



Thermal polymerization of lacquer sap and its effects on the properties of lacquer film

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ABSTRACT

A series of thermal polymerized lacquers (TPL) were prepared from a dead lacquer at the temperature of 120–200 °C under nitrogen atmosphere. The thermal polymerization of lacquer sap was analyzed by GPC, UV–Vis, FT-IR and NMR methods. The results showed that the higher the temperature, the faster the polymerization of urushiol monomer in the lacquer sap. Different from the laccase-catalyzed oxidative polymerization in air which formed the biphenyl structures, the thermal polymerization mainly occurred in the unsaturated side chain of urushiol and could involve the pericyclic reaction between the unsaturated carbon-carbon double bonds and the reactions of the side chains with the phenolic hydroxyl groups and the carbons in the aromatic ring. Addition of the thermal polymerized lacquer into a raw lacquer sap with high activity of laccase at a suitable mixing ratio promoted its drying in air, and the higher the extent of thermal polymerization of lacquer sap, the shorter the drying time of lacquer film. In addition, due to the combination of the thermal polymerization and the laccase-catalyzed polymerization, the blend lacquer films showed higher degree of crosslinking, smoother surfaces, and more uniform and compact structure. This resulted in significant improvement in the pencil hardness and gloss of lacquer film and slight enhancement of its flexibility.

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1. Introduction

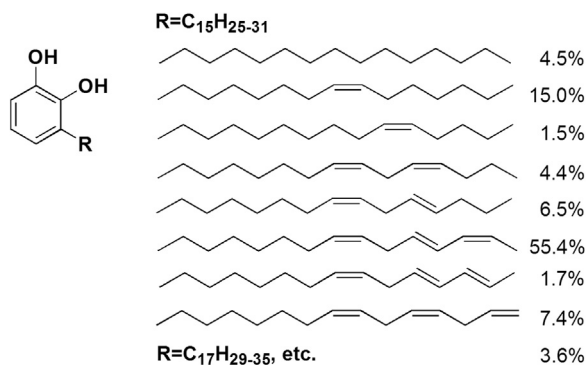
Lac tree, a member of family *Anacardiaceae*, grows widely in China and Japan (*Rhus vernicifera*), Vietnam and Chinese Taiwan (*Rhus succedanea*), and Burma and Thailand (*Melanorrhoea usitate*) [1,2]. When the bark of lac tree is cut, a milk white sap which is called raw lacquer sap gently oozes out. The lacquer sap can form solidified lacquer film with a beautiful surface, and has been used as a coating in China and Japan for more than seven thousand years [1,3,4]. Today, although many synthetic polymers and coatings have been developed, lacquer sap has still attracted increasing attention because of its natural renewable and eco-friendly feature and its excellent physico-chemical properties such as corrosion resistance, high thermal stability, good brilliance and super-high durability [2,5].

Lac tree *R. vernicifera* is extensively cultivated in China and its sap is the most highly appreciated in the world. The sap contains complex components including urushiol (60–65%), water (20–30%), gummy substance (5–7%), glycoprotein (~2%) and laccase (<1%) [6,7]. Urushiol is a mixture, mainly consisting of 3-substituted

catechols with $n = 15$ carbon alkyl chains with 0–3 olefins [8–10], as shown in Scheme 1.

Laccase is an oxidoreductase, copper glycoprotein blue enzyme whose molecular weight is $12\text{--}14 \times 10^4$ Da, with 4 atoms of copper in a molecule [1,11]. It functions as the catalyst of urushiol polymerization in the lacquer sap [12,13]. In the curing process of lacquer sap, urushiol is first oxidized by laccase to give semiquinone radical. Then, the semiquinone radical attacks on the urushiol nucleus to give urushiol dimers such as biphenyl compounds and dibenzofuran compounds, and also triggers some reactions in the side chain of urushiol. Further polymerization of the urushiol dimers produces the space network polymer and the lacquer sap dries [1]. Although an autooxidation reaction on the long aliphatic unsaturated side chain is also followed in the drying process, it is very slow [14]. Thus, the drying of lacquer sap is mainly dependent upon the oxidative polymerization of urushiol catalyzed by laccase [6,14,15]. However, laccase activity is lost under a temperature over 60 °C, or gradually decreases with the increase of storage time of lacquer sap. The lacquer with little activity of laccase is commonly called dead lacquer, which is difficult to dry and usually used to extract urushiol and prepare the synthetic paint. This leads to the loss of its environmental friendly feature and brings environmental pollution. A solution is to add some laccases into the dead lacquer [16]. However, it is very expensive to obtain the enzyme. In

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Scheme 1. Typical structures and components of urushiol.

addition, some mononuclear Cu (II) complexes were also tried to use instead of laccase [17,18]. Although some synthetic compounds have showed the catalytic performance, there are still some environmental concerns about them. In this paper, a dead lacquer sap was used to prepare a series of thermal polymerized lacquers by the direct heating under nitrogen atmosphere. The thermal polymerization process was evaluated by gel permeation chromatography (GPC) analysis and the mechanism of polymerization reaction was investigated by UV–Vis, FT-IR, and NMR spectroscopic techniques. For the purpose of its application, a thermal polymerized lacquer was also added into a lacquer sap with high activity of laccase. The drying process of the blend lacquers was analyzed by GPC and their films were characterized by IR and SEM. The effects of the thermal polymerized lacquer on the properties of lacquer sap such as the drying, the pencil hardness, the gloss, the flexibility and the chemical medium resistance of lacquer films were evaluated.

2. Materials and methods

2.1. Materials

Two raw lacquer saps were purchased from Lichuan Delong Trade Co., Ltd. (Enshi, China). One was collected from lacquer tree *R. vernicifera* in 2014 (labelled as LS14) and another in 2012 (labelled as LS12). LS14 dries quickly due to its high activity of laccase, while LS12 is difficult to dry because of its very weak activity of laccase and called dead lacquer. They have been filtered, and have naturally high water content of 25.03 wt% and 24.14 wt%, respectively. All other chemicals and reagents were of analytical grade and used as received.

2.2. Methods

2.2.1. Thermal polymerization of lacquer sap

LS12 was used to prepare thermal polymerized lacquer as follows: LS12 (100 g) was added into a closed four-neck flask (250 ml) equipped with mechanical stirrer, reflux condenser and nitrogen inlet, and then was heated in oil bath under a nitrogen atmosphere with the stirring rate of 300 rpm; After raw lacquer sap was heated for a certain time, the flask was swiftly cooled to room temperature and thermal polymerized lacquer was obtained. Five temperatures (120 °C, 150 °C, 180 °C, 190 °C, and 200 °C) were used, and the thermal polymerized lacquers (TPL) obtained were labelled as TPL1, TPL2, TPL3, TPL4 and TPL5, respectively.

2.2.2. Preparation of blend lacquer and monitoring of its drying process

TPL were mixed with LS14 in the mass ratios of 2:1, 1:1, 1:2 and 1:3 in sample cups and stirred at 25 °C for 10 min. Then, raw lacquer sap and the blend samples were applied on glass plates using a

50 μ m film applicator and dried at 30 °C and relative humidity (RH) of 80%. Their drying time was tested by a drying-time recorder. The drying process is divided into touch-free dryness (TD) and hardened dryness (HD). TD is equivalent to the time until the needle's scratch arises on the film surface, and HD is equivalent to the time until the needle's scratch can't be seen on the film surface [15]. In the drying process, samples taken from lacquer films were extracted with THF for GPC test.

2.2.3. Mechanical properties

After raw lacquer sap and the blend samples were applied on degreased tinplate panels using a 50 μ m film applicator and dried at 30 °C and 80% RH for a week, their mechanical properties were evaluated. The lacquer films' pencil hardness was tested using a QHQ film pencil scratching tester (Tianjin, China) based on national standard of GB/T 6739-2006. The flexibility was checked by a QTY-32 conical mandrel bent tester (Tianjin, China) based on national standard of GB/T 1731-1993.

2.2.4. Characterization

Weight average molecular weight (M_w) and its distribution of sample were measured by a gel permeation chromatography (GPC) on a LC-20AD instrument (Shimadzu, Japan) equipped with a TSK G3000-HXL column (TOSOH, Japan). The eluent was THF. The flow rate was 1.0 ml/min. The temperature of the column was maintained at 30 °C. The eluate was monitored with RID-10A refractive index detector (Shimadzu, Japan). The standards used for calibration the column were polystyrene. All data provide by the GPC system were collected and analyzed with the aid of the LcSolution Workstation software package.

The UV–vis spectra were recorded on a Specord 50 spectrophotometer (Analytik Jena AG, Germany). The sample was thinly applied on the quartz plate using a 25 μ m film applicator.

FT-IR spectra were recorded on a Nicolet Avatar 370 FT-IR spectrometer (Thermo, Madison, USA). The lacquer saps were thinly applied on the KBr pellets. 32 scans at a resolution of 2 cm^{-1} were averaged and referenced against air. The dry lacquer films were directly tested by a Smart iTRTM Attenuated Total Reflectance (ATR) Sampling Accessory. 64 scans at a resolution of 4 cm^{-1} were averaged and referenced against air.

¹H NMR spectra were recorded by a Bruke AVANCE III 500 MHz NMR spectrometer (Germany) with tetramethylsilane (TMS) as the internal standard. The lacquer saps were extracted by THF. After THF was removed under reduced pressure at the temperature below 40 °C, the samples were dissolved in CDCl_3 and tested.

The gloss of lacquer film was tested with an XGP20°–60°–85° specular gloss meter (Tianjin Xintongguanda Technology Co., Ltd., China). Lacquer films were prepared with 50 μ m thickness of the wet coating on tinplate panels and evaluated after one week cure at 30 °C and 80% RH.

The surface and cross-section morphologies of the lacquer films were examined using a scanning electron microscopy (SEM) Zeiss SUPRA55 (Germany).

3. Results and discussion

3.1. Thermal polymerization and characterization of dead lacquer sap

3.1.1. Molecular weight change in the thermal polymerization process

The M_w and their distribution of the lacquer sap (LS12) were monitored by GPC in the thermal polymerization process. The results are shown in Table 1. It can be seen from Table 1 that the thermal polymerization of lacquer sap was significantly influenced

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