Changes in Some Mechanical and Physical Properties and Anatomical Structure of Spruce and Larch Wood after Fire-Retardant Treatment

Chun-Won Kang,[a,b] Ming-Yu Wen,[b,]* Hee-Jun Park,[a] Ho-Yang Kang,[c]
Seog-Goo Kang,[c] and Junji Matsumura [d]

Changes in the physical and mechanical properties and anatomical structures of spruce (*Picea*) and larch (*Larix*) specimens before and after fire-retardant impregnation were studied. Results indicated that the static modulus of elasticity (MOE), dynamic modulus of elasticity (DMOE), and the Brinell hardness of the specimens decreased for both wood species upon post-treatment. This could be accounted for by the degradation of hemicelluloses by the phosphorus-based compound, the minute cracks in the latewood cell wall, and the enlarged width of the cell lumen of the specimen resulting from the vacuum-pressure treatment. However, the decreased ratio of the MOR and DMOE to density contributed to lower sound transmission, which is expected to be important in a housing environment.

Keywords: Fire retardant resin; Mechanical property; Anatomical structure; Spruce; Larch

Contact information: a: Department of Housing Environmental Design, and Research Institute of Human Ecology, College of Human Ecology, Chonbuk National University, Jeonju 561-756, Korea; b: Wood Material Science and Engineering Key Laboratory, Beihua University, Jilin Province, Jilin, China, 132013; c: Department of Bio-based Materials, Chungnam National University, Daejeon 305-764, Korea; d: Division of Sustainable Bioresources Science, Department of Agro-environmental Sciences, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan;
** Corresponding author: jlwenmingyu@163.com*

INTRODUCTION

Wood is a combustible material, and its flammability is one of the weak properties when wood or wood-based boards are used in building construction. Many types of flame retardants have been developed and used for wood materials, and sometimes a fire-retardant resin has been used to improve the fire performance of wood or wood-based materials. Although a wood treatment with such chemicals effectively retards combustion, it also may affect the physical and mechanical properties of wood. Many researchers have recognized that a fire-retardant treatment and post re-drying can reduce the initial strength properties of wood (Kunze *et al*. 2002; Wang *et al*. 2004, 2005; Zhang and Chen 2011). Moreover, it has been reported that a pressure treatment caused a decrease of 8% to 10% in the bending strength of different wood types (Islam *et al*. 2007). Furthermore, some research has investigated how much and exactly why fire retardants affect the properties of treated wood (Islam *et al*. 2009, 2012).

With respect to the utilization of fire-retardant wood materials in housing environments, in addition to the fire-retardant property, the physical and mechanical properties related to the sound absorption and transmission were investigated in this study. These properties included the static modulus of elasticity (MOE), dynamic modulus of elasticity (DMOE), and the Brinell hardness of spruce (*Picea*) and larch (*Larix*) wood after treatment with a newly developed water-soluble phosphorous-based fire retardant (WPFR). In addition, to understand the mechanical changes caused by the fire-retardant treatment, this study observed the anatomical features both before and after the treatment at the same position of the sample specimen by low-vacuum scanning electron micrograph (LV-SEM).

EXPERIMENTAL

Materials

Two wood species, spruce (*Picea*) and larch (*Larix*), were selected for this study and 20 defect-free, straight-grained squares with 20 mm × 20 mm cross-sections and lengths of 320 mm along the grain of the squares were prepared for each species. Prior to treatment, the squares were kiln-dried to 8% moisture content (MC) and then labeled and weighed.

Methods

Fire-retardant resin impregnation

A new water-soluble composite fire-retardant (FR) chemical was used in this study. Its main components are ammonium phosphate polymer (APP), guanyl urea phosphate (GUP), and a minor amount of additives. The resin content and specific gravity of this chemical were 25 wt.% and 1.13, respectively. Twenty specimens per species were randomly placed in a vertical cylindrical vessel under a pressure of -0.098 MPa for 5 min to remove the air contained within the wood prior to impregnation. When the vacuum was released, the fire-retardant chemicals refluxed into the vessel, and the pressure was raised to 10 kgf/cm^2 for 20 min. Then, the pressure was released and the specimens were removed and weighed. After impregnation, the specimens were air-dried for two weeks and then cured at 60 °C for 72 h to a MC of 12%.

Static Modulus of Elasticity (MOE) Test

The specimen size was 320 mm (length) × 20 mm (width) × 10 (thickness) mm, and 20 pieces of the specimens were prepared for each species. The static bending tests were conducted in accordance with the three-point loading method for lumber and center loading method for a specimen, using a Shimadzu autograph universal testing machine (AGS-1000G, Shimatzu Corporation, Kyoto, Japan). All of the specimens were flat loaded (wise loading) for the bending tests. The span was 28 cm, and the crosshead speed was 10 mm/min. The proportional limit, ultimate load, and deflection were obtained from load-deflection curves, and the static modulus of elasticity (MOE) was calculated as follows,

$$MOE = 23Pl^3/108bh^3f \quad (1)$$

where *MOE* is the static modulus of elasticity (MPa), *P* is the difference of initial load and final load (N), *l* is the span (mm), *b* is the width (mm), *h* is the thickness of wood species (mm), and *f* is the deformation of specimen between the initial load and final load (mm).

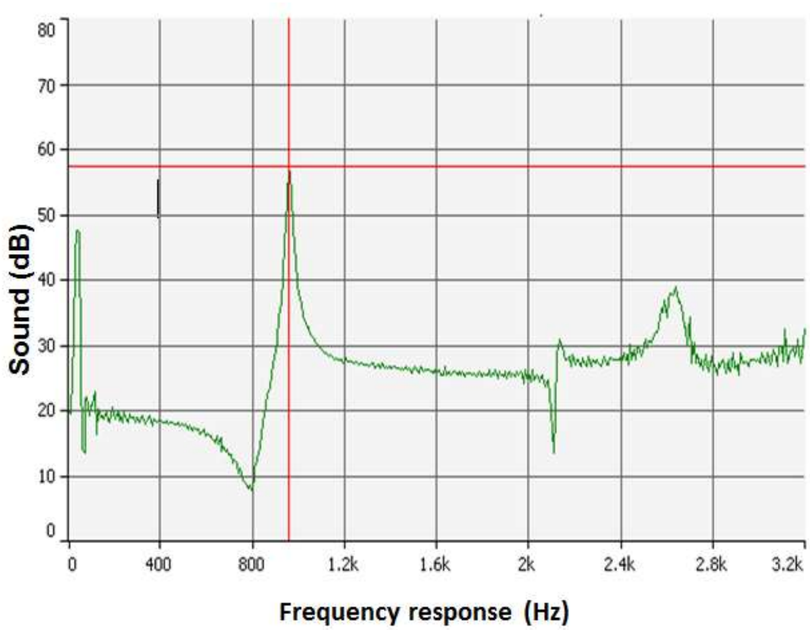
Dynamic Modulus of Elasticity (DMOE) Test

The dynamic modulus of elasticity can be computed from the density, beam shape, and resonant frequencies of wood according to Hearmon's transverse vibration theory. The resonant frequencies of wood specimens were estimated from the transverse vibration of the wooden beam with an impact hammer. The apparatus setup consisted of an accelerometer (B&K, Naerum, Denmark), impact hammer (Type 8203, B&K, Naerum, Denmark), and a FFT (Fast Fourier Transform) analyzer (Type 3065, B & K, Naerum, Denmark). First, the specimen was struck properly with an impulse hammer. The impact causes the specimen to vibrate, and the FFT analyzer transforms the signal from the accelerometer; then, a frequency response curve is acquired.

This test was repeated three times for each specimen, and the obtained data were averaged. From the spectral analysis, the resonant frequency of each small wooden board was estimated. From the estimated resonant frequencies, the dynamic moduli of elasticity (DMOE) were calculated using Eq. 1. Here, the influence of the shear stress caused by the different ratios of sample thickness to length was not considered because this study only focused on the influence of the fire-retardant resin treatment.

$$\mathrm{DMOE} = 48\pi^2 \rho l^4 f^2 / m^4 h^2 \quad (2)$$

In Eq. 2, *DMOE* is the dynamic modulus of elasticity, *p* is the density of the specimens, *f* is the resonant frequency, *h* is the thickness (cm), and *m* is a constant (4.73 for the fundamental mode of vibration).



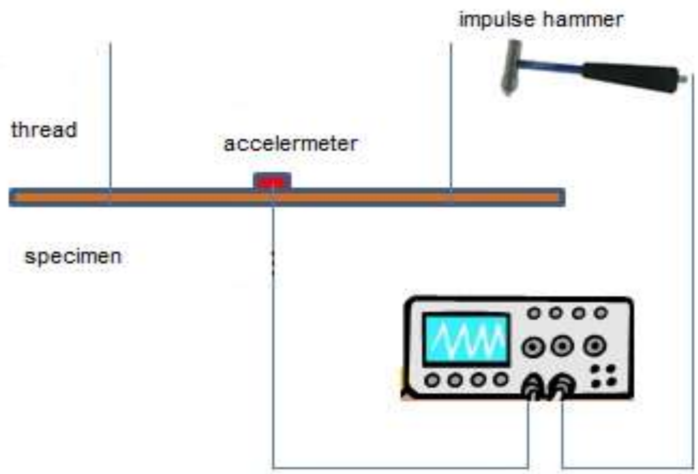


Fig. 1. Schematic diagram for dynamic MOE measuring apparatus and typical frequency response function curve for a wooden beam

Brinell Hardness

A Brinell hardness tester forced a steel ball at 500 N/mm^2 to the longitudinal-radial surface of the control and fire-retardant resin-treated wood specimens. The specimen size was 320 mm (length) × 20 mm (width) × 10 (thickness) mm, and 20 pieces of the specimens were prepared for each species. The indentation load, indentation depth, and indentation surface area were evaluated, and the Brinell hardness was determined using Eq. 2. Three points at each end of the specimens were tested. Tests were replicated with ten specimens.

$$\text{Brinell hardness} = 2P/(\pi D)(D-((D2-d2)1/2)) \qquad (3)$$

In Eq. 3, P is the load (kgf), D is the diameter of the steel ball (mm), and d is the diameter of the indentation (mm).

Low-Vacuum Scanning Electron Microscope (LV-SEM) Observation

The dimensions of the specimens for the SEM observation were 11 mm × 11 mm × 10 mm (tangential × radial × longitudinal). The SEM observations were performed on the cross sectional surfaces of the specimens both before and after the impregnation by using a low vacuum scanning electron micrograph (JSM-5600 LV, JEOL, Kyoto, Japan). The LV-SEM can observe a water-containing specimen without any additional treatment, such as ion spurting. This ability permits the same position on the specimen to be observed both before and after the treatment. Image J Software (1.44p, Bethesda, USA) measured the area and thickness of the cell lumen, tangential direction diameter of the cell wall, and the tangential diameter of the tracheid.

RESULTS AND DISCUSSIONS

Analysis of Physical and Mechanical Properties

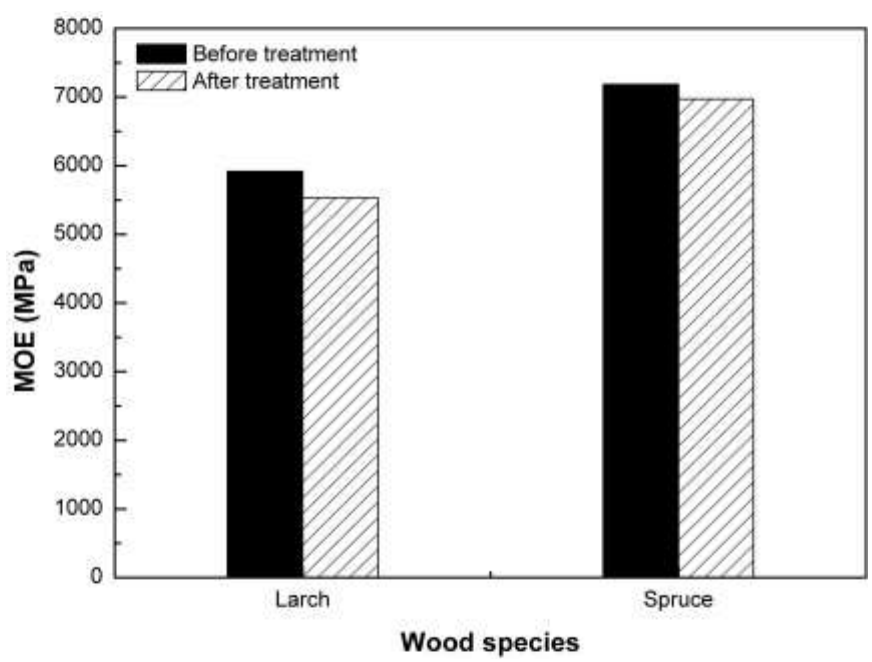
The static MOEs of spruce and larch specimens before and after the impregnation are displayed in Table 1, and the changes in the static MOEs, DMOE, and hardness are shown in Figs. 2 and 3.

Table 1. Physical and Mechanical Data of Wood Species Before and After Fire-Retardant Resin Treatment

Species	Treatment	Density (g/cm^3)	Static MOE (MPa)	Resonant Frequency	Dynamic MOE (MPa)	MOE/ Density	DMOE/ Density	*Brinell Hardness (kgf)
Spruce (*Picea*)	Before	0.43 (0.04)	7182 (1365)	613 (33)	12889 (2115)	16702	29974	50.1 (11)
	After	0.51 (0.08)	6970 (1096)	574 (31)	12880 (1916)	13667	25255	39.5 (15)
Larch (*Larix*)	Before	0.45 (0.05)	5918 (1519)	549 (27)	10645 (1869)	13151	23656	54.5 (18)
	After	0.49 (0.04)	5529 (1174)	520 (31)	10541 (1697)	11284	21512	43.7 (22)

Note: Numbers in parentheses are standard deviations

The static MOE, one of the primary indexes in evaluating the mechanical properties of wood, indicates the wood's degree of resisting distortion. A higher value of static MOE indicates that the material is not easily distorted and has a high rigidity. The static MOEs of the specimens were 7182 and 6970 MPa for spruce, which decreased by 2.95%, and 5918 and 5529 MPa for larch, which decreased by 6.57%, respectively, before and after the treatment in this study. This indicates that the static MOEs decreased, irrespective of the species. This observation was consistent with previous literature (Kunze *et al*. 2002; Wang *et al*. 2004; Wang *et al*. 2005; Zhang and Chen 2011) and can be attributed to the fire-retardant chemical treatment.



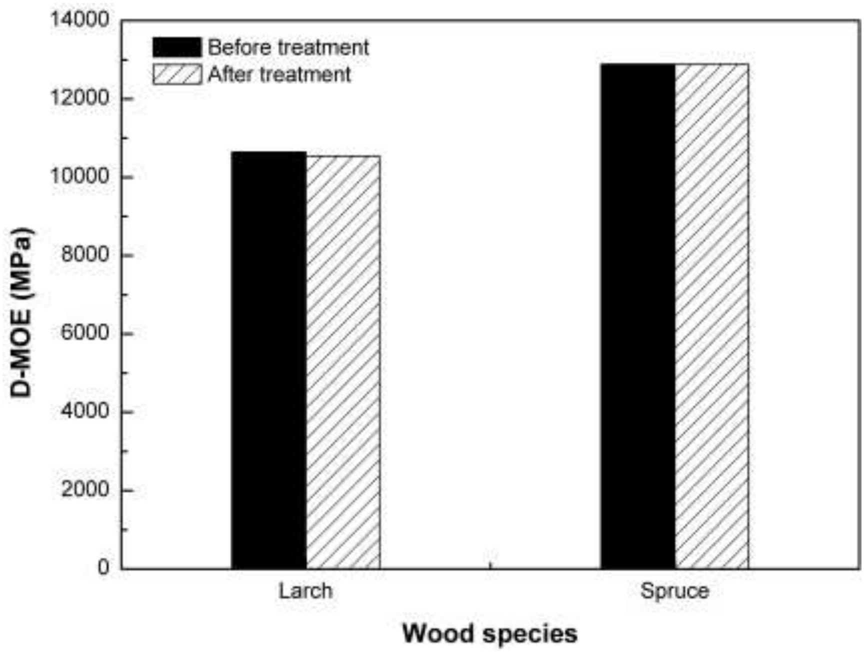


Fig. 2. Comparison of static MOEs and dynamic MOEs before and after fire-retardant treatment

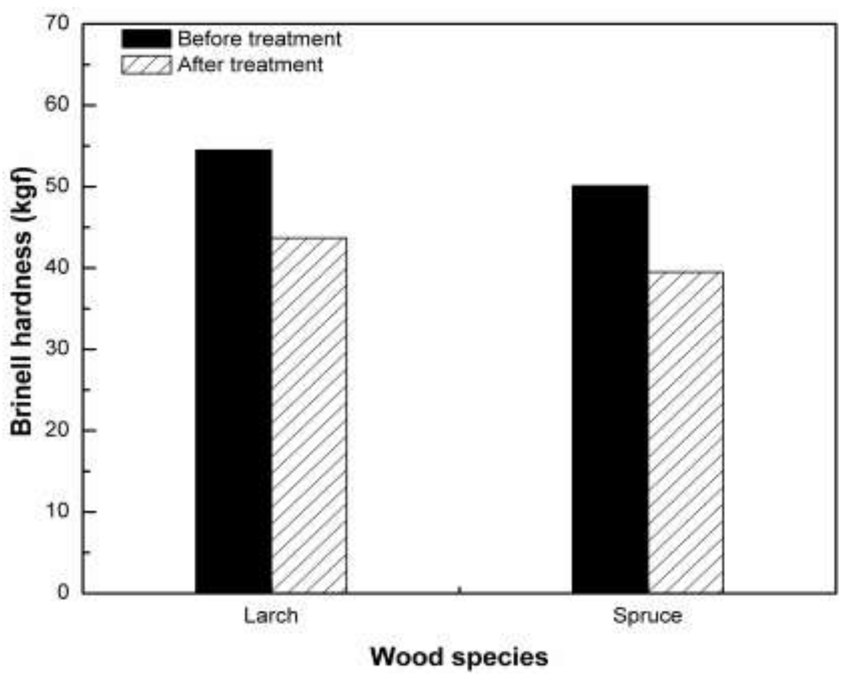


Fig. 3. Comparison of Brinell hardness before and after fire-retardant treatment

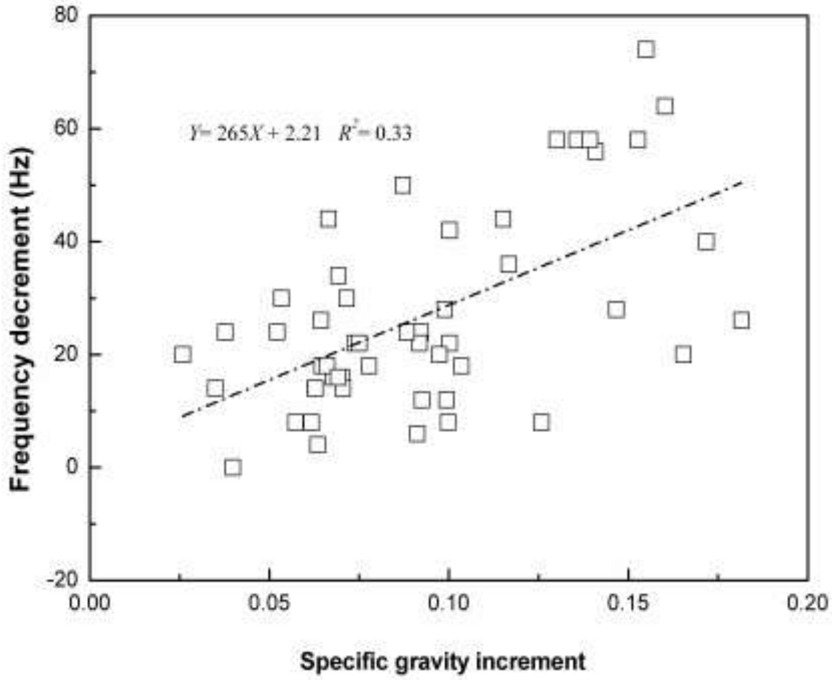


Fig. 4. Correlations between specific gravity increment and frequency decrement

Meanwhile, the DMOE was decreased by the treatment slightly (0.06% and 0.97%), and the hardness was decreased (21.2% and 19.8%) for spruce and larch, respectively. Looking at the trend between the static and dynamic MOE, the trend of the DMOE was relatively smaller than that of the static MOE. This was because the value of the dynamic DMOE was influenced more by the surface part than the inner part of the vibrating body. The hardness decrease caused by the fire-retardant resin treatment caused the dynamic MOE to decrease. In addition, the correlations between the frequency decrement and density increment of treated and control specimens are shown Fig. 4. It shows that the interrelations between the frequency decrement and density increment of the wood specimen can be represented by a positive linear regression. Therefore, after treatment the increase of density response to the decrease of frequency, and finally cause the reduction of dynamic MOE according to Eq. 2.

Furthermore, in this study it was found that the ratio of both dMOE/density and sMOE/density decreased after fire retardant treatment. Norimoto (1982) clarified that materials with higher values of dMOE/density or sMOE/density are expected to lead to good sounding boards for pianos. Therefore, on the contrary, it is considered that a low DMOE/r and MOE/r value of fire-retardant resin-treated wood contributes to lower sound transmission when it is used as flooring board, which is expected in housing environments.

Phosphorus-based compounds are some of the best-known fire retardant treatments for wood. However, a significant problem with these compounds is the reduction in strength of the treated wood products. Moreover, as previously reported by Winandy and Morrell (1998), those compounds have more noticeable negative effects on the viscoelastic properties than on the elastic properties of treated wood, the same as more acidic fire retardants. They noted that the physical and mechanical properties of wood are a complex function of cellular and polymeric structure and chemistry. They observed that changes in the chemical composition of wood directly correspond to a loss of strength. Moreover, Wang *et al.* (2005) reported that a decrease in bending strength can be attributed to the fire-retardant treatment resulting in a chemical component change in treated wood, especially in the hemicellulose content after drying.

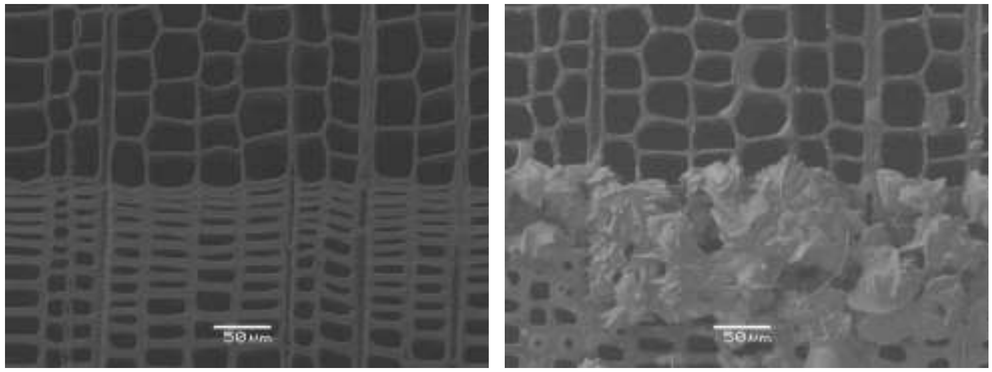
After treatment, the percentage of hemicelluloses decreased compared with the untreated specimens. Conversely, the lignin residue increased for phosphoric acid-treated specimens that were kiln-dried after treatment. The drying of phosphoric acid-treated specimens caused some changes in the wood components. The strength loss in wood might be closely related to the degradation of the branched units of hemicelluloses. Advanced strength loss that occurred later was related to further degradation of the residual hemicelluloses' main chain and the initial degradation of cellulose and lignin when wood underwent drying post-impregnation. In this study, the static MOE, dynamic MOE and hardness were decreased after impregnation treatment with the WPFR, which was consistent with the previous research.

Analysis of Low Vacuum Scanning Electron Micrograph (LV-SEM) Observations

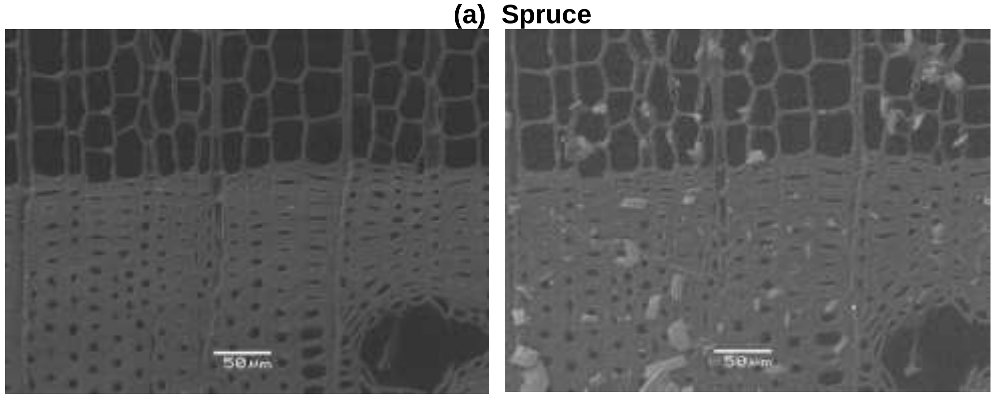
The LV-SEM observations of the specimens before and after treatment are shown in Fig. 5. Early-wood cells with thin cell walls and large lumen were mostly cut open. The lumens pointed towards the surface and can be partly filled up with the WPFR chemical. The late-wood cells with thick cell walls have a narrow cell lumen, thus the WPFR chemical deposited on the later-wood surface.

Meanwhile, it was observed by the LV-SEM that some minute cracks originated from the latewood cell wall. This may account for the external force from the vacuum-pressure treatment.

The minute cracks can directly reduce the mechanical properties of the specimen; moreover, the fact that some minute cracks originated from the latewood cell wall because of the external force suggests that some slip plane occurred in the latewood cell wall (Hoffmeyer 1993). This effect can explain why a phosphorus-based compound had more noticeable negative effects on the viscoelastic properties than on the elastic properties of treated wood (Winandy and Morrell 1998).



(a) Spruce



(b) Larch

Fig. 5. Changes of anatomical structures of the specimens before and after the impregnation

By measuring the thickness of the cell wall, as well as the area and width of the cell lumen, of the earlywood section using Image J software, it was found that the width of the cell lumen was enlarged. This also can be accounted for by the vacuum-pressure treatment. The enlarged width of the cell lumen could result in additional tensile stresses on its cell walls, which can further reduce the MOEs. Therefore, it could be concluded that the minute cracks of the latewood cell wall, as well as the enlarged width of the cell lumen during the vacuum-pressure treatment, are also causes for the decreasing MOEs.

CONCLUSIONS

1. This study showed that after the impregnation with water-soluble phosphorous-based fire retardant (WPFR), the static modulus of elasticity (MOE) decreased the most, followed by hardness and the dynamic modulus of elasticity (DMOE) for both the spruce and larch wood species. This is because the phosphorus-based compounds can reduce strength, which is caused by changes in the chemical composition of wood during the drying process after the impregnation treatment.
2. The frequency decrement and density increment of wood specimens had a positive linear regression. The lower ratio of MOE and DMOE to density of treated wood contributed to low sound transmission and better sound absorption. This will favor the application of the fire retardant wood if they were to be used in housing environments.

3. In the observation of the cell lumen, it was found that early-wood cells with thin cell walls partly filled up with the WPFR chemical, while the WPFR chemical deposited on the later-wood surfaces which have thick cell walls and narrow cell lumen. Some minute cracks that originated from the latewood cell wall might cause the decrement of the physical and mechanical properties.

ACKNOWLEDGMENTS

The authors are grateful for the support of the "Research Base Construction Fund Support Program" funded by Chonbuk National University in 2016. Also, thanks are expressed for the support of "Wood Material Science and Engineering Key Laboratory of Jilin Province Open Fund Project".

REFERENCES CITED

Hoffmeyer, P. (1993). "Non-linear creep caused by slip plane formation" *Wood Science and Technology* 27(5), 326-327.

Islam, M. N., Ando, K., Yamauchi, H., Kobayashi, Y., and Hattori, N. (2007). "Passive impregnation of liquid in impermeable lumber incised by laser," *Journal of Wood Science* 53(5), 436-441. DOI: 10.1007/s10086-006-0878-0

Islam, M. N., Ando, K., Yamauchi, H., and Hattori, N. (2009). "Effects of species and moisture content on penetration of liquid in laser incised lumber by the passive impregnation method," *European Journal of Wood and Wood Products* 67(2), 129-133. DOI: 10.1007/s00107-008-0292-y

Islam, M. N., Ando, K., Yamauchi, H., Kamikawa, D., Harada, T., and Hattori, N. (2012). "Impregnation of preservative and fire retardants into Japanese cedar lumber by passive impregnation," *BioResources* 8(1), 395-404. DOI: 10.15376/biores.8.1.395-404

Kunze, R., Schartel, B., Bartholmai, M., Neubert, D., and Schriever, R. (2002). "TG-MS and TG-FTIR applied for an unambiguous thermal analysis of intumescent spreading," *Journal of Thermal Analysis and Calorimetry* 70(3), 897-909.

Norimoto, M. (1987). "Specific Young's modulus and quality of coniferous wood," *Mokuzai Gakkaishi* 33(7), 545-551.

Wang, Q., Li, J., and Winandy, J. (2004). "Chemical mechanism of fire retardance of boric acid on wood," *Wood Science and Technology* 38(5), 375-389. DOI: 10.1007/s00226-004-0246-4

Wang, Q., Wang, W., and Winandy, J. E. (2005). "Effect of new GUP-B fire retardant on mechanical properties of Korean pine when exposed to elevated temperature," *Forest Products Journal* 55(12), 214-220.

Winandy, J. E., and Morrell, J. J. (1998). "Effects of incising on lumber strength and stiffness: Relationships between incision density and depth, species, and MSR grade," *Wood and Fiber Science* 30(2), 185-197.

Zhang, Q., and Chen, Y. (2011). "Synergistic effects of ammonium polyphosphate/ melamine intumescent system with macromolecular charformer in flame-retarding polyoxymethylene," *Journal of Polymer Research* 18, 293-303.

Article submitted: October 23, 2016; Peer review completed: December 4, 2016; Revised version received and accepted: December 31, 2016; Published: January 9, 2017.
DOI: 10.15376/biores.12.1.1358-1368