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Compressive-Molding of Wood by High-Pressure Steam-Treatment:

Part 2. Mechanism of Permanent Fixation

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Summary

Permanent fixation of the compressively transformed shape of Harigiri (*Kalopanax pictus* Nakai) specimens was attempted by steaming them, compressively transforming their shapes, and processing them with high-pressure steam again. Also, the mechanism of the shape fixation was examined. The results are summarized as follows:
(1) Compressively transformed Harigiri specimens, after being processed with high-pressure steam, did not recover to their original shape with heat and moisture, thus achieving permanent fixation of compressed shape.
(2) The conditions under which the fixed specimens would not recover to their original shape were found to be steaming with saturated steam at 200 °C for 4 min or longer or at 180 °C for 8 min or longer, within the scope of the current experiment.
(3) Hemicellulose and lignin do not affect the fixation of compressive transformation.
(4) The fixation of compressive transformation is caused by a structural change of cellulose.
(5) The mechanism of fixation of compressive transformation is supposed to be that the inner stress is released because the paracrystalline region of cellulose, which is distorted by compressive transformation, is partially hydrolyzed. Further, steam-rearrangement of hydrolyzed constituent into crystalline region occurs, keeping the transformed shape intact.

Introduction

In our previous paper (Ito *et al.* 1998), we presented a new method of processing logs into square lumbers without cutting them but by treating them with high pressure steaming in an autoclave, for the purpose of utilizing coniferous thinnings. With this method, high-pressure steam-treatment at 200 °C for 3 min for shape fixation is necessary in order to transform the shape of logs from thinnings into square lumbers and fix it permanently. Also, the inner stress at the time of processing for shape fixation gradually decreased as the processing time increased. When the inner stress was completely removed, the compressive transformation was permanently fixed.

The new equipment, a high-pressure steam compressive molding apparatus, which was employed in this method, enabled us to plasticize wood by heating it, to compressive-mold it, and to fix its transformation in one step. Also, since it does not require any chemicals, it enables us to enhance the quality of wood, to mold it with the original characteristics still intact.

Among major research on permanent fixation of compressive transformation, there are studies (Inoue and Norimoto 1991; Inoue *et al.* 1993) reporting that steam treatment after compression improves dimensional stability. According to these reports, size stability is achieved not by the dissolution of hemicellulose but by heat plasticity of matrix, i.e. cutting hemicellulose and part of lignin molecules which are rearranged under compressed condition. It is generally agreed that fixation of compressed wood structure by steam treatment is a result of steam softening of lignin-hemicellulose matrix. In the matrix are microfibrils of crystalline cellulose which move when the matrix is softened. That is that fixation of compressive transformation is achieved by relief of inner force within this matrix and the recovery of transformation of microfibrils.

We took a different approach in our research. In order to fix compressive transformation, it is necessary to prevent the activation of the molecular movement caused by moisture and heat, or to lower molecules of cellulose microfibrils that are subject to elastic transformation, for which it has been recognized that explosion is effective. In the previous studies on explosion (Tanahashi *et al.* 1989; Tanahashi 1990), it was ascertained that steam treatment could quickly hydrolyze the non-crystalline region of cellulose and hemicellulose. Hot steam treatment, without explosion, could also increase the crystallinity index values (CrI) of cellulose, width of microfibrils, and micelle width.

Based on the above mentioned studies, the current paper will discuss the mechanism of permanent fixation of compressive transformation by high-pressure steam-treatment

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using batch processing in an autoclave. Also, in order to investigate which constituent of wood affects the permanent fixation of transformation most, the set-recovery was measured during the examination of extract specimens using several kinds of solvents. The specimens were prepared from Harigiri (*Kalopanax pictus* Nakai), the hardwood, from which extract is easily taken. CrI was then measured by X-ray diffraction method, in order to investigate the relationship between crystallinity and set-recovery.

Experimental

Material

Harigiri was used as a specimen after being dried at room temperature. The size of the specimen was 20 mm long, 20 mm in radius, 30 mm thick. Air-dry specific gravity and average annual ring width were 0.52 and 2.8 mm, respectively.

Permanent fixation of compressed woods by high-pressure steam-treatment

The specimens were treated in a high-pressure steam compressive-molding apparatus (Hisaka HTP-40/58), which was introduced in our previous report (Ito *et al.* 1996). In this method, the pressure in the processing container was reduced by an aspirator for 5 min, and the specimens were softened by saturated steam at 150 °C for 3 min. After this, they were compressed in the direction of R (radial direction) to 12 mm, and the temperature was raised to 160, 180 and 200 °C, and then treatment for shape fixation was given for 2,4 or 8 min. After exhausting steam, the pressure was reduced by an aspirator for 5 min again, and the specimen was taken out. The time required for processing was 20–25 min.

The amount of compression set was defined by the following expression:

$$\text{Compression set} = \frac{To - Tc}{To} \times 100\ (\%)$$

where To and Tc are specimen sizes in the direction of R (radial direction) in oven-dried condition before and after the compression, respectively.

Recovery test

In order to determine the effects of steam-treatment before and after compression, a recovery test was conducted. Set-recovery was determined by a test where drying, water absorption, and boiling were repeated. The specimens were treated by the process which was introduced in our previous report (Ito *et al.* 1996).

The set-recovery was defined as follows:

$$\text{Set-recovery} = \frac{Tr - Tc}{To - Tc} \times 100\ (\%)$$

where Tr is the thickness in the direction of R (radial direction) under oven-dried condition and after the recovery treatment.

Changes in compressed wood constituents by high-pressure steam-treatment

In order to clarify which constituent of wood affected the fixation of the shape of compressed wood, an experiment was conducted using Harigiri, a hardwood species, with which extract operation from experimental material is easy. For the purpose of removing hemicellulose and lignin from the specimens, Soxhlet extraction was conducted for 48 hours each using hot water and 1,4-dioxane. Two different kinds of extraction were done for each condition. One of them was to mill the wood of the specimen and extract while the other was not to mill them and extract. To mill extractive residue, a Wiley mill was used.

Crystallinity measurement by X-ray diffraction

The relation between CrI and set-recovery was investigated by calculating CrI of cellulose constituent in specimens by X-ray diffraction before and after compression. The specimens that have extractive residues were milled by a Wiley mill, and 500 mg of milled wood were weighed, and processed with pill forming equipment into circular pellets with 200 kgf/cm^2 of pressure.

An X-ray diffraction image was obtained by using an X-ray diffractometer (Rigaku Geigerflex RAD-IC). The measurement was conducted by symmetrical transmission method (Nishimura *et al.* 1981; Wellwood *et al.* 1975). The specimens were scanned with the diffraction angle (2 θ) of 5 to 45° range at a scanning rate of 1°/min. As for methods to obtain CrI, the following two methods were employed: a method developed by Segal (Segal *et al.* 1959) and Area method (Jayme and Knolle 1964; Knolle and Jayme 1965).

Results and Discussion

Recovery test

Figure 1 shows the set-recovery in the test where drying water absorption and boiling of compressed specimens were repeated. The temperature for steaming at the time of shape fixation after compression was 200 °C. The compressive transformation was almost completely fixed by processing 4 min or longer, even after drying, water absorption, and boiling was repeated. This was drawn from the fact that set-recovery of the specimens was still almost zero, after the repetition of drying, water absorption, and boiling. Drying-set specimens (i.e. specimens that were treated with steam for 0 min) recovered almost to their original state after two boiling treatments. The longer the steam treatment after compression was, the smaller the final set-recovery.

Figure 2 shows the relationship between the set-recovery of compressed specimens and length of time for fixation processing at each temperature. At all temperatures, the set-recovery decreased with processing time.

It was determined that steaming at 200 °C for 4 min or longer or 180 °C for 8 min or longer after compression is necessary for fixation of compressive transformation, as clearly shown in Figures 1 and 2.

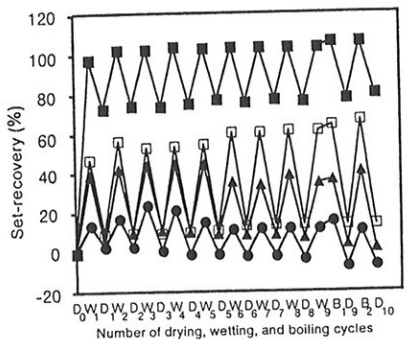

Fig. 1. Set-recovery for steamed and compressed specimens after drying, wetting, and boiling cyclic test.
Legends: Steaming time in fixation process. ■: 0 min., ▲: 4 min., □: 2 min., ●: 8 min.
Notes: Specimens were steamed at 150 °C for 3 min in softening process. The compression set was 40 %. Specimens were steamed at 200 °C in fixation process.

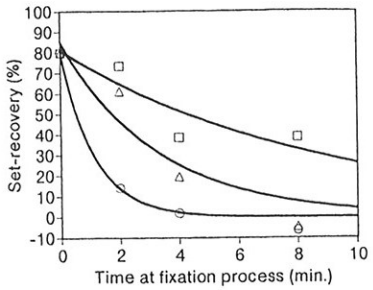

Fig. 2. The effects of steaming on the set-recovery.
Legends: Temperature at fixation process: □: 160 °C, △: 180 °C, ○: 200 °C.

Chemical changes of wood components by high-pressure steam-treatment

Table 1 shows the results of the extractive test. In the extracting operation with water, that is, extracting operation with steam and boiling water, hemicellulose is removed, whereas in the 1,4-dioxane extracting operation, lignin is removed. The weight loss (WL) in the water extracting operation and the total of all weight losses after all extracting operations tend to increase with the increase in steam processing temperature at the time of shape fixation and the increase of processing time. In Table 1, with those specimens whose transformation were fixed, i.e. those treated at 180 °C for 8 min, 200 °C for 4 min or 200 °C for 8 min, hemicellulose and lignin were removed to a significant degree. Also the amount of residual lignin in the extractive residue (RL) in those specimens that were treated for shape fixation at 200 °C for 4 min was half of that in non-processed specimens.

From the above, shape fixation was achieved even with a considerable amount of extraction of hemicellulose and lignin, and the more the amount of extraction, the firmer fixation was. Therefore, it can be surmised that hemicellulose and lignin do not affect shape fixation.

In order to analyze these points in more details, specimens, after steaming, were milled and processed using the same procedure. Under the conditions with which the shape did not recover after extraction, WL by water (steaming and boiling water extraction combined) of milled wood is, for example, 31.0 % for those specimens processed for fixation at 200 °C for 4 min. Shape fixation was achieved, even when most of the hemicellulose was removed, and RL is 6.2 %, i.e. more than half of lignin is removed. From this, it was detected that cellulose, not hemicellulose or lignin, affects the fixation mechanism.

The change of crystallinity in compressed woods

Figure 3 shows the relationship between CrI and processing time in extractive residue milled wood. In Figure 3(a), increase of CrI with the increase in fixation processing time is observed. Also, the set-recovery of the specimens after extraction decreased with an increase in CrI. In Figure 3(b), CrI reached its maximum value when fixation processing time was 4 min. This movement of CrI coincides with that of set-recovery of specimens after extraction. Also, the reason why CrI decreased when fixation processing time was 8 min could be explained from the fact that hemicellulose became furfural while 5-hydroxymethylfurfural condensed (Tanahashi 1990).

Figure 4 shows the relationship between the set-recovery and CrI. The amount of increase in CrI correlated with the

Table 1. Contents of extractives and residual lignin in Harigiri specimens

Steaming conditions				Weight loss (WL)					
Softening process		Fixation process							
Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	by steam %	by Boiling water %	by Dioxane %	Total %	Set-recovery in extractive residue %	Residual lignin in extractive residue (RL) %
Non-milled specimens									
0	0	0	0	—	1.8	1.9	3.7	—	16.9
150	3	180	2	5.4	3.8	2.8	12.0	48.3	10.6
150	3	180	4	5.1	4.8	2.7	12.6	22.6	11.5
150	3	180	8	4.7	6.9	1.0	12.6	–3.5	11.4
150	3	200	2	8.6	4.0	2.1	14.7	3.7	10.4
150	3	200	4	15.8	4.3	2.0	22.1	–1.6	8.5
150	3	200	8	9.8	5.6	3.0	18.4	0.6	13.2
Milled specimens									
0	0	0	0	—	5.9	6.0	11.9	—	15.1
150	3	180	2	5.1	5.8	4.7	15.6	—	9.5
150	3	180	4	4.7	4.0	3.7	12.4	—	9.9
150	3	180	8	4.6	7.7	7.8	20.1	—	8.2
150	3	200	2	8.8	15.2	4.5	28.5	—	7.2
150	3	200	4	14.8	16.2	8.3	39.3	—	6.2
150	3	200	8	10.2	14.5	6.1	30.8	—	6.9

Note: Compression set = 40 (%)

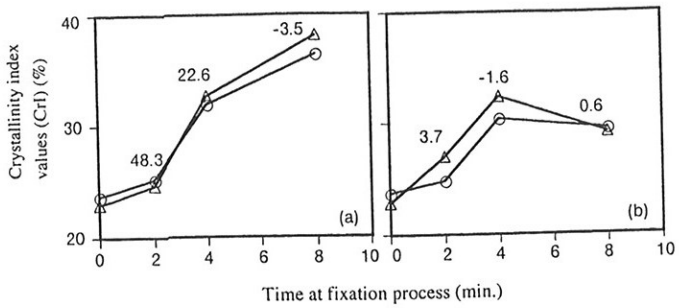

Fig. 3 .The effect of time on the crystallinity index values in extractive residue fixed at 180°C (a) and 200°C (b).
Legends: △: Segal's method, ○: Area method.
Notes: Specimens were softened at 150°C for 3 min. The compression set was 40 %. Inserted values in figure show the set-recovery.

amount of decrease in set-recovery in general. Also, the ratio of increase in CrI to the decrease in set-recovery is larger when the fixation processing temperature reached 200°C .

These results show that increase in the crystalline region of cellulose is a factor for CrI increase. However, there is another interpretation that cannot be dismissed here. Due to the extraction of non-crystalline hemicellulose and lignin constituents, the relative CrI might have increased. The results in Table 1, however, show that the fixation mechanism is affected by cellulose, which leads to the conclusion that CrI increase suggests an increase of cellulose crystalline region. Moreover, as the crystalline region of cellulose is increased by rearrangement or reorientation of the cellulose molecules of the paracrystalline regions during steaming (Tanahashi 1990), the mechanism of the fixation of compressive transformation can be thought of as follows. The inner stress is dissolved because the paracrystalline region of cellulose, which is distorted by compressive transformation, is partially hydrolyzed, and steam-rearrangement of hydrolyzed constituents into crystalline region occurs keeping the transformed shape intact.

This interpretation will be clarified further in future studies with the experiments on viscose-rayon comprised only of cellulose.

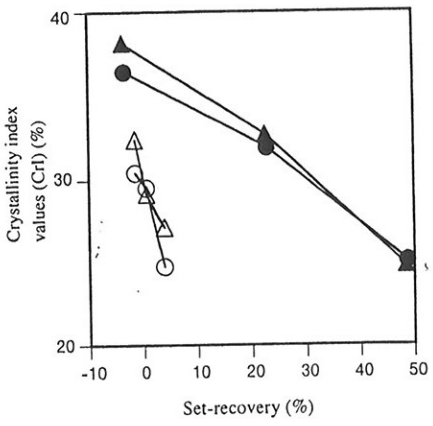

Fig. 4. The effect of the set-recovery on the crystallinity index values in extractive residue.
Legends: ▲: Segal's method (fixed at 180°C), ●: Area method (fixed at 180°C), △: Segals method (fixed at 200°C), ○: Area method (fixed at 200°C)
Notes: Specimens were softened at 150°C for 3 min. The compression set was 40 %.

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