Dielectric studies of cellulose and its derivatives: 1. Acetylation of cellulose

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Dielectric conductivity (*dc*) and water absorption measurements are reported on a series of cellulose linter samples acetylated to varying degrees. The data illustrates the effects of the original structure of the cellulose linters both on the ease of acetylation and also on the subsequent dynamic characteristics of the polymer. It is only in the most forcing conditions that the primary fibrillar structure is destroyed. A change in properties is observed to occur at 40% acetylation of the hydroxyl groups, this coincides with the concentration of accessible groups as determined by deuterium exchange. A correlation is observed between the absorption and electrical observations on these systems.

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

INTRODUCTION

Examination of the morphology of cellulose indicates that it exhibits a variety of degrees of order. Macroscopically, cellulose is organized into several distinct layers within the cell wall. An outer layer, known as the primary wall consists of cellulose fibrils interwoven in a criss-cross fashion, and embedded in a non cellulosic fraction. The secondary wall consists of two layers (S_1 and S_2) of pure cellulose, that spiral about the fibre axis in opposite directions. The inner most layer (S_3) contains fibrillar units orientated parallel to the main stem axis. This structure is typical of that found in cotton linters[1]. As a consequence, the heterogeneous chemical substitution of the hydroxyl groups in cellulose may be expected to reflect the accessibility of the reaction site. Consequently the chemical and morphological characterics of the substituted material should be sensitive to the persistence of chain interactions and as a result the dynamic properties of substituted cellulose materials may reflect the overall morphology.

When the cell wall is treated with dilute acid, alkali and other suitable chemicals in order to remove the impurities, the fibrous structure is exposed and may be examined by electron microscopy[2]. The dimensions of the fibrils depend very much on the actual source of cellulose. However, microfibrils have a width of around 100–250 Å, a thickness of approximately half the width[3] and a length that may be 500–680 Å. Each microfibril can be in turn considered to be constructed from elementary fibrils which are typically 35 Å in width[4]. These sub-units have been considered to be the basic crystalline unit formed in the bio-synthesis of cellulose. Aggregates of four elementary fibrils are bound together in the microfibril by weak interfibrillar hydrogen bonds, possibly *via* water molecules. The exact number of cellulose chains contained in each elementary fibril will again depend on the cellulose source. However, the model by Mühlethaler[5], suggests that a block of 8 × 12 cellulose chains are packed together to form the elementary fibril.

Cellulose acetate is prepared by the initial removal of the outer primary layer and subsequent acetylation of the 'pure' cellulose matrix. The extent to which the original morphology is retained depends upon the conditions used in the reaction and on the amount of acetylation produced. In this study a series of acetylated samples are prepared from cotton linters, and their dielectric behaviour discussed in terms of the effect of morphology.

EXPERIMENTAL

Materials

The cellulose linters used in this study were supplied by Dr F. S. Baker and Dr T. J. Lewis, PERME (Waltham Abbey). The linters had been previously purified and may be considered to be 100% cellulose.

The samples of linters used in this study were obtained from ICI Noble Division. They had been treated with mild alkali to remove the outer coating of waxes, proteins and soluble material. The molecular weight of the cellulose is estimated by gel permation chromatography to be approximately $M_n \sim 100\,000$ with a distribution of $M_w/M_n \approx 5$.

Acetylation of cellulose

Acetylation was achieved by immersing the purified cellulose linters in heptane and subsequent heterogeneous reaction. Initially, acetyl chloride was used as the acetylating agent but it failed to produce an acetic acid yield of greater than 10%. Acetic acid and acetic anhydride in the ratio of 3:4 produced a greater extent of acetylation, the degree depending upon the temperature and the time used in the reaction. High degrees of acetylation could only be achieved by the use of a catalyst. In the present study 3–4 ml of HCl was found to be satisfactory in this role. Care had to be taken in these latter reactions to avoid degradation of the cellulose

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Table 1 Reaction conditions for the acetylation of cellulose

Acetic acid yield (%)	Acetylating yields	Temperature (K)	Catalyst
10	CH_3COCl	293	none
20	$(CH_3CO)_2O/CH_3COOH$	338	HCl
28	"	343	"
63	"	343	"

material leading to a soluble dispersion. The reaction was performed in a 250 ml round bottom flask, fitted with a reflux condenser and stirred magnetically. The reaction time depended on the extent of substitution required, but was typically 3–4 h. A summary of the reaction conditions is shown in *Table 1*.

The resulting acetylated material was washed with dilute (3%) sodium hydroxide and subsequently washed with distilled water until the effluent had a pH of 7. The material was then dried in a vacuum oven at 333 K for at least 2 days. Acetic acid yields (AAY) were determined using the method outlined in BS 2880 (1957).

Water absorption

Previously dried samples were conditioned at various relative humidities until the required concentration of water was absorbed. In the water diffusion investigation humidities of 53% and 64% were used. The *dc* conductivities of the wet samples were measured by applying a 45 V step voltage across the sample under investigation. The resulting equilibrium current was measured on a Keithley (610c) electrometer.

Pressing of samples

In order to be made suitable for dielectric measurements the materials were pressed into uniform compact discs which were 5 cms in diameter and 0.1–0.2 cms thick. About 4 g of each sample was placed in a cylindrical mould and pressed using an Apex (type 340-4) hydraulic press. A constant pressure and temperature of 38 MPa and 373 K was maintained for each pressing for a period of 1 h.

Dielectric measurements

The dielectric data was recorded as a function of temperature at a fixed frequency of 1 kHz using a Teredyne (C.357) automatic bridge and a two terminal cell configuration. The cell was flushed with dry nitrogen prior to cooling the samples and contained a drying agent (silica gel) as an added precaution against the effects of condensation. The temperature was recorded on a Digitron 3750 K digital thermometer attached to a thermocouple located close to the sample. A temperature correction was applied to the data to allow for the effects of thermal lag in the system. No application of contact liquid was employed in this study due to a dilaterious effect on the surface of the cellulose discs.

dc *Conductivity measurements*

dc conductivity data were obtained from measurements of the current flowing through the sample in equilibrium conditions. These cellulose samples will contain low frequency relaxation components which will influence the values of the conductivity measurements obtained at short times. In practice it was necessary to leave the sample for between three to five hours before 'true' equilibrium *dc* conductivity values could be obtained.

RESULTS AND DISCUSSION

The real and imaginary parts of the permittivity of the series of dry acetylated celluloses are shown in *Figures 1* and *2* respectively as a function of temperature. The original dry cellulose exhibits a peak at 220 K consistent with the relaxation of the hydroxyl side groups[6,7]. Various studies[8,9] have shown that this relaxation amplitude is sensitive to crystallinity. Naimark *et al.*[10] calculated that the dielectric constant of amorphous cellulose is almost three times as large as that of highly crystalline cellulose. These studies indicate that the polarization is occurring in accessible regions of cellulose associated with a low degree of order.

The trisubstituted cellulose acetate (63% AAY) exhibits a relaxation at 268 K which is consistent with a study by Mikhailov *et al.*[11] in which a relaxation at 258 K (10 KHz) was absorbed for cellulose triacetate. The shift of this relaxation to higher temperatures, in comparison with the cellulose peak, reflects the increased steric constraints involved in the motion of the bulkier acetyl side groups. The effects of acetylation on the dynamic behaviour of the cellulose matrix are illustrated in *Figure 3* by plotting the position of the maximum in the dielectric loss against the AAY. It is clear from this graph that there is a significant change in the rate of shift of the peak with substitution at ~25%, which corresponds to the acetylation of 40% of the OH groups.

It has been shown[1] in studies of deuteration exchange that the amount of disordered material in cotton cellulose is around 42%. It is assumed that the remaining hydroxyl

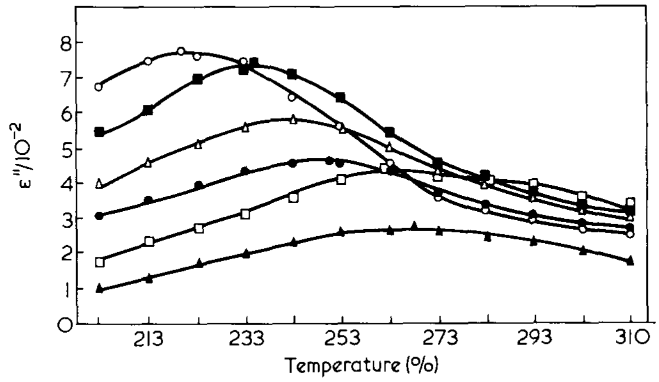

Figure 1 Dielectric loss of a series of acetylated celluloses as a function of temperature. AAY 0% (○), 10% (■), 20% (△), 28% (●), 53% (□) and 63% (▲)

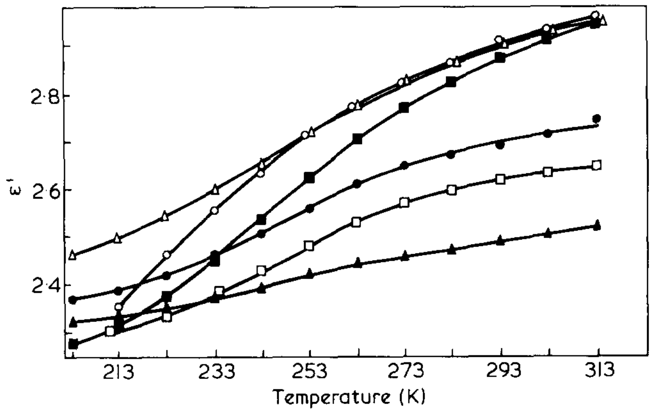

Figure 2 Dielectric constant of a series of acetylated celluloses as a function of temperature – symbols as in *Figure 1*

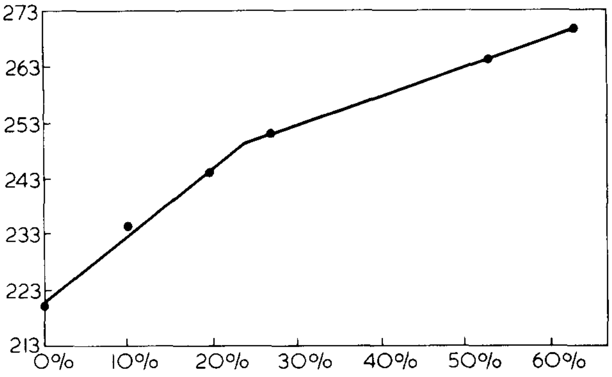

Figure 3 Relation between the relaxation temperature and the degree of acetylation. I.e. *T*. relax. vs. AAY

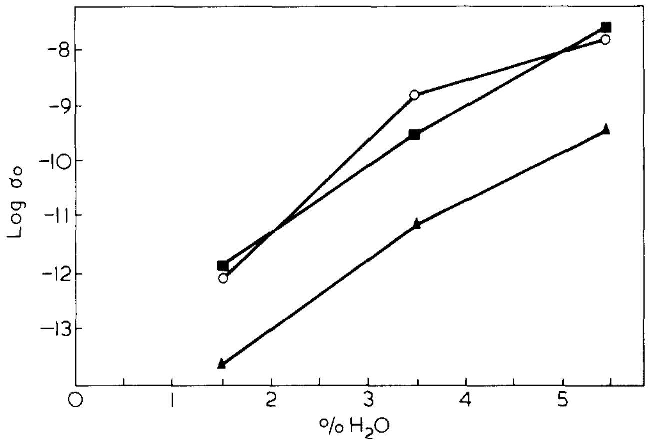

Figure 4 *dc* conductivity of wet samples – AAY 0% (■), 28% (○), and 53% (▲)

groups are in the internal structures of the elementary fibrils and as such are unable to be effectively involved in the exchange process. It would appear that in the present case, similar morphological constraints may be operative which are reflected in the dielectric behaviour of the contributing side groups.

Acetylation of the available groups leads to a rapid increase in the steric constraints on the side group motion and hence reduces the rate of rotation, which is consistent with an increase in the relaxational temperature. At $\sim$25% AAY all the accessible reaction sites are occupied. This region corresponds to the point where an increase in the severity of the acetylating conditions was required in order to achieve further substitution. The more energetic conditions lead to an operning up of the internal fibrous structure[12], which exposes the previously inert hydroxyl groups, which are subsequently acetylated. This leads to more steric constraints on the dipole mobility which results in a further shift of the relaxation to higher temperatures. The influence of the morphology on the chemistry has been identified from a study of the methylation of cellulose[13]. It was found that the rate of reaction depends critically upon the degree of substitution and can be correlated with the extent to which the fibrillar structure is destroyed.

Measurement of the *dc* conductivity as a function of the degree of acetylation, shown in *Figure 4*, indicates that cellulose and cellulose acetate (28% AAY) exhibit similar conductivity variations and have similar values as a function of water content. Increasing the degree of substitution above the critical value of $\sim$28% AAY leads to a marked lowering of the conductivity, which is indicative of a greater restriction of the charge carrier. This effect is also consistent with the observed shift to higher temperatures of the relaxation peak of the side chains.

The ease of diffusion of water in the samples is reflected in the rate of water uptake (*Figure 5*). The absolute levels of equilibrium water uptake decreases with the extent of substitution, which infers a decrease in the water affinity of acetylated cellulose. The effect of water on the dielectric properties of cellulose and cellulose acetate have been reported in a previous study[14]. Diffusion coefficients at two relative humidities are listed in *Table 2*. The diffusion coefficient measurements were carried out as indicated previously, water uptake being monitored as a function of time for a sample of well defined dimensions. The initial slopes are linear as predicted for Fickian diffusion, hence allowing the diffusion coefficients to be calculated in the usual way[14].

The diffusion data may be considered to reflect the relative degree of interaction of the matrix with the diffusing water molecules. Clearly hydroxyl side groups display a greater affinity for water than acetyl groups, which explains the observation of a highly hygroscopic cellulose, compared to cellulose acetate. In pure cellulose linters, the channel structure presented by the microfibrils, will be coated with a surface of strongly interacting hydroxyl groups. Substitution of these hydroxyl groups by acetyl groups may be expected to reduce the strength of interaction between the fibrillar surface and the water molecules. This seems to be compatible with the observation of a maximum diffusion coefficient at 28% AAY, and consistent with the high *dc* conductivity of the wet sample, indicative of highly mobile water molecules. Further substitution of the cellulose matrix above this critical point, will tend to destroy the channel structure and lead to the generation of a disrupted system. This

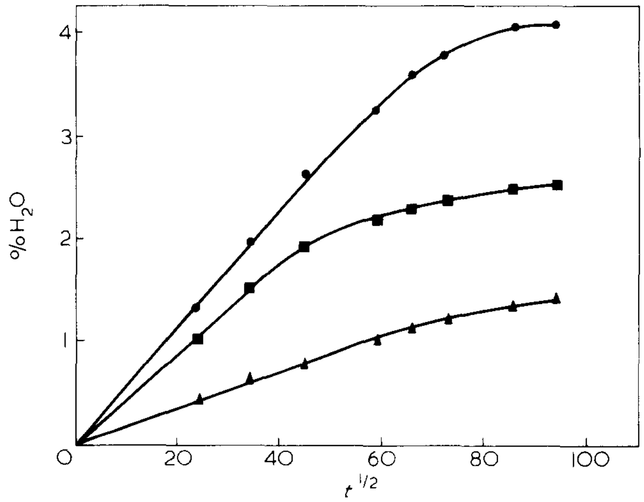

Figure 5 Effects of acetylation on water absorption at r.h. = 64% → AAY 0% (●), 28% (■), and 53% (▲)

Table 2 Diffusion of water in acetylated cellulose

AAY	r.h. = 53%	r.h. = 64%
0%	3.16×10^{-11} m^2 s^{-1}	8.11×10^{-11} m^2 s^{-1}
28%	4.54×10^{-11}	13.01×10^{-11}
23%	1.26×10^{-11}	4.47×10^{-11}

situation, whilst being less interactive to the water molecules has lost the morphological characteristics which favour diffusion, and as a consequence, a lowering of the overall coefficient of diffusion is observed.

CONCLUSION

The trends observed in this study are consistent with the influence of morphology on the acetylation of cellulose. The observations reported above infer that the initial chemical substitution occurs in amorphous and surface fibrillar states. Substitution in excess of ~28% AAY requires fibrillar disruption in order to acetylate the internal reactive sites. The substitution of hydroxyl groups by bulky acetyl groups, leads to the generation of a large degree of restriction in the side group motion with the observation of a corresponding shift of the relaxation to higher temperatures. The *dc* conductivity and diffusion studies provide relevant mobility data, which tend to highlight the change of behaviour at ~28% AAY, associated with a morphological transformation.

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