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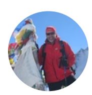
Redouane Borsali
French National Centre for Scientific Research



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Grenoble Institute of Technology

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Letters

Shear-Induced Orientation Phenomena in Suspensions of Cellulose Microcrystals, Revealed by Small Angle X-ray Scattering

T. Ebeling, M. Paillet, R. Borsali,* O. Diat,† A. Dufresne, J-Y. Cavaillé,‡ and H. Chanzy

CERMAV-CNRS, affiliated with the Joseph Fourier University of Grenoble, Box 53, 38041 Grenoble Cedex 9, France

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The alignment of cellulose microcrystals in a 6.9% (w/w) colloidal aqueous suspension under shear was characterized using small angle synchrotron radiation scattering. Prior to shearing, the microcrystals appeared randomly oriented and went through a two-step alignment process with increasing shear rate. At shear rates lower than 5 s^{-1}, the X-ray scattering patterns indicated little or no preferential alignment in the shear direction; however, in the plane perpendicular to the shear direction, the microcrystals were preferentially oriented in the vertical direction. At shear rates of 5 s^{-1} and higher, the microcrystals were aligned horizontally along the shear direction. These orientation phenomena were found to be dependent on shear rate and completely reversible. They are likely due to the presence of planar domains of randomly oriented microcrystals which align at low shear rates and are broken up at higher shear rates enabling alignment of the individual microcyrstals.

Introduction

It is known that native celluloses, when subjected to strong acid hydrolysis, readily break down into "microcrystalline cellulose" with almost no weight loss.[1] Such resultant assemblies of cellulose microcrystals are utilized in a large variety of applications in a number of flourishing businesses.[2] Due to the high aspect ratio and specific physical properties of the microcrystals, they continue to also be the focus of investigations in basic research.[3−5]

The length of these microcrystals is dependent on the sample origin. They can be as short as about a tenth of a micrometer, for cotton and wood cellulose, or as long as several micrometers for tunicates or seaweeds such as *Valonia*.[6] The width is typically between 5 and 20 nm.

A negative surface charge may be induced during cellulose microcrystal preparation which will enable specific colloidal interactions of these microcrystals in water. The nonflocculating charged microcrystals yield well-dispersed suspensions at low concentration and chiral nematic phases above a critical concentration, around 5% (w/w) for cotton microcrystals.[4] This concentration is well above the concentration at which the rotation of microcrystals is geometrically hindered (less than 1% (w/w)).

* Corresponding author: E-mail: borsali@cermav.cnrs.fr.
† ESRF-BP 220, 38043, Grenoble Cedex, France.
‡ GEMPPM; UMR CNRS-INSA #5510, INSA, 69621 Villeurbanne Cedex, France.

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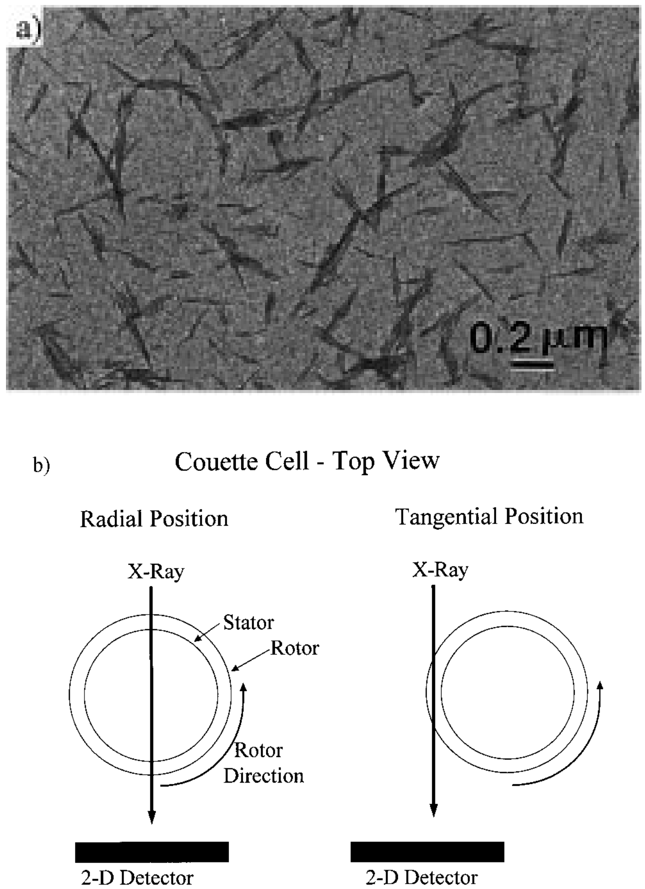

Figure 1. (a) TEM micrograph of cotton microcrystals. (b) Schematic of the experimental setup.

Recently, the utility of the cellulose microcrystals as nano-reinforcement was demonstrated. When the microcrystals are homogeneously dispersed into polymer matrices, they give a remarkable reinforcing effect, even at concentrations of a few percent.[7,8] Because the properties of such nanocomposites are very sensitive to the processing conditions, it is important to understand how the microcrystals orient under the shearing forces that are typical of polymer processing. Previous work in this area includes a study on the rheological properties of suspensions of chitin microcrystals, about 200 nm long and aspect ratio of about 13[9] and a study of shear alignment of suspensions of black spruce cellulose microcrystals, 180−280 nm long, aspect ratio of about 30, using small angle neutron scattering.[10]

We have conducted a related study of cotton microcrystals, with an average length of about 170 nm and aspect ratio of about 10, using small-angle X-ray scattering synchrotron radiation. Although the work is still in progress, we would like to communicate an important observation. The scattering results indicate microcrystal alignment under shear is a two-step process. Although a two-step alignment model was proposed based on rheological data,[9] this study reports the first structural data supporting this hypothesis.

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Experimental Section

Nonflocculating aqueous suspensions of cotton microcrystals were prepared from Whatman no. 1 filter paper following the procedure of Dong et al.[11] Figure 1a shows a TEM of the cotton microcrystals. A suspension containing 6.9% (w/v) cellulose was poured into a homemade polycarbonate couette cell for shearing. The couette cell was positioned in the X-ray beam at the small angle scattering station of the high brilliance beamline ID2 at ESRF,[12] operated at a wavelength of 1 Å and the detector distance was 6 m. The cell was mounted on motorized translation stages which allow the sample to be aligned in both the radial and tangential positions, Figure 1b. In the radial configuration the incident X-ray wavevector was perpendicular to the flow direction but parallel to the velocity gradient. Thus, in this position, the results were sensitive to ordering within the plane created by the vertical direction (V) and the flow direction (F), i.e., the V−F plane. In the tangential configuration the incident X-ray wavevector was parallel to the flow direction or the shear velocity. Thus, in this position, the results were sensitive to ordering within the plane created by the horizontal (H) and the vertical directions perpendicular to the flow direction, i.e., the H−V plane. The raw data were normalized by the transmission (taken online) and corrected for the response of the 2-D detector.

Results and Discussion

Effect of Shear Rate. The alignment process was determined to be a two-step process by coupling both the radial and tangential scattering patterns. At a low shear rate, $\gamma = 0.05\ s^{-1}$, the scattering pattern from the radial position shows an isotropic ring pattern, Figure 2a. In the radial position the beam path is perpendicular to the shear direction and is sensitive to orientation along the shear direction. These results indicate that there is no preferential alignment in the shear direction compared to the vertical direction.

The scattering pattern from the tangential position shows an anisotropy with peaks along the longitudinal arcs, Figure 2b. In the tangential position the beam path is parallel to the flow direction and thus sensitive to orientation in the H−V plane. Alignment in the vertical direction is favored over alignment in the horizontal direction. Thus, in the first step, at low shear rates, the microcrystals change from three-dimensionally random to preferentially ordered in the vertical direction as compared to the horizontal direction.

As the shear rate is increased to 500 s^{-1} both the radial and tangential scattering patterns change, patterns c and d of Figure 2, respectively. The pattern from the radial position exhibits anisotropic interference peaks along the lateral arcs. The pattern from the tangential position is an isotropic ring. These results indicate the microcrystals are aligned along the shear direction. Thus, in the second step, at higher shear rates, the microcrystals change from vertically aligned to ordered along the shear direction.

There are two possible explanations for these results. The first, the domain explanation, is based on the observation that some of the microcrystals form anisotropic domains in the suspension at rest. The domain explanation hypothesizes that the microcrystals within these domains adopt a uniplanar organization. At low shear rates, due to the their anisotropy, the planar domains orient along the shear direction. Consequently, in the radial position, the X-ray beam will be perpendicular to the planar domains containing the microcrystals. However, because the microcrystals within the domains do not align along the shear direction, the radial scattering pattern is an isotropic ring pattern. The alignment of the domains inhibits the microcrystals from lying horizontally per-

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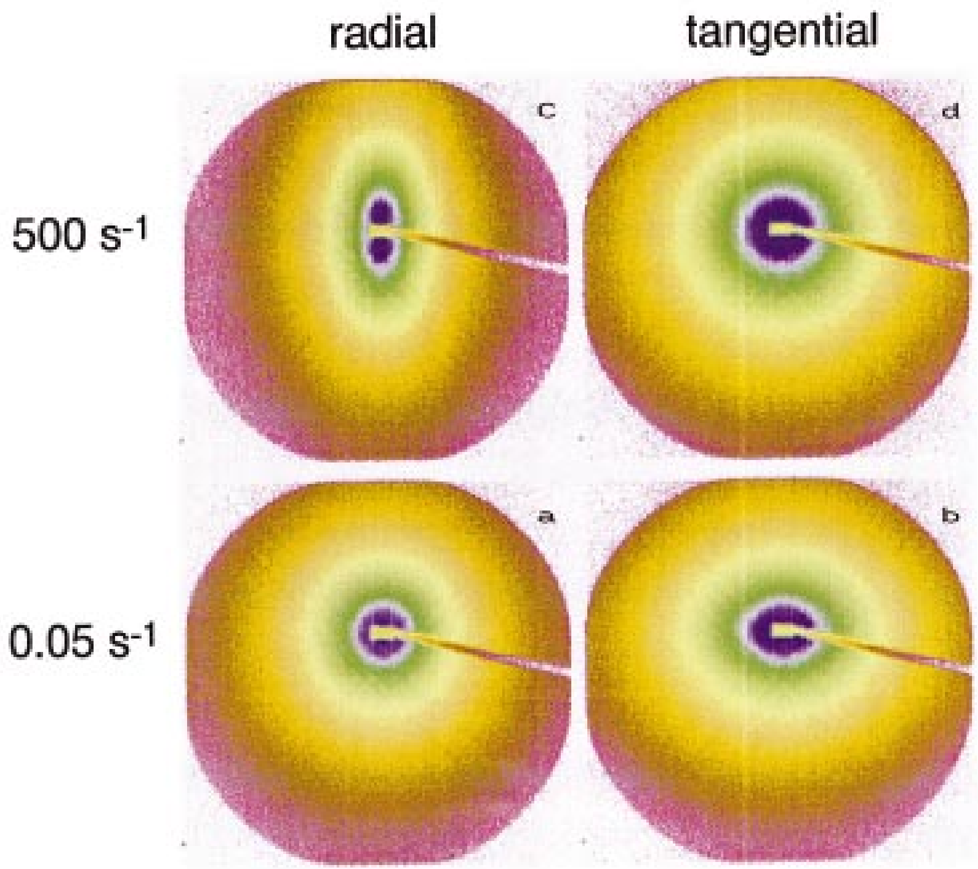

Figure 2. Two-dimensional scattering patterns collected at different shear rates.

pendicular to the flow direction. Thus, in the tangential position, where the X-ray beam strikes the side rather than the face of the planes, vertical alignment is detected. For the domain model, the second step is the disruption of the domains accompanied by alignment of individual microcrystals. This domain model was proposed as an explanation for the rheological properties of chitin microcrystal suspensions.[9]

The second possible explanation, the tumbling explanation, is based on an analogy to director tumbling of liquid crystals. This explanation hypothesizes that at low shear rates the microcrystal orientation is unrestricted in the plane of the vertical and flow directions and they possibly even “tumble” end-over-end in the vertical direction. However, the microcrystals are aligned along the flow direction in the plane of the horizontal and flow directions. In the second step, at higher shear rates, the microcrystals are no longer free to tumble vertically. The data cannot address whether the microcrystals are tumbling or merely their orientation distribution has shifted. Furthermore, with liquid crystals, the tumbling is in the horizontal direction and is a transient state, whereas our data would require steady state, vertical tumbling.

In Figure 3, the azimuthal traces of Figure 2 are shown along with results from other shear rates. At low shear rates the azimuthal traces of the radial scans were flat, Figure 3. At a shear rate of about 5 s^{-1} peaks developed at 90° and 270°, indicating alignment along the flow direction. The sharpness of the peaks increased with increasing shear rate. The order parameter, defined as $S = {}^{1}/_{2}[3(\cos^2\theta) - 1]$, where θ is the angle between the director and the microcrystal, was calculated based on the shapes of these curves using an approach described

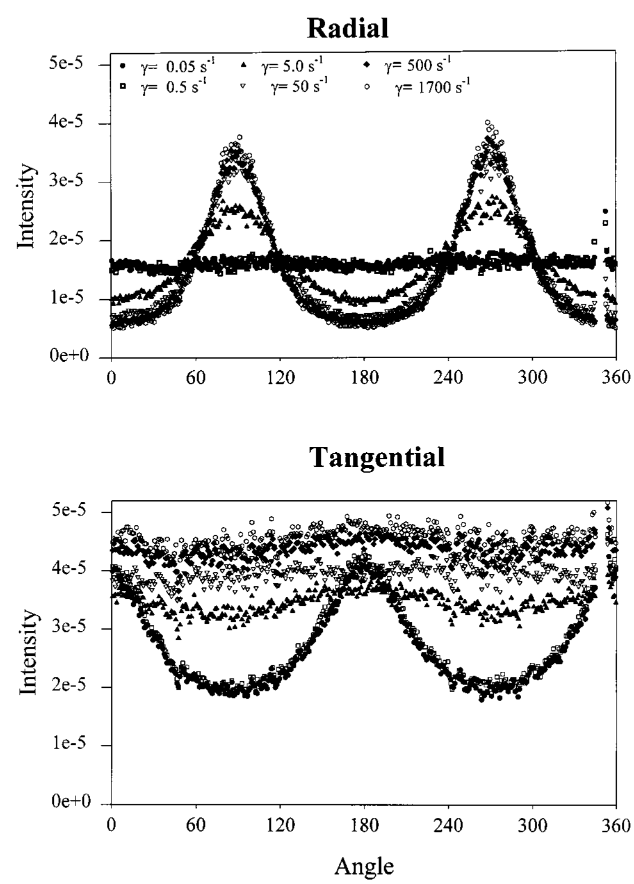

Figure 3. Azimuthal traces from scattering patterns for different shear rates.

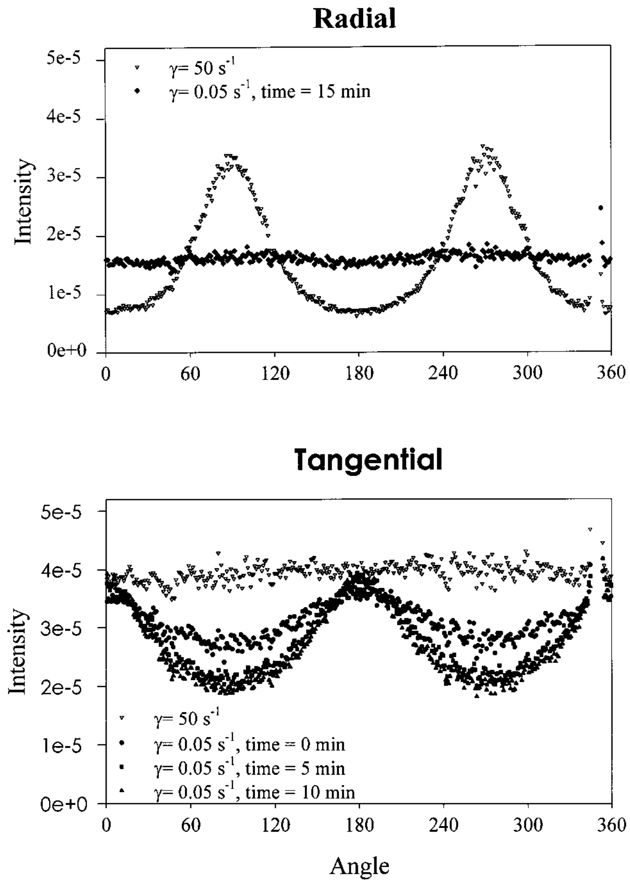

Figure 4. Azimuthal traces from scattering patterns collected at different times after the shear rate was reduced.

previously.[8] The order parameter increased from 0.00 at the lowest shear rate to about 0.75 at the highest shear rate.

The traces from the tangential position, Figure 3, showed an opposite trend, peaks appeared at low shear rates but not at the higher shear rates. Moreover, the peaks indicated vertical rather than horizontal alignment. For these experiments the order parameter decreased from a maximum of 0.59 at 0.05 s^{-1} to 0.00 at a shear rate of 50 s^{-1}. For both the radial and tangential results, the transition between ordered and random occurred between the shear rates of 0.5 and 5 s^{-1}, apparently indicating the shear rate at which the domains break up. This correlates well with the previous rheology results for chitin microcrystals which indicated domain break up at a rate of about 1 s^{-1}.[9]

Reversibility of Vertical Alignment Phenomenon. To ensure that the vertical alignment detected in the tangential direction is not due to a sample loading effect, the reversibility of the phenomenon was tested. This was done by shearing at 50 s^{-1} for 10 min and then decreasing to 0.05 s^{-1}. Scanning was initiated immediately after the shear rate was reduced. Each scan took 5 min; three tangential scans were collected consecutively followed by one radial scan. The azimuthal traces for these scans are shown in Figure 4 and they are labeled with the time at which the scan was initiated. In the radial position peaks were recorded along the latitude arcs, and the anisotropy recorded at 50 s^{-1} corresponds to an order parameter of 0.65. After shearing at 0.05 s^{-1} for 15 min another radial scan was taken. The peaks no longer appeared, and an order parameter of 0.00 was calculated. The trend recorded from the tangential scans was again the reverse. While under shear at 50 s^{-1} the trace is flat and the order parameter is 0.00. In the first tangential scan after reducing the shear to 0.05 s^{-1}, peaks appeared along the longitudinal arcs, at 0° and 180°, and the order parameter was 0.33. In the subsequent tangential scans the peaks sharpened and the order parameter increased to 0.55. This reversibility of the vertical alignment detected in the tangential position proves that it is due to the intrinsic nature of these rodlike particles rather than a loading effect.

We are presently studying, in greater detail, a number of effects such as the concentration of microcrystals, their mixture with nanoscale spheres, microcrystal aspect ratio, and the viscosity of the matrix. This work will be presented in a forthcoming paper.

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