THE SPECTROSCOPIC IMPEDANCE OF CELLOPHANE

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ABSTRACT. The electrical impedance of cellophane has been measured as a function of moisture content and temperature in the frequency range $10^{-3} - 10^5$ Hz. The data show a very strong dependence on moisture content, which is a typical characteristic of hygroscopic solids, and at low frequencies, remarkable constant phase angle spectra were obtained. Making use of the hopping model of conduction in non-crystalline solids, we explain the measured spectra. The model treats absorbed water as an impurity in the cellophane and conduction is predicted to occur by temperature-activated proton hopping between water molecules. We also propose that this model is widely applicable to prediction of the low frequency dielectric properties of hygroscopic solids.

Keywords: moisture, conductivity, proton, hopping

1. INTRODUCTION

We investigate the electrical properties of hygroscopic materials, that is materials containing water molecules retained by hydrogen bonding. This environment is similar to that in bulk water and some similarity in physical properties can be expected. It has long been accepted that electrical conduction in water occurs by proton transfer [1], and recent work has revealed the detailed mechanism as a complex process involving structural transformations in clusters of several water molecules [2]. Such processes seem improbable in hygroscopic solids, especially at low water concentrations where the probability of clustering will be very low and where cluster transformations will be strongly influenced by the substrate. Experimental data show striking similarities in the electrical properties of a wide range of hygroscopic materials, including an exponential dependence of DC conductivity on $M^{-1/3}$ where M is the concentration of absorbed water[3,4]. Low frequency dielectric data showing rapid increases of magnitude with decreasing frequency have been reported for hydrated samples of cellophane [5], wool [6], wood [7], paper [8,9], collagen [10] and bovine serum albumin [11]. Some of these data shows an approximately inverse dependence on frequency and Jonscher et al.[8] reported data for filter paper exhibiting a constant phase angle over seven decades of frequency. Sasaki [10] (collagen) and Tsuge et al. [5] (cellophane) reported "time – water content superposition", a characteristic in which appropriate simultaneous changes of frequency and water content leave the dielectric spectrum unchanged.

We have measured the dielectric spectra of cellophane, a reconstituted cellulose, in the frequency range 10^{-3} to 10^5 Hz for water contents from 9.0% to 33.4%. The low frequency conductivity slowly increases with frequency to a water-dependent turning point beyond which it rises rapidly. The dielectric loss and permittivity in the low frequency region are proportional to ω^s, where s is approximately -0.95 and ω is the frequency (radians/s). At the highest water content this characteristic extended over the whole of the measured range.

2. EXPERIMENTAL

Uncoated 42 μm cellophane samples (UCB Films NZ Ltd) were soaked overnight in a 5% solution of "decon 90"cleaning agent and then in several changes of de-ionised water to remove

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soluble ions and other substances left over from the manufacturing process[12]. The samples were then soaked for 1 hour in N/100 hydrochloric acid followed by sufficient changes of de-ionised water to remove all detectable acid then blotted and dried between sheets of filter paper. This procedure removes all mechanically deposited inorganic salts and replaces all cations bound to acidic groups in the cellulose with hydrogen[13].

110 mm wide samples were mounted in a guarded electrode with a 17 mm gap, giving a geometric cell capacitance of 2.4×10^{-15} F. Stray capacitance was measured at 2.8×10^{-13} F. The electrode was placed in a vacuum chamber and immersed in a water bath controlled to ± 0.01°C. Moisture content was controlled either by admission of water vapour into the sample chamber or by insertion of saturated salt solutions[14]. A second sample was mounted on a Mettler Toledo SAG204 weighing balance (± 0.2 mg accuracy) and placed in the chamber to determine moisture content. Dry weight of the sample was obtained by placing anhydrous P_2O_5 in the chamber. Several days were required all cases for stabilisation of moisture content after a change.

An Agilent 33120A Function Generator served as a sine wave voltage source and signal current was measured by a purpose-built I/V converter connected by guarded triaxial cable. Two methods of electrical measurement were used. In the range 10^{-3} - 30 Hz current and voltage were measured digitally and phase and amplitude determined by fitting sine waves to the data. An HP 34401A multimeter was used to measure amplitude from 3 Hz to 3×10^5 Hz, while phase was measured by a circuit comprising a zero crossing detector and RMS-to-DC converter.

3. RESULTS AND DISCUSSION

Figure 1 shows conductivity as a function of frequency at different moisture contents (dry basis) and temperatures. Comparison of the curves at 30.9°C shows strong dependence of conductivity on moisture content over most of the frequency range, a 24% increase in moisture content increasing conductivity by a factor of 10^4. At low frequencies conductivity is a slowly increasing function of frequency, but the high frequency spectra exhibit strong frequency dependence, with the transition point shifting to higher frequencies as moisture content increases. The conductivity data were converted to dielectric loss using the relation

$$\varepsilon_R'' = \frac{\sigma_{meas} - \sigma_{dc}}{\omega \varepsilon_0} \qquad (1)$$

where σ_{meas} is the conductivity (S/m) measured at frequency ω (radians/s), σ_{dc} is the dc conductivity, and ε_0 is the permittivity of free space (farad/m). Direct measurement of dc conductivity is difficult due to the very long settling time after application of a dc voltage, and complications due to electrolytic effects[3]. The values used were instead obtained by extrapolating the ac conductivities to zero frequency using an exponential function. No significant error occurs provided the dc conductivity is small relative to σ_{meas}, as indeed was indicated by the calculations. Figure 2 shows loss values obtained in this manner. This shows a remarkable example of low frequency dispersion, very similar to that observed by Jonscher[8] for filter paper. Dielectric loss is proportional to ω^s, where s is a constant, over a very wide range of frequencies, extending to at least 8 decades at the highest moisture content, with $-0.90 \le s \le -0.98$. In the same regions the data exhibit constant phase angle, as was found also by Jonscher[8].
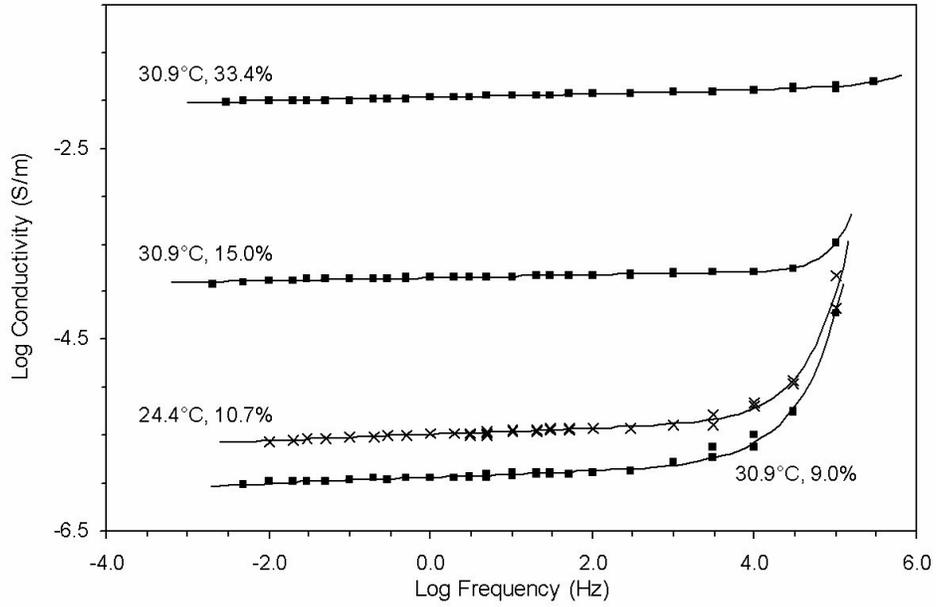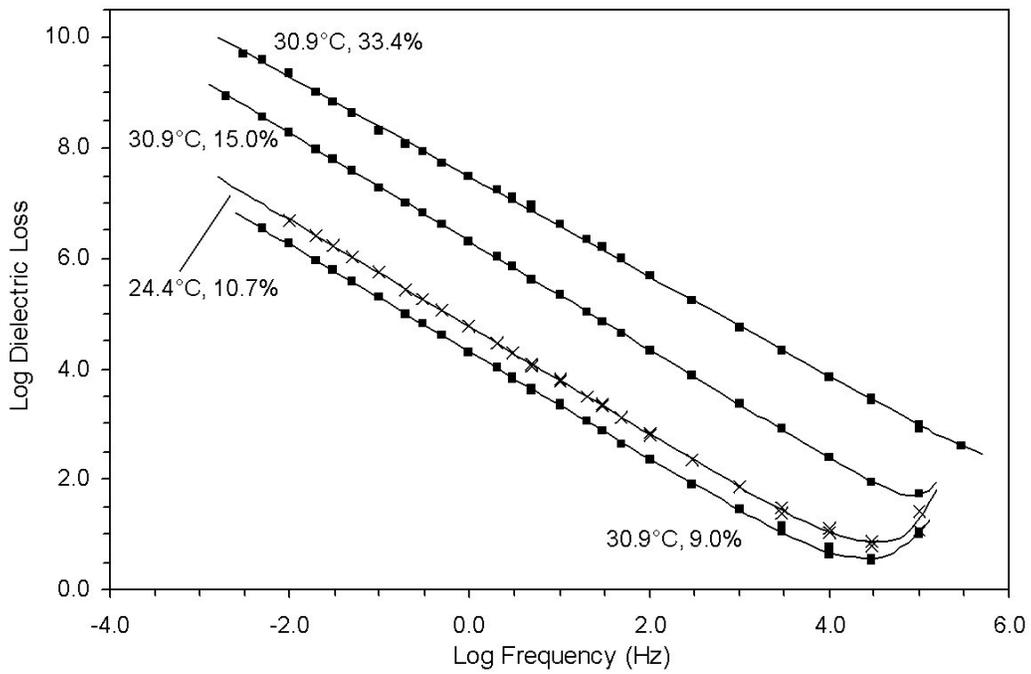
Figure 1: Conductivity of Cellophane

Figure 2: Dielectric Loss

The general relation between loss and permittivity is

(2)

$$\varepsilon_R' = \left(\varepsilon_R'' + \frac{\sigma_{dc}}{\omega\varepsilon_0} \right)\tan\theta - \frac{C_0}{\lambda\varepsilon_0}$$

where C_0 is the stray capacitance, λ is the sample cell geometric factor (area/distance) and θ is the phase angle. If the dc conductivity can be ignored ε'' will dominate at low frequencies. Substituting $\varepsilon'' = A''\omega^S$ where A'' is a constant we then get

$$\varepsilon_R' = A''\omega^s\tan\theta \qquad\qquad\qquad (3)$$

Table I gives the values of s for ε' and ε'' and Figure 4 shows permittivity calculated according to Equation 2, demonstrating the linear dependence of $\log\varepsilon'$ on frequency at low frequencies.

Table I: Values of s for ε', $\varepsilon'' \propto \omega^S$

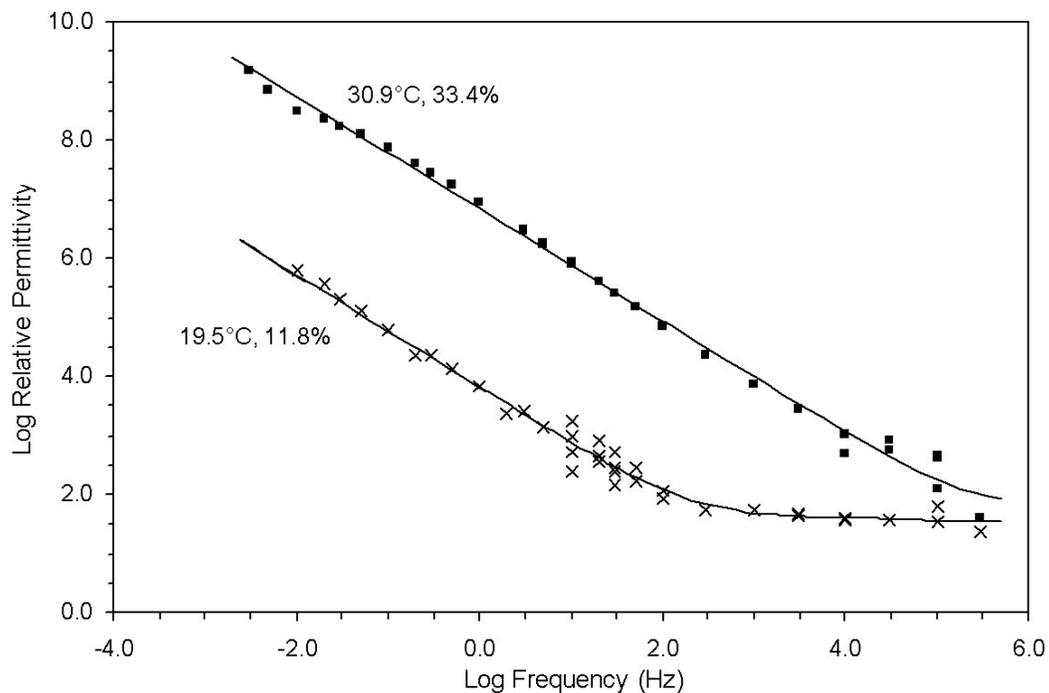| Temperature (°C)	Moisture Content (%)	s (loss ε'')	s (permittivity ε')
19.5	11.8	-0.95	-0.98
24.4	10.7	-0.97	-0.95
30.9	9.0	-0.97	-0.88
30.9	15.0	-0.98	-1.05
30.9	33.4	-0.90	-0.96

Figure 4: Relative Permittivity

The dielectric characteristics reported here are commonly observed in non-crystalline solids[15,16]. Theoretical interpretation is based on the concept of hopping conduction, i.e.

charge transport by transitions of particles between localised states. The hopping rate for charge carriers undergoing transitions between states i and j is

$$\gamma_{i \to j} = \gamma_0 e^{-\frac{2R_{ij}}{\alpha}} \quad \text{and} \quad \gamma_{j \to i} = \gamma_0 e^{-\frac{2R_{ij}}{\alpha}} e^{\frac{E_i - E_j}{kT}} \tag{4}$$

where γ_0 = attempt to escape frequency (sec^{-1}), R_{ij} = hopping distance (metres), α = the decay length of the carrier wave function (metres), $E_i > E_j$ are the energy levels of the charge carrier (joules), k = Boltzmann constant (joule/°K) and T = temperature (°K) [17,18]. Application of an electric field biases the hopping rates, leading to both charge storage and transport. In a weak electric field the net current flow can be written [17]

$$I_{ij} = G_{ij} V_{ij}, \quad G_{ij} \propto e^{-\frac{2R_{ij}}{\alpha}} \tag{5}$$

where V_{ij} is the potential difference between i and j and the quantity G_{ij} is interpreted as the conductance between the sites. In an assembly of localised sites in which the individual values of G_{ij} vary over a very many of orders of magnitude, the overall conductance is determined by a specific value of G_{ij} termed the "critical percolation conductance"[17]. From Equation (5) we see that G_C must depend on a critical distance R_C. It we regard all sites for which $R_{ij} \leq R_C$ as "connected" then the problem of evaluating R_C is equivalent to determination of the threshold value for bond percolation[19,20]. In this formulation R_C is uniquely determined by the distribution function of the localised sites and will therefore depend on the mean distance between sites, R_M. The very strong dependence of low frequency conductivity of hygroscopic solids on water concentration clearly suggests a conduction process involving the absorbed molecules and elsewhere[3] we have concluded that the conduction occurs by protonic transitions between absorbed water molecules. The distance R_M will depend therefore on the concentration of water molecules and conductivity can be expected to have the form

$$\sigma \propto e^{-\frac{B}{\sqrt[3]{M}}} \tag{6}$$

where B is a constant. This conductivity characteristic has been commonly observed[3,4]. Regarding absorbed water as an "impurity", the system is analogous to doped inorganic semiconductors for which hopping conductivity has been found to obey Equation (6) [21].

The precise origin of the characteristic frequency dependence of ac conductivity in non-crystalline solids remains controversial. According to Hunt[16] the universality of the characteristic arises from the exponential dependence of hopping rates on the random variables R_{ij} and E_{ij}. In cellophane absorbed water molecules were found to be highly mobile, with changes in sample weight and conductance detectable less than 1 second after the sample environment was changed. Similar behaviour is observed in other hygroscopic solids (see for example Watt[22]). The molecules thus can be expected to be randomly distributed throughout the solid, influenced to some extent by specific hydrophilic binding sites where these exist. In a plot of $\log \varepsilon''$ versus $\log \omega$, the universal ac characteristic shows a loss peak marking the transition from conduction in clusters of sites up to infinite size to conduction in isolated (finite) clusters[16]. Our results clearly lie on the high frequency side of the transition, in which cluster size decreases with increasing frequency. Hunt's model provides a simple explanation for the "time – water content superposition" observed by Sasaki [10] and Tsuge et al. [5] and seen also in our results (Figure 2).

Decreasing cluster size leads to decreasing values of R_C and hence increasing conductivity. An appropriately sized increase in moisture content will influence conductivity identically ($R_C \propto M^{-1/3}$).

Trapp and Pungs[7] measured the dielectric spectra of wood as a function of moisture content from 40 Hz to 3.5×10^{10} Hz obtaining spectra with identical characteristics to those reported here. In the higher frequency region a loss peak was detected which shifts to higher frequencies with increasing moisture content, approaching the dipolar loss peak in pure water (1.6×10^{10} Hz at 20°C[23]). We thus interpret the transition to rapidly increasing conductivity at high frequency in cellophane as the leading edge of a high frequency loss peak arising from dipole rotation of the absorbed water, illustrated schematically in Figure 5, which shows the summation of two Debye loss peaks.
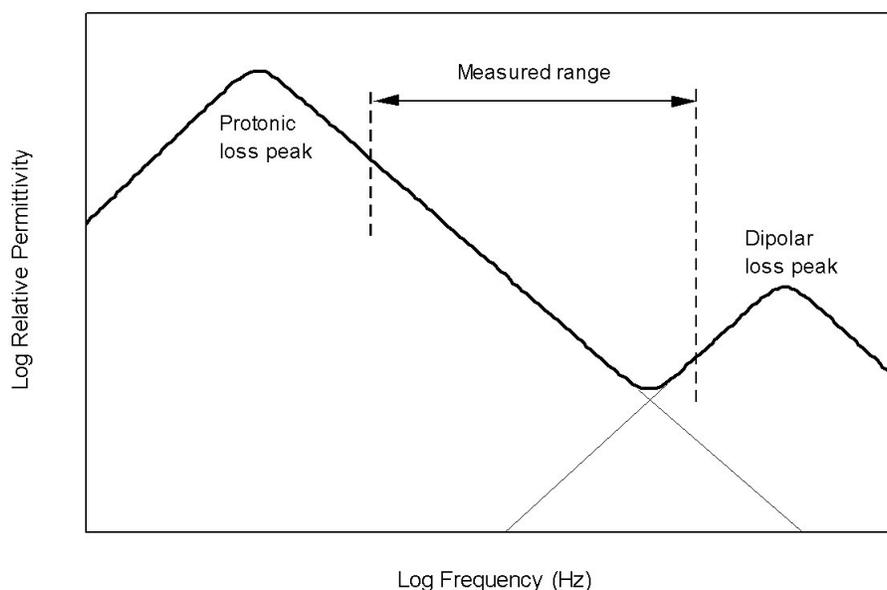

Figure 5: Schematic Loss Spectrum for Cellophane

Previous measurements on cellulosic materials have found an Arrhenius type dependence of low frequency conductivity on temperature [24], which is consistent with the temperature-activated charge transport model suggested here (Equation (4)).

4. CONCLUSION

The low frequency dielectric spectrum of cellophane arises from transitions of protons between absorbed water molecules. A previous review of dc conduction in hygroscopic solids[3] identified the proton as the charge carrier, a conclusion supported by comparison with bulk water. The hopping theory of conduction is readily applicable to this model and leads to two conclusions in accord with experimental results: the dependence of $\log \sigma$ on $M^{-1/3}$ at low frequencies, and dependence of the low frequency dielectric loss on ω^s ($-1 < s < 0$). The dielectric characteristics we have measured have been widely observed in proteins [25-29], cellulosic materials [7, 25, 30, 31] and other materials such as nylon [25], polyethylene [32] and dehydrated carrot [33]. Our model shows that these characteristics arise primarily from the properties of the absorbed water molecules, hence explaining this universality. Variations in the observed data for different

materials will occur due to the influence of specific hydrophilic binding sites, and the presence of other modes of charge transport (for example impregnation with ionic salts gives rise to ionic conduction). However such effects are secondary and we conclude that hopping protonic conduction between absorbed water molecules is the dominant low frequency dielectric process in hygroscopic solids. Our conclusion offers a solution to the longstanding problem of identifying the underlying process responsible for their low frequency dielectric characteristics [30,34,35].

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