Dielectric studies of cellulose and its derivatives: 2. Effects of pressure and temperature on relaxation behaviour

Derek J. Crofton* **and Richard A. Pethrick**
Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 *Cathedral Street, Glasgow G*1 1*XL, Scotland, UK*

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Dielectric and water absorption measurements are reported for cellulose acetate, a plasticized cellulose acetate and ethyl cellulose as a function of pressing temperature and pressure. The observed effects are explained on the basis that the work done in producing the discs used in these measurements destroys residual fibre structure and leads to an increase in the dipolar activity of the sample. The observation of gelatinization is discussed in terms of the effects on the side chain mobility and the densification of the polymer matrix. The effects observed in the case of dibutylphthalate are in agreement with data from other measurements on another cellulose derivative and indicate strong interactions between the plasticizer and the polymer. Water absorption data also reflects the changes which occur in the morpholoy with changes in the pressing conditions.

Keywords Cellulose; cellulose acetate; pressing; dielectric relaxation; morphology

INTRODUCTION

In the previous paper in this series the effects of morphology on the acetylation of cellulose were observed as changes in the dynamic spectrum. It was found that for low degrees of substitution the relaxation spectrum can be explained in terms of reaction occurring in the amorphous-interfacial regions of the cellulose fibrillar structure. Higher degrees of substitution require a modification of the fibrillar structure and the generation of a more amorphous and homogeneous overall morphology. The fibrillar structure may also be expected to be sensitive to the thermal-methanical treatment of the sample prior to being investigated dielectrically. The effects of various preparation prehistories on the dielectric relaxation forms the subject of this paper.

EXPERIMENTAL

Materials

Cellulose acetate and ethyl cellulose were obtained from Drs T. J. Lewis and F. S. Baker of PERME (Waltham Abbey). The cellulose acetate had an acetic acid yield of 53% and the ethyl cellulose had an ethoxy content of 48%. The substitution characteristics of both derivatives correspond to approximately 0.5 hydroxyl groups per gluco-pyranose ring. Cellulose acetate was doped with di-n-butyl phthalate (DBP) by immersion in heptane and stirring overnight. The remaining heptane was evaporated off in a vacuum system, and the resulting material dried at 363 K. The characteristics of the base linters used in this study were obtained from gel permeation chromatography and correspond to an M_n of approximately 90 000 with a distribution of M_w/M_n of 5.

Sample preparation

In order to be made suitable for dielectric measurements, the samples were pressed into discs in a polished stainless steel cylindrical mould using an Apex type 340-4 hydraulic press at pressures up to 46 MPa and temperatures in the range of 293–453 K. The resulting discs measured 5 cms in diameter and were approximately 0.1–0.2 cms thick. The temperature was monitored using a thermocouple (Cr/Ni) attached to the upper and lower plattens. Pressing times were typically one hour. The samples obtained were stored in an oven at 363 K until constant weight was achieved.

Dielectric measurements

The real and imaginary parts of the dielectric permittivity were measured at 1 KHz as a function of temperature using a Teredyne C.357 automatic bridge and a two terminal cell configuration. The temperature was recorded on a Digitron 3750K digital thermometer attached to a thermocouple located close to the disc. A correction was applied to the data to allow for the effects of thermal lag in the system. The cell was flushed with dry nitrogen prior to cooling the sample and contained a drying agent (silica gel) as an added precaution against the effects of condensation.

All the samples in this study received a graphite (Acheson-Aquadag) coating to improve the contact between the electrodes and the samplees.

SEM

Electron micrographs of the samples subjected to different thermal–mechanical pretreatments were obtained using a Phillips (PSEM 500) scanning electron microscope. The samples examined were fracture surfaces, coated with gold and mounted on aluminium stubs.

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[*] Present address: Leafields Marine Limited, Southfields Industrial Estate, Glenrothes, Fife, Scotland, UK

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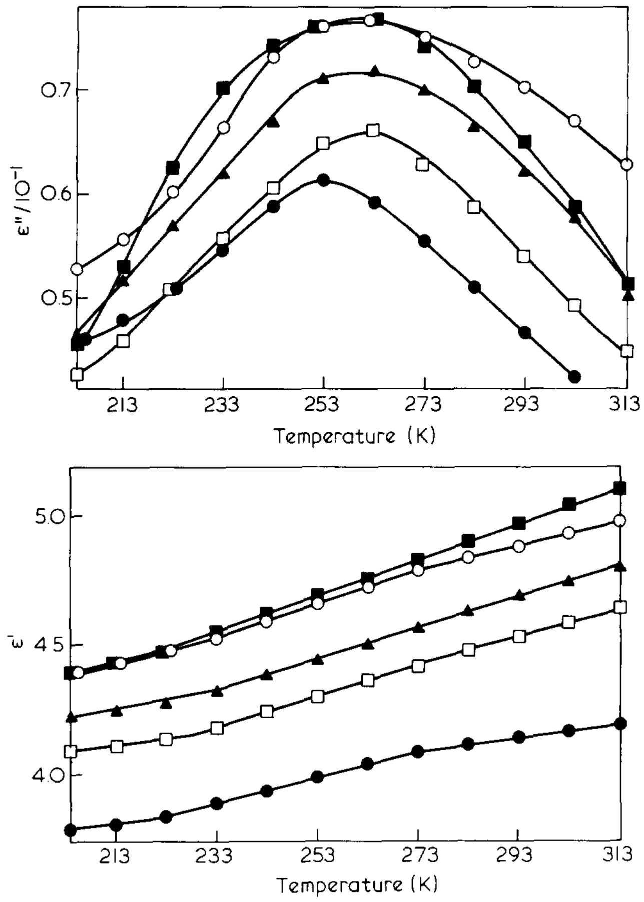

Figure 1 Effect of pressure on the dielectric properties of cellulose acetate, at pressures of 15 (●), 23 (□), 31 (▲), 38 (○) and 46 MPa (■). ε'' vs. temperature; ε' vs. temperature

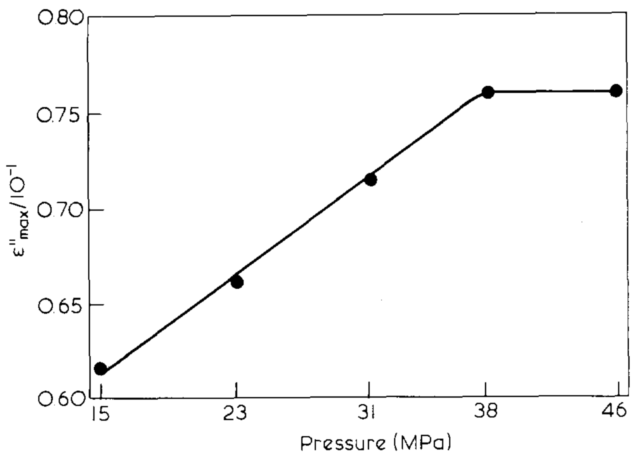

Figure 2 Effect of pressure on the maximum dielectric loss in cellulose acetate. ϵ''_{max} vs. pressure

Density measurements

The densities of the materials were measured using a flotation method, in which the samples were immersed in a measuring cylinder containing carbon tetrachloride and propanol. The density of the mixture was taken to be equal to that of the sample when the disc was suspended exactly half way up the column of liquid. The density of the mixture was measured using an Anton Paar (DMA 601) density cell. The densities determined in this way are precise to 0.1%.

Water uptake

The previously dried samples were conditioned at a constant relative humidity until the desired amount of water was absorbed. In the diffusion study the relative humidity was 57%.

RESULTS AND DISCUSSION

In an attempt to understand the effects of pretreatment on the dielectric relaxation behaviour of cellulose acetate two studies were undertaken. The first was concerned with the effect of variation of the pressure used in pressing the disc at 293 K; the second was concerned with an investigation of the effects of varying the pressing temperature between 293 and 453 K at a constant pressure of 38 MPa.

Effect of pressure

The temperature of the real and imaginary parts of the dielectric permittivity of cellulose acetate at 1 kHz are shown for a series of discs pressed at 293 K with pressures of 15 to 46 MPa (*Figure 1*). The relaxation observed at around 263 K can be attributed to the motion of acetate side groups attached to the main backbone[1,2]. Although the position of the peak in the loss curve varies very little with the effect of pressure, the magnitude of the loss process is very sensitive to pretreatment of the sample. The apparent increase in the amplitude of the loss is consistent with the pressure inducing a greater degree of disorder in the fibrillar structure and hence increasing the total amount of amorphous regions. The change of the amplitude of the loss with pressure is observed to plateau above a pressure of 38 MPa (*Figure 2*).

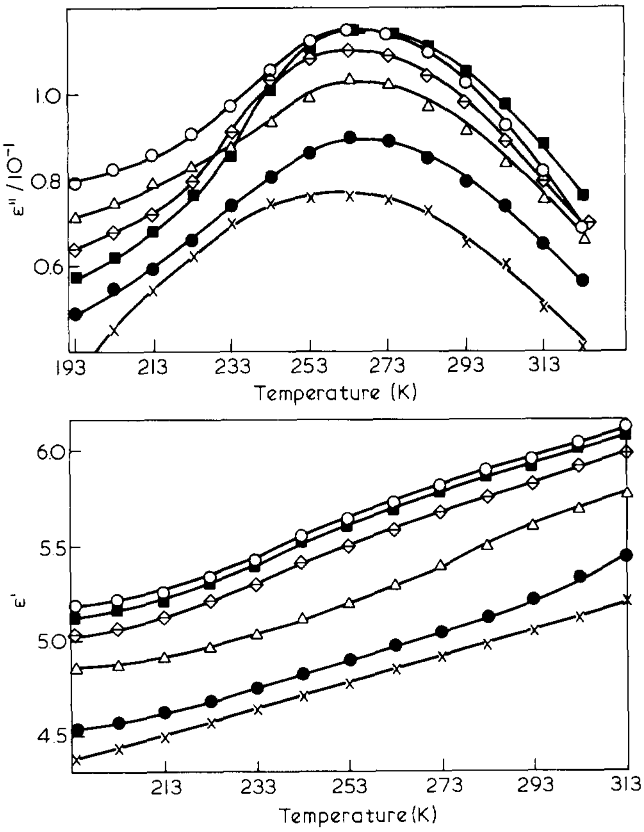

Figure 3 Effect of pressing temperature on the dielectric properties of cellulose acetate. Pressing temperatures were 293 (X), 333 (●), 373 (△), 413 (○), 433 (■) and 453 K (⊕). ε'' vs. temperature and ε' vs. temperature

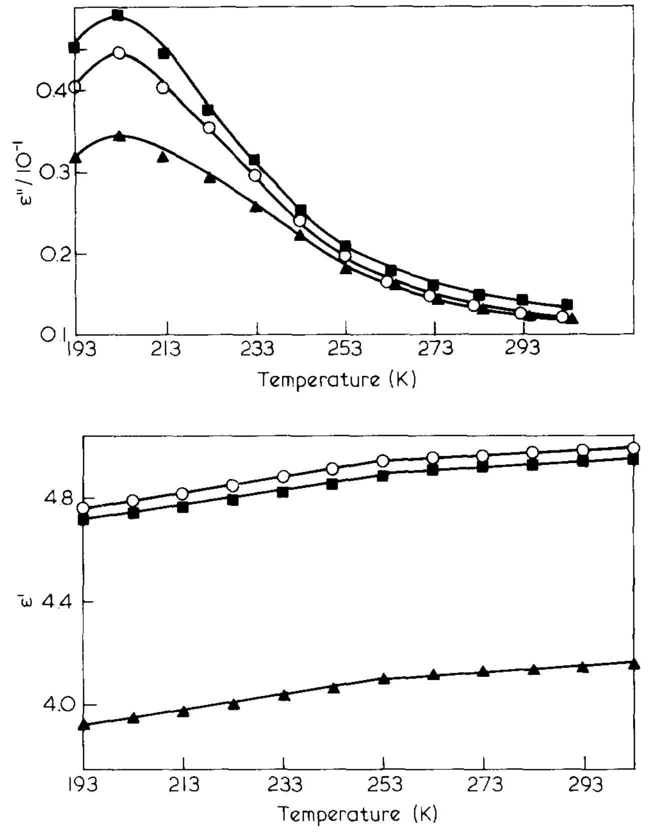

Figure 4 Effect of pressing temperature on the dielectric properties of ethyl cellulose. Pressing temperatures were 333 (▲), 373 (■), and 413 (○). ϵ'' vs. temperature and ϵ' vs. temperature

Effect of pressing temperature

The effect of pressing temperature (constant pressure of 38 MPa) on the real and imaginary parts of the dielectric permittivity for cellulose acetate and ethyl cellulose are shown in *Figures 3* and *4*. In both cases the amplitude of the dielectric loss increases with pressing temperature. This behaviour parallels that observed on the effect of pressure on the samples. Examination of electron micrographs of the fracture surfaces indicate that the materials produced at low temperatures have a more open structure than those obtained at higher temperature (*Figure 5*). A study of the variation of the density of the samples of cellulose acetate as a function of pressing temperature indicates an increase in the density (*Figure 6*) consistent with the observed densification of the structure observed by electron microscopy. Examination of the variation of the magnitude of the loss peak with pressing temperature (*Figure 7*) indicates a variation similar to that observed with pressure (*Figure 2*). In this former case the loss is observed to exhibit a maximum and this coincides with the observation of a gelatinization of the material. The phenomena of gelatinization is not well understood, but is characterized visually by the formation of a transparent yellowish coloured phase in contrast to the opaque, white-coloured material formed at lower temperatures. It may be associated with the production of a denser matrix as it involves the break up of fibres into smaller units under the application of work[3]. It is of interest to note that both the density and dielectric loss exhibit apparent peaks in the same region. It may be proposed that part of the above effects as observed dielectrically can be attributed purely to density phenomena. In an attempt to correct this effect the polarizability of the samples were calculated as follows, using a form of the Clausius Mossotti equation[4]:

$$R=\frac{4\pi}{3}.N.\left(\frac{2\varepsilon_s-2}{2\varepsilon_s+n_D^2}\right).\left(\frac{n_D^2+2}{3}\right).\mu \qquad (1)$$

where ε_s is the low frequency value of the permittivity, n_D^2 is the square of the refractive index which can be equated to the high frequency limiting permittivity (ε_∞) and μ is the dipole moment. $N=d.N_a/M$ where N_a is Avogadro's number, M is the molecular weight of the sub unit and d is

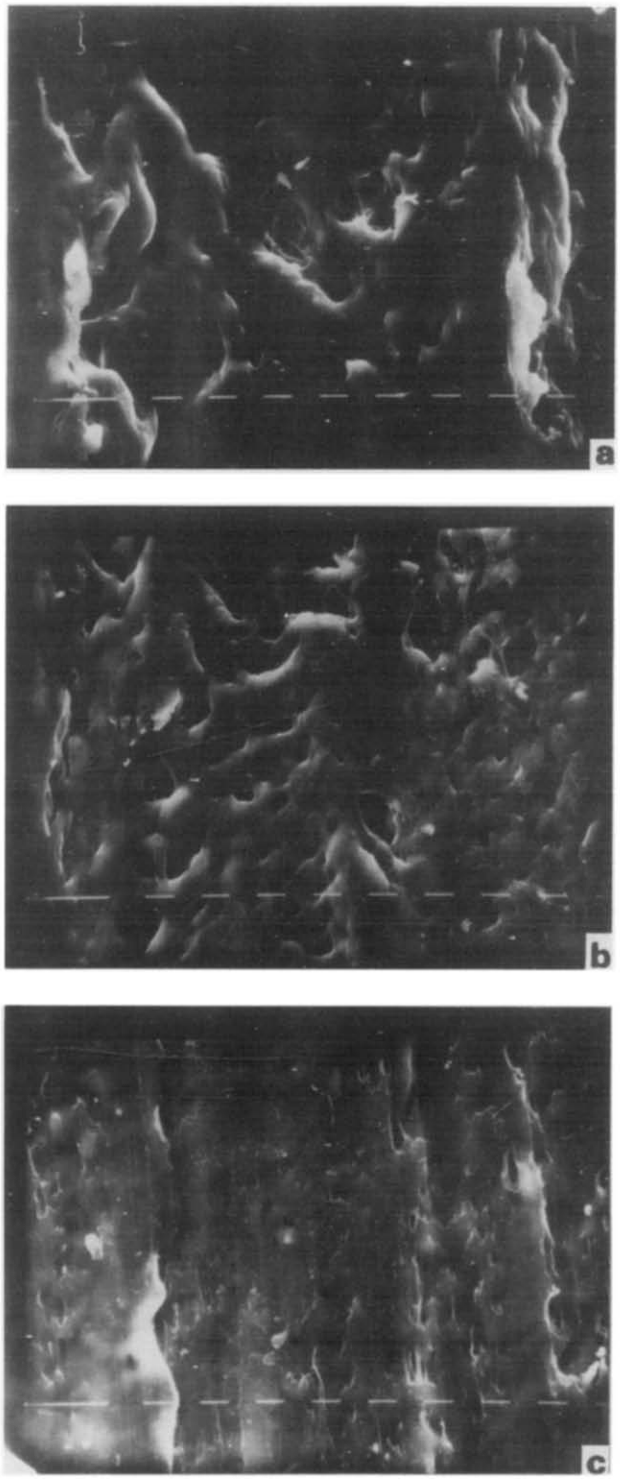

Figure 5 Scanning electron micrographs of cellulose acetate pressed at (a) 333 K (b) 373 K and (c) 433 K. Marker size = 10 μm

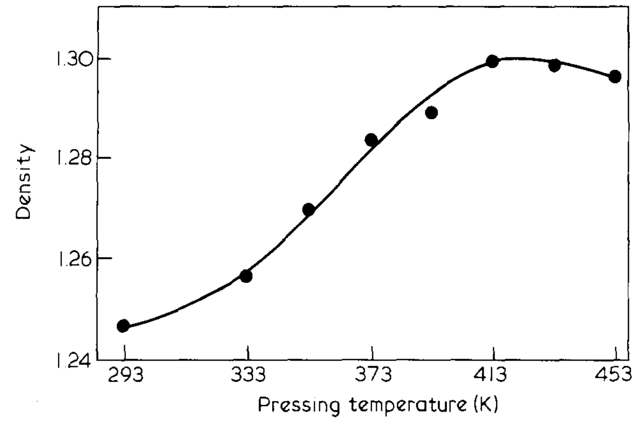

Figure 6 Effect of pressing temperature on the density of cellulose acetate. Density vs. pressing temperature

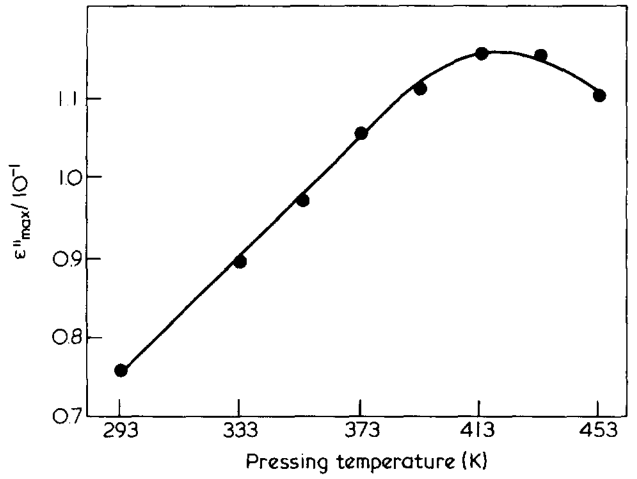

Figure 7 Effect of pressing temperature on the maximum dielectric loss in cellulose acetate. ε''_{max} vs. pressing temperature

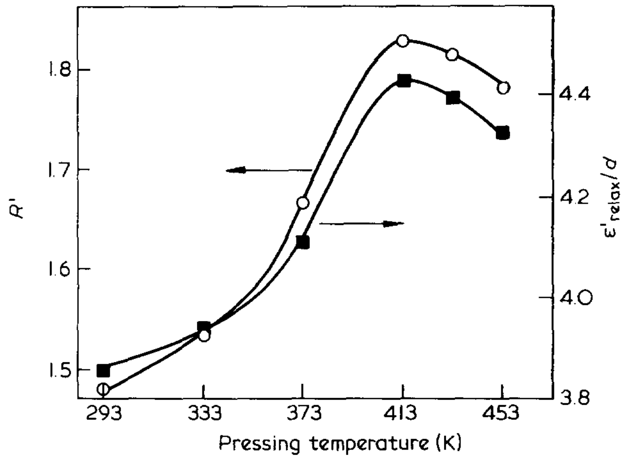

Figure 8 Density–dielectric relationship for cellulose acetate. R' vs. pressing temperature and ε'_{relax}/d vs. pressing temperature

the density. Rearranging equation (1) to include only variable parameters we can define:

$$R' = d\left(\frac{2\varepsilon_s - 2}{2\varepsilon_s + \varepsilon_\infty}\right)\cdot\left(\frac{\varepsilon_\infty + 2}{3}\right) \qquad (2)$$

Using the relationship[4] that $(\varepsilon_s + \varepsilon_\infty)/2 = \varepsilon_{\text{relax.}}$ and that $(\varepsilon_s - \varepsilon_\infty)/2 = \varepsilon''_{\text{relax.}}$, it is possible to compute values for R' and ε'/d, which are plotted in *Figure 8*. This indicates that even if we allow for the change in the density on the dielectric permittivity the variation in the increment associated with the effect of pressing temperature still exhibits a peak. It may also be noted that the shape of the temperature dependence of the loss curves (*Figure 3*) changes at 413 K which corresponds to the gelatinization temperature for this sample. Below 413 K the curves are somewhat broader and exhibit a larger increment than those obtained at higher pressing temperatures. This behaviour may be explained in terms of the way in which the polymer–polymer interactions influence the distribution of possible relaxation processes. In ungelatinized material, the dipoles may be expected to exist in or close to relatively open structured regions and hence will have activation energies which are lower than those of the average side chain motion associated with ester groups in the internal structures. The densification of the polymer associated with gelatinization leads to a sharpening of the distribution of relaxations and a consequent reduction in the number of the more mobile

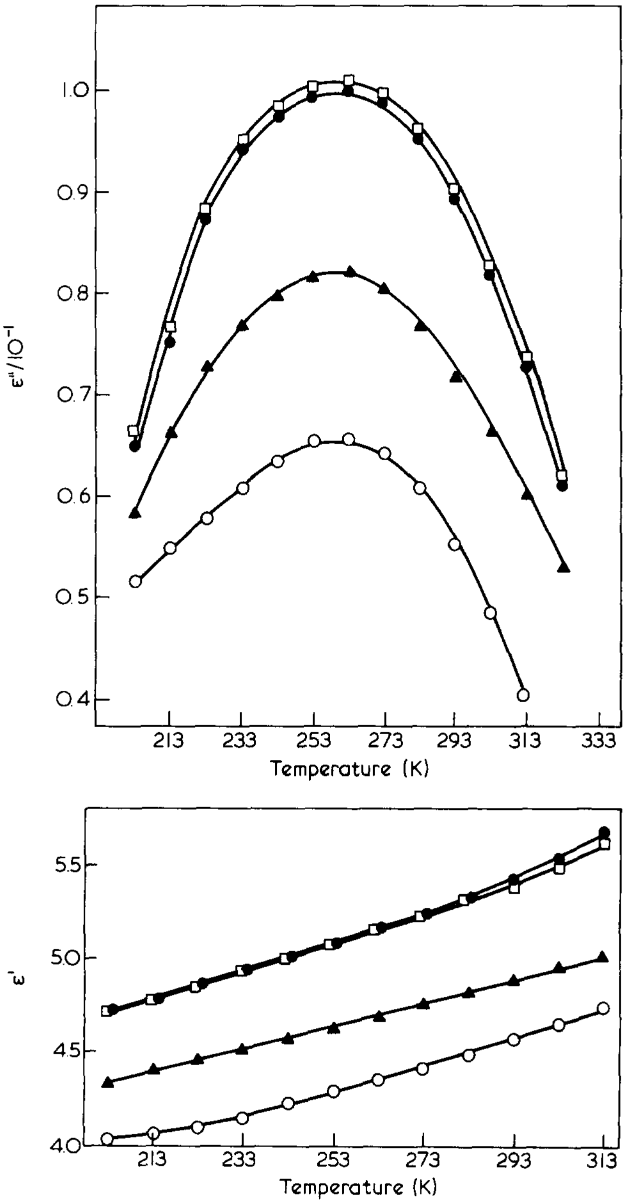

Figure 9 Effect of pressing temperature on the dielectric properties of cellulose acetate doped with DBP (26%). Pressing temperatures were 333 (○), 373 (▲), 413 (●) and 453 K (□). ε'' vs. temperature; ε' vs. temperature

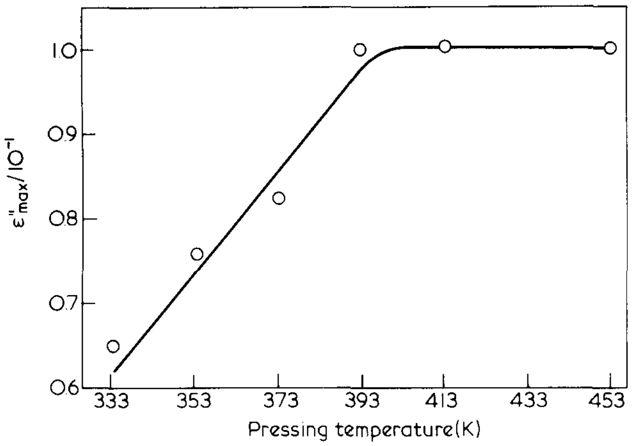

Figure 10 Effect of pressing temperature on the maximum dielectric loss in cellulose acetate doped with DBP (26%). ϵ''_{max} vs. pressing temperature

dipoles at the low temperature regions. The decrease in the amplitude on further increase in pressing temperature is also consistent with this idea.

Studies of the dielectric properties of polycrystalline powder samples[10,11] have also observed large changes in dielectric properties as a result of increases in pressure. In these systems the effects are associated with the effects of removal of internal surfaces on compaction of the samples. The changes observed in the cellulose systems are different to those observed in powder samples. It is possible that removal of internal surfaces may influence the bulk permittivity. However, the effects on the relaxation amplitude appear only to be consistent with the pressure and temperature treatments inducing changes in the actual crystalline fibre content.

In summary, the effect of increasing the pressing temperature and pressure is twofold. Firstly, there is a general increase in the dielectric activity associated with the generation of a more amorphous structure. This occurs when the fibrillar structures are distorted to form a more compact matrix. Initially these distortions will generate areas of amorphous material close to voids and have associated mobile dipoles. The second densification of the matrix, leading to a reduction in the total void content and the formation of a more homogeneous matrix. This latter process is also associated with the observation of gelatinization of the sample.

Similar behaviour was observed for the effect of pressing temperature on the change of the permittivity for ethyl cellulose (*Figure 4*) indicating that the same morphological constraints are also operative in this system. The relaxation at 203 K can be assigned to the motion of ethoxy side group[5].

Effect of dibutyl phthalate

The variation of the real and imaginary parts of the dielectric permittivity for samples of cellulose acetate doped with DBP (26%) are shown in *Figure 9*. As in the previous study of cellulose acetate the amplitude of the dielectric loss is observed to increase with increasing pressing temperature, without any appreciable shift in the position of the relaxation peak. Comparison of this data with that obtained on the pure cellulose acetate indicates that the relaxation of the side chains is unaffected in terms of its position by the presence of the DBP. However, the amplitude of the dielectric response of the cellulose acetate and plasticized materials are not identical, the latter being reduced compared with the unplasticized material at a comparable pressing temperature (*Figure 10*). It would appear that the DBP is interacting with the side chains in such a way as to reduce the number of active species, which may involve surface absorption of the plasticizer onto the residual fibrils. Measurements on cellulose nitrate[6,7] indicate a strong interaction between DBP and the fibre surface and this appears to be consistent with the above dielectric observations on cellulose acetate. It may be interesting to note that the presence of DBP seemed to reduce the degree of gelatinization observed, compared to pure cellulose acetate produced at a specific pressing temperature.

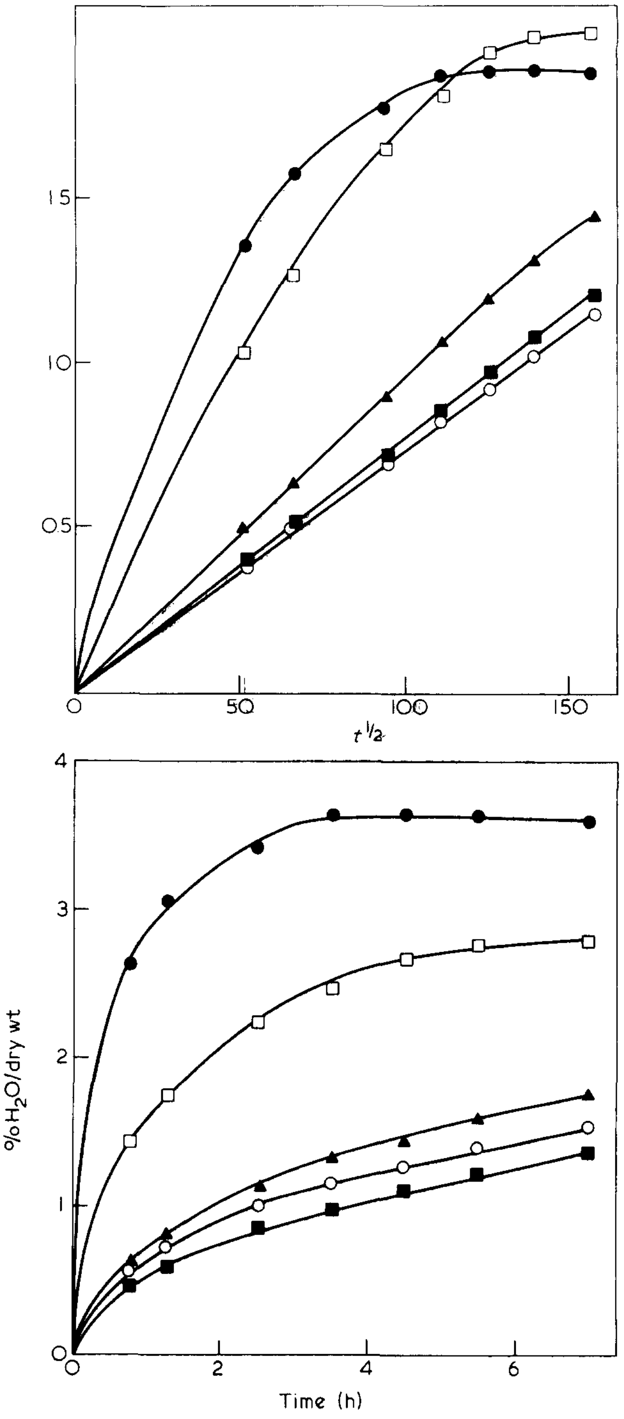

Figure 11 Water absorption in cellulose acetate at pressing temperatures of 293 (●), 373 (□), 393 (▲), 433 (○) and 453 K (■). $\%H_2O$/dry wt. vs. time (h) and $\%H_2O$ vs. $(t)^{1/2}$

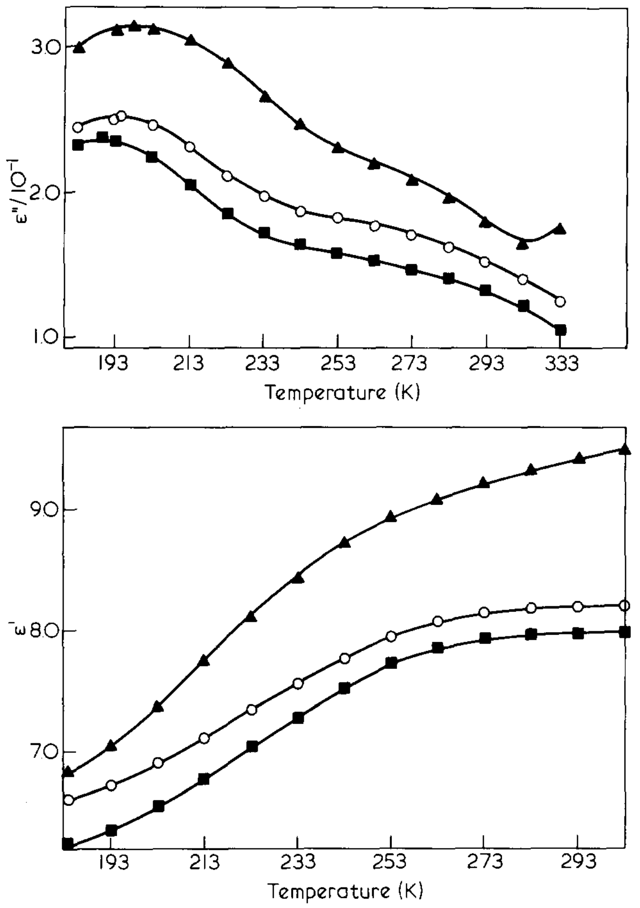

Figure 12 Effect of 4.5% water on the dielectric properties of cellulose acetate. Pressing temperatures were 293 (■), 373 (○) and 433 K (▲). ε'' vs. temperature, ε' vs. temperature

Effect of water

The percentage water uptake is shown in *Figure 11*. The equilibrium value of the water uptake decreases with an increase in pressing temperature, this presumably reflecting the formation of a closely packed, denser structure. A plot of the percentage water uptake against $t^{1/2}$ indicates that the water absorption initially follows a Fickian type behaviour[8], deviations from the ideal behaviour being observed at the lower pressing temperatures. This effect is probably a consequence of the open nature of the fibre structure which leads to the formation of large capillaries and hence allows a condensation mechanism rather than diffusion in the matrix.

Diffusion coefficients of 1.58×10^{-11}, 1.39×10^{-11} and 1.28×10^{-11} $m^2 s^{-1}$ were calculated for samples pressed at 393, 433 and 453 K respectively.

Examination of the variation of the dielectric properties for a series of wet (4.5% H_2O) cellulose acetate samples (*Figure 12*) indicates a shift of the observed relaxation peak to higher temperatures with an increase in pressing temperature. This lower temperature peak is associated with the relaxation of water, which has been investigated in a previous study[9]. These observations are consistent with the idea that increasing the pressing temperature is generating a denser matrix and hence restricting the motion of the relaxing water molecules. As observed previously the dielectric activity is increased markedly with an increase in the water content.

CONCLUSION

The above study illustrates the effect of the production of discs used in the dielectric measurements on the morphological organization of the cellulose polymers. An increase in either the temperature or pressure used in pressing the sample can lead to a destruction of residual fibrillar structure. The effects of dibutyl phthalate are consistent with observations of the effects of this plasticizer on cellulose nitrate and are indicative of relatively strong interactions presumably at the residual fibrillar surface. The studies of water absorption are consistent with this overall picture of the morphological changes which occur on pressing.

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