Some Physical Properties of Wood and Cellulose Irradiated with Gamma Rays

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Abstract—The effect of gamma irradiation from cobalt-60 on specific gravity, degree of crystallinity, thermal softening temperature, tensile strength and torsional creep behavior of wood and cellulose were investigated and the following results were obtained.

1) A dosage up to about $10^8$ rad had little effect on the specific gravity of wood and cellulose.
2) The degree of crystallinity of wood and cellulose remained almost unchanged up to $3 \times 10^7$ rad, but started to decrease rapidly at about $1 \times 10^8$ rad.
3) The softening temperature of cellulose shifted gradually to a lower temperature region up to about $3 \times 10^7$ rad and abruptly in the range exceeding $3 \times 10^7$ rad.
4) Strength of wood decreased with increasing irradiation dosage, depending remarkably on loading modes.
5) The value of creep compliance of wood at time 0.1 min did not change up to $1 \times 10^7$ rad, but increased markedly in the range exceeding about $3 \times 10^7$ rad.

Introduction

High energy radiation causes changes in the chemical and crystalline structures of wood, but does not result in significant changes of its anatomical or supramolecular structures, when radiation dosages up to $5 \times 10^8$ rad are used. As the physical and mechanical properties of wood depend on its chemical and crystalline structures, some attempts applying high energy radiation techniques to modify and improve the hygroscopicity, swelling, and decay susceptibility of wood have been made. However, prior to this an understanding of the effects of high energy radiation on the physical and mechanical properties in relation to the chemical structure is necessary. We have investigated the relationship between dielectric properties and the molecular structure of wood irradiated with gamma rays. In this paper, we outline the changes in some physical properties of wood and cellulose induced by the irradiation of gamma rays in the light of the many published references.

Experimental

The samples used were Hinoki wood (Chamaecyparis obtusa Endl., specific

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gravity: 0.41), Hoonoki wood (Magnolia obovata Thunb., specific gravity: 0.54) and Whatman cellulose powder irradiated with gamma rays from cobalt-60 under an air atmosphere for 0, 1, 3, 10, 30, 100 hours at a dose rate of 3.12 Mrad/hr for wood and at 3.20 Mrad/hr for cellulose.

The creep measurements were carried out at 20° and 50°C in water using a torsional apparatus. The dimension of the specimen was 6.60 (L) x 1.00 (R) x 0.110 (T) cm. The tensile strength of the irradiated wood was measured in water at 20°C using an instron type tensile testing instrument (TOM 5000X produced by Shinko Ltd.). Furthermore, the amount of thermal expansion for the irradiated cellulose under a constant compressive load (10 g) was measured in vacuo in the temperature range of 20° to 300°C at a heating rate of 2°C/min using a thermo-mechanical analyzer (TM 1500, Sinku Riko Co., Ltd., see Fig. 1).

On the other hand, in order to make clear the relationship between crystalline structure and mechanical properties of the irradiated wood and cellulose, X-ray diffraction measurements were performed by the transmission method (Cu-Kα) using a Rotaflex (RU-3L X-ray diffractmeter, Rigaku Denki Co., Ltd.), and the relative degree of crystallinity was estimated by the crystallinity index defined by Segal and others.

Results and Discussion

1) Specific Gravity

In Fig. 2, the relative specific gravity of the irradiated wood \( \rho_c/\rho_0 \) is plotted against logarithmic irradiation dosage log \( D \). In this figure, the data of woods
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Fig. 2. Relative specific gravity $\rho_r/\rho_o$ of wood and cellulose as a function of irradiation dosage $\log D$. $\rho_r$: irradiated, $\rho_o$: untreated.

and cellulose published by many authors\textsuperscript{19,22,23,24,32,37} are also included. SUGIMATSU et al.\textsuperscript{32} reported that the value of specific gravity of cellulose slightly increases at about $4 \times 10^6$ rad when cellulose is irradiated with gamma rays under an oxygen atmosphere. On the other hand, the data published by ISHIGURO et al.\textsuperscript{37} showed that the value of specific gravity of wood irradiated with gamma rays in vacuo decreases once up to $1 \times 10^7$ rad and then increases at irradiation levels in excess of $1 \times 10^7$ rad. However, as is evident from the figure, it seems that a dosage up to about $10^8$ rad has little effect on the specific gravity of wood and cellulose.

2) Degree of Crystallinity

TAKAMUKU et al.\textsuperscript{8} reported that the dosage of crystallinity of cellulose is almost unchanged up to $5 \times 10^7$ rad. MURAYAMA\textsuperscript{34} showed that in X-ray diffraction measurement any changes in the lattice constant of cellulose can not be detected at a dosage of $1 \times 10^8$ rad. HIRAI et al.\textsuperscript{35} also reported that the degree of crystallinity of wood remains unchanged up to $1.4 \times 10^8$ rad. However, the result published by SEIFERT\textsuperscript{44} showed that the degree of crystallinity of wood slightly decreases at a dosage of $10^8$ rad in comparison with that of the untreated wood. Furthermore, ISHIGURO et al.\textsuperscript{37} showed that the degree of crystallinity starts to decrease rapidly at about $1 \times 10^8$ rad, and GOTO et al.\textsuperscript{48} confirmed that the crystalline peaks observed in the untreated wood disappear completely at a dosage of $6.55 \times 10^8$ rad.

In Fig. 3, the relative crystallinity index $\beta_r/\beta_o$ of wood and cellulose as a function of $\log D$ are shown. The data published by many authors\textsuperscript{8,34,35,37,48} are also plotted in this figure. $\beta_r/\beta_o$ value of wood and cellulose almost remains unchanged up to $3 \times 10^7$ rad, but starts to decrease rapidly at about $1 \times 10^8$ rad. And, the value falls to 0.1 in cellulose and 0.5 in wood at about $1 \times 10^8$ rad. A similar tendency can be detected in the infrared spectra in which a broadening of the so-called crystalline sensitive bands (1110, 1060, 1040 cm$^{-1}$)\textsuperscript{61} occurs at $9.7 \times 10^7$ rad. From
the figure, it seems that the crystallinity of wood decreases gently compared with that of cellulose in the range exceed $10^8$ rad. Consequently, it may be concluded that wood is more resistant to degradation due to high energy radiation than cellulose because of the presence of encrusting substances such as lignin and extractives.

3) Degree of Polymerization

Säeman et al. studied the effect of high energy cathode ray irradiation on wood, wood pulp and cotton linters, and showed that the effect of irradiation on degree of polymerization $DP$ for cellulose is not appreciable up to a dosage of $10^6$ equivalent roentgens, but at high dosage the rapid decrease in $DP$ occurs. Cherlesby used the viscosity data of Säeman et al. to verify a theoretical relation between intrinsic viscosity and radiation dosage. Mizukami and Horio et al. found that the plots of logarithm of the difference between the reciprocal of $DP$ of the irradiation cellulose and that of the untreated cellulose against log D ranging from $5.2 \times 10^5$ to $1.1 \times 10^8$ roentgens give a straight line. On the other hand, Huang et al. reported that an approximately linear relation is obtained when $DP$ is plotted against gamma irradiation dosage on a log-log scale, and this result was in good agreement with that of Blouin and others. Furthermore, Neal et al. showed that the number of bond broken by electron irradiation is a linear function of irradiation dosage for wood pulp.

In Fig. 4, $DP$ value published by many authors is plotted against irradiation dosage on a log-log scale. From this figure, it is evident that there is a linear relationship between log $DP$ and log D in the region from $10^6$ to $10^8$ rad.
Fig. 4. Degree of polymerization DP of cellulose as a function of log D.

Fig. 5. Thermal expansion of gamma irradiation Whatman cellulose under a constant load.

Fig. 6. Softening temperature Ts of Whatman cellulose as a function of log D.
4) **Thermal Softening Temperature**

Fig. 5 illustrates the amount of thermal expansion under a constant compressive load for Whatman cellulose irradiated with gamma rays. When the amount of expansion was plotted against temperature, a clear maximum occurred. The peak position on the temperature scale, which is defined by Goring as a softening temperature $T_s$, was about $235^\circ\text{C}$ for untreated cellulose, which is in good agreement with that of Goring. Fig. 6 shows $T_s$-log D curve of Whatman cellulose. $T_s$ decreases linearly up to about $3 \times 10^7 \text{ rad}$, where any changes in the degree of crystallinity can not be detected, but DP value decreases linearly against log D. Therefore, it is assumed that $T_s$-shift to lower temperature range would be due to the scission of chemical bond such as a glucosidic bond. On the other hand, $T_s$-shift in the range exceeding $3 \times 10^7 \text{ rad}$ would be due to degradation of crystalline structure.

5) **Strength**

Siau et al. reported that there is no apparent reduction in compressive strength of wood perpendicular to grain up to $1 \times 10^7 \text{ rad}$ and Karpow et al. showed that degradation starts at $1 \times 10^7 \text{ rad}$ in bending and $1 \times 10^8 \text{ rad}$ in compression. Furthermore, Burmester found that there is an insignificant increase in tensile and compressive strengths resulting from develop of hydrogen bond in wood when low gamma irradiation dosages are used, but with increasing dosage tensile strength reduces more rapidly than compressive strength. Ramalingam et al. also found that the percent loss in bending strength of wood is directly proportional to gamma irradiation dosage beyond the level of $2 \times 10^6 \text{ rad}$. Seifert reported that the changes in the chemical properties reflect strength of the gamma irradiated wood and the decrease in tensile and compressive strengths is due to the reduction of NaOH insoluble fraction of wood up to about $10^8 \text{ rad}$. On the other hand, IjJU found that tensile strength of gamma irradiation wood depends mostly on cellulose DP and the decrease in DP reduce strength more in low DP region than in high DP region.

In Fig. 7, relative compressive strength $\sigma_c/\sigma_{0c}$, bending strength $\sigma_{b}/\sigma_{0b}$ and tensile strength $\sigma_t/\sigma_{0t}$ of wood are plotted against log D with the results reported by other authors. The results reported by Gilfilland et al. showed that the removal of water and oxygen by evacuation dose not have any effect on the strength of the beta irradiated cotton yarns. Furthermore, the study of IjJU on moisture content and temperature dependence of tensile strength of gamma radiation wood showed that tensile strength of wood with degraded cellulose is more sensitive to changes in moisture content. Siau et al. emphasized that the results published by Karpow et al., Ramalingam et al. and Kranovitskaya...
differ widely and this results from different measuring conditions. However, from Fig. 7, it is evident that both temperature and moisture content have little effect on strengths, but strength depends remarkably on loading modes. In this connection, the relative strength decrease in the order, tensile strength > bending strength > compressive strength.

6) Viscoelastic Properties

The results reported by Sugimatsu et al. shows that the value of dynamic elastic modulus reached a maximum at around $5 \times 10^6$ rad when cellulose was irradiated under an oxygen atmosphere, and they attribute it to the formation of inter-cellular bonding. On the other hand, Sulin showed that the value of dynamic bending elastic modulus of wood remains unchanged up to $1 \times 10^7$ rad, and Ishiguro et al. also showed that the ratio of dynamic elastic modulus to specific gravity as well as the degree of crystallinity rapidly starts to decreases at about $3 \times 10^7$ rad. In addition Choong et al. reported that the value of bending elastic modulus is almost unaffected by gamma irradiation. On the contrary, Hirai et al. showed that the value of dynamic compliance of wood increases by about 90 percent at $2.5 \times 10^8$ rad.

Fig. 8 illustrates the torsional creep curves of gamma irradiation Hinoki wood in water at 50°C. Furthermore, Fig. 9 shows the values of creep compliance $\mathbf{J}(0.1)$
Fig. 8. Creep curves of gamma irradiation Hinoki at 50°C in water.

Fig. 9. Creep compliance $J(0.1)$ and slope in $J(t)$ vs $t$ curve $\alpha$ of Hinoki as a function of log D. ($\triangle$: 20°C, $\circ$: 50°C)

at time 0.1 min and the slope $\alpha$ at 100 min in $J(t)$ vs $t$ curves for Hinoki wood as a function of dosage. $J(0.1)$ value remains almost unchanged up to $1 \times 10^7$ rad, but starts to increase rapidly at about $3 \times 10^7$ rad and this tendency is similar to that of crystallinity. On the other hand, $\alpha$ which is a measure of creep rate, decreases with increasing dosage.

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