Dielectric studies of cellulose and its derivatives: 3. Glycerol in cellulose acetate

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(*Received* 26 *October* 1981; *revised* 27 *March* 1982)

Dielectric studies are reported on cellulose acetate doped with glycerol. The addition of glycerol initially leads to the generation of a strongly interacting layer manifest by an increase in the amplitude of the side chain motion of the cellulose acetate and also the appearance of a higher temperature relaxation. Further addition of glycerol allows development of a multilayer situation which has relaxation properties similar to that of pure glycerol and is essentially independent of the cellulose acetate matrix. The high temperature conductivity of the samples investigated is critically dependent on the concentration of the dopant, increasing markedly for concentrations above 2–3%. This change in behaviour appears to correlate with the fibrillar surface area and is associated with the generation of proton conduction in the system. The general characteristics of this behaviour are similar to those previously reported[1] for the addition of water to cellulose derivatives.

Keywords Cellulose acetate; dielectric relaxation; glycerol; morphology; conductivity behaviour

INTRODUCTION

In a previous paper[1], the effects of water on the dielectric relaxation of cellulose acetate was discussed. It was observed that the residual fibre structure has the effects of determining the temperature–frequency–concentration dependence of the dielectric permittivity. At low water contents, hydrogen bonding between water and the polymer appears to occur at specific bonding sites associated with the residual fibre surface. Increasing the water content leads to the formation of a multi-layer absorption situation with a consequent drop to lower temperatures in the relaxation process and also a marked increase in the high temperature conductivity. Analysis of the frequency dependence of the conductivity data indicates that the Mott equation[2] for hopping between tightly bound sites is applicable to the situation at low water contents, a more mobile type of conduction mechanism being operative at higher water contents. In an attempt to understand the role of the absorbent-polymer interactions and morphology on the dielectric relaxation of cellulose materials the present study of glycerol was undertaken. Like water it is capable of hydrogen bonding to the matrix, however, it is a bulkier molecule and as such might have different relaxation characteristics.

EXPERIMENTAL

Materials

Cellulose acetate, obtained from Drs T. J. Lewis and F. S. Baker of PERME (Waltham Abbey), had an acetic acid yield[3] of 53%, which corresponded to approximately 0.5 hydroxyl groups per glucopyranose ring. The samples were pressed into discs in a polished stainless steel cylindrical mould using an Apex type 340-4 hydraulic press at a pressure of 38 MPa and a temperature of 373K, for a period of about 1 hour. The resulting discs measured 5 cms in diameter and were approximately 0.1–0.2 cms thick. The samples were stored in an oven at 363K until constant weight was achieved.

Glycerol absorption

The previously dried discs were immersed in glycerol for several hours until the desired amount of absorption was achieved. The amount of glycerol absorbed could be increased by raising the temperature to 323K. The samples were removed, carefully cleaned and stored in an oven at 363K. The glycerol content was determined by weighing.

Dielectric measurements

The dielectric data was measured at $1\mathrm{KH_z}$ as a function of temperature using a Teredyne C.357 automatic bridge and a two terminal cell configuration. Frequency dependent measurements were performed using a G.R. bridge in the range of $200\mathrm{H_z}$ to $100\mathrm{KH_z}$ at a fixed temperature. The cell was flushed with dry oxygen prior to cooling the sample and contained a drying agent (silica gel) as an added precaution against the effects of condensation. The temperature was recorded using a Digitron 3750K digital thermometer attached to a thermocouple located close to the disc. A correction was applied to the data from temperature scans to allow for the effects of thermal lag in the measuring cell. No contact coatings were applied to the samples used in this study.

RESULTS AND DISCUSSION

Variation of the real and imaginary parts of the dielectric permittivity with temperature for cellulose acetate containing varying amounts of glycerol are presented in *Figure 1*. Cellulose acetate exhibits a relaxation at 263K associated with rotational isomerism of the acetate side chains[4]. Addition of glycerol leads to an apparent shift of the relaxation to lower temperature and the development

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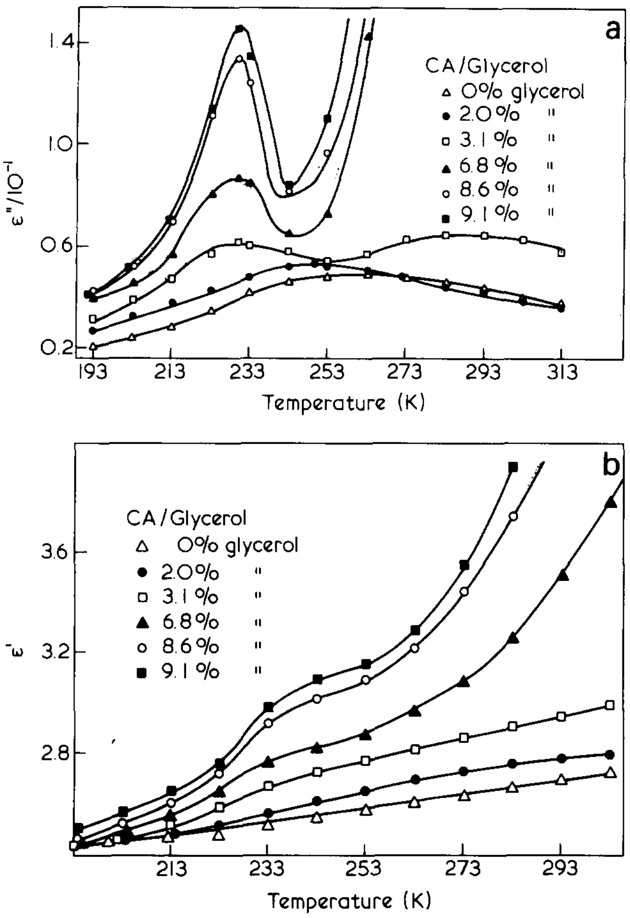

Figure 1 Effect of glycerol on the dielectric properties of cellulose acetate doped with 0% (△), 2.0% (●), 3.1% (□), 6.8% (▲), 8.6% (○), and 9.1% glycerol (■). (a) ϵ'' vs. temperature and (b) ϵ' vs. temperature

of a high temperature peak observed at 283K for 3.1% glycerol. This second feature ultimately becomes swamped by the conduction process at higher glycerol contents. For low glycerol concentrations it appears that the molecules are relatively tightly bound to the residual cellulose acetate fibrils and are presumably absorbed in the form of a monolayer. The high temperature peak is associated with the reorientational motion of this highly interactive bound phase, the lower temperature feature to a more mobile species. Further addition of glycerol leads to the formation of a distinct low temperature dielectric loss peak, the amplitude of which, when corrected for a contribution from side chain acetate motion, is linearly dependent on the glycerol concentration. Subtraction of the loss peak associated with cellulose acetate from that of the doped system yields a low temperature peak which is indicative of the dielectric relaxation of glycerol. As in the case of water, the formation of a multilayer situation leads to the observation of a marked increase in the dielectric loss associated with the generation of proton conduction in the system.

A parallel study of glycerol dispersed in PMMA *Figure 2*, indicates that glycerol relaxes at the same temperature, 230K in this matrix as in cellulose acetate, although in this case the matrix can be assumed to be purely amorphous. The explanation for this observation is that in both cases the glycerol must be existing in sufficiently aggregated clusters to appear to be similar in structure to that of the pure liquid. Further support is obtained for this hypothesis from the investigation of the low temperature, dielectric relaxation as a function of frequency, *Figure 3*. The activation energy plot derived from this data, *Figure 4*, indicates that within experimental error the same activation energy of 132 kJ mol^{-1} is observed above a critical concentration of around 3% glycerol. Further, the position of the loss peak coincides with that for pure glycerol[5], indicating that this behaviour is essentially the same as that observed for the pure liquid. The activation energy observed is similar to that calculated[5] for the pure liquid (120 kJ mol^{-1}). The rotational isomeric activation energy for the acetate group for dry cellulose acetate[1] is 47 kJ mol^{-1}. The larger activation energy and higher characteristic relaxation temperature compared to water, reflects the highly cooperative nature of the rotation of the glycerol molecules.

Frequency profiles at 295K were performed on samples containing up to 3.13% glycerol (*Figure 5*) in order to investigate more precisely the high temperature processes. A peak in the loss shifting to lower frequencies, was observed for glycerol contents between 1.20 and 1.94%. This is consistent with the effects of the 'bound' glycerol molecules on the hindered acetate side group motion, *Figure 1*. This feature is obscured by the large increase in the dielectric loss associated with proton conduction at high glycerol concentrations.

Proton conduction in cellulose materials has been shown in the case of water to involve a hopping type of mechanism[1]. Below the limiting situation of a monolayer absorption the protons are tightly bound to individual

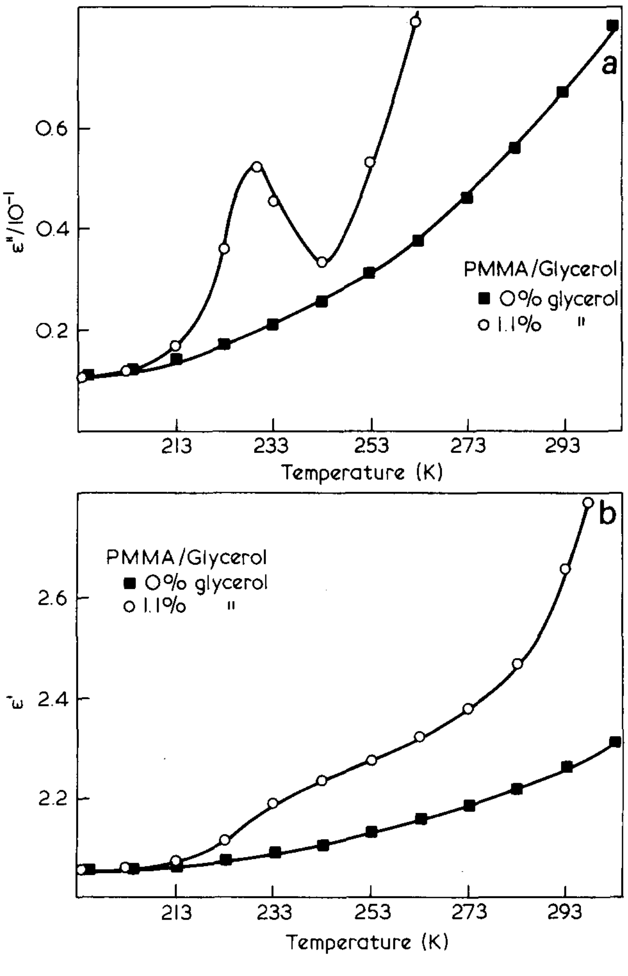

Figure 2 Effect of glycerol on the dielectric properties of PMMA doped with 0% (■) and 1.1% glycerol (○). (a) ϵ'' vs. temperature and (b) ϵ' vs. temperature

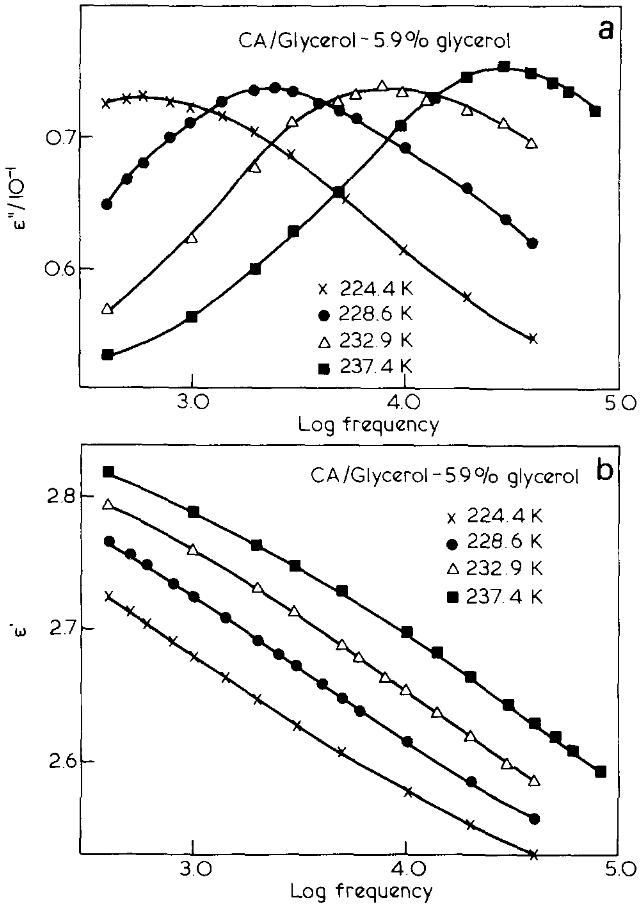

Figure 3 Frequency scans on cellulose acetate doped with 5.9% glycerol at 224.4 (X), 228.6 (●), 232.9 (△) and 237.4K (■). (a) ϵ'' vs. log frequency and (b) ϵ' vs. log frequency

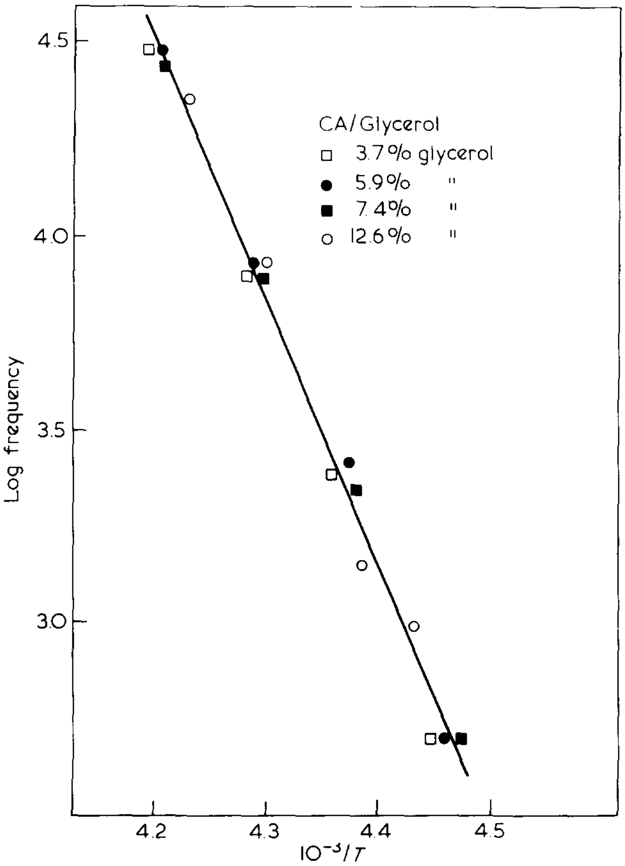

Figure 4 Activation energy plot for cellulose acetate doped with 3.7% (□), 5.9% (●), 7.4% (■) and 12.6% glycerol (O). Log frequencies vs. $10^3/T$

sites, the formation of a multilayer allows more facile migration of the protons and a change in the conductions mechanism. According to Mott[6] the conductivity of an amorphous material at low frequency may be described by the relation

$$\sigma(\omega) = A(T)\omega^{n(T)} \tag{1}$$

where $\sigma(\omega)$ is the conductivity at frequency ω and $n(T)$ is an empirical coefficient which is characteristic of the operative conduction mechanism, and $A(T)$ is a weakly temperature dependent parameter. For a trapped hop-

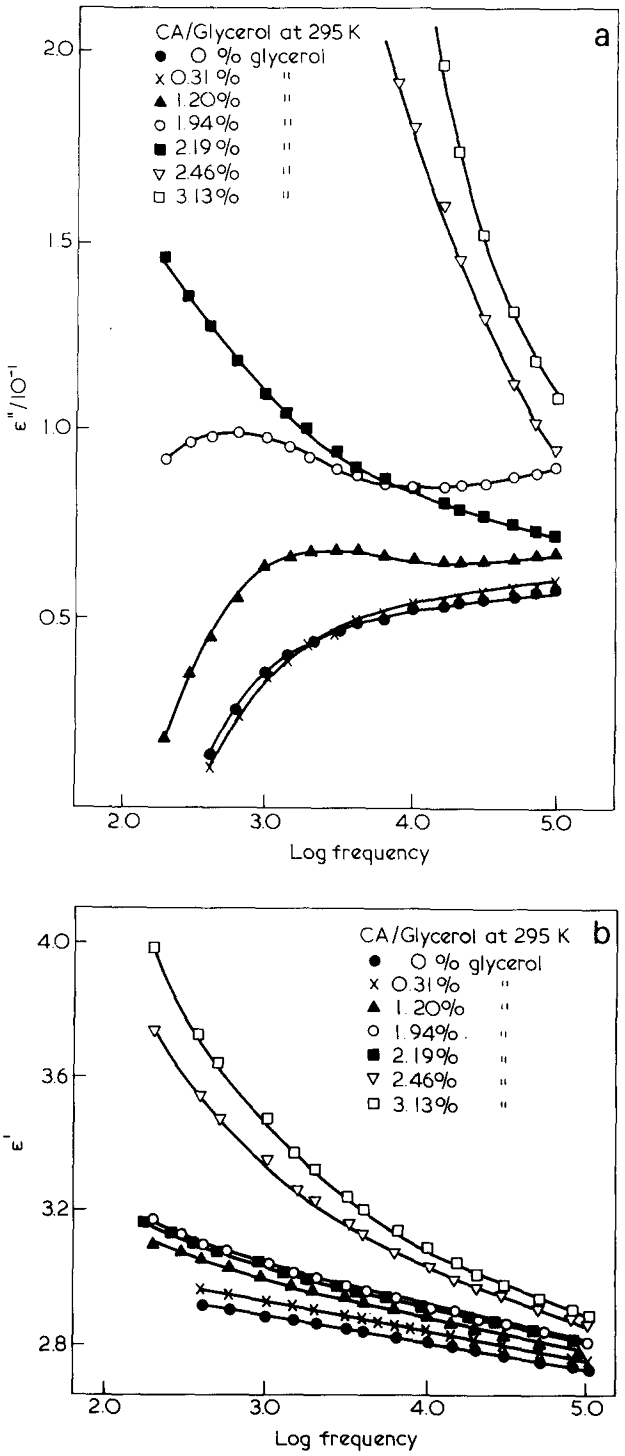

Figure 5 Frequency scans at 295K on cellulose acetate doped with 0% (●), 0.31% (X), 1.20% (▲), 1.94% (O), 2.19% (■), 2.46% (△), and 3.13% glycerol (□). (a) ϵ'' vs. log frequency and (b) ϵ' vs. log frequency

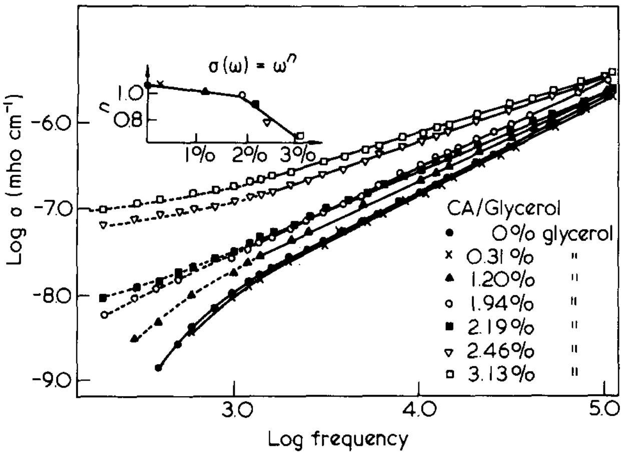

Figure 6 Variation of the a.c. conductivity with frequency as a function of glycerol contents for cellulose acetate at 295K. Inset is the variation of the coefficient in the equation $\sigma(\omega) = \omega^n$. Glycerol contents were 0% (●), 0.31% (X), 1.20% (▲), 1.94% (○), 2.19% (■), 2.46% (△) and 3.13% (□). Log 6 vs. log frequency

ping mechanism, $n(T)$ should have a value close to unity. The appropriate log plots are shown in *Figure 6*. The coefficient of n changes at a value of approximately 2% glycerol indicative of a change in the conduction mechanism.

In conclusion, the dielectric data for glycerol doped cellulose acetate resembles closely that observed with water doping. At high dopant contents the relaxation resembles that of a liquid like phase whereas at lower levels specific interactions with the fibrous matrix are readily identified. These observations would imply that doping of cellulose and its derivatives occurs in two distinct stages. Low levels of doping tend to interact with the surface of the fibres and hence exhibits relaxation characteristics which reflect the degree of interaction. Higher levels of doping lead to the formation of a more continuous phase, the dopant exhibiting properties which are more characteristic of its pure phase and are often independent of the matrix in which they are dispersed.

ACKNOWLEDGEMENTS

One of us (DJC) wishes to thank the MOD for the provision of financial support during the course of this study.

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