Cooking cellulose in hot and compressed water†

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Crystalline-to-amorphous transformation of cellulose in water, just like that for starch upon cooking called gelatinisation, is revealed at 320 °C and 25 MPa.

Cellulose and starch are polysaccharides made of glucose connected *via* β-1-4 and α-1-4 glycosidic linkages, respectively. The difference in connectivity results in a profound difference in properties of the polysaccharides. Cellulose is highly crystalline. It is the most abundant biomass on Earth and approximately 1.5×10^{12} tons are produced annually.[1] However, utilization of cellulose is hampered by its resistance to chemical or enzymatic hydrolysis. The resistance, as well as other unique characteristics such as insolubility in most solvents including water and structural rigidity, arises from hydrogen bonding networks formed between the cellulose chains in the crystals.[2] Starch is also semi-crystalline at room temperature, but it undergoes crystalline-to-amorphous transformation in water when heated to 60–70 °C (known as gelatinisation),[3] which accounts for the various changes of starchy foods when they are cooked. The starch chains become swollen upon gelatinisation and can be attacked readily by hydrolytic enzymes, resulting in better digestibility of cooked starchy foods. Gelatinisation is an indispensable step for processing starch in the food industry, and is also the preliminary process necessary to render starch suitable for enzyme-catalyzed biomass conversion.[4] Thus, a similar change would be expected if cellulose was gelatinised, but no such process is known. We found that cellulose also undergoes similar crystalline-to-amorphous transformation in water, but at a significantly higher temperature.

Gelatinisation of starch can be studied conveniently by following loss of birefringence using polarized optical microscopy.[3] We performed *in situ* polarized microscopic observation of crystalline cellulose in water at temperatures up to 350 °C and at constant pressure of 25 MPa.[5] A series of *in situ* polarized optical microscopic images in Fig. 1 show crystalline cellulose in hot and compressed water, which were taken by heating the specimen at 11–14 °C/min. Birefringence of the fibrous cellulose, which is evident from the pseudo colour under crossed polarizers, is retained up to 310 °C without any noticeable change, indicating that cellulose remains crystalline up to this high temperature. Hydrolysis of cellulose seems negligible, as the size of the fibrous cellulose does not change noticeably. However, cellulose becomes
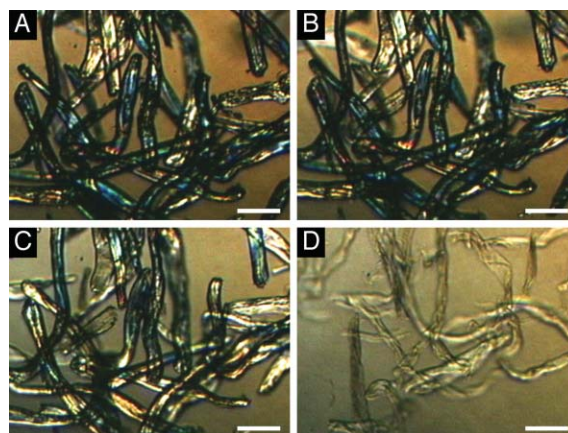

Fig. 1 *In situ* polarized microscopic images of crystalline cellulose in water taken between 300 and 330 °C and at constant pressure of 25 MPa. Temperature, (A) 300 °C, (B) 310 °C, (C) 320 °C, (D) 330 °C. Scale bar, 50 μm.

less birefringent at around 320 °C, and the birefringence is completely lost at 330 °C. The micrographs clearly show that cellulose undergoes crystalline-to-amorphous transformation in water at around 320 °C and 25 MPa. Dissolution of cellulose follows the transformation, and no cellulose remains at 340 °C. Recrystallisation is not observed when the system is cooled, confirming the previous observations that cellulose is hydrolyzed very rapidly under similar experimental conditions.[6,7]

Fig. 2 shows the change of the relative brightness of the images as a function of temperature. As is seen from Fig. 1, the image becomes brighter as cellulose loses birefringence. The relative brightness stays constant below 310 °C, but increases in the narrow temperature range (310–325 °C), and becomes constant again above 325 °C. The result suggests that the transformation proceeds in a cooperative manner.
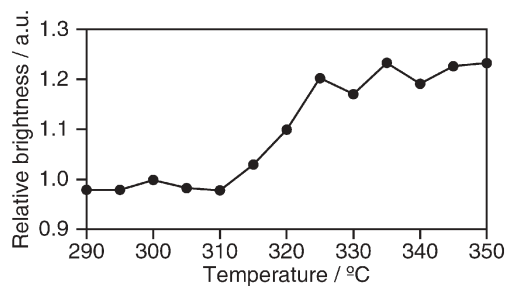
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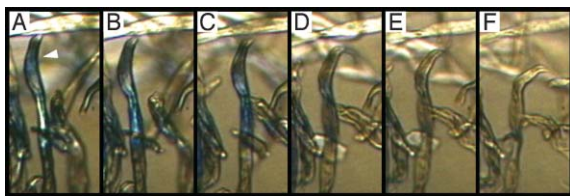
Fig. 2 Change of relative brightness of the images as a function of temperature. Detailed description of the image analysis is available in the Supporting Information.

Fig. 3 *In situ* polarized micrographic images showing a cellulose fibre (shown by a white triangle in A) during the crystalline-to-amorphous transformation. Temperature, (A) 324 °C, (B) 325 °C, (C) 326 °C, (D) 327 °C, (E) 328 °C, (F) 329 °C. Each image is 100 × 200 μm.

Fig. 3 shows a sequence of images showing a single cellulose fibre (indicated by a white triangle in Fig. 3A) near the transformation. The fibre gradually loses birefringence as it is heated (Fig. 3, A, B, C), but no significant change is seen in the shape of the fibre. The fibre starts to deform when it almost completely loses birefringence (Fig. 3D), and deforms further at higher temperatures (Fig. 3, E, F). The large deformation suggests that cellulose becomes plastic upon transformation, and the mechanical properties change dramatically upon the transformation. Twisting and bending were observed for most of the fibrous cellulose upon the transformation.

Crystalline cellulose consists of highly ordered crystallites called fringed micelles and less-ordered domains in between.[1] Under normal conditions, water only interacts with the less ordered domains.[8] The present observations clearly show that water also interacts with highly ordered domains at high temperatures under pressure, leading to a crystalline-to-amorphous transformation. It seems that water is necessary to induce the transformation because no such transformation is observed in ethanol (Tc = 243 °C, Pc = 6.4 MPa) at 7 MPa and at temperatures up to 350 °C. Birefringence is retained throughout the observation (Fig. 4), and char formation results above 330 °C. The result indicates that the transformation is not simple thermal melting, but rather interaction between water and cellulose plays an essential role.

Indirect evidence was accumulated to suggest some sorts of change of the crystalline structure of cellulose in hot and compressed water. Transformation of crystalline structure was reported after treating crystalline cellulose in hot and compressed water.[9] An anomalous increase of the hydrolysis rate of cellulose was also reported in hot and compressed water near the critical point (Tc = 374 °C, Pc = 22.1 MPa), and the kinetics of the reaction was studied in detail.[6,7] Based on the results, some sort of change in crystalline structure was inferred.[7] Our result is the

first direct evidence to show that cellulose undergoes crystalline-to-amorphous transformation in hot and compressed water, and reveals the underlying process that is responsible for the previous observations.

Elucidating water–cellulose interactions under the present experimental conditions is not straightforward, because the properties of water at high temperatures and pressures are remarkably different from those at ambient conditions. On the one hand, the dielectric constant of water, which is 78 at 25 °C and 0.1 MPa, decreases to 21 at 300 °C and 25 MPa,[10] the value of which is comparable to that of 1-propanol. The difference is ascribed to a large change in the extent of hydrogen bonding formation of the water molecules.[11] It seems unlikely that such a nonpolar solvent interacts favourably with cellulose. On the other hand, water between the crystallites might be in a supercritical state, even though the transformation takes place well below the critical temperature of water. Recent computer simulation revealed that critical parameters of water are decreased significantly when it is confined by walls that interact strongly with water.[12] Considering hydroxyl groups on the surfaces of the cellulose crystallites, it seems that this is exactly the case for the water molecules between the cellulose crystallites. Unique solvation properties of supercritical fluids such as formation of a dense solvation shell may play an important role in the transformation.[13]

In summary, we found that cellulose undergoes crystalline-to-amorphous transformation in water at around 320 °C and at 25 MPa. The transformation is associated with a large change in mechanical and chemical properties, just like gelatinisation of starch. The newly found property of the most abundant and renewable biomass is of significance to its utilization such as biomass conversion. Besides, water at high temperatures and pressures exists in the Earth's crust, and our results have important implications in considering the fate of plant deposits such as fossilization[14] or conversion to coal.[15]

Notes and references

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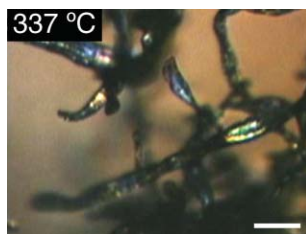
Fig. 4 *In situ* polarized microscopic image of crystalline cellulose in supercritical ethanol at 337 °C and 7 MPa. Birefringence of cellulose is clearly seen. Scale bar, 50 μm.

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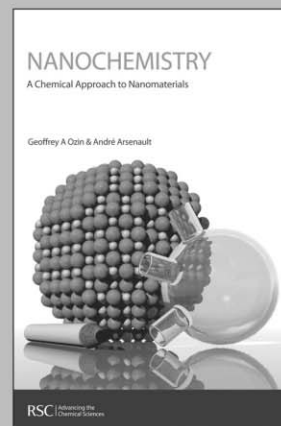15 K. B. Krauskopf, McGraw-Hill, New York, 1967, p. 306.