

# ***On the Frequency Shift of the C=O Band in the Infrared Spectrum of Gamma-Irradiated Cellulose I and Cellulose II***

## **INTRODUCTION**

In a recent communication Moharram and Hakeem<sup>1</sup> have reported that gamma ray irradiation results in the formation of a new band at 1610  $\text{cm}^{-1}$  in mercerized cellulose and at 1725  $\text{cm}^{-1}$  in native cellulose owing to C=O absorption. They have ascribed the shift in the band to transformation of the lattice from cellulose I to cellulose II. However, earlier workers<sup>2-4</sup> do not seem to have observed any new peak other than the one at 1739  $\text{cm}^{-1}$  in the irradiated celluloses. Since cellulose I and cellulose II are polymorphs built up from the same monomer unit, it appeared unlikely that the lattice transformation would confer such widely different environments for the newly formed carbonyl group in the respective lattices as to cause a shift of 125  $\text{cm}^{-1}$  in the band. To check this point, we carried out gamma ray irradiation of native and mercerized cellulose both in the sealed and open conditions. The findings are discussed in this communication.

## **EXPERIMENTAL**

Samples comprised: (1) dewaxed and kiered cotton fibers (Ce I), (2) mercerized fibres (Ce II) prepared by swelling sample no. 1 repeatedly in 24% NaOH, and (3) partially mercerized fibers produced by swelling sample No. 1 in 14% NaOH. All the samples were cut in a Wiley mill fitted with a 40-mesh screen, before being irradiated. Small portions from these samples were taken in a number of glass tubes which were left open during irradiation. One tube each containing Ce I and Ce II was, however, sealed prior to irradiation. All samples were irradiated with gamma rays from a  $\text{Co}^{60}$  source. The dose rate was 7100 rad/min. A maximum dose of about  $2.8 \times 10^8$  rad was employed. Small portions of samples were withdrawn at regular intervals from the unsealed tubes.

Infrared spectra of all the samples were recorded 24 h after irradiation. A Perkin-Elmer Model 457 Spectrophotometer operating with normal slit in the slow scan mode was used for recording the spectra in the KBr phase.

## **RESULTS AND DISCUSSION**

Table I shows the values of absorbance/mg at various doses for the newly developed peak at 1735  $\text{cm}^{-1}$  as well as for the already existing peak at 1635  $\text{cm}^{-1}$  attributable to adsorbed water. The absorbances for these peaks when the sample is irradiated in sealed tubes are also included in the table for a particular dose. Spectra for both Ce I and Ce II in the 1900–1500  $\text{cm}^{-1}$  region before and after irradiation are shown in Figure 1. The difference spectra of irradiated Ce I and Ce II against the respective controls are also included in the figure. The figure does not contain any new peak at 1610  $\text{cm}^{-1}$ . However, it may be noted from the table that the adsorbed water peak at 1635  $\text{cm}^{-1}$  shows a significant rise in intensity with increase in the dose, though not so much as the band at 1735  $\text{cm}^{-1}$ . Samples that received very high doses became yellowish in color, though this effect was subdued in sealed samples. In general, the intensity of both the peaks was found to rise with the extent of yellowing.

It is clear from the curves in Figure 1 and the data in Table I that on irradiation both Ce I and Ce II give rise to new peaks at 1735  $\text{cm}^{-1}$  while both show an increase in intensity for the already existing peak at 1635  $\text{cm}^{-1}$ . It is significant to note that similar changes were also found to occur in the spectra of irradiated samples from partially mercerized cotton as well as from hydrolysates of Ce I and Ce II, the data for which, however, have not been presented here for the sake of brevity. Of the two peaks, the one at 1735  $\text{cm}^{-1}$  can be assigned to C=O absorption without any doubt, while the additional increase in intensity in the 1635  $\text{cm}^{-1}$  region can be ascribed either to the formation of a conjugated double bond resulting from irradiation (since the intensity variation shows some colour dependence) or to increased surface for adsorption of moisture owing to the degradation (chain scission) caused by irradiation.

It is interesting to note that the X-ray diffraction patterns for Ce I and Ce II remained almost the

TABLE I  
IR Absorption Intensities at  $1735\text{ cm}^{-1}$  and  $1635\text{ cm}^{-1}$  for Native and Mercerized Celluloses  
after Gamma Ray Irradiation to Various Doses

Sample no.	Approximate dose (rad)	Native cellulose		Mercerized cellulose	
		Absorbance/mg at:		Absorbance/mg at:	
		$1735\text{ cm}^{-1}$	$1635\text{ cm}^{-1}$	$1735\text{ cm}^{-1}$	$1635\text{ cm}^{-1}$
1	0	—	0.037	—	0.046
2	$0.61 \times 10^8$	0.037	0.051	0.034	0.055
3	$1.23 \times 10^8$	0.057	0.061	0.045	0.059
4	$2.04 \times 10^8$	0.090	0.062	0.082	0.061
5	$2.86 \times 10^8$	0.124	0.777	0.114	0.075
6 <sup>a</sup>	$1.43 \times 10^8$	0.038	0.057	0.037	0.052

<sup>a</sup> This sample was irradiated in sealed tube.

same as those prior to irradiation even at such high dosages as  $2.8 \times 10^8$  rad. What may generally be expected during irradiations of polymers of the degrading type, like cellulose, is mainly oxidative degradation.<sup>5</sup> Depending on the molecular structure and constitution of the polymer and the energy of the impinging radiation, dehydrogenation and evolution of gases like CO, CO<sub>2</sub>, etc., may ensue. Such changes at the molecular level lead to intensity variations and sometimes the appearance of new peaks in the infrared spectrum of irradiated polymer. In the case of both Ce I and Ce II new peaks appeared only around  $1735\text{ cm}^{-1}$  while most of the other peaks showed small frequency shift and considerable intensity variations especially at higher doses. These intensity and frequency changes of the already existing peaks are being studied in detail.

Another interesting observation made in the course of the present study was that the effects produced by irradiation were likely to be influenced by the presence of vapors of some substance capable of being adsorbed by cellulose. Thus when traces of ethylenediamine vapor were deliberately introduced into the irradiation chamber, all the cellulose samples developed a dark orange color and showed considerable enhancement in intensity of the peak around  $1635\text{ cm}^{-1}$  unlike when irradiation was carried out in unpolluted air. Even so the spectra of Ce I and Ce II in the  $1900\text{--}1500\text{ cm}^{-1}$  region remained nearly identical.

Thus it appears that the cellulose polymorphs I and II show similar changes in their infrared spectra after gamma irradiation particularly with respect to positions (frequencies) of new peaks. If any difference exists at all, it is in the intensity of these and other peaks already present. Frequency variation, if any, for the new peaks that appear in the two polymorphs during irradiation is negligibly

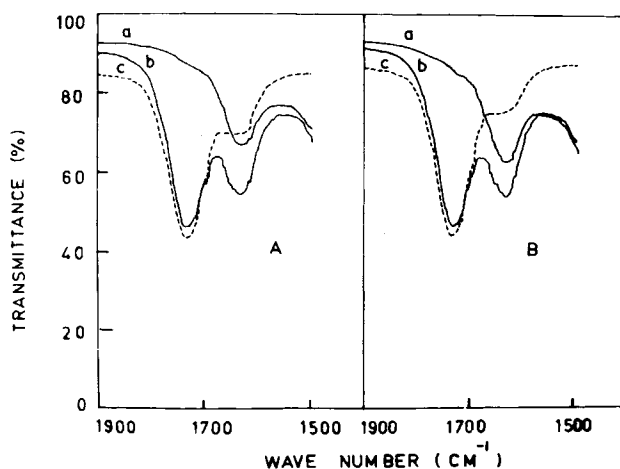


Fig. 1. IR spectra of (A) native and (B) mercerized cotton celluloses: (a) before and (b) after irradiation to a dose of  $2.8 \times 10^8$  rad. Curves (c) represent the difference spectra  $b - a$

small. This suggests that the oxidative degradation of cellulose caused by gamma radiation is independent of polymorphism as regards their IR spectra.

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