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# Twist–Bend Stage in the Relaxation of Sheared Chiral Nematic Suspensions of Cellulose Nanocrystals

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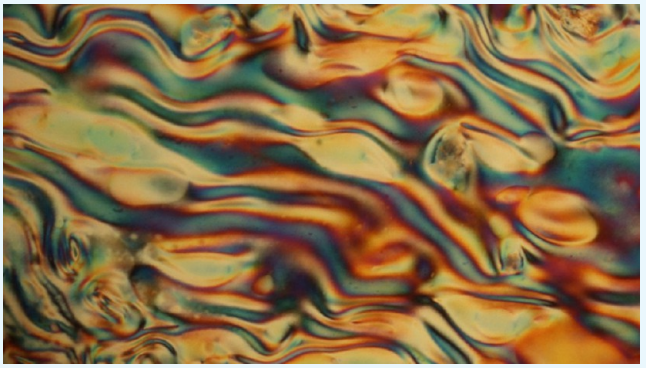
Supporting Information

**ABSTRACT:** Aqueous suspensions of cellulose nanocrystals (CNCs), prepared from natural cellulose by sulfuric acid hydrolysis, form stable chiral nematic suspensions above a critical CNC concentration. The chiral nematic organization may be preserved in films prepared from the suspensions by evaporation. However, shrinkage, gelation, and shear during film formation impair the optical properties of the dry film. In this article, we report an unusual behavior for a sample in which gelation occurred before the sample reached iridescent pitch values. In attempting to decouple changes in texture due to evaporation from those due to shear relaxation effects for this sample, we observed a transitory nematic-like texture that was induced by shear during the preparation of the sample for polarized light microscopy. We propose that the transition between chiral nematic and nematic structures involves a twist–bend-like intermediate and not an untwisting of the chiral nematic phase.



## INTRODUCTION

Cellulose, the most abundant organic material in the biosphere, occurs in nature as long, thin microfibrils, which after suitable mechanical and chemical processes form a family of nanocelluloses, with widths of the order of a few nanometers and lengths ranging from tens of nanometers to hundreds of micrometers. As the major biobased sustainable nanomaterial, nanocellulose has attracted attention for a number of applications.[1−3]

The relatively short cellulose nanocrystals (CNCs), prepared by sulfuric acid hydrolysis and stabilized by surface sulfate half-ester groups, were found to have an unexpected property. Aqueous suspensions of CNCs form a chiral nematic phase above a critical concentration.[4] Evaporation of water gives a solid film of cellulose that may preserve the chiral nematic structure.[4,5] Addition of small amounts of electrolyte to the suspension has been shown to move the pitch of the chiral nematic into the range of visible light wavelengths, resulting in iridescent films.[6,7] Despite the development of various methods to control the pitch and hence the peak reflection wavelength of CNC[8,9] and CNC-templated[10] films, the reported optical properties are usually poor, with broad reflection bands of intensities much lower than those predicted for uniform chiral nematics with planar texture;[11] thus, optimistic forecasts for optical applications have as yet failed to materialize. This note is part of ongoing attempts to understand the processes that influence the ordering of CNC suspensions at high CNC concentrations.

The most intense and pure reflection of circularly polarized light from thin chiral nematic films is expected for planar textures, where the chiral nematic axis is orthogonal to the surface of the film and the CNCs are arranged in a helicoidal arrangement, with their long axes parallel to the surface. Achieving a planar texture after the evaporation of water from the chiral nematic suspension has been elusive. A change in CNC concentration results in a change in pitch, and the shrinkage also causes the texture to break up into smaller elements, resulting in a grainy appearance. Under some circumstances, this texture may anneal to give a regular parabolic focal conic texture,[12] but the tendency of the suspensions to gel at some CNC concentration often prevents further reorganization in the liquid-crystalline state.[13] This phenomenon has been dubbed "kinetic arrest" by Honoratus-Rio et al.[14] Applying a radial shearing motion to concentrated suspensions between glass surfaces has been suggested to enhance optical properties,[15] but no reflection band wavelengths or intensities were measured. Controlling the rate of evaporation has also been investigated.[16,17]

Changes in the ordered structure caused by an increase in CNC concentration during evaporation are reflected in the rheological properties of the suspension. For example, Ureña-Benavides et al.[18] followed the changes in the rheological behavior of a cotton-based CNC sample from a dilute isotropic

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suspension through a wide biphasic region to the chiral nematic phase and finally to a gel phase. Conversely, the application of shear will generate deformation of the ordered structures in the biphasic, chiral nematic, and gel phases. The drying suspension is subject to shear, either intentionally or otherwise. In this article, we attempt to decouple changes in the texture of CNC aqueous suspension due to evaporation from those due to relaxation effects. The changes in the optical texture of thin layers of a concentrated chiral nematic CNC suspension are re-examined as a function of time, leading to a novel proposal as to how the relaxation of shear-deformed chiral nematic structures may occur.

Polarized light microscopy is used to address the question of how the texture of samples placed between a microscope slide and cover glass changes with time when evaporation is inhibited. The usual progression of chiral nematic textures in CNC suspensions is driven by increasing CNC concentration, from isotropic suspension to biphasic fluids, in which initial droplets of the chiral nematic suspension show fingerprint layers characteristic of the chiral nematic phase. As the concentration of CNCs increases, the droplets coalesce, resulting in typical planar or focal conic textures, in which the fingerprint texture remains visible for samples with pitch lengths of sufficient magnitude and helical axes in the plane of the sample. Rather than starting from dilute isotropic suspensions, preparation of samples for optical assessment usually starts with concentrations in the biphasic or liquid-crystalline regions. The shear applied during sample preparation generates a local nematic (equivalent to an infinite pitch chiral nematic), which then re-twists into a helicoidal structure, with pitch decreasing to its equilibrium value. Decreasing pitch is observed during evaporation of chiral nematic suspensions, but here we attempt to keep the CNC concentration constant and observe the change in optical textures with time.

The textures observed by polarized light microscopy have long been used to deduce the organization of liquid-crystalline phases.[11] The technique can in principal be supplemented by electron microscopy and a range of scattering techniques that give structural information regarding the orientation and spacing of CNCs in impressive detail,[19] but the lack of a uniform optical axis, the relatively rapid changes in texture with time, and the need for freeze-fracturing and sectioning hinders its application to our CNC suspensions.

Shear orientation and relaxation of chiral nematic structures is usually considered to involve an untwisting and a twisting process around the helicoidal axis,[15] but there are constraints on a simple twisting process around the helicoidal axis, as the nematic pseudolayers would have to twist relative to each other, requiring macroscopic displacements and generating intermediate pitch values. We suggest that there is an alternative mechanism for shear relaxation of CNC suspensions, involving an intermediate stage between nematic and chiral nematic ordered suspensions that is analogous in some ways to the twist−bend phase, $N_{tb}$, observed for molecular liquid-crystalline phases of bent molecular species.[20]

## TWIST−BEND STRUCTURE

For a conical helicoidal structure with axis along the $z$ direction of a right-handed Cartesian coordinate frame, the director of a twist−bend structure, $\bar{n}$, is defined by

$$\bar{n} = (\bar{x}, \bar{y}, \bar{z}) = (\sin\theta_0 \cos\varphi,\ \sin\theta_0 \sin\varphi,\ \cos\theta_0) \quad (1)$$

where $\theta_0$ is the constant oblique angle (the tilt angle) of the director with the helix axis, $z$, and $\varphi$ is the azimuthal angle of the oblique helicoid. $\varphi = 2\pi(z/P) = tz$, where $t = 2\pi/P$ and $P$ is the pitch of the conical helicoids.[20]

Note that eq 1 also describes the nematic phase, N, when $\theta_0 = 0$ and the chiral nematic phase, N*, when $\theta_0 = \pi/2$.

In essence, the twist−bend structure resembles the chiral nematic structure, except that the CNCs at a given position, $z$, along the helix axis take up a fixed tilt angle, $\theta_0$, relative to the helix axis, rather than being at 90° to the helical axis, as is the case for a normal chiral nematic structure. The twist−bend structure differs from that of a smectic C* phase[11] in that the director twist is continuous and lacks the layered structure of smectic phases.

To examine how this might affect the texture observed by polarized light microscopy, eq 1 may be used to calculate the director orientation for some arbitrary values of $\theta_0$, the tilt angle. [See Figure S1 in the Supporting Information.]

## EXPERIMENTAL SECTION

The CNC suspension was prepared as described previously[21,22] from Whatman cotton powder by acid hydrolysis with 64 wt % sulfuric acid at 45 °C for 45 min. After quenching, washing by repeated centrifugation and re-dilution with water, and dialysis against deionized water, the CNCs were dispersed by sonication. To ensure that the stabilizing sulfate half-ester groups on the surface of the nanocrystals were in the acid form, the suspension was stirred first over a mixed-bed ion-exchange resin and then over a strong acid resin. (It thus corresponds to the CNCs used to prepare suspensions SB-6 and SB-8 in ref 22.) The suspension was filtered and concentrated to 9.6% by weight, as determined gravimetrically. To measure the relative amounts of isotropic and anisotropic phases as a function of CNC concentration, the samples in sealed glass rectangular microslides were allowed to stand in a vertical position until no further change in the phase boundary was detected (at least 48 h). The results (Figure 1) indicated that a concentration of 9.6% should be essentially anisotropic. The surface charge of this CNC was 150 mmol/kg, measured by conductometric titration.

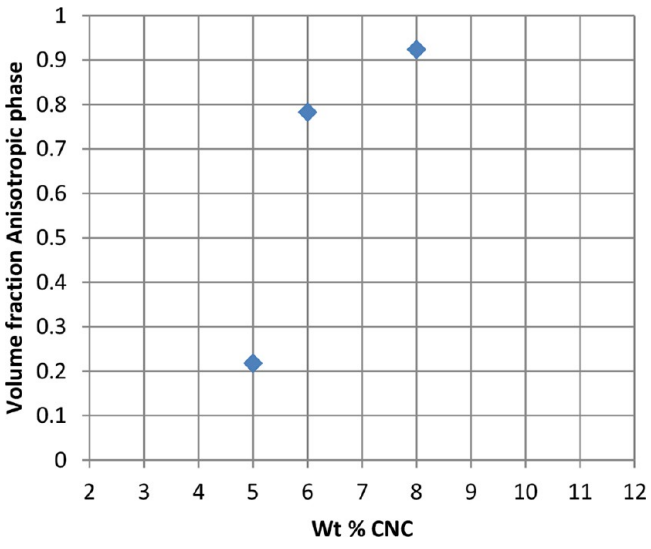


**Figure 1.** Phase composition as a function of concentration of CNCs in the suspension.



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For polarized light microscopy, samples of the suspension were placed on microscope slides to which spacers made from the plastic adhesive rings used to reinforce sheets in stationery binders were attached. Two of the rings provided suitable sample thicknesses. The microscope slides and cover glasses were used as received. A 20 $\mu$L sample of CNC suspension was pipetted into the center of the spacer ring, and a cover glass was placed on top to minimize evaporation. The sample thickness was 0.185 ± 0.005 mm, measured with a digital micrometer. To try and enhance uniformity, a gentle shearing action was applied to the samples by displacing the cover glass back and forth a small distance.

Photographs of the CNC textures were taken by a Nikon Eclipse LV100POL optical microscope equipped with a camera and a 530 nm wave plate. Unless otherwise indicated on the images, the samples were placed on the microscope stage such that the initial shearing action was in a horizontal direction on the image, the crossed polars were oriented horizontally and vertically, and the 530 nm wave plate, if used, was aligned in a direction from bottom right to top left on the images.

## RESULTS

For these observations, we started with a partially gelled suspension at a sufficiently high CNC concentration (9.6 wt %) such that it is in the chiral nematic phase (no isotropic phase) and with a pitch large enough to be visible in the optical microscope. The CNC sample used in this work differed from standard CNC samples in that gelation occurred at a relatively low concentration, trapping the pitch at sufficiently long values so that the final dry films showed no iridescence.[13]

The progression in textures of the same area of a thin sample of suspension is presented in Figures 2−5. The results are summarized in Figure 2. Initially, squeezing the suspension between the glass slide and cover plate produced a complex pattern of birefringence when viewed between crossed polars. The interference colors in the photomicrographs indicate local differences in birefringence, whereas dark lines indicate (1) liquid-crystal disclinations,[11] (2) regions where the CNCs are oriented parallel to the directions of the polars, or (3) regions where the CNCs are perpendicular to the plane of the sample. The initial pattern shows some orientation along the long direction of the image, reflecting a local shear orientation of the sample. After 30 min, the orientation has decreased and more symmetrical patches of birefringence develop, which, after a few hours, form the networklike pattern characteristic of a long-pitch chiral nematic phase (Figure 2g).

Examining each stage in more detail, the initial relaxation from the shear applied when sandwiching the CNC suspension between a microscope slide and cover glass is shown in Figure 3. The initial shear orientation (Figure 3a) becomes more uniform, until after 25 min the texture in Figure 3c is observed. This texture is characteristic of the marble texture commonly observed for *nematic* liquid-crystalline materials, in which areas of differing uniform director orientation occur.[23] Whereas the untwisting of a chiral nematic under applied shear or other fields gives a nematic-like orientation, normally high shear forces are required for untwisting CNC suspensions,[24] and the orientation of the director is uniform along the direction of shear. Neither case applies to the sample shown in Figure 3c.

After 45 min, the marble texture, indicating a randomly oriented nematic phase, starts to transform into the more ordered texture shown in Figure 4a. The patches of uniform birefringence are partially replaced by a threadlike texture,

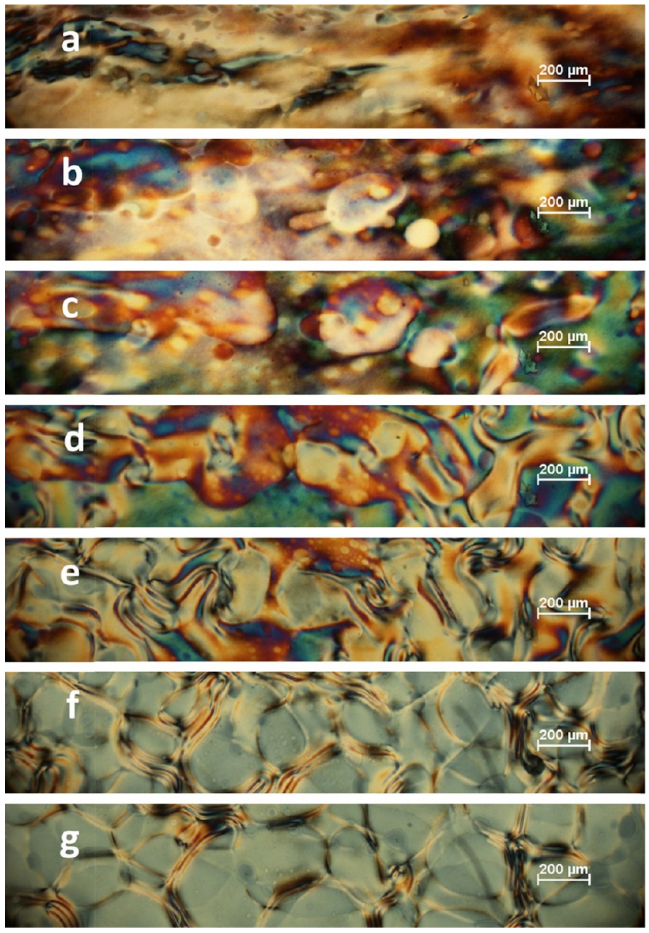


**Figure 2.** Overview of texture change with time for 9.6 wt % CNC suspension between a microscope slide and cover glass, viewed between crossed polars: (a) 5 min, (b) 30 min, (c) 60 min, (d) 110 min, (e) 170 min, (f) 330 min, and (g) 18 h. The spacer thickness is 185 $\mu$m. The same area of the sample is shown in each segment.

typical of a nematic with predominant director orientation in the plane of the sample. Evidence for a schlieren texture, characteristic of a nematic with the director normal to the viewing direction, is not readily evident, presumably because shear and surface orientation favor an orientation parallel to the constraining surfaces.

With time, the threads become more distinct and narrower (Figure 4b,c). After several hours, the pattern becomes typical of a long-pitch chiral nematic, with areas of planar orientation (director normal to the plane of the sample) separated by walls where the chiral nematic director is in the plane of the sample (Figure 5).

In Figure 5, the sample is viewed between crossed polars, and in this case, a 530 nm red plate has been added to indicate the orientation of the birefringent layers. The spacing of the fingerprint lines in the walls is relatively uniform, giving a line spacing of around 35 $\mu$m, corresponding to a chiral nematic pitch of ∼70 $\mu$m. The observations on this texture progression for a thin layer of a relatively concentrated viscous CNC sample show a clear progression from an initially *nematic* texture when freshly placed between a microscope slide and cover glass to the expected *chiral nematic* texture after standing undisturbed for a few hours.


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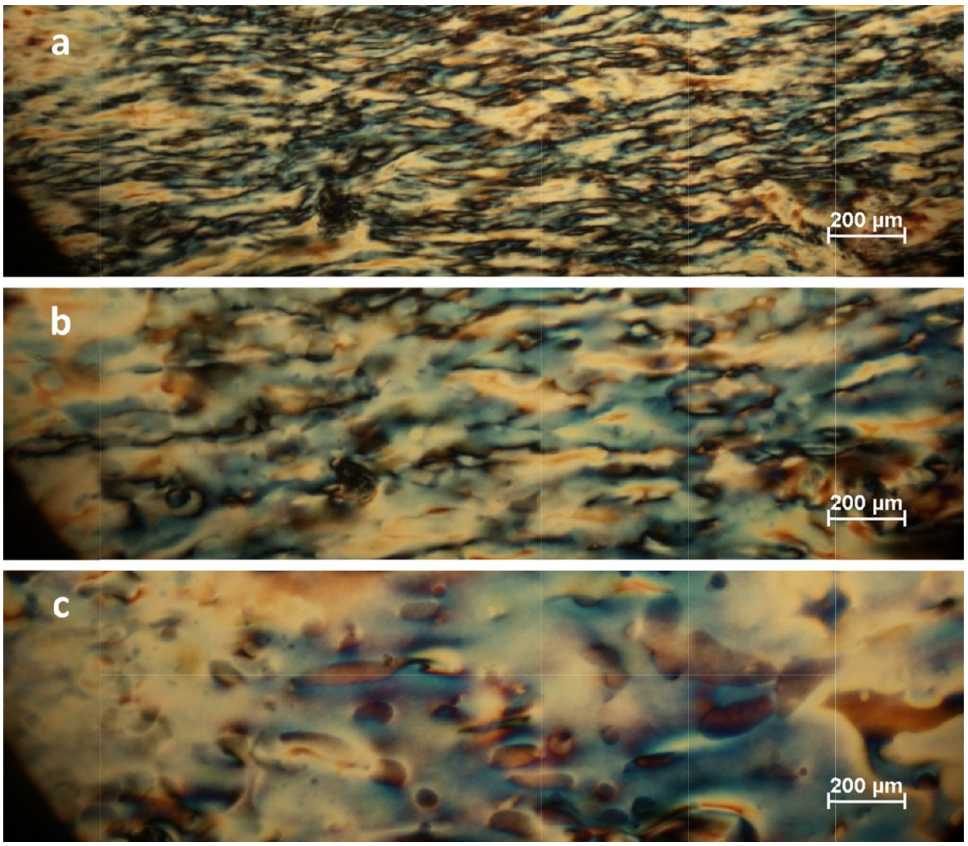


**Figure 3.** Texture change with time for 9.6 wt % CNC suspension between a microscope slide and cover glass, viewed between crossed polars: (a) immediately after preparation, (b) after 5 min, and (c) after 25 min.

## DISCUSSION

The clear evidence for an initial nematic-like rather than chiral nematic organization of the thin samples between glass surfaces was unexpected in view of the very moderate and transient shear applied during sample formation. Also unexpected was the observation that the sample showed no signs of uniform orientation under the polarized light microscope, despite the attempt to apply unidirectional shear by displacing the cover glass in a given direction (along the long direction of the microscope slide). Evidently, the radial spreading as the cover glass was pressed down onto the droplet of suspension on the microscope slide also generated shear, so no clear orientation direction was observed. Evidence for the spontaneous nematic organization of biphasic suspensions of CNCs derived from bacterial cellulose has previously been presented by Araki and Kuga.[25] On standing, a 1.58% suspension in water displayed a schlieren texture, characteristic of the nematic phase. Their CNC sample had a higher aspect ratio than those from cotton and wood, and their suspension exhibited chiral nematic properties as the ionic strength of the suspension was increased. A characteristic nematic wormlike texture has also been reported for cationic CNC thixotropic gels,[26] indicating that, in this case, the nematic director was predominantly normal to the plane of the sample. Nematic-like order in cellulose has also been observed under nonequilibrium conditions. For example, Kondo and co-workers have introduced "nematic ordered cellulose", a noncrystalline form of cellulose prepared by stretching molecularly dispersed cellulose gels.[27] Rheological and rheo-optical measurements of CNC suspensions often show evidence for a nematic-like ordering in the shear direction.[18] Factors such as suspension pH may also alter the orientational response to shear.[28] The best-controlled way to generate a nematic organization from a chiral nematic CNC suspension exploits the negative diamagnetic susceptibility of cellulose by applying a rotating magnetic field to the sample.[29,30] It seems that a range of factors may generate a transitory nematic organization, but the normal state for concentrated CNC suspensions is chiral nematic.

Experimentally, the apparent nematic texture is unstable. For the relatively concentrated suspensions examined here, the relaxation to a (presumably equilibrium) chiral nematic texture requires several hours, passing through intermediate textures such as that shown in Figure 6. Similar textures were observed for all samples after 1−3 h from sample preparation, independent of the direction and duration of the initial applied shear. In subsequent images (Figure 5), the colored lines became closer together and uniformly spaced, as expected for chiral nematic samples with the helix director in the plane of the sample. The rich variations in the width and color of the multiple lines with their orientation relative to the crossed polars (Figure 6) are in line with the patterns predicted for twist−bend textures illustrated in the Figure S3.

The response of anisotropic fluids to shear is complex and challenging, especially for polymeric and colloidal fluids, where viscoelastic phenomena may be important.[31] In practice, the transition between nematic (shear-induced) and chiral nematic states (and vice versa) is often viewed as a simple twisting or untwisting around the chiral nematic axis. This is illustrated in Figure 7e, where a nematic arrangement with the director along the $x$ direction twists through (d) to give a chiral nematic arrangement with the helicoidal axis in the $z$ direction.



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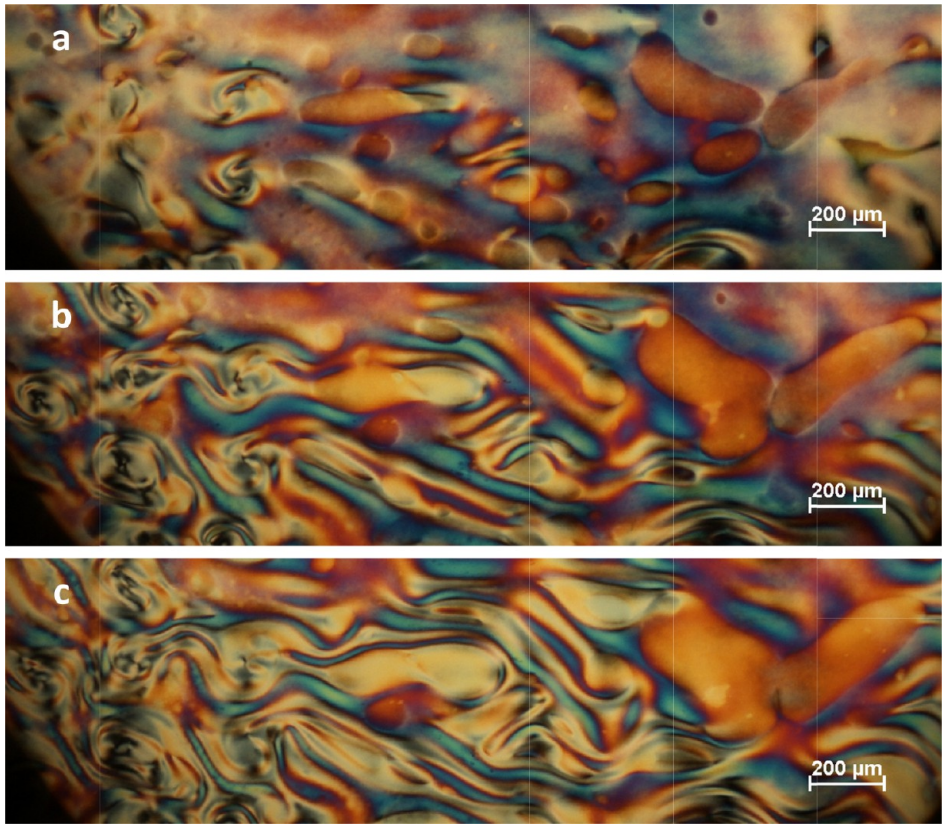


**Figure 4.** Texture change with time for 9.6 wt % CNC suspension between a microscope slide and cover glass, viewed between crossed polars: (a) after 45 min, (b) after 75 min, and (c) after 105 min.

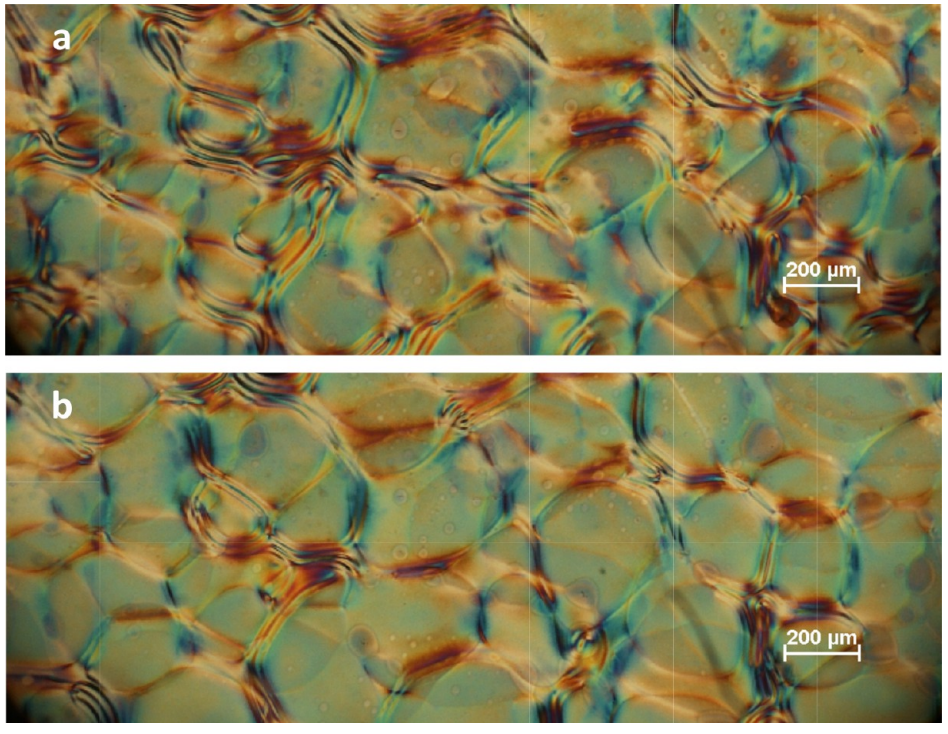


**Figure 5.** Texture change with time for 9.6 wt % CNC suspension between a microscope slide and cover glass, viewed between crossed polars with a 530 nm red plate after (a) 330 min and (b) 18 h.

Conversely, application of shear along the *x* direction causes the chiral nematic structure (c) to unwind to give an intermediate structure (d) before aligning with the shear direction. This process requires elastic distortion over a length scale of the order of the pitch, and singularities arise each half-pitch, where the orientation of the nanocrystals is orthogonal to



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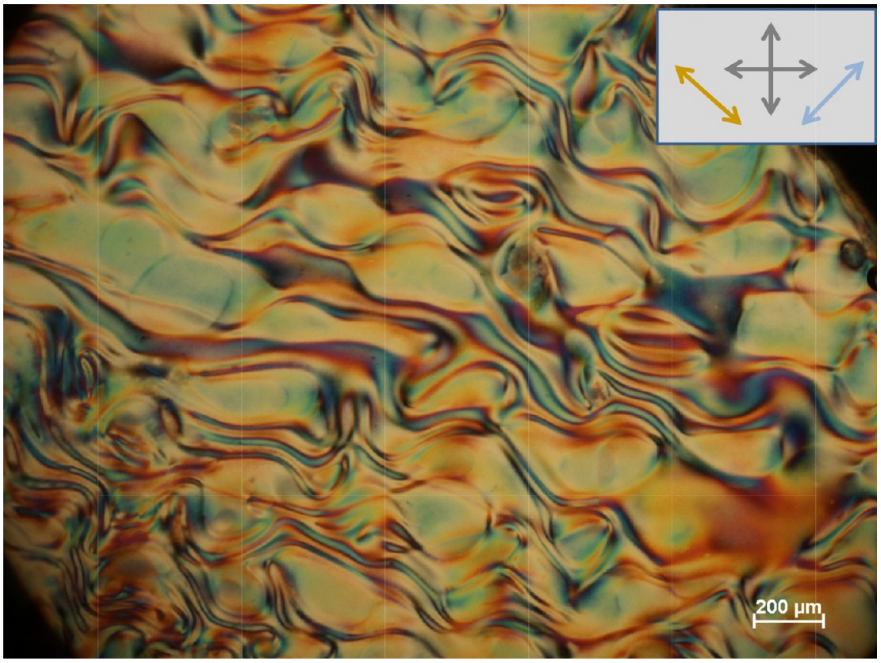


**Figure 6.** Intermediate texture between crossed polars with a 530 nm red plate, 9.6 wt % CNC suspension after 155 min relaxation.

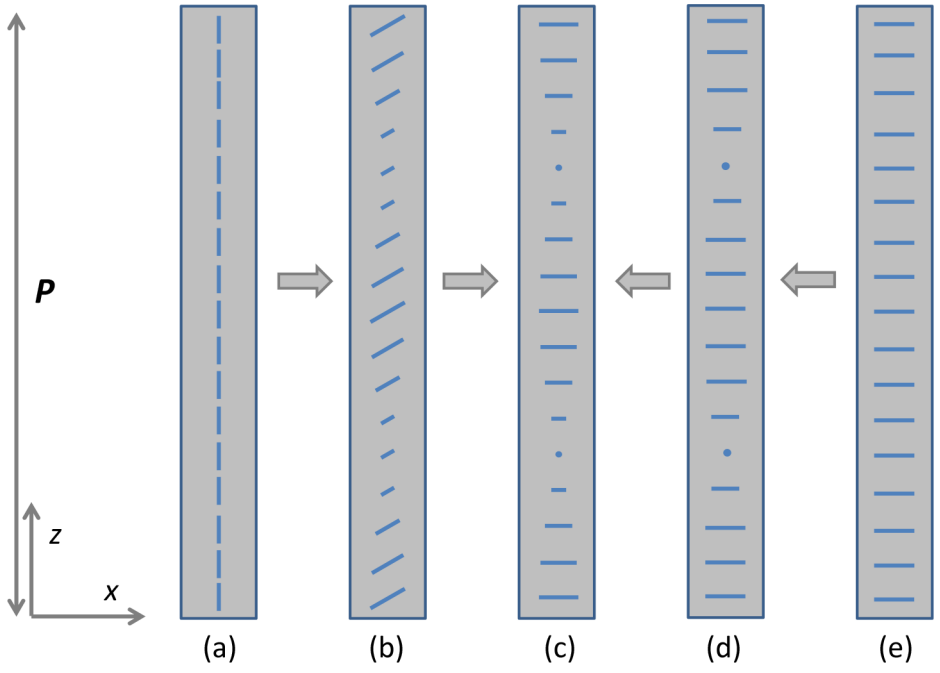


**Figure 7.** Sketch of possible relaxation routes from shear-induced nematic (a) and (e) to chiral nematic (c) structures. On the right, the transformation (e)−(d)−(c) occurs by twisting around the *z* axis. On the left, the transformation occurs via a twist−bend structure (b).

the *x*−*z* plane. We propose an alternative route between nematic and chiral nematic that starts with the nematic director along the *z* axis (Figure 7a). This corresponds to a tilt angle $\theta_0$ = 0 relative to the helix axis along the *z* direction (eq 1). Increasing the tilt angle gives a twist−bend type of CNC orientation (Figure 7b), until, at tilt angle $\theta_0$ = 90°, the equilibrium chiral nematic structure is restored. This process involves an affine deformation, with a cooperative reorientation over a length scale of the order of the CNC long dimension. Application of shear to the chiral nematic would reverse the process via (b) to (a). This mechanism might explain the relative ease with which small amounts of shear appear to generate a transitory nematic organization.

A clear distinction must be made between the twist−bend structure resulting from a nonequilibrium shear relaxation process envisaged here and the observation of equilibrium twist−bend phases observed for small molecule bent achiral mesogens. In the small molecule case, the mesogen is typically an achiral bent molecule, roughly 0.3 nm by 3 nm, that forms both left- and right-handed twist−bend nematic phases with pitch values less than 10 nm.[20] This small pitch value is of the order of the thickness of individual CNC rods and is 2 orders of magnitude smaller than typical pitch values for the left-handed



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chiral nematic CNC suspensions at the concentrations observed above. Perhaps, most importantly, the twist−bend structure envisaged for CNC suspensions is a transient, kinetically controlled state that occurs when a shear-induced nematic organization relaxes to the equilibrium chiral nematic ordered state. Evidence for a twist−bend phase includes the observation of asymmetric or incomplete "Bouligand arcs" in freeze-fracture transmission electron microscopy images of dimeric cyanobiphenyl and fluorinated terphenyl liquid crystals.[20] For the much longer pitch CNC suspensions, we propose that the variable band structure observed by polarized light microscopy during the transition from nematic to chiral nematic textures provides some evidence for a similar twist−bend structure at a larger length scale (see the Supporting Information).

Two further points on texture evolution may be noted. At very short times after relaxation of shear, viscoeleastic liquid-crystalline polymers may form regions of alternating birefringence, often termed "bands" if perpendicular to the initial shear direction and "stripes" if parallel to the initial shear direction.[31] Evidence for an initial band texture for the 9.6 wt % CNC suspension is shown in the Supporting Information. However, this phenomenon is short-lived for CNC suspensions and has little effect on the subsequent texture evolution. At the other end of the time scale, it takes hours for the reorientation of chiral nematic directors, from an initially random orientation with many disclinations to planar regions (director perpendicular to microscope slide) separated by walls where the director is parallel to the slide surface (Figure 5). Further reorganization to give a completely uniform planar texture was not achieved for the samples examined here. The time required for director reorientation is thus much longer than the time normally taken to prepare films by evaporation. This may explain the complex texture and relatively poor optical performance of most chiral nematic CNC films.

## CONCLUSIONS

1. Concentrated CNC suspensions close to gelation display a novel series of changes in liquid-crystalline texture when allowed to relax between microscope slide and cover glass.
2. The initial polarized light microscopy images, characteristic of shear-oriented samples, developed textures characteristic of nematic order before relaxing into the characteristic chiral nematic textures.
3. The relaxation from nematic to chiral nematic order passed through novel textures, which we ascribe to an organization analogous to a liquid-crystalline twist−bend structure.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00100.

Colors expected for a twist−bend nematic structure when viewed with a polarized light microscope; evidence for shear-induced band formation for 9.6% aqueous suspensions of CNC (PDF)

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### Notes

The authors declare no competing financial interest.

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