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pH-dependent warping behaviors of ancient lacquer films excavated in Shanxi, China

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Abstract

The ancient lacquer films excavated from Dongshan Han tomb M6 of the Western Han Dynasty in Taiyuan City, Shanxi, China, were found sensitive to pH variation. This paper aims to demonstrate the pH-dependent warping behaviors of the ancient lacquer film and discuss their mechanism. The samples were analyzed by surface analytical techniques including attenuated total reflectance-Fourier transform infrared spectroscopy and X-ray photoelectron spectrometry. The results suggest that the outer layer of the lacquer film is more oxidized than the inner layer and contains more carboxylates, with calcium ions and possibly ammonium cations as counter ions. The carboxylates are speculated to be formed by oxidative cleavages in the urushiol side chains and hydrolysis of glycerides of drying oils. The shrinkage and swelling of the lacquer film can be regulated by the type of cations (H^+ , Ca^{2+} , Na^+) of carboxylates through hydrogen bonds, coordination bonds and static forces. Due to the higher content of carboxylates in the outer part, it shrinks more at low pH causing warping outward and swells more at high pH causing warping inward. This paper may provide an important reference for pH control and help resolve the warping problem during conservation or restoration of ancient lacquerware.

Keywords: Ancient lacquer, pH-dependence, Warping behaviors, Carboxylates, Oxidation, XPS, ATR-FTIR

Introduction

Natural lacquer or urushi was an important natural resource for coating and adhesion in ancient times. The lacquer sap from lacquer tree (*Toxicodendron vernicifluum*) usually contains urushiol (60–65%), plant gum (5–7%), glycoprotein (2–5%), laccase enzyme (1%) and water (20–25%) [1], which together form a reverse micelle emulsion. When exposed to oxygen in the air, urushiol is oxidized with the help of laccase and starts to form polymeric network, resulting in an enduring and aesthetic lacquer film. For such merits, lacquerware was used by ancient people in the east Asia. The earliest lacquerware dating back to about 8000 years ago or even earlier was found at Kuahuqiao site [2] and Jingtoushan site [3], Zhejiang Province, China. Since the Warring States period,

the production of lacquerware became systematic on a large scale and had produced in large quantities [4]. Therefore, a large amount of lacquerware has been excavated and is requiring protection and restoration. It is then of necessity to understand the preservation states of ancient lacquerware. However, previous studies mostly focus on the technological aspects of ancient lacquers [5–8] such as layered structures, pigments, ground layer additives and the addition of drying oils. For example, the quantification methods of urushiol and drying oils have been established based on infrared spectroscopy, near infrared spectroscopy and pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) [9–11]. The degradation of lacquer film is less noticeable compared to the technological features as lacquer is well-known for its durability, but also inevitable.

Studies have found that ultra-violet can easily cause photo-degradation of lacquer films, accompanied by the increase in oxygen content and polar groups such as C=O, C–O–C and C–OH [12, 13]. Isomers

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of mono-, di-, tri-, and tetra-carboxylated benzene are identified to be products of the photo-degradation process [14]. After polymerization, the reverse micelles of the lacquer sap are kept in lacquer films as aggregates of them [15]. Larger polysaccharide particles are dispersed in urushiol particles coated with polysaccharides and glycoproteins [16]. Because of such structures, Ju believes that the oxidation process mainly takes place in the side chains of urushiol, polysaccharides and glycoproteins outside urushiol aggregates [17]. Cracks and pits are morphological signs formed as a result of photo-degradation [12, 18], which further cause a rougher surface, loss of gloss and mechanical strength [13, 19]. Although the present investigations into the photo-degradation of lacquer films have provided much information, the degradation of lacquer films buried underground poses more challenges. Tamburini found that relative high abundances of alkylcatechols and acid catechols in archaeological urushiol lacquer samples from Sichuan, China, suggesting photo-degradation is not the only cause and the degradation processes undergone by the lacquer with time [20]. The acidic degradation products may probably alter the chemical properties of the lacquer films, resulting in the ion exchange capability.

It was recently found that some ancient lacquer film samples are extremely sensitive to pH variation and consequently display different warping directions. These lacquer film samples were obtained from the excavation of Dongshan Han tomb M6 in Taiyuan City, Shanxi Province, China. This tomb is a typical wooden noble tomb of the Western Han Dynasty (202BC–8AD) in northern China. Because of the temperate continental climate, the soil provides a more aerated and drier but still wet burial environment compared to the waterlogged anoxic archaeological sites in southern China, which favors oxidation processes and biological decays. The chemical investigation in the wooden objects from this tomb shows that considerable amounts of carboxylic acids or calcium carboxylates were formed [21]. It is suspected that the lacquer films in this tomb may have also experienced severe oxidation and contain some carboxylic acids or calcium carboxylates, which grant themselves sensitivity to pH variation. This paper intends to investigate the chemical alterations of these ancient lacquer films caused by oxidation and discuss the degradation mechanism and its relationship with the warping behaviors, to provide an important guidance for properly treating deteriorated lacquer films excavated from oxidative environments during conservation or restoration.

Material and methods

Materials

The ancient lacquer samples were collected during the excavation of Dongshan Han tomb M6 in Taiyuan City, Shanxi, China. These samples were fragments of the black lacquer coffin in the tomb without any decoration. The ground layer of the lacquer film was removed by polishing it on a carborundum disc when necessary.

Observation of warping behaviors

The samples for observation of warping behaviors were at least 10 mm in length and width and the following process were repeated for 5 times. The samples were immersed in deionized water, 0.1 M HCl solution (pH1.0), and 0.1 M NaHCO₃ (pH8.3) solution successively. And the warping behaviors were observed under stereomicroscope (LEICA M80). The strong acid as 0.1 M HCl solution was chosen for demonstration because it did not cause extensive warping of lacquer films and meanwhile can completely protonate the carboxylates and release Ca²⁺ so that the equilibrium was easy to reach. 0.1 M NaHCO₃ solution was chosen for demonstration because it is a weak alkali commonly used in conservation and can already cause extensive warping of the research samples. The time durations of each immersion phase were selected based on observation of evident changes. The acidified samples for the following analysis were immersed in 0.1 M HCl solution for 24 h, rinsed in deionized water and dried naturally.

Preparation of the cross-section of the lacquer film

A small piece of lacquer film was embedded in epoxy resin, cut by microtome (Microm HM325), observed and recorded by Olympus BX53 microscope.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

The external and internal surfaces (after removing the ground layer) of the ancient lacquer films were analyzed by attenuated total reflectance-Fourier transform infrared spectroscopy (PerkinElmer Spectrum Spotlight 200) with a range from 4000 to 650 cm⁻¹, 4 cm⁻¹ resolution and 128 accumulation times.

X-ray photoelectron spectrometry

The external and internal surfaces (after removing the ground layer) of the ancient lacquer films were tested by X-ray photoelectron spectrometer (AXIS Supra from Kratos Analytical Ltd.) using mono Al source (150 W, 10 mA emission current) with a minimum analyzed area of 15 μm × 15 μm to acquire the elemental

compositions and oxidation states of carbon and nitrogen atoms. For survey spectra, the pass energy was 160 eV, energy steps 1.000 eV and dwell time 50 ms. For spectra of a particular element, the pass energy was 40 eV, energy steps 0.100 eV and dwell time 100 ms. The XPS spectra of C 1s region were analyzed by XPSPEAK software for deconvolution. The Shirley type background subtraction and Gaussian fitting were adopted. The FWHM was constrained between 1.3–1.7 eV, and peak positions of four kinds of carbon atoms were constrained at or between 284.80 eV, 286.20–286.30 eV, 287.90–288.10 eV, and 288.90–289.10 eV, respectively.

Results and discussion

Swelling and warping behaviors of the ancient lacquer film

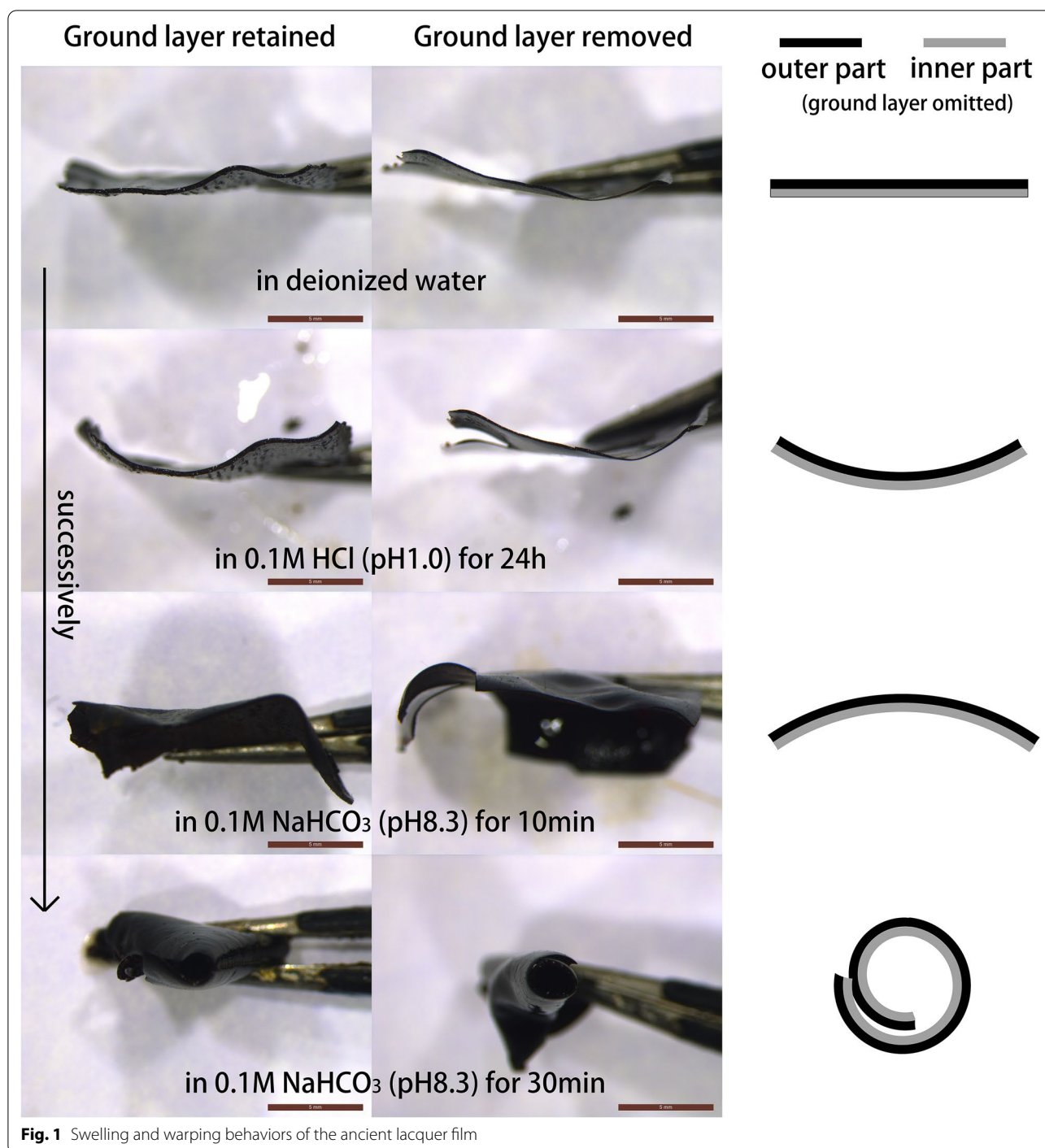
As shown in Fig. 1, the lacquer films became mildly warped outward when immersed in 0.1 M HCl solution for 24 h. They then turned warped inward after immersed in 0.1 M NaHCO₃ solution for just 10 min and continued to warp like scrolls within 30 min. As shown in Fig. 2, the lacquer film has a multilayer-structure consisting of an outer layer, an inner layer and a ground layer. After removing the ground layer, the lacquer film sample displayed consistent warping behaviors as those of the sample with the ground layer (as shown in Fig. 1). This suggests that the main cause of the warping behaviors originate from the lacquer layers, though the ground layer would at least mechanically reduce the extent of warping. When treated with acid, the outward warping implies that the outer part swelled less than the inner part. But when treated with alkali, the two parts behaved reversibly, indicating a distinction in chemical compositions. However, the outer part and the inner part of the lacquer films that cause the warping behaviors may and may not exactly correspond to the morphological bilayers. It is worth noticing that the lacquer films are more sensitive to alkali than acid, considering the relative strength of 0.1 M HCl and 0.1 M NaHCO₃. It can be speculated that these lacquer films are prone to be negatively charged or deprotonated.

Chemical differences within the lacquer film

ATR-FTIR analysis was applied on both the external surface and the backside (internal surface) of the ancient lacquer film after the ground layer was removed. Shown in Fig. 3, the spectra of both the original external and internal surfaces display strong absorption bands at 1574 cm⁻¹ and 1403 cm⁻¹, which are probably assigned to the asymmetric and symmetric stretching vibrations of carboxylate groups. Those two absorptions in the spectrum of the internal surface are less pronounced than those in the spectrum of original external surface with reference to the absorption of aromatic rings at

1630 cm⁻¹. To confirm the abundance of carboxylate groups, samples were acidified by 0.1 M HCl solution and also tested by ATR-FTIR. The absorption bands at 1574 cm⁻¹ and 1403 cm⁻¹ disappear. And a new absorption band at 1705 cm⁻¹ assigned to the stretching vibration of C=O appears. Such changes in the spectra confirm the presence of a large amount of carboxylates in the original lacquer film and carboxylic acids in the acidified one. In terms of the difference between the two layers, the absorption band at 1705 cm⁻¹ in the spectrum of the acidified internal surface is less pronounced than that in the spectrum of acidified external surface with reference to the absorption band of aromatic rings at 1630 cm⁻¹. Therefore, the outer layer of the ancient lacquer film contains more carboxylates than the inner layer. The carboxylate groups may have two sources, i.e. the oxidation of the lacquer and/or the presence of an oxidized drying oil. Further research is required to determine the exact source.

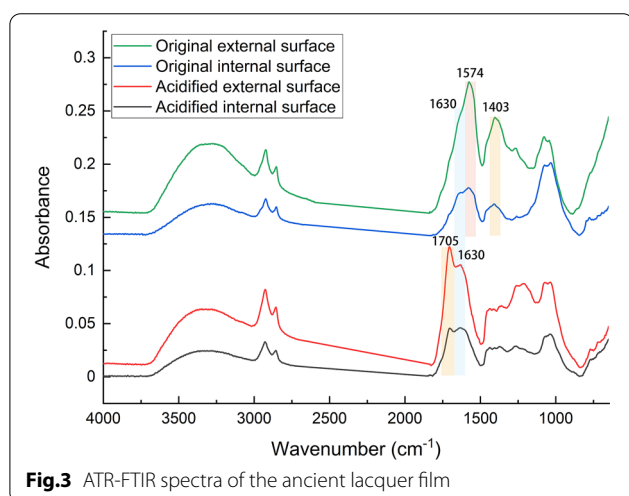
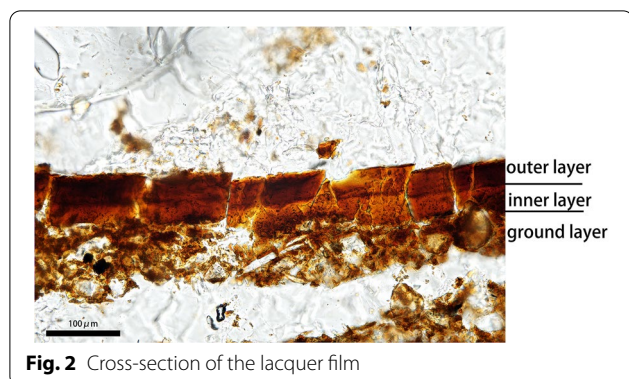
XPS analysis was adopted to investigate the difference in oxidation states between the external and internal surfaces. Because carbon atoms in COO⁻ groups have similar binding energies to those in C=O groups and may cause misidentification, only the acidified lacquer films are selected for tests of C 1s regions. Shown in Fig. 4, the XPS spectra of C 1s regions contain 4 deconvoluted peaks corresponding to four types of carbon atoms (C1–C4). The assignment of C1–C4 are summarized in Table 1 according to [22]. The C1 corresponds to a carbon atom bound by other hydrogen and/or carbon atoms. The C2 corresponds to a carbon atom bound to a single non-carbonyl oxygen atom. The C3 corresponds a carbon atom bound to a carbonyl oxygen atom or two non-carbonyl oxygen atoms. The C4 corresponds a carbon atom bound to a carbonyl oxygen atom and a non-carbonyl oxygen atom. The relative contents of the oxidized carbon atoms, including C2, C3 and C4 are obviously higher in the external surface than the internal surface, which suggests that the external surface contains more hydroxyl, carbonyl and carboxylic groups and is more severely oxidized. On the other hand, the addition of more drying oil will result in different features when compared to the current spectra. Since strong absorptions of carboxylate salts present in the FTIR spectra of the original samples, it can be inferred that the glycerides of a drying oil have already hydrolyzed if assuming the dry oil present. The C2 and C3 do not present themselves in the unoxidized hydrolyzed drying oil. As drying oils share a similar chemical structure as the urushiol side chains, the relative contents of C2 or C3 during the oxidation of both substrates can be hardly increased by a higher content of the drying oil. Besides, applying a thick layer of lacquer



sap would cause corrugation after curing and thus the multilayer technique is a way of increasing the thickness of black lacquer films. There is no reason to infer the bilayers in the research samples contain different contents of a drying oil. Therefore, the difference in the oxidation states of the carbon atoms within the lacquer films are mainly attributed to the oxidation difference

during the burial, which presumably accounts for the majority of the carboxylates.

Cation contents information are also given by XPS analysis. The elemental results based on XPS in Table 2 suggest that Ca^{2+} is a cation of the carboxylates. Ammonium cations are suspected to be another kind of cations based on the following facts. First, the unexpected high



nitrogen contents (2.9–5.9%) in the lacquer films cannot be solely attributed to the nitrogen atoms in the glycoproteins or enzymes from lacquer sap. Second, as the acidified lacquer samples shows comparable or even higher nitrogen contents than the original lacquer samples, the

nitrogenous compounds or moieties cannot be removed by acidic solution and are thus probably incorporated into the lacquer substrate. Third, the ratio of C4 atoms to Ca are obviously over 2, which suggests that Ca^{2+} are not the only type of cations. At last, XPS spectrum of N 1s region of the lacquer film (shown in Fig. 5) only includes one peak at 399.9 eV, suggesting the nitrogen atoms are all in a reduction state, possibly being amine and amide. Therefore, the cations of carboxylates probably include both calcium and ammonium cations.

Oxidative cleavage

Acid catechols, identified by Py-GC/MS and termed by Schilling, et al. [11], are a typical homologous series of compounds considered to be formed by aging and oxidation. In aged urushi reference sample and many ancient samples, the most abundant species of acid catechols are usually identified as methyl-8-(2,3-dimethoxyphenyl) octanoate (mazzeic acid) and methyl 7-(2,3-dimethoxyphenyl)heptanoate (kumanotanic acid) [8, 9, 11, 20, 23]. It can be inferred from these acid catechols that the oxidative cleavage has a close connection to the carbon–carbon double bond at C8 in the side chain of urushiol [24]. The formation mechanism and structure of the acid catechols are similar to those of dicarboxylic fatty acids that formed by oxidation of unsaturated fatty acids in drying oils [25]. With reference to the studies on the oxidation mechanism of unsaturated fatty acids [25–28], the oxidation of urushiol side chains probably involve scission reactions similar to those in the autoxidation of unsaturated fatty acids. Therefore, the possible oxidative cleavages of the urushiol side chain are speculated in Fig. 6. It's worth noting that the most abundant urushiol monomer is used for example, which is actually part of the polymeric network. After primary oxidation of urushiol, radicals (2) and (3) are formed, followed by scission of radical

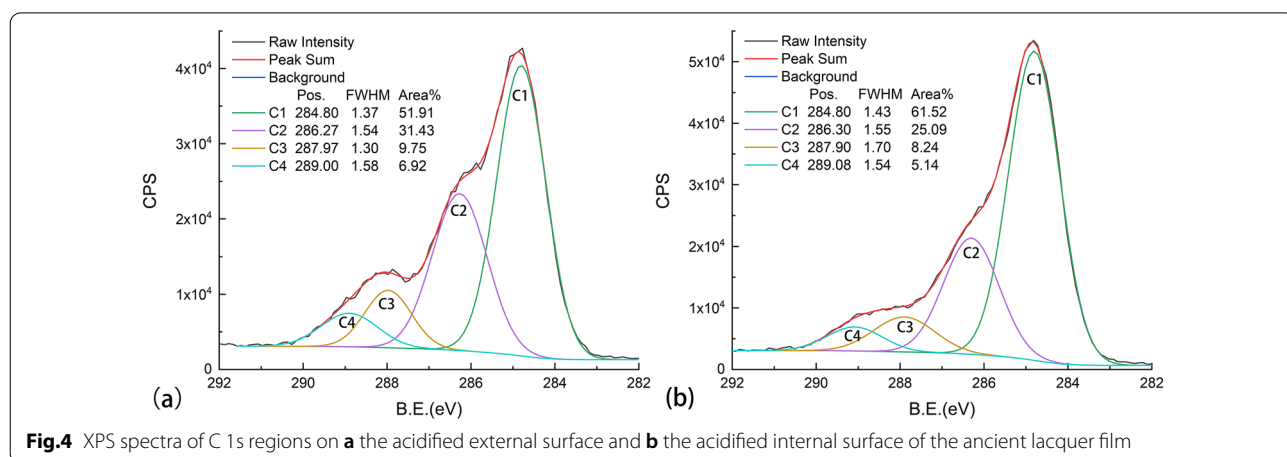


Table 1 Assignment of C 1 s regions

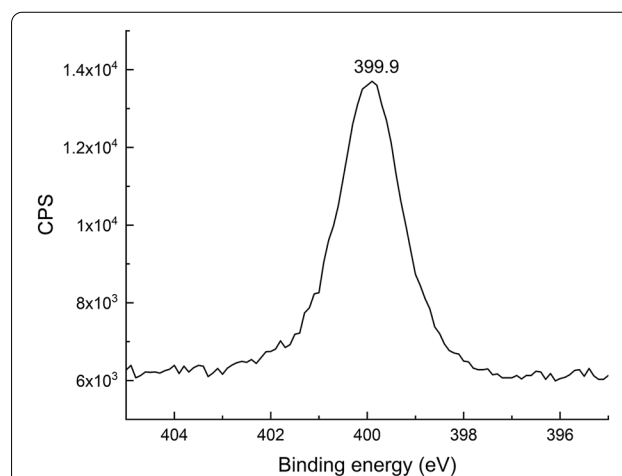
Carbon type	Binding energy (eV)	Corresponding chemical bonds
C1	284.8	C–C or C–H
C2	286.3 ± 0.1	C–O
C3	288.0 ± 0.1	C=O or O–C–O
C4	289.0 ± 0.1	O=C–OH

(2) between C8 and C9 or that of radical (3) between C7 and C8, and finally after multiple oxidation processes, carboxylic acids including mazzeic acid or kumanotanic acid are formed depending on the initial radicals. As radical (2) is easier to form than radical (3), this oxidative process is consistent with the fact that mazzeic acid is usually the most abundant species of acid catechols found in lacquer.

A study also found that oxidative cleavage of unsaturated fatty acids and production of dicarboxylic acids can be catalyzed by laccase (*Trametes* sp. Ha-1) [29]. The oxidative cleavage occurred in the unsaturated fatty acids which have carbon–carbon double bond, hydroxyl group, or carbonyl group at allylic or homoallylic position [29]. The laccase in urushi probably has a similar catalytic capability as well, which can explain the dicarboxylic acids in the lacquers containing drying oils or acid catechols found in newly prepared lacquer films [9]. Thus, the oxidative cleavage possibly happens at certain substrates (like compounds 1, 6, 7, 8, 9) shown in Fig. 6 even during the curing of lacquer. As free radical oxidation has poor regioselectivity, the products mainly depend on the chemoselectivity of the substrates. The enzymatic oxidative cleavage of urushiol should have a similar scission process as the non-enzymatic one. Therefore, the production of acid

catechols may have two stages, i.e., a fast enzymatic oxidative cleavage during curing and a slow but long-term non-enzymatic one during burial. Apart from the acid catechols, benzoic acid and alkylphenylketones were identified by Tamburini in Burmese lacquer in two cultural objects, indicating the benzylic position is likely to undergo radical oxidation [30]. Therefore, the radical oxidation of the benzylic position may also lead to oxidative cleavages between C1 and C2 in the urushiol side chain. However, the reactivity of the benzylic position in urushiol may not be the same as that in the alkylphenylcatechols in Burmese lacquer.

All the resulting moieties after oxidative cleavages are probably still connected to the polymeric network if no other cleavage happens and likely to be oxidized to carboxylic acids after a long-term burial. Therefore, it is inferred that these carboxylic acids usually present themselves in pairs as shown in Fig. 6.

**Fig. 5** XPS spectra of N 1s regions on the original external surface**Table 2** Elemental results of the ancient lacquer films

	C	N	O	Al	Si	Ca
Original external surface	65.4 ± 0.5	4.9 ± 0.5	26.9 ± 0.5	0.5 ± 0.2	1.4 ± 0.3	0.8 ± 0.2
Original external surface (Al, Si excluded) ^a	69.4 ± 1.3	5.2 ± 0.5	24.5 ± 0.8	/	/	0.9 ± 0.2
Original internal surface	66.4 ± 6.6	2.6 ± 0.2	27.1 ± 4.5	0.7 ± 0.7	2.1 ± 1.7	1.0 ± 0.1
Original internal surface (Al, Si excluded)	72.4 ± 1.6	2.9 ± 0.1	23.6 ± 1.6	/	/	1.1 ± 0.1
Acidified external surface	66.1 ± 1.7	5.8 ± 1.1	25.7 ± 0.8	0.5 ± 0.2	1.8 ± 0.5	0.1 ± 0.1
Acidified external surface (Al, Si excluded)	70.7 ± 1.6	5.9 ± 1.5	22.6 ± 1.3	/	/	0.1 ± 0.1
Acidified internal surface	66.2 ± 4.8	3.3 ± 0.2	27.3 ± 3.2	0.9 ± 0.6	2.2 ± 1.0	0.1 ± 0.1
Acidified internal surface (Al, Si excluded)	72.7 ± 1.8	3.7 ± 0.3	23.5 ± 1.6	/	/	0.1 ± 0.1

^a Al and Si are excluded and O content is reduced accordingly considering the ratio of O/(Al, Si) is 2 in common silicates like quartz, feldspar and mica

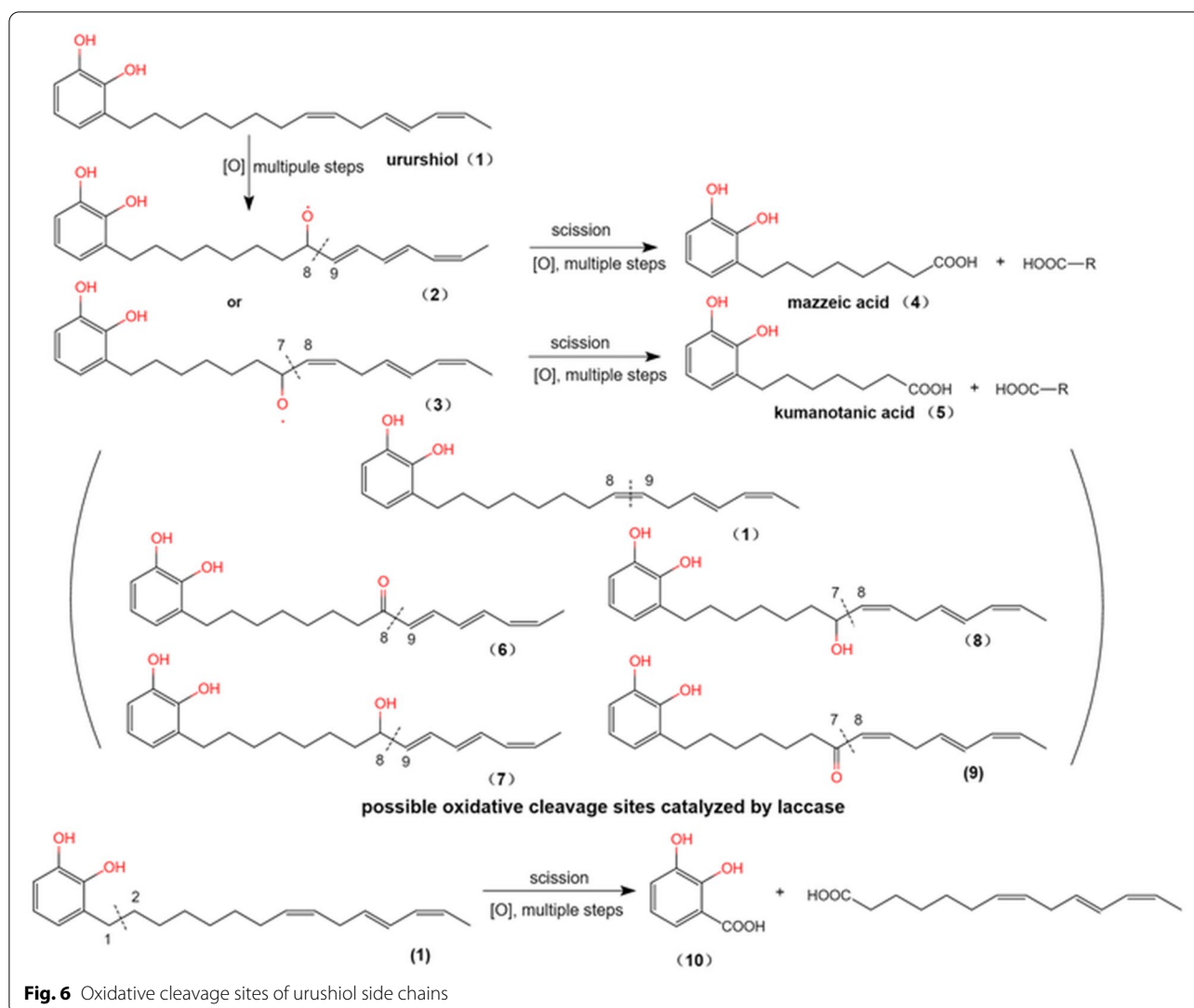


Fig. 6 Oxidative cleavage sites of urushiol side chains

Mechanism of the swelling behaviors

Based on the above results and discussions, the carboxylates in the ancient lacquer samples include calcium ones and possibly ammonium ones and are likely to be paired. Shown in Fig. 7, there are assumably five types of cation-carboxylate relations. The calcium type and zwitter type are stable at circumneutral pH. In the calcium type, the Ca^{2+} bonds the two carboxylate groups by either coordination bonds or static forces, which results in attraction. In the zwitter type, the two carboxylate groups result in repulsion while attraction exists between the nearby ammonium cation and carboxylate group, which overall does not evidently generate either repulsion or attraction. When the lacquer film is acidified by HCl, the calcium type turns in to the hydrogen type, but the attraction between the two carboxylate groups might be maintained by hydrogen bonds. Also, when the zwitter type turns into the ammonium type, new hydrogen bonds are likely

to form and generate attraction. The possible ammonium cations are not likely to evidently generate repulsion because there is no evidence suggesting they are spatially close. Therefore, the attraction forces are stronger at low pH than that at circumneutral pH. When the ancient lacquer film is then immersed in the NaHCO_3 solution, the sodium type becomes dominant, which only generates repulsion by static forces. Therefore, remarkable swelling happens when the pH is even mild alkaline. Since the outer layer of the ancient lacquer film contains more carboxylates, it shrinks more at low pH and swells more at high pH than the inner layer, which explains the warping behaviors observed.

Significance in conservation

The ancient lacquer samples analyzed in this study probably represent much more cases where the lacquer contains carboxylates and not uniformly oxidized. For

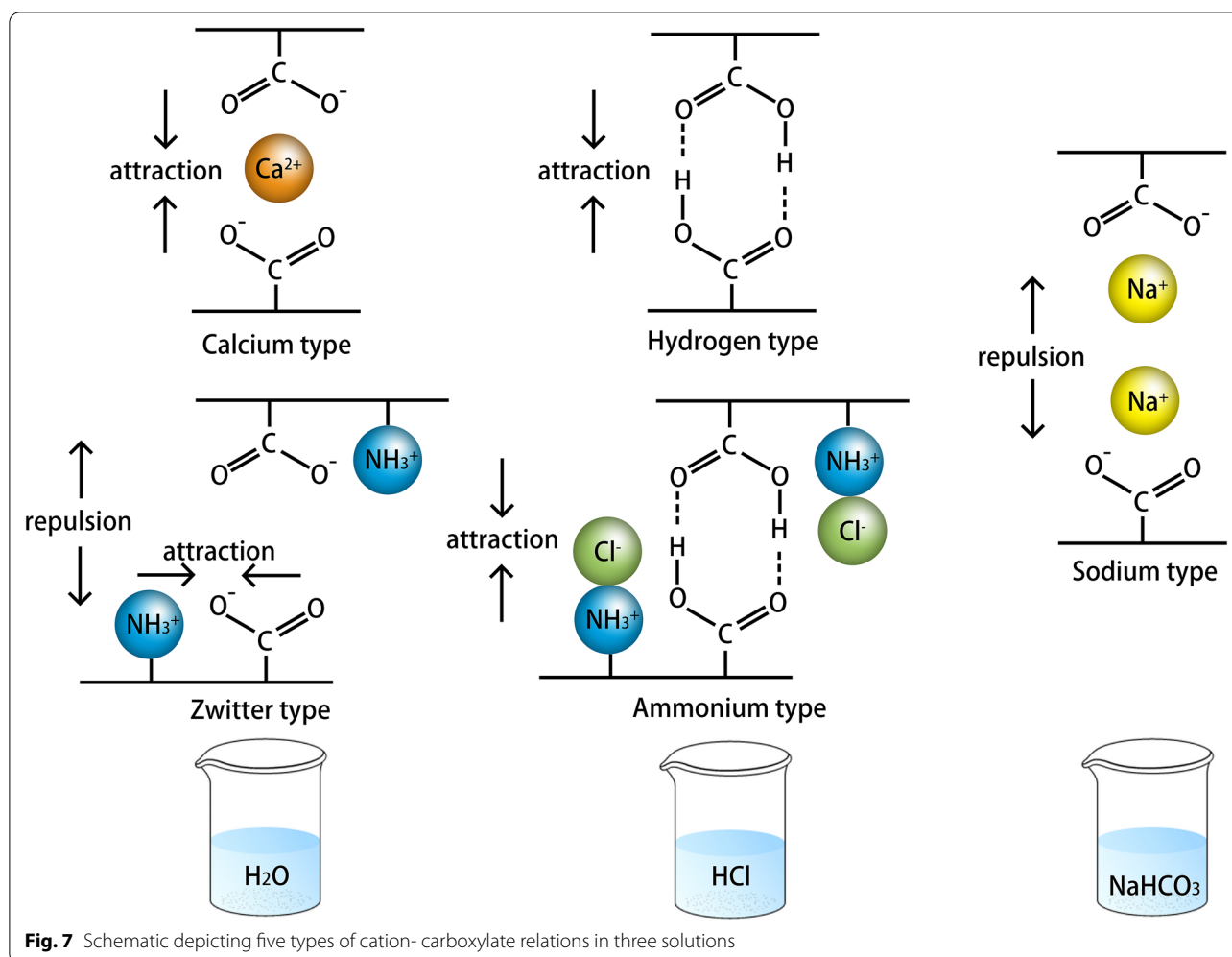


Fig. 7 Schematic depicting five types of cation-carboxylate relations in three solutions

example, evident absorption bands of carboxylates can be identified in FTIR spectra of samples elsewhere [31, 32]. In these cases, the pH of the reagents used in conservation actions, such as cleaning and consolidation of the lacquer, must be strictly regulated. The pH should be controlled below 7.0 to prevent extensive swelling and warping. In contrast, if a lacquer film is improperly dried and severely warped, it would be easier to restore it by adjusting the pH based on its warping direction and then dehydrating properly. Additionally, future research may consider using calcium-based reagents to help stabilize ancient lacquerware containing carboxylic acids.

Conclusion

Ancient lacquer films excavated from Dongshan Han Tomb M6 in Taiyuan City, China are found to have pH-dependent warping behaviors. Acidic pH results in the lacquer film mild warping outward while subsequent alkaline pH results in remarkable warping inward.

On the basis of the surface analysis of the ancient lacquer films by ATR-FTIR and XPS, it is found that the outer layer of the lacquer film is more oxidized than the inner layer and thus contains more carboxylates. The cations of the carboxylates are calcium cations and possibly ammonium cations. These carboxylates are considered to be mainly formed by enzymatic and non-enzymatic oxidative cleavages of the urushiol side chain between C8 and C9, C7 and C8, and C1 and C2. These carboxylates are likely to be paired as a result of the oxidation cleavage. The shrinkage and swelling of the lacquer film are regulated by various interactions such as hydrogen bonds, coordination bonds between Ca^{2+} and two carboxylates, and static forces. The outer part of the lacquer film is more sensitive to pH variation than the inner part due to its higher carboxylate content, which leads to the above warping behaviors.

It is suggested that the pH of the reagents applied in conservation or restoration should be normally controlled below 7. It is possible to adjust the warping of

lacquer films by pH control. Future research may also consider using calcium based reagents to help stabilize carboxylic acids in ancient lacquerware.

Acknowledgements

The research is supported by National Social Science Foundation of China (Grant No. 19CKG032).

Authors' contributions

All the experiments were designed and carried out by KW, CL and YZ. The data were analyzed by YZ and KW. The manuscript was written by YZ and KW, and revised by CL and DH. All authors read and approved the final manuscript.

Funding

The research is supported by National Social Science Foundation of China (Grant No. 19CKG032).

Availability of data and materials

The datasets analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

There is no financial and non-financial competing interests.

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Received: 17 November 2021 Accepted: 17 February 2022

Published online: 07 March 2022

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