Measurement of Length and Thickness of Cellulose Nanocrystals Using Asymmetrical Flow FFF and Multi Angle Light Scattering

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Application Natural Polymers
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Introduction

Cellulose is the most abundant natural polymer on Earth and can be found in plants, marine animals, algae and bacteria. Cellulose nanocrystals (CNCs) are mostly isolated from native cellulose using acid hydrolysis. CNCs have several attractive properties such as low thermal expansion, optical transparency, renewability, biodegradability, low toxicity and low cost. They have been used widely in industrial applications such as polymer reinforcing, photonic crystals, drug delivery, water treatment membranes, and biomedical devices [1]. Thorough size characterization of CNCs is important since their rheological and control processing properties can be affected by their size, shape and surface area. Asymmetrical Flow Field-Flow Fractionation (AF4) coupled to Multi Angle Light Scattering (AF4-MALS) [2] is an alternative to bulk characterization techniques such as Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Dynamic Light Scattering (DLS). The main advantages of AF4-MALS over the bulk characterization techniques are high resolution and fast analysis time.

In this study a CNC sample isolated from softwood sulfite pulp was analyzed by AF4-MALS to measure the length and thickness of the crystals as a function of size.

AF4-MALS Analysis of Cellulose Nanocrystals

Figure 1 shows an AFM image of the bulk CNC sample. The sample had a broad length distribution with the crystal length ranging from 20 to 550 nm. The fractogram of the CNC sample obtained from AF4-MALS analysis is illustrated in figure 2 where the scattered light intensity measured by MALS (90° angle, solid black line) was plotted against retention time. The root mean square (R.M.S.) and hydrodynamic radii profiles were also plotted as a function of retention time and shown in figure 2. The R.M.S radius (Rg, red solid circles) calculated from MALS suggested a radius range of 40 - 60 nm across the CNC distribution. Assuming a thin rod structure for the crystals the R.M.S radius can be converted to rod length and rod volume using the expressions below:

Rod Length = $2\sqrt{3}\,Rg$ ***(1)*** Rod Volume = $\pi/2\ \sqrt{3}\,Rg\,\tau^2$ ***(2)***

where τ is rod thickness.

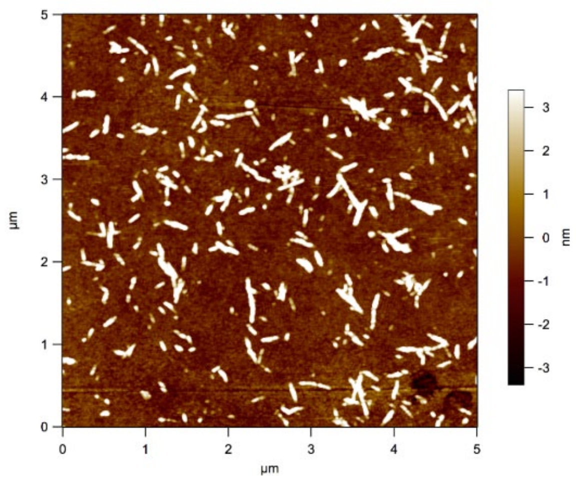

Figure 1: AFM image of the bulk CNC sample

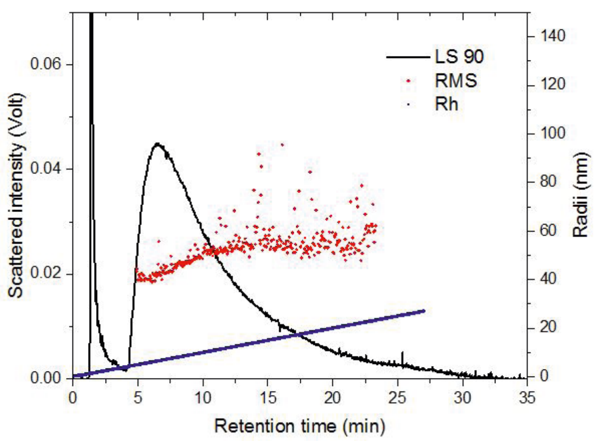

Figure 2: AF4-MALS fractogram of the CNC sample and R.M.S and Rh radii profiles

Using FFF theory, the retention time can be converted to hydrodynamic radius (Rh, blue solid circles in figure 2). The Rh profile of the CNC sample showed an equivalent spherical radius range of 5-30 nm. The CNC hydrodynamic volume can be calculated from Rh using the expression:

Hydrodynamic Volume = $4\pi/3\ Rh^3$ ***(3)***

Using expressions ***(2)*** and ***(3)***, CNC thickness can be calculated from:

Rod Thickness $\tau \cong 1.24\sqrt{(Rh^3/Rg)}$ ***(4)***

Figure 3 (left graph) compares measured CNC length distributions obtained from AFM and AF4-MALS techniques. The AF4-MALS distribution was obtained from the R.M.S radius data using expression ***(1)***. Both techniques showed similar distributions with an average length of 170 nm.

Figure 3 (right graph) illustrates the profile of CNC thickness calculated from expression ***(4)***, across the CNC distribution. The CNC thickness ranged from 1 nm to 20 nm with an average value of 4.3±3.4 nm. Comparing the trends of CNC thickness and R.M.S radius may suggest aggregation (bundling) of single CNCs for the upper end of the distribution.

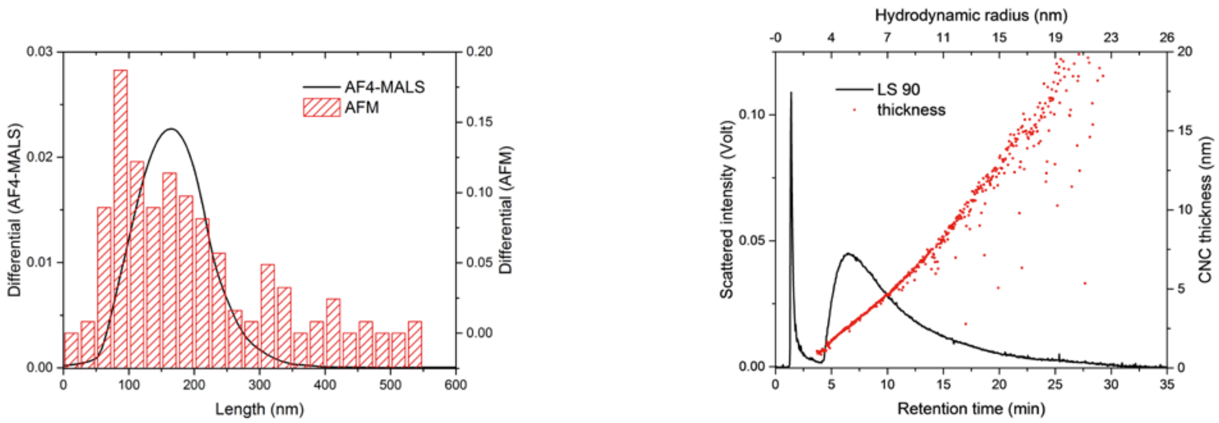

Figure 3: CNC length distributions obtained from AFM and AF4-MALS (left). CNC thickness profile as a function of retention time and hydrodynamic radius (right)

Conclusion

AF4-MALS was successfully employed to characterize a polydisperse CNC sample for measurement of size and thickness in a relatively short analysis time of 40 min. The CNC length distribution was in a good agreement with the result of the AFM analysis. CNC Rh (obtained from AF4) and R.M.S radii (obtained from MALS) are used to calculate CNC thickness. The CNC thickness profile showed a broad distribution suggesting aggregation of single crystals in the larger end of the distribution.

References

[1] Abitbol T., Rivkin A., Cao Y., Nevo Y. et al., Current Opinions in Biotechnology, 2016, 39, 76-88.
[2] Ruiz-Palomero C., Soriano L.M., Valcarcel M., Microchimica Acta, 2017, 184(4), 1069-1076.