X-RAY SCATTERING AND X-RAY DIFFRACTION TECHNIQUES IN STUDIES OF GAMMA-IRRADIATED WOOD[1]

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ABSTRACT

X-ray scattering and diffraction techniques were used to evaluate degradation of oak wood by gamma radiation. Samples were exposed to 650, 950, and 1,900 Megarads radiation. Chemical analyses (lignin, extractives, and holocellulose content) and density measurements were made on the irradiated samples. Results indicate that cellulose crystallinity was reduced with increasing irradiation and is destroyed at a dosage of 1,900 Megarads. Small-angle X-ray scattering studies were clarified by the use of these additional analytical methods.

Keywords: Irradiated wood, X-ray scattering, X-ray diffraction, cellulose crystallinity, cellulose degradation.

INTRODUCTION

Small-angle X-ray scattering is a method of determining submicroscopic porosity—the size and shape of pores in materials—by measuring the intensity of scattered X-rays in the range of 0 to 3° θ (0 to 60 milliradians) (Guinier et al. 1955; Casteel et al. 1978*a*). This technique differs from X-ray diffraction, which is a method used to determine crystallinity and crystal structure in wood and other materials, where scattered or diffracted radiation is measured at much higher angles. In the case of wood, readings are usually taken from 10 to 26° 2θ (Cutter and Murphey 1970). (Scattering angles are twice the corresponding diffraction of Bragg angles.) Frequently, both techniques may be used on the same sample since there is a zone of overlap that may prove useful to investigators.

Casteel et al. (1978*b*) described the results of small-angle X-ray scattering studies on gamma-irradiated oak and hickory wood. During the review of that paper, a question arose concerning the interpretation of a bump apparent in the plot of the relative scattering intensity (I) versus scattering angle (θ). This bump, which was observed only for the lower level irradiation levels, was ascribed to the crystalline structure of cellulose. Preliminary X-ray diffraction analyses supported the interpretation. In this paper we provide more detailed information clarifying the interpretation of the chemical composition and small-angle scattering data by means of large-angle diffraction and density measurements.

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TABLE 1. *Physical and chemical properties of gamma-radiated oak wood.*

Total irradiation dose	% Holocellulose[a]	% Lignin[a]	% Extractives[a]	SG	ρ_{ws}	CrI[b]
0 Mrads	58.1	32.6	8.98	0.54	1.449	58%
650 Mrads	14.5	30.2	52.8	0.47	1.352	33%
950 Mrads	11.0	29.6	58.0	0.18	1.347	28%
1,900 Mrads	3.7	27.0	69.1	—[c]	1.331	0%

[a] From Tabirih et al. (1977).
[b] From Casteel et al. (1978).
[c] Missing sample.

METHODS

Both the chemical data and additional physical property data for the irradiated wood are shown in Table 1. The methods used by Tabirih et al. (1977) for the chemical analyses were as follows: extractives content, TAPPI Standard T 12m; lignin content, TAPPI Standard T 13m; and holocellulose content, acid chlorite methods. Irradiation was done at the University of Missouri's 10-MW Research Reactor (Tabirih et al. 1977).

Specific gravity (SG) was determined on duplicate samples using pycnometric displacement of water (Stamm 1964, p. 56). The density of wood substance (ρ_{ws}) was determined using suspension in a mixture of carbon tetrachloride (ρ = 1.58, 20/4) and benzene (ρ = 0.88, 20/4) (Beall 1972). Wood meal ground to pass a 40-mesh screen but retained by an 80-mesh screen was used for this purpose. Four determinations were made for each treatment. The small-angle scattering data were obtained using the Kratky camera equipment with filtered Cu K α X-rays (λ = 0.154 nm) as described by Casteel et al. (1978*a*). Filtered Cu K α X-rays were also used to obtain the large-angle diffraction patterns over the range of 10 to 28° 2θ using a G. E. XRD-6 diffractometer. Crystallinity index (CrI) was determined using the intensities of diffracted radiation from the Cellulose I (020) plane, measured at 22.8° 2θ, and the amorphous background taken at 18 to 19° 2θ (Seagal et al. 1959) using the following formula:

$$\mathrm{CrI}(\%) = \frac{I_{(020)} - I_{\mathrm{Amorphous}}}{I_{(020)}} * 100$$

The planes are defined by the Cellulose I unit cell according to Blackwell et al. (1978). In the modified monoclinic unit cell, the dimensions are a = 0.817 nm, b = 0.786 nm, c = 1.038 nm (fiber axis) and γ = 97°. In this unit cell, the (020) plane is equivalent to the (002) plane of the Meyer-Misch unit cell where the b dimension is the fiber axis.

RESULTS AND DISCUSSION

Both the chemical and physical property data for the irradiated wood are shown in Table 1. There are strong correlations between the amount of holocellulose present in the sample and the ρ_{ws} (r = 0.8868), and between the crystallinity index CrI and ρ_{ws} (r = 0.8824). This is not surprising since the ρ_{ws} value is determined not only from the density of crystalline cellulose, but also from the densities of nonordered cellulose, native lignin, and hemicelluloses. Representative densities

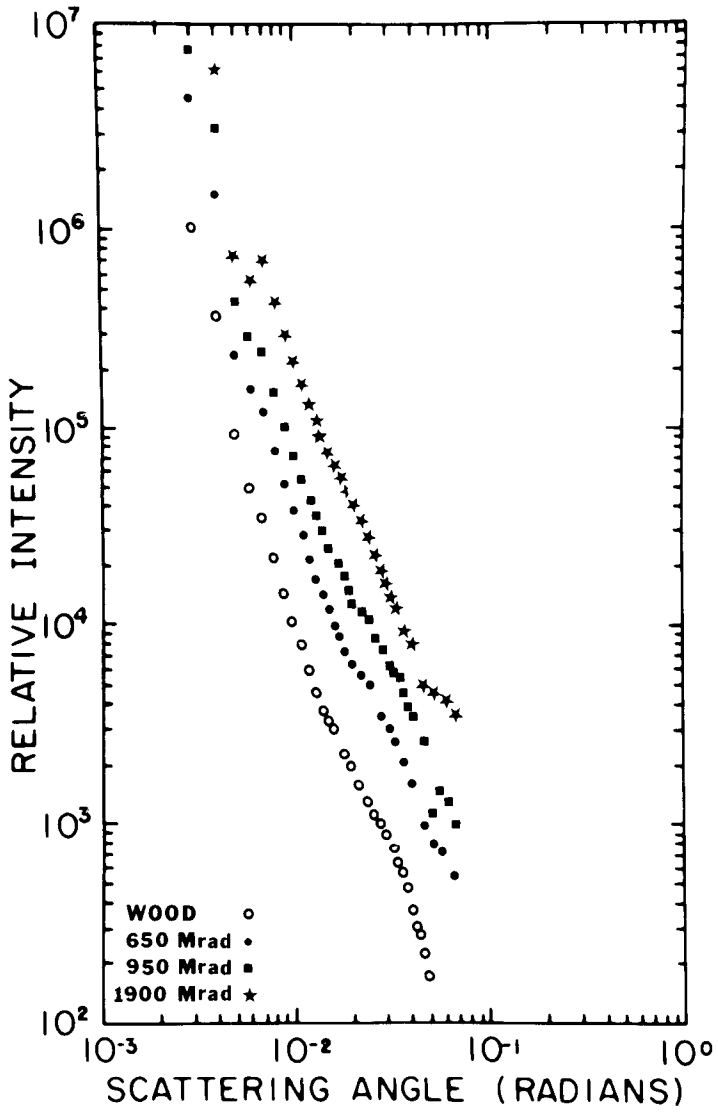

FIG. 1. Guinier plots of relative scattering intensity as a function of scattering angle. Samples have been separated vertically for visual clarity.

of the materials would be crystalline cellulose, 1.58 (Stamm 1964, p. 60), non-ordered cellulose, 1.47 (Beall 1972); hemicelluloses, 1.457 to 1.523 (Beall 1972); and lignin, 1.366 (Stamm 1969). While the chemical composition data indicate nearly a 94% loss of holocellulose after the 1,900 Mrad dose, only about 18% of the lignin was apparently lost. The ρ_{ws} after the 1,900 Mrad dose, 1.331, was close to that reported for hardwood lignin, 1.366 (Stamm 1969). The lignin shown in Table 1 might be more properly considered as sulfuric acid lignin because of the method of determination.

The small-angle scattering curves for the oak wood (Fig. 1) show a well-defined bump in the region from 10^{-2} to $10^{-1.5}$ radians. This feature can also be seen in

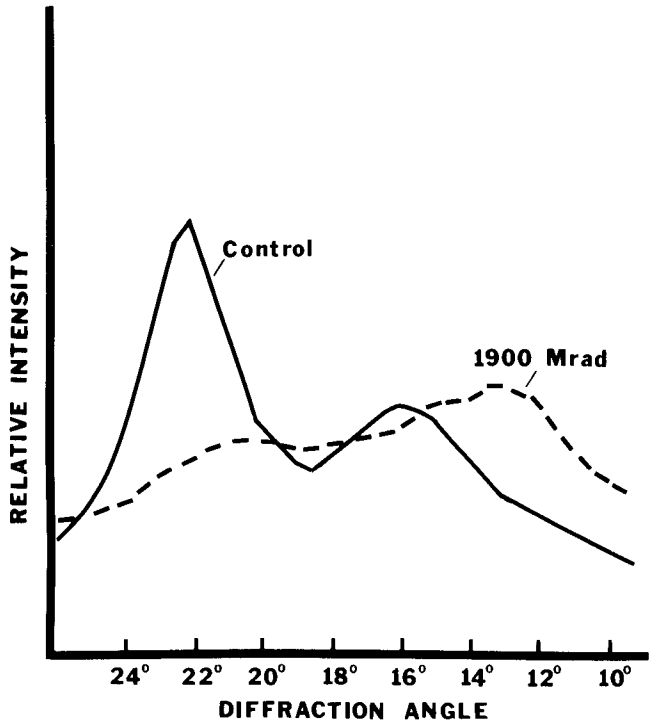

FIG. 2. Typical X-ray diffractometer patterns for nonirradiated oak wood meal (control) and 1,900 Mrad oak wood meal.

curves of the wood exposed to 650 to 950 Mrads although it is not as pronounced. The bump is not evident in the plot of the 1,900 Mrad data. Pyrolysis of wood and cellulose results in a similar scattering pattern (Casteel et al. 1978*a*).

Values for CrI of Cellulose I indicate the disappearance of crystallinity as the total radiation dose increased from 0 to 1,900 Mrads. This is clearly evident in Fig. 2, which shows X-ray diffractometer patterns of normal oak and 1,900 Mrad irradiated oak. While the (020) peak has disappeared in the 1,900 Mrad pattern, a broad diffuse peak is evident in the 13 to 15° 2θ region. This 1,900 Mrad pattern is similar to X-ray diffraction patterns for wood charcoal (von Bastian et al. 1972), white-rotted wood (Cutter and Murphey 1970), and vibratory-milled wood (Pew and Weyna 1962). One could theorize that gamma-radiation attacks the cellulose crystalline structure at the weakest link, the van der Waals forces defining the diagonal planes of the Cellulose I unit cell (Blackwell et al. 1978). This would produce a series of lamellar sheets, remnants of the (020) plane, similar to the layerlike planes in nongraphitizing carbon. Wood is considered a precursor to polymeric carbon or nongraphitizing carbon (Jenkins and Kawamura 1976). This initial point of attack on cellulose crystallinity was previously suggested for white-rotted wood (Cutter and Murphey 1970). Disruption of the relatively rigid lattice structure would obviously lead to the extensive depolymerization that occurred, as suggested by the marked increase in extractives content of the irradiated wood.

If the small-angle scattering curves are examined keeping the previous discus-

sion in mind, it becomes fairly apparent that the bump in the plots of I vs. θ in the region of 10^{-2} to $10^{-1.5}$ radians is actually due to the presence of crystalline cellulose in the samples. This bump, which is readily apparent for the plots of the control wood sample, and noticeable in the 650 and 950 Mrad plots, completely disappeared in the 1,900 Mrad curve. However, these data are not sufficiently well-defined to quantify the rate of disappearance.

CONCLUSIONS

Small-angle X-ray scattering studies and X-ray diffraction studies were used in conjunction with chemical analyses and density measurements to describe the pattern of degradation shown by oak wood exposed to increasing doses of gamma radiation. Normal wood scattering curves displayed a pronounced bump in the $10^{-1.5}$ radians region. Large doses of gamma radiation resulted in the gradual disappearance of the bump. Large-angle X-ray diffraction studies indicated that cellulose crystallinity was destroyed as total radiation dose increased. This was supported by density and chemical composition data.

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