Shape Memory Cellulose-based Photonic Reflectors

André Espinha,† Giulia Guidetti,‡ María C. Serrano,§ Bruno Frka-Petesic,‡ Ahu Gumrah Parry,‡
Wadood Y. Hamad,§ Álvaro Blanco,† Cefe López,*† Silvia Vignolini*‡

†Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Calle Sor Juana Inés de la Cruz, 3, Cantoblanco, 28049 Madrid, Spain
‡Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW UK
§Hospital Nacional de Parapléjicos, Servicio de Salud de Castilla La Mancha, Finca La Peraleda s/n, 45071 Toledo, Spain
∥FPInnovations, 2665 East Mall, Vancouver, BC, Canada V6T 1Z4.

Supporting Information – PDF

The supporting video can be found here:

https://www.dropbox.com/s/t69wsja4ja6l0rn/00003s2.mpeg?dl=0
https://www.dropbox.com/s/08xzdo80z7twguo/00004s3.mpeg?dl=0

1) Experimental Section

Chemicals: Citric acid and 1,12-dodecanediol were purchased from Sigma-Aldrich and ethanol 99.5% from Panreac. All chemicals were used as received.

Fabrication of cellulose nanocrystals films: The cellulose nanocrystal suspension was provided by CelluForce. Films of cellulose nanocrystals were fabricated by EISA by pouring 2 mL of 1 wt% CNC suspension, at pH 5.5 into polystyrene Petri dishes of 3.6 cm diameter and allowed to
dry at ambient conditions. To obtain respectively red, green and blue films the ionic strength of
the initial suspension was adjusted by subjecting it to heat treatment in a water bath at 60 °C for
12 h, 21 h and 30 h respectively. The dry films were then detached from the substrates and cut
into individual flakes of similar shape, avoiding the edge region affected by a coffee-ring strain.¹

Prepolymer synthesis: A prepolymer composed of citric acid and 1,12-dodecanediol (mol ratio
of hydroxyl to carboxyl groups 4:3) was prepared following a previously reported protocol¹ and diluted in ethanol, at a concentration of 0.5 g·mL⁻¹, with the help of mild
heating and sonication.

Preparation of SMP composites: Free-standing CNC flakes were immersed in the diluted
prepolymer overnight, drained to remove the excess of prepolymer and finally left drying for
ethanol evaporation. For further curing of the samples, they were held by three contact points, to
prevent adhesion to a substrate, and thermally annealed at 80 °C, in an oven for periods from 16
h to 20 h.

Optical characterization: Optical characterization was performed in reflection mode on a
customized Zeiss Axio microscope using a halogen lamp (Zeiss HAL100) as a light source with
Koehler illumination. The light reflected off the sample passes through a quarter wave plate and
a polarizing filter, specifically oriented to select either left-circularly-polarized or right-
circularly-polarized light before being split between a CCD camera (UI-3580LE-C-HQ, IDS)
and an optical fiber mounted in confocal configuration and connected to a spectrometer
(AvaSpec-HS2048, Avantes). This setup allowed for the spectra acquisition from specific areas
in the sample; all the spectra were normalized to the reflection of a silver mirror.

Scanning Electron Microscopy: SEM images were acquired using a Leo Gemini 1530VP
system, Zeiss, working in cross section at an angle of 90° with respect to the electron beam. The
samples were placed on aluminum stubs using conductive carbon tape and sputter-coated with a
few nanometer thick layer to Au/Pd (Emitech K550) to minimize the charging effect. The acceleration voltage used was 4 kV and the working distance was 3-4 mm.

2) Supplementary Figures

**Figure S1.** Fabrication procedure for the CNC/PDDC-HD hybrid structure and thermal activation steps.
**Figure S2.** SEM image showing the layered structure of the CNC/PDDC-HD hybrid material. The CNC thin film is sandwiched between two layers of PDDC-HD as a result of the impregnation process.

3) **Estimation of the Young modulus of a simplified hybrid CNC/PDDC-HD layered material**

The Young modulus of pure CNC films, noted $E_{cell}$, has been evaluated in the literature as being in the range of few GPa (1.5 GPa, 2.5.8 GPa). The Young modulus of pure PDDC-HD bulk polymer has been estimated to 13.7 MPa at room temperature and decreasing to a plateau of 2 MPa above $T_{trans} = 30 \degree C$.

From the cross-section profile of the film displayed in Figure S2 and assuming that the Young modulus of the edge and the middle layers are given by the pure PDDC-HD and pure CNC ones, one can estimate an effective Young modulus of the overall material corresponding to the bending stress applied in a cantilever geometry using the following formula:

$$
A_1 = t_1; \quad A_2 = t_2 \times E_{NC}/E_{PDDC}; \quad A_3 = t_3; \quad A_T = A_1 + A_2 + A_3;
$$

$$
y_1 = t_1/2; \quad y_2 = t_1 + t_2/2; \quad y_3 = t_1 + t_2 + t_3/2; \quad y_T = (y_1 A_1 + y_2 A_2 + y_3 A_3)/A_T
$$

$$
l_i = A_i[(y_i - y_T)^2 + t_i^2/12]; \quad I_T = \sum_{i=1}^3 I_i; \quad I_{PDDC} = (t_1 + t_2 + t_3)^3/12;
$$

$$
E_{hybrid} = E_{PDDC} \times \frac{I_T}{I_{PDDC}}
$$

From this simplified modeling, the effective Young modulus $E_{hybrid}$ of the overall film is expected to increase by a factor ~2.7 as compared to pure PDDC-HD.

4) **References**

(2) Cranston, E.D.; et al., Determination of Young’s modulus for nanofibrillated cellulose multilayer thin films using buckling mechanics. *Biomacromolecules* 2011, 12, 961-969.

