Decay Resistance of Polymerized Ionic Liquid-modified Woods

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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 ⁶⁰Co 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

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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

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/cm³ 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 x 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 60Co 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 60Co 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 x 4.5 mm x 10 mm) were used for the leaching and decay tests.

Table 1. Specimen Test Parameters

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wood Type</th>
<th>Absorption Method</th>
<th>Impregnation (kg/m^3)</th>
<th>Amount of Gamma Irradiation (kGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sapwood</td>
<td>Vacuum</td>
<td>752.5</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>815.4</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Ethanol</td>
<td>1015</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>1018</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>1036</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>954.9</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Heartwood</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Vacuum</td>
<td>876.1</td>
<td>100</td>
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<td></td>
<td>640.4</td>
<td>10</td>
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<tr>
<td>10</td>
<td></td>
<td>Ethanol</td>
<td>959.6</td>
<td>100</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>974.7</td>
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</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td>-</td>
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</tr>
</tbody>
</table>

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](image-url)

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*

![Sapwood Mass Loss](image1)

**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.

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