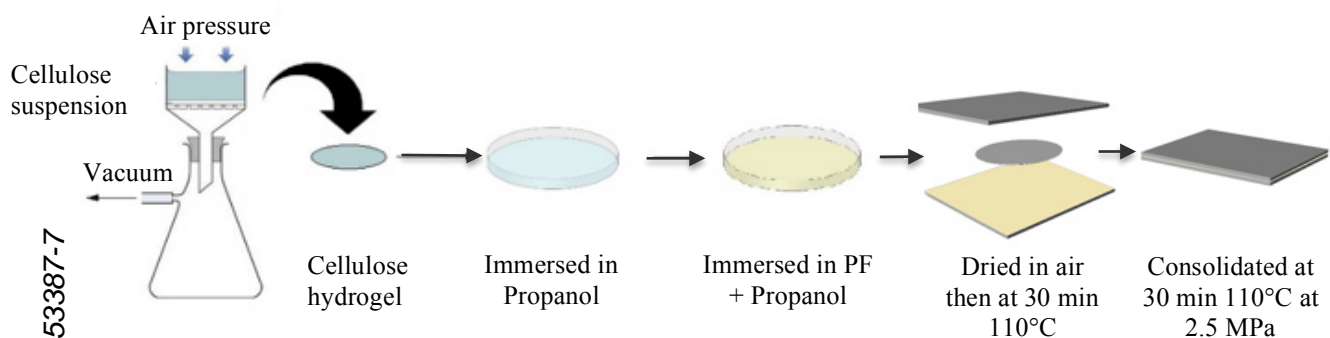


Figure 1. Schematic diagram of impregnation procedure

The degree of impregnation is taken as the amount of PF in the composite and was estimated by

$$\Phi_m = \frac{m_c - m_f}{m_c} \quad (1)$$

where m_c is the weight of the cellulose/PF composite, m_f is weight of a cellulose only network made from the same type of suspension.

The fibre mass fraction was calculated from $\phi_f = m_f/m_c$. The volume fraction of the fibres and matrix was calculated from $\phi_f = (\rho_f/\rho_c)V_f$ and $\phi_m = (\rho_m/\rho_c)V_f$, respectively. The theoretical density of the composite, assuming no voids, was calculated from

$$\frac{1}{\rho_{Tc}} = \frac{\phi_m}{\rho_f} + \frac{(1 - \phi_m)}{\rho_m} \quad (2)$$

Hence the void content could be calculated from

$$V_v = 1 - \frac{\rho_c}{\rho_{Tc}} \quad (3)$$

The morphology of the cellulose and composites was studied using a high resolution SEM (MagellanTM 400L XHR SEM, FEI Company, USA) of fracture surfaces of samples of the materials. These were sputter coated with gold to avoid charging and an acceleration voltage of 3kV was used.. Their mechanical properties were evaluated by tensile testing using a universal testing machine (AG-X, Shimadzu Corporation, Japan) equipped with a load cell of 1 kN. The material samples tested had a 20 mm gauge length and an approximate cross-section of 5.5 mm x 0.1mm. A constant strain increase was applied at a strain rate of 10% min⁻¹ and the stress measured.

3. Results

The morphology of the different films impregnated in the 5 wt.% PF solutions can be seen from the SEM images of the fracture surface of the materials after tensile testing (Fig. 2(a)). It is clear that the pulp fibres are isolated into finer material and in doing so the density of the network increases, (Fig. 2(b)). After the impregnation process, the weight increases by 30-40% in all cases, which shows that increasing the quantity of larger fibres in the networks, does not affect the degree of impregnation.

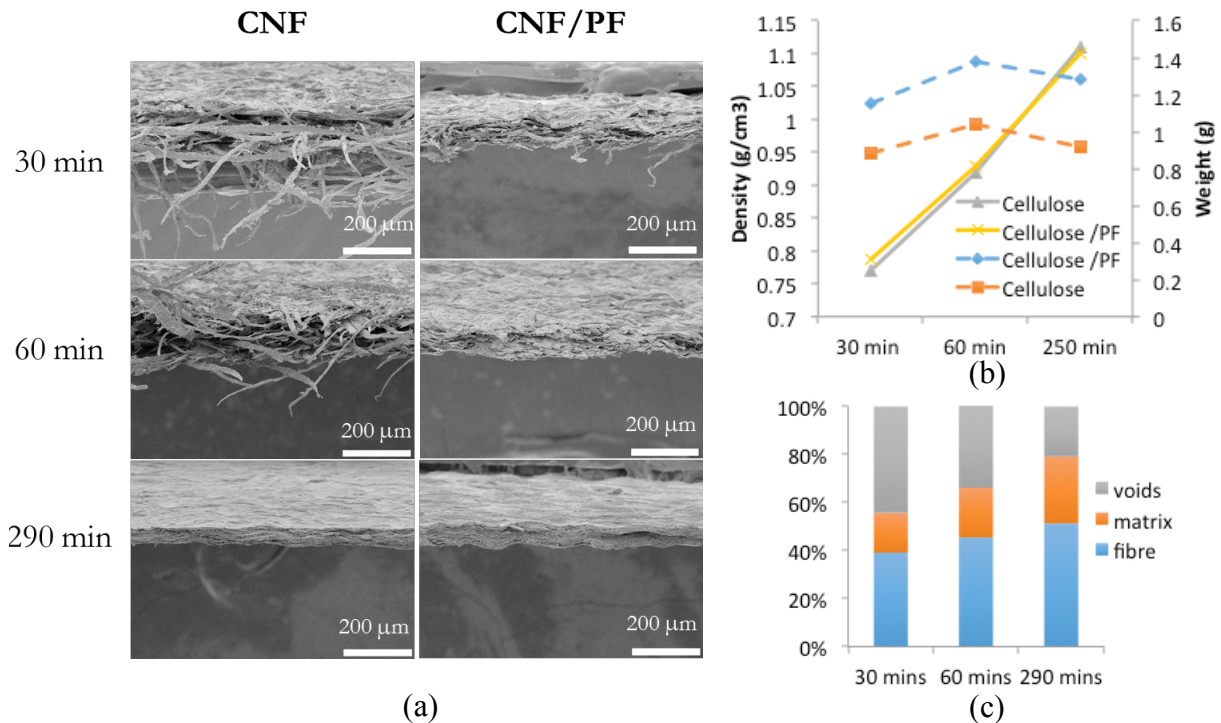


Figure 2. (a) SEM images of fracture surfaces of the samples after tensile testing. (b) Density of networks and composites. (c) Volume fractions of fibre, matrix and void in composites.

Perhaps surprisingly, it can also be seen that the density of the cellulose/PF composites is not higher than the cellulose only networks, despite a weight increase. This is due to a difference in the geometry with both the diameter and thickness of the network increasing in the cellulose/PF composites compared to the cellulose only networks. It can also be seen from Fig. 2(a) that the PF has affected the way the cellulose network consolidates rather than adding external layers of PF on the outside of the cellulose network. The composites have, as a result, a high proportion of voids as can be seen from the results of volume fractions calculations based on Eq. 1- 3 and shown in Fig. 2 (c).

Fig. 3 (a) shows the stress-strain curves for the different materials. The curves for the cellulose only networks show clearly an increase in stiffness and strength as the pulp is fibrillated to nanofibres. This can be explained by an increase in the density as the smaller diameter fibres pack more tightly. This also results in a greater number of inter-fibre bonds, which facilitate stress-transfer and reduces fibre slippage, thus increasing modulus and both yield and ultimate strength. [6], [8], [9]

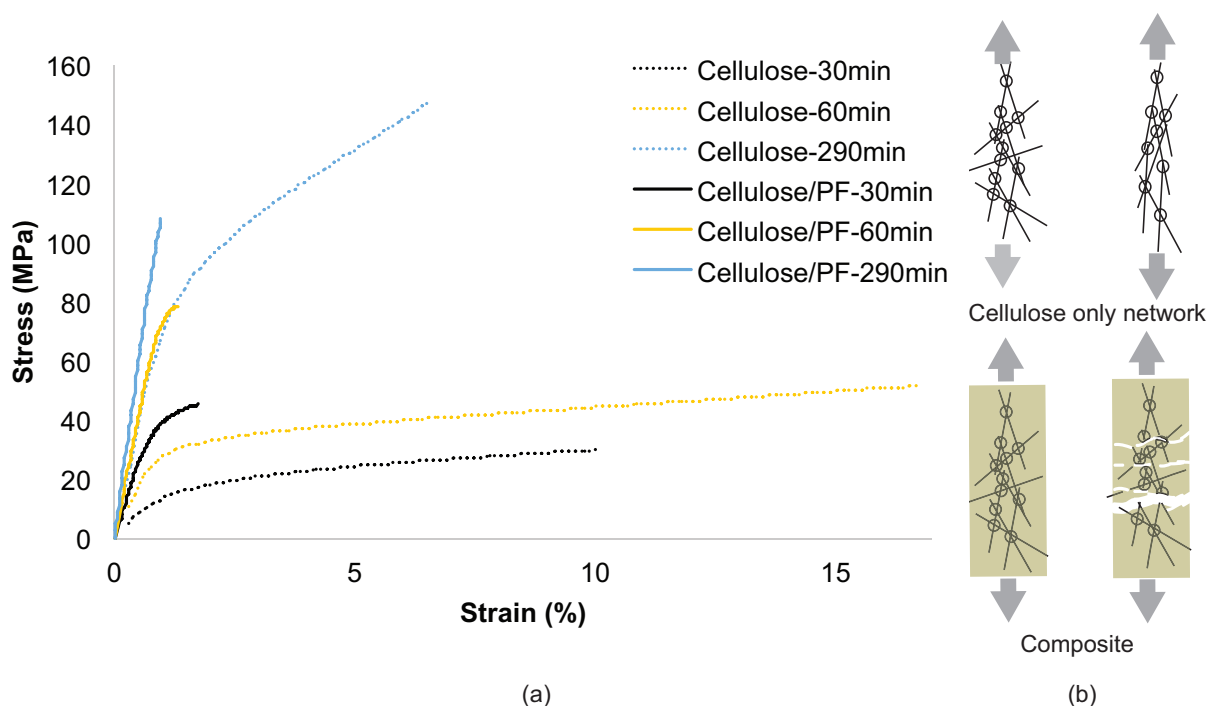


Figure 3. (a) Stress-strain curves for cellulose films from pulp with different degrees of fibrillation with and without addition of PF. (b) Mechanism of distortion and failure in the network only and in the composites

The addition of the PF increases the mechanical properties of the networks with lower processing times, hence it would appear that the PF is playing an important role in stress transfer between the fibres and supporting the load. In the composite of well-fibrillated cellulose, the modulus and yield strength increases but the ultimate strength decreases. The reason for this could be that the high ultimate strength of the cellulose only network comes from the deformation of the network. At the yield point, the inter-fibre bonds start to break allowing the network to deform as shown in Fig. 3 (b) and increasing the alignment of the fibres, thus supporting an increasing load. In the case of the composite, the network strain is restricted by both the inter-fibres bonds and the addition of the resin, thus resulting in the increase in modulus and reduced slippage leading to high yield strength. However, the PF appears to restrict the alignment of the fibres in the network and the failure therefore occurs at a lower ultimate strength.

The calculation on the volume fractions of the fibres, matrix and void content shown earlier in Fig. 2 shows that all the composites have a high void content. This will have a large impact on the modulus and strength. The effect of voids on modulus of the composite, E_c has been modeled as [10], [11]

$$E_c = (\eta_o \eta_f V_f E_f + V_m E_m)(1 - V_p)^n \quad (4)$$

where E_f is the modulus of the fibres taken as 140 GPa [2], η_o the orientation efficiency which for randomly orientated fibre in the plane is 0.38, η_f is the length efficiency which for fibres with high aspect ratio is approximately 1, V_f , V_m and V_p are the volume fractions of the fibres, matrix and voids, respectively and their values taken from Fig.2. n is a porosity efficiency exponent and found to be 2 for many cellulose based composites [10].

Using this, the theoretical modulus of the composites can be estimated and these are shown in Table 1 alongside the measured values and the theoretical value without voids.

Table 1. Theoretical and measured modulus of the composites

Composite Network base types	E_f (GPa)	E_m^* (GPa)	E_c (GPa)	E_{Tc} (GPa)	E_{Tc} (no voids) (GPa)
30 min	134	6	5.2	6.5	21
60 min	134	6	8.3	11	24
290 min	134	6	11.4	17	28

*The E_m is back-calculated from PF/glass-fibre composites and shown in the appendix.

The results in Table 1 show that theoretically the presence of voids has a strong influence on the modulus and when these are taken into account the theoretical values lie closer to the measured values. This means that the main reason for the low values of the modulus, compared to the maximum achievable value from these composites, is the presence of the voids. The measured modulus is still lower than the theoretical values and these differences could arise from inter-fibre bonding causing a weaker bond than that of a fibre embedded in a stiff matrix, as suggested by earlier study on cellulose based nanocomposites [6] or that the influence of the voids could be larger than that modelled with $n=2$, possibility due to inhomogeneity in their distribution.

3. Conclusions

In conclusion, as the degree of fibrillation and the proportion of nanofibres increase, the mechanical properties of the networks and their composites increase. Impregnation of cellulose during their hydrogel state results in a high resin content in the resulting composites of approximately 20-30 wt.% PF. The presence of larger fibres combined with nanofibres does not appear to affect the degree of impregnation using this method. The PF restricts the ductile deformation of the network, which increases the yield strength and modulus in all cellulose networks. This increases the strength of the composites based on partially fibrillated cellulose, however it reduces the strength of the composites based on well-fibrillated cellulose. In addition the method appears to restrict the consolidation and voids remain in the composite, which reduce the modulus when compared to theoretical maximum values for this material. More work on the consolidation process would therefore be necessary to achieve the full potential of composites based on cellulose nanofibre and PF.

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Appendix

The PF matrix was brittle and difficult to test hence its modulus was estimated from back-calculating the value from the modulus of glass fibre/PF composites of [0,90]₁₅ satin weave using the rule of mixtures:

$$E_c = \eta_o \eta_f V_f E_f + (1 - V_f) E_m \quad (5)$$

E_c was 23 GPa, taken from an average of 6 samples, $E_f = 73$ GPa, η_o was taken as 0.5, η_f was assumed to be 1 as the glass fibres are continuous, V_f was estimated as being 55% after compression. The estimated value was 6 GPa. Note that whilst this may not be an accurate estimation, it is only used in equation (2) where it does not have a large influence on E_c . For example changing the value from 3 GPa to 10 GPa changes E_c from 16.9 to 18.2 GPa, for the composite based on 290 min fibrillated cellulose. Hence, the accuracy of the back-calculation was assumed sufficient for this study.

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