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Supporting Information for

Hydration effects on thermal transitions and molecular mobility in Xanthan gum polysaccharide

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BDS raw data and analysis

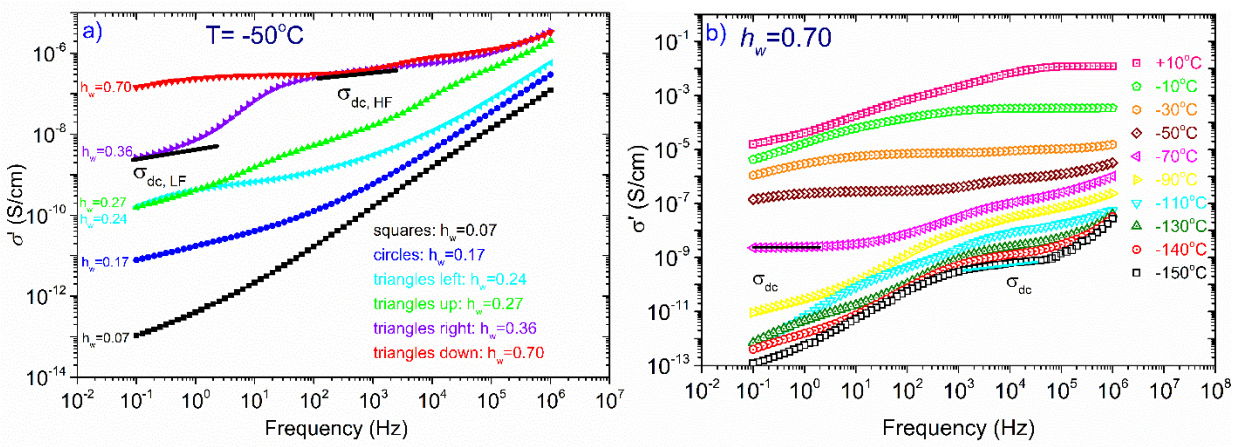

Fig. S1. (a) The real part of ac conductivity, σ', at -50ºC. A dc plateau is established for the sample with h_w=0.70 whereas two plateau (low and high frequency) are shown for the sample with h_w=0.36. The diagram in (b)

demonstrates the temperature dependence of σ' for the sample with the maximum hydration level (h_w=0.70) to emphasize on both high and low-frequency dc plateau. Symbols at (a): squares: h_w=0.07, circles: h_w=0.17, triangles left: h_w=0.24, triangles up: h_w=0.27, triangles right: h_w=0.36, triangles down: h_w=0.70.

Another aspect of great importance is how conductivity is affected by the water content inside the samples. The real part of ac conductivity, σ', was calculated from the measured dielectric loss, $\varepsilon''(f)$, using the equation $\sigma'(f)=(2\pi f)\varepsilon''(f)$. In fig. 1(a), we present σ' at -50°C and we can see that a clear dc plateau appears in the frequency range of 0.1-10 Hz only for the sample with the highest water content, which is attributed to proton conductivity in the ice phase. In higher frequencies, this plateau is interrupted by polarization processes occurring in the sample. We can also see a low frequency and a high frequency dc plateau for the sample with h_w=0.36. In fig 1 (b) temperature dependence of ac conductivity is presented for the sample with the maximum hydration level obtained (h_w=0.70) to emphasize on both high and low-frequency dc plateaus appearance.

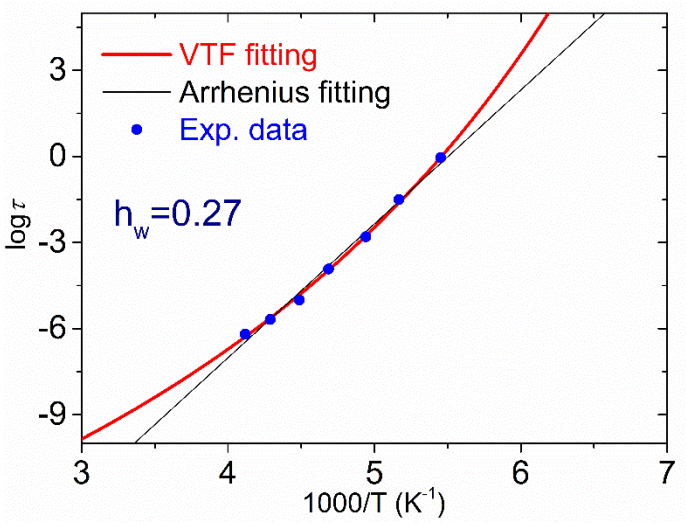

Fig. S2. Comparative VTF and Arrhenius fitting curves for the sample with h_w=0.27 (process IIccr). The fitting results show that process IIccr follows a VTF temperature dependence.

Fig. S2 represents comparative fitting curves (VTF and Arrhenius) of experimental data for process IIccr of the sample with h_w=0.27. As we can see this process follows a VTF temperature dependence rather than an Arrhenius behavior.

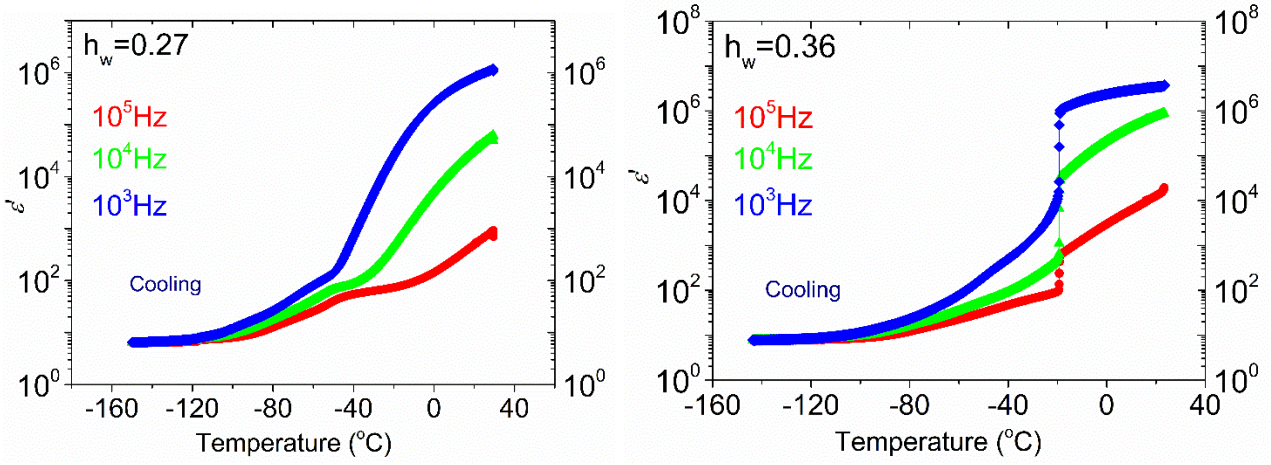

Fig. S3. ε' values recorded isochronally during cooling on BDS measurements, for the samples with h_w=0.27 and 0.36.

In Fig. S3 is presented the temperature dependence of the real part of dielectric permittivity, ε', recorded at the three frequencies (f=10^3, 10^4, 10^5Hz) during cooling, (a) for the sample with h_w=0.27 and (b) for the sample with h_w=0.36. It can be seen that there is a sudden drop on ε' values irrespective of the frequency of measurement (denoting a first order transition) only for the sample with h_w=0.36. The absence of this drop on the isochronal plot of the sample with h_w=0.27 indicates that no such crystallization phenomena occurred at this hydration level.

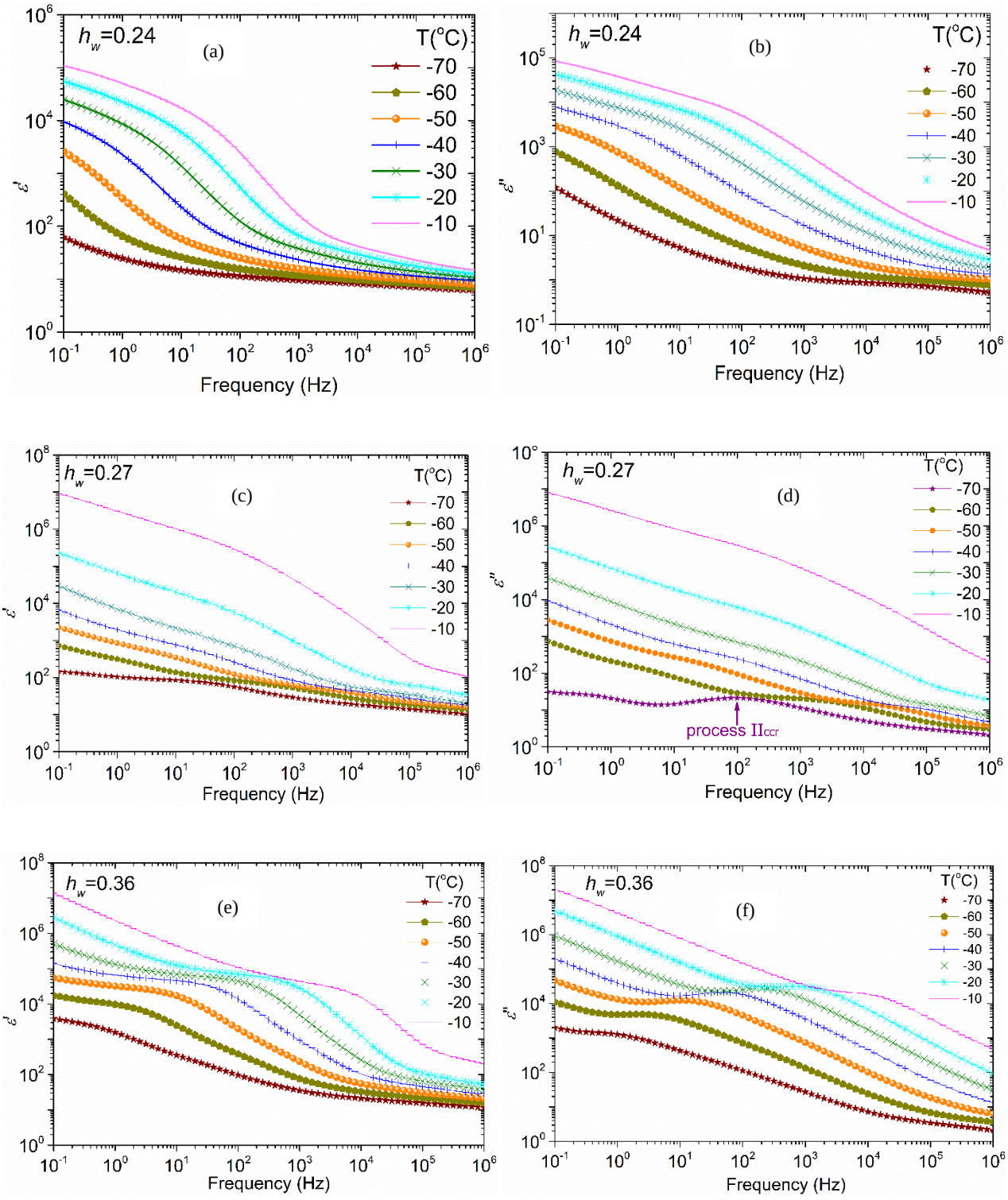

Fig. S4. Isothermal curves of ε', and ε'' for the samples with h_w=0.24 (a,b), h_w=0.27 (c,d), h_w=0.36 (e,f) at temperatures from -70 to -10°C.

Looking at the details of fig. S4, we observe that the process IIccr appears only for the sample with h_w=0.27 (at -70 °C and even lower temperatures, as is shown in Fig. 7(b) of the manuscript) neither

at lower nor at higher hydration levels. By increasing the temperature new polarization processes are recorded in all three samples of the figure that are related with interfacial polarization processes and are dependent on the water content. Consequently, we may assume that the origin of process II_{ccr} for the sample with h_w=0.27 is the particular structure of water hydrogen bonding network existed in the polymer (prior the formation of solid ice phase) giving rise to the so-called conductivity current relaxation. For higher water contents the formation of ice changes the topology of the conducting paths.