

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

Michael Giese<sup>1</sup>, Mostofa K. Khan<sup>1</sup>, Wadood Y. Hamad<sup>2</sup> and Mark J. MacLachlan<sup>1,\*</sup>

<sup>1</sup> Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, CANADA V6T 1Z1. <sup>2</sup> FPInnovations, 3800 Wesbrook Mall, Vancouver, BC, CANADA V6S 2L9.

Email: mmaclach@chem.ubc.ca

## Supporting Information

### Materials and Characterization

All compounds were used without further purification as received from the suppliers. Aqueous suspensions of cellulose nanocrystals (CNCs) were supplied by FPInnovations (5.1%, pH = 6.9) obtained by a procedure described previously.<sup>1</sup> Thermogravimetric analysis was performed on a PerkinElmer Pyris 6 thermogravimetric analyzer with 10 °C/min under air. Elemental analysis (CNH) was performed at UBC Microanalytical Services Laboratory. UV-visible/near-IR spectroscopy was carried out on a Cary 5000 UV-Vis/NIR spectrophotometer using the films on glass microscope slides perpendicular to the beam path. CD spectra were recorded on a JASCO J-710 spectropolarimeter by using the same procedure as for the UV-Vis data. For the dry films small pieces that did not completely cover the aperture were used in order to prevent saturating the detector. Infrared spectra were obtained with a Nicolet 6700 FT-IR equipped with a Smart Orbit diamond attenuated total reflectance (ATR) attachment. The SEM images were obtained on a Hitachi S4700 electron microscope after sputter-coating with gold/palladium (2.5 nm; 60/40). <sup>13</sup>C CP/MAS solid-state NMR experiments were performed at Western University NMR Facility using Bruker AV 400 MHz spectrometer with a 4 mm rotor at a spin rate of 6000 rpm with 2 ms contact time and 15000 – 20000 scans.

#### *Experimental*

*General:* The CNC solutions were sonicated for 10-15 minutes prior to mixing with MUF precursor solutions to ensure that the CNC particles were dispersed. A standard laboratory sonicator (2 A, 120 V) available from VWR (Aquasonic model 50T) was used. The used aqueous CNC suspension showed a pH of 6.9 and contained 5.1 wt% CNC.

*Preparation of the MUF precursor:* 1.00 g of urea (1.0 eq., 16.6 mmol) was dissolved in 10.00 g of a 37 wt.% formaldehyde solution (7.5 eq., 123.3 mmol) in water and stirred for 10 min. Melamine (1.00 g, 0.5 eq., 7.9 mmol) was added, the mixture was stirred for 15 min at 100 °C, then the solution was cooled for 5 min. Ten drops of an aqueous NH<sub>4</sub>OH solution (28 wt%) were added and the mixture was stirred for 4 h at ambient temperature. The resulting colorless precursor solution can be used for several days.

*Synthesis of the MUF-CNC composites (1-4):* To 5.00 mL of a suspension of CNC in water varying amounts of a 0.25 M sodium chloride solution were added (**1**: no addition, **2**: 35 µL, **3**: 140 µL and **4**: 280 µL). After sonicating the mixture for 10 min, 0.50 mL of an aqueous MUF precursor solution was

added. The mixture was stirred for 5 min and then poured into a 5 cm diameter polystyrene Petri dish. After drying for 72 h the polymer film was carefully detached from the polystyrene dish.

**1:** Red iridescent film. UV-Vis: 690 nm, CD: 670 nm. This sample was used to show the change in color by applying pressure on the composite film: UV-Vis shift from 690 nm (original film) to 510 nm (pressed sample). CD: from 700 nm to 530 nm. CHN calculated for 40% of MUF to 60% CNC. Calculated (%): C 36.89 H 6.52 N 11.32; found: C 38.64 H 6.20 N 10.86.

**2:** Red iridescent film. UV-Vis: 690 nm, CD: 670 nm. IR: 3600-3150 (OH/NH), 2970-2840 (CH), 1670 (C=O), 1550 (-C=N-)  $\text{cm}^{-1}$ . TGA: Start of decomposition at 220 °C; CHN calculated for 40% of MUF to 60% CNC. Calculated (%): C 36.89 H 6.52 N 11.32; found: C 38.26 H 6.27 N 11.46.

**3:** Yellow/green iridescent film. UV-Vis: 590 nm, CD: 610 nm. CHN calculated for 40% of MUF to 60% CNC. Calculated (%): C 36.89 H 6.52 N 11.32; found: C 38.49 H 6.21 N 11.68.

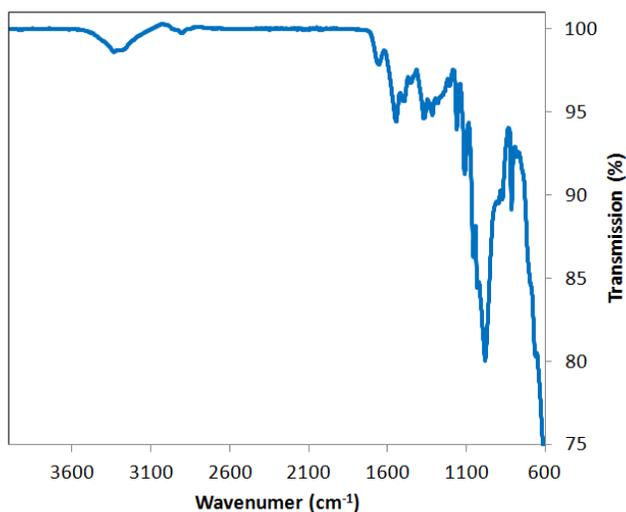
**4:** Blue iridescent film, UV-Vis: 490 nm, CD: 480 nm. CHN calculated for 40% of MUF to 60% CNC. Calculated (%): C 36.89 H 6.52 N 11.32; found: C 38.64 H 6.16 N 10.99.

*Synthesis of MUF-CNC composite for imprinting (5):* 1.50 g of urea (1.0 eq., 25 mmol) was dissolved in 10.00 g of a 37 wt% formaldehyde solution (5.0 eq., 123.3 mmol) in water and stirred for 10 min. After adding 1.00 g of melamine (0.3 eq., 7.9 mmol), stirring the mixture for 15 min at 100 °C, and cooling it down for 5 min, 10 drops of an aqueous  $\text{NH}_4\text{OH}$  solution (28 wt%) were added. The mixture was stirred for 4 h at ambient temperature to yield a stable, transparent precursor solution.

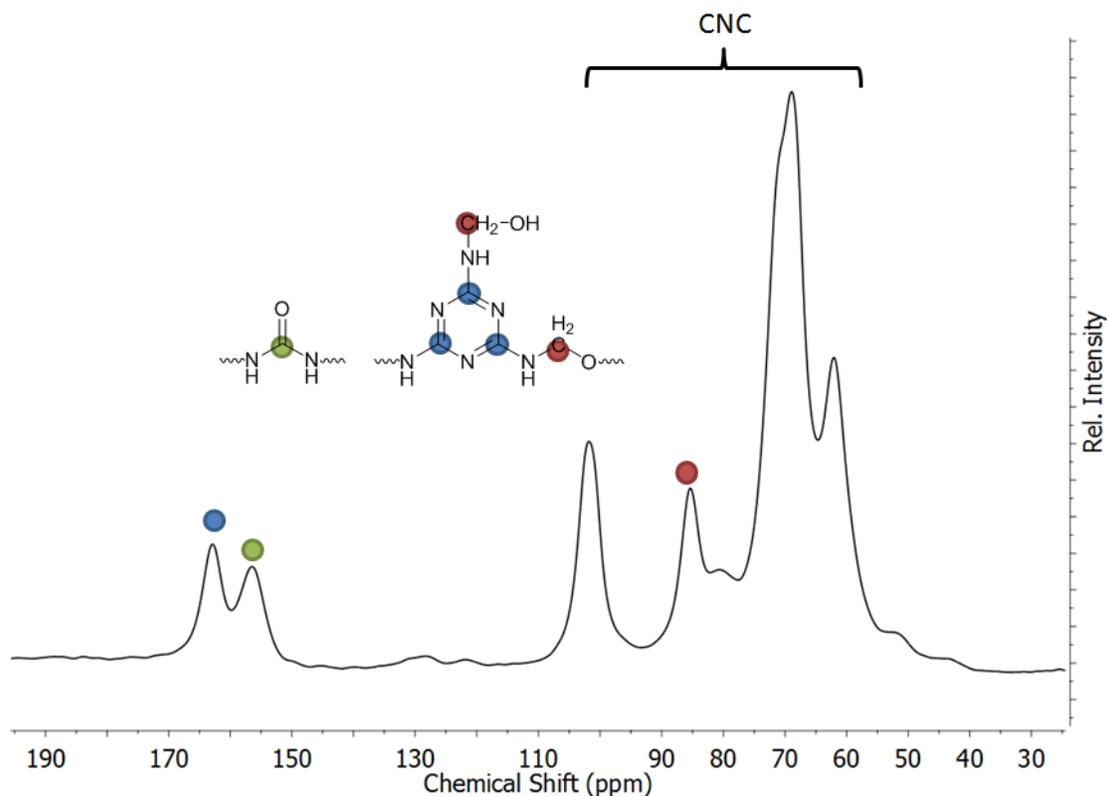
This aqueous MUF precursor solution (1.00 mL) was added to 10.00 mL of a suspension of CNC in water. The mixture was stirred for 5 min and then poured into a 5 cm polystyrene Petri dish. After drying for 72 h the polymer film was carefully detached from the polystyrene dish. The composite material was obtained as nearly colorless film.

For imprinting the UBC crest into the polymer composite films the stamp was covered with the MUF-CNC composite film as well as a 0.4 mm thick silicone elastomer slide. The pressure was carefully applied with a rolling pin (applied weight ca. 4-5 kg, 15-20 repetitions).

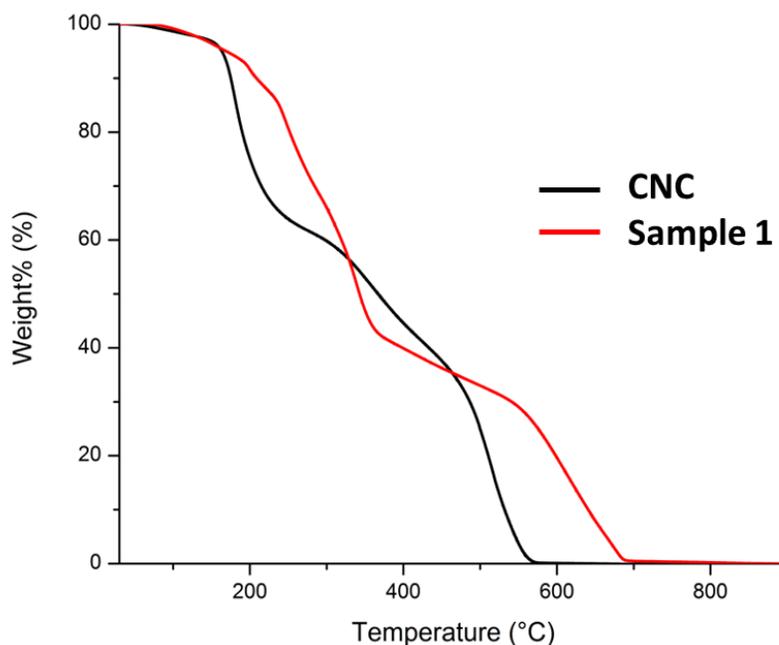
## Supporting Figures



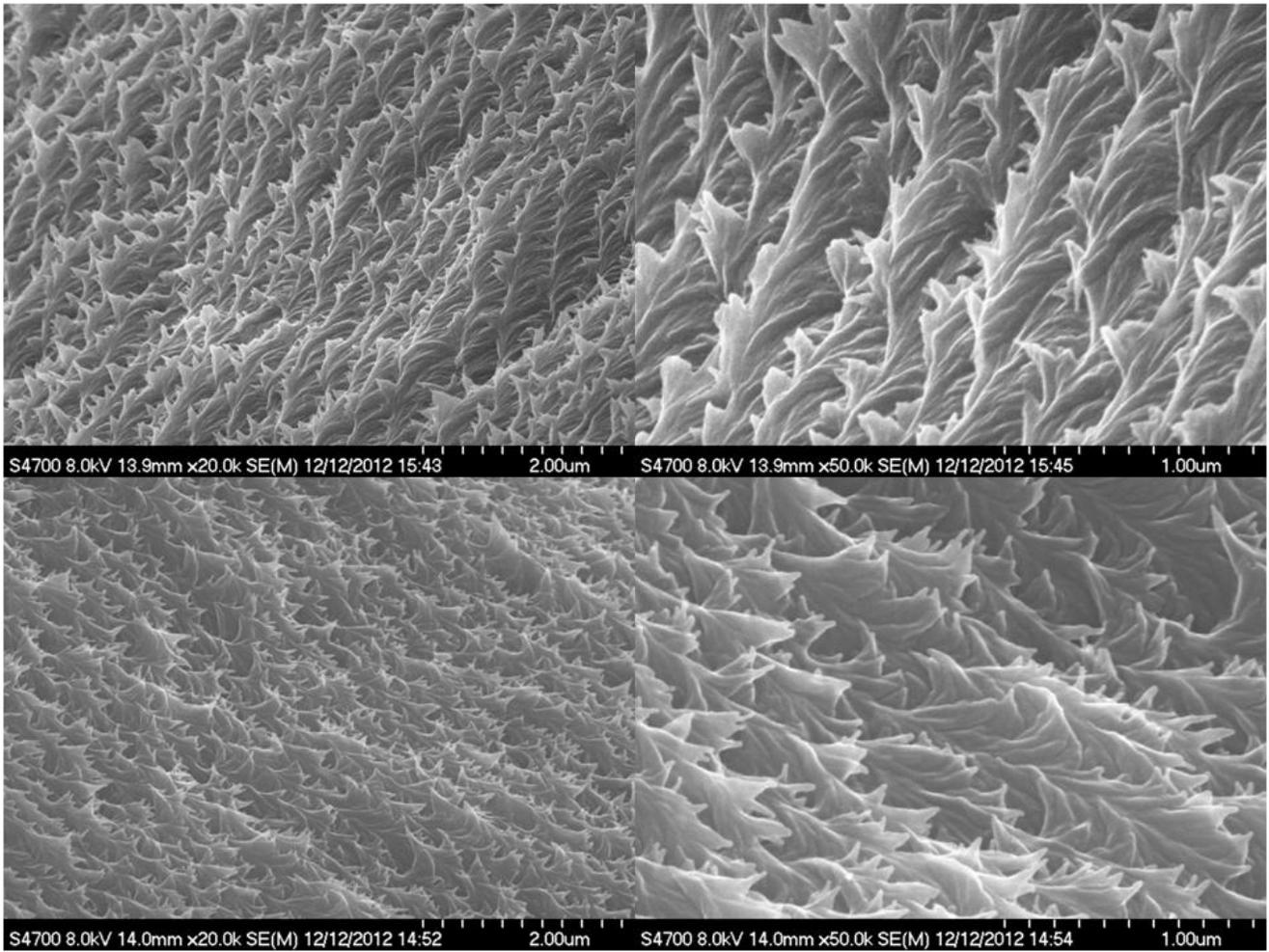
**Figure S1.** Representative IR spectrum of sample 1.



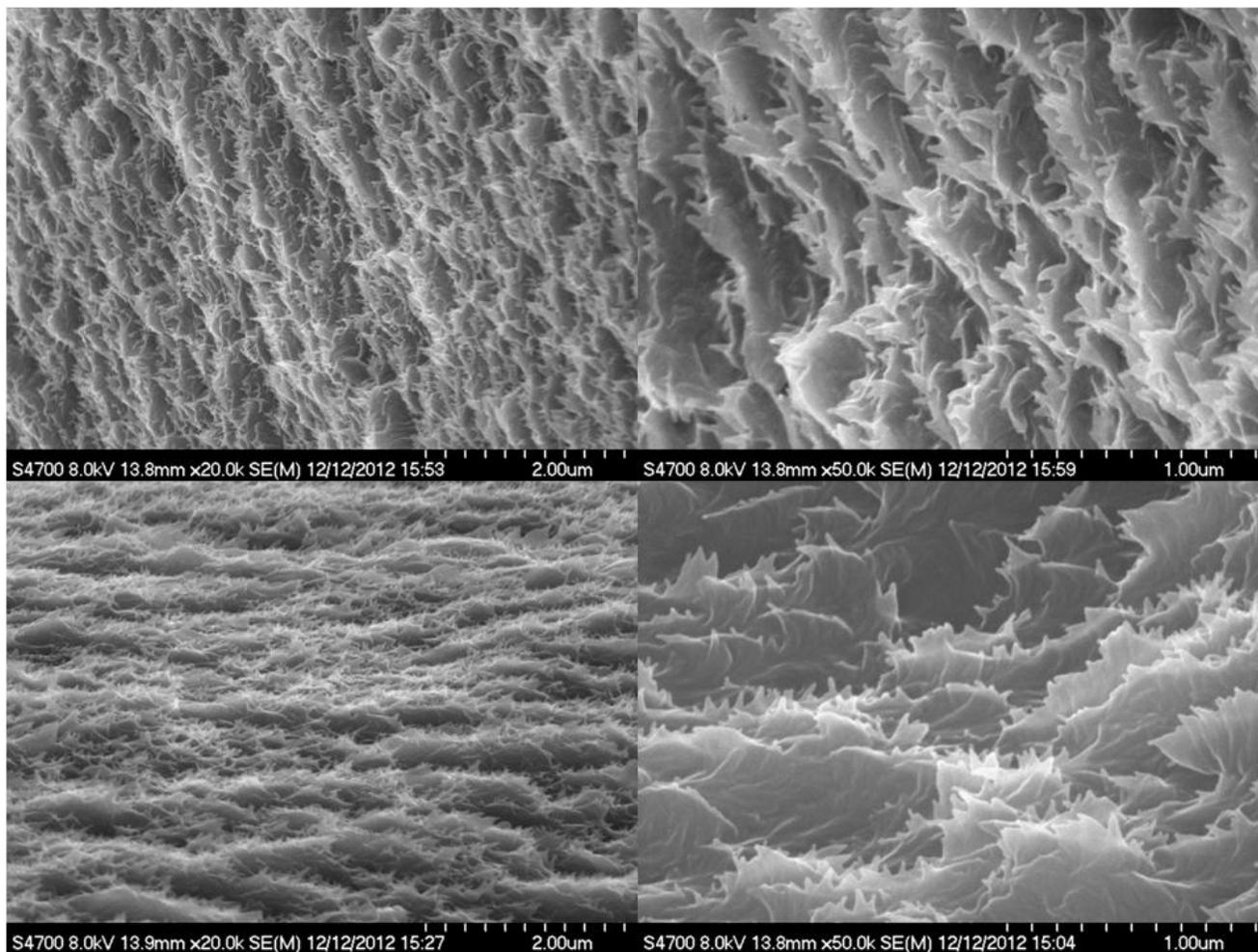
**Figure S2.** Representative  $^{13}\text{C}$  CP/MAS solid-state NMR (100 MHz, 18496 scans, spinning rate: 6 kHz, contact time: 2 msec, recycle delay: 5 sec) for sample **1**. The signal at 165 ppm is characteristic of the carbon atom in the triazine unit and the signal at 155 ppm arises from the carbonyl group. The remaining signals belong to the NCC and overlap with the methylene carbon signal of the MUF-resin at 60-80 ppm.



**Figure S3.** Representative TGA for sample **1** in comparison with a pure CNC film.



**Figure S4.** SEM images showing the high order of the composite films before pressing.



**Figure S5.** SEM images showing the disturbed order of the composite films after pressing.

<sup>1</sup> Hamad, W. Y.; Hu, T. Q. *Can. J. Chem. Eng.* **2010**, *88*, 392.