Development of a fast drying lacquer based on raw lacquer sap

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Abstract

A series of new lacquers, based on the raw lacquer sap that drying fast in the natural environment, has been developed using a repeated-kurome process. Fast drying occurred due to the repeated-kurome process from K-0 to K-4, and the 982 cm\(^{-1}\) for the dienes decreased and the 993 cm\(^{-1}\) for the trienes increased in the IR measurement. In addition, the polymerization of urushiol by laccase was revealed for the first time by the repeated-time course of GPC measurements. The results suggest that the molecular weight of urushiol was gradually increased by the repeated-kurome process, and the emulsion micelle in the raw lacquer decreased from 10 to 1\(/\mu m\) in the kurome lacquer. A lacquer based on raw lacquer that dries fast at room temperature and humidity can be obtained by stirring with additional moisture in the reaction vessel, the kurome process, with a decrease of the urushiol monomer.

Keywords: Lacquer; Repeated-kurome; Fast drying; GPC; Urushiol

1. Introduction

The oriental lacquer tree, a member of the family Anacardiaceae, consists of about 600 species and has wide-ranging growth in many countries and areas of Asia [1,2]. Lacquer sap, known as “raw lacquer”, is collected from lacquer trees grown in China and Japan (Rhus vernicifera), in Vietnam and Taiwan (Rhus succedanea) and in Burma and Thailand (Melanorrhoea) [3]. Lacquer has been used as a durable coating material in Asian countries for thousands of years [4].

The main components of lacquer are urushiol (60–65%), a gummi substance (5–7%), glycoproteins (2%), and water (20–30%) [5,6]. Parts of the structure of a Chinese lacquer polysaccharide have been determined by methylation analysis [7] and NMR measurements [8], and indicate that the Chinese lacquer polysaccharide has a 1,3-β-galactopyranosidic main chain with a 1,6-β-linked galactopyranosidic side chain attached to a 4-O-methyl-β-D-glucuronic acid in the terminal. Urushiol is a mixture of many isomers of 1,2,3-tri-O- or 1,3-di-O-substituted catechols having a long alkyl chain with double bonds [9,10], as shown in Scheme 1. Laccase is a copper-glycoprotein and functions as the catalyst of urushiol polymerization [11]. The lacquer film forms via the oxidation of urushiol catalyzed by laccase, which is followed by a coupling reaction as well as an autoxidation reaction on the long aliphatic unsaturated side chain.

Recently, many synthetic polymers and coatings have been developed that can be used simply and easily and at a lower cost [12]. However, these artificial polymers and coatings use various organic solvents that have a bad effect on the environment. Unlike the synthetic coatings, lacquer is a renewable resource and an eco-friendly biopolymer material. Further, enzymatic polymerization based on the lacquer model has attracted considerable interest as a new method of preparing synthetic polymers and coatings.

We have successively developed a small kneading mixer capable of repeated kurome, and the drying time of repeated-kurome lacquers has been investigated [13]. However, some features of dry lacquer film and the anti-oxidation property have not been clarified. As part of an on-going work, in this study, a series of new lacquers that dry fast in the natural...
2. Experimental

2.1. Materials

The raw lacquer was the sap of a Chinese lacquer tree in Chengkou, in the Hubei province of China, and was purchased from Tohityu-Urushi-Ya in Osaka, Japan. The repeated-Kurome lacquers were synthesized in our laboratory. Raw lacquer sap (20 g) is stirred in an open vessel (bottom diameter: 80 mm, capacity: 100 ml) at room temperature for about 1.5 h, then the temperature is increased from 20 to 40 °C for 2–4 h until the water concentration was reduced to 3–5%, for K-0. Water is added to K-0 to increase the moisture about 20–25%, comparable to the water concentration of the raw lacquer, and the kurome process is repeated. By repeatedly adding water and reducing it, kurome, K-1, K-2, K-3 and K-4 were obtained.

2.2. Methods

The molecular weight was estimated at 40 °C using aqueous phase gel permeation chromatography (GPC, column: Tosoh, TSK-gel, α-3000, α-4000, and α-M, Ø 7.8 mm × 300 mm × 3; eluent, DMF with 0.01 mol LiBr) running on an HPLC system with an RI detector using polystyrene standards with molecular weights of 5.00 × 10², 2.63 × 10³, and 1.81 × 10⁴. The elution rate and pressure of the DMF-eluent were 0.8 ml/min and 48 kgf/cm², respectively.

The moisture in the lacquer sap was determined at 120 °C using a simultaneous DTG–TG apparatus (Shimadzu, Japan). All substances that evaporated below 120 °C were considered to be moisture. These results were shown as a function of time.

3. Results and discussion

The molecular weight distribution of the raw and repeated-kurome lacquers measured by GPC are summarized in Table 1.

Table 1. The molecular weight distribution of the raw and repeated-kurome lacquers.

<table>
<thead>
<tr>
<th>Name of lacquer</th>
<th>Polymer</th>
<th>Oligomer</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>0.00</td>
<td>16.28</td>
<td>83.72</td>
</tr>
<tr>
<td>K-0</td>
<td>0.64</td>
<td>33.30</td>
<td>66.06</td>
</tr>
<tr>
<td>K-1</td>
<td>0.82</td>
<td>39.73</td>
<td>59.45</td>
</tr>
<tr>
<td>K-2</td>
<td>1.13</td>
<td>40.50</td>
<td>57.93</td>
</tr>
<tr>
<td>K-3</td>
<td>1.56</td>
<td>40.50</td>
<td>57.93</td>
</tr>
<tr>
<td>K-4</td>
<td>2.19</td>
<td>42.85</td>
<td>55.03</td>
</tr>
</tbody>
</table>

It is known that the water concentration of raw lacquer is about 20–30% [6]. The water concentration of the raw lacquer in this study was 24.5%. At least 3% moisture is required for the laccase oxidation of urushiol [13,14]. We controlled the water content of the kurome lacquers to 3–5% in this study. The water concentrations of the repeated-kurome lacquers were about 3.5% as shown in Table 2.
Table 2
The moisture concentrations of raw and repeated-kurome lacquers

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lacquer sap</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raw</td>
<td>24.5</td>
</tr>
<tr>
<td>2</td>
<td>K-0</td>
<td>3.55</td>
</tr>
<tr>
<td>3</td>
<td>K-1</td>
<td>3.49</td>
</tr>
<tr>
<td>4</td>
<td>K-2</td>
<td>3.48</td>
</tr>
<tr>
<td>5</td>
<td>K-3</td>
<td>3.34</td>
</tr>
<tr>
<td>6</td>
<td>K-4</td>
<td>3.47</td>
</tr>
</tbody>
</table>

The IR spectra are shown in Fig. 1. The absorption due to the ether of quinon-olefin and/or dibenzofuran appeared around 1470 and 1080 cm\(^{-1}\). The absorption of 982 cm\(^{-1}\) for the dienes decreased and the 993 cm\(^{-1}\) for the trienes increased, suggesting that the repeated-kurome made laccase polymerization occur.

Fig. 2 shows the \(^1\)H NMR spectra of raw and repeated-kurome lacquers, in which complex signals appear at 3.58–3.72 ppm due to the \(\text{C}_2\text{C}-\text{CH}_2\text{Ph}\) coupling in the side chain of the dimer, trimer, and tetramer of the urushiol[15]. The signals at 4.10–4.33 ppm were assigned to the \(\text{C}_2\text{C}-\text{CH}_2\text{O}\) coupling between the catechols of urushiol and the side chain[16] that produced the quinon-olefin and/or dibenzofuran (Scheme 2), which is not present in raw lacquer, implying that, in the repeated-kurome lacquers after K-0, enzyme had polymerization occurred.

SEM and SPM photos are shown in Fig. 3. Fig. 3A is an SEM photo of the cross-section and Fig. 3B is an SPM of the surface of the raw and K-0 lacquer film after drying at 20°C, 70% RH for 1 month.

It was revealed that the “cave” in the K-0 film is smaller than in the raw lacquer film. The K-1, K-2, K-3 and K-4 also showed the same SEM and SPM images (figures not shown). The caves are the marks of waterdrops in the lacquer sap. As kurome progressed, the emulsion micelle of lacquer became smaller. The emulsion micelle decreased to about 1 μm size, compared to 10 μm in the raw lacquer. The small “holes” in the surface of lacquer film can be considered marks of the waterdrops in the lacquer sap. They were 2.08 μm in the raw lacquer film and 0.97 μm in the K-0 lacquer film.

The lacquer drying process can be divided into three steps: dust-free drying (DF), touch-free drying (TF), and harden dry (HD)[17,18]. The raw and kurome lacquers were tested at drying conditions of 20°C with 40–50% relative humidity, 20°C with 55–65% relative humidity, and 20°C with 65–75% relative humidity using an automatic drying time.
Fig. 3. SEM (A) and SPM (B) photographs of the raw and K-0 lacquer.

The SEM photos of cross-section of (A) raw, and (B) K-0 lacquer film.

The SPM photos of surface of raw lacquer film, the diameter of the biggest cave is about 2.08 μm (between the two yellow line).

The SPM photos of surface of K-0 lacquer film, the diameter of the biggest cave is about 0.97 μm (between the two yellow line).

Fig. 3. SEM (A) and SPM (B) photographs of the raw and K-0 lacquer.

Table 3
The drying time of raw and repeated kurome lacquers (h:min)

<table>
<thead>
<tr>
<th>Name of lacquer</th>
<th>20 °C, 40–50% RH</th>
<th>20 °C, 55–65% RH</th>
<th>20 °C, 65–75% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DF</td>
<td>TF</td>
<td>HD</td>
</tr>
<tr>
<td>Raw</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>K-0</td>
<td>6:00</td>
<td>8:30</td>
<td>21:00</td>
</tr>
<tr>
<td>K-1</td>
<td>4:10</td>
<td>7:30</td>
<td>21:00</td>
</tr>
<tr>
<td>K-2</td>
<td>3:10</td>
<td>7:30</td>
<td>21:00</td>
</tr>
<tr>
<td>K-3</td>
<td>2:10</td>
<td>6:30</td>
<td>14:00</td>
</tr>
<tr>
<td>K-4</td>
<td>2:00</td>
<td>6:50</td>
<td>11:50</td>
</tr>
</tbody>
</table>
recorder. The automatic drying time recorder could be used to measure the drying process of lacquer, DF, TF and HD. The time until the marks of the needle appear on the glass board is equivalent to DF, the time until the marks of the needle disappear completely on the lacquer film surface is equivalent to HD. The drying time results are summarized in Table 3.

It can be seen that the drying time gradually decreases from the raw lacquer to the 

kurome

K-4 lacquer. Because the raw lacquer undergoes enzyme oxidation by the repeated

kurome

process, the lacquer monomer decreased. Meanwhile, the lacquer dimer, trimer, , oligomer, and polymer increased. As the lacquer monomer decreased, the anti-oxidation of the catechols of urushiol decreased, and the drying time was curtailed.

Measurement using the rigid-body pendulum physical properties testing instrument (RPT, A&D Co. Ltd., Japan) is shown in Fig. 4 (20°C, 65% RH). The frequency decrease means that the cross-linkage reaction of the urushiol had occurred. A steady change in the logarithmic-decrement means that the dry hardening of the lacquer is over. The frequency decreased (Fig. 4 A) at 500 min for the raw lacquer, 292 min for K-0, 230 min for K-1, 195 min for K-2, 130 min for K-4 lacquer, as the drying time between DF and TF. The steady states of the logarithmic-decrement values (Fig. 4 B) of raw lacquer, K-0, K-1, K-2, K-3, and K-4 were 680, 600, 580, 560, 425, and 315 min, respectively, consistent with the HD data in Table 3.

Fig. 5 shows the results of the anti-oxidation of raw and 

kurome

lacquers tested in the DTG–TG apparatus (Shimadzu, Japan), and these data are summarized in Table 4.

It is known that the air oxidation of methyl linoleate is easily carried out. In this study, oxidation required 1.50 h. After adding methyl linoleate to the lacquers (as an anti-oxidation reagent), the induction time of the air oxidation decreased according to the 

kurome

times. These results suggest that the anti-oxidation power of the lacquer decreased and that autoxidation of the side chain increased from the raw to K-4 lacquer.

It can be concluded that the dryness in an environment with a low relative humidity, depended on advance of the enzyme polymerization reaction based on the change in the molecular weight of urushiol and the IR spectra of the raw and 

kurome

lacquers. Moreover, the anti-oxidation power of urushiol decreased as the enzyme polymerization proceeded, and the autoxidation reaction of a side chain of urushiol easily occurred. In addition, the particles of the lacquer sap also became smaller after the 

kurome

occurred.

4. Conclusion

Lacquer has been limited to handcrafts applications till now because it requires severe drying conditions. Lacquer is dried at a fixed temperature and relative humidity of about 70-80%, which requires a special humidified chamber. However, raw lacquer undergoes drying by enzymes oxidation in the repeated 

kurome

technique described in this study so that
it becomes possible to use it in a low relative humidity environment. Its low monomer, low anti-oxidation power that facilitates the fast drying characteristics.

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References