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The Effect of Multiple Swelling Treatment with Ethylenediamine on Cotton Cellulose

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Synopsis

Cotton cellulose was subjected to repeated swelling treatment with aqueous solutions of ethylenediamine (EDA). Although EDA is capable of effecting a lattice change from cellulose I to cellulose II during successive swelling treatments, resistance to lattice transformation is offered during the first treatment in spite of the formation of cellulose–EDA complex. This is attributed to a structural hinderance existing in the cellulose molecule itself. There is considerable improvement in the lateral order of the treated cellulose on subjecting it to repeated swelling operations with EDA.

INTRODUCTION

The effects of aqueous solutions of alkali and amines on cotton cellulose have been studied by several workers, and these reagents have been invariably considered to cause lattice disorder in cellulose.[1] The effect of the concentration of ethylenediamine (EDA) in water has been studied by Segal and Creely,[2] Oltus and Eliasova,[3] Hennige,[4,5] and Patil et al.[6] With solutions of concentrations below 60% to 70% EDA, very little decrystallization of cellulose I lattice has been reported. At higher concentrations, the decrystallization increases with concentration, to reach a maximum at a critical concentration of 80%.[6] It has been postulated[1] that up to a concentration of about 60%, the ethylenediamine forms a complex with water, and above this concentration free ethylenediamine exists in the solution.

Most of the above swelling studies by alkali and amines, however, are on materials which have been subjected to a single swelling treatment. The possibility of observing significant changes in the fiber structure as a result of repeated swelling of the cellulose material is being studied in this laboratory. Extensive work of multiple swelling treatment of cellulosic fibers in aqueous solutions of alkali has already been reported.[7] A highly ordered cellulose II structure is obtained by repetitive treatment with alkali solutions due to hornification of fibrils. The purpose of the present communication is to report the effect of multiple swelling treatment with EDA and its aqueous solutions on cotton cellulose.

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EXPERIMENTAL

Materials

Sudan cotton was selected for the treatments. EDA of analar grade was used, and chemical assay showed that the purity of the reagent was 99%. The reagent was not dried over metallic sodium in order to avoid the presence of any free alkali. For convenience, this 99% reagent shall hereafter be referred to as anhydrous EDA. EDA solutions of 50% (wt/wt) and 85% (wt/wt) were also used.

Methods

All the treatments with 50% and 85% solutions were carried out at 0°C for the duration of 1 hr each in slack condition. The treatment with anhydrous EDA is carried out at 10°C for the duration of 1 hr each in slack condition. Thereafter, the material was thoroughly washed in ice-cold water and finally in running water before being oven-dried at 100°C. The same sample was subjected to similar treatments repeatedly.

Thus, (1) one set of cotton samples were swollen in 50% aqueous solution of EDA at 0°C ten times for 1 hr each time; (2) one set of cotton samples were swollen in 85% aqueous solution of EDA at 0°C 50 times for 1 hr each time; (3) one set of cotton samples were swollen in anhydrous EDA at 10°C ten times for 1 hr each time; and (4) one sample of cotton was continuously swollen in 85% aqueous solution of EDA at 0°C 50 hours in a single step.

X-Ray Examination

Nickel-filtered CuK_α radiation from a Philips 1009 unit operated at 35 KV and 20 mA was used. Data were gathered by reflection technique using a divergence slit of 1°, a receiving slit of 0.05, and a scatter slit of 1°. For the diffractometer studies, the samples were cut with a pair of scissors, sieved through a 300-mesh screen, and made into rectangular pellets weighing exactly 100 mg, with the aid of a special die as in earlier studies. All x-ray examinations were carried out at 50% R.H.[8]

Measurement of Lateral Order

As in previous studies,[7,8] the variations in the lateral order in cellulose II samples were followed by studying the improvement in the resolution of the $10\bar{1}$ and 002 interferences which generally overlap and are expressed in terms of the *R* factor. In the case of cellulose I diagram, the total order in the fiber was estimated by measuring the half-width of the 002 peak.

RESULTS AND DISCUSSION

It is found that on repeatedly swelling cotton cellulose with 50% EDA, the 002 reflection in the cellulose I diagram sharpens. The half-width of the 002 peak of cellulose I is reduced from 1.65° for raw cotton to 1.25° for the sample repeatedly treated ten times, indicating that the total order in the fiber is increased

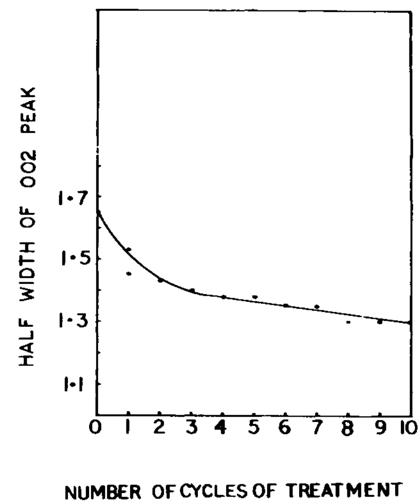

Fig. 1. Variation in half-width of the 002 peak in scans of cotton repeatedly treated with 50% EDA for ten cycles.

considerably (Fig. 1). It is also found that the repeatedly treated sample exhibits far more order than the hydrolyzed product of raw cotton which has a half-width of only 1.4° (Fig. 2). It is further observed that the repetitive swelling treatments definitely improve the resolution of the $10\bar{1}$ and 101 interference of cellulose I. In order to ascertain that 50% EDA solution does not disrupt the cellulose I lattice, an x-ray diffractogram of the sample swollen with 50% EDA for 1 hr and still wet with the reagent was taken (Fig. 3). It is found that 50% EDA solution does

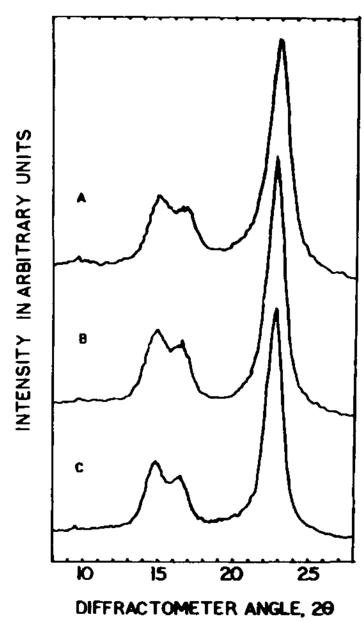

Fig. 2. Diffractometer scans of cottons: A, raw cotton; B, raw cotton hydrolyzed in 1 *N* HCl for 1 hr; C, raw cotton repeatedly treated with 50% EDA for ten cycles.

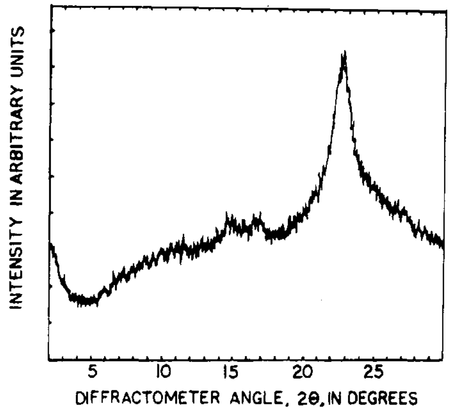

Fig. 3. Diffractometer scan of cotton wetted with 50% EDA for 1 hr.

not disrupt the lattice, and as such there is no formation of EDA cellulose complex at this concentration, as is evident by the sharp 002 reflection. It may, therefore, be inferred that during these treatments with 50% EDA, only interfibrillar swelling takes place without causing any disruption of the lattice. It is thus possible to improve the structural order of cellulose I without disrupting the lattice by repetitive swelling treatments at low concentrations of EDA in aqueous solutions. The moisture contents of native and treated cotton fibers were estimated and are found to be 6.19% and 5.21%, respectively. The decreased sorptive capacity of the repeatedly treated sample as compared to that of raw cotton confirms the increase in hydrogen bonding in the repeatedly treated samples. From this it can be concluded that it is the fibrillar aggregation which mainly contributes to the increased resolution of the x-ray diagram rather than the lattice order.

During the present study, it was observed that multiple swelling treatment with 85% EDA on cotton cellulose can produce a cellulose II structure which has not been observed hitherto after a single swelling treatment. The transformation of cellulose I to cellulose II structure to an observable extent starts taking place after the second repetitive treatment. The diffractogram of the sample treated 50 times is shown in Figure 4. The variation in the resolution of the $10\bar{1}$ and 002

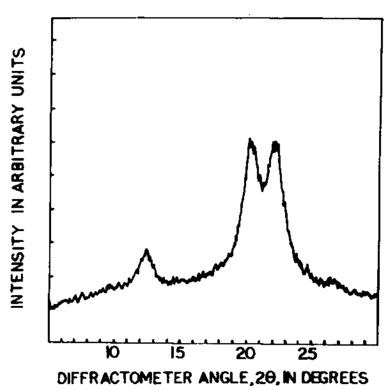

Fig. 4. Diffractometer scan of cotton repeatedly treated in 85% EDA for 50 cycles.

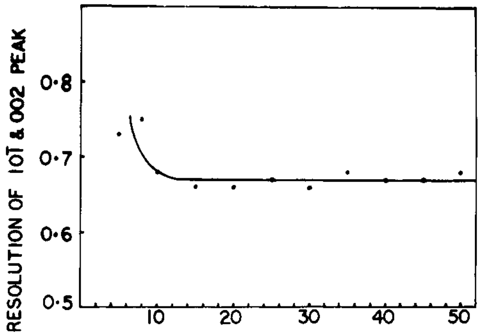

Fig. 5. Variation in the resolution of the 10Ī and 002 peaks in the scans of cotton repeatedly treated with 85% EDA for 50 cycles.

peaks in the scans of cotton treated with 85% EDA for 50 cycles is shown in Figure 5. The intensity ratios of the 002 and 10Ī peaks of cellulose II stabilizes to a value of 1.08 after 30 to 35 cycles of treatment (Fig. 6). This ratio 1.08 is quite acceptable as found in previous studies.[7,9]

The repetitive swelling treatments were found to improve the resolution of the 10Ī and 002 peaks, sharpen the 101 peak and reduce the background (Fig. 4). The final resolution attained for cotton after 50 cycles of treatment in 85% EDA is the same as that obtained by an equivalent sample repeatedly mercerized in 20% sodium hydroxide at 0°C for five cycles. That this increase in order is not due to drying of the treated sample at 100°C alone was observed in another study.[10]

The effect of multiple swelling treatments on cotton cellulose with anhydrous EDA for ten cycles is found to be nearly the same as that on the sample treated with 85% EDA for ten cycles. The ratio of 10Ī and 002 peaks is found to be almost the same after ten cycles of repetitive treatments in both the cases. The half-widths of the 002 peak after the first 1 hr of treatment with 85% EDA and anhydrous EDA are found to be 1.70° and 1.80°, respectively, which shows that the decrystallization effect on cellulose I is greater at higher concentrations of EDA. This is not in conformity with the findings of the earlier workers.[6] In the case of cotton treated with 50% EDA for 1 hr, it was found that there is no

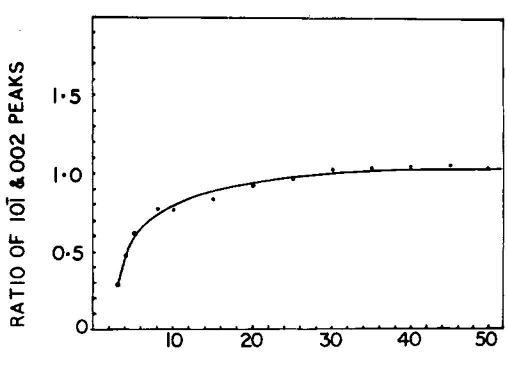

Fig. 6. Ratio of intensities of 10Ī and 002 peaks in the scans of cotton repeatedly treated in 85% EDA for 50 cycles.

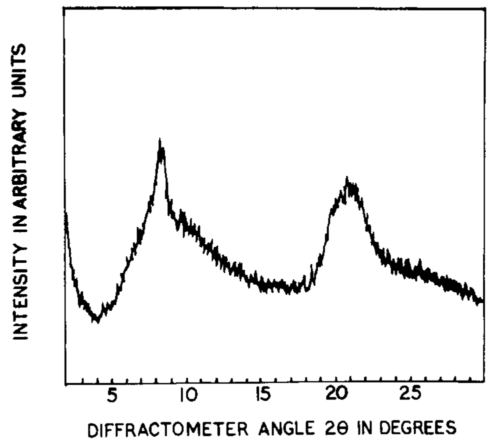

Fig. 7. Diffractometer scan of the cellulose–amine complex wetted with 85% EDA for 1 hr.

decrystallization of cellulose I taking place. On the contrary, the 002 peak sharpens which shows that there is an improvement in the total order within the fiber.

In order to compare the effect of multiple treatment with that observed during a single continuous treatment, one sample of raw cotton was swollen continuously for 50 hr in 85% EDA solution at 0°C, in a single step. It was found that continuous swelling treatment causes the broadening of the 002 peak accompanying a complete loss in resolution of $10\bar{1}$ and 101 peaks, indicating the profound decrystallization of cellulose I. There is, however, no lattice conversion from cellulose I to cellulose II in continuous swelling, irrespective of the duration of treatment. This clearly demonstrates that swelling and deswelling for short intervals of time is more effective than a single continuous swelling treatment for a long interval of time.

Thus, while repetitive treatments with EDA was able to achieve a lattice transformation from cellulose I to II, a single treatment, carried out even for long durations, failed to achieve the same result. The question then arose whether a cellulose–EDA complex was formed during a single treatment or only in subsequent treatments. To this end, an x-ray scan of cotton sample treated with 85% EDA for 1 hr with excess EDA removed was taken and is shown in Figure 7. Comparing this diffractogram with that for the sample treated with 50% EDA for 1 hr, one finds a change in the interplanar spacings of (101) and ($10\bar{1}$) planes, clearly indicating that on treatment with 85% EDA, almost all of the hydrogen bondings in cellulose I are broken and a cellulose–EDA complex is formed. But on washing, this complex reverts back to cellulose I rather than to cellulose II, which is preferred. This inability of the molecular ensemble to change its lattice to a lower energy level indicates that there is some hindrance present in the structure of the cellulose molecule which prevents the lattice transformation from cellulose I to cellulose II during the first treatment. It appears that this structural hindrance is, however, overcome during the subsequent repetitive treatments. Such behavior has not been observed in treatments with alkali solutions where the lattice transformation accompanies bond breaking and resultant soda–cellulose complex.

It has been suggested by earlier workers that the amines penetrate the crystalline regions by breaking of hydrogen bonds lying mainly in the (002) plane. With monofunctional swelling agents like methyl and ethyl amines, a lattice conversion from cellulose I to cellulose III occurred generally after the decomposition of the unstable cellulose monoamine complex. It was postulated[11,12] that anhydroglucose units, free from the interchain bonding, rotate around their long axis (*b*) to form cellulose III lattice. However, in the case of difunctional agents (diamines), crosslinking of the cellulose molecules via the swelling agent is envisaged, and this then prevents the rotation of the anhydroglucose units thereby hindering any lattice transformation. The very foundation of this hypothesis, i.e., the nonoccurrence of the lattice transformation now stands completely ruled out, as the present study shows clearly that the diamines also can cause a lattice transformation. As such, there can be no crosslinking of the cellulose chains by the diamine molecules as has been suggested earlier[11,12] as the complex decomposes to form cellulose II lattice during subsequent repeated treatments. It may be that the structural hindrance is due to an intramolecular bond other than hydrogen bonding.

CONCLUSIONS

1. It is possible to improve the total order in the cotton cellulose without disrupting the lattice or without losing the fiber structure by repetitive swelling treatments with low concentrations of aqueous solutions of EDA.

2. Although during the first hour of treatment with 85% EDA the cellulose intermolecular bonds are broken forming a cellulose–diamine complex, the structure, however, reverts back to cellulose I after washing with water. It is, therefore, concluded that there exists in the cellulose molecule a structural hindrance, apart from hydrogen bonding, which prevents the formation of cellulose II structure during a single swelling treatment with EDA.

3. It is observed that EDA of higher concentration can convert cellulose I structure to cellulose II structure. Such transformation, however, takes place only during subsequent repetitive treatments.

4. Repetitive swelling treatment is more effective than a single continuous treatment.

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