Depolymerization of Cellulose by Electron Beam Irradiation

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The depolymerization of cellulose by means of a high energy irradiation was studied using ^{60}Co gamma-ray or electron beam as an irradiation source. It was found that the number of broken bonds calculated from number average degree of polymerization (P_n) of irradiated samples is linearly proportional to the absorbed doses, and an experimental equation applicable to both types of irradiation was established. By the use of this equation, the relative absorbed dose distribution within the pulp sheets in pile irradiated with electron beams was determined from the P_n values for each sheets. Furthermore, in order to make the absorbed dose distribution narrower the utilization of electron filters as well as back-scattering bodies were studied for an electron beam at 2 and 0.5 MeV, respectively. Although both techniques are useful to prevent the samples from causing wide absorbed dose distribution, it may be to note that higher irradiation efficiency (95 % or more) and narrower absorbed dose distribution are achieved using single side irradiation method of the latter. The various samples thus irradiated were nitrated and characterized successfully for the molecular weight distributions using gel permeation chromatography.

I. INTRODUCTION

It is well known that native cellulose usually occurs with higher degree of polymerization making certain practical applications difficult. For this reason, many methods of reducing the degree of polymerization in a controlled manner have been developed, such as oxidative bleaching, alkali aging or acid hydrolysis. Thus chemical methods of reducing molecular weight are sometimes accompanied by desirable removal of impurities, while they are also accompanied by undesirable effects, such as loss of yield and non-random depolymerization of cellulose.

The use of high energy radiation to depolymerize cellulose is well known.[1~4] This method is distinguished from chemical methods since depolymerization of samples takes place in the solid state. Since irradiation can be readily and precisely controlled, it is interesting to compare this method with other conventional methods of depolymerizing cellulose. However, the scarcity of knowledge about depolymerizing cellulose by irradiation has hampered detailed discussion. The purpose of this work was to accumlate the practical knowledge about depolymerizing cellulose of which the degrees of polymerization up to 250~450, using ^{60}Co gamma-ray, 0.5 and 2 MeV electron beams.

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II. EXPERIMENTAL SECTION

Irradiation

The irradiation was carried out at following three different irradiation centers :

(1) Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, using a gamma-ray irradiation facility housing 2,000 Ci ^{60}Co source (dose rate $1.59 \cdot 10^5$ r/h in the center of the sample chamber)

(2) Takasaki Laboratory, Japan Atomic Energy Research Institute, using a resonant transformer at 2 MeV (beam current 3 mA, irradiation width 40 cm, dose rate $2.18 \cdot 10^6$ rad/sec)

(3) Katada Laboratory, Toyo Spinning Co., using an insulated core transformer at 0.5 MeV (beam current 4.1 mA, irradiation width 45 cm, distance between window and sample 20 cm)

No special precaution were taken to preclude oxygen or moisture, since such circumstances are impractical on a large scale. The commercially available regular pulp of dissolving grade (cf. Table 1) was exposed to gamma-ray or electron beams as air-dry sheets enclosed in polyethylene film. And then, the irradiated sheets were kept for three or more weeks at the room temperature taking precautions against postirradiation, before subject to various measurements.

Measurements

The intrinsic viscosity, $[\eta]$, of samples (original dissolving and irradiated pulp) was determined from a single viscosity measurement in cupriethylenediamine according to SCAN 15 : 16, and converted into the corresponding number-average degrees of polymerization P_n using Immergut equation.[5]

$$[\eta]_{OED} = 1.33 \cdot 10^{-2} \cdot P_n^{0.905}$$

Cellulose nitrates (nitrogen contents of 13 percent or more) were prepared by non-degrading Alexander and Mitchel's method[6] for gel permeation chromatographic analysis with all the samples, including aged alkali-cellulose and identically prepared rayon fibers from the same dissolving pulp by the conventional viscose process or prepared directly from an irradiated pulp by so-called "no-aging viscose process".[7]

In gel permeation chromatography, the nitrate samples in tetrahydrofuran were eluted in a Shimazu 1-A Model with column system of average pore size of 10^7, 10^6, 10^5 and 10^3 Å. The analysis was carried out at room temperature using a sample concentration of $0.10 \sim 0.5$ g per 100 ml, injection time of 120 sec and flow rate of 1.0 ml per min. for various nitrate samples.

Pulp Analysis

Alpha-cellulose, beta-cellulose, copper number, 1 % NaOH solubility and brightness of samples were determined by JIS-P 8101. Pentosan content was determined by the method of Okubo.[8] Carboxyl content was determined by chelatometric

titration method, and carbonyl content was determined by oxidizing the samples with sodium chlorite followed by the same titration procedure as in the case of carboxyl analysis.[9]

III. RESULTS AND DISCUSSION

1. Degradation of Cellulose and Change of Cellulose Properties

Depolymerization of Cellulose[16]

In our previous investigation[3] carried out using ^{60}Co gamma-ray, a fixed ratio was held between the exposure dose (in roentgen) and the fraction of bonds broken.   Denoting P_n and P_n' the number-average degree of polymerization before and after irradiation respectively, this ratio is expressed as follows:

$$\frac{1}{P_n'} - \frac{1}{P_n} = P \cdot R^{0.85}$$

where R is the exposure dose and P is the probability of bond-fractures occurring at a given monomer unit per exposure dose, which is equal to S/N giving the number-fraction of bonds broken:

where S : the number of bonds broken per gram

N : the total number of monomer units per gram

The chemical effect of the initial absorption of gamma-ray is very small: *i. e.*, the measurable chemical effects are the result of the secondary ionizations caused by the ejected electrons.   For this reason, it may be expected that high energy electron beam and gamma-ray cause very similar chemical effects on cellulose.   In the present work, the ratio between the dose and the fraction of bonds broken was investigated for both ^{60}Co gamma-ray and electron beam at 2 MeV.   The results obtained were shown graphically on a log-log plot in Fig. 1.
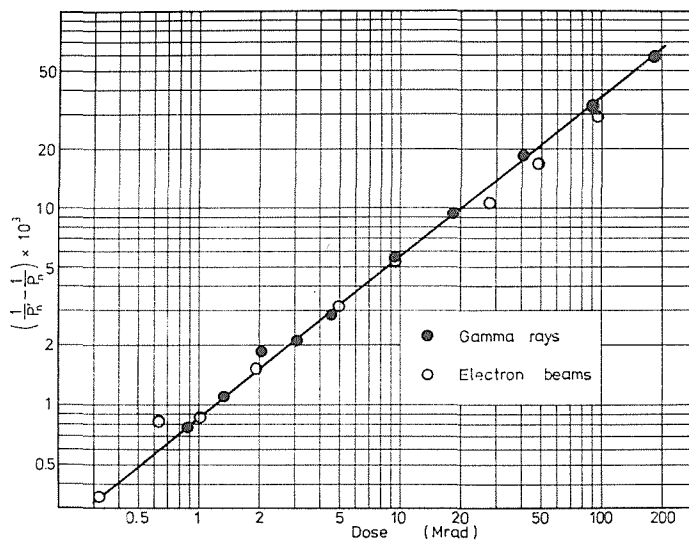

Fig. 1.   Log-log plot of $\left(\dfrac{1}{P_n'} - \dfrac{1}{P_n}\right)$ vs. absorbed dose.

In both cases, the change in dose versus $\dfrac{1}{P_n{}'}-\dfrac{1}{P_n}$ was found to be linear and if the absorbed dose (in Mrad) is used as a common unit, this relation can be also expressed with the following equation:

$$\frac{1}{P_n{}'}-\frac{1}{P_n}=8.5\cdot10^{-4}\cdot D_c{}^{0\cdot83}$$

where D_c is the absorbed dose*. This experimental equation is useful to convert the measured values of P_n into their absorbed doses of cellulose samples and was used successfully to evaluate the penetration depth of electron beam which will be shown in the following experiment.

Formation of Oxidized Groups

The interaction of radiation with cellulose leads to an oxidative degradation of the solid residue of irradiated samples. Figure 2 shows an increasing formation of oxidized groups (carbonyl and carboxyl groups) with increasing dose. These plots on a log-log are approximately linear for gamma-ray and electron beam over the range of 0.2~200 Mrad, respectively, and also indicate that the amount of oxidized groups is a little greater in carbonyl than in carboxyl group.[17] When cellulose is irradiated in an atmosphere of oxygen, the yield of these groups were reported to be greater than those obtained in nitrogen atmosphere.[10] Furthermore, the reaction of oxygen with free radicals formed in the amorphous or more accessible region of the fibrous cellulose is said to lead to the formation of these groups through the formation of peroxides. The formation of these groups by irradiating in the air may also be understood in the same manner.
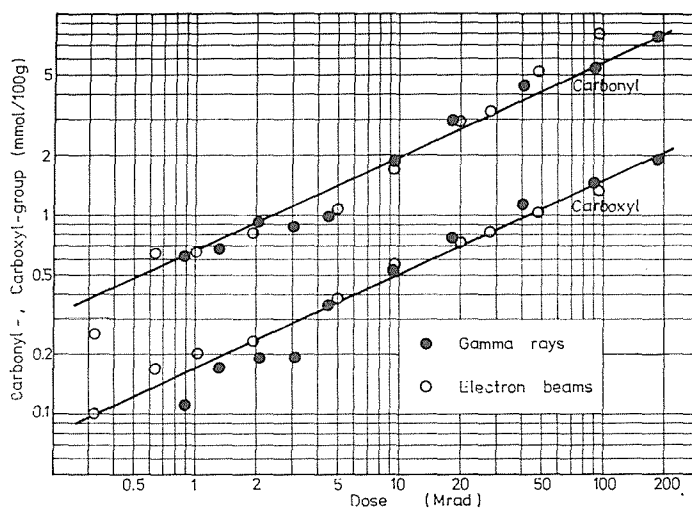

Fig. 2. Radiation-induced formation of carbonyl and carboxyl groups.

Effect on Cellulose Properties

In general, irradiation has a deleterious effect on the analytical properties of

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* In the case of cellulose, 1 roentgen was calculated to be 0.923 rad.

Table 1. Analytical Properties of Irradiated Pulps.

Radiation	Dose (Mrads)	Number average DP	α-Cellulose (%)	β-Cellulose (%)	Pentosan (%)	Copper number	Carbonyl groups (mmols/100g)	Carboxyl groups (mmols/100g)	Brightness
	0	752	90.0	5.5	3.3	1.3	0.57	3.17	90
Gamma rays	0.88	476	88.0	7.5	3.3	1.9	1.19	3.28	⋯
	1.32	412	86.7	8.9	3.3	2.2	1.24	3.34	⋯
	2.06	313	83.6	11.9	3.3	2.8	1.49	3.36	⋯
	3.08	291	82.1	13.5	3.4	3.0	1.46	3.36	⋯
	4.52	237	74.3	22.9	3.4	3.8	1.56	3.52	⋯
	9.46	144	⋯	⋯	3.4	6.2	2.46	3.71	⋯
	18.3	93	⋯	⋯	3.8	11.2	3.66	3.94	⋯
	40.6	51	⋯	⋯	3.9	24.6	4.98	4.32	⋯
	90.8	29	⋯	⋯	4.4	46.5	6.86	4.63	⋯
	188	17	⋯	⋯	5.2	70.2	8.06	5.06	⋯
Electron beams	0.32	598	89.5	6.1	3.3	1.5	0.82	3.27	90
	0.64	466	88.7	6.9	3.4	1.6	1.21	3.34	90
	1.02	456	88.0	7.7	3.4	1.7	1.22	3.37	90
	1.91	352	85.2	10.8	3.4	2.3	1.38	3.40	90
	5.00	223	73.6	23.7	3.5	3.5	1.64	3.55	89
	9.50	151	⋯	⋯	3.5	5.6	2.26	3.73	88
	20.0	101	⋯	⋯	3.5	9.1	3.51	3.90	85
	28.0	84	⋯	⋯	⋯	10.3	3.84	3.98	82
	48.0	52	⋯	⋯	3.8	15.6	5.76	4.19	82
	95.0	33	⋯	⋯	⋯	28.8	7.53	4.48	72

wood pulps which are of technical importance. As can be seen in Table 1, the alpha-cellulose content of pulps reduces with increasing dose, while the beta-cellulose content (mainly cellulose fractions of relatively low degree of polymerization) increases with increasing dose. The carbonyl and carboxyl content, 1% NaOH solubility and copper number also increase while color of pulps deepens. Thus change in pulp properties was common to both ^{60}Co gamma-ray and electron beam.

The deterioration of pulp properties, however, becomes remarkable at the dose of about 5 Mrad, where an absorbed dose lowers the number-average degree of polymerization from 752 to 230. Within the range of such depolymerization, it seems that pulp properties do not essentially change, although beta-cellulose content increases progressively.

2. Two Types of Electron Beam Irradiation

In order to depolymerize cellulose by irradiation on a large scale, electron accelerators should be considered to use. In the present work, resonance transformer at 2 MeV and insulated core transformer at 0.5 MeV were used as an electron source, as above mentioned. In general, the penetration depth varies with the energy of electron beam, as can be seen in Fig. 3.[12] In technical applications, however, "the useful range" as defined as the maximum depth in
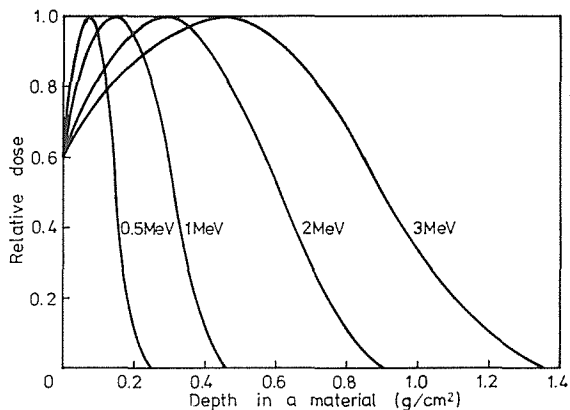
Fig. 3. Penetration depth vs. dose distribution in a material
for high-energy electrons.[12]

which the ionization does not fall below 60 per cent of peak value, should be
taken into consideration. In the present experiment, it was found that this
useful range corresponds roughly to the thickness of 7 pulp sheets for an elec-
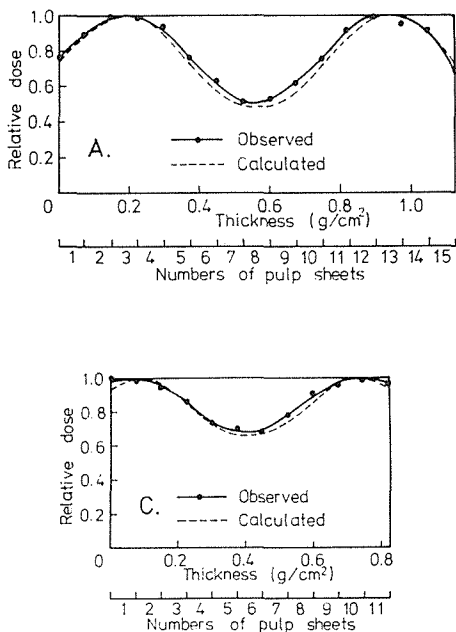tron accelerator at 2 MeV and to one pulp sheet for an electron accelerator at
0.5 MeV.[17]

Fig. 4. Relative dose distribution within pulp sheets in pile
for both sides irradiation with 2 MeV electron beam. Dotted
lines indicate the results obtained from theoretically cal-
culated values.
  A : Covered without filter
  C : Covered with aluminum plate of 0.4 mm thick

Electron Accelerator at 2 MeV

In general, a greater utilization of electron beam energy can be achieved in certain cases by irradiation of a specimen from both sides, and in such a way full use is made of the energy in the tail of beam. In the present experiment, 15 pulp sheets (basic weight of a pulp sheet $750\,g/m^2$) were irradiated by means of both sides irradiation technique. Figure 4-A shows that the relative dose reaches maximum in the third and the thirteenth sheets and minimum in the eighth sheet, while P_n value is 443 at the maximum point of the absorbed dose and 553 in the minimum point.

On the other hand, in order to provide the uniform irradiation of a specimen, the utilization of electron filters should be taken into consideration. This technique was carried out by replacing the corresponding number of pulp sheets with an aluminum plate of 0.2 mm, 0.4 mm or 0.6 mm in thickness and irradiating from both sides. In the irradiation of such 11 pulp sheets in pile covered with an aluminum plate of 0.4 mm in thickness, for example, the relative dose becomes maximum in the first pulp sheet and minimum in the seventh pulp sheet, as can be seen in Fig. 4-C. And also it is found that P_n value at the maximum point of the absorbed dose is 460 and that at the minimum point is 515. From these results, it may be expected that the fairly narrow dose distribution is achieved by a combined technique of the both sides irradiation and the utilization of an electron filter.

Electron Accelerator at 0.5 MeV

The relatively low energy electron beam, for instance, with an electron accelerator at 0.5 MeV, may be advantageous because of that shielding are relatively simple and no serious difficulties arise in insulation or power production because of the relatively low voltage used. In addition, it is said recently that this type of irradiation equipments with such a great beam current as 200 mA are on commercial. Accepting this fact, it may be possible that, even if the electron penetration depth is not so great, the irradiated materials is readily mass-produced simply by increasing velocity of belt conveyer.

From this point of view, in order to raise irradiation efficiencies and to make absorbed dose distribution narrower, the utilization of various metal plates as a back-scattering body was designed and a series of experiments were carried out by setting one of them under the handsheets in pile, which were previously formed for one sheet with a basic weight of $59\,g/m^2$.

The curve A in Fig. 5 indicates the relative dose distribution without the use of back-scattering body. Among the 25 handsheets irradiated, the relative dose is maximum in the forth handsheet rapidly dropped to very small values in the 22 th handsheet. And also the P_n value is 446 at the maximum absorbed dose point. The curves B, C and D in the same figure show the results obtained in the experiments in which aluminum, iron and lead plates are used as a back-scattering body, respectively, by setting under 13 handsheets. When any of the back-scattering bodies is not used, the energy escaped from the handsheets is estimated to correspond to an area ATR, and when back-scattering bodies are

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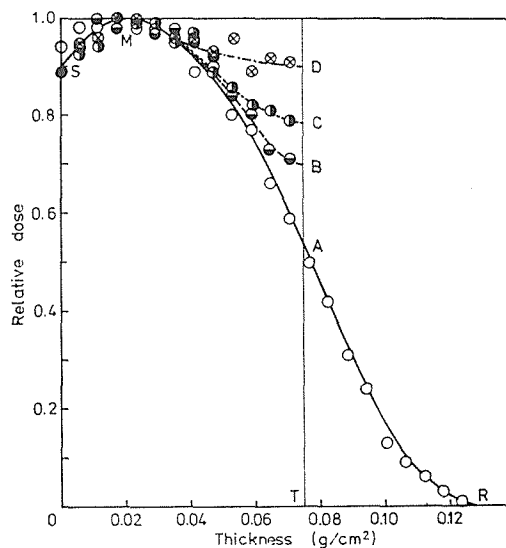
Curve	Back scattering materials
SMA R	None
SM B	Al
SM C	Fe
SM D	Pb

Fig. 5. Relative dose distribution within handsheets for single
side irradiation with 0.5 MeV electron beam.

used, the energy back-scattered are estimated to correspond to the area MAB
(Al), MAC (Fe) and MAD (Pb), respectively. Especially in the case of lead
plate, the energy deposited in the handsheets amounts to 95 per cent of total
irradiation energy. And also the P_n value is 447 at the maximum point of ab-
sorbed doses and is 465 at the minimum point. These values indicate that the
relative dose distribution is remarkably narrow in this case. From the above
results obtained, one must notice that the most effective irradiation and the
narrowest does distribution are achieved by the single side irradiation alone,
using a lead plate as a back-scattering body.

3. Molecular Weight Distribution of Irradiated Cellulose

In order to fully understand the radiation-induced depolymerization, it is
important to have a detailed knowledge of molecular weight distributions of
irradiated cellulose. In general, the molecular weight distribution of polymers
has been determined by tedious experimental techniques, such as precipitation
fractionation or solution fractionation, until a new analytical method, *i. e.* gel
permeation chromatography has been recently developed for the continuous frac-
tionation. As for the case of cellulose, some workers have already studied and,
for instance, Muller and Alexander[13] concluded that gel permeation chromato-
graphy was a useful tool in characterizing wood pulps and that it could be used
to detect small differences in molecular weight distributions of pulps. However,
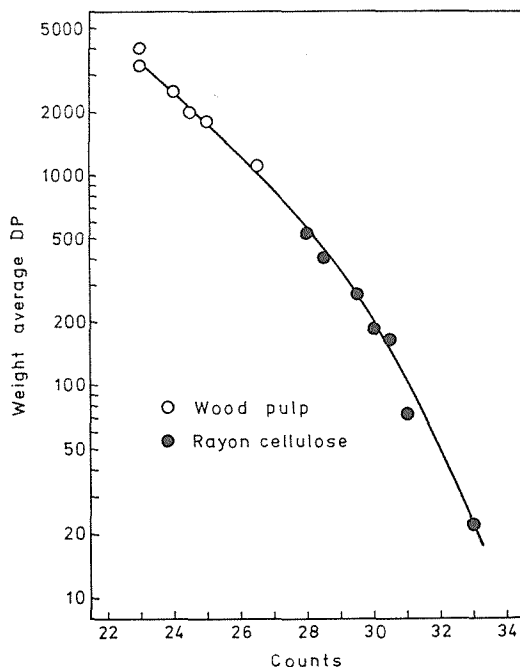a meaningful calibration curve with which the experimental gel permeation

Fig. 6. Calibration curve for cellulose nitrate in gel permeation chromatography.

chromatograms are converted to true molecular weight distribution curves is a difficult task. This is due to the fact that the cellulose samples having such a narrow molecular weight distribution as in the case of polystyrene are not commercially available and are extremely difficult to prepare by classical fractionation techniques.

Figure 6 shows the calibration curve obtained in our laboratory. As described in our previous paper,[14] this calibration curve also is not a completed one and thus the following discussion is mainly focused on the reference to "count number."

Uniform Irradiation of Cellulose

In order to accurately estimate radiation effects, it is highly desirable to work with an apparatus of uniform irradiation field. In the present work, this was achieved by sampling in the center of a sample chamber for gamma-ray irradiation, while sampled at the surface of a pulp sheet near the maximum absorbed dose for electron beam irradiation.

Figure 7 shows the gel permeation chromatograms of the original dissolving pulp having P_n of 754 and the pulp having P_n of 404 prepared by irradiating with an electron beam at 2 MeV. In the former chromatogram, it is noticed that the original pulp has bimodal distributions (count no. ca. 25 and 29) in the center and another modal in the tail (count no. 35~36). The last modal may likely be correspond to non-cellulosic components having low degrees of polymerization, considering that wood pulps in nature are seemed to contain such
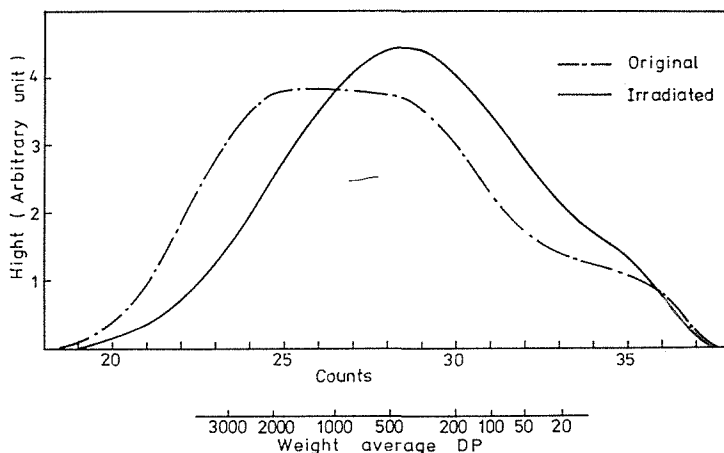
Fig. 7. Gel permeation chromatograms of nitrates from an original dissolving pulp and a uniformly irradiated pulp.

components. In the latter chromatogram, it is interesting that the shape of the distribution curve approaches that of a uniform Gaussian distribution. In the latest work, Hung and Jenkins[15] have also reported that the shape of distribution curves gradually changes from that of non-random sample and approaches that of a random sample with a normal distribution during gamma-ray irradiation.

Subsequently, the same dissolving pulp having Pn of 754 was used as a starting material for the conventional viscose process, while the same irradiated pulp having Pn of 404 was used as a starting material for "no aging viscose process".[7] In Fig. 8, the gel permeation chromatograms of alkali-cellulose prior to sulphurizing and rayon staple fibers are compared for viscose processes.
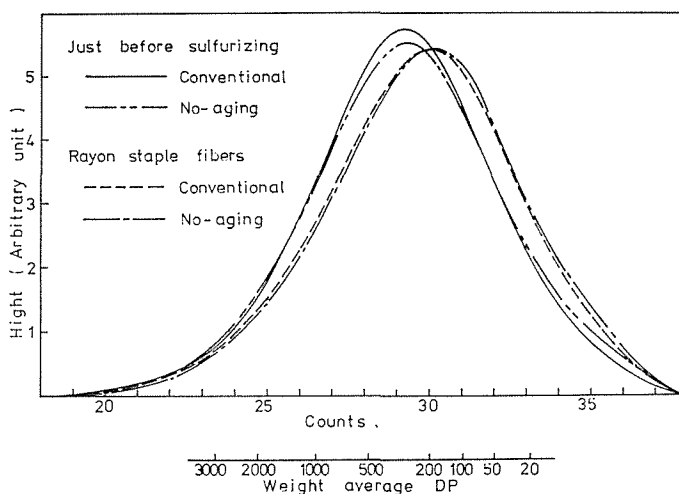

Fig. 8. Gel permeation chromatograms of nitrates from an alkali-cellulose prior to sulphurizing and a rayon fiber. Comparison of conventional viscose process with "no-aging" viscose process.

Little difference is observed in their chromatograms, if any, as such the distribution curve of alkali-cellulose prepared by alkali-aging is slightly sharper than that of alkali-cellulose prepared directly from the irradiated pulp. In spite of the fact, however, it may be important to note that the distribution curves are similar each other because of a random depolymerization of cellulose.

Irradiated Cellulose with Electron Beam

In the irradiation with electron beam on a large scale, it is more or less unavoidable that the depolymerization of cellulose becomes uneven within pulp sheets in pile because of uneven absorbed dose. Fortunately, the two effective methods is devised to minimize such uneveness in the present work. One of them is the radiation with electron beam at 2 MeV using an aluminum plate as an electron filter, and another is the irradiation with electron beam at 0.5 MeV
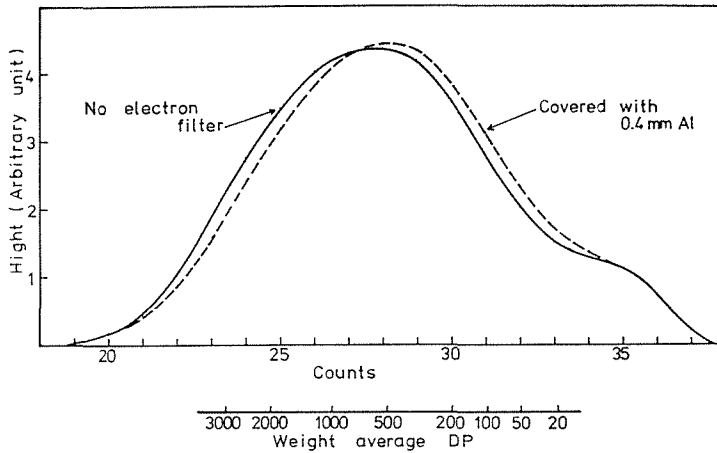
Fig. 9. Gel permeation chromatograms of nitrates from the pulp sheets in pile irradiated by both sides irradiation technique with 2 MeV electron beam.
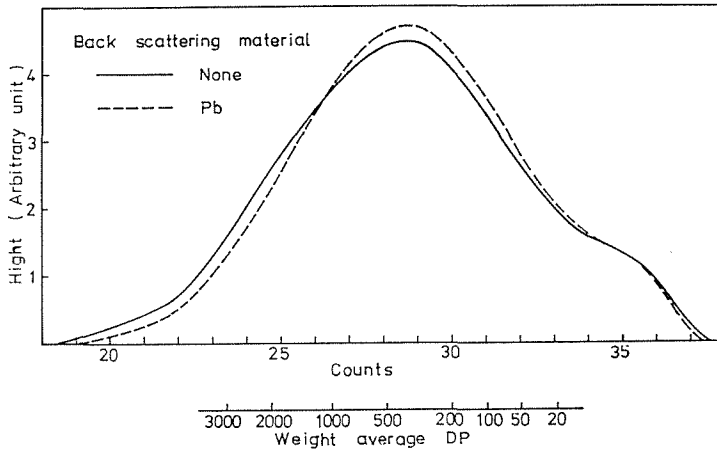
Fig. 10. Gel permeation chromatograms of nitrates from a pulp sheet irradiated by single side irradiation technique with 0.5 MeV electron beam.

using a lead plate as a back-scattering body. Figure 9 shows the comparison between the gel permeation chromatograms of the two pulps prepared by irradiating from both sides with electron beam at 2 MeV. It is interesting that a narrower distribution curve is achieved if the aluminum plate was used as an electron filter to cover the pulps, although the difference is relatively small. Further, Fig. 10 shows the comparison between the gel permeation chromatograms of the two pulps prepared by irradiating single side with electron beam at 0.5 MeV. It may be recognized that there is fairly definite difference between the cases with and without a lead plate as a back-scattering body.

IV. CONCLUSION

1. In the comparison of the effect on the depolymerization of cellulose samples and the change in their analytical properties, little difference was observed between ^{60}Co gamma-ray and electron beam irradiation.

2. The relation between the absorbed dose and the number of bonds broken calculated from the measured values of Pn can be expressed by an simple equation. By the use of this equation, the absorbed dose distribution within the pulp sheets in pile irradiated with electron beams was determined from the measured values of Pn for each sheets successfully.

3. The so-called "useful range" of electron beam penetration was evaluated for the irradiation of pulp sheets in pile. In addition, the utilization of electron filters (for example, aluminum plate of 0.4 mm thick) was studied for the both sides irradiation with 2 MeV electron beam and back-sattering bodies (for example, lead plate) designed to apply for the single side irradiation with 0.5 MeV electron beam. The results indicated that these techniques were useful to keep the absorbed dose distribution narrower. And also it was found that, in the latter case, the irradiation efficiency reached 95 per cent or more of the total irradiation energy when the single side irradiation was applied.

4. From the results obtained using gel permeation chromatography, it was observed that the shape of the molecular weight distributions of irradiated samples, generally speaking, approached that of random sample with a normal distribution. And also the above mentioned irradiation techniques were found to be applicable more or less to check the molecular weight distributions of irradiated samples to broaden.

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