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How to tailor flow-induced nanostructures of nanomaterials of cellulose nanofibrils?

Cellulose nanofibrils (NFCs) are the elementary reinforcing constituents of plant cell walls. They are isolated from cellulose fibers in the form of slender semi-crystalline nanofibers (Fig. 1) with outstanding intrinsic mechanical properties, *e.g.* a longitudinal elastic modulus E ≈100 GPa. These biosourced building blocks can be used to manufacture a variety of promising materials such as yarns, thin and flexible transparent films, aerogels and nanocomposites with interesting functional and mechanical properties. However, the selection of these biobased materials for engineering applications still requires a better understanding of their nanostructures and related end-use properties. For that purpose, it is crucial to control the rheology and to tailor the placement of their fibrous reinforcement during their fabrication and forming operations.

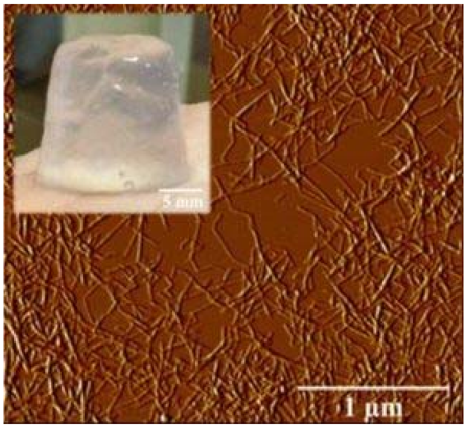

Fig. 1. Atomic force micrograph of cellulose nanofibrils (NFCs) isolated from eucalyptus fibers after chemical oxidation by a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system and mechanical grinding. The inset shows a photograph of a 0.75 wt% TEMPO-oxidized NFC water suspension.

Through these stages, NFC-based materials often behave as colloidal suspensions of semi-flexible nanofibers with a complex rheology, *i.e.*, between soft solids and liquids. Several challenges are encountered in the characterization and modeling of the rheology of these suspensions. When sheared at low strain-rates, they exhibit a solid-like behavior with a yield stress (inset of Fig. 1). At higher shear rates, these suspensions behave like fluids with shear-thinning behavior. These rheological features are closely related to the NFC nanostructure and its flow-induced evolution, both being ruled by a combination of nanoscale fluid-fiber and fiber-fiber interaction forces. Thus, modeling the rheology of NFC suspensions requires a fine description of the NFC nanostructures (geometry and spatial repartition of NFCs), flow mechanisms (NFC kinematics) and micro-mechanics (nanoscale interaction forces).

For that purpose, we prepared aqueous suspensions of electrostatically stabilized nanofibers (inset of Fig. 1). The geometry of the particles was characterized (Fig. 1) and the shear rheology of the NFC suspensions was investigated for various NFC contents. Using this experimental database, we developed a multiscale rheological model that accounts for the fibrous architecture and the particular physics of these concentrated colloidal systems. Using discrete element simulations that consist in shearing realistic elementary volumes of the NFC nanostructures (Fig. 2), it was then possible to gauge the magnitude of the different nanoscale interaction forces governing the suspension flow and the shear-induced structuration of NFCs.

Hence, the developed theoretical and numerical multiscale framework gave an insight in the scenarios at the origin of the macroscale rheological features of NFC suspensions. Particularly, the approach showed the major role of nanofiber content, waviness and flow-induced orientation on both the connectivity of NFCs in suspensions and their rheology. In addition, the model revealed the critical role played by nanoscale interaction forces arising both from the physico-chemical properties of cellulose nanofibers, namely colloidal interactions, and from short and long range hydrodynamic interactions. At low strain-rates, the origin of the yield stress of NFC suspensions was attributed to the combination of repulsive colloidal interactions and the structure of the entangled nanofiber networks in NFC suspensions (Fig. 2a). At high shear rates, both competing colloidal and short range hydrodynamic interactions could be at the origin of the shear thinning behavior of NFC suspensions (Fig. 2b).

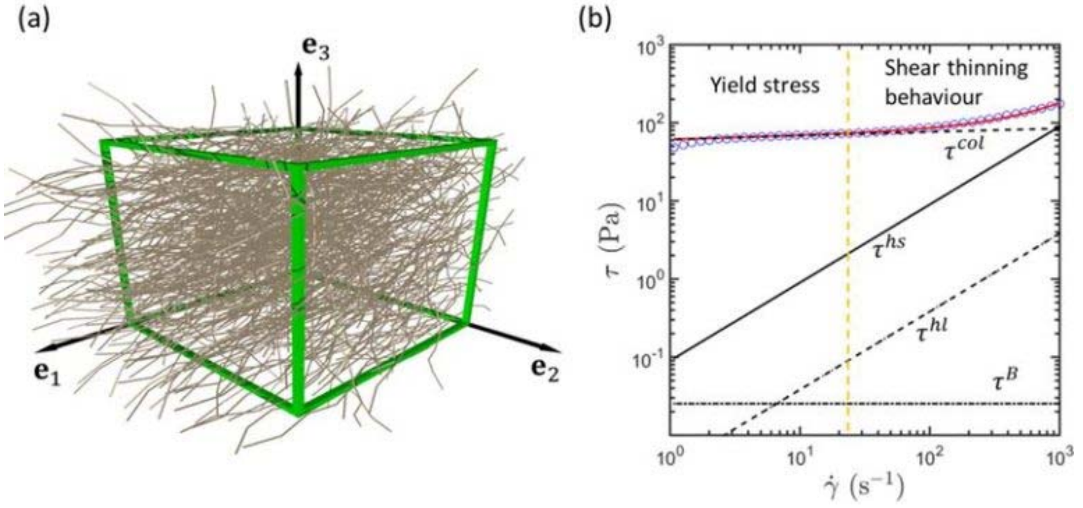

Fig. 2. a) Example of virtual NFC networks with a nanofiber content ϕ=0.004, and with shear-induced NFC orientation. (b) Corresponding steady state shear stress τ as a function of the shear rate ý obtained either from experimental rheometry measurements (blue circle symbols) or from the prediction of the micromechanical model (continuous red lines). The other lines represent the macroscale contributions induced by nanoscale interaction forces: Brownian motion τ^{B}, long and short hydrodynamic interactions τ^{hs} and τ^{hl}, and colloidal interactions τ^{col}.

The theoretical framework developed in this study could be implemented in simulation software to predict the flow-induced NFC structuration during forming of NFC-based materials.

Florian Martoïa [1], ***Laurent Orgéas*** [2], ***Pierre J.J. Dumont*** [3]
[1]*Univ. Grenoble Alpes, CNRS, LGP2, 3SR Lab, Agefpi, Grenoble, France*
[2]*Univ. Grenoble Alpes, CNRS, 3SR Lab, Grenoble, France*
[3]*Univ. Lyon, INSA-Lyon, LaMCoS CNRS UMR5259, Villeurbanne cedex, France*

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