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Biomimetic Templating

Tessellation of Chiral-Nematic Cellulose Nanocrystal Films by Microtemplating

Blaise L. Tardy,* Bruno D. Mattos, Luiz G. Greca, Tero Kämäräinen, Konrad W. Klockars, and Orlando J. Rojas*

In biological architectures, material properties are optimized by the hierarchical structuring of components with a multiscaled order, from the nano- to the macroscales. Such designs enable, for instance, programmed yield points that maximize toughness. However, research efforts in biomimetic materials have focused on the assembly of nano- or macrostructures individually. In this study, high strength cellulose nanocrystals (CNCs), assembled into chiral-nematically ordered structures, are tiled into a higher level, macro-sized, architecture by topographical templating. As templates, two meshed architectures with distinct feature sizes are evaluated, and the optomechanical properties of the resulting films are compared to featureless, flat, CNC films. Controlling capillary stresses arising during CNC assembly is shown to enable control over the orientation of the chiral-nematic director across the topography of the template. Tuning the specific reflections and multiscaled fracture propagation is demonstrated for the microtemplated CNC films. The latter phenomenon contributed to enhancing the toughness of the material through a high tortuosity of fracture propagation in all (x, y, z)directions. The presented findings are expected to pave the way towards the incorporation of current research in cellular metamaterials with the research focusing on the generation of nanoscaled biomimetic constructs.

1. Introduction

Hierarchically assembled nanoarchitectures are ubiquitous in biological materials as they enable both lightweight and

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outstanding mechanical performance.^[1-3] This has inspired recent research efforts for the formation of biomimetic materials replicating such characteristics.^[4,5] These materials uniquely combine hierarchically assembled nanoscaled "bricks" with macromolecular "mortar" in order to achieve high strength and toughness. This combination enhances the toughness of the material by channeling the stresses along a tortuous path throughout the in-plane and out-of-plane directions of the ordered structures. On another scale, bio-inspired approaches towards tough materials include multilayering or tessellation of macroscopic objects. This has been demonstrated by using, for instance, laser-cut glass or 3D-printed building blocks with dimensions much larger than those of the nanoscaled objects aforementioned.^[2,6-8] Nevertheless, in biological architectures, toughness is enhanced by combining multiple components ordered both at the nano- and the macroscales. Two examples of such materials include

flexible, natural armors with tessellated scales of highly ordered protein fibers and the multilayered, hierarchical, biomineral structures of bones, and teeth.^[9–12] Such multiscaled systems enable programmed yield points in the respective scales, which maximize toughness and minimize the otherwise high brittleness associated with stiff, high strength, building blocks. Furthermore, other beneficial attributes from multiscaled hierarchies are frequently coupled with mechanical toughness, e.g., specific optical reflections with controlled bandwidths.^[13,14] Therefore, there is an important need for biomimetic materials to include both nano- and macroscales in their designs.

Cellulose nanocrystals (CNCs) are nanoscaled building blocks that have attracted interest for the formation of biomimetic materials, principally because of their spontaneous assembly into hierarchically ordered structures that result in outstanding optomechanical properties.^[15–17] Specifically, CNCs assemble with a chiral-nematic order, with nematic planes helically arranged across the thickness of the material.^[15,18] CNCs also possess remarkable strength ($E_A > 150$ GPa),^[19–21] inherent birefringence,^[22,23] as well as high thermal (> 250 °C)^[24–26] and chemical resistances.^[27] This unique combination of properties has resulted in the development of advanced hierarchically structured materials with control over their long-range order,^[28–31] ductility,^[17] flexibility,^[32–34] and photonic response.^[32,33,35–38]





Importantly, owing to their long-range order, CNC materials can bear selective reflection properties (structural colors) that are intimately correlated with the multiscaled structures within the materials they form. Therefore, the observed structural colors can be directly correlated with mechanical performance.^[17,32,33,39,40] Indeed, depending on the pitch and orientation of the helical axis of the CNC assembly, the reflection bandwidth shifts and, also, the ability of the material to dissipate energy through tortuous fractures, particularly in the out-of-plane direction.^[39,40] Building from previous and ongoing efforts, multiscaled assemblies of CNCs may present new opportunities for biomimetic materials.

In this study, we controlled the formation of chiralnematically ordered CNCs from the nano- to the macroscale, thus bridging previous developments in biomimetic materials focusing on either of these scales individually, as illustrated in **Figure 1**. CNC films were formed and templated by evaporation-induced self-assembly (EISA) onto a substrate with well-defined macroscaled domains (Figure 1a). The CNC films were tiled into a tessellated architecture onto a flexible and soft meshed substrate with unit cells defined by the filament diameter and side length of the open areas between the filaments. To control the stresses developed during the assembly, a separate rigid support was also used (Figure 1a). In a typical film

formation, a CNC layer formed atop and around the embedded meshed substrate in an interlocked, "multilayered" configuration as a bicomponent composite (Figure 1b, left), a term that is used here to generally refer to the CNC-mesh constructs. The rigid support was key to enable the formation of chiral-nematically ordered CNC films that replicated, with high fidelity, the topography inherent to the unit cells from the given meshed substrate. By using this simple formation strategy, CNC films were templated, which enabled control of the orientation of the cholesteric director across each unit cell (Figure 1b). Consequently, the optomechanical property space of the material was expanded. Such an effect sets a new paradigm in the achievable optical-mechanical properties, which goes beyond those displayed by flat films comprising featureless chiral-nematically ordered CNC or tessellated and brittle macrocomponents (for example, as previously demonstrated with glass).^[7,8]

The high replication fidelity of the features of the template arising during EISA took place most critically by 1) controlling the capillary stresses that develop between CNCs, by addition of plasticizers, as well as 2) by controlling the capillary stresses between CNCs and the substrate, by tuning the rigid support wettability. Adjusting the interactions between CNCs and both substrates was essential since stress build-up is otherwise detrimental to the formation of composites without large,





Figure 1. a) Illustration of the methodology used for the assembly of CNC, via EISA of an aqueous suspension, on meshed substrates supported on a low-adhesion rigid support. Upon separation, the resulting composite, as shown here, was obtained with 6 mg CNC per cm² and 45% solid content of PEG. The inset illustrates the high conformability of the composite that was folded into a cylinder as shown and unfolded back into a sheet three times. The chiral-nematically ordered CNC layer, also indicated by the iridescence of the sample, replicated the topography of the mesh, resulting in a tessellated structure. b) 3D illustration of a cross-section of the composite mesh shown in a) corresponding to the CNC layer conforming around a filament, towards an open area. A distinctive orientation of the chiral-nematic director within each tessellated cells can be obtained in the case of the composite formed with the f_{30} mesh as shown in the dashed square added in a). Such system is expected to display an optomechanical response owing to the distinctive microdomains. Herein, a director orientation of 90° (yellow) is normal with respect to the main plane of the f_{30} composite, and other orientations as well their rotations respective to the main plane are color-coded as described.

Adv. Funct. Mater. 2019, 1808518

1808518 (2 of 12)



macroscopic, defects. Moreover, adjustment of such capillary interactions is key to control the orientation of the cholesteric director across the complex topography of the composite. In the latter endeavor, we demonstrate that macrotemplating of the photonic CNC films allows fine control over the width and depth of the reflection band. Additionally, fine-tuning the build-up of stresses during the assembly, easily enables scaling-up of the composite to sizes of at least 10×15 cm². Scaling-up was permitted by minimizing the adhesion between the composite material and the rigid support, which significantly facilitates their separation (Figure 1a). A particularly high composite toughness and conformability is obtained (Figure 1a, inset), with new limits for chiral-nematically ordered CNC films, remarkably higher if compared to similar composites produced as flat (featureless) films. Additionally, the integration of the two components in the composite, forming distinct microscaled domains with a contrasting nature (soft mesh versus stiff CNCs), are demonstrated to induce ductility or controlled fracture propagation depending on the direction of the applied stress. Lastly, we demonstrate that fracture generation was significantly reduced and toughness significantly improved in the single-component tessellated CNC films, compared to flat CNC films. The results indicate a multidirectional deflection of the fracture path that is imposed by the combination of the micro- and nanostructures in the composite (Figure 1b and Figure S1, Supporting Information).

We used soft Nylon meshes with unit cells defined by filament diameter-side length of their open areas. Corresponding meshes used were the 40-48 µm mesh (Figure 1, with a section of a unit cell presented to scale in b, right) and a relatively more open and stiffer 200-522 µm mesh. The latter was used to elucidate certain aspects of film conformation upon EISA of CNCs. The respective open area fraction of these two meshes, f_{OA} , correspond to 30% and 59%. A Nylon film (flat and featureless) was also used as a reference to elucidate the formation mechanism of the composite and its topography-dependent properties. For convenience the three substrates are referred to as f_{30} , f_{59} , and f_0 , respectively. When used as a substrate, the mesh having large characteristic features compared to the CNC layer thickness (f_{59}) resulted in CNC films principally suspended in the open areas without the formation of a multilayered architecture embedding the mesh, and, thus, lacking the benefits achievable by topographical templating as presented herein. In contrast, the f_{30} mesh enabled multilayered films since the size of the characteristic cell features (i.e., filaments diameter of 40 μ m) were in the order of the thickness of the formed CNC film. In this case, the formed CNC layer was connected to the substrate via the open areas (Figure 1b) and was dominant in the strength and toughness of the composite, as evaluated in conformability tests.

2. Results and Discussion

2.1. Assembly Principles of Chiral-Nematically Ordered CNC Films Formed by EISA on Meshed Substrates

The formation of CNC layers or coatings onto flexible substrate remains a challenge due to the development of large residual



stresses that deform the substrate as is the case for the f_{30} substrate. Therefore, we first investigated the factors that minimize structural defects. Such factors are associated with capillary forces, developing during EISA, between the nanoparticles as well as between the nanoparticles and the supports. Reducing capillary forces are required to avoid the otherwise significant deformation that occurs under the resulting residual stress of the dried composite. This is clearly shown by the measured deflection of a flat glass cantilever onto which a CNC film was formed by EISA (Figure 2a). The adhesion between the CNC mesogen and the (rigid) glass results in coupling of the capillary forces, e.g. from CNC-CNC capillary forces, on the solid support during EISA^[41–43] (Figure 2a,c) and, consequently, increase the overall stress on the glass substrate (illustrated schematically in Figure S2a, Supporting Information). In films formed with the same CNC areal mass (d_{CNC}) after mixing with a plasticizer (poly(ethylene glycol), PEG) added at 15% and 45% with respect to CNC mass, the cantilever deformation and associated residual stress was reduced by 56% and 95%, respectively (Figure 2a). On the other hand, capillary forces result in high cohesions between CNCs in the dried films and thus to a high strength. Therefore, the amount of plasticizers as well as other substrate effects need to be optimized for a high strength and low residual stress compromise.

For microtemplating as described herein, a good affinity between CNCs and the templating mesh is required. A good wettability is also required to enable the suspensions to wet the features of the support and to increase capillary coupling. Nylon is a material that fulfills such criteria and also engages in H-bonding interactions with CNCs through the donoracceptor pair of the amide bonds. We evaluated the formation of the microarchitectured films onto three secondary, rigid, supports with varying wettability and, thus, varying adhesive interactions with CNCs. The associated water contact angles (WCAs) were respectively below (49°), close-to (93°) or above (>150°) that of Nylon (Figure 2b, WCA of featureless Nylon = $73 \pm 2^{\circ}$). The residual stress measured on the glass cantilever correlated well with the formation of defects in the f_{30} composite, as observed in Figure 2b. Without plasticizer, a considerable deformation of the composite took place when EISA occurred on the secondary substrate with a WCA of $93 \pm 1^{\circ}$ or 150° . In contrast, composites were not deformed by the lack of plasticizer when formed on a secondary substrate with a low WCA (49 \pm 5°, Figure 2b, left-hand column). Note: the deformation, i.e., buckling and curling, of the composite was amplified in the case of non-square (rectangular) meshed substrates cut at increasing aspect ratio (Figure S2b, Supporting Information). The reduction of residual stress in CNC layers containing PEG reduced buckling of the composite (Figure 2b,d). However, for the substrate with WCA > 150° , deformation was unavoidable (Figure 2b, right-hand column). In this latter case, the residual stresses developed during EISA resulted in the filaments of the mesh being extensively pulled towards each other, even in the presence of 60% of PEG (Figures S3 and 2d, Supporting Information). Overall, the observations indicate the need for a given degree of interaction between CNC and the rigid substrate, competing with those between CNC and the mesh as well as the interparticle interactions. An appropriate interaction balance was reached with a







Figure 2. a) Normalized residual stress development during EISA of CNC aqueous suspension deposited onto a flat glass cantilever. Different amounts of plasticizer were added to the CNC suspension, as indicated. b) Effect of wettability of the rigid support and PEG content on the homogeneity of the formed f_{30} composites. c) Illustration of the three principal capillary forces arising during EISA. Coupling between these three capillary forces, via additional "capillary bridges", leads to the final residual stress of the composite, as illustrated with the orange arrows. Contact angles $\theta_1-\theta_3$ describe the wettability of the cellulose nanoparticle (CNC cross-section, yellow in the illustration) and the given substrates (shown here are polystyrene and Nylon). d) Composite materials as observed by reflection microscopy in the absence of plasticizer (left) and with addition of 15% of PEG. (in b and d, areal CNC density (d_{CNC}) = 8 mg cm⁻²).

rigid support with a wettability close or below that of the Nylon mesh (WCA = $73 \pm 2^{\circ}$).

When the hydrophilicity of the rigid support was considerably higher than the mesh (i.e., WCA = $49 \pm 5^{\circ}$), buckling was not observed, even in the absence of plasticizer. Nevertheless, in that case, the preferentially high wettability of the rigid support with a low WCA prevented high loading of CNC suspension onto the mesh. This observation is most evident after EISA of a CNC suspension with addition of 60% of PEG, leading to leakage onto the rigid support (Figure 1b, bottom left: see structural colors inhomogeneities due to leakage of the suspension outside of the mesh boundaries). Additionally, the rigid support with low WCA led to significant debonding upon separation (peeling off in this instance) of the composite (Figure S4, Supporting Information). Although PEG can increase the affinity between CNC films and the rigid polymeric surfaces, resulting in losses of CNCs bound to the rigid substrate, debonding was minimal for CNC composites formed when using rigid supports with a WCA of 93° (polystyrene, Figure S4, Supporting Information). It is also worth noting that, conventionally, CNC films are formed on rigid substrates and are thereafter separated, peeled, from the support.^[17,33,34] In the context of templating, minimizing adhesion to the rigid substrate to maintain the tessellated architecture upon peeling is particularly important and therefore required additional attention.

Overall, CNC films could be assembled without significant debonding and free of buckling-like deformations by using

a rigid support with intermediate wettability, with $WCA = 93^{\circ}$, higher than the mesh substrate (WCA = 73°), and for CNC suspensions with a PEG solid content ≥5%. From this PEG content, the contact angle on the rigid substrate decreased from a suspension contact angle of 93° to $79 \pm 2^{\circ}$ (Figure S5, Supporting Information). The contact angle on Nylon remained constant at all PEG concentrations, while for polystyrene it was constant only after >5% PEG content (Figure S5, Supporting Information). Noteworthy, the deformations from capillary stresses were considerably reduced for the stiffer Nylon substrate, f_{59} , compared to the f_{30} substrate suggesting the beneficial use of other stiffer meshes to reduce defects arising from residual stresses (Figure S3, Supporting Information). For both f_{59} and f_{30} substrates, increasing their hydrophilicity (WCA = $54 \pm 0.6^{\circ}$) did not affect the observed buckling of the composites at 0% and 15% PEG content formed onto a rigid support with WCA = 93° (data not shown). This suggests that a WCA of the templating substrate below 90° is required but increased hydrophilicity does not lead to observable improvements.

2.2. Conformational Fidelity of the Chiral-Nematic CNC Layer and Associated Reflection Bandwidths upon Templating

The assembly conditions were important to reduce defects in the composites; they also enabled control over the optical reflection properties. The deposited CNC areal mass density



 (d_{CNC}) , relative humidity (RH) during assembly and quantity of plasticizers influenced the depth and bandwidth of the specific reflections arising from the chiral-nematic films. For all composites, a clear narrowing in bandwidth for the specific reflections was observed from $d_{\rm CNC}$ of 2 and 6 mg cm⁻² for f_{30} and f_{59} composites, respectively (Figure S6, Supporting Information). Reflection bands were observed to progressively increase in depth and, to a lesser extent, in width, at $d_{\rm CNC} > 2 \text{ mg cm}^{-2}$ (f_{30}). This is a result of increased longrange order and, principally, of increased thickness of the photonic reflector.^[44,45] The same effect could be observed for CNC films formed onto hydrophilized, featureless Nylon substrates, with a lesser effect on specific reflectivity from added PEG (Figure S7, Supporting Information). Interestingly, the non-specific transmittance (measured at 800 nm), an indirect, qualitative, measure of the transparency of the material, increased by ca. 10% for the composites formed onto f_{30} in the presence of plasticizers. In contrast, for f_{59} composites, PEG had no substantial effect (Figure S6, Supporting Information). Consequentially, we systematically studied the internal structure of the chiral-nematic CNC films as a function of the topography and plasticizer

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by evaluating the specific reflection within the open areas for $d_{\rm CNC} = 10$ mg cm⁻², i.e., by studying the transmittance properties of the materials.

For films formed on flat supports the non-specific transmittance for PEG contents below 45% was constant and decreased at PEG contents of 45% and 60% (Figure S9, Supporting Information). The decrease in transmittance is likely due to be the assemblies becoming more isotropic since the amount of plasticizer is too high to maintain the CNCs' long-range order. This results in increased diffusive reflectance, common in isotropically ordered fibrillar materials.^[46] For f_{30} composites, the non-specific transmittance increased with the concentration of plasticizer or humidity, up to PEG addition of 25% or 45% for an RH of 23% and 50%, respectively (Figure 3b and Figure S8, Supporting Information). Above these two thresholds, the decrease in transmittance can be assigned to the same phenomena as the flat films. Below these two thresholds, the observed increase in non-specific transmittance is likely due to the better conformational fidelity of the CNC films formed around the filaments and open areas of the mesh. The lower threshold for the non-specific transmittance of composites formed at lower humidity highlights a more significant



Figure 3. Evaluation of the optical properties of the chiral-nematically ordered materials as a function of plasticizer concentration (a-d, f_{30} composites, $d_{CNC} = 10 \text{ mg cm}^{-2}$). a) Minimum transmittance peak as a function of PEG content and RH. The markers with an outlined color represent the respective spectra presented in c) and d). b) Non-specific transmittance at 800 nm as a function of plasticizer content and RH. c) Corresponding spectra for selected PEG contents as color-coded in a). 0%, 15%, 35%, and 60% are represented in black, grey, purple, and light blue, respectively. d) Derivative around the minimum transmittance peak. The "half-bandwidth" defined as the value measured between the maximum reflection wavelength and the closest half-maxima are represented as well.

1808518 (5 of 12)



decrease in long-range ordering of the material with faster EISA.

As previously reported, the addition of PEG shifted the maximum reflection peak of the composite films towards higher wavelengths.^[17,32–35] For f_{59} , f_{30} , and f_0 substrates the respective shifts of the CNC films per percent of PEG added was $\approx 2.2, 3.8$, and 4.4 nm (Figure 3a,c and Figures S9 and S10, Supporting Information). The shift in the reflection wavelength is due to an extension of the pitch of the helicoidal assembly, proportional to the incorporation of the plasticizer, which acted as a spacer. For f_{30} films formed at 23% or 50% RH, the corresponding shift had a similar amplitude (Figure 3a and Figure S8, Supporting Information). This highlights the fact that the maximum wavelength of the reflection peak is principally affected by the amount of plasticizer added and not by the assembly conditions, i.e., the EISA rate (slower at higher RH). Importantly, addition of PEG increases the films thickness but is not expected to increase the reflections depth or narrowing their widths, as shown for featureless films (Figure S8, Supporting Information). For f_{30} composites, the reflection shift induced by PEG was not substantially influenced by topography, since CNC films assembled on f_0 showed a similar increase in maximum reflection wavelength. In contrast, films assembled with f_{59} , with larger filaments (200 µm) in proportion to the CNC component thickness, led to a substantial decrease in the shift of maximum reflection peak.

Around the maximum reflection wavelength, the width of the reflection peak also narrowed substantially with an increase in PEG loading or humidity (Figure 3c,d and Figure S8, Supporting Information), i.e., the specificity of the reflections increased, resulting in a narrowing of the reflection bandwidth to half-bandwidths as low as 28 nm (Figure 3d, lightblue curve). This narrowing of the reflection peak further suggests that the chiral-nematic director conformation had a higher fidelity around filaments and towards the open areas in the presence of PEG or at higher humidity. The narrowing occurred from added PEG content as low as 5% and was more pronounced from 15% PEG (Figure 3 and Figure S8, Supporting Information). This suggests that a small increase in thickness of the CNC component of the composites from added PEG substantially increased the specificity of the reflections, which did not occur on featureless films (Figure S9, Supporting Information). Therefore, in the context of this study, this improvement in reflection selectivity is directly correlated with the reduction in residual stresses in the Nylon-CNC composite, and with a more ordered topographical replication of the films around and across the topography of the Nylon substrate. The same decrease in bandwidth of the reflection peaks is observed with f_{59} but to a lesser extent, whereas it is absent in flat films formed in the same conditions (Figures S9 and S10, Supporting Information). The low PEG content f_{59} had very broad half-bandwidths of up to ca. 150 nm. The opposite trend occurred for flat films, where the specific reflection bandwidth broadens with the addition of PEG. This has been previously observed for other plasticizers.^[17,33]

The cross-section of f_{59} composites formed with or without PEG reveals a better composite conformational fidelity in the presence of plasticizer (**Figure 4**), with the director of the helical assembly following the contour of the filament (Figure 4c and

larger version in Figure S11, Supporting Information), even following an abrupt turn when moving towards the open area between filaments. Nevertheless, the transition is not equally sharp across the thickness of the CNC component. Towards the bottom of the film, the chiral-nematic director makes nearly an orthogonal turn from the filament towards the open area, whereas at the top of the film, as observed in Figure 4c, the director follows a less pronounced, 45°, turn. This difference in transition between curved to planar areas highlights that the pitch of the chiral-nematic assembly is not the same atop of the filament as it is in the curved area. Indeed, the pitch atop of the filament is smaller than at the 90° turn and the latter can be estimated as a function of the thickness of the film, as described in Figure S12 in the Supporting Information. For instance, an increase in pitch by \approx 1.74-fold from the film on top of the filament to the film at the transition between filament and open area was calculated from Figure 4c. The final conformation of the films as a function of plasticizers and topography is put in perspective with the content of section 2.1 in discussion S1 in the Supporting Information, where we also highlight a potentially higher cohesion within nematic planes than between nematic planes in the constructs as can be inferred by the gap shown in Figure 4b.

As a result of differences in conformational fidelity, the reflection wavelength bandwidth is shifted as a function of the increasing curvature of the CNC films (illustrated schematically in Figure 4a).^[47] The fact that topographical factors can be used as a tool to finely control the width of the reflection band, allowing for a fine control of the optomechanical properties of the hierarchical structures, has significant implications in future designs of information-rich materials.^[48,49] It is also crucial for the formation of fracture-resistant materials that can be engineered as a function of the substrate topography, e.g., with programmable pitch gradients and ensuing fracture dissipation pathways as they enable a lighter weight and higher robustness.^[40,50]

2.3. Conformational Flexibility Limits as a Function of Plasticizer, Film Thickness and Associated Multiscaled Fracture Paths of the CNC–Nylon Composite

2.3.1. Conformability Limits

The overall mechanical characteristics of the composites were first assessed with a two-point bending test as a function of $d_{\rm CNC}$. With f_{30} , increasing $d_{\rm CNC}$ resulted in a sharp increase in the rigidity of the composite. The static force after a displacement of 2 mm increased ≈95-fold when going from $d_{\rm CNC} = 0$ to 8 mg cm⁻² (Figure S13a, Supporting Information). This strongly supports the dominant nature of the CNC layers in defining the mechanical properties of the composite, particularly for $d_{\rm CNC} > 2$ mg cm⁻². On the other hand, for the stiffer f_{59} substrate, increasing $d_{\rm CNC}$ from 0 to 8 mg cm⁻² only increased the static force by ≈2.6-fold after a displacement of 2 mm. Similarly, addition of PEG resulted only in a relatively small reduction of the flexural rigidity of the composite for f_{59} , whereas a substantial decrease in stiffness was observed upon addition of PEG for f_{30} (a maximum of 50% decrease in the static force for



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Figure 4. a) Schematic representation of the conformational fidelity of CNC layers (green) around the filaments in a mesh as a function of PEG addition and corresponding reflected wavelengths as a function of the curvature. The conformational fidelity of CNC layers in c) contrasts with non-conformable layer shown in b) for CNC assembled in the absence of plasticizer. b) Example of a high conformational fidelity of chiral-nematically ordered CNC layers around a filament (see dashed line) as observed by SEM for f_{59} ($d_{CNC} = 6 \text{ mg cm}^{-2}$) in the presence of 15% of plasticizer. A highlighted area of the central part of the film converging from an open area to a filament is shown with the cholesteric director undergoing a 90° rotation. An additional area where the curvature of the chiral-nematic director at the transition between filament and open area is obvious, as highlighted with a continuous yellow line. The helices in the insets indicate the orientation of the chiral-nematic director. In b) and c), the dashed line highlights the contour of the filament's cross-section.

2 mm displacement at 8 mg cm⁻², Figure S13a,b, Supporting Information).

The insights obtained from the two-point bending experiments as well as the remarkable flexibility of the composites motivated an effort to probe the conformability limits of the materials. To do so, f_{30} composites prepared at varying d_{CNC} and PEG content were bent or conformed around solid cylinders of progressively smaller radii of curvature, exerting a progressively higher tensile stress at the uppermost layer of the material and compressive stress at the lower layer of the material, until crack initiation and propagation occurred (Figure 5a, and Figure S14 and schematic in Figure S15a, Supporting Information). The composites were conformed around the solid cylinders, with a given radius of curvature, in the longitudinal (weaving) X-Y direction (Figure 5a). For all conformability tests, the films were additionally conformed in the direction orthogonal to the first one, resulting in the formation of "macrotiles". Importantly, even after crack formation, the individual CNC macrotiles remained tethered to the Nylon mesh, through the openings between the overlapping nylon filaments. The macrotiled composite reached new conformability limits while maintaining the optomechanical properties provided by the chiral-nematic component. This offers an alternative strategy for the design of macroscaled hierarchically structured materials with high strength and significantly reduced brittleness, as has previously been demonstrated using non-nanostructured materials.^[7,8,51] In contrast with the behavior observed in Figures S14 and 5 in the Supporting Information, single-component CNC layers shatter into several fragments when reaching conformational limits.^[39]

The minimum cylinder radius that would promote crack initiation of the composite was reduced by decreasing d_{CNC} and by increasing the amount of PEG in the composite (Figure S14, Supporting Information). For instance, for $d_{\rm CNC} = 4 \text{ mg cm}^{-2}$ and 60% of PEG, few fractures were generated when conforming the composite around a solid cylinder with a radius as small as 3 mm. In contrast, a composite with the same d_{CNC} but at a PEG content of 15%, fractured considerably when conformed around the same cylinder. When increasing d_{CNC} to 8 mg cm⁻², numerous fractures were generated when the composite was placed around a cylinder with radii of 13 and 3 mm, for a respective PEG content of 15% and 60%. At a low $d_{\rm CNC}$, the topography has more pronounced features, whereas at higher d_{CNC} the films become smoother. It is therefore likely that both, increased thickness and decreased fidelity of the replication, contributed to the large difference in fracturing as a

1808518 (7 of 12)





Figure 5. Fracture propagation and macro tiling of the composite materials (15% PEG, $d_{CNC} = 6 \text{ mg cm}^{-2}$). a) Composite material after macro tiling by longitudinal conformation around a solid cylinder with a radius of 3 mm (blue in schematic inset). The photo was taken with a light source close to parallel to the principal plane to highlight the fractures and reduce structural colors. b) SEM image of the fracture path between four individual tiles. c) Map of a unit cell of the meshed substrate as a function of the chiral-nematic director orientation, with respect to the solid support orientation as represented in Figure 1b, with dashed lines corresponding to hypothetical fracture propagation paths, while the red line corresponds to the fracture path typically observed in panel b. Straight reference lines are added for analysis in d). d) Fracture propagation paths illustrated in c) as a function of height and distance traveled.

function of the conformational curvature (as imposed by the solid cylinders).

2.3.2. Multidirectional Fracture Propagation Mechanisms

Multidirectional and tortuous fracture propagation are desirable features necessary to obtain materials of high strength and toughness (as schematically depicted in Figure S1, Supporting Information). Herein, besides the "brick and mortar" architecture present over the thickness of the CNC layers, the topographical features also extend the fracture propagation towards the outer rims of the open areas of the unit cells (Figure 5b, right and magnified image in Figure S20, Supporting Information). The latter is to avoid the sharp vertical to horizontal curvature transitions occurring between the curved CNC layer that formed around the filaments of the mesh and the planar CNC layer in the open areas. The tortuous fracture path corresponds to the path of minimal resistance, imposed by the high strength microdomains of hierarchically ordered CNCs and their associated chiral-nematic director orientation. Noteworthy, the fracture paths do not match with the highest local tensile strain generated upon bending the woven architecture as the highest tensile strain exists directly above the point where two filaments intersect.^[52] The latter is confirmed experimentally when observing the paths for orthogonally strained composites

in which the CNC components are arranged isotropically, without long-range order, across the thickness of the material (Figure S17, Supporting Information, where the composite was prepared by EISA of an isotropically ordered gel).

The contributions of the tessellation to the fracture tortuosity, and associated toughness, were studied using a model unit cell of the composite architecture, also presented in Figure 1 (Figure 5c,d with corresponding 3D model in Figure S19, Supporting Information). The model unit cell represents a CNC layer where the features are pronounced (thin film case) and thus where the effect of the director orientation and curvature is also the most pronounced. Four hypothetical fracture paths across the architecture are represented (Figure 5c) with corresponding height (z) positions plotted as a function of the fracture length (Figure 5d). The two straight vertical paths impose both a slightly longer fracture distance and sharper transitions between Z-planes, whereas the tortuous path observed in Figure 4c, approximated by the red curve in Figure 5c, reduces markedly the height difference. The tortuous path induces the smallest height differences, thus corroborating with the hypothesis put forward in Section 2.3 and previous findings on fracture dissipation by imposition of angled yield points.^[7] Additionally, fracture toughness may also be promoted by the distribution of pitch gradient at the transition between filaments and open areas, providing set yields points with longer pitches that, ultimately, contribute to crack deflection.



The directionality-dependent response of the composite was also assessed and showed that ductile response or fracture propagation can be observed as a function of the orientation of the applied strain (discussion S2 and associated Figures S15, S16, and S18, Supporting Information). The directional dependence of the mechanical response is similar to that from woven fabrics, which have a reduction in their elastic modulus of more than 15 times if comparing loading conditions at 0° or 45° respective to the weaving directions, i.e., with flexural strains applied longitudinally or diagonally, respectively.^[53]

2.4. Conformational Flexibility and Toughness of the Microarchitectured, Single-Component, CNC Layer

The mechanical response of the composite observed thus far emphasizes that the fracture pattern can be engineered to follow the longest possible path on the *X*–*Y* plane and over the thickness of the material (Z-X and Z-Y planes). We therefore compared the fracture propagation of free-standing flat films with the isolated upper layer of the composite, consisting of a free-standing CNC film replicating the topography of the f_{30} mesh. Both CNC films were adhered onto smooth adhesive tape and conformed around a solid cylinder with a radius of curvature of 3 mm. Noteworthy, the conformability tests presented herein bare a level of comparison to conventional indentation tests carried out with large probes, where conformability around the spherical tip is probed normal to the surface. To emphasize that the difference in mechanical response is not related to the potentially thinner films formed around the larger surface area of the meshed substrate compared to a flat support, a topographically templated CNC film formed at a d_{CNC} of 8 mg cm⁻² and a flat film formed at 6 mg cm⁻² were compared. The film was separated from the Nylon substrate and the backside of the surface indicated minimal defects due to the highly laminated nematic layers in the architecture (Figure S21, Supporting Information). This further supports the observed contouring of the cholesteric director around the filaments and across the open areas. The surface area normalized d_{CNC} for the tessellated film, obtained using the topography presented in Figure S18 in the Supporting Information, can be calculated to correspond to a $d_{\rm CNC\text{-}normalized}$ of 5.7 mg cm^-2 (~1.4 reduction factor), a value comparable to that of the flat CNC film. In other words, while the cross-sectional area is larger for the tessellated CNC film (across the micro features, from a higher overall $d_{\rm CNC}$), the thickness of the corrugated CNC film is similar to that of the smooth/planar one.

For both diagonal and longitudinal strains, the tessellated films fractured to a lower extent than the control formed on a flat surface (**Figure 6**a–e and Figure S22, Supporting Information). The total fracture length was observed to be doubled for the flat film compared to the tessellated film, with tile sizes ca. 5 times larger for the tessellated film (Figure 6e). The tile size is directly proportional to the size of the smallest element that can be conformed around a 3 mm radius of curvature without cracking. Therefore, these differences highlight a high flexibility and toughness of the tessellated CNC films compared to the flat films.

When observing the fracture surface and delamination distance, the material with a flat topography had clear and consistent delamination over ca. 20 μ m (Figure 6e). In contrast, as was observed for the composite material, the fracture surface for the topography-templated CNC films followed a substantially more tortuous path along the *X*–*Y*, *Z*–*X*, and *Z*–*Y* planes (Figure 6b, with a delamination distance of more than 100 μ m). Additionally to increased delamination, the higher toughness of the tessellated films may also arise from a distribution of the strain favoring plastic deformation of the whole construct. The latter may prevent the generation of new fractures as previously demonstrated for similar, tessellated architectures obtained from non-nanostructured components.^[54,55]

The higher toughness of the single-component tessellated films was also observed using tensile testing for samples formed at high plasticizers content (Figure 6f). A PEG addition of 60% was used to ensure that the effect of remaining residual stresses was minimal, which otherwise could have introduced biases (Figure 2a).^[56] In tension, toughness is principally affected by the hierarchical structures across the thickness (or cross sectional area) and by the sliding of individual nanocrystals over each other to align with the direction of the applied stress.^[17] When comparing tessellated to featureless films, a considerable increase in toughness can be measured for topographically templated films compared with flat films (Figure 6f). For a comparable maximum stress, the strains at rupture were 0.58 \pm 0.12%, 0.9 \pm 0.17%, and 0.69 \pm 0.09% for featureless films and tessellated films strained longitudinally or diagonally, respectively. A toughness of 166 ± 62.6 kJ m⁻³ was obtained for the flat film. For the tessellated films strained diagonally and longitudinally, toughnesses 5.1% lower (157 \pm 33.3 kJ m⁻³) and 62.1% higher (269 \pm 72.8 kJ m⁻³), respectively, were obtained. Interestingly, applying the strain diagonally to the tessellated unit cells reduced the toughness, suggesting that the inflection points introduced by templating have a directional response to mechanical strains, similarly to the meshed substrate or the composite.[53,55]

2.5. Conclusions

In conclusion, we demonstrated the topographical templating of CNC films by using combinations of meshed and rigid substrates as a function of their respective wettability. The preparation strategy enabled simple, scalable formation, and isolation of CNC films with extended property spaces, allowing new limits for long-range ordered CNC materials that could not be achieved, for instance, by using additives. We highlight that the fidelity of the replication of the features represents a simple mean to control the optical properties of the materials, i.e., control of the reflection peaks over a wide range of reflection bandwidths. The topographical features introduced affected the mechanical properties of the materials, which showed increased conformability because of their greater toughness. Compared to polymeric liquid crystals, the "rigid" colloidal nature of the lyotropic liquid crystalline suspension is demonstrated to be key as capillary forces onto the colloids are shown to promote topography-dependent orientation of the cholesteric director. Importantly, although the geometry used herein for

1808518 (9 of 12)





Figure 6. Comparison of fracturing for free standing, top layers, isolated from Nylon substrates and longitudinally conformed around a solid cylinder with a radius of 3 mm as a function of micro tessellation. Images in a) and d) were taken with a light source close to parallel to the principal plane to highlight the fractures. The films (15% PEG) were adhered to ca. 30 μ m thick adhesive tape to prevent shattering upon testing. a) Illustration of fracture development after conformation of topographically templated CNC films formed at a density of 8 mg cm⁻² and isolated post EISA. d) Illustration of fracture development after conformation of smooth CNC films formed at a density of 6 mg cm⁻² and isolated post EISA. b,e) Illustration of fracture delamination as observed by SEM for a) and d), respectively. c) Tile size (mm²) (polydispersity indicated) and total fracture length density (mm cm⁻²) for images observed in a) and d). f) Stress–strain curves obtained by tensile tests of films formed (60% PEG) and isolated from $f_{OA} = 30\%$ (black and orange curves) or a smooth nylon substrate (blue curve) ($d_{CNC} = 8$ and 10 mg cm⁻² for tessellated and smooth films respectively.

topographical templating is simple, more complex architectures can be envisioned with the aid of computational simulations to generate new bioinspired composite materials. Furthermore, in this study the smallest topographical features replicated were of the order of the thickness of the film. Further evaluation of the relation of the features to the thickness of the films may prove key to exploit the potential of microtemplating as described herein. Overall, the presented findings pave the way towards bridging the large body of research in cellular metamaterials comprising, e.g., 3D tessellation of repetitive motives or origami patterns,^[55] with the generation of nanoscaled biomimetic materials (including those from mismatched layers of clay, CNCs or even chitin). The combination of cellular metamaterials and long-range ordered nanoparticle composites, can be envisioned to form new ranges of light-weight yet extremely strong and tough materials that would match biological architectures. The latter remains a challenge to be achieved.

3. Experimental Section

Materials: PEG (10 kDa) was purchased from Sigma–Aldrich and used as received. High-grade precision Nylon 66 (poly(hexano-6-lactam)) meshes (NITEX) were obtained from Finntex, Finland and used as received. Flat Nylon substrates (thickness of 300 μ m), acetone

and poly(tetrafluoroetylene) (PTFE) particles (35 μ m) were obtained from Sigma–Aldrich. The CNCs (CAS No. 7789-20-0) were from the USDA's Forest Products Laboratory (FPL, Madison, WI) and acquired through the Process Development Center in the University of Maine, USA. They were obtained as an 11.8% slurry and used as received. A thorough characterization of the CNC suspension was performed in previous studies including for the specific batch used herein.^[30,57] Millipore (Synergy UV) milli-Q water was used to dilute the CNC suspension. Photographic images were taken using a digital camera at a resolution of 4128 × 3096 at a fixed working distance or lightning on top of a black background.

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Superhydrophobization of Polystyrene Petri Dishes: Superhydrophobized polystyrene Petri dishes were formed as previously described.^[58] Briefly, the Petri dishes were exposed to acetone for 30 s after which excess acetone was removed. Subsequently, PTFE powder was rapidly added (ca. 100 mg). Evaporation of the remaining solvent and removal of the excess PTFE powder resulted in an embedded layer of PTFE particles forming a superhydrophobic surface.

Hydrophilization of Polystyrene Petri Dishes and Nylon Meshes: Polystyrene Petri dishes or Nylon meshes were hydrophilized as previously descried.^[30] Briefly, the substrates were exposed to high UV intensity for 30 min, using a Biofore Nanosciences UV-ozone chamber, after which they were thoroughly washed and rinsed with deionized water for 30 min.

Measurement of Contact Angles: Contact angles were measured on pristine, superhydrophobized, and hydrophilized polystyrene surfaces, as well as on a flat Nylon surface, using suspensions with varying amounts of PEG. A droplet size of 7 μ L was utilized and the contact



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angles were captured with a KSV Instruments CAM 200 optical contact angle meter. Results are average of three separate measurements.

Preparation of CNC Suspensions: A stock solution of 10% of PEG was prepared and mixed at appropriate ratios with the 11.8% suspension of CNC. The volume was adjusted using milli-Q water. The PEG content is reported in w:w relative to the dry weight of CNC. For instance, a 57.5 mg films formed from a suspension labeled "15%" contains 50 mg of CNC and 7.5 mg of PEG. The suspensions were left to sit for at least 1 h prior to casting.

Casting of CNC Suspension onto Meshes and Flat Nylon Substrates: The meshes were laid down onto the supporting layer and thereafter the suspension was cast homogeneously on the Nylon. EISA was left to occur under a controlled humidity for a duration of several hours to several days as a function of $d_{\rm CNC}$. The suspension was constrained to the area of the Nylon support due to preferential wetting of the meshes. To prevent the flat Nylon substrates from being affected by residual stresses they were taped to a rigid support. Additionally, after separation from the support, the films were placed on a thin tape to avoid shattering upon testing of conformability.

Conformability Tests Using Solid Cylinders: The composite samples were repeatedly conformed around a solid cylinder of a given radius and under a pressure sufficient enough to induce a tight fit between the composite films and the cylinders. For a given direction, the films were conformed then rotated 90° and conformed again so that the strain was applied symmetrically onto the unit cells of the composites or single-components films. The films presented in Figures 5 and 6, and Figures S14, S17, and S20 in the Supporting Information were conditioned at 23% RH for 6 h, whereas the films presented in Figure S13 in the Supporting Information were conditioned at 23% RH for 1 week.

UV–Vis Spectroscopy: Transmission spectra were obtained with a Perkin Elmer Lambda 950 UV–Vis spectrometer. Three positions within the central part of each film were measured. All experiments were carried out at room temperature. For films formed across the meshed substrates, the data were normalized to the transmittance in the absence of CNCs. The transmittance corresponded approximately to T = 100 - (open area density). Non-specific transmittances were recorded from 250 to 900 nm, giving values of 37% and 60% for $f_{OA} = 30\%$ and 59%, respectively. The half-bandwidths were calculated based on the distance on the *x*-axis (wavelength, nm) between the local lower maxima in transmittance and the minima in transmittance specific to the specific CNC reflections.

Scanning Electron Microscopy: The morphology of the composite materials was examined using a field emission scanning electron microscope (FE-SEM, Zeiss SigmaVP, Germany) operating at 1.6 kV and a working distance of 4 mm. A small piece of the sample was fixed on a carbon tape and then sputtered with Pd–Au alloy (4 nm). For imaging cross-sections of the film onto the mesh, the meshes were pre-cut in small areas prior to casting of the suspension and were fractured in the pre-cut areas post-EISA.

Two-Point Bending Experiments: The bending resistance of the hybrids was evaluated using a dynamic mechanical analysis instrument with a single cantilever mode (Q800 from TA instruments), whereas the sample was clamped in one end (fixed end) and flexed at the other end (loading end) at 10 mm from the clamping point. The loading end was not clamped and, therefore, sliding of the surface of the sample against the top part of the clamp was not restricted. The sample size was 20 by 10 mm ($L \times W$), while the loading rate was 0.2 N min⁻¹. The test was carried for the plain meshes with $f_{OA} = 30\%$ and 59% and for the meshes containing concentrations between 2 and 12 mg cm⁻² at PEG concentrations of 0 and 15%.

Residual Stress Measurements: Residual stress measurements were performed using Borosilicate glass coverslips (VWR) with nominal dimensions of $22 \times 50 \text{ mm}^2$ and thickness number 1 (which corresponds to 150 μ m) as substrates. The coverslips where cut with a glass cutter to a final width of 5 mm. After attaching the glass substrate to a holder, the free length of the cantilever was 39 mm. 100 μ L of the CNC suspensions with PEG contents of 0%, 15%, and 45% were cast over

the cantilever. The values obtained were normalized to the total mass. For the displacement measurement, the free end of the substrate was recorded using a KSV CAM 200 (KSV Instruments, Finland) at a rate of 30 points per hour until the displacement was negligible. The acquired images were subsequently analyzed by measuring the displacement of a fixed point at the tip of the substrate using Image J 1.52e.

Tensile Tests: Tensile tests were carried out on a dynamic mechanical analysis instrument (Q800 from TA instruments) at room temperature. The samples were conditioned at 50% RH for 12 h and the measurements were performed at 23% RH. The composites were cut into samples with dimensions of 30 by 1.1 mm. A gap width of ca. 1 cm was used for the measurements and then a force ramp of 0.5 N min⁻¹ was used.

The thickness was evaluated by SEM. For the microtemplated samples, the thickness above the filament was used and averaged from at least 10 points. The presented results were generated from five measurements for each condition. The toughness was obtained by integrating at least five curves.

Chiral-Nematic Director Orientation Mapping: A 3D model was constructed (Blender 2.79b, Blender Foundation) that obeyed the film surface topography as determined by SEM imaging for the 40–48 μ m mesh. The surface normal vector angle relative to the *z*-direction was then numerically assessed in Matlab R2018a (MathWorks) to compare a set of paths along the surface.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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1808518 (11 of 12)

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