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Influence of the degree of substitution and pretreatments on the surface structure of cellulose nitrate fibres *

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Summary: Cellulose nitrate fibres of three different degrees of substitution (DS) were prepared by heterogeneous reaction. The fibre surfaces were observed in the scanning electron microscope. Apart from the DS the influence of pretreatments such as prenitration and boiling of the fibres prior to nitration was studied. The results reveal an interaction between the cell wall layers and the esterification and swelling capacity of the nitration medium. In all cases the DS was determined by the composition of the nitration medium. A pretreatment influenced the fibre surfaces after nitration. The peculiar role of the primary wall during esterification is emphasized.

Introduction

Native cellulose forms a well organized system within the plant cell walls in order to guarantee their mechanical stability. The structural elements of the cell wall are the fibrils in which the cellulose molecules are well ordered by mutual formation of hydrogen bonds. In addition, the fibrils are more or less densely packed within the various cell wall layers.

For the derivatization of cellulose in a heterogeneous system these structural factors have a great influence on the accessibility and reactivity of the hydroxy groups. The nitration of cellulose represents the oldest kind of derivatization on an industrial scale. For the reactions which take place during the nitration two different models are discussed (Balser et al. 1986; Munro, Short 1987). In the heterogeneous model type, the reaction takes place primarily in the easily accessible domains. The reaction is inhibited in the crystalline domains because of the relatively strong H-bonds of the hydroxy groups in the crystalline lattice. The average degree of substitution (DS) is determined by the ratio of the totally substituted accessible domains to the unsubstituted core of the crystalline domains. The other model of reaction starts from a uniform reaction of cellulose in all structural domains. In this case the DS is determined by the chemical equilibrium between the nitration and denitration reactions.

The derivatization causes a variation in the chemical structure of the cellulose molecule, which influences the supramolecular structure of the cell wall and the entire fibre. The aim of this study was to observe the fibre surfaces regarding various degrees of substitution and pretreatments.

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Experimental

Bleached and ground cotton linters (Type E 4000, Hercules) were used as starting material for nitration. Different degrees of substitution (DS) were obtained by treating the fibres with mixtures of nitric acid, sulfuric acid and water of varying component concentrations (Green 1963). Cellulose nitrates of three DS were prepared, corresponding to the substitution of approximately one, two or three OH groups (Table 1).

Apart from a one-step nitration the cotton fibres were also nitrated in two or three steps starting from a low nitrated cellulose (DS 0.9). This nitrate was treated with a nitration mixture that had been used previously to produce a medium nitrated sample (DS 1.8). A portion of the latter sample was further treated with a nitration mixture that had been used previously to produce a highly nitrated sample (DS 2.8) (Table 1).

Another portion of linters was boiled in water for 10 minutes before it was subjected to the nitration procedure. The boiling was carried out either by heating on a hot-plate or by microwave radiation (2.45 GHz, 600 kW).

Before the specimens were observed in the scanning electron microscope (SEM; Leitz AMR 1200 B) they were coated with gold-palladium.

Results

Cotton linters

For comparison with the nitrated fibres, the starting material was also observed in the SEM. The linters fibres are flat ribbons with diameters between 10 and 30 µm. According to the ground condition the fibres are fragmented and have frayed ends. The surfaces are relatively smooth, and only some fibrils or fibrillar bundles are torn out of the surface (Fig. 1).

It is worth mentioning that the linters fibres are more sensitive to the electron beam than the nitrated fibres. The fibre walls tend to form a bubble during the exposure of a small area to the electron beam (Fig. 1).

One-step nitration

Nitrate fibres of low DS already show a changed surface structure compared to the original linters fibres. The surface is partially covered with a fluffy layer of fine fibrils (Fig. 2). Under this coating a loose fibrillar texture appears.

Table 1. Degrees of substitution of the cellulose nitrate samples

Nitration procedure	Degree of substitution		
One-step nitration	0.9	1.8	2.8
Two-step nitration	–	1.8	–
Three-step nitration	–	–	2.7
Bioling prior to one-step nitration	1.0	1.9	2.7

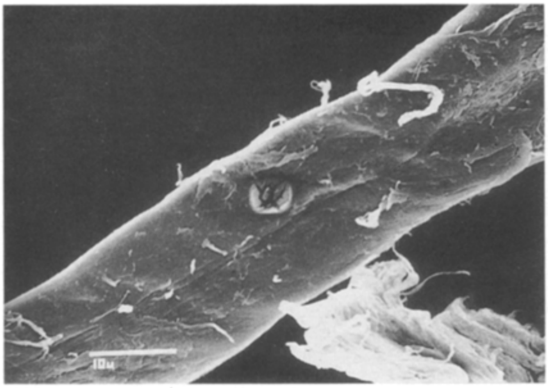

Fig. 1. Linters fibre with a damage by electron beam radiation (centre)

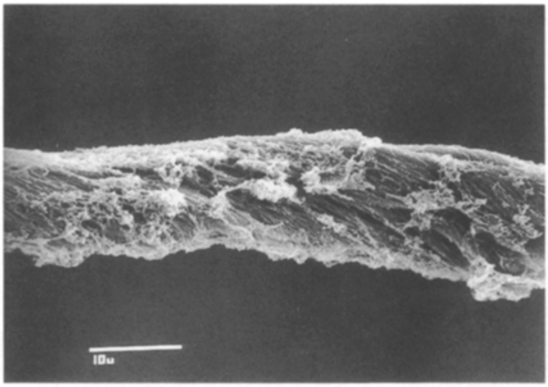

Fig. 2. Cellulose nitrate fibre (DS 0.9) prepared by one-step nitration

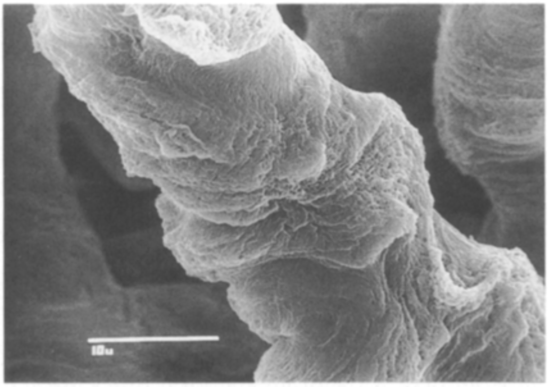

Fig. 3. Cellulose nitrate fibre (DS 1.8) prepared by one-step nitration

The nitration resulting in a medium DS (1.8) completely changes the fibre form. Most of the fibres are strongly bent and twisted. They show a warped and swollen surface (Fig. 3). The fibre fragments are aggregated and their ends are rounded (Fig. 4).

The highly nitrated fibres (DS 2.8) are similar to the original linters. A higher magnification, however, reveals a dense network of fine pores at the fibre surface

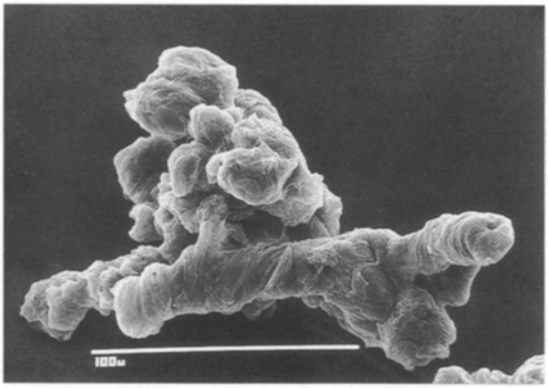

Fig. 4. Aggregated fibres of cellulose nitrate (DS 1.8) prepared by one-step nitration

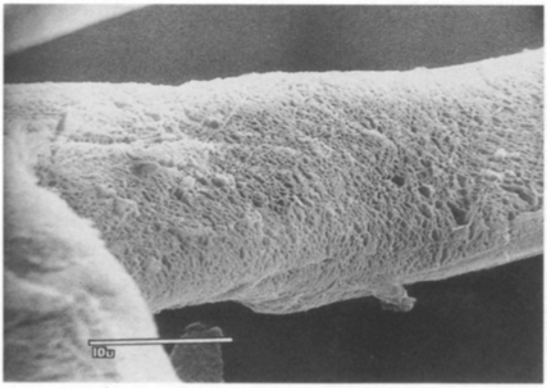

Fig. 5. Cellulose nitrate fibre (DS 2.8) prepared by one-step nitration

(Fig. 5). The pore sizes are between 0.2 and 1.0 µm in diameter. They show a regular arrangement and follow the screw-like texture of the fibrils in parallel lines. The fibres themselves seem to be rigid with occasionally sharp-edged cracks.

Multiple-step nitration

Great differences were observed with nitrate fibres obtained by two- and three-step nitration compared to samples from a one-step nitration. Although the same DS was reached the surface structures are not comparable.

The behaviour of the low nitrated fibres in the nitration mixture used for increasing the DS was already quite different from that of the original cotton fibres as they dispersed easily in the reaction mixture and did not aggregate.

The nitrate fibres of DS 1.8 derived from the two-step nitration are very similar to the fibres of low DS (Fig. 6). The surface is covered with a fluffy coating and the fibrillar texture of the layer below is clearly visible. By twisting during the chemical treatment the fibrillar texture is more or less split.

After the third nitration step, which results in a high DS, the structures formed during the preceding nitration steps are maintained: fluffy coating, split fibrillar

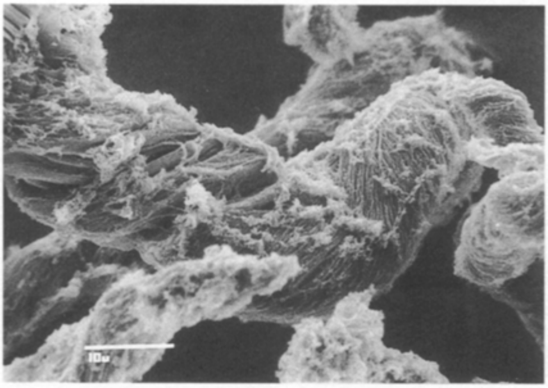

Fig. 6. Cellulose nitrate fibre (DS 1.8) prepared by two-step nitration

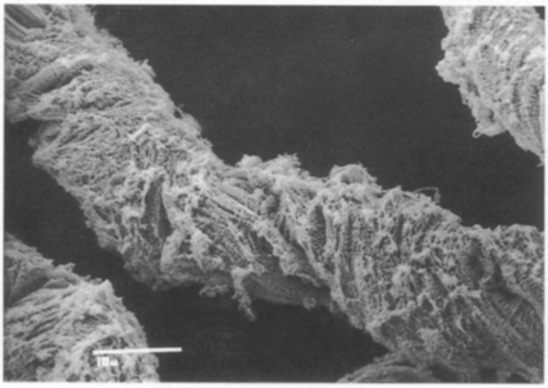

Fig. 7. Cellulose nitrate fibre (DS 2.7) prepared by three-step nitration

texture underneath. Additionally, fine pores appear along the fibrillar bundles (Fig. 7).

Effects of boiling

As shown in Table 1, the DS obtained by nitration of pretreated cotton linters was the same for the original fibres. Nevertheless, boiling of fibres prior to the nitrating procedure resulted in some changes of the fibre structure. No different effects, however, could be found in the structure when comparing boiling by heating and boiling by microwave radiation.

The nitrate fibres of low DS are relatively smooth without any coating. The fibrillar texture of the fibre surface is helically split to varying extents (Figs. 8 and 9). Fibrillar bundles and lamellae may be torn out of the surface (Fig. 9).

During nitration to a medium DS the fibres are obviously subjected to extensive swelling; thus the nitrate fibres are warped and deformed. The fibre in Fig. 10 shows a screw-like shape and a rounded end. Deep notches and indentations follow the screw thread.

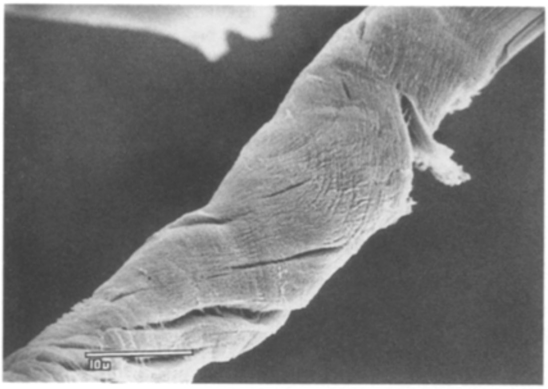

Fig. 8. Cellulose nitrate fibre (DS 1.0) boiled by heating prior to nitration

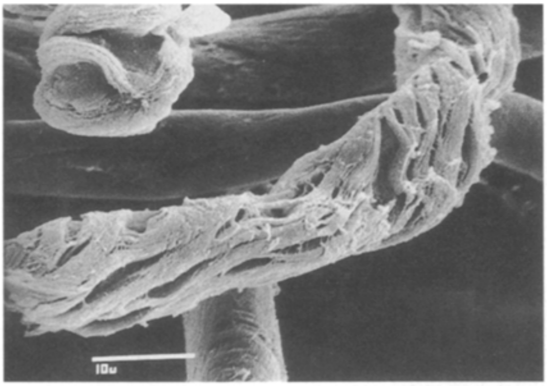

Fig. 9. Cellulose nitrate fibre (DS 1.0) boiled by microwave radiation prior to nitration

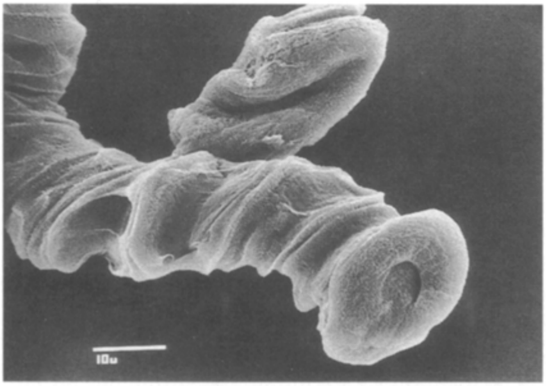

Fig. 10. Cellulose nitrate fibre (DS 1.9) boiled by microwave radiation prior to nitration

Highly nitrated fibres seem to be very rigid and brittle. They are often split along the run of the fibrils, resulting in a helical shape (Fig. 11). At higher magnification a dotting of the fibre surface with fine pores is visible (Fig. 12).

Discussion

The polyalcoholic character of cellulose is used for variation of the properties of cellulose by esterification and etherification. One of the cellulose derivatives of indus-

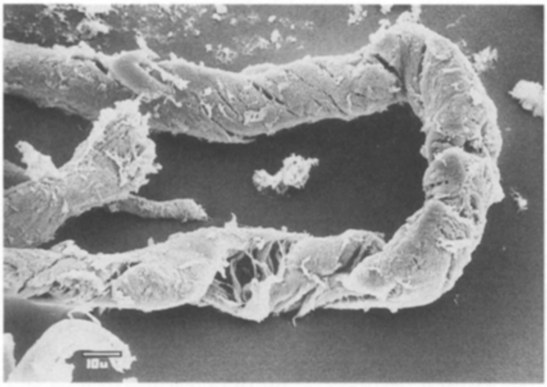

Fig. 11. Cellulose nitrate fibre (DS 2.7) boiled by microwave radiation prior to nitration

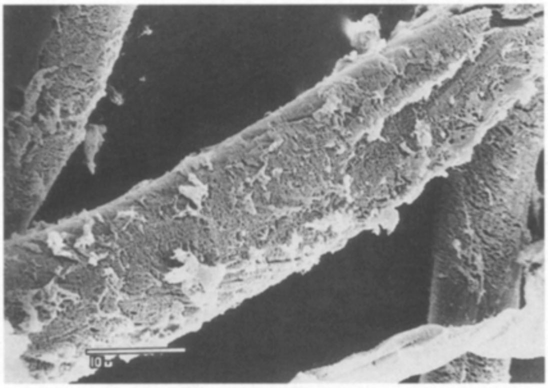

Fig. 12. Cellulose nitrate fibre (DS 2.7) boiled by heating prior to nitration

trial interest is cellulose nitrate, which is produced with different degrees of substitution for various purposes.

The reaction for nitrating cellulose fibres is generally carried out in a heterogeneous system. Thus the reaction is influenced by the supramolecular organization of the cellulose molecules. The esterification is impeded on the one hand by the H-bonds between hydroxy groups within the crystalline domains of the fibrils and on the other hand by the texture of the cell wall layers. A peculiar role as a constricting layer for swelling of the cell wall is attributed to the primary wall (Bucher, Widerkehr-Scherb 1948; Rollins, Tripp 1963; Philipp, Purz 1977). The results of this study reveal an interrelation between cell wall layers and the esterification and swelling capacity of the nitration medium.

The nitration resulting in a cellulose nitrate of low DS occurs mainly at the fibre surface. The primary wall forms a fluffy coating and is obviously completely nitrated. The secondary wall layer underneath seems to be nitrated only on the surface, and the nitration mixture was obviously prevented from penetrating the inner layers of the fibres. The core of the cellulose fibres remains unsubstituted as proved by polarization microscopy and micro-FTIR spectroscopy (Ludwig 1990; Ludwig, Fengel 1992).

The nitration mixture applied for a di-substitution has a high swelling capacity, and the mixture can penetrate the whole fibre. The esterification capacity, however, is not sufficient for the substitution of all OH groups. Cellulose molecules with an average of two nitrate groups per anhydroglucose unit are not able to form crystalline lattices; they aggregate in an amorphous state. The amorphous arrangement at the molecular level results in a distended, warped shape of the nitrate fibres, which may be further influenced by the primary wall.

For an approximately tri-substituted cellulose nitrate a complete penetration of the fibres by the reaction mixture is required. Cellulose nitrate molecules containing three nitrate groups per anhydroglucose unit are able to form crystal lattices (Meader et al. 1978; Viney, Windle 1987). Therefore, the nitrate fibres show almost the same shape as the original cotton fibres. A characteristic feature of highly nitrated cellulose is a system of tiny pores at the fibre surface. The formation of these pores was explained by Mann and Patrick (1983) by a partial dissolution and by drying effects.

A pretreatment of the fibres such as prenitration or boiling did not influence the degree of substitution. The DS was determined in all cases by the composition of the nitration mixture. The pretreatment, however, influenced the surface structure of the fibres.

The stepwise nitration shows that the structure of the monosubstituted cellulose persists in higher substituted samples. The loosening and separation of the primary wall and the partial nitration of the surface of the secondary wall make the wall layers underneath more accessible to penetration. Therefore a reaction mixture with a high swelling capacity results in a loosening of the fibrillar texture.

Boiling of the fibres prior to nitration obviously removes most of the primary wall. Thus the chemical reaction distends the fibrillar texture of the secondary walls. Even the swelling effects of the di-substituted fibres follow the run of the secondary wall fibrils in a screw-like shape.

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