A NEW METHOD FOR OBTAINING HIGH STRENGTH PHENOL FORMALDEHYDE RESIN-IMPREGNATED WOOD COMPOSITES AT LOW PRESSING PRESSURE

MI Shams[1, 2, *] & H Yano[1]

[1]*Research Institute for Sustainable Humanosphere, Kyoto University, Japan*
[2]*Forestry and Wood Technology Discipline, Khulna University, Bangladesh*

Received May 2008

SHAMS MI & YANO H. 2009. A new method for obtaining high strength phenol formaldehyde resin-impregnated wood composites at low pressing pressure. To obtain high strength phenol formaldehyde (PF) resin-impregnated compressed wood at low pressure, we investigated the effects of sodium chlorite treatment followed by sodium hydroxide treatment prior to low molecular weight PF resin impregnation. Sawn veneers of Japanese cedar (*Cryptomeria japonica*) were first treated with 2% aqueous solution of $NaClO_2$ followed by 0.5% aqueous solution of NaOH. A total weight loss of 12% was obtained by the combination of these two treatments. It was found that the treatments showed potential for the marked deformation of PF resin-impregnated wood at low pressure. The result suggests that depolymerization or partial removal of lignin can be effective for the removal of hemicellulose, which softens the cell wall swollen by PF resin and makes it possible to compress wood remarkably at low pressing pressure. Pressure holding during compression caused creep deformation of resin-impregnated wood and resulted in density, Young's modulus (MOE) and bending strength (MOR) of 1.16 g cm^{-3}, 29 GPa and 307 MPa respectively at a pressing pressure of 1 MPa. This technique imparts high strength and attractive surface to plywood and other wood composite materials with conventional hot press equipment.

Keywords: PF resin-impregnated wood, densification, mechanical properties, sodium chlorite treatment, sodium hydroxide treatment

SHAMS MI & YANO H. 2009. Kaedah baru menghasilkan komposit kayu berisi resin fenol formaldehid berkekuatan tinggi pada tekanan mampatan rendah. Bagi mendapatkan kayu mampat berisi resin fenol formaldehid (PF) berkekuatan tinggi pada tekanan rendah, kami menyiasat kesan rawatan natrium klorit diikuti dengan rawatan natrium hidroksida yang dijalankan sebelum mengisi PF yang mempunyai berat molekul rendah. Venir gergaji daripada pokok sedar Jepun (*Cryptomeria japonica*) mulanya dirawat dengan 2% larutan akues $NaClO_2$ dan seterusnya dengan larutan akues 0.5% NaOH. Kehilangan berat sebanyak 12% dicapai dengan kombinasi kedua-dua rawatan ini. Kami dapati kedua-dua rawatan ini menunjukkan potensi untuk menghasilkan canggaan jelas bagi kayu berisi resin pada tekanan rendah. Keputusan mencadangkan bahawa penyahpolimeran atau penyingkiran sebahagian lignin mungkin berkesan untuk membuang hemiselulosa yang melembutkan dinding sel yang cekang akibat resin PF. Justeru kayu dapat dimampat dengan sangat baik pada tekanan rendah. Tekanan semasa proses mampatan menyebabkan canggaan rayap pada kayu berisi resin dan menghasilkan ketumpatan, modulus kekenyalan (MOE) dan modulus kepecahan (MOR) masing-masing sebanyak 1.16 g cm^{-3}, 29 GPa dan 307 MPa pada tekanan mampatan 1 MPa. Teknik yang menggunakan alat pemampat panas ini dapat menjadikan papan lapis serta bahan komposit kayu kuat dan mempunyai permukaan menarik.

INTRODUCTION

The establishment of a sustainable society based on renewable and sustainable resources is a real challenge and responsibility of all nations in the 21st century. In this sense, the promotion of wood as a future-oriented material must be emphasized as it is a natural renewable resource that is environmentally friendly. As reserves of coal and oil become exhausted, future advanced materials have to be derived from renewable resources such as wood. For these potentials to be realized and to substitute other resources derived from synthetic plastic, ceramics and metals, the utilization of inherent properties of wood should be taken into account. However, some properties of wood are a bane in its utilization; these include dimensional instability with changing moisture, low durability and unsatisfying mechanical properties. Phenol formaldehyde (PF) resin

E-mail: shams_rish@yahoo.com

impregnation and compression at considerably high hot pressing pressure have been used for the enrichment of bending-strength properties (MOR), dimensional stability and durability of wood against decay (Stamm 1964, Ryu *et al.* 1991, Yano *et al.* 1997, Yano *et al.* 2000, Yano 2001, Yano *et al.* 2001). However, high hot pressing pressure limits the commercial application of the products. In studies of the compressive deformation of resin-impregnated wood in relation to mechanical properties, it was found that high strength resin-impregnated wood product could be achieved at a lower pressure by effective utilization of the collapse region of cell wall (Shams *et al.* 2004, Shams & Yano 2004, Shams *et al.* 2005, Shams *et al.* 2006). In this case, PF resin caused significant softening of cell walls and decreased the Young's modulus (MOE) of wood fibre and resulted in collapse at lower pressure. Furthermore, it was found that with increased resin content, the MOE of cell wall perpendicular to fibre direction decreased and collapse-initiating pressure decreased linearly with the MOE. This shows that plasticization of cell wall without any damage to microfibril is effectual for densification of wood at lower pressure (Shams & Yano 2004).

The plasticization of cell wall can be enhanced either by changing the cell wall material or by adding a plasticizer. The lignin in cell wall is thermoplastic, i.e. it softens upon heating. Under water or ethyl glycol saturated conditions, wood shows clear softening at temperatures of 80–100 °C due to the softening of lignin (Salmen 1984, Olsson & Salmen 1997, Furuta & Yano 1997). Thus, to allow more PF resin to be added into wood and to obtain a further deformation of PF resin-impregnated wood under compression, the effect of partial removal of lignin by $NaClO_2$ treatment prior to resin impregnation was studied. Using $NaClO_2$ to remove lignin significantly reduce the MOE of wood perpendicular to the fibre and is effective in utilizing collapse efficiently to obtain a high-strength resin-impregnated wood at a pressing pressure as low as 1 MPa (Shams *et al.* 2005).

In this paper, we studied the effects of two treatments, namely, NaOH treatment for the removal of hemicellulose and $NaClO_2$ treatment for the removal of lignin and their combination in order to obtain high strength PF resin-impregnated wood at lower pressing pressure.

MATERIALS AND METHODS

Sliced veneers were used in this study since it was easy to remove lignin and hemicellulose from veneers than solid wood and also because their density and mechanical properties were not significantly different (Yano *et al.* 2000). Sawn veneers of Japanese cedar (*Cryptomeria japonica*), with density of 0.34 g cm^{-3} and dimensions of 60 × 40 × 1.5 mm were used in the experiment. In general, it is more difficult to remove hemicellulose from softwood than hardwood due to the differences in cross-linking density of lignin (Yano *et al.* 2001). Hence, veneers were then first treated by 2% aqueous solution of $NaClO_2$ at 45 °C for 12 hours (referred to as 1T). This treatment was repeated (2T) and veneers were soaked in 0.5% aqueous solution of NaOH at 40 °C for 12 hours. The weight loss was evaluated based on the oven-dry (105 °C for six hours) weight by using the following equation:

$$WL = \frac{W_a - W_b}{W_a} \times 100$$

where
W_a = original oven-dry weight
W_b = oven-dry weight after treatment.

An aqueous solution was prepared using a commercial PF resin with a molecular weight of about 300 (Gun Ei Chemical Industry Co. Ltd., PL 2771, pH 5.5 and gelation time of 10 min at 150 °C). Chemically treated and untreated veneers were immersed in a 20% aqueous solution of PF resin for three days. The specimens were taken out from the solution and kept at ambient conditions for three days before being vacuum dried at 50 °C for 12 hours to obtain oven-dried PF resin-impregnated wood. To regulate moisture content, specimens were conditioned at 20 °C and 60% relative humidity for one week after oven drying. The percentage of weight gain (WG) due to resin impregnation was expressed using the following equation:

$$WG = \frac{W_b - W_a}{W_a} \times 100$$

Four plies of oven-dried veneer (without adding extra glue) were parallel laminated (approximately 6 mm in the radial direction) and compressed using plates fixed to a universal testing machine (Instron 5582). The compression procedure has been described in a previous study (Shams *et al.* 2004). Two compressed laminates were produced at each condition. For comparison with previous results (Shams *et al.* 2005), the hot pressing was carried out at 150 °C with a pressing speed of 20 mm min^{-1} and later cooled for 10 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.

The MOE and MOR were evaluated in the oven-dried condition by a three-point load-bending test at a crosshead speed of 5 mm min^{-1} and a test span of 40 mm using an Instron 3365 universal testing machine. The values recorded were an average of four samples.

RESULTS AND DISCUSSION

Table 1 shows the weight loss of veneers due to chemical treatment and weight gain after PF resin impregnation. When veneers were subjected to only NaOH treatment, a weight loss of 1.7% was noticed. Alkaline treatment (in this study NaOH treatment) requires higher temperature to remove hemicellulose (Yano *et al.* 2001). It has been shown that when veneers were first treated with 2% $NaClO_2$ before being soaked in 0.5% NaOH solution, about 6% weight loss occurred (Shams *et al.* 2005). In this study, the one time $NaClO_2$ treatment followed by NaOH treatment produced a weight loss of 9.2% (Table 1). Repeating the $NaClO_2$ treatment resulted in 12.4% sample weight loss. It was assumed that partial removal of lignin allows the removal of hemicellulose under mild NaOH treatment and, thus, more PF resin was impregnated into the wood. However, the weight gain due to PF resin treatment was about 60% regardless of chemically treated or untreated conditions, which may be due to sample variation (Table 1).

Effects of $NaClO_2$ treatment followed by NaOH on the densification of PF resin-impregnated wood after adding moisture are shown in Figure 1. A more practical expression of the stress–strain relationship is the pressing pressure–density relationship, since density is an important parameter in determining the change in mechanical properties of resin-impregnated compressed wood (Shams *et al.* 2004, Shams & Yano 2004). When $NaClO_2$ treated PF resin-impregnated wood was compressed at oven-dried condition, the deformation was similar to that of untreated PF resin-impregnated wood (Shams *et al.* 2005). In general, wood can be regarded as an elastic material in dry conditions. However, it becomes soft and exhibits plasticity to some extent when heated in wet conditions. This is mainly due to the softening of the matrix components containing hemicellulose and lignin.

Table 1 Effects of $NaClO_2$ treatment followed by NaOH treatment on weight loss and weight gain due to PF resin impregnation

Treatment condition	Weight loss (%)	Weight gain (%)
Untreated	–	64.0
NaOH	1.7	58.6
$NaClO_2$*	2.3	58.4
$NaClO_2$*– NaOH	9.2	57.7
$NaClO_2$**– NaOH	12.4	56.7

* and ** refer to one time and two times $NaClO_2$ treatment respectively.

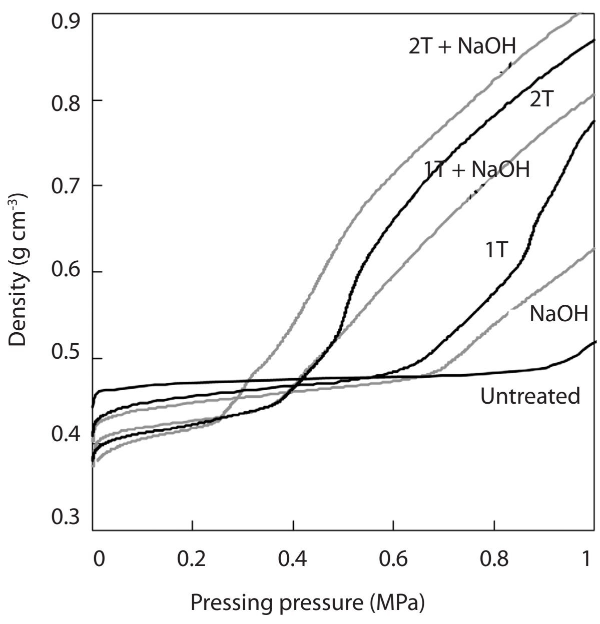

Figure 1 Effects of $NaClO_2$ followed by NaOH treatment on the densification of PF resin-impregnated wood. MC: 10–11%, pressing temperature: 150 °C and pressing speed: 20 mm min^{-1}. 1T and 2T refer to one time and two times $NaClO_2$ treatment respectively.

The heating of wet wood above the softening temperature of the matrix components results in a considerable reduction in its MOE and a slight increase in its breaking strain (Goring 1963). Hence, deformation behaviour of $NaClO_2$ treated resin-impregnated wood was investigated by adding moisture and a moisture content of 10–12% was suitable for the large deformation of resin-impregnated wood.

From Figure 1, it can be concluded that treatment using one time $NaClO_2$ followed by NaOH (1T + NaOH) has more potential to deform PF resin-impregnated wood. The density reached 0.8 g cm^{-3} at pressing pressure of 1 MPa, almost double the density of untreated wood. Although there was not much difference in density of the laminates at 1 MPa between one time $NaClO_2$ treatment (1T) and $NaClO_2$ followed by NaOH (1T + NaOH), there was a substantial difference in their deformation behaviour. At pressing pressure of 0.6 MPa, $NaClO_2$ followed by NaOH (1T + NaOH) had a considerable effect on the densification of PF resin-impregnated wood in that it deformed well compared with the treatment using $NaClO_2$ (1T) alone. This can be attributed to the difference in the collapse-initiating pressure (Shams *et al.* 2004). $NaClO_2$ treatment followed by NaOH (1T + NaOH) initiated collapse at about 0.4 MPa while $NaClO_2$ treatment (1T), at about 0.6 MPa. Since most of the densification occurred in the collapse region the density of wood treated with $NaClO_2$ followed by NaOH (1T + NaOH) was greater compared with 1T treatment**.** This suggests that partial removal of lignin can be useful for the removal of hemicellulose which softens cell wall swollen by PF resin and allows initiation of collapse at low pressing pressure. It was further observed that the density of resin-impregnated wood was accelerated with increasing $NaClO_2$ treatment time followed by NaOH treatment (2T + NaOH) reaching a density of 0.9 g cm^{-3} at 1 MPa.

Pressure holding is a feasible method to enhance the deformation of PF resin-impregnated wood (Shams *et al.* 2004). Pressure holding causes substantial creep deformation of the resin-impregnated wood. This also makes it possible to initiate collapse at lower pressing pressures. In this study, densities after pressure holding at different treatment conditions are shown in Figure 2. Effects of pressure holding on density differed among different treatment conditions. Although the deforming pattern between $NaClO_2$ treatment (1T) and that of $NaClO_2$ followed by NaOH (1T + NaOH) was different, the density after pressure holding did not differ significantly, presumably due to collapse attained by creep deformation. Within one minute of holding, all densities increased regardless of treatment condition and thereafter, densities were almost consistent. Thus, $NaClO_2$ followed by NaOH treatment with 1 min pressure holding is suitable to obtain highly compressed resin-impregnated wood at low pressure as long as the deformation is fixed. Two times $NaClO_2$ treatment followed by NaOH (2T + NaOH) with a pressure holding at 1 MPa for 30 min increased the density of Japanese cedar from 0.34 to 1.16 g cm^{-3}.

The effects of $NaClO_2$ treatment followed by NaOH treatment on the mechanical properties of PF resin-impregnated compressed wood are shown in Figure 3. Delamination due to the release of internal pressure occurred when treated samples were hot pressed at 1 MPa and taken out from the hot plates without cooling**.** This may be due to the fact that wood with higher density has a higher compaction ratio. This prevents the escape of vapour from inside the board and, thus, produces higher internal pressure. $NaClO_2$ treatment followed by NaOH is effective to improve mechanical properties

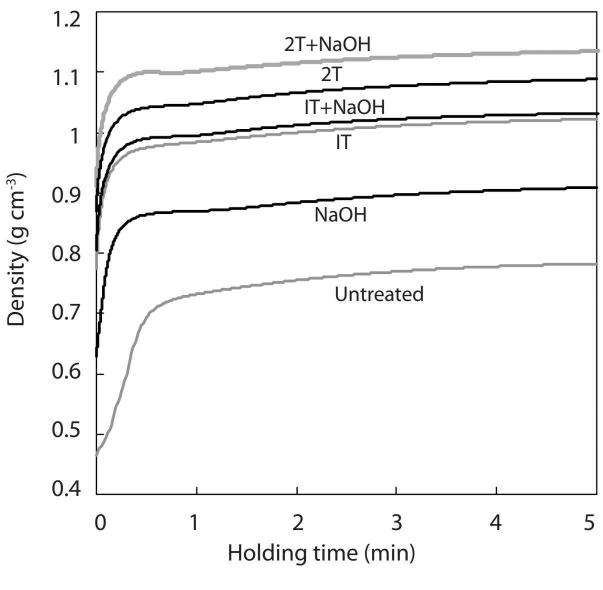

Figure 2 Effects of pressure holding on the densification of PF resin-impregnated compressed wood at different treatment condition. 1T and 2T refer to one time and two times $NaClO_2$ treatment respectively.

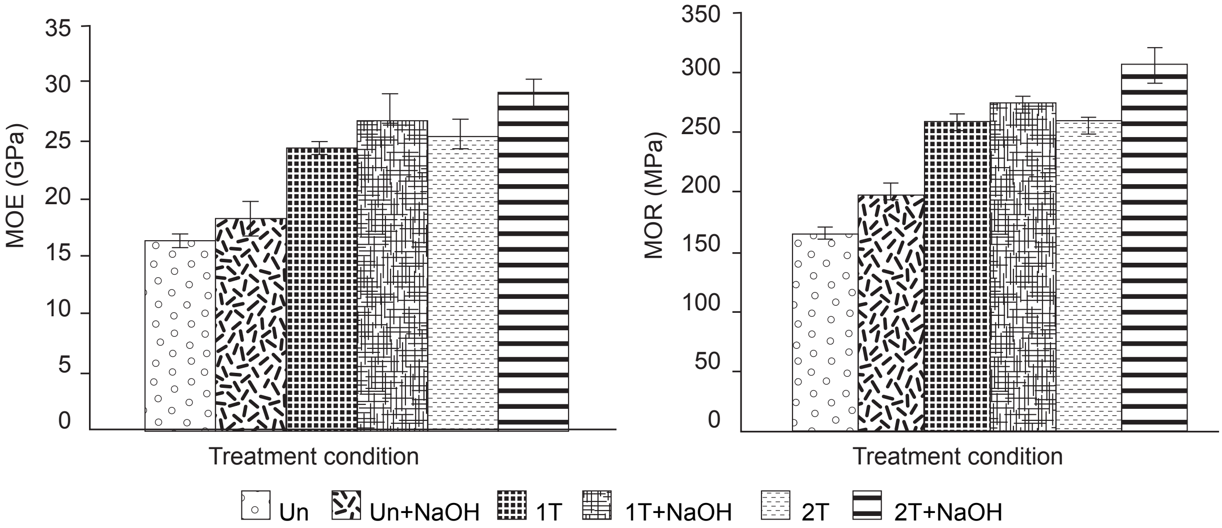

Figure 3 The effect of $NaClO_2$ treatment followed by NaOH treatment on the mechanical properties of PF resin-impregnated compressed wood. 1T and 2T refer to one time and two times $NaClO_2$ treatment respectively. Un = untreated.

of wood at low pressing pressure. At a pressing pressure of 1 MPa, values for MOR and MOE of laminates subjected to two times $NaClO_2$ treatment followed by NaOH were 29 GPa and 307 MPa respectively. The specific MOE and MOR of this treatment was 25% higher than untreated wood. Our results also showed that the specific MOE and MOR of $NaClO_2$ followed by NaOH treatment was about 10 and 5% higher respectively than that of $NaClO_2$ treatment. This may be attributed to the increment of the volume ratio of microfibril (Yano *et al.* 2001). Even after weight loss of 12.4%, the integrity of the cellular structure is still preserved and PF resin plays a role to conserve the compressed microstructure of the material. It can be concluded that two times of $NaClO_2$ treatments followed by NaOH treatment under a mild condition can be viable for the development of high strength wood at lower pressing pressure.

ACKNOWLEDGEMENTS

The authors would like to thank Gun Ei Chemical Industry Co. Ltd. for supplying low molecular weight phenol formaldehyde resin. M. I. Shams is grateful for the financial support by the JSPS Postdoctoral Fellowship for Foreign Researchers from the Japan Society for the Promotion of Science.

REFERENCES

Goring D. 1963. Thermal softening of lignin, hemicellulose and cellulose. *Pulp and Paper Magazine Canada* 64: 512–527.

Furuta Y & Yano H. 1997. Thermal-softening properties of water-swollen wood III. Ethylene glycol-swollen wood. *Mokuzai Gakkaishi* 43: 642–646. (In Japanese)

Olsson AM & Salmen L. 1997. The effect of lignin composition on the viscoelastic and properties of wood. *Nordic Pulp Paper Research Journal* 12: 140–144.

Ryu JY, Takahashi M, Imamura Y & Sato T. 1991. Biological resistance of phenol-resin treated wood. *Mokuzai Gakkaishi* 37: 852–858. (In Japanese)

Salmen L. 1984. Viscoelastic properties of *in situ* lignin under water saturated condition. *Journal of Material Science*: 19: 3090–3096.

Shams MI, Yano H & Endou K. 2004. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin I. Effects of pressing pressure and pressure holding. *Journal of Wood Science* 50: 337–342.

Shams MI & Yano H. 2004. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin II. Effects of processing parameters. *Journal of Wood Science* 50: 343–350.

Shams MI, Yano H & Endou K. 2005.Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin III. Effects of sodium chlorite treatment. *Journal of Wood Science* 51: 234–338.

Shams MI, Kagemori N & Yano H. 2006. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin IV. Species dependency. *Journal of Wood Science* 52: 189–193.

Stamm AJ. 1964. *Wood and Cellulose Science*. Ronald Press Co., New York.

Yano H, Hirose A & Inaba S. 1997. High strength wood based materials. *Journal of Material Science Letters* 16: 1906–1909.

Yano H, Mori AK, Collings PJ & Yazaki Y. 2000. Effects of element size and orientation in the production of high strength resin-impregnated wood based materials. *Holzforchung* 54: 443–447.

Yano H, Hirose A, Collings PJ & Yazaki Y. 2001. Effects of removal of matrix substances as a pretreatment in the production of high strength resin-impregnated wood based materials. *Journal of Material Science Letters* 20: 1125–1126.

Yano H. 2001. Potential strength for resin impregnated compressed wood. *Journal of Material Science Letters* 20: 1127–1129.