Rubber Materials from Elastomers and Nanocellulose Powders:

Filler Dispersion and Mechanical Reinforcement

Matthieu Fumagalli, Julien Berriot, Benoit de Gaudemaris, Anne Veyland,

Jean-Luc Putaux, Sonia Molina-Boisseau, Laurent Heux

SUPPORTING INFORMATION

Figure SI-1. Liquid-state ^{1}H NMR spectrum of 3'-dithiodipropionic acid chloride (DTACl) in deuterated acetone.

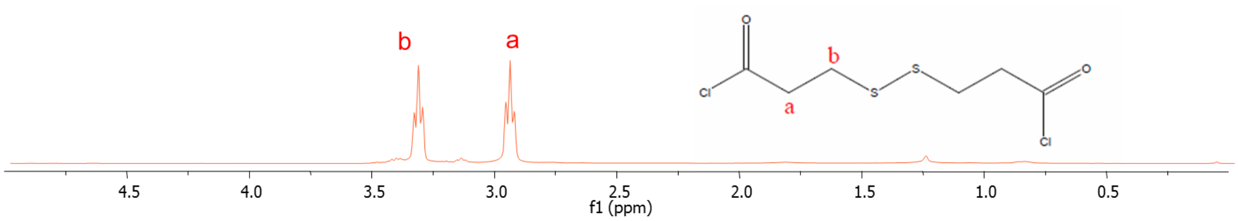


Figure SI-2. Curing kinetics followed by rheology measurements.

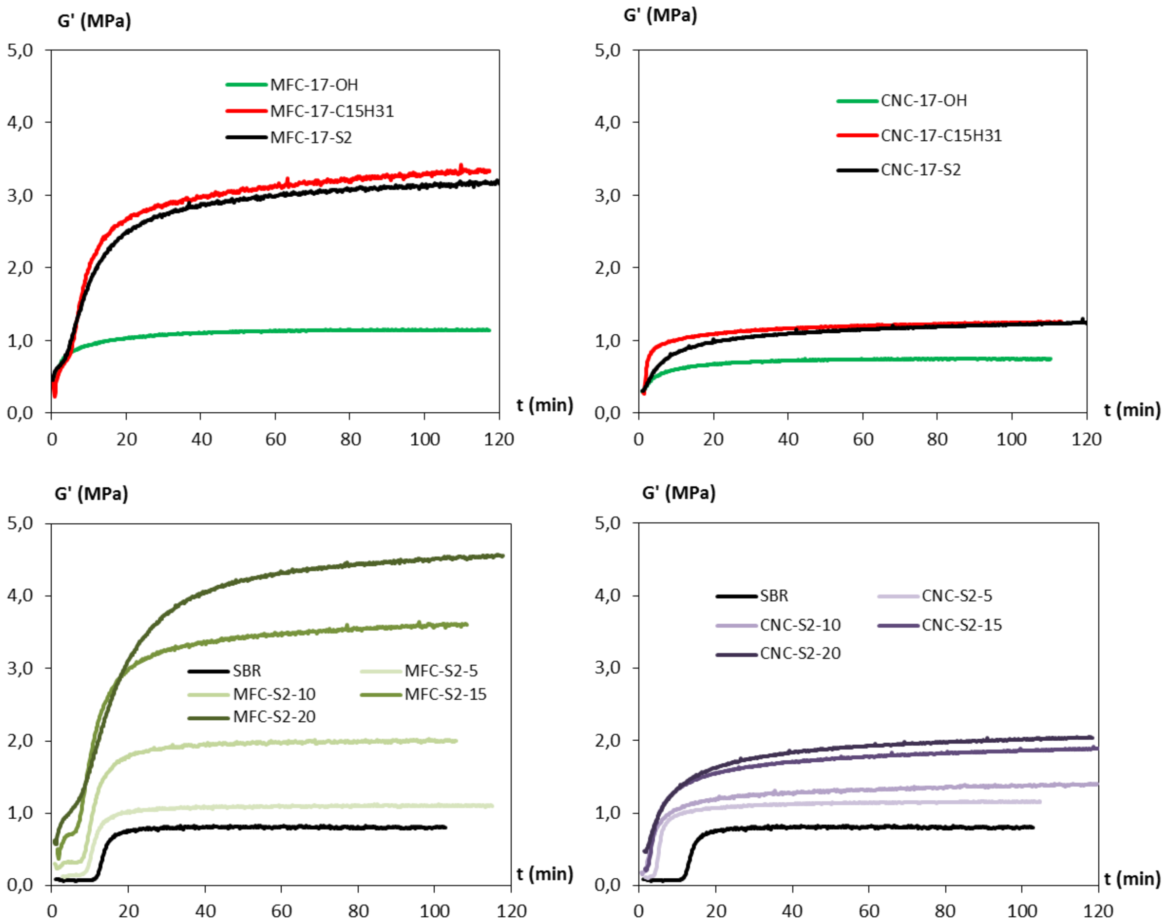


Figure SI-3. Low magnification TEM micrographs of cryosections of elastomers nanocomposites loaded with 5 vol. % CNC-S_2 (a), 10 vol.% (b), 15 vol. % (c), 20 vol. % (d), 17 vol. % MFC-OH (e), 17 vol. % MFC-$C_{15}H_{31}$ (f), 17 vol. % MFC-S_2 (g), 5 vol. % and MFC-S_2 at (h), 10 vol. % (i), 15 vol. % (j), 20 vol. % (k).

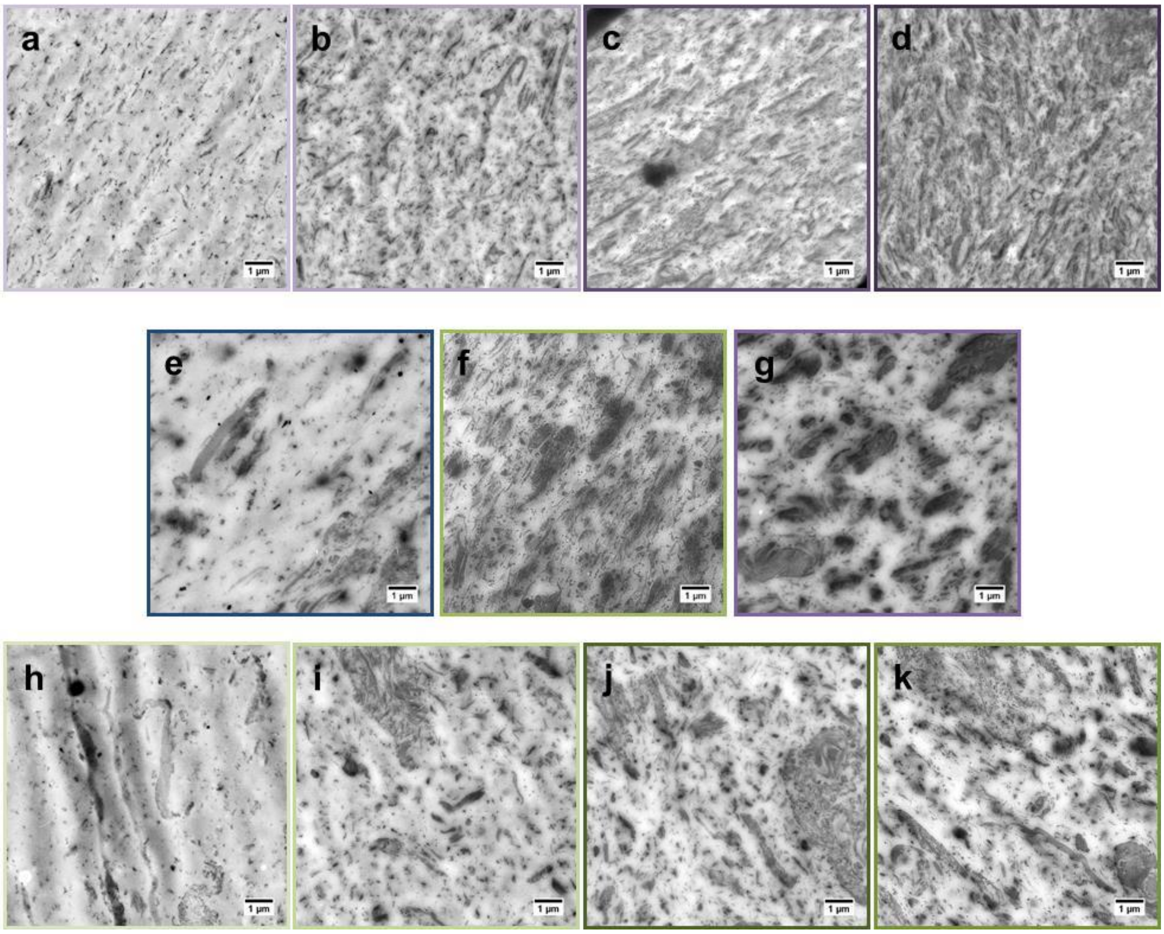


Figure SI-4. High magnification TEM micrographs of ultrathin cryosections of elastomer nanocomposites loaded with 5% vol.% S_2-modified MFCs (a), 10 vol.% (b), 15 vol.% (c), 20 vol.%.

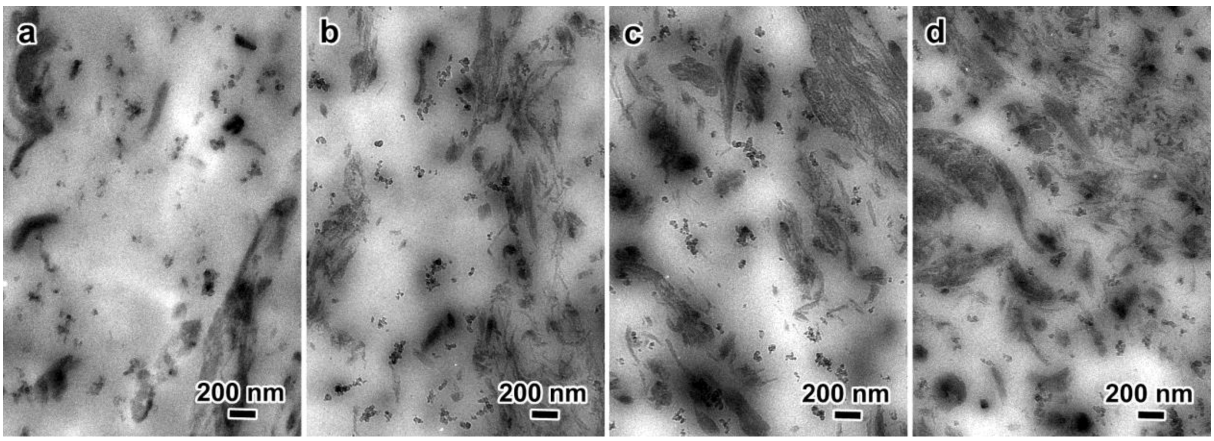
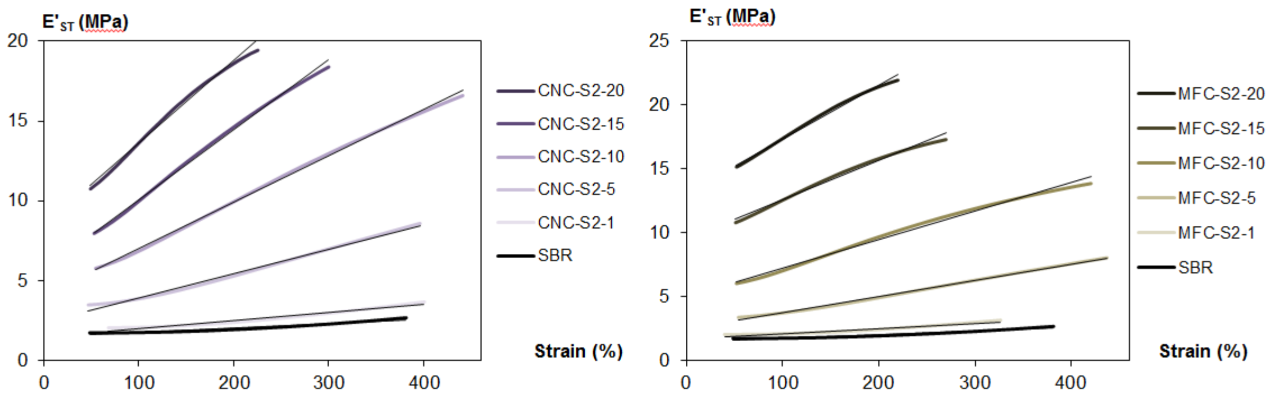


Figure SI-5. Tensile curves plotted as the true secant modulus E'_{ST} (true stress divided by strain). Left panel CNC-S_2 and right panel MFC-S_2 at several filler volume fraction. From strains above 50% the curves are fitted by an affine function (thin dark lines in the figures), and $\alpha E'$, their slope coefficient reflects the magnitude of the stress stiffening phenomenon.



Mechanical models for describing the nanocomposites reinforcement phenomenon. We have used the following parameters: filler form factor f = 10, nanocellulose filler network modulus $E'_{cell\ net}$ = 1 GPa, nanocellulose longitudinal modulus $E'_{cell\ L}$= 150 GPa, nanocellulose transverse modulus $E'_{cell\ T}$ = 15 GPa, nanocellulose shear modulus G'_{cell} = 5 GPa, nanocellulose Poisson coefficient ν_{cell} = 0.3, matrix Poisson coefficient ν_m= 0.5, matrix elastic modulus E'_m = 2 MPa, matrix shear modulus G'_m = 0.5 MPa.

- **Reuss model**[1] $$E = \frac{E_{cell\ L} * E_m}{E_{cell\ L}(1-\phi) + E_m\phi}$$

- **Halpin Kardos model**[2] $$E = \frac{4U_5(U_1 - U_5)}{U_1}$$

$$U_1 = {}^1/_8\,(3Q_{11} + 3Q_{22} + 2Q_{12} + 4Q_{66}) \qquad U_5 = {}^1/_8\,(Q_{11} + Q_{22} - 2Q_{12} + 4Q_{66})$$

$$Q_{11} = \frac{E_L}{1 - \nu_{12}\nu_{21}} \qquad Q_{22} = E_T(1 - \nu_{12}\nu_{21}) \qquad Q_{12} = \nu_{12}Q_{22} = \nu_{21}Q_{11} \qquad Q_{66} = G_{12}$$

$$\nu_{12} = \phi\nu_{cell} + (1-\phi)\nu_m \qquad G_{12} = \frac{G_m(1+\eta\phi)}{1-\eta\phi} \qquad \eta = \frac{{}^{G_{cell}}/_{G_m} - 1}{{}^{G_{cell}}/_{G_m} + 1}$$

$$E_L = \frac{E_m(1 + 2f\eta_L\phi)}{(1 - \eta_L\phi)}\ with\ \eta_L = \frac{{}^{E_{cell\ L}}/_{E_m} - 1}{{}^{E_{cell\ L}}/_{E_m} + 2f}\quad and\quad E_T = \frac{E_m(1 + 2f\eta_T\phi)}{(1 - \eta_T\phi)}\ with\ \eta_L = \frac{{}^{E_{cell\ T}}/_{E_m} - 1}{{}^{E_{cell\ T}}/_{E_m} + 2f}$$

- **Percolation model**[3]

$$E = \frac{(1 - 2\psi + \psi\phi)E_{cell\,net} * E_m + (1 - \phi)\psi {E_{cell\,net}}^2}{(1 - \phi)E_{cell\,net} + (\phi - \psi)E_s}$$

$\phi_c = \frac{0.7}{f}$ and $\psi = 0 \; if \; \phi < \phi_c \quad or \quad \psi = \phi(\frac{\phi - \phi_c}{1 - \phi_c})^{0.4} \; if \; \phi > \phi_c$

[1] Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J., Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites. *Chem. Soc. Rev.* **2011,** *40* (7), 3941-3994.

[2] Hajji, P.; Cavaillé, J.-Y.; Favier, V.; Gauthier, C.; Vigier, G., Tensile Behavior of Nanocomposites from Latex and Cellulose Whiskers. *Polymer Composites* **1996,** *17* (4), 612-619.

[3] Favier, V.; Chanzy, H.; Cavaillé, J.-Y., Polymer Nanocomposites Reinforced by Cellulose Whiskers. *Macromolecules* **1995,** *28* (18), 6365-6367.