Polymer Degradation and Stability 134 (2016) 251–264

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

An investigation into the curing of urushi and tung oil films by thermoanalytical and mass spectrometric techniques

Diego Tamburini [a, 1], Dario Sardi [a], Alessio Spepi [a], Celia Duce [a], Maria Rosaria Tinè [a], Maria Perla Colombini [a, b], Ilaria Bonaduce [a, *]

[a] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, I-56124, Pisa, Italy
[b] Institute for the Conservation and Valorization of Cultural Heritage (ICVBC), National Research Council, Via Madonna del Piano 10, Sesto Fiorentino, I-50019, Florence, Italy

ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form
19 October 2016
Accepted 24 October 2016
Available online 24 October 2016

Keywords:
Urushi
Tung oil
Curing
Mass spectrometry
Py-GC-MS
EG-MS
EGA-MS
TG
DSC
Autoxidation

ABSTRACT

Urushi is the oldest and most precious lacquer used since antiquity in East Asia. For artistic purposes, in order to obtain suitable rheological properties, the lacquer is usually mixed with a vegetable oil. In this work we investigated the curing process of urushi/tung oil mixtures in order to highlight the chemical interactions at the molecular level between the two materials.

A multi-analytical approach was adopted, based on thermogravimetry (TG), differential scanning calorimetry (DSC), gas chromatography-mass spectrometry (GC-MS), evolved gas analysis-mass spectrometry (EGA-MS), analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) and high performance liquid chromatography-mass spectrometry (HPLC-MS). Fresh and aged mixtures were analysed and the results were compared with those obtained from the analysis of the individual materials.

The data highlighted that different polymerisation and oxidation mechanisms take place in oil/urushi mixtures compared to the pure materials. Py-GC-MS and GC-MS showed that the profile of aliphatic mono- and di-carboxylic acids was drastically different for the aged film of pure tung oil compared to the mixtures. The ratio between the relative content of azelaic and palmitic acids was much lower in the mixtures than in the pure oil, highlighting a lower level of oxidation. On the other hand, the relative content of short chain carboxylic acids, which are produced by pyrolysis of the cross-linked oil network, increased as the concentration of urushi in the mixtures increased, thus indicating an increasing level of reticulation. HPLC-MS showed a relatively higher amount of triglycerides with hydroxylated fatty acids – the intermediate oxidation product of polyunsaturated fatty acids - in the mixtures with respect to pure tung oil.

1. Introduction

Tung oil and urushi are two natural organic materials, which spontaneously form solid long-lasting films. This feature makes these materials extremely suitable for artistic and protective purposes. Tung oil has long been used as a binding medium [1–3] and as a coating material, especially for wooden artefacts [4]. Urushi lacquer is considered as the oldest and most precious lacquer in East Asia, and has been used for thousands of years as a coating material, because of its capacity to lend great and lasting brightness, toughness and water resistance to the object [5].

Tung oil is a vegetable oil extracted from the nuts of the tung tree (*Vernicia fordii*). Its triglyceride composition mainly consists of polyunsaturated fatty acids. In particular, α-eleostearic acid ((9*Z*,11*E*,13*E*)-octadeca-9,11,13-trienoic acid) accounts for *ca.* 80% of the fatty acids [6]. Tung oil thus belongs to the group of drying oils that polymerise under exposure to air and light [7].

This process is referred to as autoxidation, a well-studied free-radical chain reaction, which can be divided into three main steps: 1) beginning, 2) propagation, 3) termination [8].

In the first step a radical initiator begins the formation of radicals by H-abstraction from the unsaturated alkyl chains of fatty

* Corresponding author.
E-mail address: ilaria.bonaduce@unipi.it (I. Bonaduce).
[1] Present address: Department of Scientific Research, The British Museum, Great Russell Street, London WC1B 3DG, England.

http://dx.doi.org/10.1016/j.polymdegradstab.2016.10.015
0141-3910/

acids. Allylic and in particular bis-allylic positions are favoured for this process, because the radicals formed are stabilised by resonance. The second step involves the attack of molecular oxygen to form peroxyl radicals. The peroxyl radicals can perform an H-abstraction from another chain, propagating the reaction and forming hydroperoxides, which are considered as the first oxidation products of polyunsaturated fatty acids [9]. Hydroperoxides can further degrade to form alkoxyl and hydroxyl radicals, which contribute to propagate the reaction. During these two phases, for unconjugated fatty acids, H-abstraction to form radicals is highly preferred with respect to the addition of a radical to double bonds, which is instead favoured in conjugated fatty acids, especially when they are in cis-configuration [10]. The formation of a cross-linked network, as well as of cyclic peroxides or polyperoxides is a consequence of this latter phenomenon [10–13].

The termination step includes all the cross-linking reactions where two radicals are combined to form non-radical, stable species, leading to the formation of C–C and C–O–C bonds. For conjugated systems, the disproportion of the compounds formed by the addition of a radical to a double bond can also occur [14]. The decomposition of primarily formed hydroperoxides and peroxides can also be followed by β-scission and other side reactions, leading to the formation of low molecular weight compounds, such as alcohols, ketones, aldehydes, acids, and alkanes [8,15–18]. The photo- and thermo-instability of alcohols, aldehydes and ketones, and the presence of oxygen create favourable conditions for the production of dicarboxylic acids, which are considered as the final oxidation products in these systems [15,19].

Urushi is a lacquer produced from the sap of the *Rhus Vernicifera* tree. The sap is composed of water (30%), glycoproteins (2%), plant gum (7%), laccase enzyme (1%), and a mixture of catechol derivatives (60–65%) referred to as urushiol [20]. The most abundant catechol in urushiol is (8*Z*,11*E*,13*Z*)-3-pentadecatrienylcatechol [21]. Laccase enzyme is a copper-containing enzyme, fundamental in the polymerisation of urushi, as it catalyses the reduction of Cu^{2+} to Cu^{+}, which reacts with oxygen to form a peroxyl intermediate. The peroxyl intermediate reacts with the catechol, leading to the formation of a semiquinone radical and to the loss of a water molecule. The semiquinone radicals react with each other to form C–C bonds between two aromatic nuclei (biphenyl dimers, trimers, etc.). With further electron transfer, quinone species are formed, which can react with the unsaturated side chains to form C–C bonds between aromatic nuclei and aliphatic chains, and C–O bonds between phenolic oxygens and aliphatic chains [22]. These mechanisms consume the urushiol monomers, and when their concentration drops below 30%, auto-oxidation reactions take place at the side chains, according to the same mechanisms described for polyunsaturated fatty acids [20,23,24].

Tung oil and urushi have often been used in mixtures in oriental art [25], as the resulting film shows enhanced rheological and mechanical properties. The mixture dries more slowly and the resulting film is less hard than that obtained with pure lacquer, thus facilitating manual polishing to obtain the finishing layers.

Despite much research has been dedicated in the literature at improving the quality of urushi lacquer films, acting on its formulation or on its curing [23,26–28], molecular studies of the curing and quality of the film that is produced by mixing urushi and tung oil have not been reported.

The aim of this study was to understand the chemical interactions taking place at the molecular level between the two materials when they cure together. We also investigated whether it is possible to identify one or more molecular markers that can be used to determine whether tung oil and urushi belong to the same layer, and thus curing occurred at the same time, or if they were applied in two distinct layers, and thus curing occurred separately.

We used a multi-analytical approach, based on thermogravimetry (TG), differential scanning calorimetry (DSC), gas chromatography-mass spectrometry (GC-MS), evolved gas analysis-mass spectrometry (EGA-MS), analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) and high performance liquid chromatography-mass spectrometry (HPLC-MS). The study revealed that urushi acts as an antioxidant, favouring the cross-linking of the oil polyunsaturated fatty acids over oxidation. Copolymerisation between the two materials also takes place and auto-oxidation reactions of catechol alkyl substituents occur at a higher rate in urushi, when it is mixed with tung oil.

2. Experimental section

2.1. Reagents

Lauric acid, suberic acid, myristic acid, azelaic acid, sebacic acid, palmitic acid, oleic acid, stearic acid, tridecanoic acid, hexadecane (Sigma-Aldrich, 99% purity). Acetone, diethyl ether, ethanol, *n*-hexane and isooctane (Sigma-Aldrich, HPLC grade). *N,O*-bis(-trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) (Sigma-Aldrich, 98.5% purity). 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (Sigma-Aldrich, purity 99.9%). The solvents used for the HPLC analyses were: *iso*-propanol, *n*-hexane, trichloromethane and methanol (HPLC/MS grade; Fluka, U.S.).

2.2. Samples

Tung oil was purchased by Kremer Pigmente and the raw material for urushi lacquer was bought from a local producer in the northern slopes of the Qinling mountains near Xi'an (China) in 2007. Both fresh and aged samples were analysed. Fresh tung oil, fresh urushi and a 1:1 (w/w) fresh mixture of the two materials (M1*) were used for TG and DSC analyses. Films were prepared by depositing a few milligrams of the materials on laboratory glass plates. The tung oil film was analysed after two years of natural ageing. Films of urushi and mixtures of urushi and tung oil in w/w ratios 1:1 (M1), 2:1 (M2) and 4:1 (M4) were prepared in 2007 and analysed after eight years of natural ageing. These samples were analysed by mass spectrometric techniques.

2.3. TG and DSC

A TA Instruments Thermobalance model Q5000IR was used. Isothermal experiments were performed on fresh materials under a constant air flow (90 mL min^{-1}) at 80 °C for 6000 min (*ca.* four days). The amount of sample used for these analyses ranged from 3 to 4 mg. DSC measurements were performed by a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter in the temperature range of 30–300 °C, with a heating rate of 10 °C min^{-1} and using nitrogen as purging gas. Fresh tung oil and a 1:1 (w/w) fresh mixture of the two materials (M1*) were analysed after different curing times: 0, 3, 21, 45, 93, 140, 190, 282, 450 and 2800 h. The amount of sample used for these analyses ranged from 5 to 6 mg, and samples were prepared in aluminium pans.

2.4. EGA-MS

The instrumentation consisted of a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab) coupled with a gas chromatograph 6890 Agilent Technologies (Palo Alto, USA) equipped with a deactivated and uncoated stainless steel transfer tube