Decay Resistance of Polymerized Ionic Liquid-modified Woods

Hiroki Sakagami,[a,*] Saki Higurashi,[b] Tetsuya Tsuda,[c] Satoshi Seino,[c] Susumu Kuwabata [c]

A functional ionic liquid 1-butyl-3-vinylimidazolium iodide ([BuVyIm]I) was synthesized, and it exhibited the features of both decay resistance and leaching resistance after *in-situ* polymerization within wood. Treated wood specimens of *Cryptomeria japonica* were evaluated in this preliminary study using leaching tests with distilled water and decay tests for 12 weeks with brown rot fungi *Fomitopsis palustris*. The [BuVyIm]I polymerized by 100 kGy ^{60}Co gamma irradiation was retained in wood after 10 wash and dry cycles, whereas nearly all of the [BuVyIm]I was washed out in the cases of 10 kGy and no irradiation. The decay testing of these specimens showed that sapwood had a different decay resistance depending on the strength of gamma irradiation used, whereas the treated heartwood did not support fungal growth. The results of this study imply that [BuVyIm]I polymerized by 100 kGy gamma irradiation have potential for wood preservation.

Keywords: Wood; Ionic liquid; Preservative; Decay; Polymerization; Fungal growth

*Contact information: a: Division of Sustainable Bioresources Science, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka, 812-8581, Japan; b: Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka, 812-8581, Japan; c: Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan; *Corresponding author: h-sakagami@agr.kyushu-u.ac.jp*

INTRODUCTION

Ionic liquids (ILs) are organic liquid salts at room temperature. Research interest in these materials has increased in recent years because of their attractive characteristics, including negligible vapor pressure, high flame resistance, relatively high conductivity, and high chemical stability. These are also considered to be green chemicals because they can be efficiently recycled due to their non-evaporating characteristics. Many kinds of ILs have been synthesized and used in many fields since the first report of air and water stable 1-ethyl-3-methylimidazolium-based ILs by Wilkes and Zaworotko (1992). Several studies have applied ILs to wood samples, as reviewed by Han *et al.* (2009). Many of these studies have focused on the dissolution of lignocellulose, as these ILs are known to dissolve cellulose (Swatloski *et al*. 2002) and lignin (Pu *et al.* 2007), which are the main chemical components of wood. While many of these reports regarding dissolution of cellulose were conducted using purchased or isolated cellulose, more recent studies have moved towards examining naturally-occurring wood materials. Fort *et al*. (2007) confirmed the dissolution of finely divided wood shaving specimens of pine, poplar, eucalyptus, and oak. Kilpelainen *et al.* (2007) examined the variable solubility of thermomechanical pulp from wood, ball-milled wood powder, sawdust, and wood chips.

An IL treatment of veneer wood can change its surface characteristics (Croitoru *et al.* 2011), enhance its ultraviolet (UV) stability (Patachia *et al.* 2012), and act as a wood

preservative against fungal growth (Pernak *et al.* 2004, 2005, 2006, 2009; Stasiewicz *et al.* 2008).

Many wood preservatives have been developed to prevent wood materials from being decayed by fungi. The most popular methods to cut off the moisture necessary for fungal growth are finishing with oil, wax, and stain. These methods have the advantages of cost effectiveness and easy treatability; however, their performance cannot be maintained for long in comparison with the treatment of chemical preservatives (Wood Handbook 2010). Chemical preservatives have been developed to prolong the service life. One of the most popular wood preservative was chromated copper arsenate (CCA), but its use has been withdrawn in most countries because of its toxicity and leachates (Hingston *et al.* 2001). Arsenic-free wood preservatives, such as alkaline copper quaternary (ACQ) and copper azole (CUAZ), are widely used as replacements for CCA. It is indispensable for modern wood preservatives to have a low impact on human and environmental health, and ILs featuring green and sustainable chemistry are expected to be used as a new class of wood preservatives.

In cases where ILs characterized as environmentally friendly and recyclable are used as wood preservatives, it is important to prevent the wood preservative from seeping out of wood and into the environment over a long period of use. However, water-soluble ILs are easily removed unless they form the complexes with wood components, such as copper amine solutions (Ruddick *et al.* 2001; Xiao and Ruddick 2004) contained in ACQ and CUAZ. Polymer treatment of phenol formaldehyde (PF) resin, first introduced by Stamm and Seborg (1936), is considered as an efficient method for use on wood preservatives (Ryu *et al.* 1991, 1993) to retain these ILs in wood and for retaining dimensional stability (Deka and Saikia 2000) due to polymerization after the monomer PF is impregnated into the cell wall (Furuno *et al.* 2004).

The primary focus of this work was to confine ILs within wood. The effect of the polymers to shield cell walls from chemicals, and the synthetization of the polymerizable IL 1-butyl-3-vinylimidazolium iodide ([BuVyIm]I) were considered. This IL can be synthesized at a low cost and through simple means compared to other ILs. Using this IL, the leaching and decay resistance of polymerized wood specimens of *Cryptomeria japonica* with gamma rays were preliminarily evaluated after monomeric [BuVyIm]I was absorbed.

EXPERIMENTAL

Materials

Synthesis of monomeric IL

[BuVyIm]I was synthesized using purified 1-vinylimidazole and 1-iodobutane, which were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). These were reacted at a molar ratio of 1:1.02 (1-vinylimidazole:1-iodobutane) at approximately 80 °C. Synthesized [BuVyIm]I was purified by precipitation from dry acetonitrile with dry ethyl acetate by referring to the previous paper (Wilkes *et al.* 1982), and eventually vacuum-dried at 70 °C. The density of [BuVyIm]I is 1.49 g/cm^3 at 25 °C.

Wood specimens

Fourteen small samples (10 mm × 5 mm × 20 mm) were prepared from air-dried sapwood and heartwood of *Cryptomeria japonica* D. Don.

Methods

Treatment using IL

Synthesized monomeric [BuVyIm]I was absorbed into specimens through two different methods to accelerate absorption. In one method, [BuVyIm]I was absorbed under different pressure conditions. That is, the pressure was returned to ambient after the specimens were immersed in [BuVyIm]I under vacuum conditions ($<1.3 \times 10^3$ Pa) at room temperature for 24 h. In the other method, the specimens pre-saturated in ethanol for 12 h were immersed in [BuVyIm]I for 24 h. The amount of impregnation (kg/m^3) was calculated from the weights of specimens before and after absorption, divided by the volume. Afterwards, the specimens impregnated with [BuVyIm]I were irradiated with ^{60}Co gamma rays at 10 kGy, 40 kGy, and 100 kGy in an effort to polymerize the [BuVyIm]I within the specimens. This procedure was performed at the ^{60}Co Irradiation Facility, Institute of Scientific and Industrial Research, Osaka University. A summary of the specimens and their treatments is presented in Table 1. The impregnation of [BuVyIm]I in wood is also shown. Specimens No. 7 and No. 14 were not treated by IL. Half-sized, cut specimens (7.5 mm × 4.5 mm × 10 mm) were used for the leaching and decay tests.

Table 1. Specimen Test Parameters

Sample No.	Wood Type	Absorption Method	Impregnation (kg/m^3)	Amount of Gamma Irradiation (kGy)
1	Sapwood	Vacuum	752.5	100
2			815.4	10
3		Ethanol	1015	100
4			1018	40
5			1036	10
6			954.9	0
7		-	-	-
8	Heartwood	Vacuum	876.1	100
9			640.4	10
10		Ethanol	959.6	100
11			974.7	40
12			1037	10
13			923.7	0
14		-	-	-

Leaching tests

Leaching tests were conducted in accordance with JIS K 1571 (2010). The IL-treated specimens were washed under magnetic stirring in a glass filled with distilled water with a specimen to water volume ratio of 1 to 10 for 8 h and kiln-dried at 60 °C for 16 h. This procedure was repeated ten times. The specimens were weighed before the leaching test and after every wash and dry cycle.

Decay testing

Fomitopsis palustris (FFPRI 0507), a brown rot fungus, was used for the fungal decay tests. Decay tests were conducted in accordance with JIS K 1571 (2010). Sterilized specimens from the leaching tests were placed in culture bottles for 12 weeks to allow for *Fomitopsis palustris* growth. Decay tolerance was evaluated by mass loss (%) from the ratio of specimen weights before and after decay testing after the surface hyphae were removed. Transverse and radial surfaces inside the wood specimens after decay tests were

observed *via* scanning electron microscopy (SEM, JSM 5600LV; JEOL Ltd., Akishima, Japan).

Supplementary Tests

To confirm the results, supplementary tests were conducted at 100 kGy gamma ray irradiation. Samples of size 20 mm × 20 mm × 10 mm treated with [BuVyIm]I were prepared from two sapwoods and a heartwood of *Cryptomeria japonica* D. Don. The weight ratios of the treated samples after 10 leaching tests based on the initial weights, and the mass losses after the decay tests were evaluated. Leaching and decay tests were conducted using the same procedure followed for primary tests.

RESULTS AND DISCUSSION

Leaching Tests

A key factor for outdoor wood use is that the wood preservative must be stable for a long time and maintain its high decay resistance performance even in moist conditions. Some polymerized IL is expected to remain after leaching tests if sufficient polymerization had been achieved as a result of gamma ray irradiation. Figure 1 shows the specimen weight ratios after each wash and dry cycle based on the weight before the leaching tests. The graphs of sapwood and heartwood show decreasing ratios of specimen weights for [BuVyIm]I after every wash and dry cycle. Samples 5 and 6 for sapwood, and samples 12 and 13 for heartwood released the most [BuVyIm]I. It was difficult to determine the wood specimen weight before treatment, because the specimen weight without polymerized IL before treatment could not be measured due to half cutting the sample after impregnation. However, the weight ratios in samples 5 and 12 (the lowest values) without IL after 10 wash and dry cycles were estimated as 0.236 and 0.198, as calculated from the specimen density under air-dry conditions. This indicated that almost all of the [BuVyIm]I in samples 5 and 12 was washed away. In contrast, the ratios in samples 1 and 3 for sapwood, and samples 8 and 10 for heartwood were higher (approximately 0.7). Based on these results, a higher applied gamma radiation resulted in less weight decrease, which indicated that polymerized IL was retained in these wood specimens.

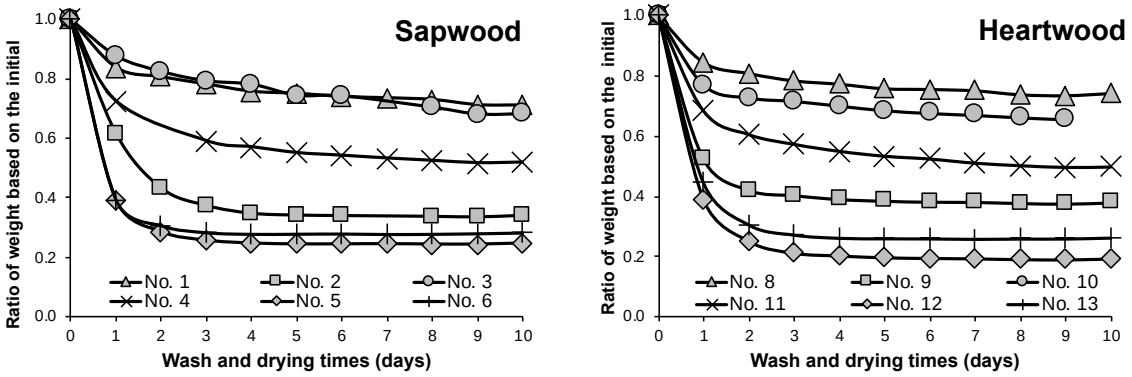

Fig. 1. Decrease in specimen weight after ten wash and dry cycles; each weight is given as the ratio of weights before and after leaching tests.

Decay Testing

Specimens after the leaching tests were placed in culture bottles for 12 weeks to allow for brown rot fungi growth. Figure 2 shows the specimens after 11 weeks in culture bottles and without fungi after 12 weeks decay testing, and their mass losses after decay testing are shown in Fig. 3. Samples 7 and 14 that were not treated with [BuVyIm]I featured extensive fungal growth. The specimens without fungi retained their shapes, but they featured a darker color. The sapwood in sample 7 was more brittle than the heartwood in sample 14, and its mass loss was higher.

Sapwood samples treated with [BuVyIm]I exhibited different decay resistances depending on the strength of gamma irradiation used, while the heartwood samples, which are naturally durable, were more resistant to fungal growth. Samples 1 and 3 (with 100 kGy gamma irradiation) and sample 4 (40 kGy) did not show the presence of fungi, compared to the extensive fungal growth in samples 2 and 5 (10 kGy). This tendency was strongly related to the IL residue in the specimens, as shown in Fig. 1. The mass losses of specimens with no fungi were low, except in the case of sample 3, where it was considered that the weight loss in this specimen was due to IL leaching during 12 weeks decay testing, as sample 3 showed slight emissions of [BuVyIm]I. Further research on polymerization of [BuVyIm]I will be required to explain this phenomenon.

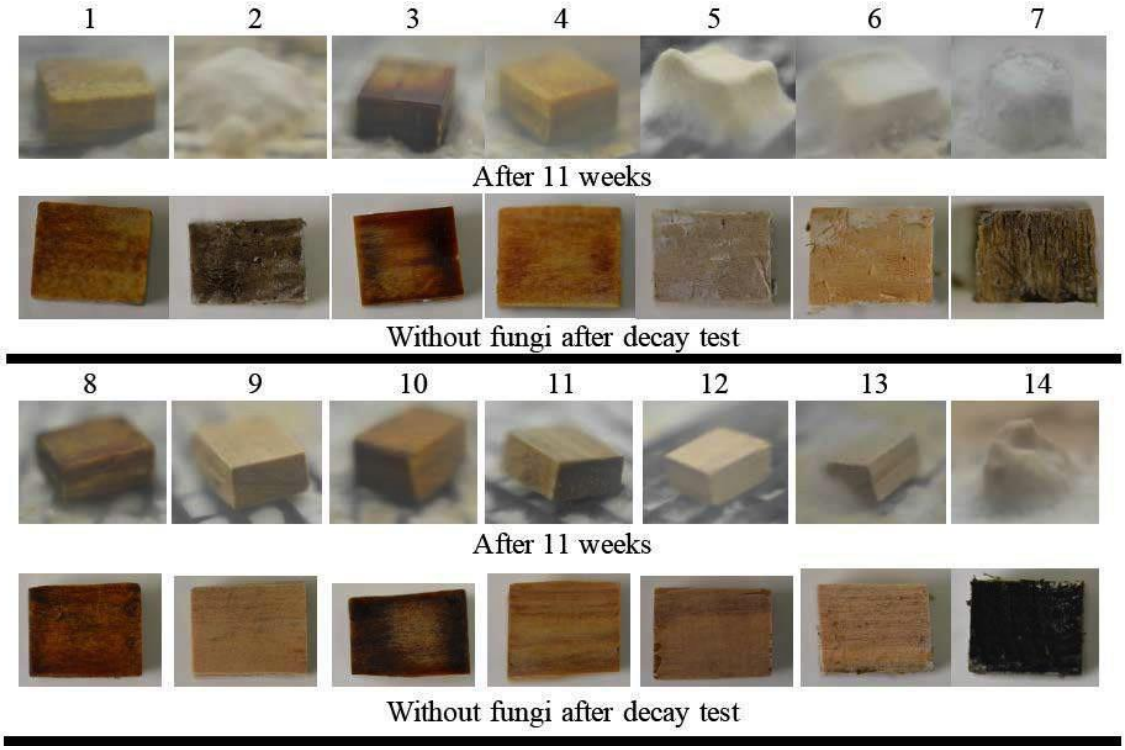

Fig. 2. Images of specimens in culture bottles after 11 weeks incubation, and specimens without fungi after 12 weeks decay testing

To determine why the treated specimens did not decay, the authors observed the inner parts of the specimens through SEM. Figure 4 shows the inner transverse and radial surfaces of samples 3, 5, and 6. Some lumens of tracheids embedded with substances, which look like polymerized [BuVyIm]I, were observed in sample 3, as shown in Fig. 4a. These substances appeared to cover the cell walls, and it is believed that they prevented

fungi from moving into the cell walls. In contrast, widespread fungal growth occurred inside sample 6, and some areas were partially decayed (Fig. 4c) with microcracks causing mass loss (Fig. 4d).

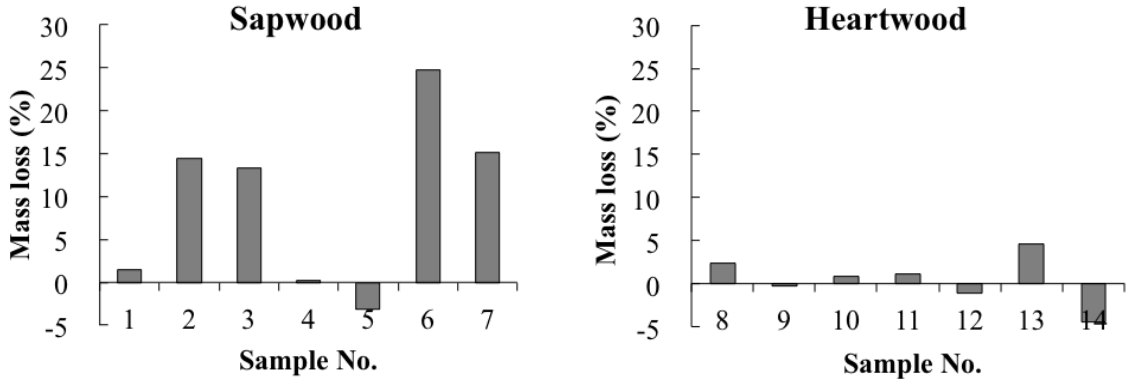

Fig. 3. Mass loss of specimens after twelve weeks decay testing with brown rot fungi *Fomitopsis palustris*

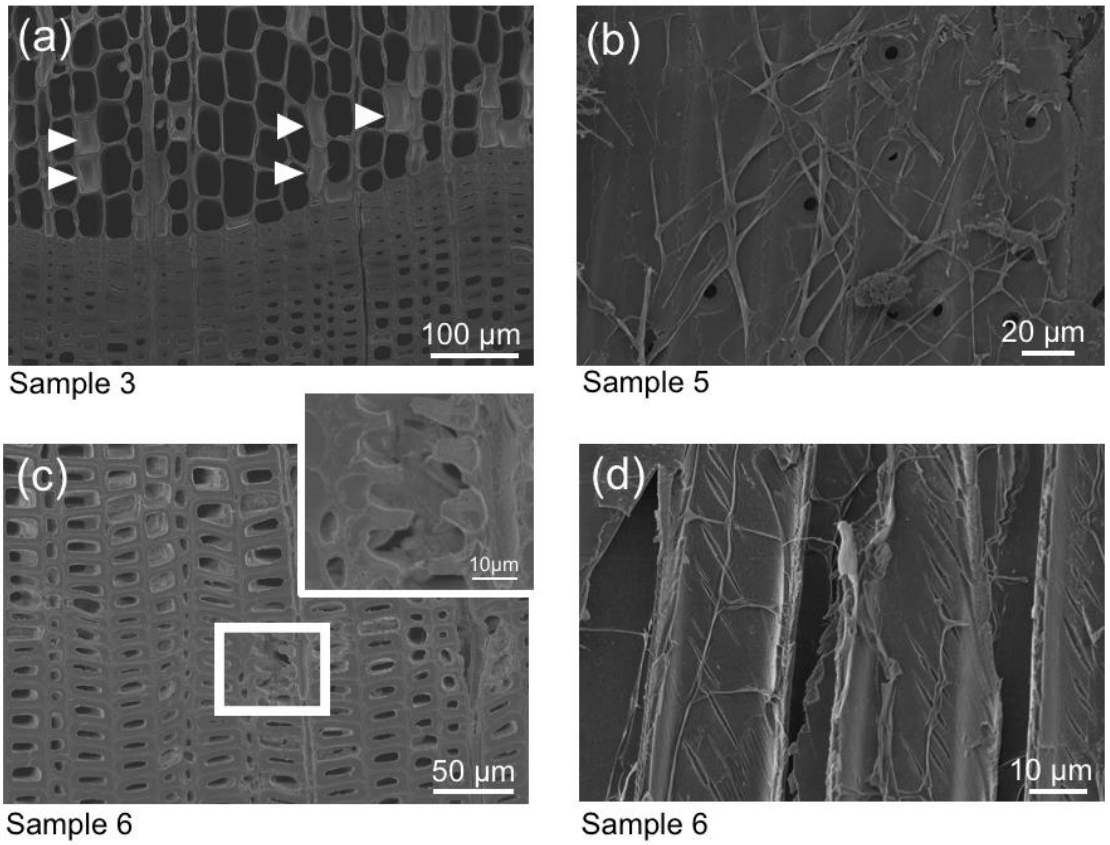

Fig. 4. SEM images of inner wood surfaces, transverse surface inside sample 3 (a), radial surface inside sample 5 (b), transverse surface inside sample 6 (c), and radial surface inside sample 6 (d); the arrowheads show the substances that appear like [BuVyIm]I.

Based on these results, [BuVyIm]I polymerized by 100 kGy gamma irradiation was retained inside wood after 10 wash and dry cycles, and the [BuVyIm]I treatment was

effective for wood preservation. However, one contradiction lies in the mass loss values derived for samples 2 and 5, both of which were irradiated at 10 kGy and were similarly covered with fungi. Based on SEM observations, the morphology of decayed cell walls with microfibrils (Schwarze 2007) was observed in sample 6 (Fig. 4d) but not in sample 5 (Fig. 4b). Slightly more residual IL in sample 5 (ethanol-treated) may enhance the penetration or polymerization of IL to protect from fungi.

Supplementary Tests

The results of primary leaching and decay testing showed that 100 kGy gamma irradiation was the most effective treatment. However, this is not a reliable conclusion because the number of specimens was only one, and the size of the specimen was small. Supplementary examinations were conducted to support the results. The results showed that the ratios of sample weights after 10 leaching tests based on the initial were 0.91 and 0.93 for two sapwood samples, and 0.91 for the heartwood sample. The larger specimens were assumed to resist leaching, so that more [BuVyIm]I was left in the specimens when compared with the primary tests. The results of decay testing were that all samples were not decayed, and the lumens of the tracheid were embedded with substances that looked like polymerized [BuVyIm]I under SEM observation. However, the mass losses were 5.6% and 12.3% for sapwood and 0.1% for heartwood. As with the case of sample 3 in the primary test, higher mass loss was observed in sapwood. It was considered that substances insoluble in water, which could not be removed during the leaching test, would have been released from the sapwood during the decay test for three months. On the other hand, low mass loss was seen in heartwood because the substances would be encapsulated due to low liquid penetration. Unidentified substances that arose after polymerization should be analyzed without the wood samples. This study examined the efficiency of 1-butyl-3-vinylimidazolium iodide, a poly IL, for wood preservation based on leaching and decay tests. However, further research is required with larger-scale specimens and a higher sample count to support the results. Additionally, this study does not discuss treatability because this monomeric IL is too adhesive to penetrate into wood specimens at room temperature. Moreover, cost improvements of this treatment must also be addressed.

CONCLUSIONS

A polymerizable IL 1-butyl-3-vinylimidazolium iodide, which exhibits both decay resistance and leaching resistance after polymerization, was synthesized. Treated wood specimens of *Cryptomeria japonica* were preliminarily evaluated.

1. The leaching tests indicated that the decrease in the specimen weight after 10 wash and dry cycles was minimal when 100 kGy gamma irradiation was applied to the samples. The ratios were approximately 0.7. In contrast, nearly all of the [BuVyIm]I was washed from the specimens irradiated with ≤ 10 kGy.
2. Decay testing of these specimens after leaching tests showed that sapwood had variable decay resistance depending on the strength of gamma irradiation. The specimens with 100 kGy and 40 kGy gamma irradiation were not covered with fungi, and their mass losses were slight except for one sample, whereas the specimens irradiated with 10 kGy or no gamma ray were covered with fungi. The treated heartwood samples did not support fungal growth.

3. The SEM observations revealed that some lumens of the tracheid in the specimens exhibiting leaching resistance and decay resistance were embedded with substances considered to be the polymerized [BuVyIm]I with gamma irradiation.
4. Supplementary tests irradiated with 100 kGy gamma rays supported the findings of the preliminary test.

ACKNOWLEDGMENTS

This work was supported in part by JSPS KAKENHI (Grant Nos. JP16K14539 and JP15H03591). The authors gratefully acknowledge Dr. Hayato Masuya of Forestry and Forest Products Research Institute for helping with the decay test.

REFERENCES CITED

Croitoru, C., Patachia, S., Cretu, N., Boer, A., and Friedrich, C. (2011). "Influence of ionic liquids on the surface properties of poplar veneers," *Appl. Surf. Sci.* 257(14), 6220-6225. DOI: 10.1016/j.apsusc.2011.02.041

Deka, M., and Saikia, C. N. (2000). "Chemical modification of wood with thermosetting resin: Effect on dimensional stability and strength property," *Bioresource Technol.* 73(2), 179-181. DOI: 10.1016/S0960-8524(99)00167-4

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., Moyna, G., and Rogers, R. D. (2007). "Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride," *Green Chem.* 9(1), 63-69. DOI: 10.1039/b607614a

Furuno, T., Imamura, Y., and Kajita, H. (2004). "The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: A properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls," *Wood Sci. Technol.* 37(5), 349-361. DOI: 10.1007/s00226-003-0176-6

Han, S., Li, J., Zhu, S., Chen, R., Wu, Y., Zhang, X., and Yu, Z. (2009). "Potential applications of ionic liquids in wood related industries," *BioResources* 4(2), 825-834. DOI: 10.15376/biores.4.2.825-834

Hingston, J. A., Collins, C. D., Murphy, R. J., and Lester, J. N. (2001). "Leaching of chromated copper arsenate wood preservatives: A review," *Env. Pollut.* 111(1), 53-66. DOI: 10.1016/S0269-7491(00)00030-0

JIS K 1571 (2010). "Wood preservative - Performance of requirements and their test methods for determining effectiveness," Japanese Industrial Assoc., Tokyo, Japan.

Kilpelainen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., and Argyropoulos, D. S. (2007). "Dissolution of wood in ionic liquids," *J. Agr. Food Chem.* 55(22), 9142-9148. DOI**:** 10.1021/jf071692e

Patachia, S., Croitoru, C., and Friedrich, C. (2012). "Effect of UV exposure on the surface chemistry of wood veneers treated with ionic liquids," *Appl. Surf. Sci.* 258(18), 6723-6729. DOI: 10.1016/j.apsusc.2011.12.050

Pernak, J., Goc, I., and Fojutowski, A. (2005). "Protic ionic liquids with organic anion as wood preservative," *Holzforschung* 59(4), 473-475. DOI: 10.1515/HF.2005.078

Pernak, J., Smiglak, M., Griffin, S. T., Hough, W. L., Wilson, T. B., Pernak, A.,

Zabielska-Matejuk, J., Fojutowski, A., Kita, K., and Rogers, R. D. (2006). "Long alkyl chain quaternary ammonium-based ionic liquids and potential applications," *Green Chemistry* 8(9), 798-806. DOI: 10.1039/B604353D

Pernak, J., Świerczyńska, A., Walkiewicz, F., Krystkowiak, E., and Maciejewski, A. (2009). "Long alkyl chain bis-quaternary ammonium-based ionic liquids as biologically active xanthenes dyes," *J. Brazilian Chem. Soc.* 20(5), 839-845. DOI: 10.1590/S0103-50532009000500006

Pernak, J., Zabielska-Matejuk, J., Kropacz, A., and Foksowicz-Flaczyk, J. (2004). "Ionic liquids in wood preservation," *Holzforschung* 58(3), 286-291. DOI: 10.1515/HF.2004.044

Pu, Y., Jiang, N., and Ragauskas, A. J. (2007). "Ionic liquid as a green solvent for lignin," *J. Wood Chem. Technol.* 27(1), 23-33. DOI: 10.1080/02773810701282330

Ruddick, J. N. R., Xie, C., and Herring, F. G. (2001). "Fixation of amine copper preservatives. Part 1: Reaction of vanillin, a lignin model compound with monoethanolamine copper sulphate solution," *Holzforschung* 55(6), 585-589. DOI: 10.1515/HF.2001.095.

Ryu, J. Y., Imamura, Y., Takahashi, M., and Kajita, H. (1993). "Effects of molecular weight and some other properties of resins on the biological resistance of phenolic resin treated wood," *Mokuzai Gakkaishi* 39(4), 486-492.

Ryu, J. Y., Takahashi, M., Imamura, Y., and Sato, T. (1991). "Biological resistance of phenol-resin treated wood," *Mokuzai Gakkaishi* 37(9), 852-858.

Schwarze, F. W. M. R. (2007). "Wood decay under the microscope," *Fungal Biol. Reviews* 21(4), 133-170. DOI: 10.1016/j.fbr.2007.09.001

Stamm, A. J., and Seborg, R. M. (1936). "Resin-treated plywood," *Ind. Eng. Chem.* 31(7), 897-902. DOI: 10.1021/ie50355a023

Stasiewicz, M., Fojutowski, A., Kropacz, A., and Pernak, J. (2008). "1-Alkoxymethyl-X-dimethylaminopyridinium-base ionic liquids in wood preservation," *Holzforschung* 62(3), 309-317. DOI: 10.1515/HF.2008.028

Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. (2002). "Dissolution of cellulose with ionic liquids," *J. Amer. Chem. Soc.* 124(18), 4974-4975. DOI: 10.1021/ja025790m

Wilkes, J. S., Levisky, J. A., Wilson, R. A., and Hussey, C. L. (1982). "Dialkylimidazolium chloroaluminate melts: A new class of room-temperature ionic liquids for electrochemistry, spectroscopy, and synthesis," *Inorg. Chem.* 21(3), 1263-1264. DOI: 10.1021/ic00133a078

Wilkes, J. S., and Zaworotko, M. J. (1992). "Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids," *J. Chem. Soc. Chem. Comm.* 1992(13), 965-967. DOI: 10.1039/C39920000965

Wood Handbook (2010). "Wood as an engineering material," U. S. Department of Agriculture, Forest Products Laboratory, Madison, WI.

Xiao, J., and Ruddick, J. N. R. (2004). "Leaching resistance of copper amine-treated Scots pine," *Forest Prod. J.* 54(12), 213-216.

Article submitted: February 28, 2018; Peer review completed: April 29, 2018; Revised version received: May 29, 2018; Accepted: May 30, 2018; Published: June 8, 2018.
DOI: 10.15376/biores.13.3.5702-5710