Structure of Fibrous Cellulose Acetate: X-ray Diffraction, Positron Annihilation and Electron Microscopy Investigations

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Synopsis

X-ray diffraction, positron annihilation, electron microscopy and bulk density measurements are reported as a function of the degree of acetylation for a linters cotton. Heterogeneous reaction proceeds with a retention of ordered structure in the fibers. Substitution does increase the extent of disorder but is not sufficiently extensive to disrupt completely order at the fiber, fibril, micro fibril, and crystallite levels. The generation of disorder is associated with an increase in the interfibrillar distance, a breakup of the microfibrillar structure without a total disruption of the microcrystalline structure.

INTRODUCTION

The acetylation of cellulose under certain circumstances proceeds heterogeneously with the retention of the original fibrous texture.[1] In contrast, commercial cellulose acetate produced via mercerization and then acetylation yields a powdery product. The heterogeneous reaction to yield fibrous material has been studied by Warwicker[2] and Hess and Trogus.[3] X-ray diffraction studies[3] of heterogeneously acetylated cellulose indicate that solvent absorption increases the lattice spacing consistent with reorientation of the CTA (I) lattice. Heat treatment also improves the crystallinity consistent with reorganization in the solid state. Recent molecular and crystal structure determinations of the CTA (I) lattice indicate[4] an orthorhombic unit cell with dimensions $a = 23.63$ Å, $b = 6.27$ Å, and $c = 10.43$ Å. The proposed structure has two chains or four glucose units, in the cell with the chains having the same direction. This structure is similar to that of native cellulose (I),[5] indicating that the acetylation conditions do not disrupt the crystal structure. Stipanov and Sarko[6] have reported a strong equitorial (200) reflection in fibrous cellulose acetate and related studies of cellulose triacetate (II).[7,8] This indicates that in both polymers the large a dimension results from the projection of the ester group along the axis.[8] In this paper we explore, using electron mixtroscopy, X-ray diffraction, and positron annihilation methods, the changes in structure at various levels of organization which occur on acetylation of cellulose linters using heterogeneous conditions.

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Positron annihilation occurs in an organic matrix via a spin exchange process. The positron, in the process of thermalization, generates a number of free electrons which can combine with the positron to form positronium. The thermalized positronium can have two spin states: ortho or para. The spin allowed para decay occurs in approximately 125 ps, whereas the ortho, which undergoes a spin forbidden annihilation process has a lifetime of 100 ns. In a polymer matrix, thermalization of the ortho positronium occurs in voids in the structure, and decay occurs via a spin exchange process between the electron density of the surrounding cavity and the positronium. The intensity of the ortho positronium signal is proportional to the number of voids in the matrix, and the lifetime is inversely proportional to their size.

EXPERIMENTAL

Synthesis of Fibrous Cellulose Acetate

Samples with varying degrees of acetylation were prepared from cotton linters by heterogeneous acetylation using the method of Tanghe et al.[9] A 10-g portion of linters (Holden Vale type II, cleaned and dewaxed, supplied by Dr. T. J. Lewis and F. S. Baker PERME, Waltham Abbey) was placed in a 250 mL conical flask and a mixture of glacial acetic acid (80 mL), toluene (120 mL), and 71–73% perchloric acid (2 mL) added. The reaction mixture was vigorously shaken for a few minutes and then as much of the liquid phase as possible was poured into another flask containing 50 mL of acetic anhydride. This mixture was vigorously swirled and immediately poured back into the flask containing the linters.

This procedure minimizes the possibility of a high initial concentration of acetic anhydride contacting fibers closest to the neck of the flask and producing material with a higher than average degree of acetylation. The flask was stoppered and maintained at 303 K for periods from 5 min to several hours, the mixture being agitated periodically. Reaction was stopped by removal of the linters and washing with ethanol and then with water. The washing with water was continued until one drop of 0.05*M* sodium hydroxide imparted a faint pink color to a 100 mL aliquot of the washing water containing phenolphthalein. The acetate was then washed a final time in ethanol and subsequently dried *in vacuo* overnight at 333 K.

All samples were stored in screw-capped glass jars and dried overnight in a draught-assisted oven at 363 K prior to being used. The degree of acetylation was determined using wet analysis as described previously.[10]

X-Ray Diffraction Measurements

The method used has been described previously.[11] The residual air scatter in the camera was determined using a silver foil reference. Corrections were not applied for Lorentz or polarization factors since these effects will be common for all samples. The percentage crystallinity was determined using the method of Hermens and Weidinger,[11] whereby the ratio of crystalline to amorphous material was determined by drawing a smooth curve through the

minima of the principal diffraction features and the areas above and below the curve were compared over an angular range of 2θ from 4 to 41° (d = 23–2.2 Å).

Positron Lifetime Measurements

A fast slow coincidence method was used and has been described in detail elsewhere.[12] The ^{22}Na source was sandwiched between two pieces of polymer and the sample sealed in an evacuated tube. Computer analysis of the lifetime measurements indicated the presence of three components; two short lifetime components (τ_1 = 125 ps and τ_2 = 430 ps) and a longer lifetime component. The longest lifetime component was essentially free of correlation with the other components, and had an intensity of approximately 20% and lifetimes in the range 1.6–2.5 ns.

Electron Microscopy

Samples of the polymer mounted on aluminium stubs and coated with gold were examined using a Philips PSM 100 scanning electron microscope. The micrographs were recorded photographically.

Density

The density of the pure materials and the partially acetylated samples were determined by a bouyancy method. The composition of a mixture of two nonsolvents; toluene and carbon tetrachloride were adjusted until the sample just floats. The density of the mixture was then determined using a digital densiometer (Anton Paar). These values were compared with data obtained by accurate measurement and weight of compressed discs of the fibres. Good agreement was observed between the two sets of data.

RESULTS AND DISCUSSION

Cellulose fiber exhibit a range of morphological features. Macroscopically, cellulose is organized into several distinct layers. There is an outer layer, composed of proteins and waxes and in the case of the linters used in this study removed by sodium hydroxide. The wall of the cellulose fibre consists of fibrils interwoven in a crisscross fashion. The secondary wall consists of two layers (S_1 and S_2) of pure cellulose that spiral about the fiber axis in opposite directions. The inner most layer (S_3) contains fibrillar units orientated parallel to the main stem axis. The dimensions of the fibrils depend on the actual source of the cellulose; however, the microfibrils have widths of around 100–250 Å, a thickness of approximately half the width and a length of between 500 and 680 Å. Each microfibril is constructed from elementary fibrils typically 35 Å in width and are the basic crystalline unit obtained from the biosynthesis of cellulose. Aggregates of elementary fibrils are bound together into the microfibril by weak interfibrillar hydrogen bonds, possibly via trapped water molecules. The exact number of cellulose chains per elementary fibril

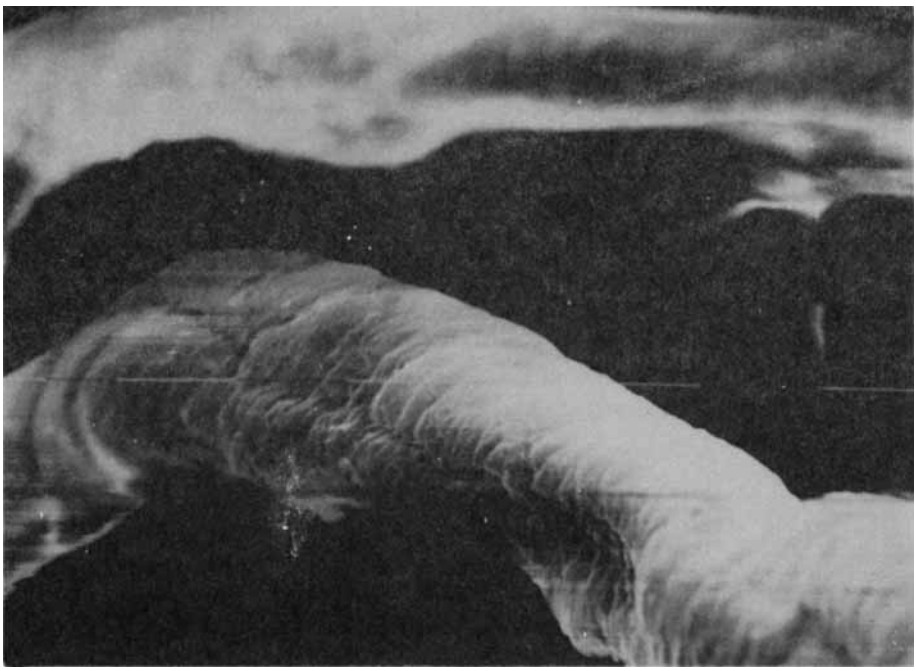


Fig. 1. Electron micrographs of cellulose linters. Striations on the surface are the fibrillar structure.

depends on the source of the cellulose but would typically be a matrix of 8×12 chains.

Substitution of hydroxyl groups in the formation of cellulose acetate is likely to reflect accessibility of the reaction sites and also influence the structure of the product formed.

Electron Microscopy

Electron micrographs of unsubstituted cellulose and also cellulose with a DOS of 2.5 are shown in Figures 1 and 2. Acetylation leads to an opening of fiber structure (Fig. 2) with associated rupture of the internal fibrillar morphology. Normal commercial cellulose triacetate would, however, have degraded at this DOS to a powder. It is clear that the heterogeneous method used in this study leads to a very fibrous product, strongly resembling the form of the original cellulose linters.

X-Ray Diffraction Measurements

Diffraction patterns obtained for three specimens orientated so as to give a fiber pattern are shown in Figure 3. The unmodified cellulose linters were relatively long—about 5 mm and therefore easily aligned—so that the azimuthal spread of reflections is due only to the misorientation of the

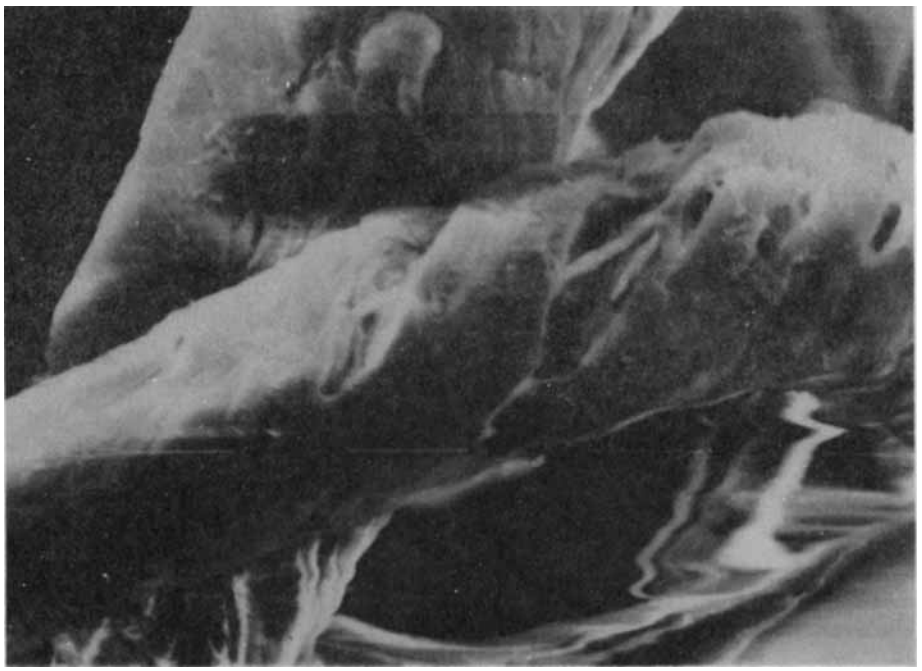
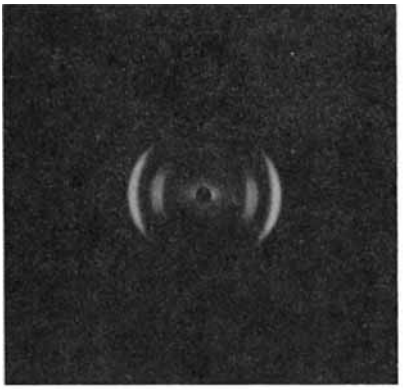
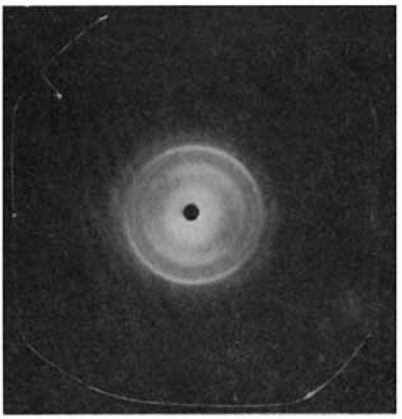


Fig. 2. Electron micrographs of acetylated cellulose linters with a DOS of 2.5. Acetylation leads to an opening of the microfibrillar and some rupture of fibrillar structures.

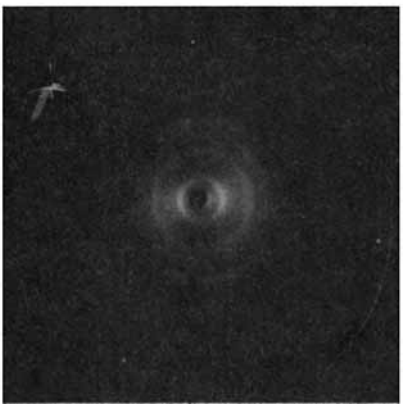
microfibrils in the fiber. Due to its very short length, ~ 1–2 mm, and brittle nature, the cellulose triacetate gave a poorer orientational pattern. The most obvious change occurring during acetylation is the development of a lattice spacing at 11.7 Å. Table I summarizes the lattice spacings for both cellulose and cellulose triacetate and corresponding spacings for the various models. Analysis of powder diffraction patterns for a series of acetylated samples leads to the intensity profiles shown in Figure 4. A plot of the [200] reflection as a function of the degree of acetylation, Figure 5 indicates an approximately linear variation. An increase in the intensity of the [200] reflection for the lowest degrees of acetylation indicates that reaction leads rapidly to a crystallizable cellulose triacetate structure. Warwicker and Spedding[2] have shown from infrared and X-ray measurements that crystalline triacetate exists at a DOS of 0.4. Dulmage[7] has shown that the crystallinity of cellulose can be enhanced by swirling the acetic acid. However, other authors have indicated that crystalline triacetate does not form below a DOS of 1. The X-ray data presented in Figures 4 and 5 indicates that acetylation increases the amorphous content but does also increase the crystalline content of cellulose acetate, consistent with Warwicker and Spedding's observations.[2] The samples with the highest degree of acetylation have a diffraction pattern almost completely due to the crystal lattice of cellulose triacetate, although the general increase in the level of amorphous scattering indicates a more imperfect structure than in the original cellulose linters.



(a)



(b)



(c)

Fig. 3. Diffraction patterns obtained cellulose and sense of the acetylated samples; (a) cellulose; (b) cellulose acetate DOS = 1.74; (c) cellulose acetate DOS = 2.94.

TABLE I
Comparison between X-Ray Spacings Observed in the Present Study and Those Calculated Using the Least Squares Approach of Arnott and Wonacott[15]

		d_{obs} (Å)	d_{calc} (Å)	Crystal plane
		Cellulose		
Equatorial reflections	(1)	6.13	6.10	(110)
	(2)	5.32	5.50	(110)
	(3)	3.91	3.93	(020)
Meridional reflections	(4)	5.06	—	(002)
	(5)	4.30	—	—
	(6)	3.18	—	—
	(7)	2.59	—	(004)
		Cellulose Triacetate I		
Equatorial reflections	(1)	11.74	11.8	(200)
	(2)	5.36	—	—
	(3)	4.14	—	—
Meridional reflections	(4)	3.41	3.48	(003)
	(5)	2.63	2.61	(004)

An absolute determination of the degree of crystallinity is limited by the uncertainty in the initial estimates of the amorphous scattering intensity. A comparison of the amosphous scattering halo with the intensity from the crystalline regions (Fig. 6) indicates a general increase in the noncrystalline content with increasing DOS. No significance should be attached to the actual values; however, the observed trend is real. These observations are consistent with the electron microscopic data, which reveals an opening of the structure on acetylation.

Positron Lifetime Measurements

The positron annihilation lifetime data is composed of three components. The two shortest lifetime components corresponding to annihilation of free and para positronium and a long lifetime component corresponding to ortho annihilation via a pickoff mechanism. The variation of the ortho positronium (σP) lifetimes and intensity as a function of the degree of acetylation and temperature are shown in Figure 7. As in other studies of polymers,[13] it is found that the free and para positronium annihilation rates were insensitive to any measurable physical or chemical characteristics of the material. In contrast, the ortho positronium annihilation does change with DOS and temperature.

The σP's is formed in voids in the polymer matrix. The nature of the process necessitates that these voids should be between 15 and 200 Å^3. The intensity of the σPs signal is proportional to the probability of the free positronium finding a void of molecular dimensions. The lifetime of the σPs is a function of the probability of electron exchange and is directly proportional to the overlap of the wavefunctions associated with the electron density of the

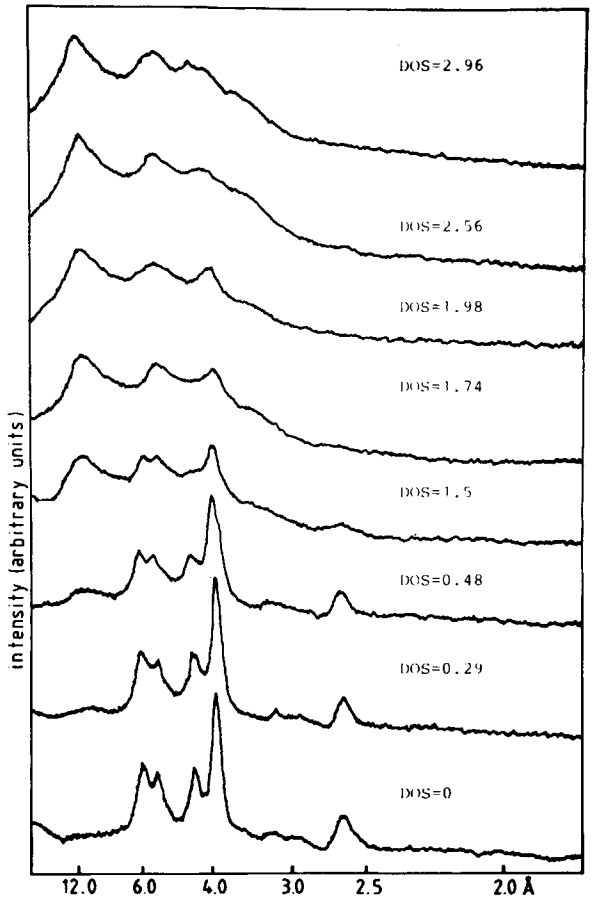


Fig. 4. Analysis of the intensity profiles of cellulose and cellulose acetate.

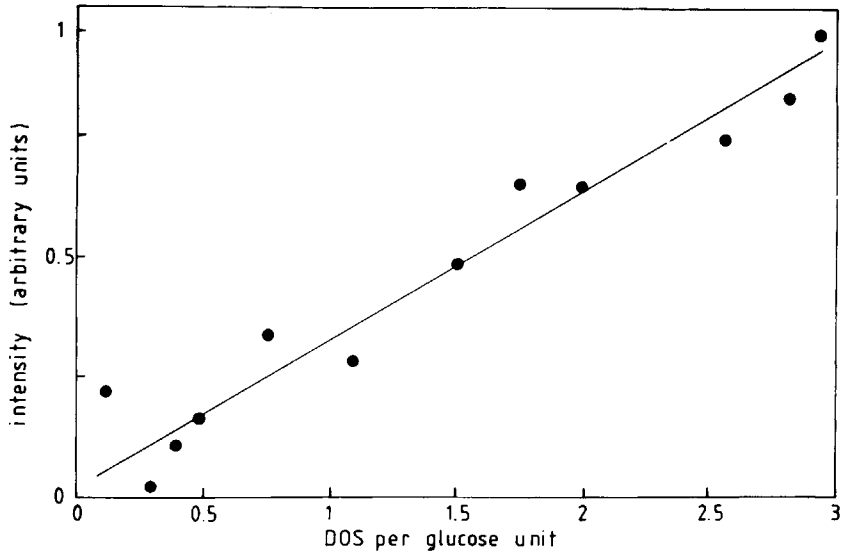


Fig. 5. Variation of the [200] reflection intensity as a function of the degree of acetylation.

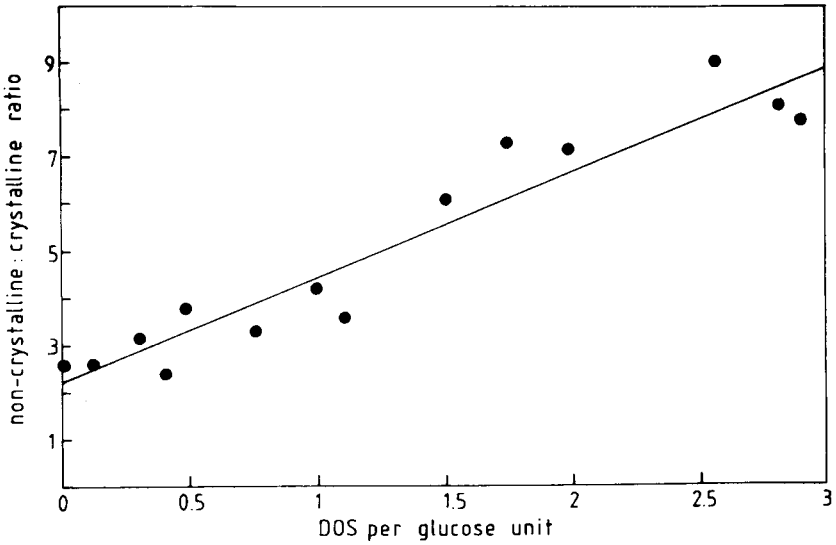


Fig. 6. Variation of the relative degree of crystallinity as a function of the degree of acetylation.

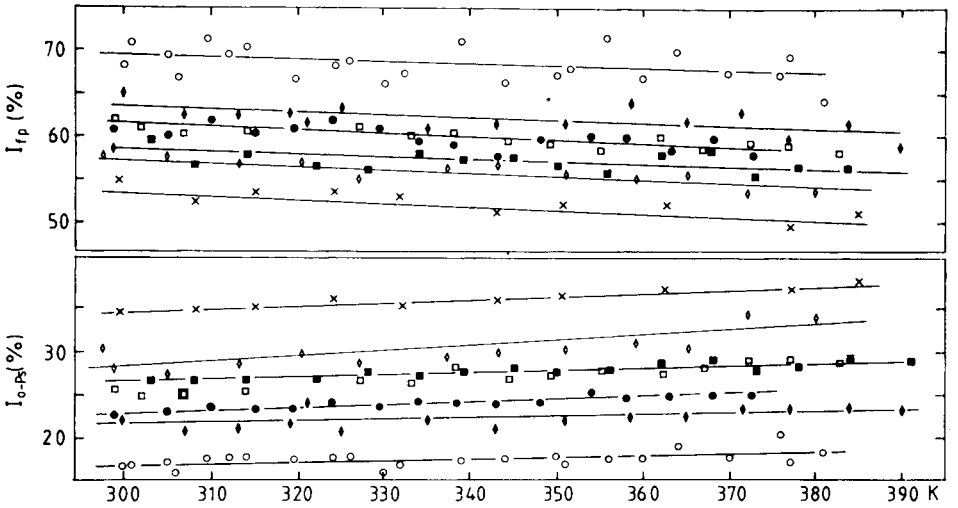


Fig. 7. Variation of the positron lifetimes and intensities with temperature for cellulose and cellulose acetates: (○) cellulose; (◆) DOS = 0.48; (●) DOS = 1.5; (□) DOS = 1.74; (■) DOS 2.53; (◇) DOS = 2.8; (×) DOS = 2.96.

positronium and that of the molecules forming the walls of the cavity. As a consequence, the lifetime is inversely proportional to the mean size of the cavity containing the positronium. Increasing the degree of acetylation has the effect of increasing the σPs lifetime; consistent with an increase in the fraction of noncrystalline material and an increase in the lattice spacing in the unit cell and the formation of a more open structure. A plot of the variation of the lifetime and intensity as a function of DOS, Figure 8 indicates that both the average size and number of defects increase significantly with extent of

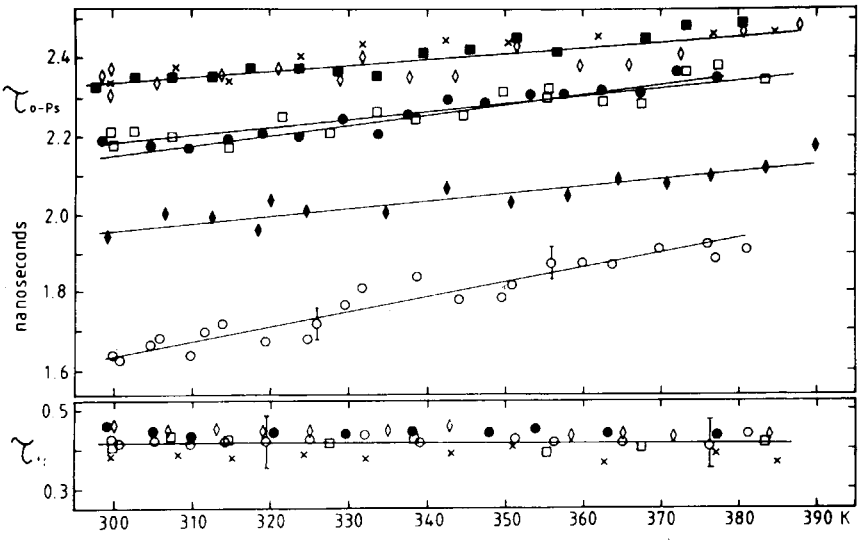


Fig. 7. (*Continued from previous page.*)

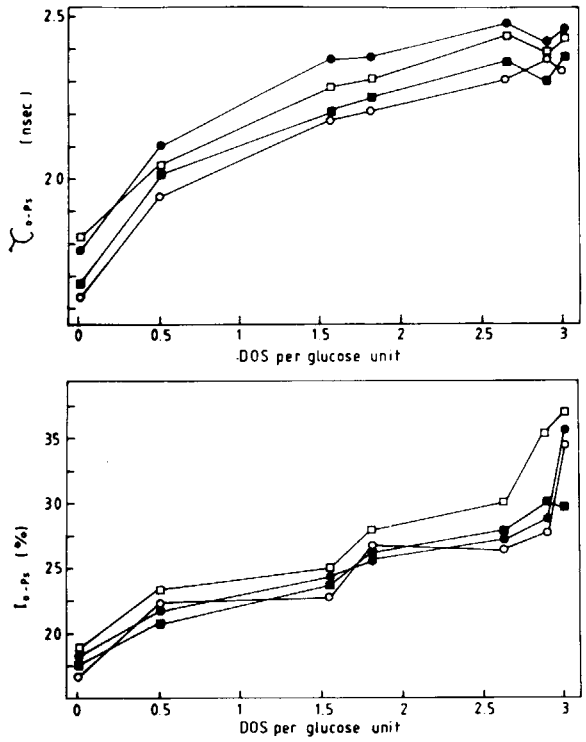


Fig. 8. Variation of the ortho positronium lifetime and intensity as a function of degree of acetylation: (○) −300 ± 1 K; (■) 325 ± 1 K; (●) −350 ± 1 K; (□) 375 ± 1 K.

acetylation. This data is consistent with the analysis of the amorphous content obtained from the X-ray data.

Density Variation with Degree of Acetylation

The density of cellulose based on its unit cell is 1.594 g cm^3 and the value for crystalline cellulose triacetate is 1.24 g cm^3. The variation of the bulk density with degree of substitution is shown in Figure 9. Departures from these theoretical values are due to imperfections in the crystal lattice and also in the interfibrillar arrangement.

CONCLUSIONS

Heterogeneous acetylation leads to a product which retains elements of the original order of cellulose, but has a slightly increased amorphous content. The X-ray data indicates that crystallization of the acetylated regions can occur at low degrees of substitution. Further acetylation leads to a breakup of the ordered crystalline regions in cellulose; yet reaction appears to be able to proceed with a retention of the crystalline structure originally present in cellulose. The electron microscopy and bulk density measurements indicate that the interfibrillar separation is increased by acetylation. The positron studies confirm the conclusions based on the X-ray data, which indicate that a loss of order occurs with acetylation; however, even in the triacetate there is a significant retention of structure at both the macro and microscopic levels.

In a recent paper,[14] we have compared solution and solid state ^{13}C NMR of cellulose and cellulose acetate prepared as indicated above. The solution spectra obtained in a mixture of morpholine *N*-oxide and dimethyl sulphoxide for samples with a degree of acetylation below 10% (DOS = 0.48) is a superposition of the spectra of cellulose, cellulose triacetate, and some partially substituted cellulose rings. Above a DOS of 0.48, the solution spectrum corresponds to that of the triacetate and lacks evidence of either partial substitution or of unsubstituted cellulose. However, the solid state spectrum indicates the existence of unsubstituted and partially substituted cellulose above a DOS of 0.48, indicating that the acetylation reaction are generating nonsoluble partially substituted ordered regions. Above a DOS of 2.0, the presence of unsubstituted cellulose in the spectrum is not detected and the spectrum is consistent with acetylation occurring in ordered regions.

Heterogeneous acetylation of cellulose can be subdivided into three stages. Initial reaction occurs in amorphous regions and on the surface of the microfibrillar structures. This reaction occurs with an increase in the average number and size of defects present. There is little evidence for selective substitution of the cellulose ring at the 3, 4, and 6 positions, and some crystallization of these substituted chains appears possible.

Once acetylation has occurred at these accessible sites, subsequent acetylation must involve reaction in the crystalline regions. Reaction appears to be able to proceed without destruction of the original cellulose structure. Up to a DOS of 2.0 unsubstituted cellulose structures are detected. Above a DOS of 2.0, acetylation is occurring at all levels, and there is a loose of the spectrum of unsubstituted cellulose in the solid state ^{13}C NMR. The X-ray, positron, and electron microscopy data support the retention of structure in the partially and completely substituted cellulose acetate.

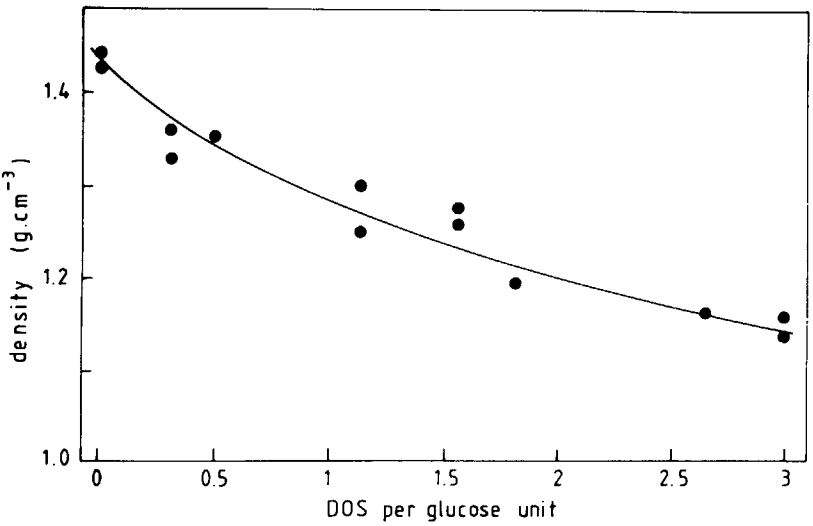


Fig. 9. Variation of bulk density as a function of the degree of substitution of cellulose linters.

It is clear that conversion of cellulose to cellulose acetate is a complex process morphologically; however, the reaction is possible with both a high level of local order at the molecular, microfibrillar, fibrillar, and fiber levels. Amorphous structure is generated during the acetylation process; however, this is not sufficiently extensive to destroy the overall fibrous structure of the product.

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