

Investigation of the Hydration Process in Cellulose with aspect of dielectric and physiochemistry

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ABSTRACT

The hydration system of characteristic cellulose and microcrystalline cellulose is examined by water sorption isotherms estimation, and additionally by thermally fortified depolarization streams (TSDC) and Broad Band Dielectric Relaxation Spectroscopy (DRS), in the temperature go 77 - 300 K and the recurrence go 10 106 Hz. The reliance of the hydration system on cellulose crystallinity is researched and an examination of results acquired by water sorption, TSDC and DRS is endeavored. The conduct of dc-conductivity and its part on the natural elements of living creatures is underscored.

Keyword : - Sorption isotherm , TSDC, Spectroscopy, plasticizing action of water, etc....

1. INTRODUCTION

Polysaccharides are mind boggling multifunctional, sugar atoms, made out of countless joined through glycosidic linkages. Cellulose, a basic polysaccharide which makes up most of the plant cell divider, is a direct atom comprising just of 1,4-connected P-D-glucopyranose units. Upon finish hydrolysis it yields P-D-glucose particles [1]. In this work, we display aftereffects of our examination of the hydration system of two cellulose sorts, a-cellulose, which is a characteristic item, and microcrystalline cellulose, MCC, by methods for physicochemical and dielectric spectroscopy techniques, utilizing: (a) harmony and dynamic water sorption isotherms, (b) thermally invigorated depolarization streams (TSDC) procedures in the temperature run from 77 to 300 K and (c) Dielectric unwinding spectroscopy (DRS) in the recurrence run 10 - 106 Hz. On the premise of the trial comes about got with the above various examination techniques, this investigation points fundamentally in gathering data and making a few determinations concerning the impact of crystallinity of cellulose on its hydration flow and instrument, and in addition on properties as proton conductivity, a procedure surely understood as basic numerous natural capacities.

2. MATERIALS AND METHODS

For the readiness of tests, cellulose powder was packed at 7 tons to barrel shaped pellets of 13 mm distance across what's more, around 1.5 mm tallness. For a nitty gritty depiction of the techniques utilized for the assurance of the water content in our test and for the harmony water sorption estimations we allude to [2,3]. The hypothesis of the TSDC technique, the exploratory mechanical assembly what's more, strategy, and in addition the systems took after to compute the different parameters are depicted somewhere else [4,5]. DRS estimations and the examination of the recorded information were done with a totally programmed hardware, containing a Novo control alpha (impedance) Analyzer [6] in mix with the Novo control Quatro Cryosystem

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Sorption isotherms

The equilibrium water sorption isotherms obtained with the α -cellulose and MCC samples at room temperature are typical of multilayer type absorption followed by capillary condensation at high humidities. The data were analyzed according to the Guggenheim - Anderson - De Boer (GAB) equation [7], which could be satisfactorily fitted to the experimental data, with the value of the fitting parameter h_m , corresponding to monolayer absorption, higher in α -cellulose than in MCC. Moreover, the maximum value of sorbed water content, for a relative humidity value equal to 100%, in MCC (14% w/w) has been found equal to about 2/3 of the corresponding value in native cellulose (21% w/w).

3.2 Thermally Stimulated Currents (TSDC)

Fig. 1 indicates TSDC plots recorded for α -cellulose tests with three distinctive water substance. TSDC spectra measured with microcrystalline cellulose (MCC) are appeared in Fig. 2. In understanding with comes about got in a huge number of natural and natural materials, the wide low temperature (LT) crest, evident even at low water substance, is ascribed to the reorientation of short-side chains of the sugar (principally methylol side gatherings), though the one showing up for higher hydration esteems is for the most part due to freely bound water atoms unwinding [4,5,8,9]. It is a typical conviction that hydration in local cellulose takes primarily put in its scattered or undefined fragments. Truth be told a plot of the variety of the commitment of the LT top to the static permittivity, As, with water content for α -cellulose and MCC [10] has demonstrated that the measure of firmly bound water in α -cellulose is equivalent to around 7 - 8%, though for MCC, which has a significantly higher level of crystallinity, it is substantially lower (- 4%), and similar holds for the most extreme estimation of sorbed water content, as per water sorption isotherms comes about, detailed above (III A). No TSDC top relating to mass ice has been identified in cellulose or in some other researched polysaccharide, demonstrating that water does not separate as mass ice for water substance up to 20% w/w.

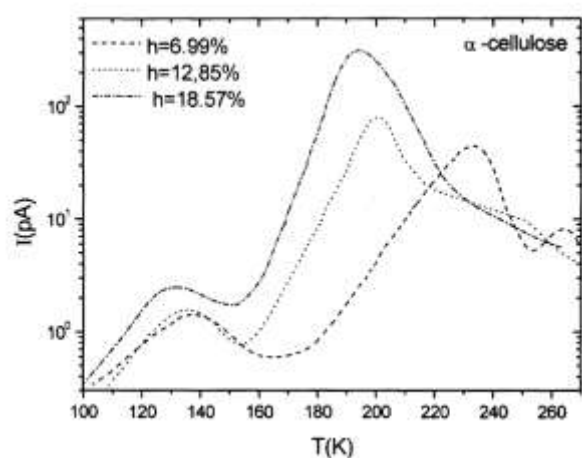


Figure -1 TSDC plots recorded for native (a) cellulose samples with three different water contents.

The high-temperature (HT) band is arranged between 160 also, 260 K and moves extraordinarily to bring down temperatures with expanding water content. As per many creators [5, 11], it is ascribed, to water helped reorientation of dipoles, generally a mix of methylol-water edifices or potentially glucopyranose rings, and additionally to charge unwinding (MWS) or exchange identified with dc-conductivity [12]. The move to lower temperature with expanding water content is like what has been seen with many hydrated regular and engineered polymers [13] and is clarified by the solid plasticizing activity of water in the homogeneous polymer/water framework.

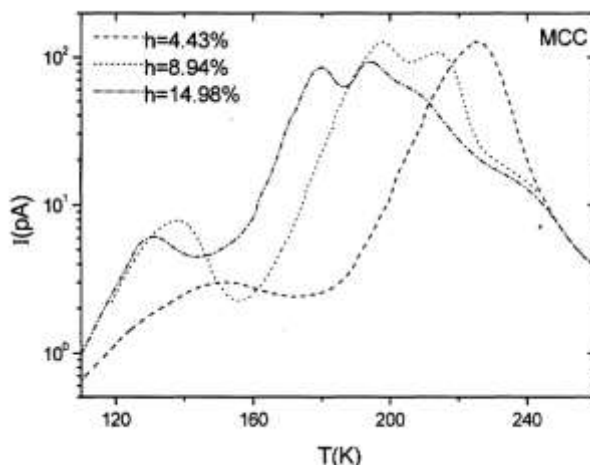


Figure -2 TSDC plots recorded for microcrystalline cellulose (MCC) samples with three different water contents.

The pinnacle related to the glass progress of the material, can't be recognized for our situation, since the glass change temperature (T_g) of dry cellulose fluctuates in the vicinity of 200 and 250°C [14] and is the fate of the request of room temperature just for water substance higher than around half w/w [15].

3.3 Thermally Stimulated Currents (TSDC)

The reliance of the fanciful piece of the dielectric permittivity, c'' , and of air conditioning conductivity, Sac , on recurrence and water content at room temperature [10] has demonstrated that unwinding instruments are conceal by the high dc conductivity of the specimen. Truth be told, in all DRS spectra we have measured up to now [5-7,9] with either common or engineered polymers, unwinding crests turn out to be typically clear just at below zero temperatures, where dc-conductivity impacts are stifled. Figs. 3 and 4 indicate individually the spectra of c' and c'' for a test containing 9,65% w/w of water, recorded at different temperatures between -120 and 0 °C. In both spectra, an unwinding component is exceptionally well recognized, moving to higher frequencies with expanding temperature because of the warm initiation of the procedure.

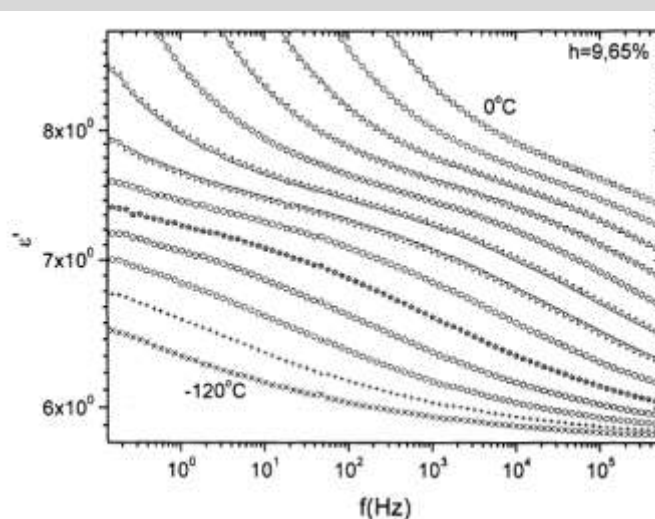


Figure -3 DRS spectra of the real part of the dielectric permittivity, E' , as a function of temperature, between -120 and 0 °C, for an a-cellulose sample

containing 9.65% w/w of water. In actuality, the c'' top (Fig. 4) is uprooted from around 1 Hz, at -120 °C, to around 1 MHz, at 0 °C. Spectra of air conditioning conductivity, aac , and also of the dielectric

misfortune factor, $\tan\delta$, and the nonexistent piece of modulus, M' , appear a comparable conduct, displaying an unwinding system in the same recurrence go. In addition, M' shows a moment system at bring down frequencies, identified with dc-conductivity, as examined later in connection to Fig. 8. All instruments are plasticized by water as will be appeared in connection to Figs 6 and 7. The expansion of c'' at low frequencies is an indication of dc-conductivity, moving to higher esteems with expanding temperature and water content. Truth be told, dc-conductivity is well clear in our specimens over a specific temperature contingent upon water content, moving from 10^{-10} to 10^{-6} S/cm, for T shifting between -140 and 20 °C.

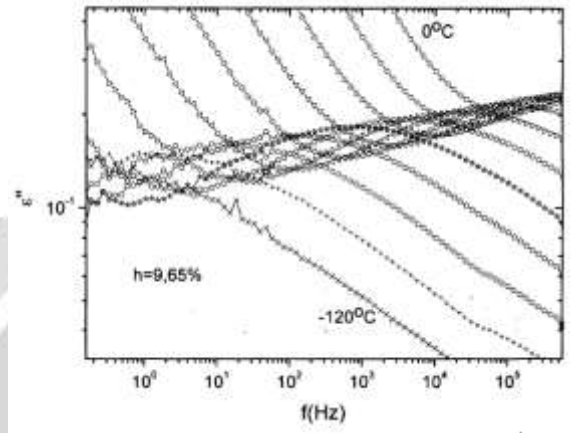


Figure -4 DRS spectra of the imaginary part of the dielectric permittivity, a'' , as a function of temperature, between -120 and 0 °C, for an a-cellulose sample containing 9.65% w/w of water.

Appropriately, the increment of c' at low frequencies and high temperatures is credited to cathode polarization. With a specific end goal to take after the conduct of the unwinding instrument as an element of temperature, we have plotted, in Fig. 5, the alleged Arrhenius plots, i.e. the pinnacle recurrence as an element of reverse temperature ($1/T$), for every one of the three amounts, c'' , $\tan\delta$ and M' (just the high recurrence top), for an acellulose test with water content $h = 9.65\%$. It is promptly observed that every single trial point take after an extraordinary straight plot, recommending that each of the three pinnacles mirror the same component and should in this manner have a similar root. The relating initiation vitality esteem has been discovered equivalent to 0.56 eV (0.54 kJ/mol). The point to the most distant right of the outline compares to the TSDC low temperature crest, with an identical recurrence equivalent to 1.6×10^{-3} s $^{-1}$. It lies not far from the expansion of the straight Arrhenius plot, proposing that the unwinding instrument recorded with DRS, may have the same starting point with the LT TSDC crest, credited to neighborhood short side-chain (methylol gathering) reorientation

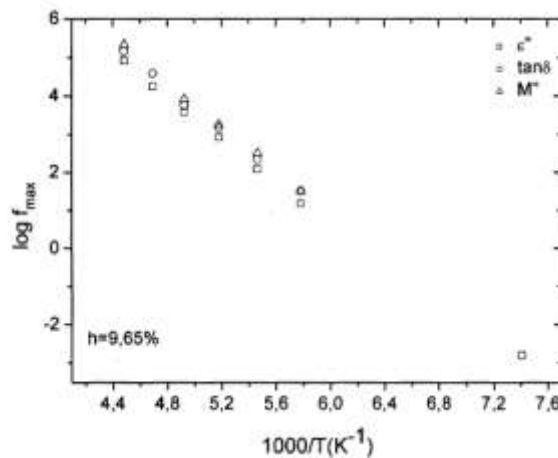


Figure -5 Variation of the logarithm of the peak frequency, $\log f_{max}$, with inverse temperature, $1/T$, for the imaginary part of dielectric function, E'' , the imaginary part of modulus, AM' , and $\tan\delta$.

The plasticizing activity of water on the distinguished unwinding component is well evident in Figs. 6 and 7, which demonstrate the reliance of the c'' top position, recorded at $T = -40\text{ }^\circ\text{C}$, on the water content, for α -cellulose and MCC tests, individually. It is intriguing to take note of that, in normal cellulose, the pinnacle position stays consistent for water substance as high as 8%, while for MCC it begins moving towards the higher frequencies as of now for h lower than 5%. This is as per comes about acquired above by water sorption isotherms and TSDC spectra (see Figs. 1 and 2), demonstrating that plasticization begins considerably prior in MCC than in normal cellulose, because of that higher level of crystallinity of MCC and thus to the way that irrotationally bound water rate is much lower in the second case. When the principal hydration layer has been finished, extra water ties all the more freely and goes about as a plasticizer, moving all tops to higher frequencies or, alternatively, to bring down temperatures. The piece of the TSDC high temperature band which has its root in dc-conductivity (Figs 1 and 2,) ought to be identified with the development of dc-conductivity, as assessed from the even part (level) of the air conditioner conductivity spectra. In [10] we have demonstrated that dc-conductivity in α -cellulose begins been obvious for a water content, h , in the vicinity of 7% and 8% and achieves the estimation of right around 10^{-6} (S/cm) for a water substance of around 16%, at room temperature.

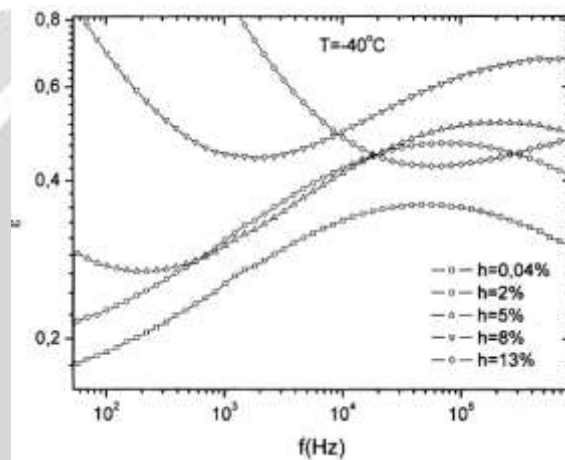


Figure -6 DRS spectra of the imaginary part of the dielectric permittivity, a'' , as a function of water content, recorded at $T = -40\text{ }^\circ\text{C}$, for MCC.

This outcome affirms the permeation character of charge (for the most part proton) transport, which can be depicted as takes after: at water substance lower than the permeation limit, water atoms are confined, though over this edge a connective way for long-go movement is built up [16], offering ascend to proton conductivity, whose esteem increments strongly with expanding hydration. Fig. 6 demonstrates the reliance of air conditioning conductivity, uac , (left pivot) spectra on temperature, for temperatures between -30 what's more, $20\text{ }^\circ\text{C}$, for an α -cellulose test containing 9.65% of water. The relating M' spectra (right hub) are appeared on a similar outline. The level of the Uac spectra gives the estimation of dc conductivity, as commented above, while the drop of clear conductivity at low frequencies underneath its dc esteem, recorded for temperatures over $0\text{ }^\circ\text{C}$, is an unmistakable sign of the terminal polarization impact, because of charge movement inside the material [17]. The pinnacle of M' in this recurrence and temperature extend mirrors the development of conductivity, and shows up at the same T -run where air conditioning conductivity begins commanding once again the dc one, while the crest at higher frequencies and lower temperatures (not appeared here obviously) relates to the unwinding pinnacle of Figs 3 - 6. The initiation vitality of this low recurrence high temperature M' crest, identified with conductivity, has been found to diminish with expanding water content, because of the plasticizing activity of water. The impact of proton conductivity on the natural capacities of living creatures has been widely treated by a few creators [16,18] and is scientifically examined in [8].

4. CONCLUSIONS

The research shows that The hydration mechanism of natural cellulose and microcrystalline cellulose is studied by water sorption isotherms measurement, as well as by thermally stimulated depolarization currents (TSDC) and

Broad Band Dielectric Relaxation and The behavior of dc-conductivity and its role on the biological functions of living organisms is emphasized.

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