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Resistance of wood coated with oriental lacquer (urushi) against damage caused by subterranean termite

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Abstract
The sap of urushi tree (Toxicodendron vernicifluum (Stokes) F.A. Barkley) has been used for coating materials and is known as urushi or oriental lacquer in East Asia. The potential of termite attacks against wood samples coated with four types of urushi: Ki-urushi, Sugurome-urushi, Kuro-Sugurome-urushi, and Bengara-urushi, in correlation with their chemical and mechanical properties was investigated in this study. Mortalities of the subterranean Formosan termite (Coptotermes formosanus Shiraki) after a 3-week no-choice feeding tests in samples coated with all types of urushi showed no significant difference from those of control samples. However, mass loss of the sample coated with urushi was lower than that of the control sample especially for Sugurome-urushi (Tukey’s test: \( p < 0.05 \)). Results of Fourier transform infrared spectra analysis suggested that the degree of crosslinking reaction of Sugurome-urushi was higher than that of other urushi. The highest indentation stiffness was detected in the sample surface coated with Sugurome-urushi and Sugurome-urushi film, which have better ductile properties when compared with others. Moreover, the tangential section of Sugurome-urushi was smoother than that of the others. Increasing the hardness and smoothness of wood samples by coating with urushi could be effective in preventing termite penetration.

Keywords: Oriental lacquer, Subterranean termite, Mortality rate, Wood consumption rate, Surface roughness, Surface stiffness

Introduction
The sap of urushi (Toxicodendron vernicifluum (Stokes) F.A. Barkley) trees contains typically 60–65% urushiol, 25–30% water, 5–7% water-soluble polysaccharide, 3–5% glycol-protein, and < 1% laccase. This sap is a water-in-oil emulsion [1, 2]. Urushi sap has been used for coating materials, and is known as urushi, oriental lacquer, in East Asia over the past 5000–7000 years [3]. Urushi coating provides solvent resistance, excellent toughness, and beautifies the products.

Urushi ware has been found in its original state from the graves of Ma Wong Dui, B.C. 2, concluding that urushi has a high durability [1]. Urushiol in the sap of the lacquer tree is a small molecule consisting of catechol derivatives with long alkyl side chains that vary, including 1–3 double bonds in different locations, and can produce an extremely strong coating with a waterproof effect. Watanabe et al. [4] reported that urushiol coating has a contact angle of over 90°, which means strong hydrophilicity. It was also reported that the urushi coating had higher water-repellent property than that obtained using silicon finishing [5].

In Japan, traditional techniques are used for preparing several types of urushi. The filtrate sap of urushi, called Ki-urushi, is used for painting surfaces. Refined urushi from Ki-urushi using traditional Nayashi (stirring/homogenization) and Kurome (agitated/dehydration) methods [6], is called Sugurome-urushi. For the coloration, a small amount of ferric hydroxide or Bengal red is added to Ki-urushi or Sugurome-urushi. All types of urushi are cured by enzymatic catalysis in nature without any organic solvents. Recently, urushi coating systems have received considerable attentions because of...
their environmentally benign processes [7]. They have been used as coating products for building materials, such as floors and walling, as well as lacquer products. Urushi has been limited to use in the shade because it is easy to degrade by ultraviolet light [8, 9]. Therefore, other expected uses of urushi coating for building is coating for structural materials such as underfloor not only floors.

Termites cause serious damage to building materials in Asia including Japan. Chemical prevention and control has been used as a practical method to protect wooden materials from termite attack. Recently, physical barriers have gained significant interest due to their non-toxic activity to humans and environmental friendliness. Some studies suggested that tunneling of termites could be inhibited by controlling surface hardness or smoothness of materials [10, 11].

One of the advantages of coating urushi is surface smoothing of wooden materials even though a small amount of urushi is used. In Japan, there is a simple wood coating technique with urushi called Suri urushi for several thousand years [7]. A layer is wiped gently with a soft cloth to ensure that the layer of urushi left behind on the surface of the object is extremely thin and even [12], and this procedure is repeated several times for surface smoothing [13]. It was observed that the wooden surface became flat and smooth by 1-time Suri urushi process and urushi layers were formed by 4-time Suri urushi process [7]. It was also reported that the roughness was decreased and degree of brightness was increased with every process [7]. Improving surface characteristics of wooden materials would be effective for the prevention of termite feeding. In the present study, we evaluated the potential of termite attacks against wood samples coated with urushi in correlation with their chemical and mechanical properties.

**Materials and methods**

**Materials**

Ki-urushi (KU), Sugurome-urushi (SU), and Kuro-sugurome-urushi (KSU) manufactured in 2018 were used for coating materials (Tsutumi asakichi urushi, Kyoto, Japan) (Fig. 1a). KU is filtered sap of the lacquer tree and contains 25–30% water in emulsion form. SU was obtained by agitating and evaporating Nayashi and Kurome KU with a stirring machine to reduce the water content to 3–5%. In contrast to KU, water bubbles in SU emulsions were smaller, 1 µm diameter or less, and more uniform.

KSU was prepared by agitating KU with the addition of ferric hydroxide (<1 wt%) to produce a black compound. Bengara-urushi (BU) was obtained by mixing SU with Bengal red (w/w = 3:1) to produce a red product. All of these have been commonly used for coating wooden materials in Japan.

Bengara-urushi (BU) was obtained by mixing SU with Bengal red (w/w = 3:1) to produce a red product. All of the sample surfaces were coated with urushi in correlation with their chemical and mechanical properties.

**No-choice test for termite feeding**

The laboratory no-choice test for termite feeding was conducted according to the Japanese Industrial Standards (JIS) K 1571:2010 [14]. Each specimen was introduced in the center of a plastic cylinder (6 cm in height by 8 cm in diameter) with a hard plaster bottom. Each cylinder housed 150 workers and 15 soldiers of Coptotermes formosanus, which were obtained from a laboratory colony of the Deterioration Organisms Laboratory (DOL) at the Research Institute for Sustainable Humanosphere (RISH) Kyoto University. The cylinders were placed in the plastic container in a termite breeding room with wetted cotton pads to supply water to the termites. After 21 days, termite mortality and mass loss of the test samples were determined using three replicates. Sapwood blocks (10 × 10 × 20 (L) mm) of Japanese cedar were used as controls. Tukey’s test was used to determine statistical significance.

**Characterization**

Urushi films were analyzed using FTIR (Spectrum One, PerkinElmer, Inc., USA) with attenuated total reflection (ATR-FTIR). Roughness of sample surfaces was evaluated using laser microscopy (VK-100, Keyence Corporation, Japan) according to the JIS B 0601:1994 [15]. The indentation test was conducted with scanning probe microscopy (SPM, AFM5100N, Hitachi High-Technologies Corp., Japan) in force curve mode to determine the indentation stiffness of the sample surface. Sample surface stiffness (modulus of the sample surface) is given by the slope ΔF, the reaction force that a cantilever receives by tapping on the sample surface/ΔD, displacement of a cantilever by...
Fig. 1 Schematic of each urushi sample and micrographs of each urushi sap (a), the samples coated with each urushi (b) images of each samples coated with four types of urushi (c), and structures of typical urushiol.
bending, of the reaction curve [16]. The lower the $\Delta F/\Delta D$, the softer is the sample surface [17]. Ten trials were performed for each sample. Dumbbell samples according to the ISO 5893-2002 standard of each film were prepared for tensile tests [18]. The tensile test was conducted using a universal material testing machine (MCT-2150, A & D Company, Japan) with a crosshead speed of 50 mm/min. The average values $\pm$ standard deviations of the elastic modulus, tensile strength, and tensile strain were evaluated using five independent specimens.

Results and discussion

Termite test

The samples coated with each urushi after termite feeding test are shown in Fig. 2. All sections of control sample were attacked by termite. The tangential surfaces of the samples coated with all types of urushi were attacked by termite, while the radial and the cross sections of urushi-coated samples especially for SU show no/less penetration by termite. There were no clear differences of the surface morphology among the samples after termite feeding test, it was suggested that urushi coating was ineffective in preventing termite feedings once through the coating (Fig. 3).

Mortalities of workers and soldiers after the 3-week no-choice termite feeding tests in samples coated with KU, SU, KSU, and BU showed no significant difference from those of the control samples (Table 1). One of the major phyto compounds possessing both termiticidal and antioxidant properties in plant extracts is phenol [19]. The function of antioxidant enzyme systems can be disturbed by antioxidants, and lead to insect mortality by destroying the bonds in the DNA strands [20]. Urushiol has been found to possess both antimicrobial and anti-oxidative effects [21]. However, the anti-oxidant activity of urushiol

![Fig. 2 The samples coated with each urushi after termite feeding test. 1 indicates the tangential surface, 2 indicates the radial surface, and 3 indicates the cross section](image)

![Fig. 3 The microscopic observation of sample surface after termite feeding test](image)

| Sample | Worker mortality (%) $\pm$ S.D | Soldier mortality (%) $\pm$ S.D |
|--------|---------------------------------|---------------------------------|
| KU     | 30.0±5.2                        | 1.8±0.8                         |
| SU     | 31.8±2.5                        | 4.7±2.5                         |
| KSU    | 29.8±1.6                        | 0.7±0.5                         |
| BU     | 25.8±2.2                        | 1.1±0.3                         |
| Control| 23.3±4.3                        | 1.1±0.3                         |
decreased as enzyme polymerization proceeded [22]. It was expected that there would be no termiticidal property in samples coated with any type of urushi because it was fully cured during storage in the present study.

Figure 4 shows mass loss of the samples after termite tests. The mass loss of samples coated with KU (31.5 ± 5.3), KSU (31.1 ± 5.3) or BU (31.5 ± 7.7) was slightly lower than that of the control (40.3 ± 4.7); whereas, mass loss of sample coated with SU (10.9 ± 4.1) was significantly lower than that of the control sample (Tukey’s test: \( p < 0.05 \)). It was suggested that the surface characteristics or mechanical properties, not chemical characterization, of the sample coated with urushi especially for SU could resist termite damage because there was no termiticidal property in samples with this coating. Therefore, surface characterization and evaluation of mechanical properties of the samples were conducted.

**Fourier transform infrared spectra**

The FTIR spectra of urushi film are shown in Fig. 5. Intensity changes of characteristic peaks were standardized using a peak at 2930 cm\(^{-1}\) owing to C–H stretching vibration of the terminal methyl group [2]. Urushiol consists of a variety of isomers of 1,2,3-tri-o- or 1,3-di-o-substituted catechol and a long alkyl side chain (Fig. 1c). The peaks at 992, 1070, 1210, 1270, 1460, 1580, and 1618 cm\(^{-1}\) were assigned to conjugated triene, polysaccharides, aromatic C–O–C, phenolic OH, bending vibration of CH\(_3\), glycoprotein, and phenyl ring, respectively. All these peaks are associated with urushi (Fig. 3a) [1, 23]. A broad band between 3600 and 3200 cm\(^{-1}\), which is attributed O–H stretching, of SU was higher than that of other types of urushi film (Fig. 3b). This is possibly the highest urushiol content in SU. SU contains less water and impurities than do other samples. It was reported that the molecular distribution of raw urushi sap was increased after stirring and homogenization for water evaporation—the Kurome process [22]. Raw urushi contains no polymer, 16.28% oligomer, and 83.72% monomer. After the Kurome process, neat urushi contains 0.64% polymer, 33.30% oligomer, and 66.06% monomer [22]. Enzyme polymerization of neat SU could have occurred during the Kurome process. Moreover, curing the urushi sap is proceeded by laccase-catalyzed oxidative coupling of the urushiol phenol moiety and then auto-oxidation of the unsaturated hydrocarbon chain in air. The peak owing to O–H stretching increased after auto-oxidation of the unsaturated group in the side chain [2], which suggests that the degree of crosslinking reaction of SU is higher than that in other urushi.

**Mechanical properties of urushi-coated surface and urushi film**

Table 2 shows the results of surface stiffness and modulus in the samples coated with urushi. The highest indentation stiffness was detected in the sample surface coated with SU. It has been reported that the universal hardness of urushi films reached maximum values after autoxidation of the side chain of urushiol occurred [2]. In the present study, maximum autoxidation could have occurred in SU.

A test of tensile strength was performed for each urushi film, and the results have been plotted in Fig. 6. A clear difference among the stress–strain behavior of each sample was observed. The value of tensile strength and elastic modulus was the lowest in SU film and highest in KU. While, the highest tensile strain occurred in the SU film, and lowest occurred in KU. The SU film has better ductile properties than do the other urushi films. These differences might be caused by the materials present in each urushi. Water, ferric hydroxide, and Bengal red were present in KU, KSU, and BU, respectively. The water in KU could enhance curing by enzyme catalysis [22]. The mineral materials present in ferric hydroxide and Bengal red might perform as nucleus, and also enhance curing rather than SU. Notably, wood hardness is a key determinant of wood resistance to termites, as well as of wood density [24], and differences in the consumption rate could be attributed to differences in wood hardness rather than to feeding preferences [25]. The differences in mechanical properties of urushi might have inhibited termite attack on coated samples.

**Surface roughness of the urushi-coated sample**

The results of RMS (root mean square) of tangential, radial, and transverse sections are shown in Table 3. The lowest RMS in tangential and transverse sections was obtained in the SU-coated sample. In the present...
in the samples coated with urushi

|       | Force (nN) | Modulus (nN/nm) |
|-------|------------|-----------------|
| KU    | 13.3 ± 2.5 | 1.22 ± 0.13     |
| SU    | 14.3 ± 2.9 | 1.31 ± 0.07     |
| KSU   | 12.5 ± 1.6 | 1.25 ± 0.10     |
| BU    | 13.3 ± 2.1 | 1.26 ± 0.18     |

*Calculated by ΔF/ΔD; ΔF means the reaction force that a cantilever receives by tapping on the sample surface, ΔD means displacement of a cantilever by bending.

study, termite damage was mainly observed in the tangential section (Fig. 3). The tangential section of SU was smoother than that of the others. Uniformity in water bubbles in neat urushi emulsion after the Kurome process led to a smoother surface of the urushi-coated samples (Fig. 1a). It has been reported that samples with smoother surface were effective against both tunneling and penetration of termites [26]. In particular, the surface roughness of bamboo affects the feeding activity of termites [11]. Surface smoothness obtained by coating with SU could prevent tunneling and penetration of termites.

**Conclusions**

Mortalities of workers and soldiers after the 3-week no-choice termite feeding tests in samples coated with KU, SU, KSU, and BU showed no difference when compared with the control samples. However, mass loss of the sample coated with urushi was lower than that of the control sample especially for SU. It was suggested that the degree of crosslinking reactions of SU was higher than that of
Increased hardness and smoothness of wood samples obtained by coating with urushi could be effective in preventing termite penetration.

**Abbreviations**

KU: Ki-urushi; SU: Sugurome-urushi; KSU: Kuro-sugurome-urushi; BU: Bengara-urushi; FTIR: Fourier-transform infrared spectroscopy; AFM: atomic force microscope; RMS: root mean square, roughness value.

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**Authors’ contributions**

YO designed the study, analyzed data and wrote the initial draft of the manuscript. CN contributed to analysis and interpretation of data, and assisted in the preparation of the manuscript. TY contributed to data collection and interpretation, and critically reviewed the manuscript. All authors agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. All authors read and approved the final manuscript.

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**Availability of data and materials**

The authors confirm that the data supporting the findings of this study are available within the article.

**Competing interests**

The authors declare that they have no competing interests.

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