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Fibril orientation redistribution induced by stretching of cellulose nanofibril hydrogels

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The mechanical performance of materials reinforced by cellulose nanofibrils is highly affected by the orientation of these fibrils. This paper investigates the nanofibril orientation distribution of films of partly oriented cellulose nanofibrils. Stripes of hydrogel films were subjected to different amount of strain and, after drying, examined with X-ray diffraction to obtain the orientation of the nanofibrils in the films, caused by the stretching. The cellulose nanofibrils had initially a random in-plane orientation in the hydrogel films and the strain was applied to the films before the nanofibrils bond tightly together, which occurs during drying. The stretching resulted in a reorientation of the nanofibrils in the films, with monotonically increasing orientation towards the load direction with increasing strain. Estimation of nanofibril reorientation by X-ray diffraction enables quantitative comparison of the stretch-induced orientation ability of different cellulose nanofibril systems. The reorientation of nanofibrils as a consequence of an applied strain is also predicted by a geometrical model of deformation of nanofibril hydrogels. Conversely, in high-strain cold-drawing of wet cellulose nanofibril materials, the enhanced orientation is promoted by slipping of the effectively stiff fibrils.

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I. INTRODUCTION

Cellulose nanofibrils (CNFs) disintegrated from wood pulp have been the focus of intense research during the last decade.¹ The mechanical properties of CNF materials are of interest for many potential applications. The stiffness and strength in the axial direction of CNFs give impetus for load-carrying applications. The CNFs are ideally constituted by elementary fibrils from the cell wall of tracheids from trees.² The microfibrils are co-oriented to merely a few degrees to the longitudinal direction in the dominant secondary layer S2 of the cell-walls of normal wood, resulting in remarkable mechanical properties considering that wood is a low-density biopolymer material with a high moisture content. In manufactured CNF materials, this almost perfect orientation is lost, and the orientation is typically random in-plane for thin CNF films. It is of interest to develop manufacturing methods to improve orientation, since many structural components are subjected to uniaxial stresses. If the CNFs can be oriented in the maximum principal stress direction, the mechanical performance of the component could be radically improved. Development of processing routes to control the orientation is therefore of significance. To facilitate materials development, measurement and analysis of the CNF ability to reorient are useful. The present work is a contribution in this area.

The most common and direct way to manufacture CNF materials is to cast films through deposition of CNFs on a fine wire or in a Petri dish. The final films will have essentially a random in-plane orientation of the nanofibrils and the films

can be tested mechanically with tensile tests. Typical values of the in-plane Young's modulus of such films are 14–16 GPa.^{3–5} However, the orientation of the CNFs highly affects the mechanical performance of the films, and a more advantageous use of the stiff CNFs would be in an aligned configuration. To be able to control the mechanical performance of the CNF based materials, a technique to orient the nanofibrils is desirable. In the last years, many researchers have focused on producing materials with aligned CNFs. Iwamoto *et al.*⁶ produced wet-spun fibers from CNFs by various spinning rates, resulting in different degrees of alignment of the CNFs in the fibers. The structure and the mechanical properties of the fibers were studied. For the highest spin rate, a fiber with a Young's modulus of 23.6 GPa was produced. Walther *et al.*⁷ produced macrofibers from CNFs by wet-extrusion. The fibers were prepared by extrusion of CNF hydrogels into a coagulation bath of an organic solvent. The bath creates a surface layer on the macrofibers, preventing interfiber aggregation and helps to maintain the distinct macrofiber. The macrofibers obtained by the wet-extrusion had a stiffness of 22.5 GPa. Torres-Rendon *et al.*⁸ continued on the work done by Walther *et al.* by adding an additional wet-stretching of the extruded macrofibers to achieve higher alignment of the CNFs. The procedure resulted in CNF fibers with a Young's modulus of 33.7 GPa. Jalal Uddin *et al.*⁹ produced composite fibers of polyvinyl alcohol and highly oriented cellulose whiskers from cotton. The composite fibers were manufactured by extrusion followed by hot drawing. By adding 30 wt. % of CWs, the Young's modulus increased from 30 GPa, for the pure PVA fibers, to 56 GPa for the oriented composite.

This paper analyses films of oriented CNFs, produced by cold-drawing. CNF hydrogel strips were stretched mechanically in order to reorient the nanofibrils. The method has been used by Gindl and Keckes¹⁰ for films of microcrystalline cellulose and by Sehaqui *et al.*¹¹ for films of CNFs. Both studies showed films with a high degree of alignment and improved mechanical properties, with a film Young's modulus of 33 GPa. The micromechanical behavior of cellulose hydrogels has been investigated by Lopez-Sanchez *et al.*¹² where the hydrogels were compressed in the direction perpendicular to the plane of the in-plane randomly oriented fibrils and the viscoelastic behavior was studied. The present study focuses on the realignment of the CNFs that occurs during the cold-drawing when strain is applied in the direction of the plane of the in-plane randomly oriented CNFs. The orientation distribution of the CNFs was quantified by X-ray diffraction (XRD). The hydrogel strips were subjected to increasing strain, ranging from 35% to 50%. The orientation behavior was qualitatively compared with the theoretical orientation distribution obtained by a simple geometrical model for reorientation of CNFs in a hydrogel due to an applied strain. The model is presented in Sec. II.

II. NANOFIBRIL REORIENTATION MODEL

In wet CNF films, the nanofibrils are dispersed in water forming a malleable hydrogel, where the nanofibrils are not fully bonded to each other. From the casting procedure, the CNFs have originally an in-plane orientation. When subjected to a strain in x -direction, the film will have a positive elongation in the x -direction and a resulting negative elongation in the y -direction. The stress transfer between the nanofibrils is necessary for the fibrils to reorient during stretching. Stress transfer arises from mechanisms where the fibrils interact, e.g., entanglement and flow-induced orientation. Ideally, an applied strain would directly translate of into a change in fibril orientation. For a nanofibril originally oriented with an angle φ from the x -axis, the applied strain will result in a new nanofibril angle φ' from the x -axis, as shown schematically in Figure 1.

The relation of the new nanofibril angle and the strain can be expressed by

$$\tan \varphi' = \frac{l(1 - \nu_{xy}\varepsilon_x)}{L(1 + \varepsilon_x)}, \quad (1)$$

where ε_x is the applied strain and ν_{xy} is the in-plane Poisson ratio of the matrix. For incompressible materials, such as water-saturated hydrogels, the Poisson ratio may be assumed

to be $\nu_{xy} = 0.5$. The length l can be related to the original angle φ by

$$l = L \tan \varphi \quad (2)$$

and substituted in Eq. (1), which gives the expression for the angle φ' in the deformed configuration as

$$\varphi' = \tan^{-1} \left(\frac{1 - \nu_{xy}\varepsilon_x}{1 + \varepsilon_x} \tan \varphi \right). \quad (3)$$

This expression can relate the initial orientation distribution function $p(\varphi)$ of the undeformed configuration to the orientation distribution function $p(\varphi')$ of the deformed configuration.

III. MATERIALS AND METHODS

A. Disintegration of cellulose nanofibrils from softwood sulphite pulp

The CNFs were produced from softwood sulphite pulp, with a lignin content of 0.7% and a hemicellulose content of 13.8%, supplied by Nordic Paper Seffle AB. The pulp was treated with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation according to Saito *et al.*¹³ The pulp was then dispersed in water containing 1 mmol bromide and 0.1 mmol TEMPO per gram of cellulose. The final suspension had a concentration of 2 wt. % cellulose. Sodium hypochlorite of a concentration of 10 mmol per gram of cellulose was added stepwise to the suspension and the pH was kept at 10 by sodium hydroxide addition. The suspension was then filtered and washed, followed by dilution with water to obtain a neutral suspension of 1 wt. % cellulose. The suspension was treated mechanically with a Microfluidizer M-110EH (Microfluidics Ind., USA) which resulted in individually separated CNFs.

B. Film preparation

The CNF suspension of 1 wt. % cellulose was dispersed to 0.1 wt. % by adding water under stirring. The suspension was carefully poured in a funnel with a diameter of 72 mm and vacuum filtered using a filtering membrane (0.65 μm DVPP, Millipore). The flow in filling the bottom of the mold was minimized in order to avoid a preferential nanofibril orientation. From the filtering process, wet hydrogel films were formed. The hydrogel films contained 70%–90% water, had a jelly like texture, and had relatively large thickness (millimeter range). The hydrogel films were carefully peeled from the filtering membrane, and cut into 10 mm wide strips. The hydrogel strips were mounted in a tensile tester (Instron

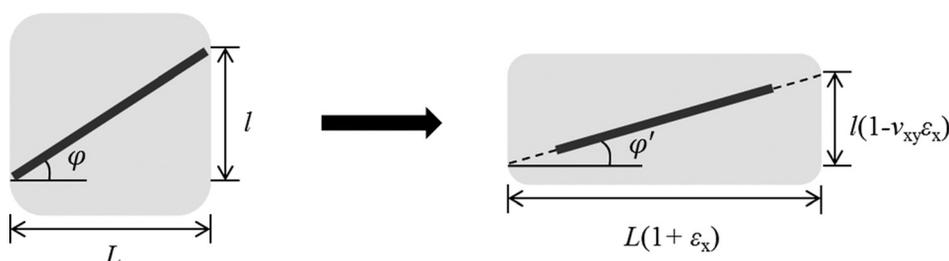


FIG. 1. A wet film of CNFs subjected to a strain in the x -direction will undergo a reorientation of the structure in the film. For a nanofibril oriented with an angle φ from the x -axis, the strain will cause a rotation of the nanofibril to the angle φ' .

5944), and stretched with controlled strain rate of 0.5 strain per minute. In total, 6 strips were subjected to a strain of 35%–50%. The strains were estimated from the position of the calibrated stroke of the clamps under no-slip conditions. The CNF films were stretched immediately after the vacuum filtration and thereafter directly dried in the final strained configuration in a semi-automatic sheet dryer (Rapid Kouthen-Rycobel Group) for 12 min at 93 °C in a vacuum of about 70 mbar.¹⁴ The dried sample had a thickness of 50–100 μm . The in-plane shrinkage was negligible to the out-of-plane shrinkage during drying. The shrinkage strains in the axial direction of the strips were not considered in the present study. Only the applied strains in the hydrogels were considered in the orientation study. Reference films with randomly orientated CNFs were also produced by direct drying of the hydrogels without any applied strain.

C. X-ray diffraction

The XRD was measured from each sample subjected to strain and also from a reference sample dried in the undeformed state. The X-rays were generated with a rotating Cu-anode X-ray source (Rigaku), with a voltage of 50 kV, a current of 80 mA, and monochromatised (copper K_{α} , wavelength of 1.541 Å) with a bent Si (1 1 1) crystal. Each sample was exposed for 1 h. The distance from the MAR345 image plate detector to sample was 120 mm. Calibration of the scattering angles was done with silver behenate and lanthanum hexaboride samples.

Detector read-out noise and air scattering were subtracted from the measured two-dimensional data. Polarization correction and flat-panel geometrical correction were then performed. Due to the low sample absorption, no angle-dependent absorption correction was employed. The remaining non-crystalline contribution was subtracted by linear fitting before the fibril orientation analysis. The orientation distribution was calculated from the 200-diffraction peak at the scattering angles of $2\theta = 21.5\dots 23^\circ$, and the regions of $2\theta = 13\dots 15^\circ$ and 23.25° were assumed to comprise fully non-crystalline contributions. Further, the latter two regions were limited in azimuthal angles to two 40° sections perpendicular to the two maxima of the 200-peaks. Since the thicknesses of the samples are much smaller than the optimal scattering thickness, the raw data were noisy. For the purpose of visualizing the trend of the nanofibril orientation in the films and for easier comparison of the distributions, smoothing was done on the data using a moving average with a span of 20° in the azimuthal direction.

IV. RESULTS AND DISCUSSION

When cold-drawing a never-dried CNF hydrogel, a reorientation of the CNFs will occur. In the wet hydrogel films, the interacting nanofibrils are suspended in the water matrix and are not fully bonded to each other. When a strain is applied, the nanofibrils will reorient and align towards the direction of the applied strain. The films investigated in this project were subjected to a strain of 35%–50%. An undeformed reference sample was also analyzed. To determine the orientation distribution of the CNFs as a function of the

applied strain, XRD measurements were acquired from all the samples. The XRD data provided information of the crystal orientation in the sample. For cellulose, the 200-diffraction peak can be used to determine the orientation of the cellulose crystals. As the c axis of these crystals is oriented along the direction of the nanofibrils, the orientation of the cellulose crystals corresponds to the orientation of the CNFs.¹⁵ The XRD patterns were carefully analyzed and the 200-peak investigated. An example of a XRD pattern, showing the 200-diffraction peak, the axes of the scattering angle 2θ and the azimuthal angle φ , is shown in Figure 2.

For thin samples, as used in this project, the scattering from the sample is weak and it is difficult to accurately separate the scattering intensity into crystalline and amorphous cellulose contributions. Resolving the crystallite orientation distribution from the XRD data requires that the relative scattering intensities depend only on the crystalline cellulose contribution. The use of linear background ensures that all contributions from other scattering material, such as amorphous cellulose, water, and air, are removed and the calculated intensity is attributed to scattering from only the crystalline cellulose. By integration of the intensity on a ring corresponding to strong scatter from crystalline cellulose (the 200-diffraction peak), the orientation distribution of the nanofibrils can be plotted with respect to the azimuthal angle. In Figure 3, the orientation distributions of the CNFs in the different samples are shown.

As can be seen in Figure 3, the orientation distribution of nanofibrils in a film is a function of the applied strain. When the applied strain increases, the alignment of the CNFs is more pronounced. The experimental data can be compared with the model predicting the nanofibril reorientation in a hydrogel subjected to a strain in one direction, as derived in Eq. (3). The predicted orientation distributions of nanofibrils in such composites subjected to the same amount of strain as in the experimental procedures are shown in Figure 4.

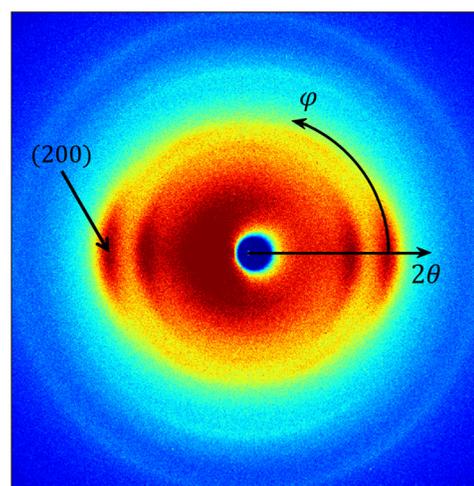


FIG. 2. An example of XRD pattern obtained from a CNF film subjected to a strain. The image shows the difference in intensity by the different colors and the axes of the scattering angle 2θ and the azimuthal angle φ .

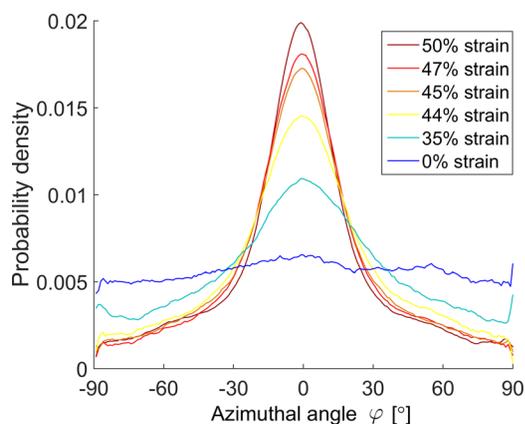


FIG. 3. Orientation distributions of the CNFs in the films subjected to various strain levels.

As can be seen in Figure 4, the CNF alignment predicted by the model is not as strong as that seen in the experimental results. All of the probability density curves are flatter than those observed in the XRD measurements. The model of CNF reorientation predicts the ideal reorientation of CNFs in a hydrogel subjected to an external strain. In the model, the Poisson ratio was set to 0.5 as the matrix material is water, which is essentially an incompressible material. The composite hydrogel can therefore also be regarded as incompressible. The difference in the orientation distributions measured in the films and the orientation distributions predicted by the model could probably be explained by additional CNF orientation mechanisms, as well as the difference in local and average strain. The presented geometrical model is in principle based on an idealized elastic situation, where the CNF is tilted and the matrix is deformed according to the global strain. In practice, there is a flow in the liquid matrix, which also contributes to further alignment. Furthermore, the experimental strain was measured by the displacement of the end clamps, which gives the average strain of the sample. Each XRD measurement was done on a spot in the middle of the sample where the local strain can be higher than the average strain subjected to the sample.

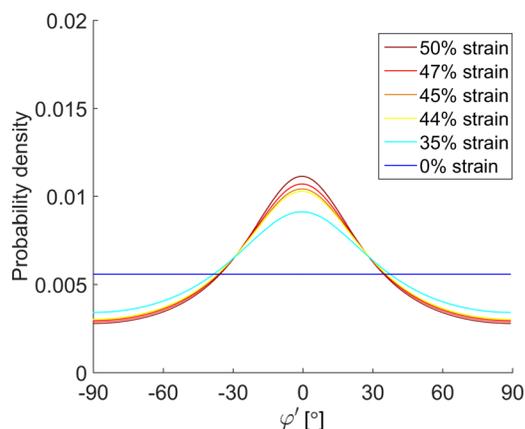


FIG. 4. Predicted orientation distributions of CNFs in hydrogel composites subjected to various strain levels.

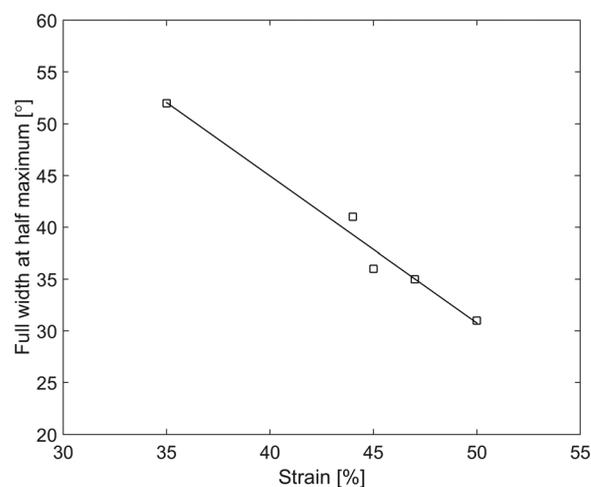


FIG. 5. Full width at half maximum of the orientation distribution peaks as a function of the applied strain where the squares are the experimental results and the line is a linear fit to the experimental data.

One way to quantify the degree of orientation with a single parameter is to determine the full width at half maximum (FWHM) of the unimodal bell-shaped distributions. The FWHM can be determined as a function of the applied strain, as plotted in Figure 5. As the ends of the probability curves are based on information of low intensity diffraction, it is subjected to considerable scatter. As the FWHM is just a relative measurement, the baseline levels used to determine the FWHM were chosen at the value corresponding to an azimuthal angle of 20° for each curve. Being based on experimental orientation distribution functions determined by XRD, there is a remarkable linear correlation between the FWHM and the applied strain. The high degree of linear correlation indicates that an orientation-strain relationship can be formulated, preferably based on the physical deformation mechanisms. Only geometrical tilting of the CNFs under elastic conditions as described in the suggested model is, however, not enough to describe the observed CNF alignment shown in Figure 3.

With an improved predictive model for the case of ideal and unhindered CNF orientation, it would be useful to compare the experimental results to the predictions. The difference could then be attributed to the resistance to alignment. Such a parameter describing the resistance or propensity to CNF orientation may be used to qualitatively compare different processing routes. For instance, Tang *et al.*¹⁶ have recently shown that polyethylene glycol-coated CNFs in hydrogels orient more readily than untreated CNFs in hydrogels when subjecting the hydrogels to a strain. The interfibrillar hydrogen bonding was reduced by the surface treatment, thus facilitating the nanofibril alignment. Fibril-fibril bonds are, however, desirable in providing stress transfer between the nanofibrils, when the final material carries load. There is thus a trade-off between processability (nanofibril alignment) and mechanical performance (stiffness and intrinsic strength) of the material. Material mechanics can provide insight into these processes and provide a suitable balance between processing and performance.

V. CONCLUSIONS

The reorientation of CNFs in films subjected to different amount of strain was studied. Characterization by X-ray diffraction showed that cold drawing of wet films of CNFs results in alignment of the nanofibrils, assuming that the CNF orientation is the same as that of the cellulose crystallites. The measured alignment was higher than predicted by the model describing mere geometrical tilting of the CNFs. Additional flow-induced orientation is therefore expected. The experimental method to estimate the CNF orientation distribution can be used to compare the alignment ability of different CNF materials. Furthermore, a high linear correlation was found between the full width at half maximum of the CNF orientation distributions and the applied strain.

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