# Infrared Spectroscopic and Dielectric Studies of Swollen Cellulose

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## Synopsis

Infrared spectra of treated cotton linters and bleached cotton stalk pulp with different concentrations of ethylene diamine and zinc chloride solution are studied. The structural changes brought about by these treatments have been studied from infrared spectral diagrams. It is found that the crystallinity index calculated from the infrared spectral data of these treated pulps decreases with increasing concentration of ethylene diamine and zinc chloride. The decrease in the crystallinity index (CrI) of the treated pulp with zinc chloride is higher than in case of treatment with ethylene diamine (EDA). The detectable frequency change at the hydrogen bonded OH of cotton linters by treatment with zinc chloride and ethylene diamine reflects the contributions of this bond in the swollen pulp. The dielectric study of these treated pulps confirmed the molecular structural changes determined from IR spectroscopic study.

## INTRODUCTION

Fine structural changes in cellulose brought about by different swelling agents have been studied extensively. Segal and co-workers[1,2] as well as Patil et al.,[3] in their extensive studies on the swelling and decrystallization of cellulose with ethylene diamine, reported that the cellulose I lattice structure is retained in the treated fiber. However, most of these studies are based on a single step swelling of cotton in reagents. Manjunath and Venkataraman[4] reported that the lattice order obtained after successive treatments in sodium hydroxide solution is higher than that obtainable during single step swelling. On the other hand, metal chloride solution (e.g., Zn and Li chloride) are used as swelling and decrystallizing agents for cellulosic materials.[5,6] Petitpas and Mering[7] reported that the transition of form cellulose I to form cellulose II is not only due to molecular rearrangement but also to rotation of glucose rings around the glucosidic bonds. This could happen only if the swelling agent is a monofunctional reagent, e.g., ethylamine.

The aim of this work is to study the structural changes and dielectric properties of cotton linters and bleached cotton stalk pulp brought about by different concentrations of ethylene diamine and zinc chloride solutions.

## EXPERIMENTAL

### Materials

The raw materials used in this study were cotton linters (delivered from Factory of 81, Abu-Zaable, Egypt) and bleached cotton stalk pulp.[8] These pulps have the following analysis:

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| | α-Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|
| Cotton linters | 99.1 | — | — |
| Cotton stalk pulp | 82.1 | 16.2 | 1.64 |

Reagent grade ethylene diamine and zinc chloride were used.

### Methods

The pulps were subjected to the following treatments:

1. Treatment with EDA of different concentration (25–100% v/v) with liquor ratio of 30 : 1 for 20 min at 10°C. Treated samples were filtered and washed until free from ethylene diamine.
2. Treatment with zinc chloride solution of different concentrations (66, 75, and 85% w/w) with liquor ratio of 30 : 1, for 20 min at 35°C. Other samples were treated with 66% zinc chloride solutions for 30 and 40 min. After treatments, samples were washed with water until free from $ZnCl_2$.

Loosely held water in the treated samples was removed by suction and final traces were removed by a solvent exchange technique using dry methanol and dry ether.

The infrared spectra of the samples were recorded on a Beckman 4250 spectrophotometer. The samples were prepared for spectral scanning as KBr discs. Each sample was scanned five times. The resolution of the instrument is 2 $cm^{-1}$.

For the dielectric measurements, the samples were prepared in the form of discs 12 mm in diameter and 2 mm thick under a constant pressure of 10 ton/$cm^2$ using a hydraulic pressing machine. An automatic precision bridge type ALCB from Rhode and Schwartz (Munchen, West Germany) was used for capacitance measurements from which the permittivity $\epsilon'$ is obtained and also for measuring the power tan $\delta$ from which the dielectric loss $\epsilon''$ is obtained. The measurements were carried out at frequency of 1 kHz and temperature of 25°C. The accuracy of measurements in capacitance was ± 0.1% while for tan $\delta$ it was ± 5%. The investigated samples were heated in an oven at 70°C for 24 h and kept in a desiccator to avoid water absorption.

## RESULTS AND DISCUSSION

The IR spectra of the treated cotton linters with ethylene diamine of different concentrations (25–100% v/v) are shown in Figure 1. O'Connor and co-workers[9] assigned the 7 μm (1430 $cm^{-1}$) absorbance band to crystalline form and 11 μm (900 $cm^{-1}$) to the amorphous form in origin.

From Figure 1 it is clear that the treatment of cotton linters with ethylene diamine produced a detectable change in the intensities of the two bands (1430 and 900 $cm^{-1}$). This means that the treatment causes a change in lateral order of cellulose I and cellulose II. The crystallinity index (CrI) of the treated cotton

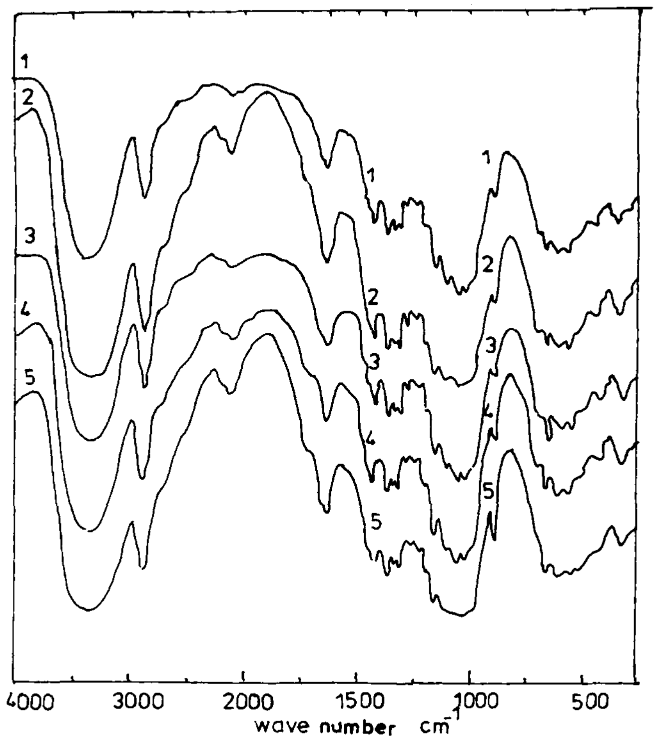


Fig. 1. IR spectra of untreated cotton linters (1) and cotton linters treated for 20 min with EDA concentrations of 25% (2), 50% (3), 75% (4), and 100% (5).

linters with different concentrations of ethylene diamine, measured according to the absorbance ratio ($a_{1430}/a_{900}$), are found in Table I. These results of (CrI) are the mean value of the results produced from five charts of five discs of the same sample with experimental error ± 2%. From this table, it is clear that the crystallinity index decreased (i.e., increase of decrystallization and disordered

TABLE I
Effect of the Treatment with Ethylene Diamine and Zinc Chloride on the Crystallinity Index of Cotton Linters

| Treatments | Time (min) | CrI ($a_{1430}/a_{900}$) | Decrease in CrI (%) |
|---|---|---|---|
| Untreated pulp | — | 2.15 | — |
| 25 EDA | 20 | 1.90 | 11.15 |
| 50 EDA | 20 | 1.66 | 21.90 |
| 75 EDA | 20 | 1.36 | 36.80 |
| 100 EDA | 20 | 0.65 | 74.70 |
| 66 $ZnCl_2$ | 20 | 1.30 | — |
| 75 $ZnCl_2$ | 20 | 1.14 | — |
| 85 $ZnCl_2$ | 20 | 1.75 | — |
| 66 $ZnCl_2$ | 30 | 1.14 | — |
| 66 $ZnCl_2$ | 40 | 1.09 | — |

regions) even by treatment of the cotton linters with low concentrations of ethylene diamine. The decrease in crystallinity index changed from 2.15 for the untreated sample, to 1.9 and 0.65 for samples treated with 25 and 100% ethylene diamine, respectively. Thus, it can be concluded that, during the swelling of cellulose with ethylene diamine solutions, bridge formation takes place through hydrogen bonding between the $NH_2$ groups of the swelling agent and OH groups of cellulose[10] to form a cellulose amine complex (two anhydroglucose units and one ethylene diamine molecule). This complex decomposed when solvent or water were added. As a result of this, the original lattice agent is removed from the swollen samples.[1,3,4] This previous mechanism can be supported by the observed detectable shift of the hydrogen bonded OH of the absorbance band at 3350 $cm^{-1}$ for the untreated cotton linters. This band shifted to 3400 and 3450 $cm^{-1}$ for the treated cotton linters with 75 and 100% ethylene diamine, respectively. This shift (100 $cm^{-1}$) is due to the decrease of hydrogen bond strength of the treated samples.

From Figure 2(a) it is shown that the crystallinity index decreases with increasing ethylene diamine concentration. It decreases gradually for concentrations of ethylene diamine increasing from 25 to 75%. By increasing the concentration from 75 to 100%, the decrease in CrI was sharp and reached 0.65. The treatment of cotton linters with 25 and 50% EDA, has little effect on the decrystallization of cotton linters. The percent decreases in their CrI were 11.15 and 21.9%, while in the case of 100% it was 74.7% (Table I). This is due to the fact that the concentration of ethylene diamine must be more than 60%[11] for free unhydrate amine molecules to be present to promote intercrystalline swelling and forming the cellulose amine complex. In another explanation, there must be a certain concentration of ethylene diamine ($< 60\%$) to swell cellulose. Below this concentration, amine is found as a com-

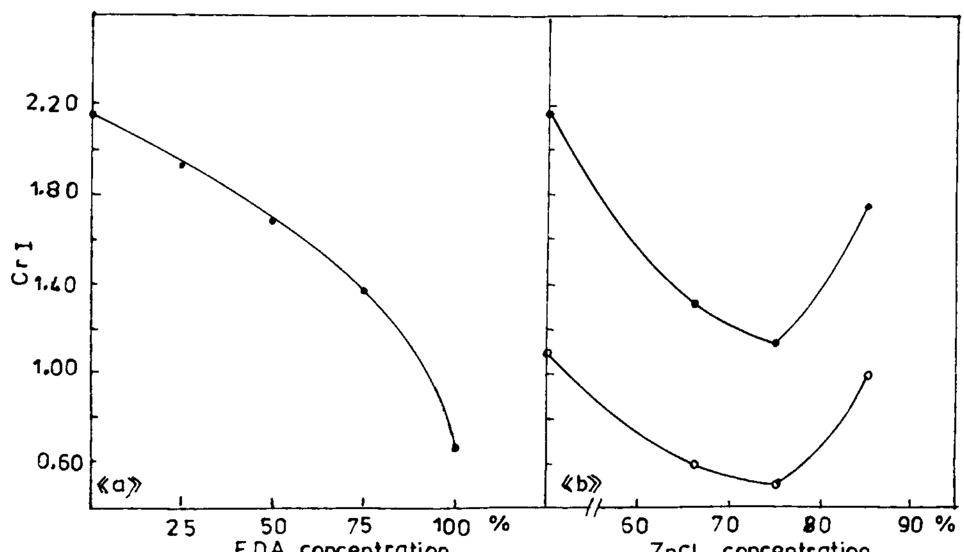


Fig. 2. Effect of: (a) EDA concentration on CrI of treated cotton linters and (b) $ZnCl_2$ concentration on CrI of the treated, (●) cotton linters and (O) bleached cotton stalk pulp.

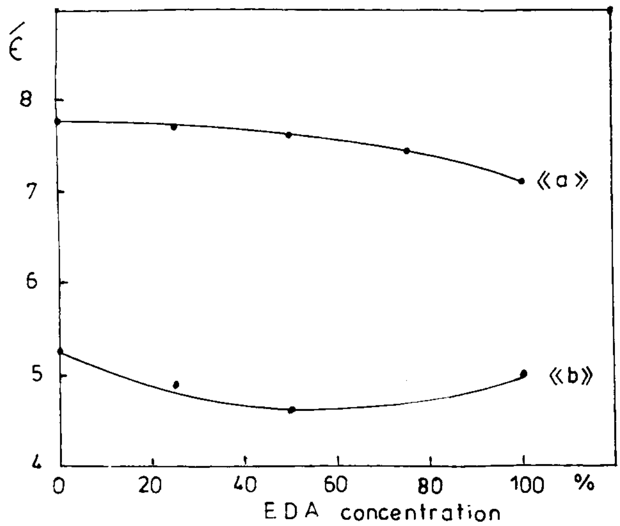


Fig. 3. Permittivity ε″ of the treated cotton linters with different concentrations of EDA, for 20 min: (a) before drying; (b) after drying.

plex with water in its solutions.[1,3,12] Above this concentration, there exists free EDA in the solution which increases the swelling of cellulose.

Figure 3, curve a, shows the variation of permittivity ε′ of treated cotton linters with different concentrations of EDA. ε′ is found to decrease slightly by increasing the concentration of EDA. After drying (curve b) where the moisture content was evaporated from those samples, it is interesting to find that the decrease in ε′ is only noticed up to 50% EDA after which ε′ starts to increase. This increase could be attributed to the decrease in hydrogen bond strength and consequently the high decrease of CrI of the treated samples with 75 and 100% EDA. On the other hand, no pronounced change in the dielectric loss ε′ was noticed by increasing the concentration of EDA (Table II).

Figures 4 and 2(b) upper line show the effect of zinc chloride solutions on the infrared spectra pictures and the crystallinity index of treated cotton linters.

TABLE II
Effect of the Treatment with Ethylene Diamine and Zinc Chloride on the Dielectric Loss ε″ of Cotton Linters

| | ε″ | |
|---|---|---|
| Treatments | Before drying | After drying |
| Untreated pulp | 0.026 | 0.017 |
| 25 EDA | 0.026 | 0.016 |
| 50 EDA | 0.024 | 0.015 |
| 75 EDA | 0.024 | 0.016 |
| 100 EDA | 0.023 | 0.016 |
| 66 $ZnCl_2$ | 0.026 | 0.018 |
| 75 $ZnCl_2$ | 0.029 | 0.017 |
| 85 $ZnCl_2$ | 0.055 | 0.017 |

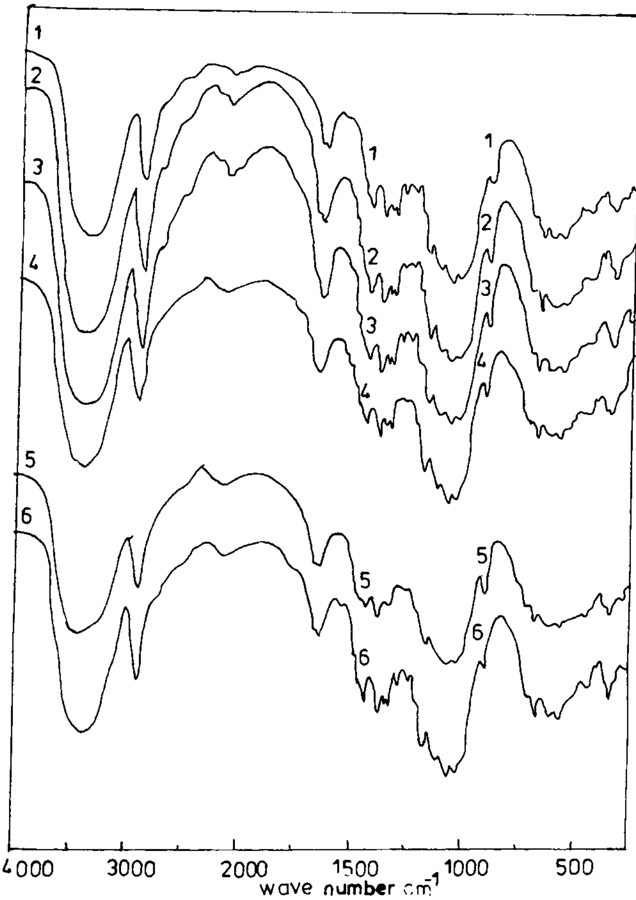


Fig. 4. IR spectra of untreated cotton linters (1), cotton linters treated with a 66% solution of $ZnCl_2$ for 20 min (2), 30 min (3), 40 min (4), and cotton linters treated for 20 min with a $ZnCl_2$ solution of 75% (5) and 85% (6).

From Figure 2(b) upper line, it is demonstrated that CrI decreased for increasing zinc chloride concentrations from 66 to 75% (w/w). The swelling and decrystallization effect of zinc chloride solution on cotton linters is due to the hydration of the ion adsorbed on cellulose[13] and its ease of hydration and high solubility in water. Also, as explained by Williams,[14] the reaction of cellulose with zinc chloride solution should be exothermic, which causes the dissociation of the salt hydrate, produced by the adsorption of salt molecule by cellulose. The free water molecules so formed cause the swelling. On the other hand, by increasing the concentration of zinc chloride solution up to 85% (w/w), the CrI increases. This can be attributed to the high viscosity of the chloride solution which decreases the penetration velocity of the solution into cellulose, and, consequently, the rate of swelling is decreased.

From Table I, it is clear that the crystallinity index of the treated cotton linters with 66% (w/w) zinc chloride solution decreased by increasing time of treatment. Concentration less than 60% (w/w) zinc chloride are reported[15] to have little effect on the crystallinity.

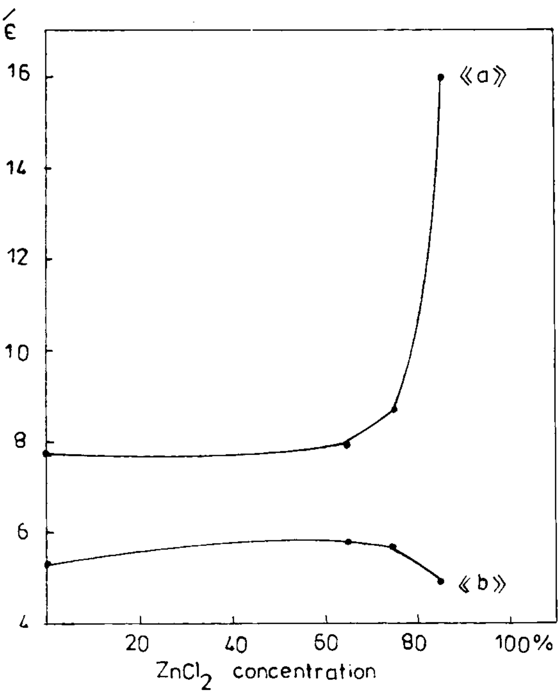


Fig. 5. Permittivity $\epsilon''$ of the treated cotton linters with different concentrations of $ZnCl_2$, for 20 min: (a) before drying; (b) after drying.

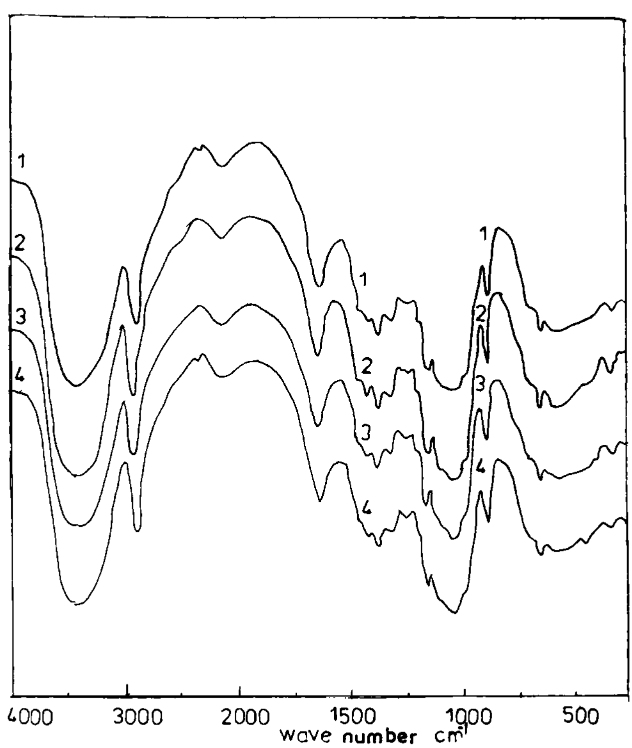


Fig. 6. IR spectra of untreated cotton stalk pulp (1) and cotton stalk pulp treated for 20 min with a $ZnCl_2$ solution of 66% (2), 75% (3), and 85% (4).

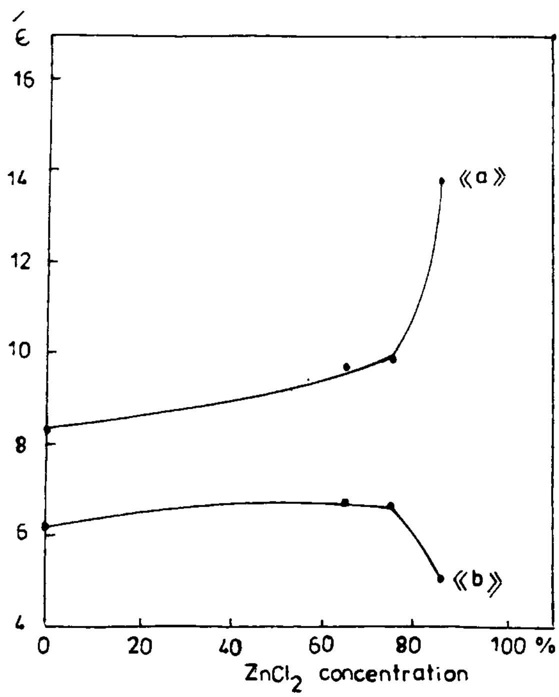


Fig. 7. Permittivity $\epsilon''$ of the treated cotton stalk pulp with different concentrations of $ZnCl_2$ for 20 min: (a) before drying; (b) after drying.

Figure 5, curve a, shows the variation of $\epsilon'$ of the treated cotton linters with different concentrations of zinc chloride. $\epsilon'$ increases by increasing zinc chloride concentration. At 85% $ZnCl_2$, the increase in $\epsilon'$ becomes sharp. This increase may be attributed to the presence of moisture in the treated samples. For the dry samples (Fig. 5, curve b), it is interesting to find that the increase is only seen for the treated samples with zinc chloride up to 75%. This result supports the crystallinity index measurements. For those samples, the dielectric loss values were measured and given in Table II. For the dry samples, no detectable change is noticed.

The crystallinity index of the treated cotton linters with ethylene diamine is higher than that formed by the zinc chloride solution (Table I). This is in agreement with the variation in the OH band position at 3375 and 3400 $cm^{-1}$ for the treated cotton linters with 75% ethylene diamine and zinc chloride solutions, respectively.

The infrared absorbance spectra of the untreated and treated bleached cotton stalk pulp with zinc chloride solution is shown in Figure 6. The effect of different concentrations of zinc chloride on the crystallinity index of treated cotton stalks is shown in Figure 2(b) lower line. From Figures 2(b) and 7, the effect of zinc chloride solution on the CrI and permittivity $\epsilon'$ of the treated cotton stalks has the same trend as in the case of treated cotton linters. On the other hand, $\epsilon'$ for cotton stalk pulp is higher than that for cotton linters. This may be due to the lower CrI of cotton stalk than cotton linters and also to the difference in the chemical constituents of the two pulps.

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