Correlation Between Chain Architecture and Hydration Water Structure in Polysaccharides

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Supporting Information

This document contains additional technical details and 2 supporting data figures.

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Water Sorption Isotherms

Lyophilized samples (~ 0.1 g) of phytoglycogen, hyaluronic acid (sodium salt), and chitosan were equilibrated at 25 °C in a series of sealed chambers containing saturated salt solutions (LiCl, CH₃COOK, MgCl₂, Mg(NO₃)₂, NaNO₂, NaCl, KCl, and K₂SO₄) and the change in mass was measured using a Mettler Toldeo analytical balance. The water mass fraction at each relative humidity is reported with respect to the dry basis weight.

Water sorption isotherms relate the polysaccharide water content to the relative humidity of the surrounding environment, which is directly related to the water activity. Fig. S1 shows the gravimetric water sorption isotherms for phytoglycogen and hyaluronic acid. The sorption isotherms show that hyaluronic acid and chitosan sorb a greater mass fraction of water at a given relative humidity than phytoglycogen, which is likely due to the presence of more polar groups in HA and chitosan, than in phytoglycogen. The gravimetric water sorption isotherms provide a simple measurement of water sorption, relating polysaccharide water content to RH. This basic information is important for our discussion of the ATR-IR measurements of the hydrogen bonding structure of water in the polysaccharide films.
Figure S1: Water sorption isotherms of phytoglycogen (red), hyaluronic acid (blue) and chitosan (black). The water mass fraction is calculated with respect to the dry basis weight measured for the lyophilized samples.

ATR-IR Difference Spectra

In Fig. S2 we show the ATR-IR difference spectra between each successive RH step. These spectra show incremental changes in the $\nu$(OH) band of water sorbed by the phytoglycogen, HA, and chitosan films. The spectral parameters shown in Figure 5 are calculated from these spectra.
Figure S2: ATR-IR difference spectra for a) phytoglycogen, b) hyaluronic acid, and c) chitosan. Each spectrum corresponds to $\Delta A = A(\text{RH}\% + \sim10\% \text{ RH}) - A(\text{RH}\%)$, ranging from $\sim10\%$ (bottom traces) to $90\%$ RH (top traces). The arrow shows the progression of increasing RH.