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On the UV-Induced Polymeric Behavior of Chinese Lacquer

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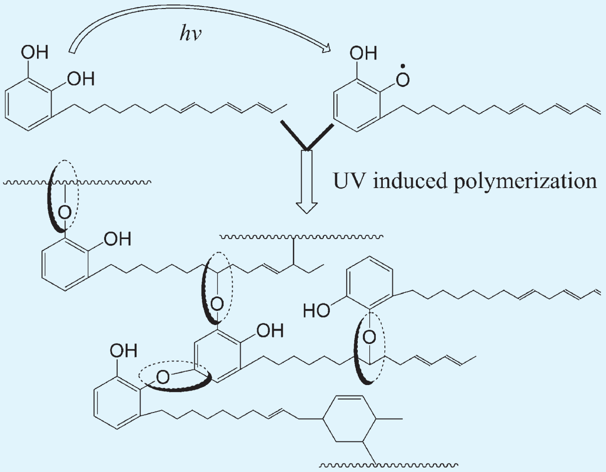
ABSTRACT: To dry Chinese lacquer rapidly for the protection and restoration of archeological findings coated by lacquer or excavated lacquer wares and the development of new application of this lacquer, we carried out UV curing technology to improve its curing rate using a high-pressure mercury lamp as a UV source in the absence of any additional photoinitiator. The effects of mainly specific components in Chinese lacquer sap and the role of each reactive group of urushiol, namely hydroxyl groups, hydrogen on the phenyl ring, and olefins in the side chain, in the course of UV exposure were well-investigated. The UV-cured Chinese lacquer films were also characterized by FT−IR, ^{1}H NMR, SEM, TGA, and Py−GC/MS. The results showed that urushiol was the main component to form Chinese lacquer films, and decomposed to generate the urushiol semiquinone radicals, which sequentially induced the polymerization of Chinese lacquer by radical polymerization, as well as radical substitution under UV irradiation. In addition, the TG analysis suggested that polysaccharide and glycoproteins were integrated with the UV-cured films by covalent bonding. Furthermore, this method could be suitable to fast cure other phenol bearing long aliphatic unsaturated chain, such as CNSL.



KEYWORDS: Chinese lacquer, coatings, UV irradiation, cross-linking, photopolymerization, semiquinone radicals, radical polymerization, pyrolysis

INTRODUCTION

Oriental lacquer with a high gloss and superhigh durability are dried by enzyme-catalyzed process at room temperature, which is a natural, biodegradable, energy-saving coating, as well as an environmentally friendly product and, most importantly, a people-friendly material. In Asia, there are three kinds of lacquer trees, that is *Rhus vernicifera* (China, Korea, and Japan), Rhus succedanea (North Vietnam and Formosa), and Melanorrhea usitate (Thailand and Burma).[1] The lacquer saps are the mixed "blood" flowing out from these trees, and different in quality from the species of lacquer tree, grown region, collection method, and season. The yield of Chinese lacquer adds up to more than 85% in the world, and the processing industry of lacquer in China is pervasive. The facts of the lacquer-coated excavated cultural treasures and/or archeological findings, such as vermilion lacquered wooden bowl,[2] the graves in Ma Wong Dui, and the Chinese Terracotta Army in Lintong,[3] show that Oriental lacquer has been used to coat objects for more than 7000 years in China.

Since the 19th century, many researchers have reported on the sap of the lacquer tree. Research on the chemistry of lacquer was begun through isolation of the sap constituents.[4] Lacquer sap is a very complex mixture including urushiol, glycoproteins (also named plant gum), laccase enzymes, polysaccharides, and water.[5] By now, the main components of the lacquer can be identified and isolated.[6] Urushiol, the main film-forming constituent, is a mixture of three substituted catechol derivatives with $n = 15$ carbon chains bearing 0−3 olefins, with impurities of other minor phenolic liquids such as those having $n = 17$ carbon chains instead of $n = 15$ carbon chains, in which the triene side urushiol makes up to 60−70 wt %.[7] A typical urushiol is shown in Scheme 1A. Laccase enzyme is another important ingredient in lacquer saps. The oriental lacquer films are formed by a laccase-catalyzed oxidation polymerization, following a coupling reaction as well as an autoxidation reaction on the long aliphatic unsaturated side chain.[8−11] In fact, the enzyme-catalyzed polymerization has attracted much interest because it is an energy-saving and environmentally friendly technology.[12−19] The laccase-catalyzed process of oriental lacquer sap is shown in Scheme 1B. However, as laccase is a bioenzyme, to keep its activity, the lacquer drying process requires severe and specific conditions (about 80−90% relative humidity at 20−30 °C).[20] And this procedure needs a long drying period. Additionally, when the laccase is inactivated (we call it dead lacquer), the lacquer can not dry, so these limit the applications of lacquer.

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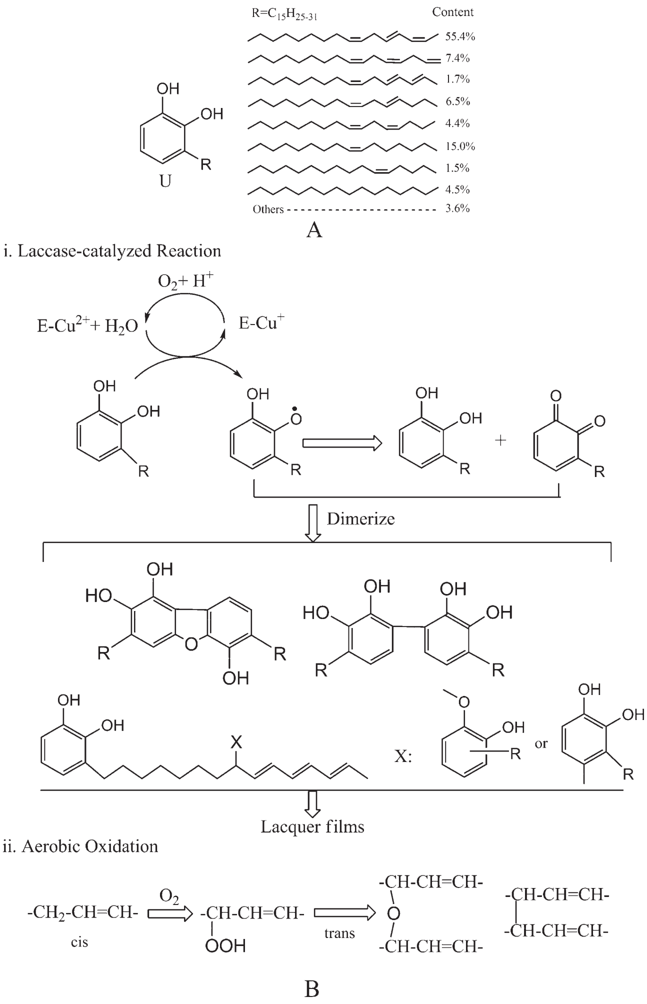
Scheme 1. (A) Structure of Typical Urushiol in Chinese Lacquer, and (B) Schematic Process of Laccase-Catalyzed Oxidation Polymerization of Chinese Lacquer and Autoxidation Reaction on the Long Aliphatic Unsaturated Side Chain



To fabricate fast drying lacquer or to be free of the restriction of relative humidity and temperature, many efforts have been performed in this field. They could be mainly divided into two avenues: one is to improve the drying rate under this condition, in which the activity of laccase is kept; the other is to modify the extraction, e.g., urushiol. Lu et al. have reported a fast drying Chinese lacquer based on raw lacquer sap using a repeated-kurome process.[21] They have found that raw lacquer could dry fast by stirring with additional moisture in the reaction vessel at room temperature and humidity. They also reported a hybridized lacquer by mixing Chinese lacquer with N-(2-aminoethyl)-3-aminopropyl-frimethoxysilane (AATMS) that could be fast dried in low relative humidity environment[22] with good physical properties.[23,24] The alcoholysis between urushiol hydroxyl groups and alkoxy group of organic silanes, as well as the sol—gel reaction of silanes, was believed to promote the autoxidation of the urushiol unsaturated side chain.[25] During the last three decades, Hu and Lin have reported the fabrication of urushiol—metal polymers by making use of the reaction between metal ion and the hydroxyl groups on the phenyl ring of urushiol.[26−33] Free of the restriction of relative humidity and temperature, urushiol—metal polymers could be dried themselves without laccase catalysis. More excitedly, they have the improved excellent properties such as resistance against chemical media, especially against alkali, and thermostability.[34] In fact, the urushiol—metal polymers have achieved industrial production, and been used as a heavy anticorrosive coating in chemical industry in China.[35,36] However, these methods still need a few hours to form lacquer films.

Soon after people were amazed and excited at the first excavations of coated lacquer, they were grateful that these were not only extraordinary archeological findings but also special conservation and restoration challenges.[3,37] Of all these problems, to further improve the drying rate of lacquer saps is of high importance. Previously, we have used UV-curing technology to cure urushiol rapidly, and obtained UV-cured films within 2 min[38]. In this paper, the UV-curing technology was introduced to dry Chinese lacquer quickly by using a high-pressure mercury lamp of 365 nm wavelength as a UV source. Compared with the other methods, the UV-cured Chinese lacquer films could be completely dried within 2 min in the absence of any additional photoinitiator. The effects of mainly specific components and the role of each reactive group of urushiol in the course of UV exposure were well-studied. The UV-induced polymeric behavior of Chinese lacquer was also investigated by FT—IR, ^{1}H NMR, SEM, TGA, and Py—GC/MS.

EXPERIMENTAL SECTION

Materials. Chinese lacquer and cashew nut shell liquid (CNSL) were purchased from the Institute of Lacquer, Xi'an, China. Acetic anhydride, acetone, pyridine, xylene, and absolute ethanol, obtained from Sinopharm Chemical Reagent Co, Ltd., were analytically pure and used without further purification. Palladium carbon catalyst (10 wt %) was supplied by Xukou Reagent Feaduct Factory, Suzhou, China. Dead lacquer in which the laccase is inactivated was obtained by cooking Chinese lacquer sap for 3 h at 60 °C. 94 wt % urushiol was obtained after extraction with ethanol. Glycoproteins, polysaccharide, and laccase were isolated by the method in ref 39. Urushiol acetate (UA), hydrogenated urushiol (HU), and hydrogenated urushiol acetate (HUA) were prepared according to the methods we had previously reported,[40] and HUA was hydrogenated for 3 h.

Measurement. The hardness of the lacquer films were measured with pencil hardness testing, which is one of the methods for the physical characterization of polymer films. The adhesion, flexibility, impact strength of the lacquer films were measured by standard test method (GB1720—79, GB/T1731—93 and GB/T1732—93), which are the test methods for reflecting properties of the UV -cured coatings and some important characterizations of network structure.[41].The gel content method was performed with the following procedure. Gel content is expressed as

$$\text{Gel content} = m_t/m_0 \times 100\%$$

Where m_0 is the initial weight of the film, and m_t is the final weight after extraction with xylene.

FT-IR spectra were obtained by ATR method on a NICOLET5700 FT—IR spectrometer (America-Switzerland). ^{1}H NMR was performed on a 400 MHz Bruker NMR spectrometer (AVANCE III) in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. SEM images of the products were carried out on a JSM-7500F scanning electron microscopy (Japan). The thermo—gravimetric analysis (TGA) was carried out using METTLER TGA/SDTA851 thermo—gravimetric apparatus (Switzerland, Metter—Toledo Inc.) under nitrogen atmosphere with a heating rate of 10 °C/min. The scanned temperature range was from ambient temperature to 600 °C. Pyrolysis GC/MS analysis was carried out using THERMO TRACE DSQ (USA). The MS spectrum was measured by the EI mode at 70 eV. The carrier gas (helium) was flowed at the rate of 1 mL/min using a splitter. The sample was introduced directly into the furnace at 500 °C and the GC was programmed with a heating rate of 20 °C/min from 50 to 280 °C.

Preparation of UV-Cured Films. Chinese lacquer saps were coated on a clean glass slide, and the film thickness was about 25 μm. All the other samples were mixed with xylene to about 50 wt % solution. The xylene solution was dropped on a clean glass slide, and then flowed to form evenly films at room temperature in the air; the film thickness was ca. 25 μm. The samples were continually exposed to a high−pressure mercury lamp of 365 nm wavelength and 2 kW power capacity [GY.UV 2 kW/II(s), Baoding specialty light source electrical equipment factory]; the light intensity at the film surface was 103 mW/cm^2 (UV−A light radiometer, Photoelectric Instrument Factory of Beijing Normal University, China), and the surface was 10 cm from the lamp envelope. All the irradiation experiments have been carried out in the presence of air at 65−70 °C.

RESULTS AND DISCUSSION

UV technology is an eco-efficient and energy-saving process, and the driving forces for future developments of this environment−friendly technology become evident.[41] However, oxygen inhibition reactions of the radical induced polymerization are still a struggle in radiation curable systems, mainly at the surface. In the photoinduced radical polymerization of monomers, the efficiency of cross-linking is due to the efficiency of the propagation step. In the presence of air, the oxygen diradical reacts much faster with the photoinitiator or propagating radical to form a relatively stable peroxy-radical,[42] which does not initiate the polymerization, but rather acts as an inhibitor. This inhibition results in an induction period of the polymerization until all oxygen is consumed.[43] Therefore, the complete polymerization is retarded in thin films and the conversions at the air−coating interface are very low in thicker films. Taguchi and co-author[44] reported in 2007 that when mixing photocuring monomers bearing epoxy, oxetane, or vinyl ether functional groups with urushi lacquer, together with a photocationic initiator, the wrinkled and inner part incompletely cured coatings were obtained by using an unfiltered Hg−Xe lamp (Matsushita ElectricWorks Ltd.; UV-curing system, Pana Cure, ANUP5252L, 250 W) as a UV source. It is generally accepted that a high light irradiance would decrease the oxygen inhibition reactions. The increase in irradiance has been shown not only to increase the rate of polymerization, but also the conversion of double bonds, thus the extent of cure is much higher. This effect has been explained by the increase of the sample temperature at higher irradiance, because of higher heat production of the lamp itself as well as to higher heat of polymerization produced within the short polymerization time, leading to higher mobility and thus higher conversion.[41] Considering all mentioned above and to tackle these disadvantages, we select a rather high light intensity in our experiments.

Curing of Chinese Lacquer. The drying of Chinese lacquer involving laccase-catalyzed polymerization and aerobic oxidative polymerization,[1] which is a slow cross-linking reaction, is a time-consuming and temperature- and humidity-dependent procedure. When Chinese lacquer films (~50 μm) coated on glass substrates were placed in the air about 55−60% relative humidity at 20−26 °C, 48 h later, the hardness of the lacquer films was 2 B, and 15 days later, it was 4 H. A high-pressure mercury lamp (365 nm) was introduced to dry Chinese lacquer fast in this paper. Photo−polymerization of Chinese lacquer films could be roughly confirmed by measuring the hardness of the films immediately after UV irradiation. A few seconds after UV exposure, the film became brown and insoluble in xylene. The hardness (pencil method) of the UV-cured films irradiated for 1 min was B, and it was 4 H after exposure for 2 min. These results proved that Chinese lacquer could be polymerized under UV irradiation more rapidly than polymerized by laccase-catalyzed oxidation. The polymerization of Chinese lacquer could also be proved by FT−IR analysis. Figure 1 shows the FT−IR spectra of UV-cured films of Chinese lacquer irradiated for different time. Concerning a broad peak at 3200−3500 cm^{-1} due to O−H stretching vibration, its intensity gradually decreased with the UV irradiation time, probably owing to the decrease in the number of the hydroxyl group on the phenyl ring of urushiol. A peak at 3012 cm^{-1} ascribed to stretching vibration of the unsaturated group in the side chain decreased significantly at UV curing period, suggesting that urushiol had been cross−linked in the side chain. The crab-leg-like peaks at 1621 and 1595 cm^{-1} in Figure 1A, assigned to the vibration of phenyl ring, had taken place great change during UV irradiation and disappeared in Figure 1D; these were the changes of the vibration of $-C{=}C-$ bonds on phenyl ring, because of the formation of dimers or polymers. The peak at 1644 cm^{-1} in Figure 1A−D, assigned to urushiol quinones, was shifted to 1710 cm^{-1} in Figure 1E−G, and become broader, indicating that more urushiol quinones were appeared, and that the Chinese lacquer could be almost perfectly cured after irradiated for 2 min. The several peaks at 1360−1100 cm^{-1} have greatly changed at UV curing period; the peak at 1354 cm^{-1} due to β_{O-H} was rapidly disappeared, and the peaks at 1280 and 1189 cm^{-1} due to γ_{O-H} have rapidly decreased with the increasing of irradiation time, because of the formation of dimers and polymers. The peak at 1087 cm^{-1} due to ν_{C-OH} stretching vibration rapidly decreased with the increase of exposure time, and a peak at about 1205 cm^{-1} assigned to aromatic ether vibration became stronger and broader; these indicated that more aromatic ether bonds were performed in the process of UV irradiation. Concerning several peaks in 1000−600 cm^{-1} at UV curing period,

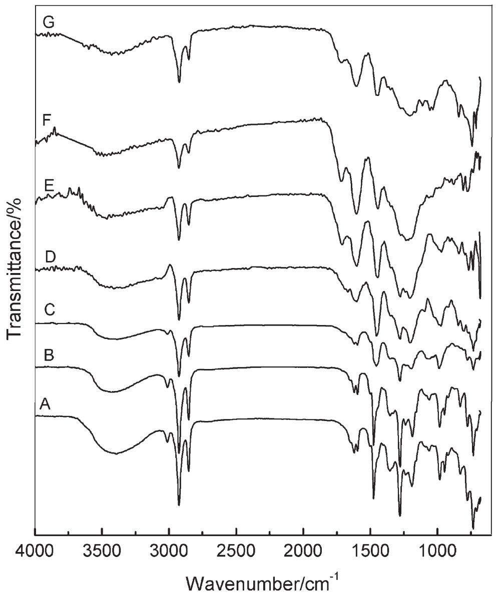


Figure 1. FT−IR spectra of UV-cured Chinese lacquer films irradiated for different times: (A) 0, (B) 30, (C) 60, (D) 90, (E) 120, (F) 150, and (G) 180 s.

the peaks at 982 and 945 cm^{-1} ascribed to the conjugated group obviously decreased; and the peak at 970 cm^{-1} ascribed to trans–olefin appeared in Figure 1D, E, and then disappeared in Figure 1F, G. The disappearance of distinctive absorption peak at 920 cm^{-1} demonstrated the polymerization of –C=C– bond in the end of the side chain; these also proved that urushiol had been cross–linked in the side chain. The decrease of the peak at 730 cm^{-1} and the increase of the peak at about 840 cm^{-1} suggested that more substituted groups are performed on the phenyl ring[20]. All these results clearly proved that UV irradiation was an effective technique to dry Chinese lacquer within 2 min. All the above results show the formation of urushiol quinones and aromatic ether, the cross-linking in the side chain, and the change of the number of substituted group on the phenyl ring under UV irradiation. The UV-induced polymerization was further confirmed by ^{1}H NMR analysis. For the completely cross-linked polymers were insoluble in any organic solvents or water, the incompletely cured urushiols were investigated in this experiment, and even so, only a part of urushoil oligomers was soluble in $CDCl_3$. The ^{1}H NMR spectra of urushiol irradiated for different time are shown in Figure 2. The protons of the –CH=CH–CH=CH– bonds were detected at about 5.6–6.4 ppm with three peaks (Figure 2A). However, these peaks weakened in Figure 2B,C, and decreased with the increase in exposure time, implying that the polymerization occurred in the side chain of urushiol.

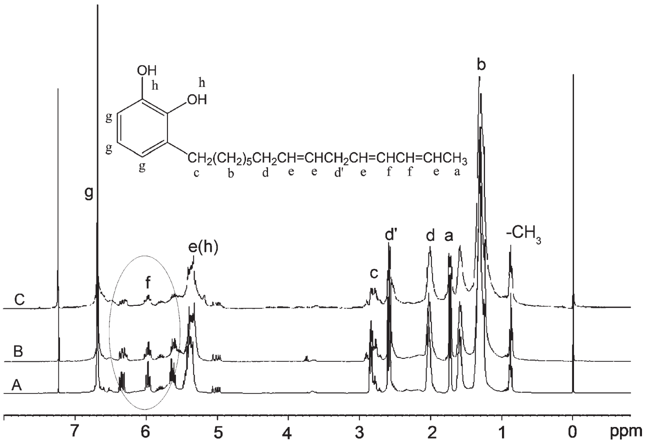


Figure 2. ^{1}H NMR spectra of urushiol irradiated for different times: (A) 0, (B) 30, and (C) 50 s.

Typical SEM images of UV-cured films of Chinese lacquer are shown in Figure 3A and B. For comparison, Figure 3C and D represent the SEM images of Chinese lacquer films dried by laccase–catalyzed polymerization at about 60% relative humidity and ambient temperature for 15 days. As can be seen from Figure 3, porous structure, formed by the constantly absorbed water in the polymeric matrix[45] and the marks of waterdrops in the lacquer sap[21], was the main morphology of the laccase-catalyzed Chinese lacquer films, whereas no porous morphology was found in the

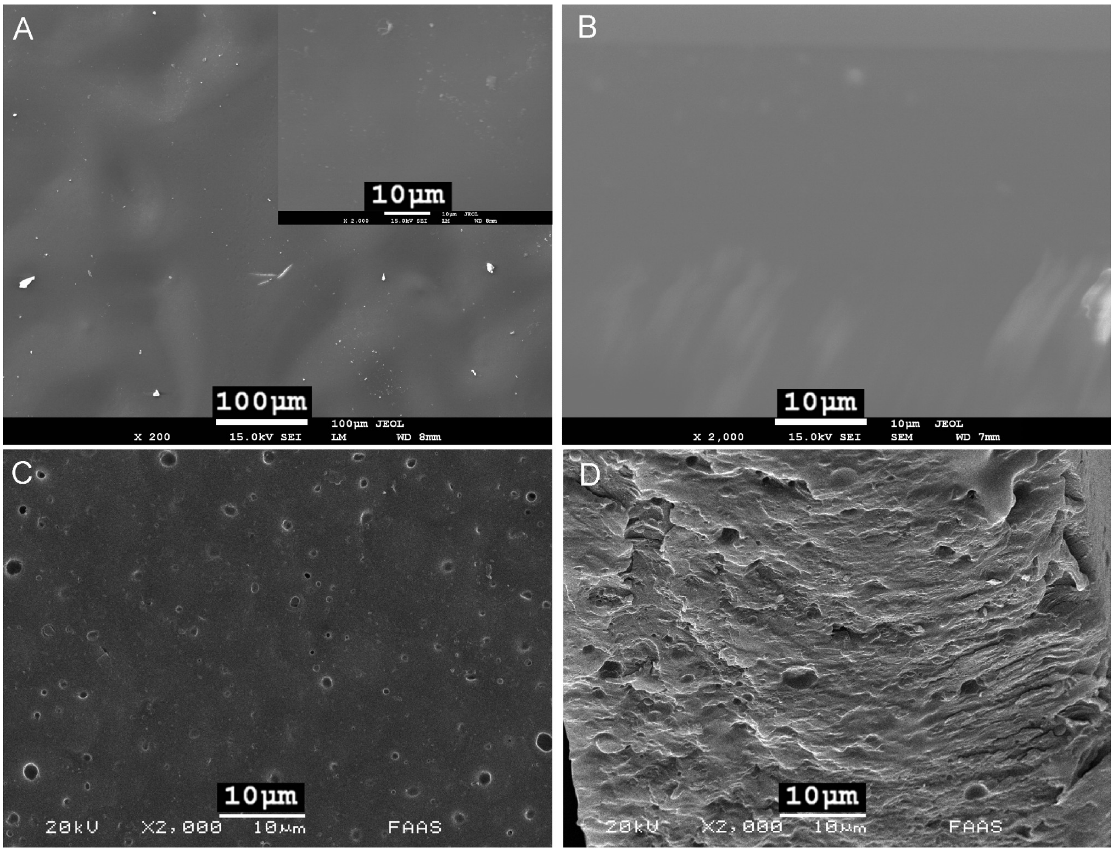


Figure 3. SEM images of (A) surface morphology of the UV-cured Chinese lacquer film irradiated for 90 s, on which the minute wrinkles were observed, and the inset is a high-magnification image; (B) cross-sectional morphology of the UV-cured Chinese lacquer film irradiated for 90 s, the inner part of which was also completely cured, and no porous morphology was found in the film; (C) surface morphology of Chinese lacquer films dried at about 60% relative humidity and ambient temperature for 15 days; and (D) cross-sectional morphology of Chinese lacquer films dried at about 60% relative humidity and ambient temperature for 15 days.

Table 1. Effect of Different Constituents in Chinese Lacquer on UV-Induced Polymeric Behavior

	samples					
irradiation time/s	Chinese lacquer	urushiol	urushiol + polysaccharide	urushiol + glycoproteins	urushiol + laccase	glycoproteins/polysaccharide/laccase
30	not drying	not drying	not drying	not drying	not drying	scorched
60	brown film	brown film	brown film	brown film	brown film	scorched
120	dark film	dark film	dark film	dark film	dark film	scorched

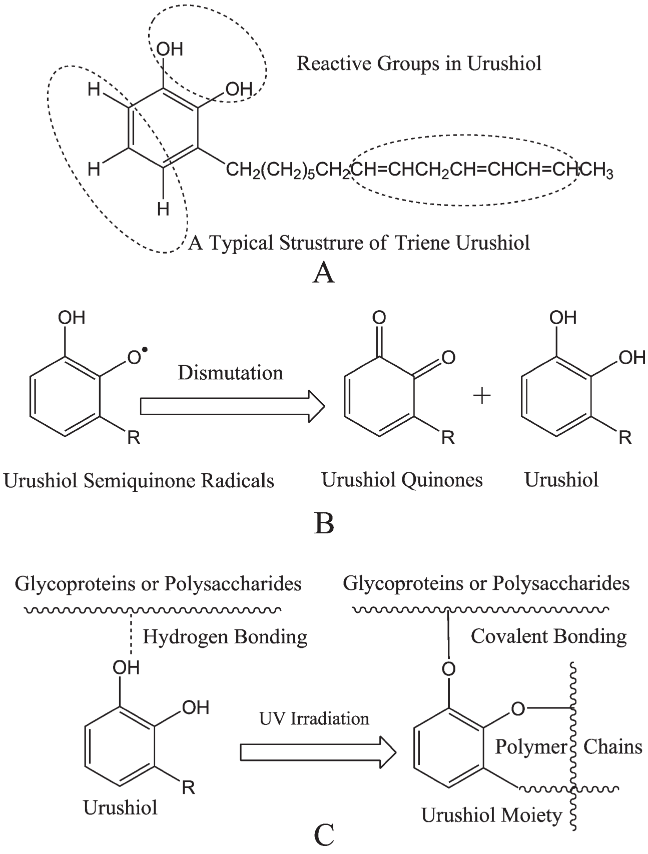


Figure 4. (A) Reactive groups on urushiol (in the dashed circle loop), (B) dismutation of urushiol semiquinone radicals, and (C) transformation from hydrogen bonding into covalent bonding between urushiol and glycoproteins or polysaccharides in the course of UV exposure.

Table 2. Effects of Reactive Groups on the Gel Content Value after Different Exposure Time

	gel content (%)								
irradiation time (s)	urushiol	HU1	HU2	HU3	HU4	HU20	UA	HUA	CNSL
30	0	0	0	0	0	0	0	0	0
50	26.3	17.5	10.9	0	0	0	0	0	6.1
60	100	98.4	88.1	36.7	34.1	28.5	26.7	3.2	15.3
90	100	100	98.1	46.6	43.6	35.5	39.6	8.8	43.9
120	100	100	100	100	100	100	100	15.8	100

UV-cured films. These may be caused by fast curing of urushiol and rapid evaporation of water in Chinese lacquer during UV irradiation period. Also, minute wrinkles were observed on the surface of UV curing films (Figure 3A), which was presumably ascribed to the existence of the retarded polymerization between the surface and the inner part of the film, and could be transformed into glossy smooth surface by adding hydrogenated urushiol.[40] As Taguchi and co-author reported,[44] when mixing photocuring monomers bearing epoxy, oxetane, or vinyl ether functional groups with urushi lacquer, together with a photocationic initiator, the wrinkled and inner part incompletely cured coatings were obtained. However, the inner part of the film was also completely cured in our experiments (Figure 3B). The results of SEM analysis showed that both the outer and inner part of the Chinese lacquer films could be completely cured under UV irradiation within 2 min.

It should be noted that Chinese lacquer is a mixture of urushiol, glycoproteins, polysaccharide (or named Plant gum), and laccase, together with other minor ingredients. Therefore, to identify the influence of mainly specific components, we isolated the constituents, and then made them or their mixture irradiated under UV light. Table 1 shows the effect of different constituents in Chinese lacquer on UV-induced polymeric behavior. As can be seen from Table 1, the sample of urushiol could be cured under UV irradiation within 2 min. In addition, the samples of urushiol + polysaccharide, urushiol + glycoproteins, and urushiol + laccase, together with Chinese lacquer, could also be dried under this condition. However, the samples of single glycoproteins, polysaccharide, or laccase and their mixture would become carbonized and/or scorched after exposure to UV light for 30 s. With further investigating the mixture of the components, it was found that only samples containing urushiol would be cured completely within 2 min, otherwise, they would become carbonized and/or scorched. Obviously, urushiol was the necessary and sufficient components to form cured films of these samples. All these proved that urushiol was the main component to form films in Chinese lacquer under UV irradiation.

Urushiol, the basis of Chinese lacquer, is a mixture of three substituted catechol derivatives with $n = 15$ carbon chains with 0−3 olefins, so it has three reactive groups, namely two hydroxyl groups on the phenyl ring, hydrogen on the phenyl ring, and olefins in the side chain (see Figure 4A). To determine the function of each reactive group in the course of UV exposure, urushiol was reacted with acetic anhydride to terminate hydroxyl groups, and hydrogenated urushiols with varying degrees were fabricated in this experiment. Among various measurements concerning coatings, gel content play an important role in the characterizations of relative structure, especially to those which could not be soluble in any organic solvents or water. The measured values corresponded to the different samples are summarized Table 2. Considering the urushiol sample, it could be cured after irradiating for 60 s, whereas there was a relatively long induced period before 50 s. This was assumedly due to the formation of urushiol quinones by dismutation to consume urushiol semiquinone radicals (see Figure 4B), which were the mainly reactive species to induce polymerization of urushiol-radical polymerization. At the same time, the high gel content values were measured in the HU1 and HU2 samples hydrogenated for 1 and 2 h, respectively, and a gradual decrease in gel content was observed with the increase in hydrogenation time. When urushiol was hydrogenated for 3 h, the C=C bond in the side chain would be most hydrogenated. For it is well-known that the C=C bond is one of the bases of photo−polymerization of the monomers, as expected, the gel content values were sharply decreased after hydrogenating for 3 h or late. Compared with the gel content value of CNSL sample, the sample HU4, even hydrogenated for 4 h, had almost the same gel content value, which added up to 43.6% after irradiating for 90 s. This was estimated to be induced by radical substitution. While when the hydroxyl groups were terminated with acetic anhydride, the gel content value of UA sample only reached to 39.6% after irradiating for 90 s. All these results showed that the hydroxyl groups of urushiol, as well as the C=C bonds in the side chain, were an important role to induce the polymerization. It was interesting to find that the HUA still had some gel content value, and all of the samples could be completely cured after exposure for 2 min, except for HUA.

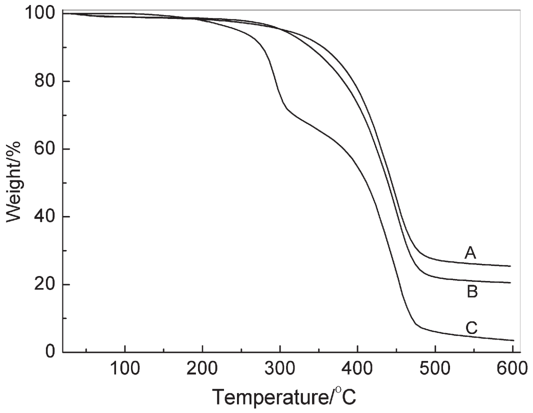


Figure 5. TGA curves of (A) the UV-cured Chinese lacquer film irradiated for 120 s, (B) irradiated for 90 s, and (C) lacquer films dried at about 60% relative humidity and ambient temperature for 15 days.

Thermal Property of the UV-Cured Chinese Lacquer Films. It is believed that the laccase-catalyzed Chinese lacquer films have excellent thermo−stability. If matches with spark after burning are placed on the lacquer-wares coated by Chinese lacquer, they can not damage the lacquer films. To investigate the thermal stability of the UV-cured Chinese lacquer films, we used TGA to trace the degradation process of the UV-cured films. Figure 5 presents the TGA curves of (A) the UV-cured Chinese lacquer film irradiated for 120 s, (B) irradiated for 90 s, and (C) lacquer films dried at about 60% relative humidity and ambient temperature for 15 days. The gradual weight loss of the UV-cured films both irradiated for 120 s and for 90 s (Figure 5A, B) was about 3.5% before 300.0 °C. This was due to the evaporation of residual urushiol oligomers. Compared with the TGA curve of the UV-cured films (Figure 5A, B), the gradual weight loss of the lacquer film (Figure 5C) was about 6.5% before 278.0 °C, and the TGA curve of the laccase-catalyzed Chinese lacquer films could be mainly divided into two stages. The first stage was from 278.0 to 304.0 °C (weight loss was 21.3%). This might be caused by the thermal degradation of the not completely cross-linking urushoil oligomers, and because of decomposition of other constituents, such as glycoproteins and polysaccharide, which exited in Chinese lacquer through hydrogen bonding, as reported by Kumanotani[45] (see Figure 4C). The second weight loss in the range of 409.0−471.7 °C (weight loss was about 49.8%) was ascribed to the decomposition of polymer. However, there was only one stage thermal degradation in the curves of the UV-cured films. This revealed that urushiol was completely cross−linked and glycoproteins, together with polysaccharides, were integrated with urushiol polymer by covalent bond during the course of UV exposure (see Figure 4C). Additionally, the residual mass of the UV-cured films irradiated for 120 s, 90 s, and the laccase-catalyzed Chinese lacquer films at 500.0 °C was 27.6%, 22.4%, and 5.8%, respectively, indicating that the UV-cured films had more excellent thermostability than that of laccase-catalyzed lacquer films.

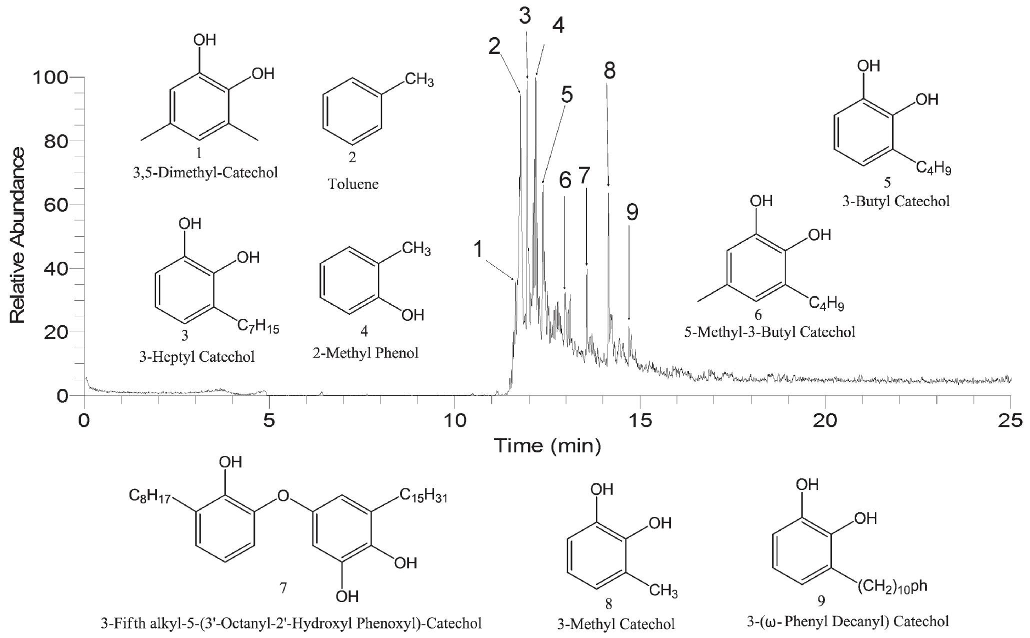
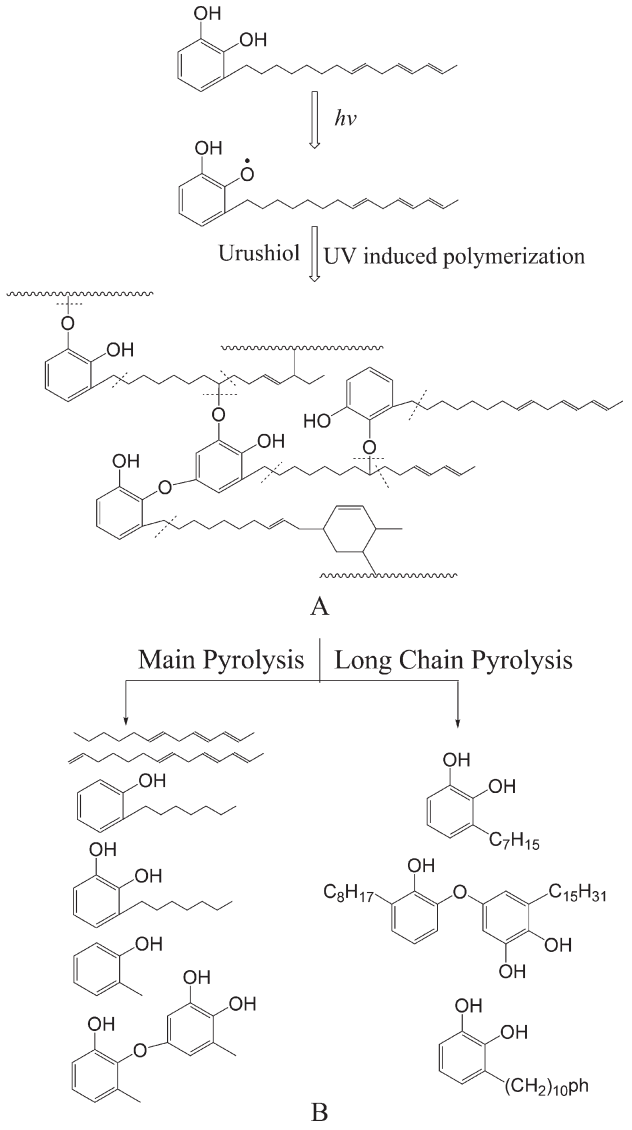


Figure 6. Total ion chromatograms (TIC) of the pyrolysis GC/MS measurement of the UV-cured urushiol lacquer films irradiated for 2 min, and insets are the pyrolyzed compounds assigned by their mass fragmentations.



Scheme 2. (A) Estimated Formation of UV-Cured Chinese Lacquer Films and (B) Pyrolysis Process of UV-Cured Films

Py−GC/MS Analysis of the UV-Cured Urushiol Films. Pyrolysis−gas chromatography/mass spectrometry (Py−GC/MS) is one of a fast technique to characterize the cross−linking materials, especially to those insolubly complex structure polymers.[46−49] Therefore, it may be considered as an effective method to identify and characterize the structure of oriental lacquer films, and to estimate the drying mechanism. Figure 6 represents the total ion chromatograms (TIC) of the py−GC/MS measurement of the UV-cured urushiol films irradiated for 2 min. The compounds illustrated in Figure 6 were assigned by their mass fragmentations. Many absorptions due to catechol derivatives appeared in TIC. The appearance of two absorptions at 11 min 36 s (no. 1) and 13 min (no. 6) due to 3,5-dimethy catechol and 5-methyl-3-butyl catechol, respectively, suggested that urushiol might be substituted at the 5-position, which might be caused by radical substitution or by radical coupled termination. The three peaks at 11 min 57 s (no. 3), 12 min 23 s (no. 5), and 13 min (no. 6), assigned to 3-heptyl catechol, 3-butyl catechol, and 5-methyl-3-butyl catechol, respectively, suggested that the polymerization mainly occurred on the side chain on the phenyl rings of urushiol. The absorption at 13 min 34 s (no. 7) ascribed to 3-fifth alkyl-5-(3′-octanyl-2′-hydroxyl phenoxyl) catechol demonstrated the radical substitution between phenoxyl radical and urushiol. The pyrolysis process of UV-cured films is schematically shown in Scheme 2B.

Estimated Mechanism. The results from the influence of mainly specific components in Chinese lacquer and the role of each reactive group in the course of UV exposure showed that urushiol was the main component to form films in Chinese lacquer under UV irradiation, and that three reactive groups, namely two hydroxyl groups, hydrogen on the phenyl ring, and olefins in the side chain, contributed to polymerization. When the hydroxyl groups were terminated with acetic anhydride, the polymeric rate sharply decreased. Our previous research had found that there was an intense radical signal in the ESR spectra, which was deemed to be urushiol semiquinone radicals,[38] and that the oxygen content of the films did not increase considerably, suggesting that they were not polymerized through an aerobic oxidative mechanism, as could be one of the film-forming process in the laccase-catalyzed Chinese lacquer films. The FT-IR spectra observed the increasing absorptions of aromatic ether bonds and multisubstituted phenyl rings with the increasing of exposure time. All these showed that hydroxyl groups on the phenyl ring was decomposed to generate the phenoxy radical, which then attacked the C=C bonds in the long aliphatic unsaturated side chain to form polymer by radical polymerization, or attacked phenyl nucleus to form polymer through radical substitution. When the C=C bonds in the long aliphatic unsaturated side chain of urushiol have been gradually hydrogenated, the latter become increasingly dominant, and this was the reason why the curing rate decreased with the increase of hydrogenation time. In all, the UV-induced polymerizations were estimated in Scheme 2A. In fact, the chemistry of these formations is more complex than the given reactions in the scheme.

It is worth noting that the alternative and fast curable technology could also be used to dry dead lacquer, urushiol-based polymers, urushiol−metal polymers,[33] together with other phenol derivatives containing long aliphatic unsaturated chain such as CNSL, and they could be rapidly dried within 2 min without additional photo−initiator. Additionally, the as-prepared UV-cured Chinese lacquer films had excellent properties. The adhesion, flexibility, impact strength of Chinese lacquer films formed by laccase-catalyzed oxidation polymerization in the air about 55−60% relative humidity at 20−26 °C for 15 days were 2°, 0.5 mm, and 12 cm, whereas they were 1°, 0.5 mm, and 50 cm, respectively, in the UV-cured Chinese lacquer films. Also, the UV-cured films had improved resistance against chemicals and solvents than that of laccase-catalyzed films. So the as-reported method is an effective way to obtain Chinese lacquer films with good properties. This will further improve the application environment of Chinese lacquer.

CONCLUSIONS

The Chinese lacquer films were fabricated by using UV irradiation as a fast cured technology, and the films with completely cross-linking structure and nonporous morphology could be formed within 2 min in the absence of any additional photoinitiator. It was found that urushiol was the main component to form Chinese lacquer films, which was decomposed to generate the phenoxy radicals—urushiol semiquinone radicals that were responsible for the film-forming in the course of UV exposure. Furthermore, the phenoxy radicals produced were considered to attack the unsaturations of side chain to promote the curing process by radical polymerization, as well as to attack phenyl nucleus through radical-substituted polymerization. Different from the polymerization of laccase-catalyzed oxidation, these reactions did not involve the aerobic oxidative polymerization, and glycoproteins, together with polysaccharides, existed in UV-cured Chinese lacquer films through covalent bonding.

Free of the restriction of relative humidity and temperature, this fast curable technology would bring bright and significant prospects in the field of the protection and/or restoration of archeological findings coated by lacquer or excavated lacquer wares and the new application of this lacquer. Additionally, the dead lacquer, urushiol-based polymers, together with other long aliphatic unsaturated chain phenol derivatives such as CNSL, could also be rapidly dried within 2 min by using this method without an additional photoinitiator.

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