

Polymer and Colloid Highlights

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Assembly, Aggregation and Gelation in Nanocellulose Dispersions

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Nanocellulose represents an important class of sustainable bio-colloids with great promise for use as rheology modifier, structural reinforcement or as functional template in new advanced materials.^[1] In order to fully utilize its material properties, one needs, however, to understand the nanocellulose phase behavior and the relations between processing and final material structure.

We have recently studied the aggregation behavior of various nanocelluloses from bacterial and wood origin as a function of (1) their type and amount of surface charge, (2) their aspect ratio and (3) their concentration.^[2] The results, using a combination of dynamic light scattering (DLS) and inverted cuvette tests, showed that, as the concentration of nanocellulose particles increases, the samples transition from a dispersed state to a trapped gel like or glassy state at a transition volume fraction that correlates well with the inverse particle aspect ratio (see Fig. 1). Charges, on the other hand, were, in the samples studied here, found not to significantly influence the critical volume fraction of gel formation, suggesting that the main driving force for the dispersion to gel transition is an increased mobility constraint of the nanocellulose particles. The transition to a gel phase occurs before the development of a liquid crystalline (LC) nematic or cholesteric phase is predicted based on the classical Onsager treatment (indicated by the dark green area in Fig. 1). This suggests that one needs to carefully take the interactions between the nanocellulose particles into account, allowing them to self-assemble before reaching a trapped gel state, if a well ordered fibrillar phase is desired. Indeed, lower aspect ratio samples, known to demonstrate cholesteric LC ordering,^[3,4] develop their structures at volume fractions below or just slightly above those where the transition to the gel phase is predicted in ref. [2] (see data points in the gray area of Fig. 1).

Interestingly, small angle neutron scattering (SANS) revealed ordered structure formation further down in the semi-dilute dispersion regime (see data points in the blue shaded area of Fig. 1) for a system of carboxylic acid functionalized cellulose nanocrystals (CNCs).^[5] This structure formation occurred on two different length scales. First, a two-dimensional aggregation behavior was observed on the particle length scale. This lateral aggregation was traced back to the amphiphilic nature^[6] of the cellulose nanocrystals, where the more hydrophobic sides of the particles were hypothesized to face inward in the side-by-side aggregates. Second, a semi-dilute liquid crystal like formation

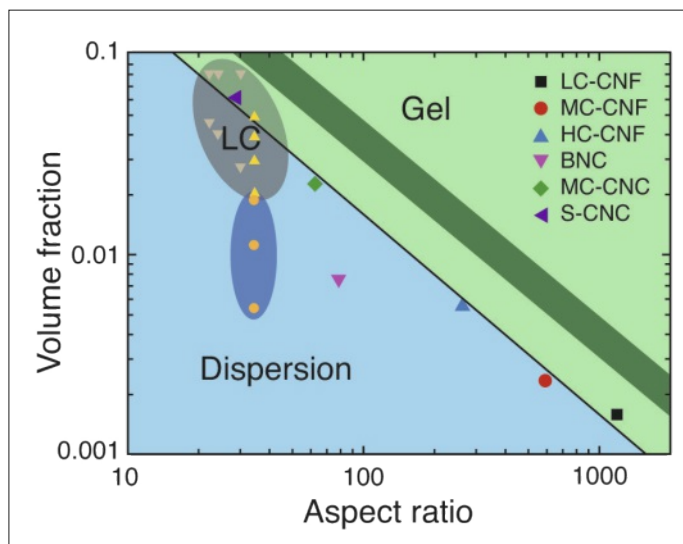


Fig. 1. Threshold volume fractions for the dispersion to gel transition for nanocellulose of varying type, charge and aspect ratios (adapted from ref. [2]). The data points within the shaded gray and blue areas represent compositions displaying liquid crystal (LC) ordering collected from ref. [3] (yellow triangles), ref. [4] (brown triangles) and ref. [5] (orange circles).

was observed, prior to any macroscopic signs of ordering, in the form of the development of a structure peak at length scales corresponding to particle aggregate distances of ~40–80 nm.

These two examples illustrate that the phase behavior of nanocellulose include subtle effects that may be difficult to observe, but which may have a large influence on the final properties of nanocellulose dispersions and materials. Future efforts should therefore aim to improve our understanding of the inter-particle interactions, identifying pathways to tune the self-assembly in order to control the final nanocellulose properties.

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