Supplementary Materials

Micro-mechanics of electrostatically stabilized suspensions of cellulose nanofibrils under steady state shear flow

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Appendix S1

For a prolate ellipsoid with an aspect ratio $\hat{r} = a/b$ (where $a$ and $b$ are the major and minor axes of the prolate ellipsoid, respectively), the shape factor writes $\lambda = (\hat{r}^2 - 1)/(\hat{r}^2 + 1)^{1}$. For more complicated particles such as the studied NFCs, the estimate of $\lambda$ is not straightforward$^2$. For simplicity sake, as shown in Fig. 8, a first order estimation of $\lambda$ was used. Hence, the
coefficient $\lambda$ was calculated from the prolate ellipsoid that displays the same inertia axes and moments as NFC $i$.

Figure 8. Sketch that shows (a) the NFC $i$ and (b) its associated equivalent prolate ellipsoid with the same inertia axes and moments.

Appendix S2

Each tortuous nanofiber $i$ of diameter $d$ and length $l$ contained $n_{seg}$ straight segments of length $l_{seg}$ that had a random relative misorientation $\theta_{seg}$. Their center of mass $G_i$ was randomly placed in the elementary volume $\Omega$. Following this procedure, various fibrous networks with various nanofiber contents $\Phi$ were generated with random orientation of nanofibers, i.e., the generated microstructures exhibited isotropic fiber orientation with second order orientation tensors $A = \frac{1}{3} e_i \otimes e_i$ (Fig. 5a and Fig. 5c for the corresponding pole figure of orientation). This type of microstructures was chosen because it constituted a reference state, potentially close to that of NFC suspensions at rest (where Brownian motion presumably induces particle dispersion$^{3,4}$).
To mimic microstructures with a pronounced NFC orientation along the flow direction\(^3\) under shear flow, \(i.e.,\) for \( \mathbf{v} = \dot{\gamma} \mathbf{e}_1 \otimes \mathbf{e}_2 \), the evolution of the mean orientation vector \( \mathbf{p}_i \) of each NFC \( i \) was computed up to the steady state overall orientation of the fibrous networks, solving the Jeffery-based model (eqn (17)) with \( D_r = C_r \sqrt{2D : D} \) and \( C_r = 10^{-3} \). For convenience, calculations were done using the expansion in spheric harmonics up to the fourth order\(^7\) of the orientation distribution \( \Phi \). Hence, the following approximation was used\(^8\):

\[
\psi \frac{\partial \psi (\mathbf{p})}{\partial \mathbf{p}} \approx \frac{4}{3} \left( -21 \mathbf{A} \cdot \mathbf{p} + 63 \mathbf{p} : \mathbf{A} \otimes \mathbf{p} \right) + 2 \mathbf{p} \cdot \mathbf{A} : \mathbf{p} \otimes \mathbf{p} + 63 \mathbf{p} : \mathbf{A} \otimes \mathbf{p} : \mathbf{p}
\]

(22)

All the simulations were run using Matlab and a suitable time step \( \Delta t = \Delta \gamma / \dot{\gamma} \) such that \( \Delta \gamma = 0.01 \) until reaching a steady state, which was close to a shear strain \( \gamma = 100 \). Then, the simulation procedure led to orientated fibrous microstructures with \( A \approx 0.9 \mathbf{e}_1 \otimes \mathbf{e}_1 + 0.05 \left( \mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3 \right) \) (Fig. 5b and Fig. 5d for the corresponding pole figures of orientation). In accordance with the Jeffery-based models, it is worth to note that the resulting fiber orientation only depended on initial orientation state and on the applied shear strain, but not on the shear rate \( \dot{\gamma} \).

References