Irradiation of Cotton Fibers in the Presence of Liquids

INTRODUCTION

It is well known since several years ago that γ-irradiation of native cotton has become one of the most common processes in graft copolymerization as a means of mixing compounds. The γ-induced modifications in the structures of these fibers have been related to the degree of order in the cellulosic fibers and the type of the crystalline lattice. For examples the effects of crystalline modifications of cellulose and of water on the infrared spectra and ESR spectra of γ-irradiated cellulose I, II, III, and IV, ball-milled cotton, and hydrocellulose were investigated.[1-8]

The present study is carried out to investigate the effects of γ-irradiation on cotton fibers in the presence of water, chlorinated hydrocarbon solvents, and aqueous solutions of NaOH by using infrared spectroscopy.

EXPERIMENTAL

The fibers were first washed and dried in an electric oven at 70°C over night. The dried fibers were then ground in a hardened steel vial containing two hardened steel balls. The powder was then irradiated from a Co^{60} source, a noratom control A-S gamma a 3500 unit, 32.41 rad/s in the presence of water, carbon tetrachloride, chloroform, 1,2-dichloroethane, methylene dichloride, and aqueous solution of 14% and 18% NaOH. The solvents are free of water. The material:liquor ratio was 1:50. The samples were then washed with distilled water.

KBr discs were prepared from the treated samples. The infrared spectra were recorded on Beckman spectrophotometer. The X-ray diffraction patterns were obtained on a Siemens D 500 diffractometer.

RESULTS AND DISCUSSION

The infrared spectra of samples of cotton fibers irradiated as such or in the presence of solvents were recorded over the spectral range 200–4000 cm^{-1}. Figure 1 presents partial infrared spectra of cotton fibers exposed to 14 Mrads of γ-radiation in the presence of carbontetrachloride, chloroform, 1,2-dichloroethane, and methylenechloride.

Examination of the spectra of the samples revealed that the only difference observed in the spectral curves of the exposed samples from the spectral curve of unexposed sample is the appearance of an absorption band at about 1735 cm^{-1}. The presence of this band confirms the presence of both carbonyl and carboxylic groups.[1,2,9]

The degree of oxidation was measured by the carbonyl index. This is simply the ratio of the absorbance of the C=O band at 1735 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 1735 and 2900 cm^{-1} bands, respectively.

The degree of oxidation together with the dipole moment of the solvents are given in Table I. The table indicates that irradiation of cotton fibers in the presence of the mentioned solvents results in considerable increase of the degree of oxidation of cotton fibers. The highest value of this degree is obtained when the samples are irradiated in the presence of the nonpolar solvent, CCl$_4$. It is also evident from the table that, in case of polar solvents, the degree of oxidation depends on the polarity of the solvent; it increases as the dipole moment increases.
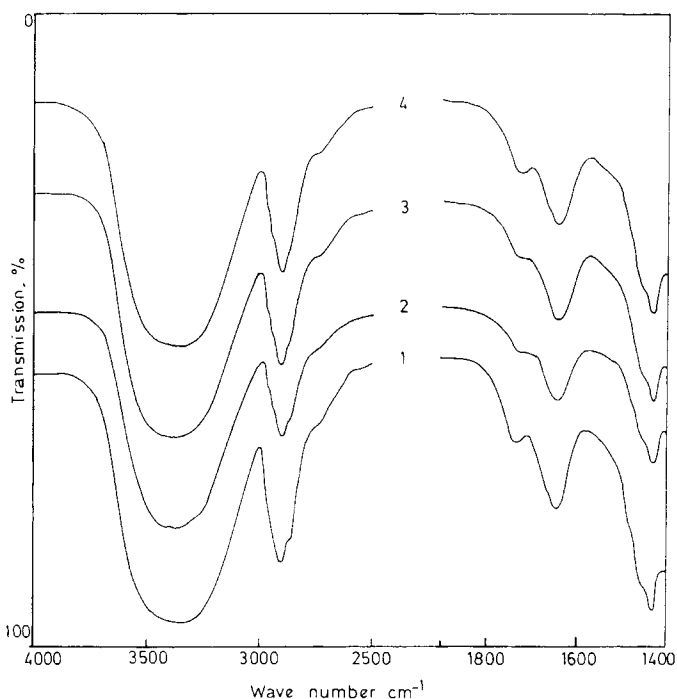
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Fig. 1.   Partial ir spectra of cotton fibers γ-irradiated in the presence of: 1) Carbon tetrachloride, 2) Chloroform 3) 1,2-Dichloroethane, and 4) Methylene chloride.

Based on the above-mentioned results one can conclude that solvents such as carbon tetrachloride, chloroform, 1,2-dichloroethane, and methylenechloride which can readily yield free radicals help in oxidation and cleavage of cellulose molecule.

It is well known that mercerization is the swelling of cotton fibers in aqueous solution of sodium hydroxide.[10] This swelling results in reorganization of the cellulose fiber, which becomes cellulose II when the swelling agent is removed. The swelling in sodium hydroxide breaks hydrogen bonds and weak van der Waal's forces between the cellulose chain molecules. Once the forces are broken between chains during swelling, the chains are freed to rearrange, expand, and reorient. When the sodium hydroxide is removed, these chains will form new bonds in this reorganized state.

Samples of cotton fibers were also irradiated in the presence of water and in aqueous solution of 14% (wt) and 18% (wt) NaOH. For comparison two dry samples of mercerized cotton (pretreated with 14% and 18% NaOH solutions) were irradiated with the same dosage. Figure 2 illustrates partial infrared spectra of some of the irradiated samples.

Analysis of the spectra of the samples under investigatioon revealed the following:

TABLE I

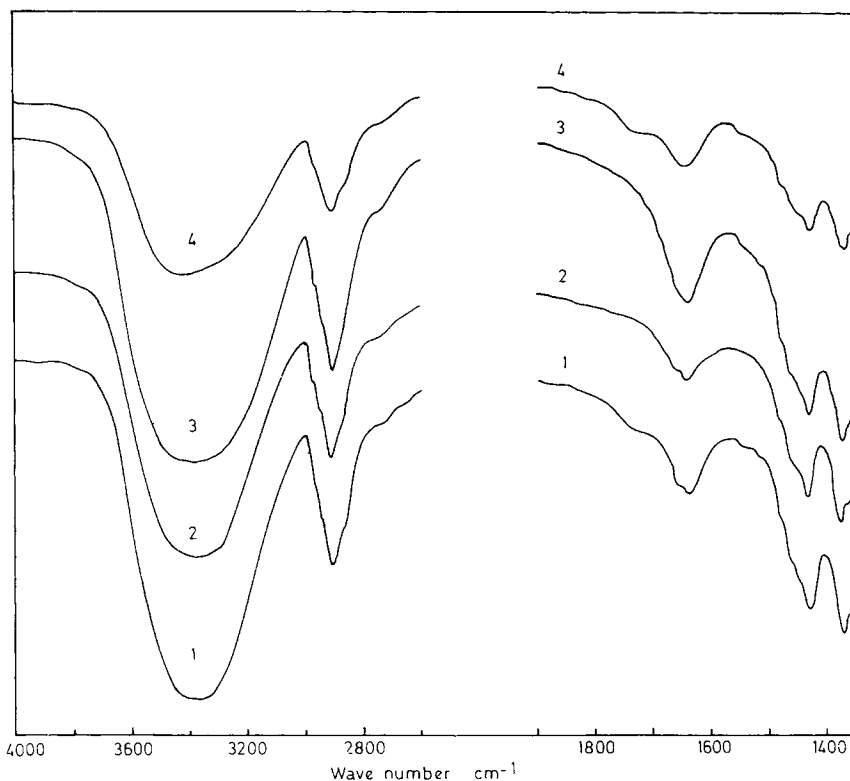| Solvent	Degree of oxidation	Dipole moment $\mu \times 10^{-18}$ esu
(Dry sample)	0.28	—
Carbon tetrachloride	0.44	0
Chloroform	0.31	1.02
1,2-dichloroethane	0.35	1.19
Methylene chloride	0.42	1.6

Fig. 2. Partial ir spectra of: 1) cotton fibers γ-irradiated in the presence of water, 2) in the presence of 14% NaOH solution, 3) in the presence of 18% NaOH soln., and 4) γ-irradiated mercerized cotton fibers pretreated with 14% NaOH soln.

(i) The spectrum of the irradiated mercerized sample, pretreated with 14% NaOH solution and that of the sample irradiated in the presence of water exhibit C=O band at about 1735 cm^{-1} while the spectrum of the irradiated mercerized sample pretreated with 18% NaOH solution shows the same band at 1610 cm^{-1}.

(ii) The C=O band has no evidence in the spectrum of the sample irradiated in NaOH solutions. This means that oxidation of cotton fibers exposed to γ-radiation in the presence of NaOH solution is not possible.

(iii) The carbonyl indices for the mercerized sample (14% NaOH) and for the sample irradiated in water are 0.29 and 0.17, respectively. Comparison of the value for the dry sample with that for the sample irradiated in water shows that the presence of water decreases greatly the degree of oxidation.

The XRD patterns of the mercerized samples and of the samples irradiated in NaOH solutions are given in Figure 3.

As can be seen from Figure 3 that the diffractogram (1) of γ-irradiated native cotton shows the (101) peak at $2\theta = 14.8°$, the (101) peak at $2\theta = 16.5°$ and the (102) peak at $2\theta = 22.6°$, which are the characteristics of cellulose I lattice.[11,12] The diffractogram (5) of the irradiated mercerized sample (18%) exhibits the mentioned peaks at $2\theta = 12, 20, 2$, and 21.8°, which are the characteristics of cellulose lattice type II.[11,12] It can be seen from Figure 3 diffractogram (4) that the sample pretreated with 14% NaOH solution indicates the presence of cellulose II in addition to a small fraction of cellulose I. The diffractograms (2) and (3) of the samples irradiated in the presence of 14% and 18% NaOH solutions, respectively, show the characteristic peaks of cellulose I in addition to a very weak peak at $2\theta = 20.2$ which indicates the presence of very small fraction of cellulose II.
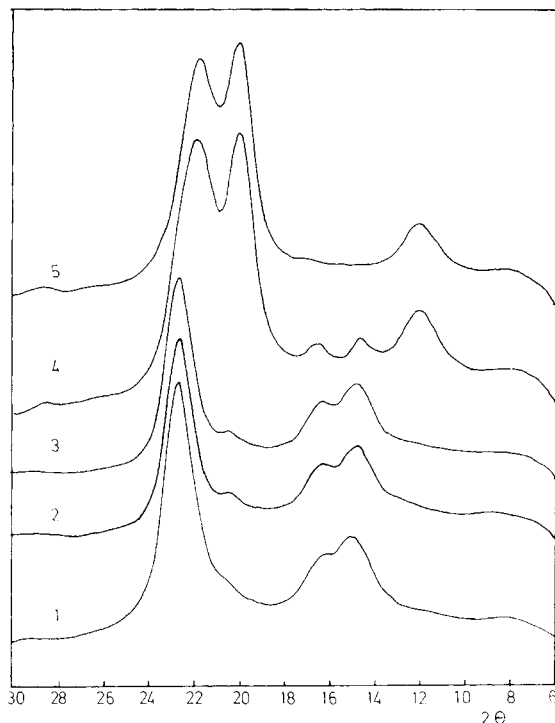
Fig. 3.   X-ray diffraction patterns of γ-irradiated cotton fibers: 1) Native cotton 2) cotton fibers immersed in 14% NaOH, 3) cotton fibers immersed in 18% NaOH, 4) mercerized with 14% NaOH and 5) mercerized with 18% NaOH.

The foregoing result means that γ-irradiation of cotton fibers during swelling in 14% and 18% NaOH solution even for long periods of time hinders the transformation of cellulose material from cellulose I lattice type to cellulose lattice type II.

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