Revisiting the phenomena of cocrystallization and moisture-induced shift in XRDs

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ABSTRACT

Of the many observations reported in cellulose literature, the phenomena of "cocrystallization" and "moisture-induced shift in XRD" (XRD-shift) need re-examination. Does cocrystallization really occur or, entirely, something else is going on? Recent research carried out by the authors suggests that upon hydrothermal treatment of wood-cellulose, where cocrystallization has been reported to be occurring, the cellulose becomes partly crystalline from the pre-existing non-crystalline arrangement.[1, 2]. Similarly, although the XRD-shift of wood's (200) diffraction plane is real, based on the new non-crystalline wood-cellulose model, an alternate explanation is proposed wherein the XRD-shift results from the reorganization of cellulose molecules.

KEYWORDS

Cellulose, crystallinity, hydrothermal treatment, microfibrils, non-crystalline, wood

INTRODUCTION

What is meant by cocrystallization? A cocrystal is a single-phase crystalline solid composed of two or multiple components.[3] In the field of cellulose-materials, this concept/phenomenon has been increasingly invoked when the experimental findings are difficult to interpret in light of the conventional wisdom.[4 - 7] Although there are many examples, here, this is illustrated by the transformation of wood-cellulose by the hydrothermal treatment.[2, 4] In XRD, the resultant significant sharpening of the equatorial reflections of cellulose has been observed by many researchers,[2, 4, 8] considering the traditional crystalline model of the cellulose, the researchers explained the observed increased crystallinity in terms of cocrystallization or increase of crystallite thickness.[4, 8] Additionally, it was reported that with higher treatment temperature, more crystalline cellulose was produced.[2, 4] If wood-cellulose was already crystalline in the native state, this proposed cocrystallization of the microfibrils is the only way to explain the experimental results. In the present context, the crystalline cellulose is defined as a structure that has a crystal lattice which extends in all directions (translational periodicity) and consequently, has long-range positional order. Moreover, water and most other small molecules cannot get inside crystalline cellulose.

However, based on the work of the authors, it was pointed out that the traditional crystalline model of wood-cellulose is incorrect, and a new model was proposed.[1, 2, 9] The new model successfully explained many of the inexplicable observations reported in the literature[9, 10] Under that model, the cellulose is non-crystalline in native state, though it is organized and aligned. Moreover, water can get inside the fibril and interact with cellulose (Fig. 1).

Similarly, although the (200) XRD-shift in wood and low-crystallinity celluloses is real, the generally accepted interpretation of the shift is based on an assumption. Namely, that the shift results from the environmental-stress caused changes in the cellulose crystal. An alternate explanation was proposed by the authors wherein the moisture-induced reorganization of cellulose molecules is responsible for the shift.[11] This interpretation is grounded in the non-crystalline model of wood cellulose, details of which would be discussed later (see text below).

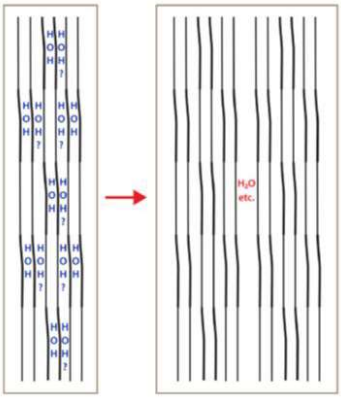

Figure 1. Proposed non-crystalline model of wood-cellulose in native state. Reproduced with permission from Ref. [1]. Copyright Springer Nature 2015.

EXPERIMENTAL

All chemicals, reagents, celluloses, and other materials were as described in the cited works. These publications also describe how the various treatments/analyses/investigations were carried out. These consisted of AFM/TEM imaging, compositional analysis of the samples, anatomical observations of woods, investigation of wood cell walls by confocal Raman microscopy, analyses of various materials by FT-Raman and estimation of cellulose-crystallinity by this technique, analysis by X-ray diffraction and estimation of cellulose crystallinity by Segal-WAXS method.

RESULTS AND DISCUSSION

Cocrystallization:

On the basis of the traditional model, Fig. 2 shows the transformation of wood-cellulose by the hydrothermal treatment. Under this explanation, the original crystal size increases significantly and is

responsible for the observed higher crystallinity in XRD and ss NMR.[4]

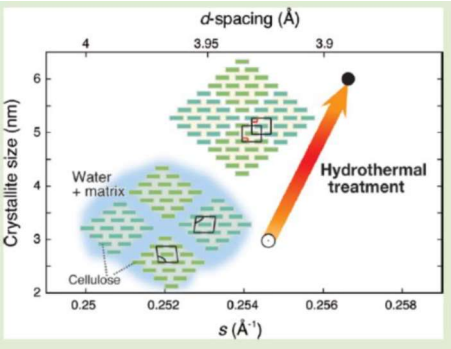

Figure 2. Proposed schematic drawing of cocrystallization of cellulose microfibrils in lateral view. Each small rectangle denotes the projection of a cellulose molecule perpendicular to the chain length, and the different green shades indicate different molecular polarities. The black parallelograms in (a) and rectangles in (b) represent the unit cells in projections perpendicular to the chain axis. Reproduced with permission from Ref. [4]. Copyright American Chemical Society 2016.

The proposed non-crystalline model of wood-cellulose is based on many findings,[1, 2, 9] chief among them - a) wood-cellulose in the never-dried native state is laterally aggregated where internal chains are water-accessible, b) hydroxymethyl groups (CH_2OH) in cellulose exist not only in the *tg* conformation but also in the *gt* rotamer form, c) in native-state fibrils, low-frequency Raman bands due to cellulose crystal domains are absent, indicating the lack of crystallinity, d) failure of the normal 64 % H_2SO_4 hydrolysis procedure to produce cellulose nanocrystals from untreated wood, e) deuterated-CNCs could be generated from the hydrothermally treated poplar indicating that cellulose chains were accessible to water and thereby became partly crystalline upon hydrothermal treatment, (f) crystalline wood cellulose, present in G-layer (in aspen tension wood), was not destroyed by the standard 64 % H_2SO_4 hydrolysis, implying that if such cellulose existed in normal wood, CNCs should have been produced, (g) presence and absence of the 93 cm^{-1} Raman band, respectively, in TW G-layer and TW S_2 layer, and (h) supporting evidence based on Raman spectra of TW-CNCs, wood holopulps, as well as those of mixture-samples of crystalline cellulose and xylan.

Based on the non-crystalline model shown in Fig. 1, how the hydrothermal treatment modifies the cellulose is shown in Fig. 3 where it is depicted that not only cellulose gets partly crystallized but additional domains/phases – such as coalesced and disordered/consolidated, are also generated. Currently, it is not clear how the structural dynamics of wood happens upon hydrothermal processing. As seen in Fig. 3, the new model explains the higher crystallinity of the hydrothermally treated cellulose in terms of crystallization and not due to cocrystallization (Fig. 2).

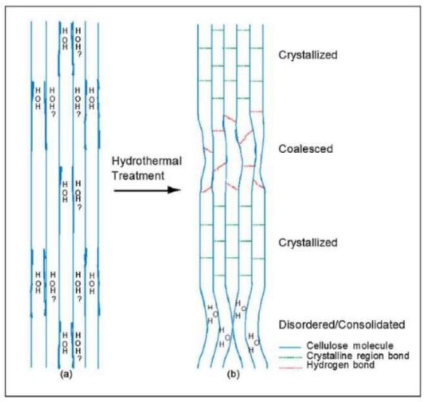

Figure 3. Proposed hydrothermal treatment caused transformation of non-crystalline native wood cellulose (a) to partly crystalline cellulose (b).[1, 2] The "?" means that it is unknown if such a location is accessible by water. Reproduced with permission from Ref. [2]. Copyright Elsevier 2018.

In the context of cocrystallization, actually, evidence that contradicts the existence of the phenomenon exists .[12] This is because if the fibrils in the bleached kraft pulp, which was used in the TEMPO oxidation, were cocrystallized by the thermochemical treatment, post oxidation, the cocrystallization (in the cellulose nanofibrils) should have been detected. However, that was not the case and only individually separated 3 nm wide pulp fibrils were obtained (Fig. 4). [12] This negated the existence of cocrystallization in the bleached kraft pulp.

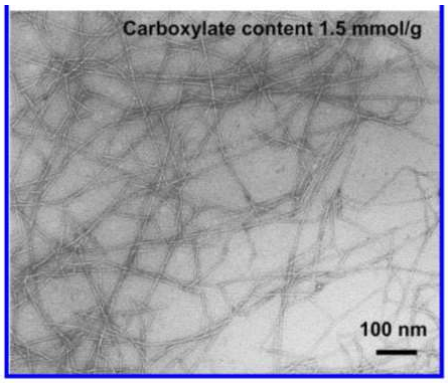

Figure 4. TEM images of dispersions of the TEMPO-oxidized celluloses with carboxylate contents of 1.5 mmol/g. Image was taken after stirring in water for 10 days. Reproduced with permission from Ref. [12]. Copyright American Chemical Society 2016.

Moisture-induced shift in XRDs:

In wood and cellulose fields, literature points to many studies where the obtained results can be better interpreted by invoking a model of cellulose that is semi-crystalline or non-crystalline instead of crystalline. Some of such studies have to do with the

changes in the X-ray diffractogram upon drying and rewetting of woods,[13 - 16] effects of cyclic drying and moistening on the mechanical and physical properties of wood,[16] and upon wetting of the dried materials.[17] Moreover, higher NMR- and XRD-crystallinities of cellulose materials in the wet state compared to the values in the dry state have been reported. [11, 17, 18]

Here, for the cellulose materials, only the case of XRD changes upon sample moisture change would be discussed.[11] As was reported in the literature, a number of materials with wide range of cellulose crystallinities were studied. These consisted of untreated wood (loblolly pine, W; non-crystalline) to highly crystalline cellulose (tunicin, T; highly crystalline). The other samples with in-between crystallinities were – cotton microcrystalline cellulose (MCC1), Avicel-PH-101 (pulp microcrystalline cellulose, softwood-pulp derived cellulose nanocrystals (CNC), softwood kraft-pulp (KP), NaOH treated aspen holopulp (HP1), oven-dried HP1 (HP1od), NaOH treated red pine holopulp (HP2), and oven-dried HP2 (HP2od).

For the wood sample, Fig. 5 shows the changes upon wetting in the (200) peak-normalized XRD pattern of dry wood. For all the samples, the changes in their XRD parameters are plotted in Figs. 6 - 8.

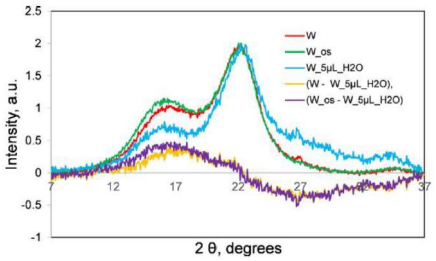

Figure 5. 2θ max position for (200) reflection (~ 22°) , W in dried state (W) and after 5 µL water addition (W_5 µL_H2O); os means other side of the pellet. Subtracted spectra (W – W_5 µL_H2O), and (W_os – W_5 µL_H2O) are shown as well. Reproduced with permission from Ref. [11]. Copyright Springer Nature 2017.

For loblolly pine wood, in the wet state, there were significant changes compared to its dry state XRD (Fig. 5). In this Figure, where the (200) peak normalized XRDs of dry and wet state are compared, in the wet state, the intensity in the 12 - 20° 2θ region declined, the $2\theta_{max}$ position for (200) peak increased from 21.8 to 22.3°, and higher diffraction intensity was seen in the 2θ region > 24°. Moreover, these changes were accompanied by a decline in the (200) peak FWHM (full width at half maximum), from 4.49 (dry) to 3.03° (wet state). Further, when the results from the other samples were included, it was shown that such changes to the XRD parameters were correlated with samples' dry state Segal CrIs. [11]

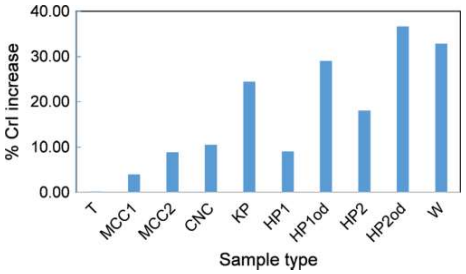

Figure 6. Percentage of increase in CrI upon 5 µL water addition; IDs of samples – page 3, left column. Reproduced with permission from Ref. [11]. Copyright Springer Nature 2017

Although, changes in CrI and crystallite size were reported in this work assuming the traditional crystalline model, in light of the new model (Fig. 1 and Fig. 3), the changes in most cases, seem to be associated with the reorganization of the cellulose chains. Further, in hemicellulose containing samples, role of the latter in the XRD changes cannot be ruled out because the contribution might be a function of how the hemicelluloses are organized with respect to the cellulose microfibril. Nevertheless, between the samples, the extent of the cellulose reorganization is likely to vary and particularly, in the case of wood, where the cellulose is not crystalline, significant reorganization is expected to happen in the interior of the sample. [1, 9] Moreover, strictly speaking, for the wood sample, word like CrI and crystallite size cannot be used because there are no crystals of cellulose. And in some other materials, like KP, the peak intensities in XRD arise from both non-crystalline and crystalline cellulose and therefore, one has to exercise caution while interpreting the data.

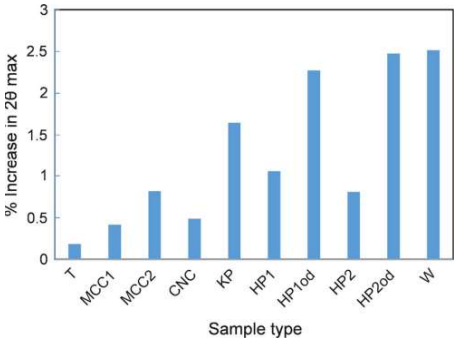

Figure 7. Percentage of increase in (200) 2θ max position upon 5 µL water addition; IDs of samples – page 3, left column. Reproduced with permission from Ref. [11]. Copyright Springer Nature 2017.

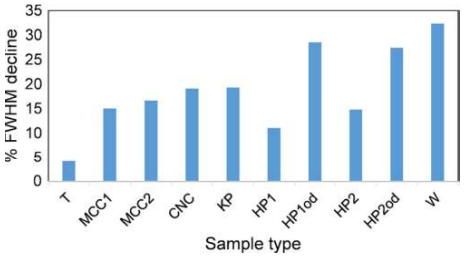

Figure 8. Percentage of FWHM decline upon 5 µL water addition; IDs of samples – page 3, left column. Reproduced with permission from Ref. [11]. Copyright Springer Nature 2017.

Although not reported here, when the moistened samples were dried for longer duration, it was observed that these changes were reversible to a degree. [11] This pointed to the physical nature of the phenomenon which was reversible to some extent.

CONCLUSIONS

In this report, phenomena of cocrystallization and moisture-induced shift in XRDs have been revisited and it is shown how the experimental findings can be better explained using a newly-proposed model of wood cellulose. Considering that in the literature there are many examples where the traditional crystalline model of cellulose has limited applicability, the expectation is that, in future, researchers in the field would invoke the new model of cellulose structure to understand the results. The reasonings behind the XRD-shift and increased-crystallinity, provided here, would afford better interpretation of the data and therefore, more accurate insights with regards to the ultrastructural changes of cellulose and cellulose materials. Knowledge of the supramolecular structure of cellulose is essential in a great number of areas, for example, in fields such as - plant science and wood technology, biofuels and bioeconomy, pulp and paper, and cellulose nanomaterials.

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