High-Energy Radiation-Induced Changes in the Crystal Morphology of Cellulose

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Introduction

Sunlight, X-rays, and electron beams darken and weaken paper as they depolymerize cellulose.[1−4] X-rays, electrons, and ultraviolet photons with at least 5 eV energy can initiate direct photolysis of cellulose even without oxygen; however, aerobic irradiation results in the production of carbonyl and carboxyl groups.[5−7] Because the effects of ionizing radiation on pulp fibers increase their subsequent susceptibility to chain cleavage by acid hydrolysis,[8−10] they have some similarities to thermal aging of paper which also darkens, weakens, and depolymerizes paper through acid hydrolysis.[11−13] The effects of electron, X-ray, or UV irradiation are similar because the high-energy electrons or X-rays both trigger an avalanche of lower energy electrons and photons.

Bombardment of cellulose with high-energy electrons is of interest for at least three reasons: the photolysis is more direct than with UV light because cellulose is transparent to many sufficiently energetic photons; electron irradiation is assumed to cleave cellulose chains with equal ease in crystalline and amorphous regions in contrast to the preferential hydrolysis of noncrystalline regions by photons; and the practical reason that the high-energy electron beams are currently used in the USA to neutralize suspected terrorist biohazards in the mail.[14] To characterize the effects of controlled high-energy electron beam irradiation on the two crystalline allomorphs[20] of cellulose (I_α, I_β) in paper, we have undertaken a solid-state ^{13}C NMR and X-ray diffraction study and report the findings herein.

Experimental Section

Various fine papers were exposed at the facilities of EBEAM Services Inc. to either 4.5 or 10 MeV electrons through a range of dosages from 10 to 240 kGy. To minimize the influence of additives, this study focuses on a chromatographic paper made from cotton linters and used in the paper industry for reflectance calibration. The initial degree of polymerization was about 1100 (from supplier) and compares with a softwood fully bleached Kraft pulp. A dosage of 1 kGy corresponds to the adsorption of 1 J of energy per gram of material, which is equivalent to about $^1/_4$ cal/g. The exposures were done in multiple passes, ensuring minimum increase in temperature of the paper.

^{13}C CPMAS NMR spectra were obtained at 75.4 MHz using a Chemagnetics CMX-300 spectrometer. Samples were spun in 7.5 mm zirconia rotors at 4000 Hz. For the cross-polarization a contact time of 2 ms and a recycle delay of 2 s were used for all spectra. The proton $\pi/2$ pulse width was 4 μs, giving a decoupling power of 62.5 kHz. The free induction decays were sampled with 1K points and zero-filled to 16K before Fourier transformation. For the determination of the I_α/I_β ratio no sensitivity or resolution enhancement was used. For the determination of crystallinity the FIDs were Fourier transformed after the application of 25 Hz of Lorentzian broadening. Deconvolution of the peaks was accomplished using the routines available in the spectrometer's Spinsight software. The C1 peak was fit assuming one peak for the I_α and two for the I_β form. (The results of the fits consistently put the I_α peak at 105.4 ppm and the I_β peaks at 104.4 and 106.2 ppm.) A third peak was added to account for noncrystalline material. In all fits the functional form of the peaks was purely Lorentzian, purely Gaussian, or any linear combination of the two. The crystalline peaks were found to be a combination of Lorentzian and Gaussian shapes, and the relative contribution of the two shapes did not vary as a function of irradiation amount. The noncrystalline peak was found to be purely Gaussian.

Disks of the paper irradiated at 4.5 or 10 MeV were cut and mounted in an X-ray powder diffractometer employing a cobalt anode and scanned at constant intensity. The integrated intensity of a diffraction peak will be proportional to the crystallinity of the cellulose, the intensity of the X-ray beam, and the mass per unit area of the disks of paper. If crystallinity were depleted due to electron irradiation, the integrated intensity of the main diffraction peak would reduce commensurately.

Results and Discussion

A typical deconvolution of the peaks in the 100−106 ppm range of a sample irradiated by 10 MeV electrons to a dosage of 20 kGy is shown in Figure 1. A plot of the results of the deconvolutions as a function of irradiation dosage is given in Figure 2. The amount of the I_α form as a percentage of the crystalline fraction continuously decreases with irradiation amount. This finding is consistent with the effect of aqueous alkali annealing treatments[16] of celluloses where such treatments are known to bring about a reduction in the I_α/I_β ratio. This is the first time that it has been shown that high-energy electron beam irradiation has the same effect on native cellulose. Moreover, the conversion of the I_α form to the I_β form is less at the higher dosage (10 MeV). It has also been determined that the higher energy electrons have a lesser effect on the strength properties of these papers.[17] Electron microscopists have long been aware that higher energy electrons are less damaging to native cellulose than lower doses.

Interestingly, transmission electron microscopy (TEM) has allowed observation of lattice spacing transformation in cellulose using much weaker electron beam energy than reported here. In a seminal paper, Revol[18] recorded successive diffraction changes for *V. ventricosa* microfibrils (under continuous TEM observation) through 0.53, 0.536, to 0.54 nm. In a TEM diffraction study on cellulose the irradiation energy is 50−100 times less than the high-energy radiation used in this study, but the continuous lower energy irradiation eventually causes loss in mass and destroys crystallinity. However, the periodicity of the area exposure for high energy electron beams ensures that overheating and decomposition do not occur. In the transmission electron microscope heat may play a significant role in lattice transformations. Sugiyama and Okano[19] have explored how spacings observed in transmission electron microscopy diffraction related to crystal size of microfibrils in pulps.

Atalla and Vanderhart[20] have noted that a resonance from noncrystalline cellulose is a complicating factor in

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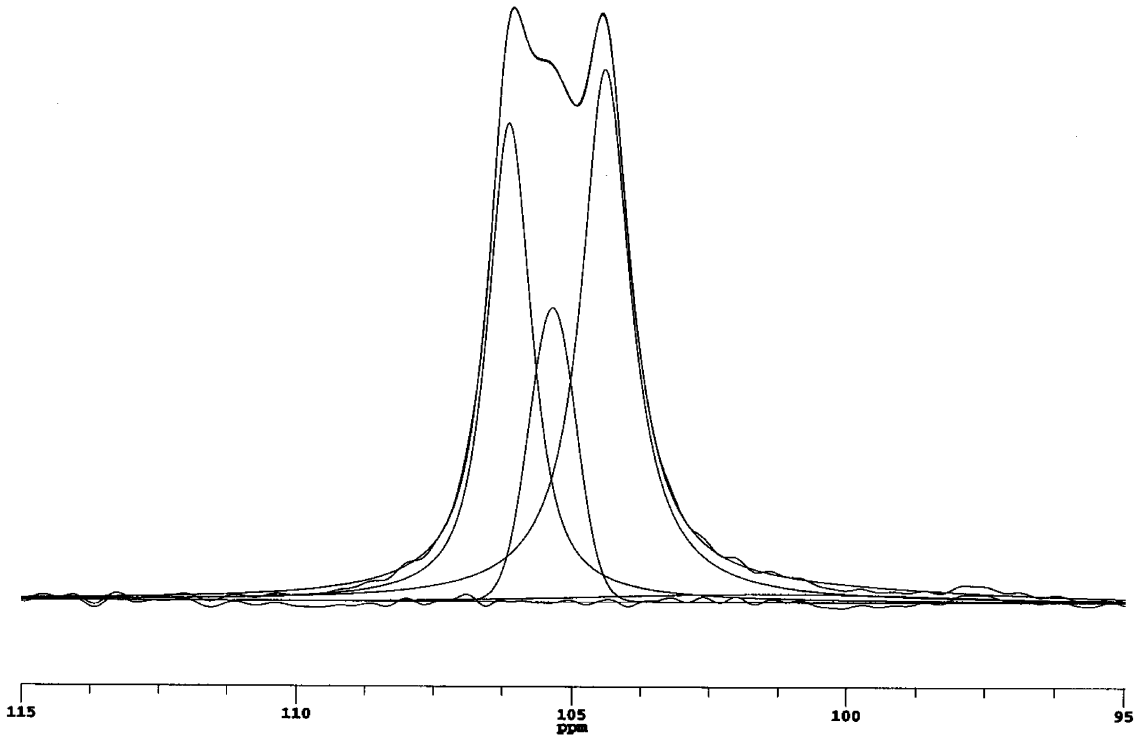

Figure 1. Experimental and best fit spectra of the C1 region of chromatographic paper irradiated by 10 MeV electrons to a dosage of 20 kGy. See text for details regarding the experimental parameters and the fitting procedure.

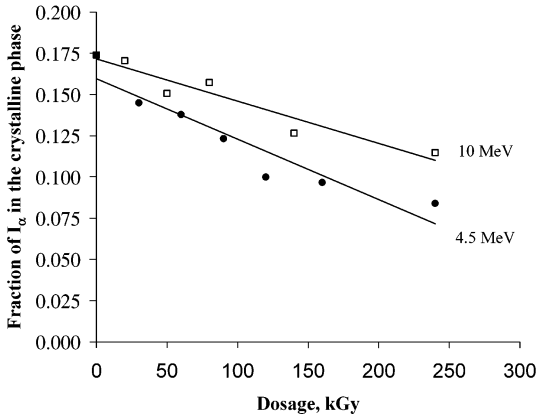

Figure 2. Dependence of the fraction of I_α form in the crystalline phase as a function of the radiation dosage.

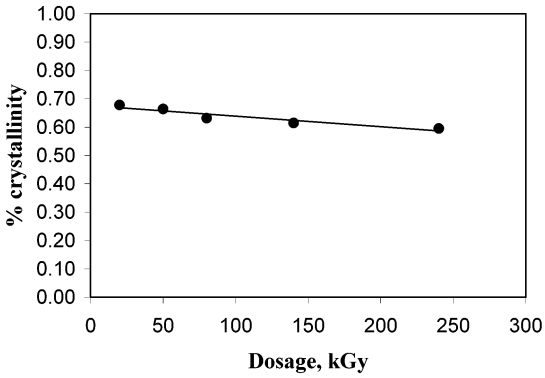

Figure 3. Percent crystallinity of chromatographic paper irradiated by 4.5 MeV electrons as a function of dosage, as determined from the relative areas of the C4 crystalline peak (89 ppm) and the noncrystalline peak (84 ppm) in the solid-state ^{13}C spectra.

fitting the line shapes of celluloses. As described above, we have included in the fits a peak to account for the ^{13}C CP/MAS noncrystalline material. To confirm that our determination of the I_α/I_β ratio is not affected by a change in the amount of noncrystalline material present as a function of irradiation, the degree of crystallinity was also determined by deconvolution of the C4 peaks at 84 ppm (noncrystalline fraction) and 89 ppm (crystalline fraction). The degree of crystallinity is essentially unaffected by the irradiation, decreasing only slightly with irradiation amount (Figure 3). Similar results were found for the degree of crystallinity of the 4.5 MeV samples as measured by X-ray diffraction. No change is apparent in the diffractograms, and the 4% decrease in crystallinity shown in Figure 4 is not statistically significant. This increase in the amount of noncrystalline material is not large enough to affect our conclusion regarding the effect of irradiation on the I_α/I_β ratio. While the exact interpretation of the results obtained from line shape fitting of solid-state ^{13}C NMR spectra of cellulose is a matter of some debate in the literature, we feel the observed trends are meaningful. All the spectra have been carefully processed in order to ensure reproducibility, and the deconvolutions were done in a consistent manner across both series.

As expected for a pulp sample, the I_α content is relatively small and the degree of crystallinity is modest compared to algal samples.[21] Nevertheless, a steady increase in I_β is generated by the irradiation; since this cannot be attributed to the effect of heat energy, which require temperatures[22,23] above 200 °C, it must be due to the high-energy electrons themselves. The effect of electron energy can be considered as statistically distributed in the pulp fiber microfibrils as are the I_α and I_β domains. If native cellulose crystals are composites of two allomorphs,[15,16,20] the local phase transition can be thought of as an energy-sensitive yield point, based on a conformational change. This can lead to local irreversible change in the conformational features of O_2 and O_6 atoms, which have been proposed[24,25] as forming

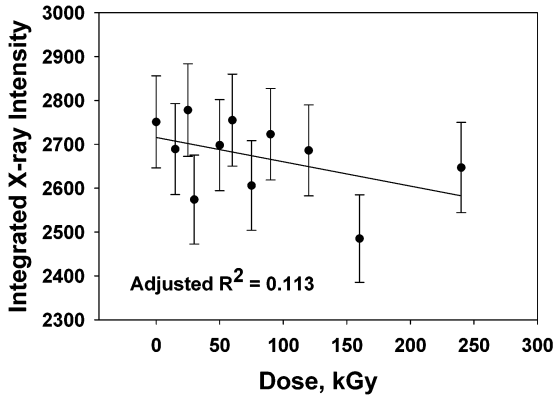

Figure 4. Degree of crystallinity of chromatographic paper irradiated by 4.5 MeV electrons as a function of dosage, as determined from the integrated X-ray intensities.

multiple geometry intramolecular H-bonds. Each transition creates a new minimum-energy condition within the *tg* conformational range of the hydroxymethyl group.[24,25] This transformation has a minimal effect on cellulose crystallinity or paracrystallinity as demonstrated here. It has also been suggested that noncovalent bonding between the sheets of crystalline cellulose may be the weak link, which yields more readily in the I_α phase compared[25,26] to I_β.

When applied to plant fibers and pulp, as in this study, the I_α and I_β noncovalent bonding differences are probably less well-defined. Low-order materials have poor sensitivity to diffraction, and solid-state NMR can benefit from the lateral order distribution interpretation as proposed by Hult et al.[21]

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