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ORIGINAL ARTICLE

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Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin III: effects of sodium chlorite treatment

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Abstract To obtain high-strength phenol–formaldehyde (PF) resin-impregnated compressed wood at low pressing pressure, we investigated the effects of sodium chlorite ($NaClO_2$) treatment on wood prior to low molecular weight PF resin impregnation. Sawn veneers of Japanese cedar (*Cryptomeria japonica*) were treated with 2% aqueous $NaClO_2$ solution at 45°C for 12 h to remove lignin, and the process was repeated up to four times, resulting in weight loss of 21%. $NaClO_2$ treatment has shown considerable potential for high compression of PF resin-impregnated wood at low pressing pressure, especially after adding moisture to a content of 10%–11%. This deformation is further enhanced during pressure holding by creep deformation. The density, Young's modulus, and bending strength of PF resin-impregnated veneer laminated composites that were treated with $NaClO_2$ four times and compressed at 1 MPa, reached 1.15 g/cm^3, 27 GPa, and 280 MPa, respectively. The values in untreated PF resin-impregnated wood reached 0.8 g/cm^3, 16 GPa, and 165 MPa, respectively.

Key words Phenol formaldehyde resin · Densification · Mechanical properties · Sodium chlorite treatment

Introduction

Phenol formaldehyde (PF) resin impregnation and compression is one of the promising techniques for overcoming shortcomings in wood such as dimensional instability due to moisture, low durability due to biodeterioration, and relatively low mechanical properties compared with other engineering materials. However, considering the production of composites on a large scale, the commercial use of this admirable material has been severely limited by its high pressing pressures of 7 MPa or above.[1] Hence, a method to obtain highly compressed PF resin-impregnated wood at low pressing pressure is desirable.

In our previous studies,[2,3] we described our study of the compressive deformation of PF resin-impregnated wood with regard to mechanical properties and found that when wood is plasticized by low molecular weight PF resin, the cell wall softens significantly, which results in collapse at low pressing pressure. Due to the collapse, PF resin-impregnated wood could be compressed significantly by applying slightly increasing pressing pressure, which is in turn accompanied by an increment of mechanical properties. In addition, pressure holding during compression caused creep deformation of resin-impregnated wood, also making it possible to initiate collapse at low pressure.

To clarify the optimum processing conditions for obtaining highly compressed wood, we studied the effects of processing parameters such as resin content, preheating temperature, pressing temperature, and pressing speed on the deformation behavior of PF resin-impregnated wood and found that with an increase of PF resin content, the Young's modulus of the cell wall perpendicular to fiber direction decreases and collapse-initiating pressure decreases linearly with the Young's modulus. This clearly shows that the occurrence of cell wall collapse is strain dependent rather than stress dependent.[3] In other words, plasticization of the cell wall is the dominant factor for initiating collapse at low pressing pressure.

Considering that the lignin polymer comprising around 50% of the cell wall matrix shows clear softening at a temperature of 80°–100°C when swollen under water or ethyl glycol,[4–6] removal or depolymerization of lignin seems to be effective in reducing the Young's modulus of the cell wall when it is swollen by PF resin. In this article we discuss the effects of sodium chlorite ($NaClO_2$) treatment, that is, a lignin-removal treatment on the compressive deformation of low molecular weight PF resin-impregnated wood, including effects on mechanical properties.

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Materials and methods

Raw material

Sawn veneers of Japanese cedar (*Cryptomeria japonica*), with a density of 0.34 g/cm^3 and dimensions of 60 mm in the longitudinal direction (L), 40 mm in the tangential direction (T), and 1.5 mm in the radial direction (R), were cut in a series from a large block. The average annual ring width was 1.7 mm.

Sodium chlorite treatment

Sawn veneers were used in this study, because it is easier to treat the inside of the veneers with aqueous $NaClO_2$ solution than thicker solid wood. The density and mechanical properties were not found to be significantly different between solid woods and veneer-laminated wood as long as delamination is avoided during bending testing.[7] Thus, oven-dried veneers were treated with 2% aqueous solution of $NaClO_2$ at 45°C for 12 h. Acetic acid was added to adjust the pH to 4.5. The treatment was repeated up to four times followed by rinsing with running water for 6 h. The weight loss due to this treatment was evaluated based on oven-dried weight before and after the treatment.

Impregnation with PF resin

An aqueous solution was prepared using a commercial PF resin with a molecular weight of about 300 (PL 2771, pH 5.5, Gun-ei Chemical, gelation time: 10 min at 150°C). Sodium chlorite treated and untreated veneers were soaked in a 20% aqueous solution of PF resin for 3 days. Then specimens were kept under ambient conditions for 3 days and were then vacuum dried at 50°C for 12 h. The weight gain due to resin impregnation was evaluated based on oven-dried weight before and after treatment. To regulate moisture content, specimens were conditioned at 20°C and 60% relative humidity (RH) for 1 week after oven drying.

Measurement of deformation behavior

We investigated the deformation of wood in the radial direction. Four plies of veneers were laminated in parallel (approximately 6 mm in the radial direction) and compressed using plates fixed to the universal testing machine (UTM, Instron 5500). The compression procedure is described in our previous report.[2] The UTM allows precise movement of the crosshead, thus providing data on how wood can be compressed. The crosshead movement, load, and accumulated time were logged using a computer attached to the UTM. After the removal of the deformation of the hot plates and their attachments, we evaluated precisely the deformation of wood in the thickness direction. Two compressed plates were produced for each condition. For comparison with previous results,[2,3] the hot pressing was carried out at 150°C and at a pressing speed of 5 mm/min for oven-dried PF resin-impregnated veneers. A pressing speed of 20 mm/min was adopted to clarify the effect of adding moisture, because the pressing speed of 5 mm/min is not adequate to retain moisture inside specimens during compression.

After reaching the desired pressing pressure level, the pressing pressure was held for 30 min, called pressure holding in this study. The relationship between pressing pressure and density was determined based on stress–strain curves.

Evaluation of bending properties

Two 50 × 8 mm samples were prepared from each plate. The specimens were then oven dried for 6 hours at 105°C to evaluate their oven-dried weight and dimensions. The Young's modulus and bending strength were evaluated in the oven-dried condition by a three-point load bending test at a crosshead speed of 5 mm/min and a test span of 40 mm, on an Instron 4411 universal testing machine. The values recorded were an average of three samples.

Results and discussion

After $NaClO_2$ treatment was repeated up to four times, veneers turned a whitish color. Weight loss due to this treatment was above 21% noted. This weight loss could be attributed to the removal of lignin.[8] The weight gain due to PF resin was about 60% regardless of $NaClO_2$ treatment.

Figure 1 shows the effects of $NaClO_2$ treatment on the densification of PF resin-impregnated wood in the

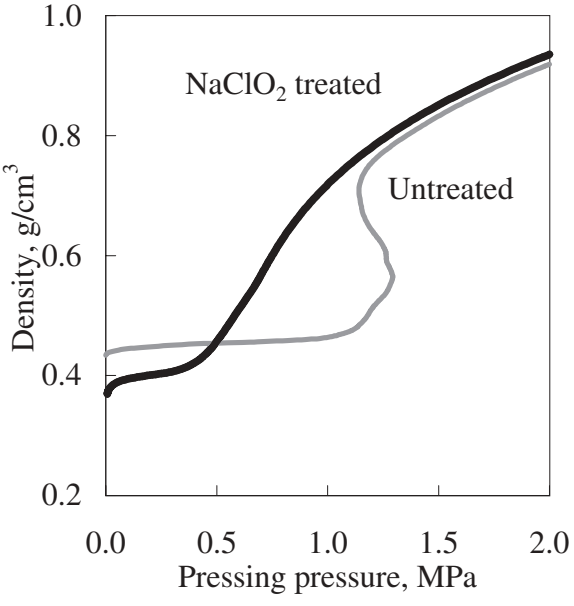

Fig. 1. Effects of $NaClO_2$ treatment (four times) on the densification of phenol–formaldehyde (PF) resin-impregnated wood in oven-dried condition. Pressing temperature, 150°C; pressing speed, 5 mm/min

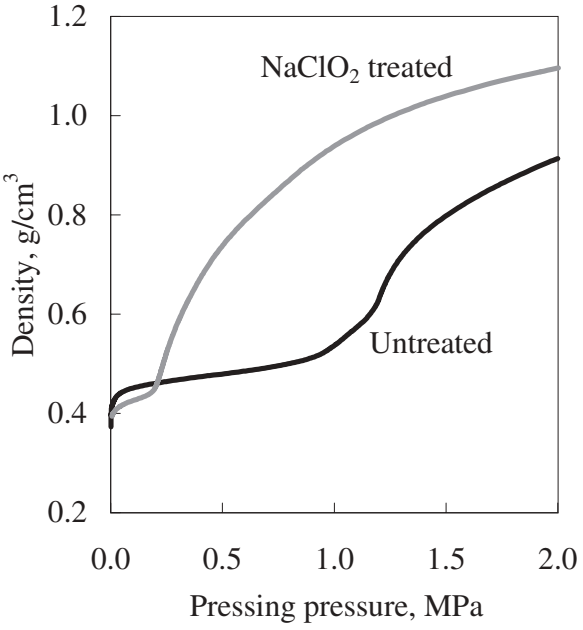

Fig. 2. Effects of $NaClO_2$ treatment (four times) on the densification of PF resin-impregnated wood after adding moisture (10%–11%). Pressing temperature, 150°C; pressing speed, 20 mm/min

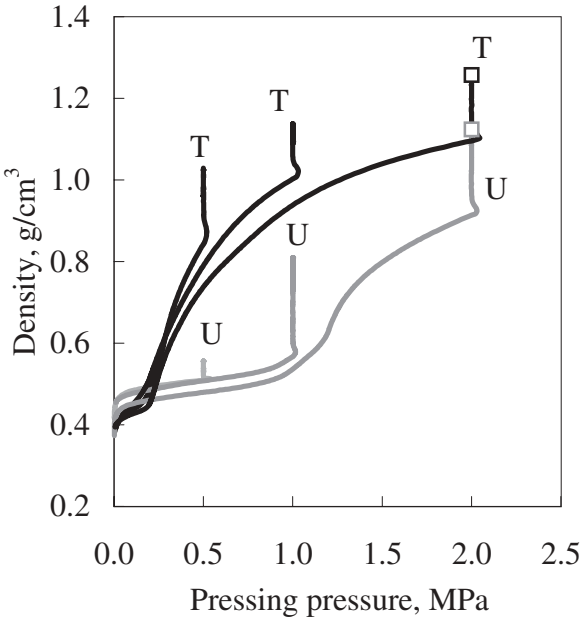

Fig. 3. Effect of pressing pressure with pressure holding on the densification of PF resin-impregnated wood. *U*, untreated; *T*, four times $NaClO_2$ treatment. Moisture content, 10%–11%; pressing temperature, 150°C; pressing speed, 20 mm/min; holding time, 30 min

oven-dried condition. The results show that PF resin-impregnated Japanese cedar was deformed at a density of 0.92 g/cm^3 at a pressing pressure of 2 MPa regardless of $NaClO_2$ treatment. However, at a pressing pressure of 1 MPa, that $NaClO_2$ treatment had a considerable effect on the densification of PF resin-impregnated wood; that is, $NaClO_2$ treated wood deformed significantly whilst untreated wood did not. This can be explained by the differences of collapse-initiating pressure. For example, $NaClO_2$ treated wood initiates collapse at around 0.5 MPa whilst untreated wood initiates at above 1 MPa. As in the collapse-dominant region, wood deforms considerably by applying a slightly increasing pressing pressure, and the density of $NaClO_2$ treated wood increased significantly from 0.5 MPa to 1 MPa.

In order to enhance the deformation of wood, moisture was added because wood softens thermally to some extent in wet conditions due to the thermal softening of the matrix components such as hemicellulose and lignin.[9] Pre-experimental work on $NaClO_2$ treated wood showed that high moisture content such as 15%–20% tends to cause splitting of veneers resulting in unsuccessful densification. Thus, in this study we compared the compressive deformation behavior at a moisture content of 10%–11%, as shown in Fig. 2. It was apparent that the deforming behavior was significantly different between $NaClO_2$ treated and untreated wood. By adding moisture of 10%–11%, the density of $NaClO_2$ treated wood reached 0.94 g/cm^3 at a pressing pressure of 1 MPa, which is almost double that of untreated wood at the same pressing pressure. To attain such a density, untreated wood required a pressing pressure of 2 MPa. The differences in the curve of untreated wood between the oven-dried condition and the air-dried condition could be explained by the differences in pressing speed.[3] Thus, it is reasonable to conclude that adding moisture helps to plasticize the cell wall significantly in $NaClO_2$ treated wood and results in considerable reduction in pressing pressure required to initiate collapse compared with oven-dried wood. However, the effect of adding moisture could not be observed in untreated PF resin-impregnated wood, and the reasons for this are not clear. Hence, we conclude that the removal of lignin is a highly promising approach for marked deformation of PF resin-impregnated wood at low pressing pressure, especially when moisture is added.

In our previous studies,[2,3] we found that pressure holding caused significant creep deformation of wood plasticized by low molecular weight PF resin. This allows the initiation of collapse at low pressing pressure. Thus, the effect of $NaClO_2$ treatment during pressure holding was studied on PF resin-impregnated wood with added moisture, at different pressing pressures. After reaching the desired pressing pressure, it was held for 30 min, as shown in Fig. 3. When PF resin-impregnated wood not treated with $NaClO_2$ was compressed at 0.5 MPa, the effect of pressure holding on density was negligible. However, $NaClO_2$ treated wood deforms well at 0.5 MPa and density increased from 0.84 to 1.03 g/cm^3. In the case of untreated wood, a significant increment in density occurred during pressure holding at 1 MPa. The density of untreated wood increased from 0.50 to 0.80 g/cm^3, while that of $NaClO_2$ treated wood increased from 0.97 to 1.14 g/cm^3.

Analysis of the stress–strain curve, including pressure holding at 1 MPa, revealed that the strain of PF resin-impregnated wood untreated with $NaClO_2$ was in an elastic deformation region up to 1 MPa before starting pressure

Table 1. Effect of $NaClO_2$ treatment on the mechanical properties of phenol–formaldehyde (PF) resin-impregnated compressed wood

Conditions	Pressing pressure (MPa)	Density (g/cm^3)	Young's modulus[a] (GPa)	Bending strength[a] (MPa)
Un	0.5	0.49	9.4 (.01)	79.0 (13.2)
T	0.5	1.02	23.5 (2.8)	247.1 (8.9)
Un	1	0.80	16.4 (0.5)	165.3 (4.2)
T	1	1.15	26.8 (0.7)	279.1 (8.7)
Un	2	1.14	22.3 (0.5)	238.4 (2.4)
T	2	1.24	27.0 (1.2)	278.6 (8.7)

Un, untreated; T, four times treatment with $NaClO_2$
[a]Each value is the average of three samples; values in parentheses show the standard deviation

holding, and it showed a significant increment in strain during pressure holding due to collapse attained by creep deformation. On the other hand, $NaClO_2$ treated wood crossed the collapse-dominant region up to 1 MPa and entered the post collapse region before pressure holding.

In the post collapse region, the slope of the stress–strain curve increases as the strain increases. This means that the resistance of the cell wall against deformation increases with increasing strain. In addition, the relationship between pressure-holding time and density revealed that within 1 min of holding time, the density increased significantly and then stabilized. Such stabilization is due to the resistance of the cell wall, not the curing of PF resin, which takes 10 min at 150°C. Thus, it is of paramount importance to design a suitable combination of pressing pressure and pressure holding, taking into account the deformation characteristics such as elastic deformation, collapse and post-collapse deformation in order to obtain marked deformation at low pressing pressure.

Table 1 shows the effect of $NaClO_2$ treatment on the mechanical properties of PF resin-impregnated compressed wood. $NaClO_2$ treatment is an effective way to improve the mechanical properties of wood at low pressing pressure. The Young's modulus and bending strength of $NaClO_2$ treated wood increased considerably compared with untreated wood and reached 27 GPa and 280 MPa respectively, at a pressing pressure of 1 MPa. Furthermore, it is interesting to note that the specific values of Young's modulus and bending strength (that is, Young's modulus and bending strength each divided by density) are about 20% and 30% higher respectively, than untreated wood at the same pressure. This could be attributable to the effects of the removal of lignin, or, in other words, to an increase in the volume ratio of microfibril, the framework of the cell wall.[8]

Finally, we studied the relationships between the degree of $NaClO_2$ treatment and deformation behavior of resin-impregnated wood. Figure 4 shows that weight loss increased with increasing number of $NaClO_2$ treatment times. With one time treatment, the weight loss was 2%. The weight loss increased significantly after two times treatment and 21% weight loss was attained after four times treatment. The weight gain due to PF resin impregnation was not significantly different regardless of the number of $NaClO_2$ treatments.

The relationships between pressing pressure and density after successive $NaClO_2$ treatment times are shown in Fig. 5.

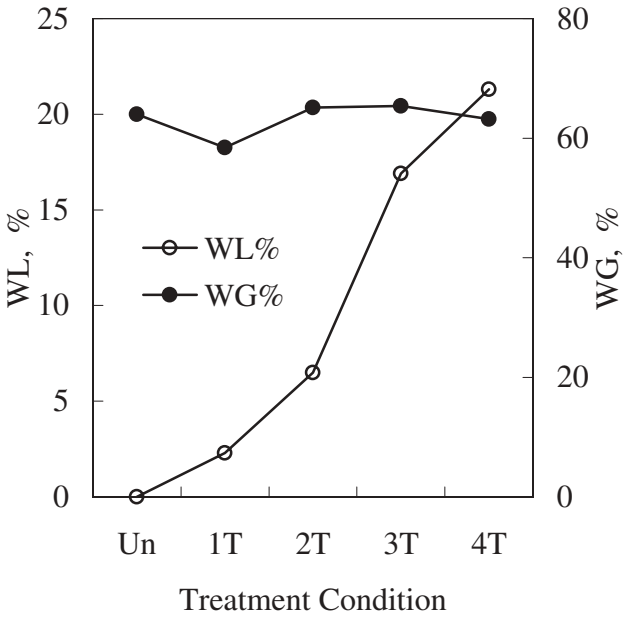

Fig. 4. Effects of number of $NaClO_2$ treatments on the weight loss (*WL*, %) and weight gain (*WG*, %) due to PF resin impregnation. *Un*, untreated; *1T*, one time treatment; *2T*, two times treatment; *3T*, three times treatment; *4T*, four times treatment

We found that the density of PF resin-impregnated wood at the pressing pressure of 1 MPa increased with the number of $NaClO_2$ treatment times. The differences of density among the treatment times can be attributed to the differences of collapse-initiating pressure. For example, wood treated with $NaClO_2$ once initiated collapse at 0.6 MPa, while it occurred at around 0.2 MPa in the case of four times treatment. The most interesting observation was found during pressure holding. Wood treated with $NaClO_2$ twice reached a density similar to that of wood treated four times at the pressing pressure of 1 MPa after pressure holding. The Young's modulus and bending strength of wood treated with $NaClO_2$ twice were nearly the same as those of wood treated four times and reached around 26 GPa and 260 MPa, respectively, at a pressing pressure of 1 MPa. Thus it is reasonable to conclude that partial removal of lignin attained by treating wood with $NaClO_2$ twice with pressure holding is adequate to obtain high strength PF resin-impregnated Japanese cedar at a low pressing pressure such as 1 MPa.

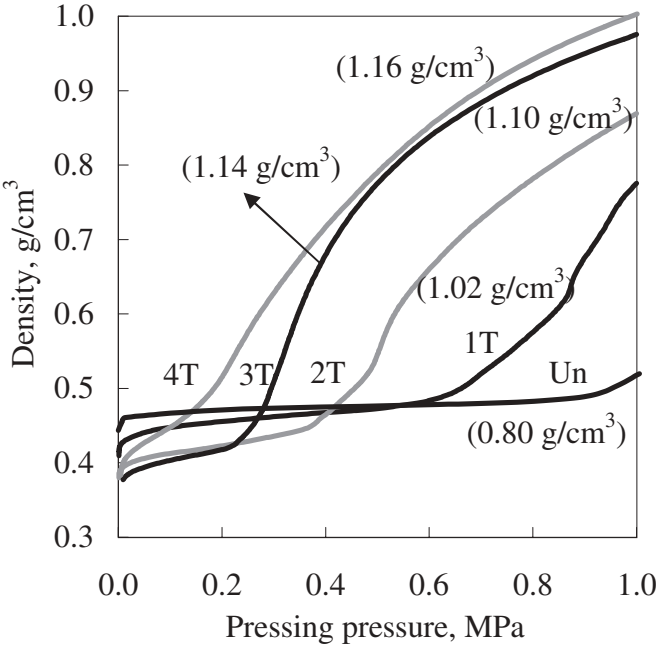

Fig. 5. Effects of degree of $NaClO_2$ treatment on the densification of PF resin-impregnated wood. Moisture content, 10%–11%; pressing temperature, 150°C; pressing speed, 20 mm/min. Values in parentheses show the density after pressure holding at 1 MPa

Conclusions

We concluded that the lignin removal treatment by $NaClO_2$ is a promising method for the densification of wood at low pressing pressure, especially with the addition of moisture at a level of 10%–11%. By a combination of $NaClO_2$ treatment and pressure holding, high-strength PF resin-impregnated wood can be obtained at low pressing pressure. Such treated wood elements are promising surface materials for the manufacture of sandwich panels at one shot, which gives high strength and dimensional stabilization with a moderate specific gravity.

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