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Promotion by copper (II)-modified montmorillonite of the drying property of oriental lacquer sap

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ABSTRACT

A series of hybrid lacquer saps were prepared by adding copper(II)-modified montmorillonite (Cu(II)-MMT) into the raw lacquer. Cu(II)-MMT can effectively accelerate the polymerization of urushiol over a wide humidity range. Addition of 5 wt% of Cu(II)-MMT suspension (concentration, 5 wt%) into the raw lacquer sap made its touch-free drying time and hardened drying time decrease from each > 36 days and > 36 days to 6 days and 9 days at 36 °C and 50% relative humidity and from each > 120 h and > 120 h to 5 h 40 min and 23 h 30 min at 34 °C and 65% relative humidity, respectively. GPC tests proved the acceleration of the urushiol polymerization. Based on the results from UV–vis, FT-IR and NMR, the urushiol polymerization catalyzed by Cu(II)-MMT is similar to that catalyzed by laccase. However, a distinct difference is that the degree of crosslinking of lacquer films increased due to the formation of Si—O—C and Al—O—C bonds between urushiol and MMT in the drying process. Furthermore, addition of Cu(II)-MMT also improves the gloss and thermo-stability of lacquer films.

1. Introduction

Oriental lacquer is a natural sap tapped from lacquer trees. Its collection method is similar to that for latex obtained from rubber trees [1]. Lacquer sap is secreted by three kinds of lacquer trees: *Rhus vernicifera*, growing in China, Japan and Korea; *Melanorrhoea usitata*, growing in Cambodia, Myanmar and Thailand; *Rhus succedanea*, growing in Chinese Taiwan and Vietnam [2,3]. Lacquer sap collected from *Rhus vernicifera* is the most famous and has the best quality in the world. As a kind of natural coating, it has been used to protect and decorate dishes, tools and crafts for more than several thousand years in China because of its excellent performance such as high thermal stability, gloss and durability [3–5]. The world's earliest unearthed lacquer ware is a red lacquer bowl found in 1978 at Zhejiang Hemudu site in China. It has a history of more than 7000 years, yet its original elegant beauty has been retained [6,7]. Recently, despite the rapid development of synthetic coatings, there is still no paint that exceeds it in terms of comprehensive performance and it is still in use today. However, although the lacquer film has excellent performance, its drying property is its "Achilles heel". The lacquer sap dries under a special condition, about 70–90% relative humidity (RH) at 20–30 °C [8]. In a low humidity environment, the lacquer film dries slowly, or even not at all [9], which hinders its popularization and application.

Lacquer sap collected from *Rhus vernicifera* is composed of urushiol (60–65%), water (20–30%), gummy substance (5–7%), glycoprotein (~2%) and laccase (~0.2%) [10]. Its curing involves a complex polymerization process of urushiol, including enzyme-catalyzed and autoxidation reactions [3,11–13]. However, laccase-catalyzed urushiol polymerization plays a decisive role in the drying of lacquer sap. Urushiol monomers are first oxidized to produce semiquinone radicals. Then the radicals attack the unsaturated groups in the side chain or the catechol moiety of urushiol to produce urushiol dimers, and the dimers further polymerize to form oligomers and polymers [14]. Laccase is a kind of multi-copper enzyme, with four copper ions per molecule of laccase [15–19]. The copper ions are the key in the laccase-catalyzed reaction and are responsible for electron transfer. So far, some mononuclear Cu (II) complexes such as cupric potassium chloride dihydrate ($K_2CuCl_4 \cdot 2H_2O$) and cupric complexes with pyridines have been used to the mimic laccase to catalyze the polymerization of urushiol and showed good catalytic performance [20,21]. However, these water soluble Cu (II) complexes can be leached from the cured lacquer film, which will lead to some environmental concerns. Thus, the development of new catalyst for the drying of lacquer sap is still a concern.

Recently, composites of inorganic nanoparticles and organic polymers have attracted increasing attention. Some inorganic nanoparticles have been added into the lacquer to improve its performances. Xu et al.

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had fabricated the polyurushiol/CdS nanocomposite. This nanocomposite showed excellent thermo-stability [22]. A raw lacquer/organophilic montmorillonite/multihydroxyl polyacrylate nanocomposite had also been prepared and the UV resistance of its film was greatly improved [23]. Montmorillonite is a natural layered clay. Its main building unit is a negatively charged layer composed of two tetrahedral Si-O sheets sandwiching an octahedral Al-O sheet [24]. The presence of Al in the framework introduces negative charges, which are neutralized by the charge balancing cations such as K^+, Na^+ or alkali earth metals in the interlayer space. These charge-balancing cations can be partially substituted by other metal ions such as Cu^{2+} [25]. Copper-bearing montmorillonite (Cu-MMT) has been prepared and used as an efficient catalyst to degrade some types of organic contaminant in wastewater [26]. But its catalytic polymerization of urushiol has not been studied, yet. In this paper, a copper-modified montmorillonite (Cu(II)-MMT) was prepared and added into the raw lacquer to obtain copper(II)-montmorillonite/lacquer blend (CML). CML's polymerization process was investigated using GPC, UV–vis and NMR techniques and its film was characterized by FT-IR, TG, TEM and SEM methods. The influence of Cu(II)-MMT on the drying property of lacquer sap and lacquer film performance such as gloss and thermo-stability were assessed.

2. Materials and methods

2.1. Materials

Montmorillonite was purchased from Tianyu Chemical Co. (Neimenggu, China). Lacquer sap was collected from lac tree *Rhus vernicifera* in China. It contains 27.5% of natural water. Cupric potassium chloride dehydrate ($K_2CuCl_4 \cdot 2H_2O$) was purchased from Wuhan Huashun Co. (Wuhan, China). All other chemicals were of analytical grade.

2.2. Preparation of Cu(II)-MMT

4 g of montmorillonite (MMT) was dispersed in 100 mL distilled water and then the pH value of the suspension was adjusted to 2 with 2 mol/L HNO_3 aqueous solution. After the suspension was stirred with a stirring rate of 300 rpm for 8 h at room temperature, the acid-modified MMT was obtained by filtering the suspension and the product was washed with distilled water and centrifuged 3 times. Then the acid-modified MMT (2 g) was mixed with 200 mL of 1 mol/L $NaNO_3$ aqueous solution and stirred for 8 h at 80 °C. After filtration, the filter residue was washed with distilled water and centrifuged 3 times to obtain sodium-modified MMT (Na(I)-MMT).

1 g of Na(I)-MMT was dispersed in 200 mL of $Cu(NO_3)_2$ aqueous solution (0.05 mol/L). After the clay suspension was stirred for 8 h at 80 °C, it was filtered and rinsed with distilled water to get Cu(II)-MMT. Cu(II)-MMT was dried at 105 °C and ground in an agate mortar to pass through a 200 mesh sieve.

2.3. Preparation of Cu(II)-MMT/lacquer hybrid sap and monitoring of its drying process

Cu(II)-MMT was dispersed into distilled water to form the clay suspension, and the concentration of the suspension was 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%, respectively. Then the lacquer sap was blended with the Cu(II)-MMT suspensions in mass ratios (w/w, 95:5). These mixtures were labelled as CML-1, CML-2, CML-3, CML-4 and CML-5. 5 wt% of MMT suspension was also introduced into the lacquer sap. The resulting sample was labelled as ML. In the experiment, the raw lacquer sap was also mixed with H_2O in the mass ratio of 95:5 as a control and it was recorded as RL. In addition, a cupric potassium chloride (K_2CuCl_4)/lacquer hybrid sap (CPCL) was also prepared by adding K_2CuCl_4 aqueous solution. It contained the same copper content as CML-5.

RL, CMLs and CPCL were coated on glass panes using an applicator with 50 μm clearance gap and dried in a 302A constant temperature and humidity chamber (Shanghai, China). The drying time was measured using an automatic drying time tester. Samples were also obtained from lacquer films and extracted with tetrahydrofuran for GPC test during the drying process.

2.4. Leaching test

2 g of CPCL and CML-5 films were placed in 100 mL of deionized water at room temperature. After 24 and 48 h, the leachate solutions of all samples were filtered. 80 mL of filtrates were concentrated to 10 mL under reduced pressure at 45 °C and 1 mL of 1 mol/L HNO_3 was added. Finally, concentrations of copper were analyzed using a NovAA 300 atomic absorption spectrometer (Analytik Jena, Germany). All the experiments were carried out in triplicate.

2.5. Characterization

The copper content of Cu(II)-MMT was measured using a NovAA 300 atomic absorption spectroscope (Analytik Jena, Germany). 0.1 g of Cu(II)-MMT and 0.3 g of lithium metaborate were mixed in a graphite crucible. After the mixture was melted in a muffle furnace at 950 °C for 20 min, it was dissolved in 50 mL of 0.4 mol/L nitric acid aqueous solution. After dilution to a certain volume, the content of copper was measured.

X-ray diffraction (XRD) data was collected with a Rigaku D/max-2500 diffractometer (Japan), with CuKα radiation running at 40 kV and 100 mA. The scanning range was 2°–80°.

Molecular weight distribution of samples was tested using a GPC on a Simadzu LC-20AD instrument with RID-10A detector (Japan). A TSK G3000-H_{XL} column was used with THF as the eluent at 30 °C. The flow rate was maintained at 1.0 mL/min. Data collection and analyses were made with LCsolution Workstation.

UV–vis spectrum of sample was investigated by a Specord 50 spectrometer (Germany). The sample was coated on the quartz plates using an applicator with 25 μm clearance gap. The film was dried at 23 °C and 65% RH for the first 7 h, and then was transferred into a constant temperature and humidity chamber with 80% relative humidity at 30 °C.

IR spectra of samples were recorded by a Nicolet Avatar 370 FT-IR spectrometer with an iTR™ ATR Accessory (USA). NMR data were recorded on a Bruker AVANCE III 500 MHz NMR spectrometer (Bruker). The samples were dissolved in $CDCl_3$.

TEM images were recorded on a JEM-2100 microscope (Japan). All samples subjected to TEM measurement were embedded in araldite resin, and cut into 80 nm thick sections using a Leica EM UC7 Ultra microtome (Germany) and fixed on copper grids.

The surface morphologies were recorded by a scanning electron microscope Zeiss SUPRA55 (Germany).

The lacquer films (wet coating thickness of 50 μm) were dried at RH 80% and 30 °C for 7 days. Their thermal behavior was tested with a thermogravimetry analyzer (NETZSCH TG209F3, Germany). The samples were heated from 48 °C to 648 °C under N_2 atmosphere, a rise of 10 °C/min.

The gloss of sample films was measured by an XGP20°–60°–85° specular gloss meter (Tianjin, China). Sample films were coated on the tinplates with a wet coating thickness of 50 μm and evaluated after 7 days of curing at RH 80% and 30 °C.

3. Results and discussion

3.1. Cu(II)-MMT

Fig. 1 shows the XRD patterns of the MMT, Na(I)-MMT and Cu(II)-MMT samples. The (001) diffraction peak of MMT appeared at 2θ of