Characterization of Explosion Wood*1

1. Structure and Physical Properties

Mitsuhiko TANAHASHI*2, Shinsuke TAKADA*3, Tsutomu AOKI*4,
Toshiyuki GOTO*5, Takayoshi HIGUCHI*2 and Shiro HANAI*6

Abstract——Wood chips of Shirakaba (*Betula platiphilla* Skatchev var. *Japonica* Hara) and Karamatsu (*Larix leptolepis* Gordon) were treated with a high pressure steam (12–28 kg/cm^2) for 1–16 min., and the steam pressure was released instantaneously to result in explosion wood. When the treating time was longer more fibrillation of cell walls of Shirakaba occurred. However, Karamatsu chips gave small non-fibrillated block fragments. Fibers of the explosion wood of both woods were observed to be vigorously ruptured. Glycosidic linkage of hemicelluloses and alkyl-aryl linkages of lignin were hydrolyzed to give low molecular weight fragments. Cellulose, on the other hand, remained apparently intact. The crystallinity and micelle width were found to be increased by explosion.

1. Introduction

Annual consumption of wood in Japan is about one hundred million m^3 of which 70% is imported. Since we have entered the energy shortage age the importance of wood as a renewable resource of energy and chemicals has increased. For the continuously maintained utilization of wood, development of useful chemicals, cattle feed, and energy from wood residue is keenly demanded.

Explosion wood process which was developed by STAKE Technology, and IOTEK in Canada has attracted attention in utilization of woody biomass[1]. The present investigation was carried out to characterize the structure and physical properties of explosion wood in relation to the utilization of woody biomass.

2. Experimental

Apparatus for Explosion

The apparatus was made on trial in collaboration with TAKARA-SHUZO Co. Ltd. and TSUKISHIMA KIKAI Co. Ltd. Maximum steam pressure attained by the electric boiler is 30 kg/cm^2, and digester has the capacity of 2 l and pressure resistant of 40 kg/cm^2. For batch-wise operation of this apparatus the digester was

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*2 Research Section of Lignin Chemistry
*3 Faculty of Agriculture, Kinki University, Kowakae, Higashi-Osaka 577
*4 Faculty of Education, Kobe University, Tsuruko 3, Nadaku, Kobe 657
*5 Osaka Medical College, 2-7, Daigakucho, Takatsuki, Osaka 569
*6 Takara Shuzo Co., Ltd. Shimogyo-ku, Kyoto, 600-91

constantly heated with saturated steam inside the jacket.

Preparation of Explosion Wood

Four hundred gram chips (ca. $50 \times 50 \times 2$ mm) of Shirakaba (*Betula platiphilla* Skatchev var. *japonica* Hara) and Karamatsu (*Larix leptolepis* Gordon) were put into the digester. The air in the digester was replaced with steam for 20 seconds at 1–2 kg/cm^2. Then the pressure was rapidly raised to the desired pressure (12, 16, 20, 24 and 28 kg/cm^2, respectively) and the chips were treated with saturated steam for desired period (1, 2, 4, 8 and 16 min., respectively). Reaction temperature for these pressure conditions were about 190, 200, 210, 220 and 230°C, respectively. After the steaming, the steam pressure was released instantaneously to the atmospheric pressure via a ball bulb. The wood chips were exploded by this treatment. For observation of the explosion wood (EXW) by optical- and transmission electron microscopy a small portion of the EXW was taken and the major portion was lyophilized.

Observation by Optical Microscope

EXW was suspended in water and drops of the suspension were observed by an optical microscope (Olympus Vanox).

Observation by Scanning Electron Microscope

Freeze-dried sample of EXW was directly mounted on a specimen holder, coated with gold and observed by a scanning electron microscope (Hitachi S-450).

Observation by Transmission Electron Microscope

EXW was suspended in water, and a drop of supernatant solution was mounted on a grid and mixed with a drop of aqueous solution of uranyl acetate. The excess solution was removed by a filter paper and air-dried. The preparations were observed by a transmission electron microscope (Hitachi H-500) at the accelerating voltage of 100 KV.

Determination of Crystallinity and Micelle Width of EXW with X-ray Diffraction

Five hundred mg of freeze-dried EXW was pressed at 200 kg/cm^2 for 3 min to make a tablet and X-ray diffraction curve was measured by a Rigaku Geiger Flex (CuKα).

The degree of crystallinity was calculated by the Segal's equation.[2]

$$CrI = \frac{I_{002} - Iam}{I_{002}} \times 100 \qquad (\%)$$

And the width of micelle was calculated by the Scherrer's equation[3]

$$D = \frac{K\lambda}{B \cos \theta} \qquad (\mathrm{A})$$

K : constant=0.9
λ : wave length of X-ray=1,542 Å
B : half width (rad)
2θ : angle of the peak for (002) plane

Thermal Softening Analysis of EXW

Freeze-dried EXW was used for measurement of thermal softening point. Thermal softening point was determined using a thermomechanical analyzer (TM 1500, Shinku Riko Co. Ltd.) as the collapse of a column (4×2 mmo) of EXW under a constant load of 200 g in a heated glass capillary tube. The measurement was conducted over the temperature range from 20°C to 400°C at a programmed heating rate of 1°C/min.[4]

3. Results and Discussion

The Explosion Process of Wood

The process contains a physical rupture of wood structure by adiabatic expansion of water in small pores in wood tissues, and autohydrolysis of cell components. General aspects of the explosion process of wood have been reported by Marchessault.[5,6] However no detailed investigation has been reported on the effect of processing con-

Table 1. Distribution of the Size of Fragments of Explosion Woods.

sample	kg/cm²	min (meshes, mm)	Weight % of fragment on sieves: 7 on 2.830	14 on 1.190	28 on 0.590	42 on 0.350	80 on 0.117	80 pass	average size of EXWs
SHIRAKABA	28	1	14.0	54.7	21.1	5.1	3.1	2.0	1.74 (mm)
	28	2	8.9	55.0	25.8	6.0	2.7	1.6	1.64
	28	4	4.1	60.4	16.3	10.7	4.6	3.9	1.55
	28	8	0.7	12.5	22.9	20.1	20.4	23.4	0.65
	28	16	0.0	4.2	8.9	17.9	18.9	50.1	0.34
	20	16	8.7	40.9	22.9	12.6	8.9	6.0	1.38
	24	16	2.3	23.0	25.5	18.3	18.9	12.1	0.91
	28	16	0.0	4.2	8.9	17.9	18.9	50.1	0.34
KARAMATSU	28	1	16.1	49.4	22.7	6.8	3.8	1.3	1.72
	28	2	12.5	55.4	22.7	5.3	2.5	1.6	1.72
	28	4	5.2	43.4	31.1	9.4	5.5	5.4	1.37
	28	8	2.0	27.1	32.3	13.9	11.2	13.5	1.00
	28	16	2.2	28.3	30.4	14.2	10.9	14.0	1.01
	20	16	9.8	47.3	31.6	7.2	2.8	1.3	1.57
	24	16	4.6	34.8	29.9	12.1	11.6	7.0	1.20
	28	16	2.2	28.3	30.4	14.2	10.9	14.0	1.01

dition. In development of the utilization of EXW and understanding of the process it is required to characterize EXW in different conditions in pressure, temperature and time of the treatment. In this paper, morphological structure and physical property of EXW were investigated. One of the most important characteristics of explosion process is that wood chips were finely ruptured to fibers and/or powder. Table 1 shows the effect of explosion condition on the destruction of wood chips. Distribution of the size of fragments of EXW inherently indicates the degree of effect of explosion process. The average size of the fragments and the whiteness of EXW decreased with increase of the reaction time.

Microscopic Analysis of EXW

Fig. 1 shows the appearance of the EXWs of Shirakaba and Karamatsu examined by optical microscopy. In Shirakaba EXW, when the steam pressure was lower and reaction time was shorter (ex. 20 kg/cm^2, 2 min.) shivers were frequently observed. When the steam pressure was higher (28 kg/cm^2) single fibers were mainly observed (Fig. 1A). Brown colored oily substances were frequently detected both inside and outside of exploded cell walls (Fig. 1C-a and 1A-a). These substances were insoluble in water but soluble in MeOH, and considered to be originated from lignin, resinous extractives and/or polyphenols. Production of these substances is one of the important characteristics of explosion wood, because they were hardly detected in Thermomechanical pulp (TMP) and Ground pulp (GP). It seems that lignin both in middle lamellae and secondary walls could be liberated considerably from cellulose. It is concluded consequently, as steaming time is longer (28 kg/cm^2, 16 min.) fibers are almost fibrillated (Fig. 1B).

In Karamatsu EXW, which is different from Shirakaba EXW, single fibers could scarcely be produced by these conditions. Karamatsu EXW does not form fiber but particles, and the particle size decreased with the longer steaming time. However, the microscopic structure of Karamatsu EXW at different conditions changed little. Most of tracheids were not disintegrated to fibers but ruptured to small particles (Fig. 1D and 1E). Lignin was scarcely eluted from tracheids cell walls. Tracheids crossed with ray tracheids were particularly difficult to be exploded and remained as a block.

To investigate the fibers of Shirakaba EXW in detail, observations by scanning electron microscopy was performed (Fig. 2). In Fig. 2A, vessels (a), fibers (b) and amorphous substances (c) which are considered to be formed by freeze-drying from hydrolyzed hemicellulose, and/or lignin were observed. As shown in Fig. 2A intact vessels (a) were scarcely found in fact. Most of vessels were found to be destroyed to small fragments. Most of fibers (b) suffered from some damage, too, as found in a buckling (Fig. 2A-d), a cleft along the fiber axis (Fig. 2B), rupture at the end

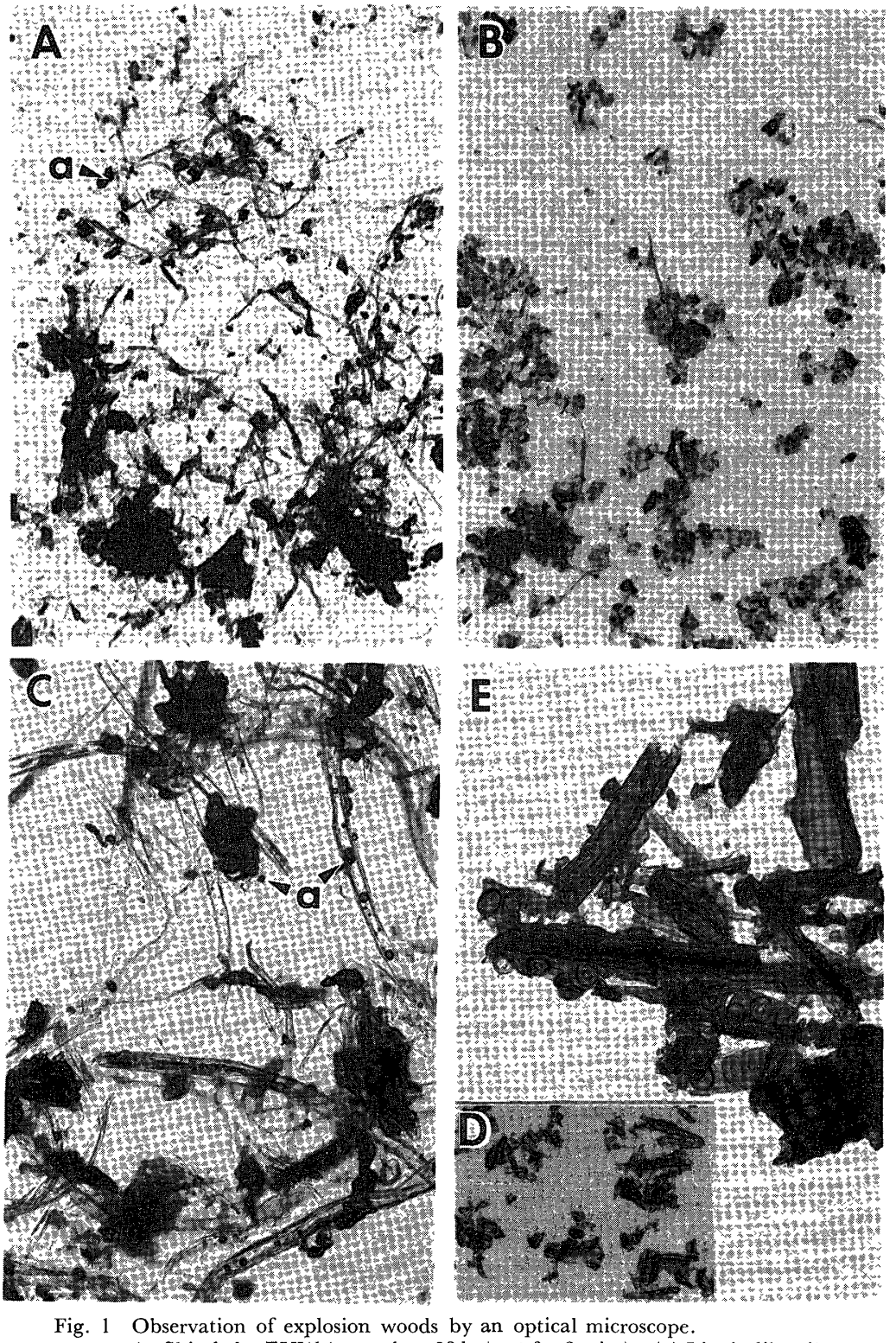

Fig. 1 Observation of explosion woods by an optical microscope.
A. Shirakaba EXW (treated at 28 kg/cm^2 for 2 min.) (a) Lignin-like oily substance released from fibers. B. Shirakaba EXW (treated at 28 kg/cm^2 for 16 min.) C. Enlargement of A D. Karamatsu EXW (treated at 28 kg/cm^2 for 2 min.) E. Enlargement of D

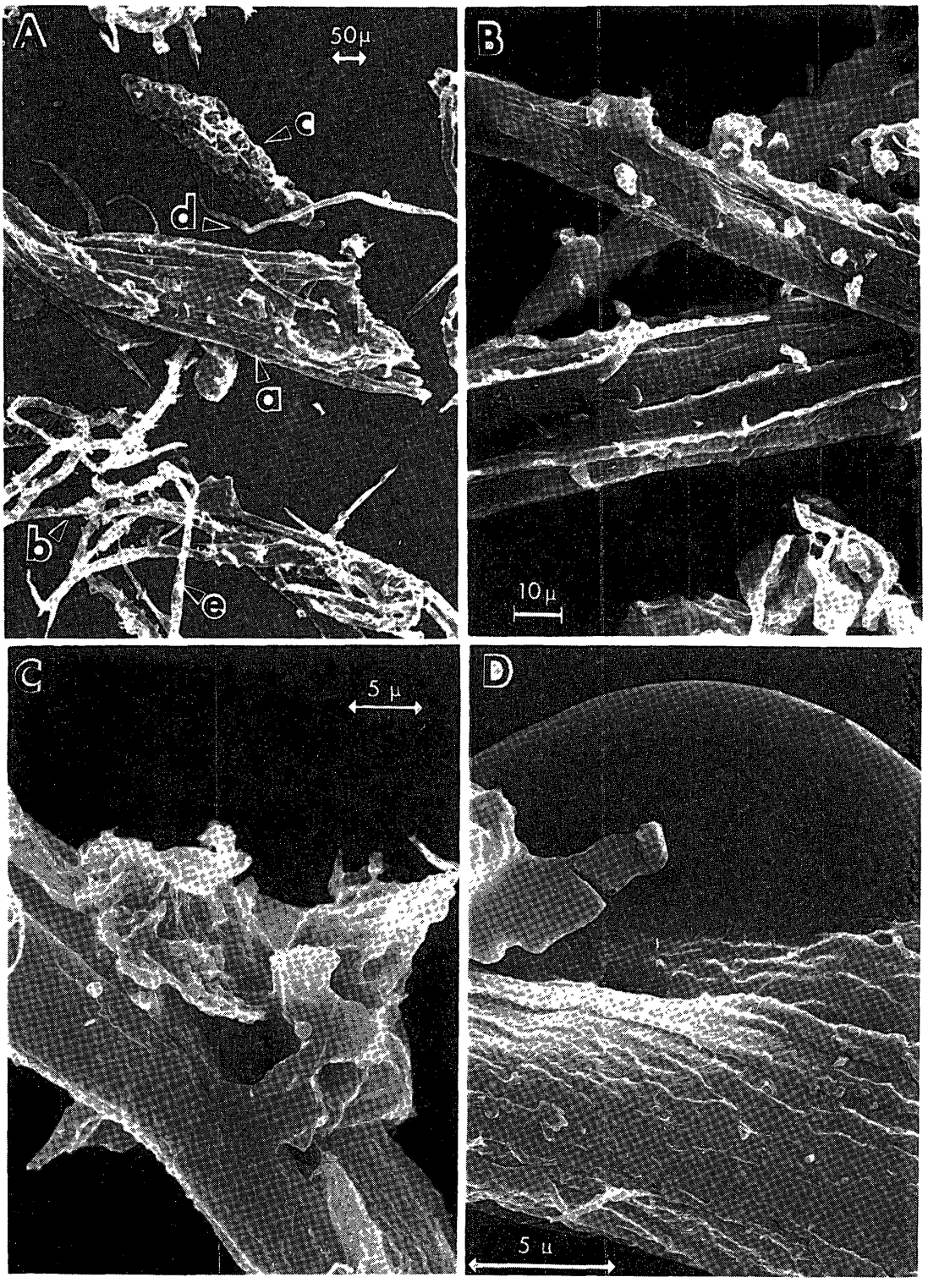

Fig. 2 Observation of Shirakaba explosion wood (treated at 28 kg/cm for 2 min.) by a scanning electron microscope.
A. Observation of EXW at the lower magnificaiton (a) vessels, (b) fibers, (c) Amorphous substances, (d) Buckling and (e) Expansion of a fiber B. A cleft along a fiber C. Explosion at a middle of a fiber D. Expansion of a fiber

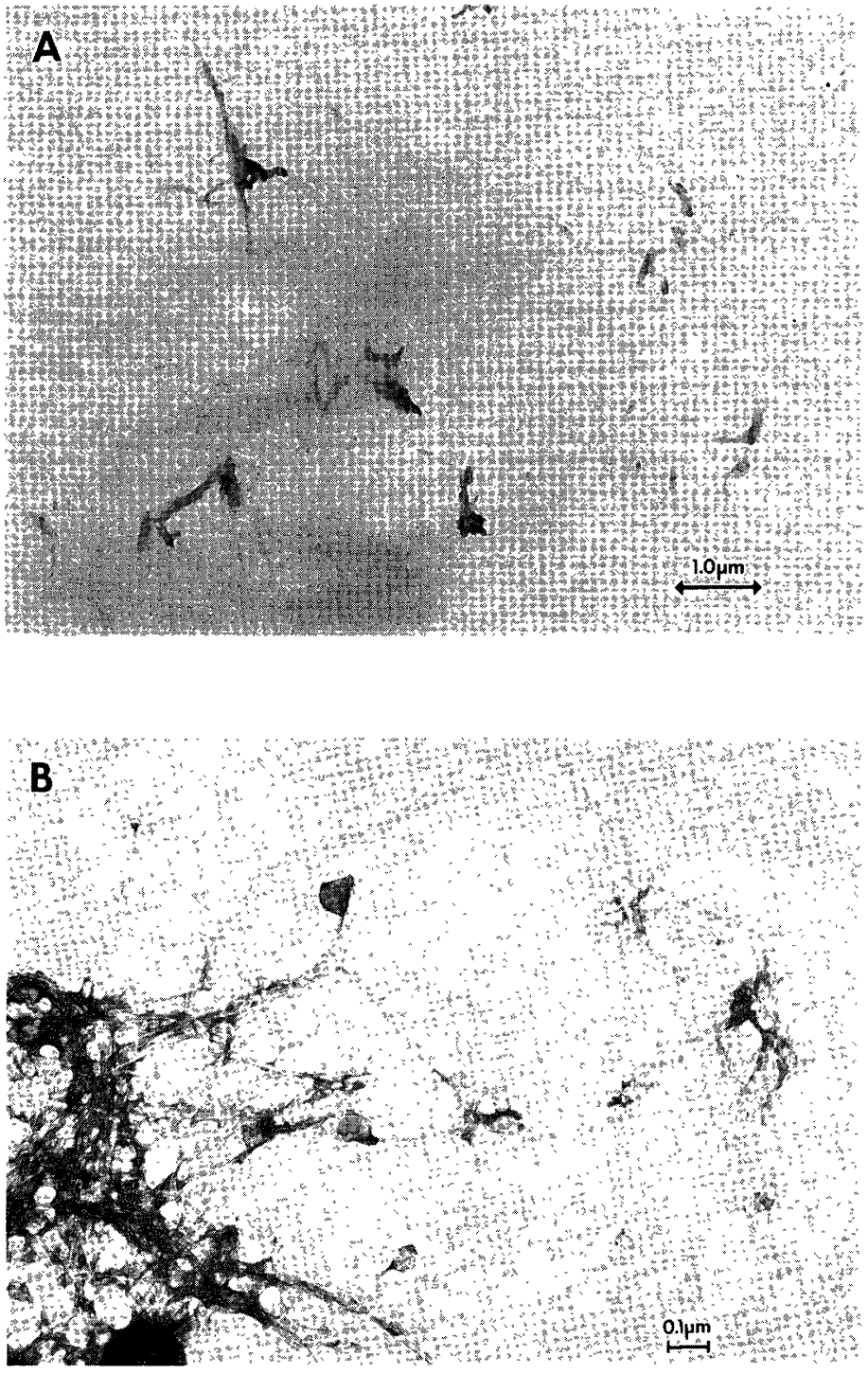

Fig. 3

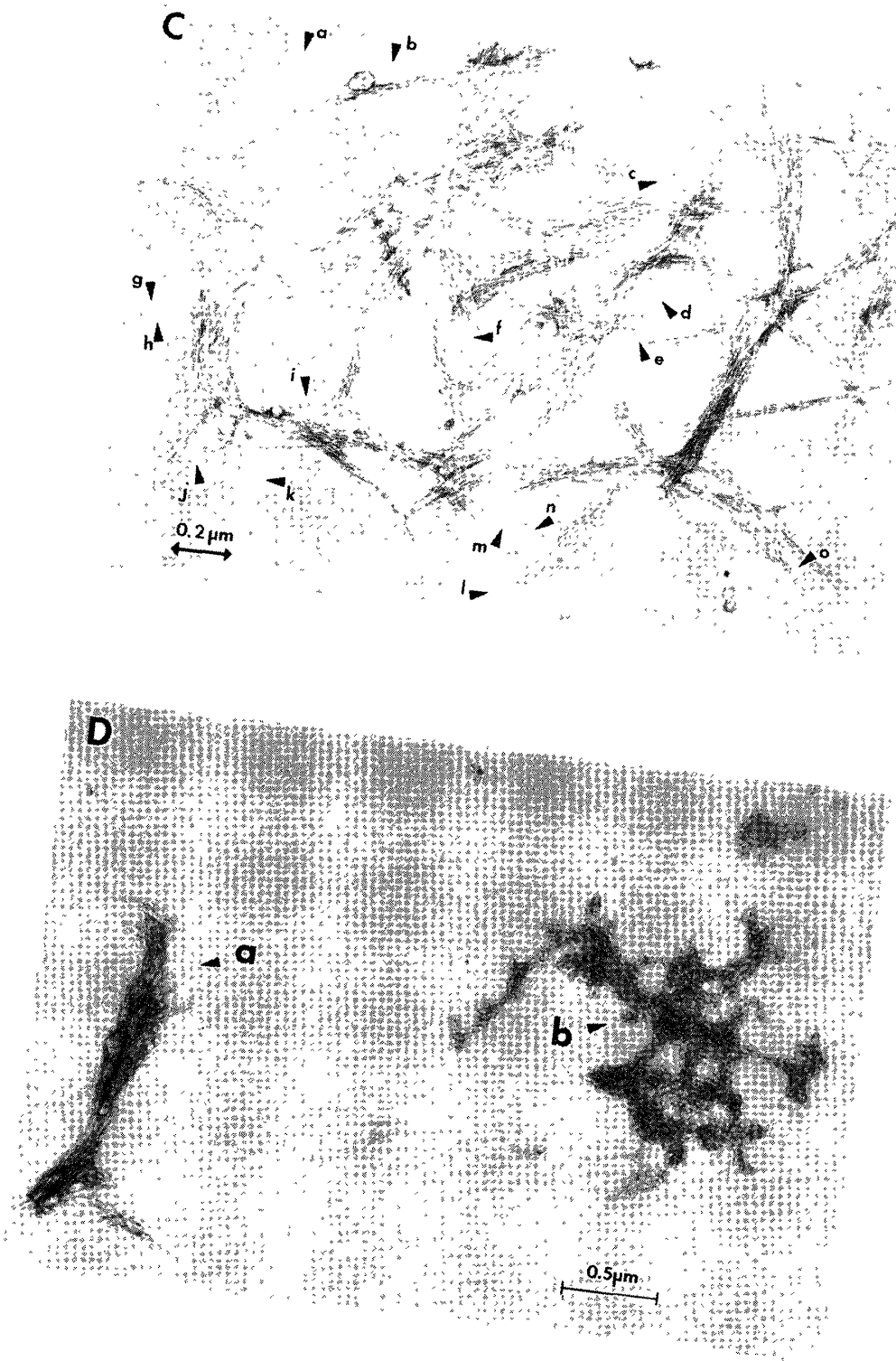

Fig. 3

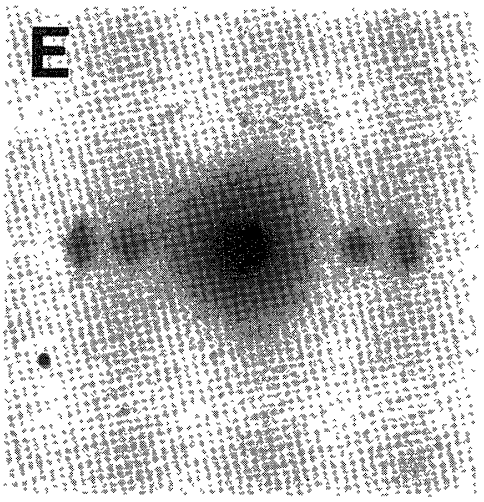

Fig. 3 Observation of EXW by a transmission electron microscope.
A. Observation of Karamatsu EXW at the lower magnification
B. Shirakaba EXW (treated at 28 kg/cm^2 for 1 min.)
C. Shirakaba EXW (treated at 28 kg/cm^2 for 8 min.)
Width of microfibrils (Å)

Width	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
Å	66	53	40	66	40	26	79	46	92	66	105	53	92	66	33

D. Karamatsu EXW (treated at 28 kg/cm^2 for 16 min.)
(a) Cellulose microfibrils and (b) Lignin-like substances
E. Electron diffraction diagram of microfibrils from Shirakaba EXW

and middle of a fiber (Fig. 2C), expansion in a dome shape (Fig. 2D) and tear at middle lamellae and S_1 layers. Thus, the exploded fibers were so deformed and different from fibers in GP and KP.

Previous investigation of EXW showed that the filtrate of the water extract by a general analytical filterpaper contains cellulose[7]. Then the observation of the water extract (suspended fine fibrils) by transmission electron microscopy was performed. A similar observation of EXW by TEM has recently been carried out by Marchessault.[8] When the explosion condition was weeker than 28 kg/cm^2, 8 min., a few microfibrils were detected. However, in the EXWs treated at the conditions of 28 kg/cm^2, 8 and 16 min. many microfibrils were observed as shown in Fig. 3A. Observation at high magnification showed that microfibrils were completely separated to each other (Fig. 3 B, C and D). Microfibrils were thicker and shorter with increase of the steaming time (Fig. 3 C as compared with B). In Karamatsu EXW, the same characteristics were observed, too (Fig. 3 D). Such fibrillation hardly occurs in the process of GP and KP manufacturing, and such free microfibrils have not been obtained by other methods. It is noteworthy that

fibrillation of cellulose fibers occurs easily for a very short time by explosion. Small particles as shown in Fig. 3D-b were observed in some cases. They were stained negatively and insoluble in water. This observation suggests that the particle is lignin-like substance but not sugar. To confirm this point, methanol solution of the methanol soluble fraction of EXW was added dropwise into the excess of water, and a drop of the mixture solution was observed by TEM. Similar particles were again detected as shown in Fig. 3D-b, suggesting that the particles were lignin-like substances. Further investigations are in progress to characterize the substance. On the other hand, the microfibrils were confirmed to be cellulose I by electron diffraction (Fig. 3E).

Analysis of Crystallinity and Micelle Width of EXW by X-Ray Diffraction

Marchessault and co-workers reported that X-ray diffraction analysis of aspen EXW showed little or no loss in the degree of crystallinity of EXW cellulose, and that the cellulose retains its basic crystalline structure.[5] However, the present investigation is not consistent with their conclusion. Fig. 4 shows the X-ray dif-

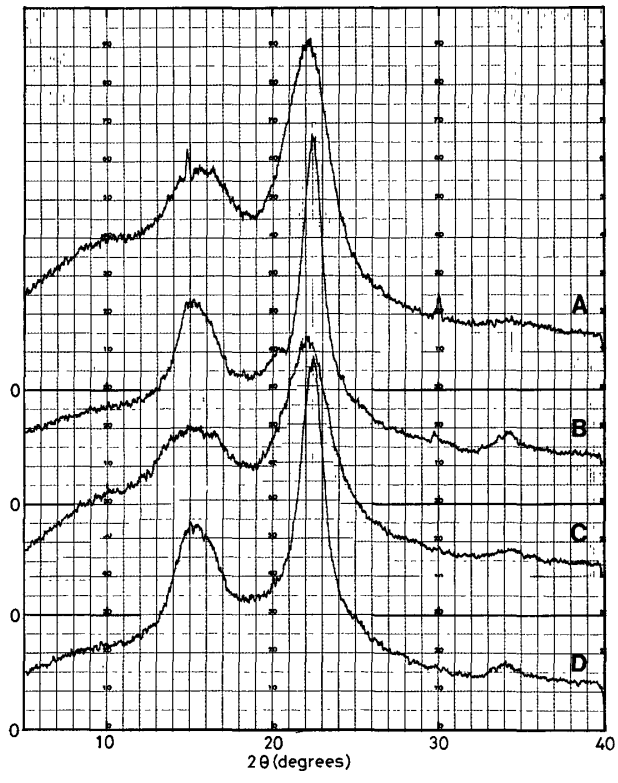

Fig. 4 X-Ray diffraction curves of EXW.
A. Shirakaba untreated wood powder
B. Shirakaba EXW (treated at 28 kg/cm for 16 min.)
C. Karamatsu untreated wood powder
D. Karamatsu EXW (28 kg/cm^2, 16 min.)

fraction curves of exploded (28 kg/cm^2, 16 min.) and untreated woods of Shirakaba and Karamatsu, respectively. The diffraction patterns showed that the EXWs are composed of cellulose I. However, the peak of (002) diffraction by EXWs was sharper than that by untreated woods, and the degree of crystallinity and micelle width increased by explosion treatment. Fig. 5 shows the effect of steaming time at 28 kg/cm^2, on the degree of crystallinity and micelle width. Within 4 min. of explosion the degree of crystallinity increased rapidly with increase of steaming time and attained maximum at 4 min. (Shirakaba: 69.8%, Karamatsu: 67.7%, and the EXW/untreated ratios (E/U) are 1.39 and 1.50, respectively) and then decreased slowly. Micelle width of cellulose rapidly increased and attained maximum at about 8 min. steaming (Shirakaba: 57.9A, Karamatsu: 49.1A, and the E/U ratio is 2.04 and 1.82, respectively).

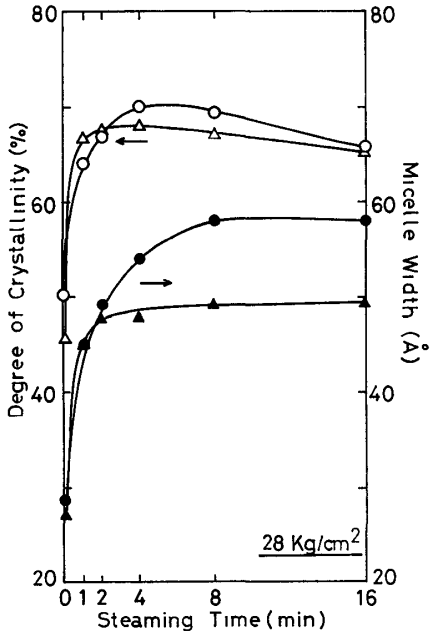

Fig. 5 The effect of steaming time on crystallinity and micelle width of EXW.

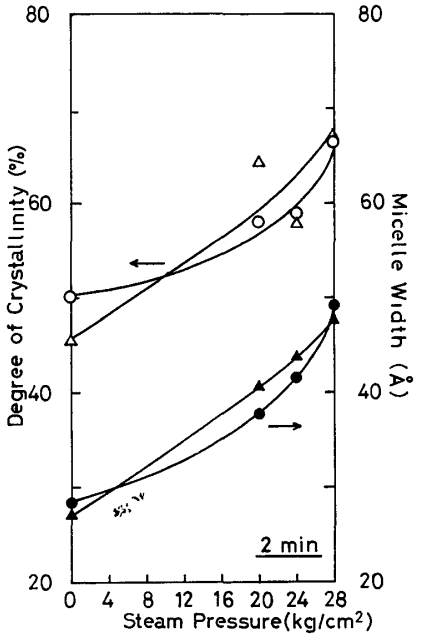

Fig. 6 The effect of steam pressure on crystallinity and micelle width of EXW.

On the other hand, Harada and Goto found that the width distribution of uranyl acetatestained microfibrils observed by TEM was correlated with micelle width of corresponding sample determined by X-ray diffraction.[9] The observation of EXW by TEM in the present investigation showed that the average width of microfibrils of EXW treated at the condition of 28 kg/cm^2 G for 8 min. was about 63 Å. Thus, the degree of the crystallinity and width of micelle increased about 1.5 and 2.0 times, respectively by the explosion. These results suggest that most of amorphous

region of cellulose transformed to crystalline region by the explosion, resulting in the increase of the crystallinity and micelle width of the explosion wood.

Fig. 6 shows the effect of steaming pressure on the crystallinity and micelle width of EXW at 2 min. steaming; it is indicated that the degree of crystallinity and micelle width increased with the higher steam pressure.

Thermal Softening Property of EXW

Fig. 7 shows the effect of steaming time on the thermal softening behavior of Karamatsu and Shirakaba explosion woods at 28 kg/cm^2 of steam pressure, and

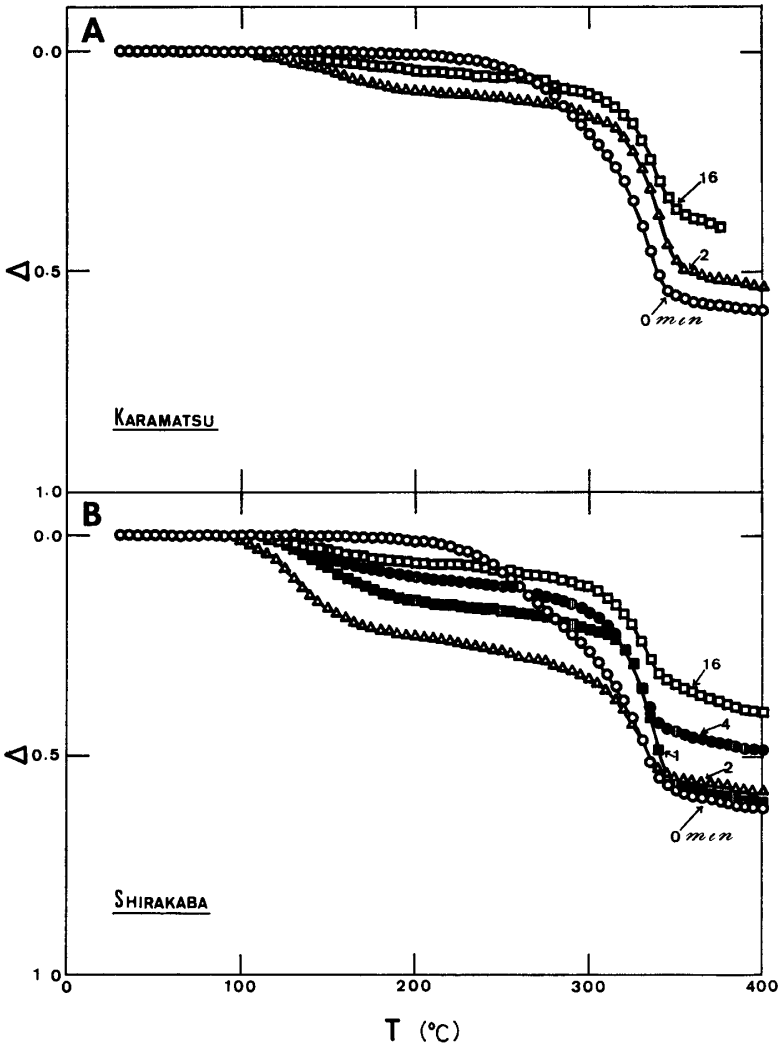

Fig. 7 The effect of steaming time at 28 kg/cm^2 of the steam pressure on the thermal softening process
A. Karamatsu EXW B. Shirakaba EXW
Δ: Normalized deformation function $\left(\frac{\Delta l}{l_0}\right)$

Fig. 8 and Fig. 9 show the differential thermoanalysis curves. In the Shirakaba untreated wood, there was a shoulder around 200–300°C which is probably attributed to L.C.C.[10] In the EXW, on the other hand, the shoulder disappeared and a new peak at about 125°C was observed (Fig. 8): methanol extract mostly composed of guaiacyl-syringyl lignin gave the softening point (120°C) which corresponds to the new peak. In the Karamatsu EXW, the same tendency as in Shirakaba was observed, except that the new peak was shifted at about 165°C which would correspond to guaiacyl lignin (Fig. 9). These results suggested that hemicelluloses and lignins were hydrolysed to low molecular weight fragments by explosion.[11] However, the height of the new peak decreased with the increase of the steaming time (Fig. 8, 9 and 11B). It seems that the depolymerized substance was repolymerized and transformed to the unsoftened product. In agreement with this view, the rate of

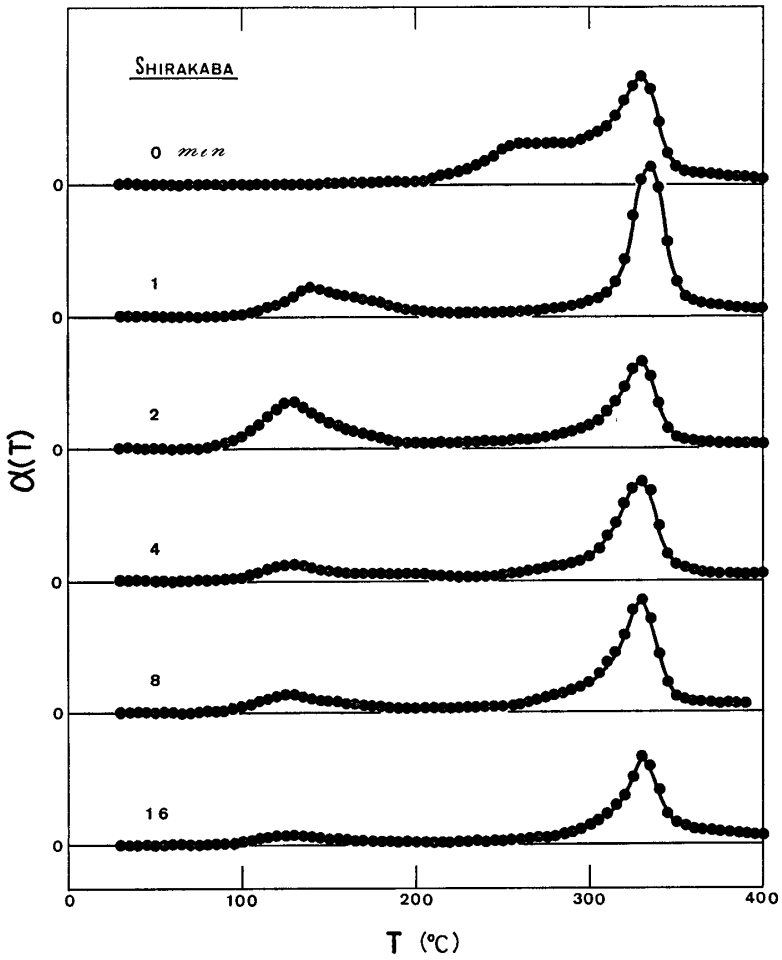

Fig. 8 The differential curves of thermal softening process for Shirakaba EXW at 28 kg/cm² of the steam pressure. α: Rate of deformation at each temperature T $\left(\frac{d\Delta}{dT}\right)$

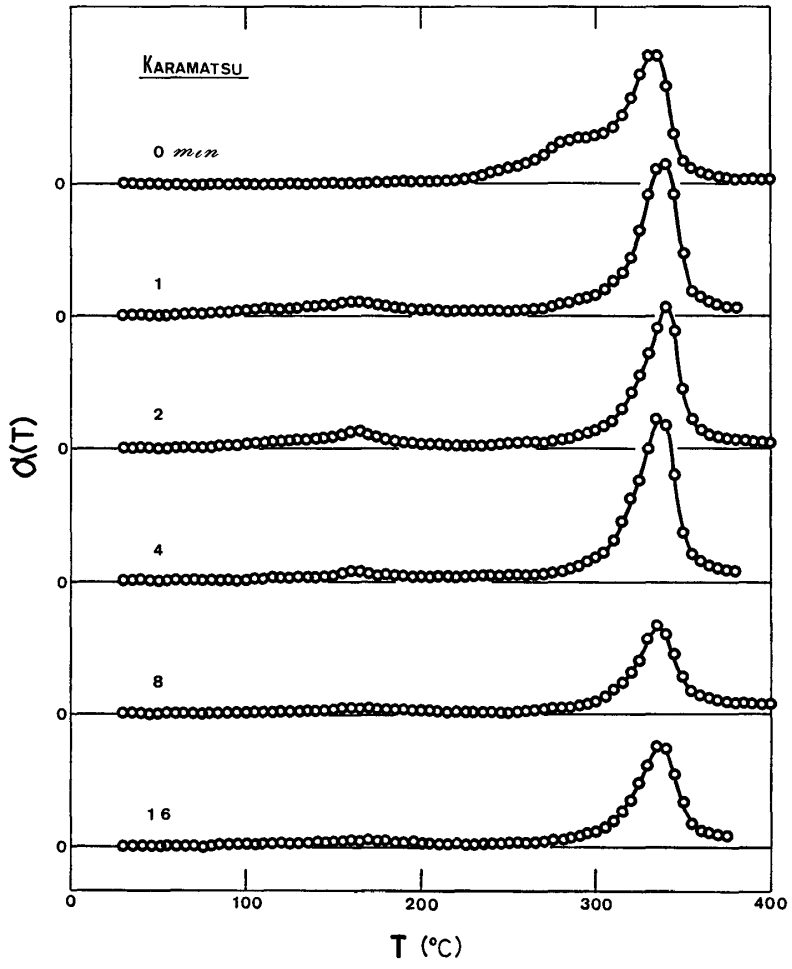

Fig. 9 The differential curves of thermal softening process for Karamatsu EXW at 28 kg/cm^2 of the steam pressure.

deformation at 350°C decreased with the increase of the explosion time as shown in Fig. 11A. These results conclusively indicated that the best condition of delignification from wood is 28 kg/cm^2, 2 min. both for Shirakaba and Karamatsu in the present investigation. However, a considerable amount of lignin remained in fact in Karamatsu EXW, and the total amount of eluted lignin was lower than that of Shirakaba.

In Shirakaba EXW, treated at 28 kg/cm^2 for 1 min, the thermal softening temperature of the new peak slightly shifted to higher temperature than that of EXW treated for 2 min. (Fig. 8). The pattern of the new peak of EXW (at lower temperature) under different pressure for 1 min. showed that the shoulder which probably attributed to the lignin connected with hemicelluloses was gradually shifted to the lower temperature up to 130°C corresponding liberated lignins.[10,11] The amount of the dissolved substances increased with the increased steam pressure (Fig. 10, 11D).

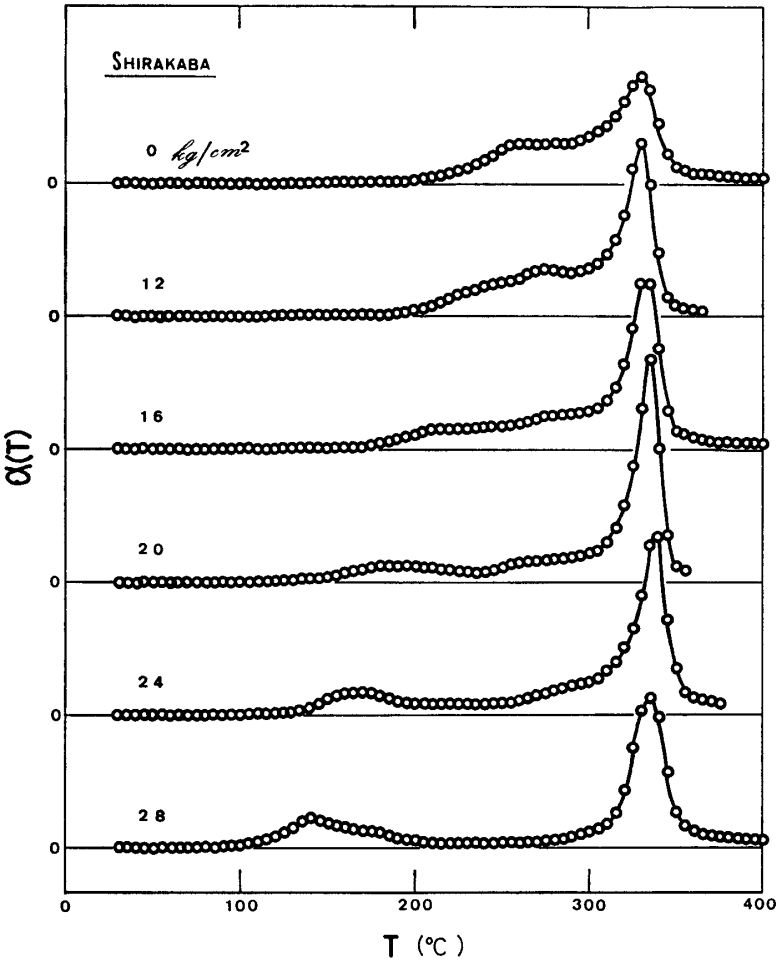

Fig. 10 The effect of steam pressure on the thermal softening process of Shirakaba EXW for one min. steaming.

The present investigation conclusively showed that lignin and hemicelluloses were hydrolyzed to low molecular weight products, and that amorphous region of cellulose crystallized by the explosion. The results also indicated that the explosion gave a highly crystallized cellulose and a good delignification, which is useful for preparation of cellulose microfibrils and lignin from wood.

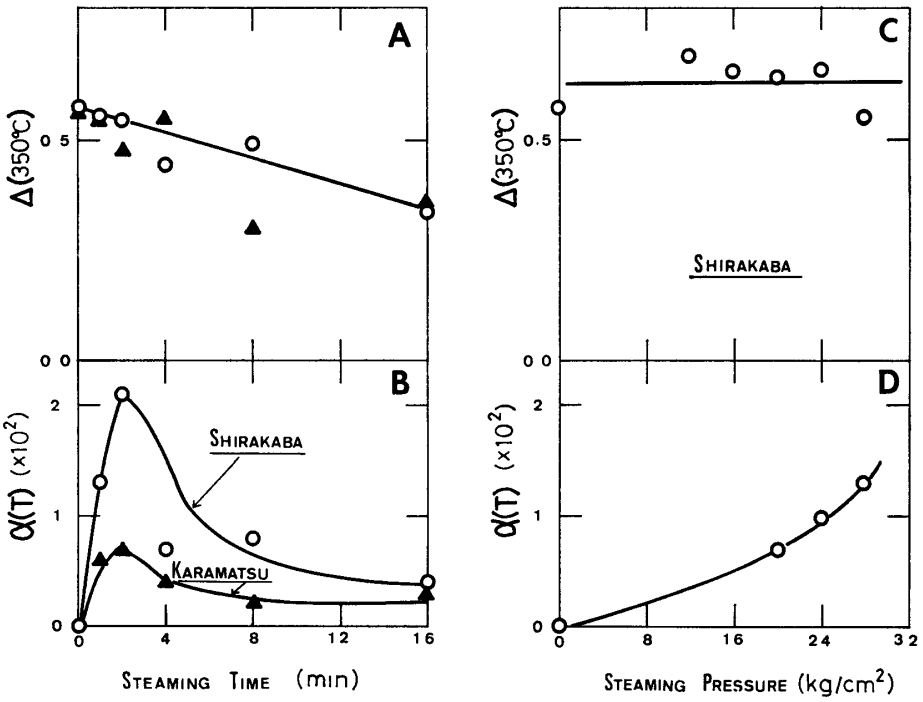

Fig. 11 The effects of the explosion processing on thermal softening process
A. Calibration curve for the deformation rate at 350°C against the steaming time.
B. Calibration curve for the height of the peak at 120–170°C against the steaming time.
C. Calibration curve for the deformation rate at 350°C against the steam pressure.
D. Calibration curve for the height of the peak at 120–170°C against the steam pressure.

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