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Automated characterization of varnishes photo-degradation using portable T-controlled Raman spectroscopy

I. Osticioli *, D. Ciofini, A.A. Mencaglia, S. Siano

Institute of Applied Physics "Nello Carrara" (IFAC-CNR), Florence, Italy

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ABSTRACT

In this work, a portable-Raman device (excitation wavelength 1064 nm) was employed for the first time for continuously monitoring the complex molecular dynamics of terpenoid resins (dammar, mastic, colophony, sandarac and shellac), which occur during their ageing under artificial light exposure. The instrumentation was equipped with a pyroelectric sensor allowing for temperature control of the sample's irradiated surface while the acquisition of spectra occurs by setting fixed maximum temperature and total radiant exposure. Resins were dropped into special pits over a dedicated rotating wheel moved by a USB motor. The rotation allowed samples sliding between the positions designated for the acquisition of the Raman spectra and that for artificial ageing. Samples were exposed to artificial light for 45-days and almost 400 spectra for each resin sample were collected. The exposure to artificial light led to significant changes allowing the characterization of the alteration process. The automated acquisition of a large number of spectra overtime during light-exposure has given the possibility to distinguish fast dynamics, mainly associated to solvent evaporation, from those slower due to resins photo-degradation processes.

1. Introduction

All natural varnishes undergo ageing and degradation course overtime, changing their chemical and physical properties. The characterization of the alteration is a crucial issue concerning cultural heritage artefacts in order to have a reliable and trustful diagnosis of their state of conservation [1].

The ageing process can definitely affect the stability of the artefact because of the destruction of the material itself as well as the loss of its flexibility and cohesion properties. Similarly, change in color and growth of cracks can alter the legibility as well. Depending on external factors, degradation can be of thermal, hydrothermal, chemical, photochemical or mechanical origin.

In this scenario, the understanding of molecular changes involved in degradation becomes crucial for a more correct and durable conservation intervention. Among the materials used in the field of art, organic polymers are indeed those subject to more complex ageing and degradation processes [2]: auto-oxidative processes through chain radical reactions, photo-dissociative processes along with the generation of cross-linking, condensations, chain shortening and defunctionalization as well as bond breaking and disintegration are example of what may happen during the alteration processes.

The identification of altered compounds is usually carried out by means of mass spectrometry, which requires sampling and sample pre-treatment [3–5]. FTIR spectroscopy is used for the identification and discrimination between organic and inorganic species [6] as well as for the assessment of the photodegradation kinetics of solvent and oil-based varnishes [7].

These techniques are nowadays employed not only to assess molecular changes due to the degradation of the polymer itself but also to understand how its interaction with other materials (i.e. heavy-metals ions, pigments and other binders) may affect the time of ageing and determine the formation of specific compounds [8–11].

In this scenario, Raman and non-contact IR spectroscopy can allow to assess chain reactions and identify the formation of specific degradation products without any sampling and sample preparation [12,13]. However, in the present application IR spectroscopy is more suited for describing molecular processes involving mainly C═O molecular vibrations, whereas Raman spectroscopy can provide a wider and more detailed picture of the alteration dynamics thank to the higher spectral resolution and sensitivity with respect to the C═C, C—C, C—O, and C—N bonds. Thus, the latter can better assess microstructural changes (polymerization, de-polimerisation) and formation of new compounds containing conjugated C═C bonds.

Effects of ageing were assessed through the comparison of Raman bands (frequency shifts, intensity and shape changes) of the fresh and aged samples of proteins binders [14,15], lipids [16,17], and natural resins [18,19]. Recently, micro-Raman spectroscopy has been also

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* Corresponding author at: Institute of applied physics "Nello Carrara" (IFAC - CNR), via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy.
E-mail address: i.osticioli@ifac.cnr.it (I. Osticioli).

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Table 1
Resins, solvents and illuminance used for the experiment.

Resins	Group	No. of carbon atoms	Solvent	Illuminance at sample surface (lx)	Total illuminance (Mlx in 45 days)
Dammar	Triterpenoid	30	Ligroin	19,000	14.0
Mastic	Triterpenoid	30	Ethanol	17,750	12.5
Colophony	Diterpenoid	20	Ethanol	11,200	9.0
Sandarac	Diterpenoid	20	Ethanol	19,500	14.0
Shellac	Sesquiterpenoid	15	Ethanol	19,400	14.0

used for assessing the chemical changes induced by UV laser radiation on naturally cured and artificially aged varnishes [20].

In this work, for the first time, Raman spectroscopy has been employed for continuously monitoring the complex molecular dynamics of natural resins, which occur during their ageing under artificial light exposure. In particular, a portable, temperature-controlled, Raman device (excitation wavelength 1064 nm) has been developed in order to automatically monitor the ageing process by preventing phase changes and other undesired alteration effects. Temperature control of the sample's irradiated surface was achieved by means of a pyroelectric sensor and dedicated software producing a feedback on the laser power supply and then a suitable modulation of the output beam. It allows collecting a sequence of spectra in the same area of analysis by setting fixed maximum temperature and total radiant exposure.

One spectrum every 4 h has been measured during the whole ageing period of 45-days. Samples were prepared by applying various terpenoid resins (colophony, shellac, dammar, sandarac, mastic) on Polyethylene (PE) thin film and subjected to artificial ageing in order to simulate natural light exposure in indoor museum conditions. Total irradiance of 9–14 Mlx was used which can be compared, assuming reciprocity, to about 16–28 years of exposure in recommended museum conditions (150–200 lx 8 h/day). Natural resins have been intensively used in the past and they are still employed as adhesives, binders and varnishes.

Intensity changes of the bands in Raman spectra have indicated structural modifications after the ageing process which allowed describing the chemical alteration dynamics of molecular bonds over time.

2. Materials and methods

Homogeneous saturated solutions of fresh grinded natural terpenoid resins (constituted of units of C_5 compound isoprene) were prepared, dissolving the material in the appropriate solvent and stirred for 1 day. All the formulations were dropped on very thin polyethylene (PE) slides. Ethanol and ligroin were used as solvents for dissolving the resins according to Table 1. Resins employed for the experiment are dammar, mastic, colophony, sandarac and shellac. Dammar is a triterpenoid resin largely composed of tetracyclic dammarane series ($C_{30}H_{54}$), the pentacyclic compound ursonic acid ($C_{30}H_{46}O_3$) and a proportion of polymeric hydrocarbon. Mastic is a triterpenoid resin composed of several tetracyclic compounds of the euphane series, including masticadienonic acid ($C_{30}H_{46}O_3$). Colophony and Sandarac are diterpenoid resins composed mainly of abietic acid ($C_{20}H_{30}O_2$) and sandaracopimaric acid ($C_{20}H_{30}O_2$) respectively. Shellac is a sesquiterpenoid extracted from insects with very complex composition: probable primary components are jalaric ($C_{15}H_{22}O_5$) and laccijalaric acid ($C_{15}H_{20}O_4$) [21].

A portable Raman device was conveniently assembled in the lab by using a narrow-band CW diode-pumped Nd:YAG(1064 nm) laser and a NIR-spectrometer equipped with an InGaAs linear array. A specific probe was designed in order to control the local temperature rise of the area under analysis. To this goal a pyroelectric sensor was used, which provides the feedback for suitably modulating the output power of the laser source and then limiting undesired heating effects within the gauge volume. Furthermore, a dedicated rotating wheel moved by a USB servo motor was designed as sample holder (Fig. 1).

Resins solutions were dropped into special pits over the wheel surface. The rotation allowed samples sliding between the positions designated for the acquisition of the Raman spectra and that for artificial ageing. All the experimental parameters including the time of exposure to light and spectra acquisition were set in the control code and a completely automated measurement cycles was launched.

Light ageing was carried out under six 55 Watt OSRAM DULUX® (range 380–780 nm) daylight fluorescent tubes (5400 K color temperature). As the ultraviolet content of the light emitted by these lamps is relatively low no further ultraviolet filter was used.

The light flow in lux, or illuminance, was measured at the surface of each sample through a lux meter in order to consider irradiation slight inhomogeneity. The illuminance (lx) and light dose (Mlx∗h) delivered to each sample during 45-days of irradiation are reported in Table 1.

During the early 5-days of measuring, Raman spectra were acquired after every ½ h irradiation in order to follow the initial fastest molecular changes in more detail, as, for example, those associate with the solvent evaporation.

During the following 40-days Raman spectra were collected every 4 h for a total irradiance of 9–14 Mlx which can be compared, assuming reciprocity, to about 16–28 years of exposure in recommended museum conditions (150–200 lx 8 h/day). Acquisition time for Raman spectra of 4 min and laser output power of about 300 mW were employed during the experiment. In these conditions a maximum temperature of 35 °C was reached during laser irradiation, which is lower than those of the glass transition of the various resins [22].

Peak deconvolution was carried out using Origin Pro 2015 in order to investigate molecular changes induced by light ageing over time. The local maximum method with high sensibility was used as peak finding settings and the Lorentzian peak function was preferred to Gaussian and Gaussian-Lorentzian profiles since it provided the highest R-square value.

The need of an automated measurement protocol has been justified by the following reasons. First, Raman measurements of this work need very high spatial accuracy because the samples cannot be considered

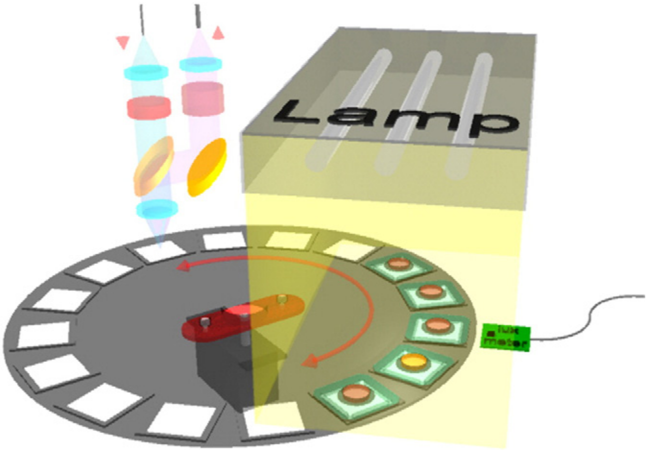

Fig. 1. Automated Raman setup used for characterizing resins degradation.

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