Irradiation of Cotton Celluloses I and II in Presence of Organic Solvents.

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Synopsis

The infrared spectra and dielectric properties of cotton celluloses I and II, γ-irradiated in the presence of organic solvents have been investigated. The obtained data showed that irradiation of cotton celluloses I and II in organic solvents helps in oxidation of these celluloses and increases their dielectric constant. Examination of the infrared spectra and X-ray diffraction (XRD) patterns revealed that irradiation of cotton celluloses I and II in organic solvents produces considerable changes in their crystallinity. It was found that the highest values of crystallinity and dielectric constant are obtained when the samples are irradiated in chloroform whereas the lowest values are obtained when the samples are irradiated in toluene.

INTRODUCTION

In the past few years the effects of ionizing radiation on the properties of cotton fibers have received considerable attention. This is undoubtedly due to the great importance of these effects in the cotton industry. It is generally accepted that oxidation of cellulose and cleavage of cellulose molecules are the principal reactions that cotton cellulose will undergo on exposure to ionizing radiation. In most of the earlier studies the samples were irradiated in either atmosphere of air or atmosphere containing oxygen or nitrogen.[1-8] But the irradiation of cotton celluloses in the presence of organic solvents has not yet been fully explored. The aim of the present work is to investigate the induced changes in the infrared (IR) spectra and dielectric properties of cotton celluloses I and II, γ-irradiated in the presence of organic solvents.

EXPERIMENTAL

The fibers were first washed and dried in a drying oven at 70°C for 24 hr. The dried fibers were then ground in a hardened steel vial containing two hardened steel balls. The mercerized samples were prepared by immersing part of the powder in an aqueous solution of 18% (w/w) NaOH at room temperature for 10 minutes. The material: liquor ratio was 1:50. The fibers were washed with distilled water and then treated with 1% acetic acid solution for 5 minutes. The fibers were again washed with distilled water and dried at 50°C. The samples were then irradiated in air and in (carbon tetrachloride, chloroform, 1,2-dichloroethane, methylene chloride, toluene, hexane, and benzene), from a Co^{60} source, anoratom control A-S gamma a 3500 unit, 32, 41/rad/s (γ dose = 16.5 MR). KBr discs were prepared from the treated samples. The infrared spectra were recorded on

Beckman Spectrophotometer. The X-ray diffraction patterns were obtained on the Siemens D 500 Diffractometer.

The samples prepared for the dielectric measurements were in the form of discs of 12 mm diameter and 2 mm thickness. These samples were prepared by pressing the powder under constant pressure of 10 ton/cm² using a hydraulic pressing machine. An automatic precision bridge type RL CB from Rhode and Schwartz was used for capacitance measurements from which the dielectric constant ϵ' is obtained and also for measuring the power factor tan δ at 1 KH3. The measurements were carried out at room temperature ($\sim$ 25°C). The accuracy of measurements in capacitance was $\pm$ 0.1% while for tan δ it was $\pm$ 5%. The samples under test were dried in an oven at 105°C. The amount of water in the samples can be expressed in terms of either the percent relative humidity or the moisture content

$$\% \text{ Relative humidity} = \frac{\text{wt of humid sample} - \text{wt of dry sample}}{\text{wt of dry sample}} \times 100$$

$$\text{Moisture content} = \frac{\text{wt of humid sample} - \text{wt of dry sample}}{\text{wt of humid sample}} \times 100$$

RESULTS AND DISCUSSION

The XRD patterns of untreated and NaOH-treated cotton samples are shown in Figure 1, where the diffractogram (a) of native cotton shows the 110 peak at 2 θ = 14.8°, the 110 peak at 2θ = 16.5°, and the 200 peak at 2 θ = 22.6° which are the characteristics of cellulose I lattice.[9,10] The diffractogram (b) of the mercerized sample (18%) exhibits the mentioned peak
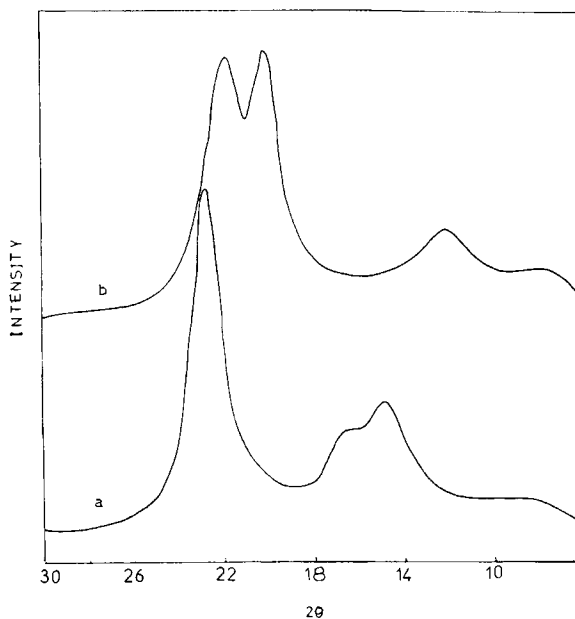

Fig. 1.   X-ray diffraction patterns of cotton celluloses I and II (a) cellulose I ; (b) cellulose II.

at 2 θ = 12.20 and 21.8° which are the characteristics of cellulose lattice type II.[9,10]

The IR spectra of both cotton cellulose I and II γ-irradiated in atmosphere of air or in the presence of some organic polar and nonpolar solvents are shown in Figures 2 and 3 respectively.

These figures indicate the following:

1. The spectra of all samples of cellulose I irradiated either in air or in the presence of solvents exhibit absorption band at 1725 cm^{-1}. The only difference between these spectra is that the intensities of their bands vary from sample to sample. The presence of the 1725 cm^{-1} band confirms the presence of carbonyl or carboxylic groups.[1,2]

2. The spectrum of the sample of cellulose II irradiated in air shows an absorption band at 1610 cm^{-1}. Previous investigation of the IR spectra of cellulose II revealed that the γ-irradiated species absorbs at this frequency 1610 cm^{-1} which is an indication of the presence of C = 0 groups. It seems very interesting to mention here that it is not easy to observe the band at 1610 cm^{-1} since it is always overlapped by the H$_2$O band at about 1640 cm^{-1}.

3. The spectra of the samples of cellulose II irradiated in presence of solvents exhibit an absorption band at 1725 cm^{-1}, the intensity of which varies from sample to sample.
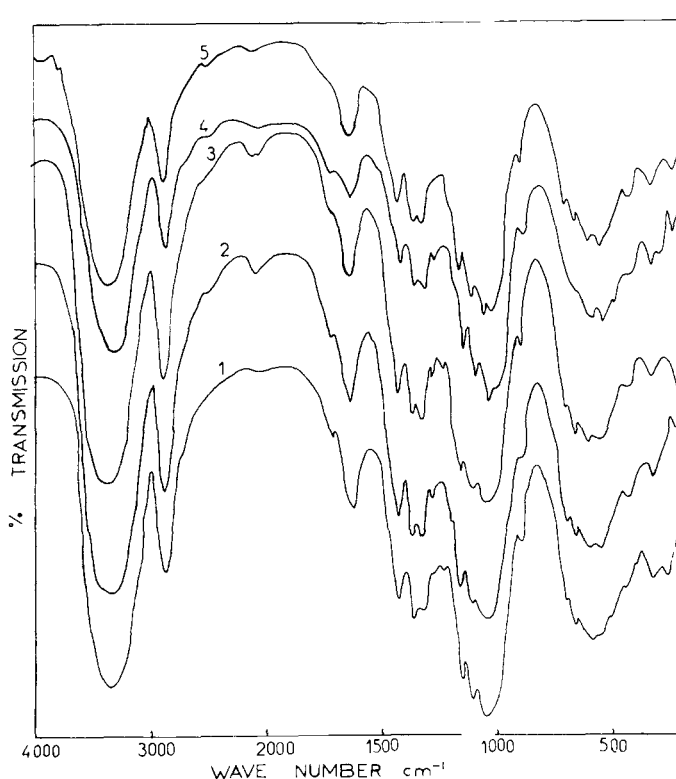

Fig. 2.   Infrared spectra of cotton cellulose I irradiated in: (1) air, (2) benzene, (3) toluene, (4) methylene chloride, and (5) chloroform.
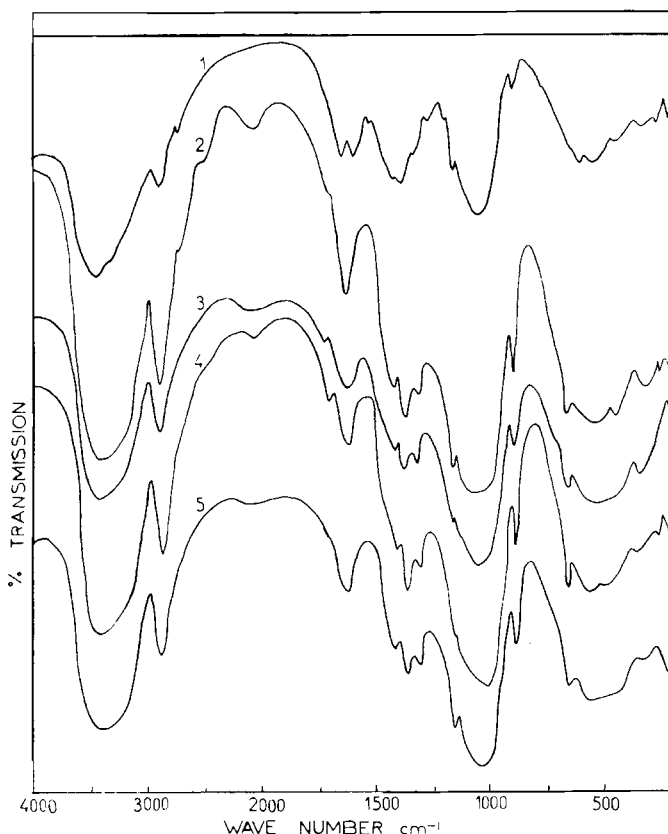
Fig. 3.   Infrared spectra of cotton cellulose II irradiated in: (1) air, (2) benzene, (3) toluene, (4) methylene chloride.

The degree of oxidation was measured by carbonyl index. This is simply the ratio of the absorbance of the C = O band at 1725 cm^{-1} to that of the C-H stretching band at 2900 cm^{-1}. The absorbances of these two bands were measured by using the base-line method. Base lines were drawn from 1580 to 1800 cm^{-1} and from 2810 to 3000 cm^{-1} across the 1725 cm^{-1} and 2900 cm^{-1} bands, respectively. The determined values are given in Table I.

Table I indicates that for any given solvent the degree of oxidation of cellulose I is always higher than that of cellulose II. For both celluloses the highest values of degree of oxidation are obtained when the samples are irradiated in presence of methylene chloride (in case of chlorinated hydro-carbons) and in toluene (in case of aromatic hydrocarbons). The lowest values are obtained when the samples are irradiated in the presence of chloroform and benzene. It seems very important to mention that methylene chloride and toluene have the highest values of dipole moment among the two groups of solvents. The degree of crystallinity of the samples under investigation were determined by using Nelson[11] crystallinity ratio

$$\frac{a\ 1375\ cm^{-1}}{a\ 2900\ cm^{-1}}$$

TABLE I
The Degree of Oxidation, Degree of Crystallinity, and Dielectric Constant of Cotton
Cellulose I and II Irradiated in Organic Solvents

Solvent	Degree of oxidation		Degree of crystallinity		Dielectric constant	
	Cell. I	Cell. II	Cell. I	Cell. II	Cell. I	Cell. II
CCl$_4$	0.45	0.39	0.74	0.478	3.92	4.38
Chloroform	0.32	0.27	0.82	0.551	4.06	4.40
1,2-dichloro-ethane	0.343	0.30	0.675	0.469	2.98	3.75
Methylene chloride	0.46	0.41	0.59	0.485	2.93	3.63
Toluene	0.51	0.32	0.477	0.366	2.42	3.53
Hexane	0.43	0.27	0.566	0.41	2.45	3.85
Benzene	0.37	0.20	0.66	0.41	2.48	3.61
Raw cotton	0.31	—	0.66	0.39	2.40	3.23

The determined values given in table I. indicates that:

1. The highest value of crystallinity is obtained when cellulose I or II are immersed in chloroform, while the lowest values are obtained when these samples are immersed in toluene.

2. For both celluloses I and II, the degree of oxidation decreases as the degree of crystallinity increases.

Samples of cotton powder were immersed in chloroform and toleune separately for a time equal to the time of exposure of these samples to γ doses in the presence of solvents. The determined values of degree of crystallinity for these samples are 0.70 and 0.68 for chloroform and toluene, respectively. The difference between these values is very small compared to the difference between the corresponding values for the samples irradiated in the presence of the mentioned solvents.

The XRD patterns of the samples irradiated in air and in the presence of chloroform and toluene were recorded. The resolution of the (110) and (110') peaks of the XRD scans of these samples were measured by using the relation of Chidombareswaran and co-workers.[12] The determined values are 2.36, 2, 2.11 for the samples irradiated in chloroform, toluene, and air, respectively. These values provide strong evidence that irradiation of cotton in the presence of chloroform increases the resolution of its XRD peaks whereas irradiation of cotton fibers in presence of toluene decreases its resolution. It is well known that the higher the resolution index the better is the resolution. Also better resolution is generally correlated with a higher degree of crystallinity.

The dielectric properties of the samples under investigation were measured. Figure 4 shows the effect of relative humidity on the dielectric constant of (a) untreated cotton samples (cellulose I) irradiated either in air or in the presence of the different solvents and (b) sodium hydroxide-treated samples (mercerized cotton cellulose II) irradiated either in air or in the presence of different solvents. From this figure, it is noticed that ϵ' for cellulose I are lower than those for cellulose II. Tan δ is also changed from about 0.12 for cellulose I to about 0.15 for cellulose II. As the relative
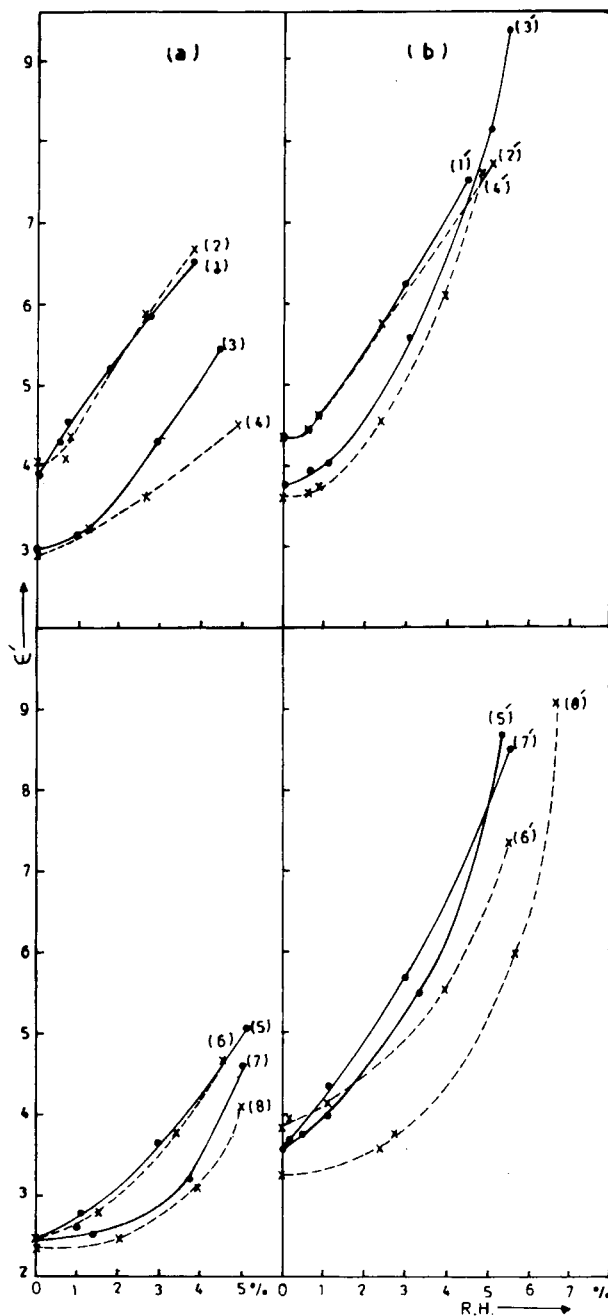
Fig. 4. Relation between the relative humidity in the sample and the dielectric constant of (a) cellulose I irradiated in: (1) Carbon Tetrachloride, (2) chloroform, (3) 1,2-dichloroethane, (4) methylene dichloride, (5) toluene, (6) hexane, (7) benzene, (8) air; and (b) cellulose II irradiated in: (1') carbon tetrachloride, (2') chloroform, (3') 1,2-dichloroethane, (4') methylene dichloride, (5') toluene, (6') hexane, (7') benzene, (8') air.

humidity decreases, ϵ' and tan δ are also decreased until a complete dryness is obtained. For the dry samples, tan δ is found to about 0.04 for cellulose I and about 0.05 for cellulose II. The increase in ϵ' and tan δ with relative humidity is attributed to the high dielectric constant of water as compared to the relatively low value of cellulose, and also the increased freedom of rotation of polar groups with the increase of relative humidity.[13] The dielectric constant for the whole dried samples are illustrated in Table I. From the table it is found that ϵ' for cellulose I and cellulose II irradiated in air are smaller than those irradiated in the presence of solvents. The values of ϵ' and tan δ for the dry raw cotton samples irradiated in air are comparable with those values reported in literature.[14] From the table, it is also clear that the highest value of ϵ' is obtained when cellulose I or cellulose II are irradiated in the presence of chloroform, while the lowest value is obtained when these samples are irradiated in the presence of toluene. This result is in good agreement with those obtained by infrared and X-ray measurements.

From the above-mentioned data, it could be concluded that irradiation of cotton cellulose I and II in the presence of organic solvents increases its degree of oxidation as well as its dielectric constant. The highest values of degree of oxidation are obtained when the samples are irradiated in the presence of methylene chloride (in the case of chlorinated hydrocarbons and toluene in case of aromatic hydrocarbons) while the lowest values are obtained when the samples are irradiated in the presence of chloroform and benzene. It is also found that the highest value of crystallinity and dielectric constant are obtained when the samples are irradiated in the presence of chloroform while the lowest values are obtained when these samples are irradiated in toluene.

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