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Quartz crystal rheometry: A quantitative technique for studying curing and aging in artists' paints

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ABSTRACT

In this paper we demonstrate the use of a quartz crystal microbalance (QCM) as an effective new tool to measure the physical properties of artists' paints during cure in real time, with unprecedented sensitivity to both mass changes and mechanical properties. While QCM-based dosimeters have been used in the conservation field primarily as mass sensors, the limits of the technique are here extended so that the rheological properties of the materials are obtained as well. The capabilities of the technique are illustrated with alkyd resins, a binder for artists' paints developed in the late 1920s that became widely used in the 1950s. Curing of an alkyd film was monitored both in ambient conditions and at elevated temperatures. By using the QCM as a thin film rheometer, the changes in the film's mass and high-frequency dynamic shear modulus were monitored, and the ability to quantify temperature-dependent changes in the cure rate was demonstrated. The film was also exposed to water and showed slight mass loss but no significant changes in mechanical properties. This work demonstrates that the QCM can be a useful tool for quantifying changes in the mechanical properties of artists' paint films during aging and exposure to different environmental conditions.

1. Introduction

During the lifetime of a painting, the paint undergoes a variety of stresses, from the initial curing and natural aging to the changing conditions of humidity or temperature and conservation interventions such as cleaning, consolidation and lining. All of these factors have an impact on the chemical and physical properties of the paint itself. Despite extensive research on the chemistries involved in the curing and aging of linseed oil films [1–4], as well as pigmented paints [5,6], recent research has demonstrated the shortcomings of most artificial aging regimes for predicting long-term behavior of the mechanical properties of actual historic paint layers [7–10]. It has also been shown that mature oil-based paint films show a significantly more dynamic behavior than previously thought [5,8,9,11,12]. Conservation treatments or environmental conditions that introduce an imbalance in relative humidity or temperature can cause detrimental rearrangements in the mobile phases of these paint systems, which are mostly composed of free fatty acids and organometallic carboxylates [13,14]. Thus, new experimental and theoretical models are needed for oil-based paints in order to accurately measure and predict the effects of a range of environmental conditions and of different conservation treatments on the physical properties of aged samples in real time.

The present research focuses on the development of a technique for the measurement of the total mass and linear viscoelastic properties of paint films that is based on the use of the quartz crystal microbalance (QCM). Widespread use of these QCM sensors, with their capability to provide large amounts of data from samples that are being aged according to different artificial aging protocols, can both enhance the data-driven approaches traditionally used to study materials degradation, and also contribute to the development of new scientifically-based conservation treatments. Indeed, the portability and simplicity of the experiment have motivated previous applications of the QCM technique in the field of art conservation [15–19]. These previous applications of the QCM in art conservation all involve the use of the quartz crystals qualitatively or as mass sensors mainly for applications to assess

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environmental conditions in museums, historic buildings, and inside microclimate frames. Such use of QCMs as dosimeters to define damage thresholds for environmental exposure of artworks is based on a linear relationship between the mass loading of the quartz crystal and its resonant frequency. In this work, we seek to expand the range of applications of QCMs in the cultural heritage field based on the fact that deviations in this linear relationship become important for films that are sufficiently thick. The quantitative details of these deviations depend on the thickness and mechanical properties of the film, and an appropriate quantitative analysis enables the mechanical properties of the film to be determined [20–22]. Thus in addition to mass measurements, the elastic and dissipative components of the complex dynamic modulus of the coatings at the quartz crystal resonant frequency can also be obtained. Using the approach outlined in this paper the 'quartz crystal microbalance', with its sensitivity to very small changes in the mass of a film, becomes a 'quartz crystal rheometer', with an ability to measure the linear viscoelastic properties of the film at discrete frequencies corresponding to the crystal resonances. Availability of this rheometric capability enables more detailed investigations of curing and aging of paint films to be undertaken in real time.

The rheometric application of the QCM places additional constraints on the film that is being investigated. In particular, the thickness must be thick enough so that the device becomes sensitive to the film properties, but not so thick that the crystal resonance becomes too strongly damped. The optimum thickness depends on the properties of the film itself, and is in the range of several micrometers for a fully cured paint coating. In order to understand this constraint, and the errors inherent in the technique, we begin in the following section with a discussion of the operating principles of the rheometric QCM. In the experimental section which follows we describe our experimental implementation, and introduce the alkyd paint coating that we have used to validate the technique. An error analysis is included in this section because this analysis informs our choice of the most appropriate film thickness to use in the experiments. In the results and discussion section our rheometric technique is applied to alkyd coatings in the early stages of the cure process. In a proof of concept experiment aimed at illustrating our ability to probe effects of temperature and on exposure to solvents, we use a test protocol that includes changes in temperature and that also involves a water immersion step.

2. Rheometric quartz crystal microbalance

Applications of the quartz crystal microbalance (QCM) to the determination of rheological properties of the coating are based on the coupling of mechanical loading and electrical response of thin, single crystal piezoelectric quartz disks oscillating in a shear mode near their resonant frequency [20]. The basic experimental geometry is shown schematically in Fig. 1a. Commercially available quartz crystals with gold electrodes on the opposing surfaces are used as the substrates, and the paint coatings are deposited onto the larger electrode surface. The crystal resonance can be quantified by either time-domain or frequency-domain experiments [23]. In the frequency domain experiments, which are used here, impedance spectroscopy is used to monitor the response of the crystal at different odd harmonics of the fundamental resonant frequency. As illustrated in Fig. 1b, the resonant frequency at the nth harmonic, f_n, is defined as the frequency where the conductance of the circuit is maximized, and the dissipation, Γ_n, is defined as the half-width at half the maximum of the resonance peak. Together, these quantities are used to define the complex resonant frequency, f_n^*:

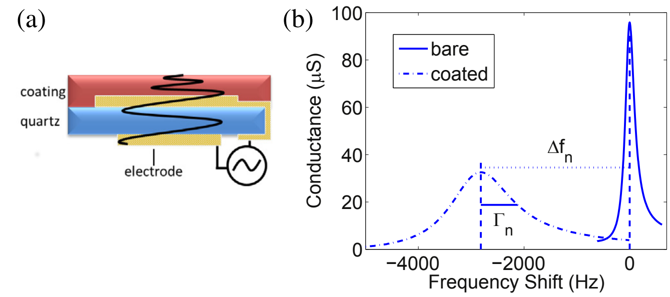

Fig. 1. (a) Schematic representation of the quartz crystal microbalance. (b) Electrical conductance spectra for an unloaded (solid line) and loaded (dashed line) crystal. Δf_n is represented by the dotted line, and the value for Γ_n is indicated by the solid line.

$$f_n^* = f_n + i\Gamma_n \tag{1}$$

When a paint film is deposited onto the electrode surface on one side of the crystal, there is a shift in the complex resonant frequency, with both the resonant frequency and dissipation changing as a result. In our case we simultaneously measure the response of the crystal for $n = 1$ ($f_1 = 5$ MHz), $n = 3$ ($f_3 = 15$ MHz) and $n = 5$ ($f_5 = 25$ MHz).

The QCM technique is based on the coupling between Δf_n^*, the change in f_n^* arising from the deposition of the film on the electrode surface, and the load impedance, Z_n^*, which is associated with the mechanical response of the film. This load impedance is defined as the ratio of the shear stress over the shear velocity at the coating/electrode interface. If the load impedance is small in comparison to the impedance of the quartz crystal, a condition that is always met in any practical QCM experiment [24], a linear relationship exists between Δf_n^* and Z_n^*:

$$\frac{\Delta f_n^*}{f_1} = \frac{iZ_n^*}{\pi Z_q} \tag{2}$$

here Z_q is the acoustic impedance of quartz, $8.84 \cdot 10^6$ kg m^{-2} s^{-1}. If we assume that the film in contact with the QCM electrode surface has uniform viscoelastic properties, the expression for the complex frequency shift can be written in the following way [22,24–26]:

$$\frac{\Delta f_n^*}{\Delta f_{sn}} = \frac{-\tan\{(2\pi d/\lambda_n)(1 - i\tan(\phi_n/2))\}}{(2\pi d/\lambda_n)(1 - i\tan(\phi_n/2))} \tag{3}$$

where d is the thickness of the coating and ρ is its density and φ_n is the phase angle of the complex shear modulus at the measurement frequency, f_n. Note that the normalization for the film thickness is λ_n, the wavelength of the shear wave in the film, and the normalization for the frequency shift is the Sauerbrey shift [27], Δf_{sn}:

$$\Delta f_{sn} \equiv \frac{2nf_1^2}{Z_q}\rho d \tag{4}$$

The ability to measure material properties with the QCM originates from the relationships between λ_n and the properties of the coating [22,26,28]:

$$\lambda_n = \frac{1}{nf_1}\left(\frac{|G_n^*|}{\rho}\right)^{1/2}\frac{1}{\cos(\phi_n/2)} \tag{5}$$

here $|G_n^*|$ is the magnitude of the complex dynamic shear modulus at f_n. Note that $|G_n^*|$ and φ_n are related to the storage and loss moduli, G_n' and G_n'', respectively, by the following relationships:

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