ORIGINAL ARTICLE

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Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin V: effects of steam pretreatment

Abstract This study evaluated the potential of steam pretreatment for making highly compressed phenol–formaldehyde (PF) resin-impregnated wood at a low pressing pressure. Sawn veneers of Japanese cedar (*Cryptomeria japonica*) were first subjected to saturated steam at different steaming temperatures (140°–200°C), followed by impregnation with a 20% low molecular weight PF resin aqueous solution resulting in a weight gain of around 50%–55%. Four oven-dried treated veneers were laminated and compressed up to a pressing pressure of 1 MPa at a pressing temperature of 150°C and pressing speed of 5 mm/min, and the pressure was held for 30 min. Steam treatment, causing partial hydrolysis of hemicellulose, accelerated the compressibility of Japanese cedar in the PF resin-swollen condition. As a consequence, a discernible increment in density was achieved at a pressing pressure of 1 MPa due to steam pretreatment between 140° and 200°C for 10 min. It was also found that even a short steaming time such as 2 min at 160°C is sufficient for obtaining appreciable compression of PF resin-impregnated wood. The density, Young's modulus, and bending strength of steam-treated (200°C for 10 min) PF resin-impregnated wood composite reached 1.09 g/cm^3, 20 GPa, and 207 MPa, respectively. In contrast, the values of untreated PF resin-impregnated wood composite were 0.87 g/cm^3, 13 GPa, and 170 MPa, respectively.

Key words Compressed wood · Steam treatment · PF resin impregnation · Compressive deformation · Mechanical properties

Introduction

Phenol–formaldehyde (PF) resin-impregnated compressed wood has been studied since the early half of the 20th century. This material, called Compreg, exhibits high strength, good dimensional stability, and high resistance to decay and termites.[1,2] However, processing this material is severely curtailed by the need for high hot-pressing pressures in order to achieve its highly compressed condition, which results in a high-cost product thus having limited applications. Hence, the present authors developed a method to obtain highly compressed wood at low pressing pressure based on the analysis of the deforming behavior of PF resin-impregnated wood.[3–6]

First, we found that low molecular weight PF resin deposited in the cell wall causes considerable softening, inducing the reduction of Young's modulus perpendicular to the fiber direction, which results in cell wall collapse at low pressing pressure.[3] Because of this collapse, PF resin-impregnated wood can be compressed significantly by the application of a slightly increasing or steady pressing pressure, which is in turn accompanied by an increment in mechanical properties.

The effects of processing parameters such as resin content, preheating temperature, pressing temperature, and pressing speed were further investigated. It was demonstrated that by controlling these processing parameters properly, a highly compressed wood with high strength could be obtained at low pressing pressure.[4] In addition, we studied species dependency in terms of the compressibility of wood after PF resin impregnation and identified that low-density wood species are potential candidates for the production of high-strength PF resin-impregnated wood at low pressing pressure.[6]

To obtain a further drastic deformation of PF resin-impregnated wood under compression, the effect of the removal of the matrix substances of the cell wall prior to resin impregnation was studied. It was found that a lignin-removing treatment using NaClO$_2$ could significantly reduce the Young's modulus of wood perpendicular to the

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fiber and is effective in utilizing collapse efficiently to obtain a high-strength resin-impregnated wood at a pressing pressure as low as 1 MPa.[5]

The above treatment is attractive; nevertheless it is complicated in processing. Furthermore, it is somewhat difficult to remove the harmful chemical, NaClO$_2$, completely from the treated wood, a factor that poses a major drawback in the application of this treatment.

For this reason, based on previous research,[7–12] we focused on steam treatment as an alternative pretreatment. An application of steam treatment for the production of dimensionally stable wood-based composites was developed by Hsu et al.[7] They found that steam treatment causes partial hydrolysis of the hemicellulose components, which greatly increases the compressibility of wood. The increase in compressibility by steam treatment is due to partial breakage of the matrix network cross-linked by lignin and carbohydrate components.[10] Furthermore, it was found that the compressibility varied with steam temperature; at temperatures above 180°C wood shows significant deformation.[11] Thus, we have studied the potential of steam treatment in the range of 140°–200°C to enhance the compressibility of PF resin-impregnated wood.

Materials and methods

Raw material

Sawn veneers of Japanese cedar (*Cryptomeria japonica*), with 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 sapwood portion of a large block. Because density has a significant effect on the deformation behavior of PF resin-impregnated wood,[6] veneers with a similar density were selected carefully. Two series of wood samples were arranged: one for steaming temperature and the other for steaming time. Their ranges of air-dried density were 0.32–0.34 g/cm^3 and 0.35–0.36 g/cm^3, respectively.

Steam pretreatment

Veneers were subjected to saturated steam at different temperatures and times: 140°C, 160°C, 180°C, and 200°C for 10 min and 160°C for 2, 5, 10, 20, and 30 min (Table 1). The resultant steam pressures were 0.25 MPa for 140°C, 0.5 MPa for 160°C, 0.89 MPa for 180°C, and 1.4 MPa for 200°C. The weight loss was evaluated based on the oven-dried (105°C for 6 h) weight before and after steam treatment.

PF resin impregnation

An aqueous solution was prepared using a commercial low molecular weight PF resin with a molecular weight of about 300 (Gun-ei Chemical, PL 2771, pH 5.5, gelation time: 10 min at 150°C). Steam-treated and untreated veneers

Table 1. Effect of steam treatment on weight loss (WL) and weight gain (WG) due to phenol–formaldehyde (PF) resin impregnation

Temperature (°C)	Time (min)	WL (%)	WG (%)
Control	–	–	52.2
140	10	1.8	59.2
160	2	0.7	54.1
160	5	0.9	51.4
160	10	2.5	53.3
160	20	3.6	53.5
160	30	5.0	52.6
180	10	4.8	57.7
200	10	7.4	54.5

were immersed in a 20% aqueous solution of PF resin for 3 days. The specimens were taken out of the solution and kept at ambient conditions for 3 days and vacuum dried at 50°C for 12 h, which is designated as oven-dried condition for PF resin-impregnated wood. The weight gain due to resin impregnation was evaluated based on the oven-dried weight before and after treatment.

Measurement of deformation behavior

Four plies of oven-dried veneer (without adhesive) were parallel laminated (approximately 6 mm in the radial direction) and compressed using an ordinary open system hot platens fixed to a universal testing machine (Instron 5500). The compression procedure was the same as described previously.[3] Two compressed laminates were produced for each condition. The hot pressing was carried out at 150°C at a pressing speed of 5 mm/min. After reaching a pressing pressure of 1 MPa, the crosshead movement was stopped and the pressure maintained for 30 min, hereafter called pressure holding. The relationship between pressing pressure and density was determined based on stress–strain curves.

Evaluation of mechanical properties

Two samples, 50 mm in the longitudinal direction by 8 mm in the tangential direction, were prepared from each plate. 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, using an Instron 3365 universal testing machine. The values recorded were an average of the results of four samples.

Results and discussion

Weight loss

Table 1 shows the weight loss (WL, %) due to steam treatment and weight gain (WG, %) due to PF resin impregnation. The color of the samples became darker after steam
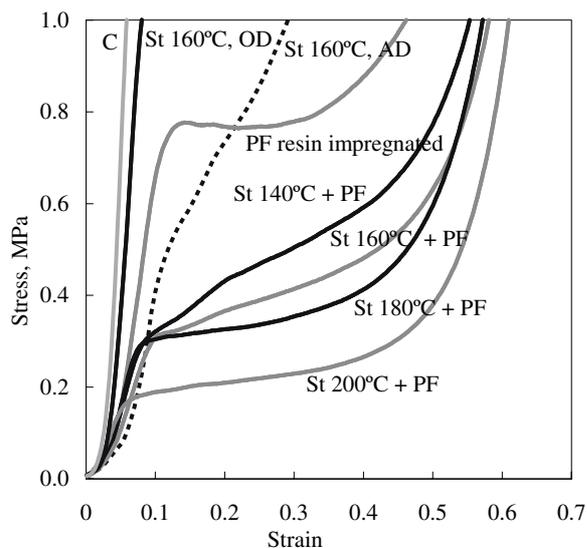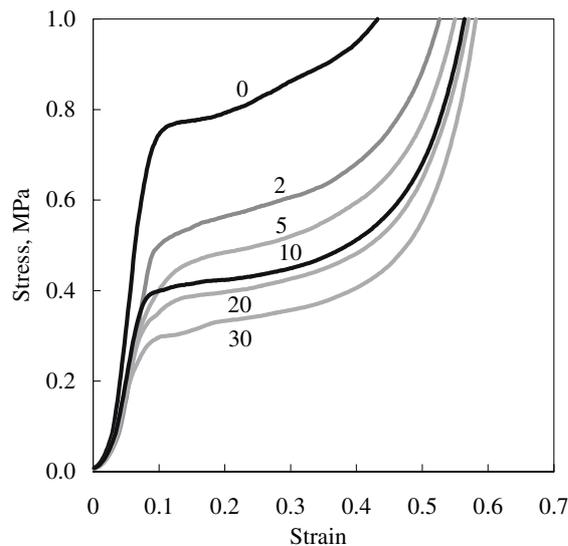
Fig. 1. Stress–strain curves of oven-dried phenol–formaldehyde (PF) resin-impregnated wood as a function of steaming temperature at a pressing temperature of 150°C and pressing speed of 5 mm/min. *C*, control (oven-dried untreated Japanese cedar); *St*, steam temperature; *PF*, phenol-formaldehyde resin impregnated; *OD*, oven-dried condition; *AD*, air-dried condition. Steaming time was 10 min


Fig. 2. Stress–strain curves of PF resin-impregnated wood for different steaming times at 160°C. The pressing temperature and pressing speed are the same as in Fig. 1. The *numbers* on the curves show steaming times (min)

treatment. The brownish color intensified with increases in the steaming temperature, especially at 200°C for 10 min. The weight loss tended to increase with increasing steaming temperature and time as reported previously.[9,10] A maximum weight loss of 7.4% was observed at 200°C for 10 min. The weight gain due to PF resin impregnation did not vary considerably, irrespective of steaming temperature and time as shown in Table 1.

Stress–strain relationships

Figure 1 displays the stress–strain curves of PF resin-impregnated wood as a function of steaming temperature. Steaming time was 10 min. In general, wood compressed in the radial direction, shows an elastic region followed by a long collapse-dominant region with roughly constant stress, leading to the final region of steeply rising stress called the postcollapse region. When solely steam-treated wood was compressed at oven-dried condition (St 160°C, OD), we could not detect any collapse deformation up to a pressing pressure of 1 MPa, showing to some extent the similar deformation behavior of untreated oven-dried Japanese cedar (C).

Hence, moisture was added to steam-treated wood, because wood softens thermally to some extent in wet conditions due to the thermal softening of the matrix components such as hemicellulose and lignin.[13] As shown in Fig. 1, steam-treated wood after adding moisture (St 160°C, AD) showed to a great extent deformation when compared with the oven-dried condition. It started collapsing at up to 1 MPa, although it was difficult to point out the exact position of the collapse-initiating stress. This behavior corresponds to the previous findings that steam treatment is

effective to enhance the compressibility of wood.[7,10] However, as clearly demonstrated in Fig. 1, the behavior is not as distinct as that of oven-dried PF resin-impregnated wood (PF resin impregnated) especially in the collapse-dominant region.

The collapse-initiating stress was dramatically reduced by the combination of steam treatment and PF resin impregnation (St + PF). Steam treatment at a relatively lower temperature such as 140°C prior to PF resin impregnation reduced the collapse-initiating stress from 0.8 MPa of solely PF resin-impregnated wood to 0.3 MPa. The collapse-initiating stress remained constant over the range of temperatures from 140° to 180°C despite the decomposition of the cell wall polymers demonstrated by increased weight loss, although a long collapse-dominant region with roughly constant stress was distinct at 180°C. The collapse-initiating stress decreased with increasing steaming temperature from 180°C to 200°C, and it was noted that cell wall collapse started at 0.2 MPa when steam treatment was performed at 200°C for 10 min.

The compressibility of steam-treated PF resin-impregnated wood was further studied at 160°C as a function of steaming time. As shown in Fig. 2, the stress required to compress PF resin-impregnated wood was greatly influenced by the steaming time. Interestingly, at a steaming treatment time of 2 min, which resulted in a small weight loss of 0.7%, the collapse-initiating stress reduced from 0.8 to 0.5 MPa. As steaming time increased, the collapse tended to start at lower stress. At a steaming time of 30 min and a weight loss of 5.0%, the collapse-initiating stress fell to 0.3 MPa, which is comparable with that for 180°C for 10 min having a weight loss of 4.8%. This implies that the collapse-initiating stress closely corresponded to the degree of decomposition of the cell wall polymers as indicated by weight loss.
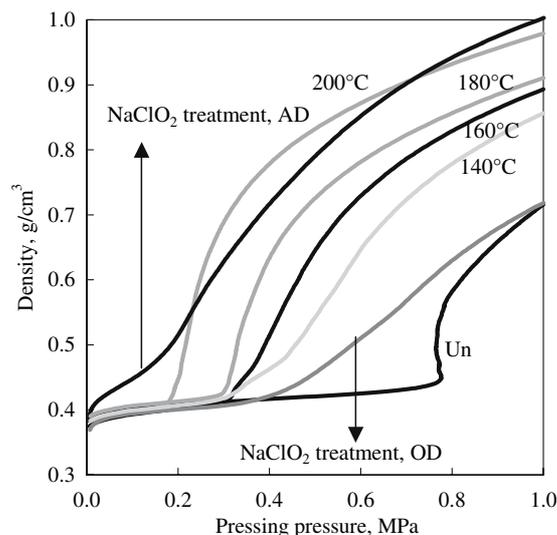
Fig. 3. Changes of density of PF resin-impregnated wood as a function of steaming temperature and comparison with NaClO₂ treatment.[5] *AD* and *OD* refer to air-dried and oven-dried conditions for NaClO₂-treated PF resin-impregnated wood, respectively. *Un* refers to PF resin-impregnated wood. Steaming time was 10 min

The decomposition of cell wall polymers due to steam treatment has been studied extensively.[14–18] The chemical structure of wood differs among species, especially between softwood and hardwood; thus, the decomposing manner of cell wall polymers differs among wood species. In the case of Japanese cedar, Higashihara et al.[15] reported that the hemicellulose decreased remarkably by steam treatment at 180°C for 60 min whilst the lignin of Japanese cedar apparently did not change. Dwianto et al.[12] considered that steaming up to 200°C for 60 min induces the decomposition of hemicellulose and is probably accompanied by slight decomposition of lignin. Thus, it appears that for up to 180°C for 10 min or 160°C for 30 min, the change in chemical components of Japanese cedar is attributable to the decomposition of hemicellulose. Thus, it can be said that the decomposition of hemicellulose due to steam treatment accelerates the compressibility of Japanese cedar in the PF resin-swollen condition.

Pressing pressure–density relationships

A more practical expression of the stress–strain relationship is the pressing pressure–density relationship, because density is an important parameter in determining the change in mechanical properties of resin-impregnated compressed wood.[3] The pressing pressure–density relationship was evaluated based on the final density of the compressed samples and thickness changes during compression. The relationship is depicted in Fig. 3 as a function of steaming temperature. There was a drastic change in density due to steam treatment. A steaming temperature of 140°C caused a weight loss of 1.8% and enabled a discernible increment of density: about 20% higher than in the untreated condition (Un) at 1 MPa. The difference can be explained by the

difference of collapse-initiating stress shown in Fig. 1. The density at 1 MPa did not differ between 140° and 180°C, as could be expected from Fig. 1. However, the density showed a marked increment from 180° to 200°C, attaining a density of 0.98 g/cm³ at 1 MPa, which is about 1.4 times higher than that of untreated PF resin-impregnated wood (Un).

When the pressing pressure–density relationship was evaluated as a function of steaming time at 160°C, it was observed that the density increased with increasing steaming time and attained around 0.93 g/cm³ when the steaming time was 30 min. Furthermore, it is interesting to show that the density of PF resin-impregnated wood reached a density of 0.8 g/cm³ at a short steaming time such as 2 min, about 15% higher than that of untreated PF resin-impregnated wood (Un).

The pressing pressure–density relationship of steam-treated resin-impregnated wood is compared in Fig. 3 with those of NaClO₂-treated (a lignin removal treatment) resin-impregnated wood.[5] The weight loss due to NaClO₂ treatment was 21%, and the weight gain due to PF resin impregnation for NaClO₂-treated wood was 60%. As reported previously,[5] there was a significant difference in compressibility between air-dried and oven-dried conditions for NaClO₂-treated PF resin-impregnated wood. The density of NaClO₂-treated resin-impregnated wood was 0.7 g/cm³ for the oven-dried condition (NaClO₂ treatment, OD) at a pressing pressure of 1 MPa. After adding moisture of 10%–11% to the NaClO₂-treated resin-impregnated wood (NaClO₂ treatment, AD), the density reached 1.0 g/cm³. This is similar to the density attained by oven-dried steam-treated resin-impregnated wood (200°C). It is worth mentioning that the decomposition of hemicellulose is as effective in increasing the compressibility of PF resin-impregnated wood as is the removal of lignin. Based on the chemical analysis of Higashihara et al.,[15] it is believed that a large amount of low molecular weight substances derived from decomposition of hemicellulose still remain in the cell wall after steaming. From these facts, it may be speculated that the decomposed hemicellulose maintained in the cell wall acts as a plasticizer in combination with the low molecular weight PF resin, and reduces the Young's modulus of the cell wall. It is thus recommended that steam treatment can be substituted for chemical treatment in the fabrication of highly compressed PF resin-impregnated wood, because steam treatment is much easier to perform than NaClO₂ treatment and is harmless to humans.

Mechanical properties of compressed wood

Figure 4 shows the density and mechanical properties of steam-treated PF resin-impregnated wood after pressure holding for 30 min at 1 MPa. The steaming time was 10 min. The density of PF resin-impregnated wood increased during pressure holding. For example, untreated PF resin-impregnated wood (Un) showed an increment of density from 0.70 to 0.87 g/cm³, and steam-treated (140°C) PF resin-impregnated wood increased from 0.85 to 1.03 g/cm³.
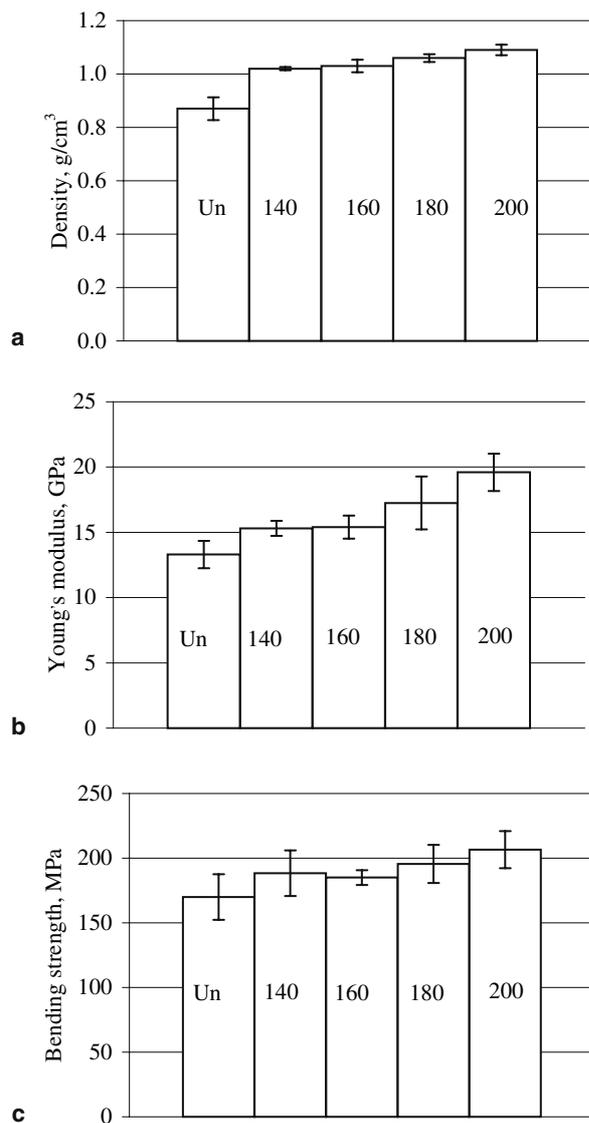
Fig. 4a–c. Effects of steam treatment on **a** density, **b** Young's modulus, and **c** bending strength of PF resin-impregnated compressed wood. All samples were compressed at 1 MPa with a pressure holding of 30 min. *Un* refers to PF resin-impregnated wood. The *numbers* are the steaming temperatures (°C). Steaming time was 10 min. *Bars* represent standard deviations

Pressure holding causing creep deformation of the cell wall is effective for the further densification of PF resin-impregnated wood. Furthermore, it was observed that within 1 min of pressure holding, the density increased considerably irrespective of the steaming temperature and afterward became stabilized, as reported previously.[3]

The Young's modulus and bending strength of PF resin-impregnated wood at a pressing pressure of 1 MPa increased due to steam pretreatment, and attained 20 GPa and 207 MPa, respectively, when the steaming treatment was 200°C and 10 min as shown in Fig. 4. This improvement is mainly attributable to the increased compressibility by the combination of steam treatment and PF resin impregnation. Furthermore, the specific Young's modulus (the ratio of Young's modulus to the specific gravity) was found to increase due to steam pretreatment. This increment is likely to cause the increase of the volume fraction of cellulose microfibril. The specific bending strength (the ratio of bending strength to the specific gravity) did not show any significant decrease, even when pretreated at a high steaming temperature such as 200°C. Thus, it can be concluded that steam treatment prior to PF resin impregnation and pressure holding is desirable in obtaining high-strength PF resin-impregnated compressed wood at low pressing pressure.

Because the Young's modulus and bending strength of untreated oven-dried Japanese cedar in this study were 5.0 GPa and 40.8 MPa, respectively, the mechanical properties of Japanese cedar improved four- to fivefold by the combination of steam pretreatment, PF resin impregnation, and hot pressing at 1 MPa. Considering that 1 MPa is a typical pressing pressure used for ordinary plywood and laminated veneer lumber (LVL) production, our finding indicates that when steam-treated PF resin-impregnated Japanese cedar veneers are laminated on both surfaces of stacked untreated veneers prior to hot pressing, high-strength plywood or LVL having dimensionally stabilized surfaces and a moderate specific gravity can be obtained by one-shot hot pressing. The application of this promising technique in making high-strength plywood and LVL is underway and will be reported in a future article.

Conclusions

We have demonstrated that steam treatment prior to PF resin impregnation enables marked deformation of PF resin-impregnated wood at low pressing pressure. The density of steam-treated PF resin-impregnated compressed wood was much higher than that of $NaClO_2$-treated PF resin-impregnated wood when compared in their oven-dried conditions. It is recommended that steam treatment be substituted for chemical treatment in the fabrication of highly compressed PF resin-impregnated wood. Steam treatment is much easier to perform than $NaClO_2$ treatment and is harmless to humans. Such treated wood elements present a promising surface material in the manufacture of sandwich panels, giving high strength and dimensional stabilization with a moderate specific gravity using a one-shot application.

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