

# Imprinting of Photonic Patterns with Thermosetting Amino-Formaldehyde-Cellulose Composites

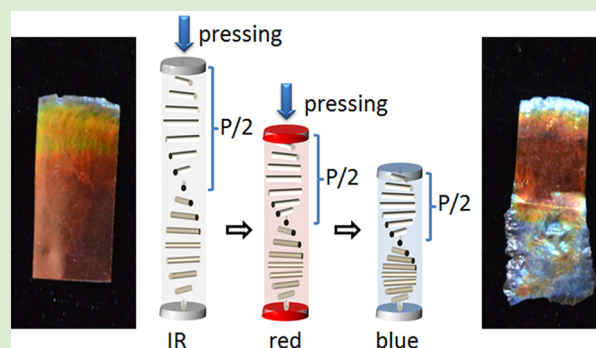
Michael Giese,<sup>†</sup> Mostofa K. Khan,<sup>†</sup> Wadood Y. Hamad,<sup>‡</sup> and Mark J. MacLachlan<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

<sup>‡</sup>FPIInnovations, 3800 Wesbrook Mall, Vancouver, British Columbia, Canada V6S 2L9

## S Supporting Information

**ABSTRACT:** A family of new amino resin-cellulose nanocrystal composites is reported. Owing to the chiral nematic order of the cellulose nanocrystals (CNCs) embedded in the amino resin polymer, the materials appear highly iridescent and their color can be controlled by the addition of salt. The freshly prepared samples are highly flexible and their color can be manipulated by applying pressure to the films. Colored chiral nematic patterns can be permanently recorded in the composite films, suggesting their application for security features, pressure sensors, and decoration.



Structural color is ubiquitous in nature<sup>1</sup> and has important roles in signaling, mimicry, or mate choice among organisms. It is found in minerals like opals,<sup>2</sup> shells of mussels and insects,<sup>3</sup> bird feathers,<sup>4</sup> and even in plants<sup>5</sup> and their fruits.<sup>6</sup> While nature is rich with examples of structural color, our fabricated buildings and belongings are mainly colored with dyes and pigments.

There has been growing interest in structural coloration over the past few decades in both academic and industrial circles. Structural color opens the door to new markets and novel applications.<sup>7</sup> In this regard, materials like photonic crystals<sup>8</sup> or Bragg stacks<sup>9</sup> offer the possibility for brilliant structural colors by prohibiting propagation of specific wavelengths due to their photonic band gap (PBG). Photonic materials are generally prepared using self-assembly of monodisperse spheres to yield a highly ordered crystalline lattice with photonic properties. Besides photonic crystals and Bragg stacks, chiral nematic liquid crystals (LCs) exhibit interesting photonic properties.<sup>10</sup> Iridescence can be observed when the helical pitch of the chiral nematic LC is in the region of the wavelength of visible light. Owing to the chirality of the structure, the incident light is selectively reflected with circular polarization. Tuning the reflective color of these materials by variation of the periodic arrangement may lead to new applications.<sup>11</sup>

Extraction of cellulose nanocrystals (CNCs) was first reported by Rånby in the early 1950s.<sup>12</sup> In 1959, Marchessault and co-workers reported lyotropic liquid crystalline behavior of CNC, which was extensively studied by Gray et al. and assigned to the helicoidal self-assembly of the CNCs.<sup>13</sup> CNCs prepared from sulfuric-acid catalyzed hydrolysis of cellulose have a net negative surface charge, are typically 5–10 nm in diameter, and have a high surface area (ca. 400 m<sup>2</sup>/g). When dried, solutions of CNCs have been shown to retain their liquid crystalline

characteristics and organize into iridescent solid films with chiral nematic organization.<sup>14</sup> The self-assembly of CNCs in aqueous solutions makes them a potentially effective template for structurally colored materials.<sup>15,16</sup> We have recently demonstrated that CNC-templating can be applied to construct flexible photonic hydrogels and mesoporous phenol-formaldehyde resins with tunable colors.<sup>17</sup>

Amino resins, on the other hand, are an important, broad family of polymers with a long history.<sup>18</sup> They are accessible by the reaction of amino groups (mostly from urea or melamine) with aldehydes (e.g., formaldehyde). Amino resins have been produced industrially for many applications, including laminated structures and adhesives for wood furniture,<sup>17b</sup> but their stand-alone applications are limited by their poor stability against water.<sup>17a</sup> They have not been applied to the construction of photonic crystals.

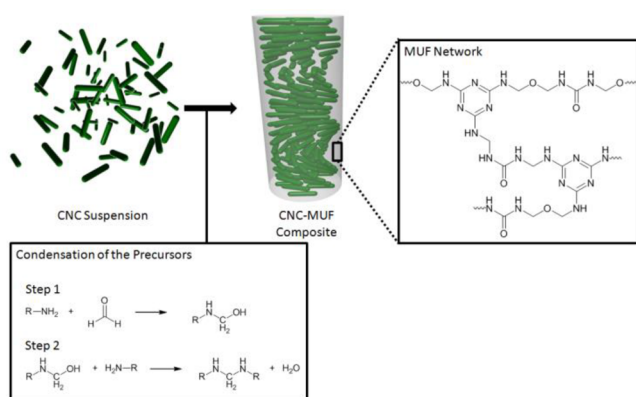
In this paper we explore, for the first time, the use of amino resins for the construction of photonic crystals. We specifically report the use of a new family of amino resin composites derived from condensation of melamine, urea, and formaldehyde in the presence of CNCs. These melamine-urea-formaldehyde (MUF)-CNC composites capture the chiral nematic structure of CNC assemblies in aqueous solution and integrate them into a cross-linked polymeric network, leading to the production of colorful films with tunable optical properties (Scheme 1). The color of the polymer composite can be controlled either by changing the ratio of polymer to CNC or by manipulating the ionic strength of the CNC

Received: July 18, 2013

Accepted: August 20, 2013

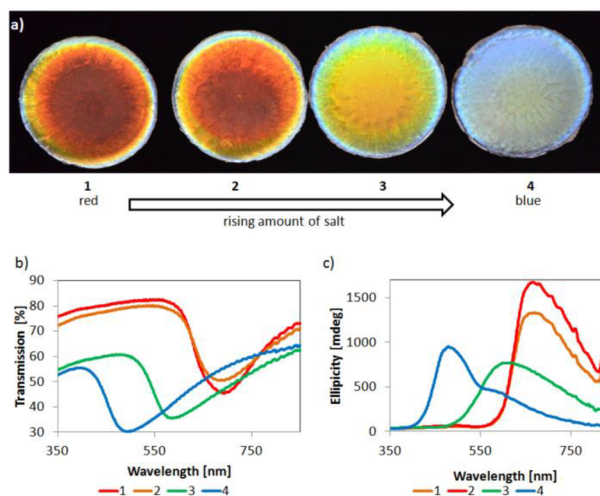
Published: August 26, 2013

## Scheme 1. Synthesis of the Novel Chiral Nematic MUF-CNC Composites



solution through salt addition. Significantly, we demonstrate that the application of external pressure leads to structures with variable optical properties. These materials can essentially form a new type of imprintable photonic resin that may be useful for security features and decorations.

For our current synthesis,  $H_2SO_4$ -catalyzed CNC aqueous suspensions were prepared from commercial bleached kraft wood pulp.<sup>19</sup> It was uncertain if the basic polymer precursor solutions would be compatible with the chiral nematic self-assembly of CNCs in water. A slightly cloudy but homogeneous mixture was obtained by mixing an aqueous suspension of CNCs (5.1 wt %, pH = 6.9) with a basic solution of MUF precursor. After allowing the composite mixture to dry in a polystyrene Petri dish for 72 h under ambient conditions, highly flexible and iridescent polymer films were obtained (Figure 1a).

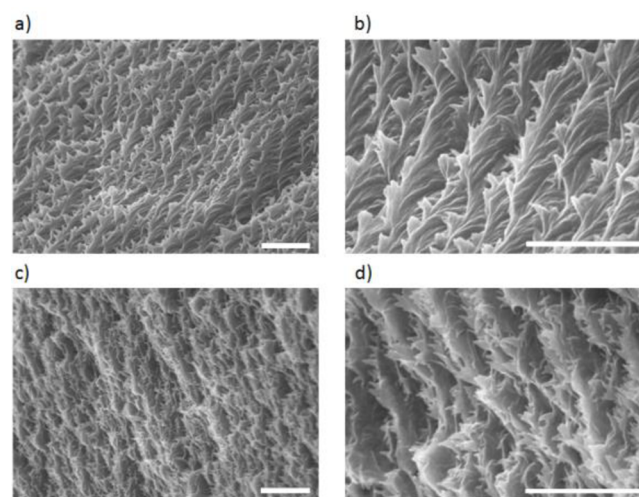


**Figure 1.** (a) Photograph of the MUF-CNC composite films obtained with addition of salt during the synthesis (5 cm diameter). (b) UV-visible transmission spectra of 1 (red), 2 (orange), 3 (yellow/green), and 4 (blue). (c) CD spectra of 1–4.

Formation of the MUF-CNC composite was confirmed by IR spectroscopy and solid-state  $^{13}C$  cross-polarization/magic angle spinning (CP/MAS) NMR spectroscopy. The IR data show signals at  $1670\text{ cm}^{-1}$ , assigned to the carbonyl band, and at  $1550\text{ cm}^{-1}$ , which arises from the C-N stretching of the triazine (Figure S1).<sup>20</sup> The presence of the MUF polymer in

the composite was further confirmed using solid-state  $^{13}C$  CP/MAS NMR spectroscopy (Figure S2). The signal at 165 ppm is characteristic of the carbon atom in the triazine unit<sup>21</sup> and the signal at 155 ppm arises from the carbonyl group.<sup>22</sup> The remaining signals belong to CNCs and overlap with the methylene carbon signal of the MUF resin at 60–80 ppm.<sup>14c,20</sup> On the basis of the calculated stoichiometry, the composites contain about 40% MUF and 60% CNC, and elemental analysis was close to the theoretical value. Our data gives no information about cellulose–resin interactions, which have been debated in the cases of UF and MF composites.<sup>23,24</sup> Thermal stability of the samples was measured thermogravimetrically and showed comparable thermal stability to the corresponding CNC films (see Supporting Information, Figure S3). By adding different amounts of NaCl solution (0.25 M) to the reaction mixture (1, no salt addition; 2, 35  $\mu\text{L}$ ; 3, 140  $\mu\text{L}$ ; 4, 280  $\mu\text{L}$ ), the color of the composite films could be varied from red to yellow/green to blue (Figure 1a).

The composite samples show peak reflectance wavelengths from 490–670 nm (Figure 1b). We attribute the broadness of the peaks to the polydispersity of the CNC and disordered structure. To confirm that this reflection arises from the chiral nematic structure of the composite films, small pieces of the polymer films (in order to prevent saturation of the detector) were used to obtain circular dichroism (CD) spectra (Figure 1c). The contribution of linear birefringence was eliminated by repeating the CD spectra upon rotation of the samples, which showed no significant change in the spectra. In each case, the samples show a peak with positive ellipticity that matches closely with the reflectance peak observed by UV–vis spectroscopy. Scanning electron microscopy (SEM) images of cross sections of sample 1 (Figure 2a,b) show a layered



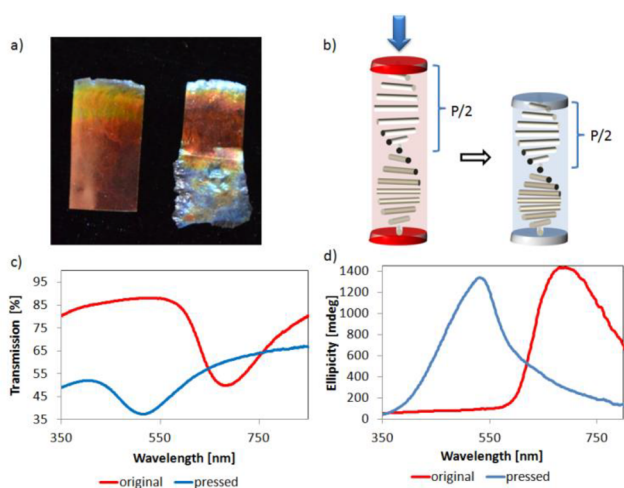
**Figure 2.** SEM images of the chiral nematic MUF-CNC composites (scale bar, 1  $\mu\text{m}$ ). (a,b) Side views of an unpressed region of the cracked composite film looking down the edge. (c,d) Side views of a pressed region of the same film.

structure with details that are reminiscent of the structure observed in chiral nematic CNC films. The observed colors of the composite films arise from the selective reflection of light from the planar chiral nematic structure. For incident light normal to the film's surface, the peak reflected wavelength,  $\lambda_{\text{max}}$  of a chiral nematic structure obeys the following equation:

$$\lambda_{\max} = n_{\text{avg}} \cdot P$$

where  $n_{\text{avg}}$  is the average refractive index and  $P$  is the helical pitch (nm).<sup>25</sup> A change in color can therefore be caused by a change in the refractive index or the helical pitch of the chiral nematic assembly. Because the composition of samples 1–4 is nearly identical, the observed blue shift arises from a change in the helical pitch of the CNCs rather than a change in refractive index. As previously reported for CNC films, this behavior can be explained by masking of the electrostatic repulsion of the CNC units during self-assembly with increased ionic strength. As a result of the decreased repulsion through salt addition the helical pitch is smaller and the UV–vis signal of these films is blue-shifted.<sup>26</sup>

As mentioned above, the freshly prepared films are highly flexible. Using this mechanical flexibility we tried to manipulate the optical properties of the composite films by squeezing or stretching the material. Therefore, sample 1 was rolled with a piece of metal. Depending on the applied pressure, the color of the composite films shifts from red to blue (Figure 3a). The



**Figure 3.** (a) Photograph of composite film 1 before (left) and after (right, bottom of the strip) applying pressure to the material. (b) Schematic representation of the change in helical pitch that occurs upon pressing the material. (c) UV–vis spectrum and (d) CD spectrum of 1 before and after applying pressure.

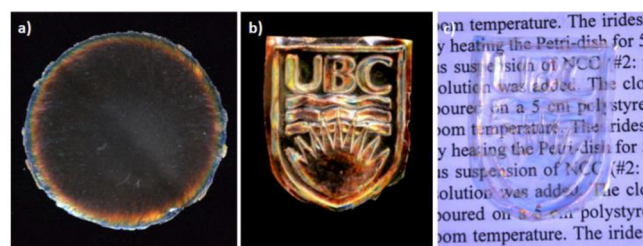
material appears to have a positive Poisson ratio and the compression is accompanied by stretching. After curing the films at ambient temperature for an additional 120 h or at 120 °C for 2 h, the material is obtained as a dimensionally stable polymer. The color originating from the chiral-nematic order is slightly blue-shifted (~20 nm) and locked. The samples no longer show changes with applied pressure.

UV–vis spectroscopy confirms a shift of the reflection peak from 690 to 510 nm (Figure 3c). CD spectroscopy verified that the chiral nematic order remained after mechanical manipulation, with the peak signal (with positive ellipticity) shifting from ~700 nm to ~530 nm (Figure 3d). This 170 nm blue shift in the reflection peak is explained by a decrease in the pitch of the chiral nematic structure upon application of pressure, as depicted in Figure 3b. The line width of both the UV–vis and the CD signals did not show a significant change.

We also used SEM to observe the structural change that results from pressing. Whereas the layered structure before pressing appears fairly homogeneous and well ordered (Figures

2a,b and S4), the structure after pressing appears more disordered, but still retains the characteristic layered structure (Figures 2c,d and S5). Also, the separations between the layers appear smaller after pressing the sample, but one must be cautious in overinterpreting this as the spacing between the planes is very sensitive to sample preparation and imaging conditions.<sup>16k</sup> Tilting of the layers upon pressing could also contribute to the change in color.

As the application of pressure to the film leads to changes in color, we thought this could be useful for imprinting colored patterns into composite films. A related MUF-CNC polymer composite film was synthesized (sample 5) that is twice as thick as samples 1–4. This film contains a higher amount of polymer precursor and, therefore, its reflection from chiral nematic order is red-shifted into the IR region, leading to a nearly transparent film (Figure 4a). Pressure was applied to the film by using a



**Figure 4.** (a) MUF-CNC composite film 5 after synthesis. (b) MUF-CNC composite 5 after imprinting of the crest. (c) Imprinted MUF-CNC composite 5 in front of a sheet of paper to show the transparency of the composite material.

metal stamp embossed with the UBC crest. Since pressure was not applied homogeneously to the film, the change in color is not uniform over the whole sample. However, this simple experiment shows that the new photonic amino resins are suitable for irreversibly imprinting patterns by applying pressure. The film with the crest imprinted shows up well on a black background (Figure 4b) but remains transparent when observed on a white background (Figure 4c). This application strongly benefits from the chiral nematic order in our composites that allows color tuning by changing of the pitch of the structure. We believe this is a novel way to impart a photonic imprint in materials, and is distinct from other methods (typically reversible) to change the color of photonic materials.<sup>27</sup>

We attempted to quantify the relationship between the applied pressure and the degree of change in the pitch and, hence, color in the composite films. With the MUF resins, however, we found that repeated rolling of the resin with a nearly constant pressure resulted in a continuous change in pitch and color. We are now pursuing a less pliable resin that can systematically change color with applied force.

In conclusion, we synthesized a new family of polymers, namely, MUF-CNC composites, with structural coloration arising from the chiral nematic order of the CNCs. The color of these composites can be tuned from red to blue by the addition of salt. Furthermore, the color of the composite films can be manipulated by applying pressure to the materials, which causes a blue shift in the wavelength of light reflected from the materials. Additionally, we demonstrated that chiral nematic patterns can be imprinted into the composite films by using a stamp. These new structurally colored, mechanically manipulable amino resin composite materials with chiral nematic order

may be useful for the construction of security features, labels, and optical components.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Supporting spectra and thermal analysis details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [mmaclach@chem.ubc.ca](mailto:mmaclach@chem.ubc.ca).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank NSERC, NORAM Engineering and Constructors Ltd., FPInnovations, and ArboraNano for their support. M.G. thanks the German Academic Exchange Service (DAAD) for a postdoctoral fellowship.

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