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REVIEW

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After the paint has dried: a review of testing techniques for studying the mechanical properties of artists' paint

Gwen dePolo¹, Marc Walton¹, Katrien Keune^{2,3} and Kenneth R. Shull^{1*} 

Abstract

While the chemistry of artists' paints has previously been studied and reviewed, these studies only capture a portion of the properties affecting the response of paint materials. The mechanical properties of artists' paints relate to the deformation response of these materials when a stress is applied. This response is dependent on many factors, such as paint composition, pigment to binder ratio, temperature, relative humidity, and solvent exposure. Here, thirty years of tensile testing data have been compiled into a single dataset, along with the testing conditions, to provide future researchers with easy access to these data as well some general discussion of their trends. Alongside the more commonly used techniques of tensile testing and dynamic mechanical analysis, new techniques have been developed to more fully investigate the mechanical properties, and are discussed along with salient results. The techniques have been divided into two categories: those that are restricted to use on model systems and those that are applicable to historic samples. Techniques applied to model systems (tensile testing, dynamic mechanical analysis, quartz crystal microbalance, vibration studies) require too large of a sample to be taken from art objects or focus on the mechanical properties of the liquid state (shear rheometry). Techniques applied to historic samples incorporate the use of small sample sizes (nanoindentation), optical techniques (laser shearography), computational simulations (finite element analysis), and non-invasive comparative mechanical properties (single-sided nuclear magnetic resonance) to investigate and predict the mechanical properties of paints.

Keywords: Mechanical properties, Tensile testing, Dynamic mechanical analysis, Shear rheometry, Quartz crystal microbalance, Nanoindentation, Laser shearography, Single-sided nuclear magnetic resonance, Vibration studies, Finite element analysis

Introduction

Overview

Paint is a ubiquitous component of art objects and a research subject that has received prominent attention for many years in both industry and cultural heritage. A great amount of research has focused on understanding the chemical changes of the curing processes of paints, but they only partially capture the overall stability of a

paint film [1–4]. The mechanical properties play a key role in assessing its stability over the lifetime, providing information about the stiffness, toughness, and the likelihood of crack formation, among other things. The most recent review paper discussing the mechanical properties of paint was published thirty years ago, emphasizing the role that temperature (T) and relative humidity (RH) play on brittleness of these films [5]. In the present review our aim is to compile the innovative mechanical testing techniques that have been developed in the last two decades, together with the data derived from these experiments. It is shown how this area of research has grown and begun

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to provide possibilities for contributing to improved conservation practices.

Paints are typically comprised of a pigment for coloration, a binding medium, and other additives that can adjust the optical properties and workability of the paint film. All paint materials have several properties that change over time, initially being a liquid-like film that evolves into a solid-like paint film. This transition from liquid- to solid-like behavior can occur two ways: through a drying process, where solvents added to the system evaporate out of the paint film, or through curing, where crosslinking and other chemical reactions occur within the paint film to increase the stiffness. The timescale over which these drying and/or curing processes occur can vary greatly, from a few hours (acrylics) to months (alkyds) to decades (oil-based paints) [6, 7]. As the paint transitions from liquid-like to solid-like, the stiffness of the paint film can typically increase several orders of magnitude. For oil-based paints, the mechanical properties can continue to change over the long periods of time that the curing process is ongoing, motivating active research into the mechanical properties of these paints. Alkyd and acrylic paints, since they are modern paints that have been in use for less than 100 years, have also been a strong focus of research efforts in the last few decades. Other historic paints, such as distemper or egg tempera, are known to have a short drying phase and to form stiff, brittle films [6, 8]. Once tempera paints solidify, the mechanical properties remain fairly stable, so they have not been the focus of more recent research efforts. Distemper paintings are rare to find in a pristine condition, as many have been subjected to a varnish treatment, which alters the original mechanical properties of the film [9].

The mechanical properties of a paint film are affected by the paint composition, interactions between paint layers for a composite painting structure, and the environmental conditions (temperature, relative humidity, transportation, etc.) to which a paint is subjected. Each of these contributions will be discussed in further detail in the following sections, followed by an overview of the techniques discussed in the review and at what point during the lifetime of a painting they are relevant for use.

Pigment to binder ratio

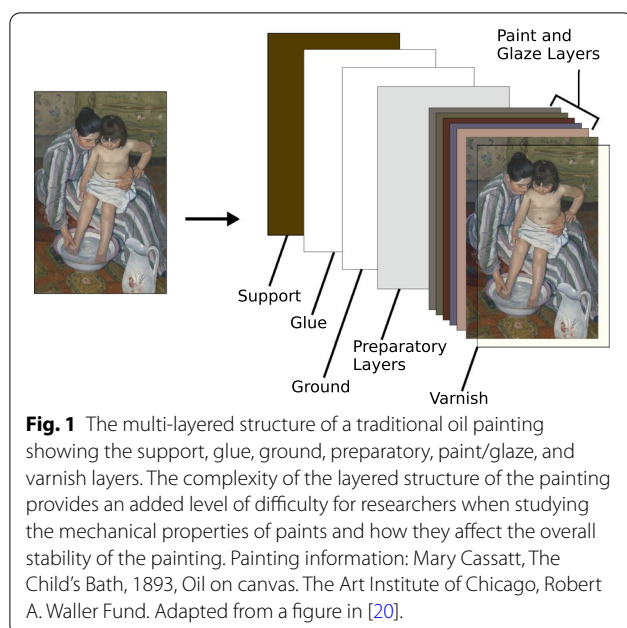
A simplified definition of a paint film is a composite material comprised of rigid pigment particles suspended in a more flexible binding medium. The concentration of pigment or additive present tends to have a strong contribution to the mechanical properties of the paint. The concentration can also vary widely depending on the desired properties and particular combination of pigments used in the paint. These relative concentrations

can provide insights about the expected stiffness of paints since the additives function as rigid fillers within the binding medium matrix. The added filler is typically much stiffer than the corresponding binding medium matrix, and thus contributes to an increased stiffness of the overall paint [10, 11]. A challenge for researchers is accurately determining the pigment to binder ratio of fully cured historic paints, which provides relevant information for understanding the mechanical properties of the paint and for understanding an artist's technique by making paint reconstructions. Two approaches to determine pigment to binder ratio that have been previously used various imaging and spectroscopic techniques to analyze these cross sections. The first approach used a sequence of μ X-ray diffraction (μ XRD), particle induced X-ray emission (PIXE) and backscattering spectrometry (BS) to determine the light and heavy elements present in a historic paint cross section, using the techniques together to identify the pigment(s) and estimate of the ratio of pigment to binder in the sample [12]. Alternatively, researchers have looked into the quantification of the ratio between pigment and binder on stable, liquid-like paint systems using Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy [13]. The use of these spectroscopic techniques becomes difficult on dried historic paints where the pigment, binder, or both are not stable over long periods of time, since the particular chemical peaks tracked in this study can change quite a bit over longer periods of time. Some more recent work has used X-ray micro- or nano-tomography to determine the pigment to binder ratio for the full volume of a paint sample [14].

Some studies focused on the mechanical properties of paint have used a measurement of pigment content based on volume, pigment volume concentration (PVC), instead of pigment-to-binder ratio, which is a weight-based measurement [15–17]. Mathematical models have also been developed to describe the effects of pigment particle concentration and shape on the stiffness of the sample and have been explored in some of the studies that will be highlighted in Section 2 [18, 19].

Paintings as multi-layer structures

The complexity of paint mechanical properties goes beyond the effect of a rigid filler on the stiffness of the paint. Multiple layers of paint ranging from tens of microns to 1 mm in thickness are generally utilized in the creation of a painting. These layers are placed on a support, forming a multi-layer structure where the mechanical properties of a given paint layer can be affected not only by the environmental fluctuations or conservation treatments, but also by changes in the surrounding layers (Fig. 1) [20].



Obtaining information about this complex multi-layer structure presents challenges to researchers, especially understanding how each layer contributes to an overall response of the object and how the material/chemical composition influences that response. The range in size of single paint layers to entire paintings also provides a challenge for determining which length scale (e.g., micron, millimeter, or meter) and therefore which technique is most relevant for understanding the mechanical response of an object. Any expansion or swelling of a given layer (such as the swelling of a canvas in response to increased RH) or significance differences in stiffness between layers (i.e. a much stiffer ground layer below a paint layer) can lead to small applied strains on the surrounding layers, causing stresses that increase the potential for cracks to form and propagate through the painting. Paint layers can also be subject to issues of adhesion, which can lead to delamination or paint loss, which is also problematic. Understanding the mechanical properties of these layers the mechanical response to neighboring layers or environmental fluctuations are relevant when determining the overall structural stability of a painting and will be discussed within this review.

Craquelure

One of the main concerns for conservators is the formation or propagation of new cracks within the painting due to fluctuations in environmental conditions or as a function of transporting a painting. The craquelure present in a painting is acknowledged as an inherent part of the drying process of the paint, but the

formation of new cracks from an impact, transportation, or a drastic change in environmental conditions can increase the chances for paint delamination and paint loss. The development of craquelure in paint has been an area that has been discussed fairly extensively in a qualitative nature, but has experienced difficulties in developing a standardized metric for characterizing the craquelure [21–24]. Some models have been discussed with regards to how ground layers may develop cracks as a result of environmental fluctuations [25]. Research on the craquelure formed using model colloidal systems, which can be tuned to have similar particle size and distribution as historic paint layers, has provided some information about the distinctions between drying and aging cracks, as well as the insight that as paintings age, the degree of cracking increases [26]. The research was also extended to discuss how craquelure on paintings can relate to the mechanical properties of the visible and underlying paint layers, as well as the implications of these craquelure in the routine conservation work performed on paintings [27]. These colloidal system studies provide some experimental data to correlate with the qualitative descriptions of craquelure patterns, but it can still be difficult to understand the underlying mechanisms influencing crack formation and propagation within the paint.

Two distinct length scales need to be considered when discussing crack formation in a paint layer. The first of these is the macroscopic scale of the entire painting, which determines the stresses that the paint layer is exposed to. In fracture mechanics terms these stresses define the driving force for continued growth of a crack, typically expressed in terms of an energetic driving force, \mathcal{G} . This quantity has units of energy per unit area, and quantifies the energy that is recovered by the overall system as the crack grows. Crack growth occurs when \mathcal{G} exceeds a critical value, \mathcal{G}_c , that is characteristic of the paint. Growth of the crack alters the stress field around the crack itself, affecting its own trajectory and the ability of neighboring cracks to grow. These interactions determine the craquelure patterns that are observed in actual paintings, and motivate the need to understand the system behavior at the length scale of the cracks themselves. Because of the complexities of the experimental geometries in real paintings, numerical finite element methods have an important role to play at both of these length scales, although considerable insight can also be obtained from appropriate analytic expressions. [27]. The main point we want to make here is that it is generally not sufficient to understand the properties of the paint in absence of an understanding of the relevant driving forces for crack propagation. These driving forces originate from a combination of external forces imposed

Table 1 Summary of the techniques and defining characteristics (age of the paint, type of samples, the amount of strain applied to the sample, how invasive the technique is, and the relevant mechanical properties) for each technique discussed within this review.

Technique	Paint age	Sample type	Applied strain	Sample size	Invasiveness	Relevant data
Tensile testing	Dried/aged paint	Model systems	Large strain	Bulk	Invasive	Elastic stiffness, ultimate mechanical properties (E , e_f , σ_T)
Dynamic mechanical analysis	Dried/aged paint	Model systems	Small strain	Bulk	Invasive	Solid/liquid-like behavior (E^* , $\tan\phi$)
Shear rheometry	Fresh Paint	Model systems	Small strain	Bulk	Invasive	Viscosity (η)
Quartz crystal microbalance	Fresh & dried/aged paint	Model systems	Small strain	Thin-film	Invasive	Elastic stiffness, swelling ($d\rho$, $ G^* \rho$, ϕ)
Nanoindentation	Dried/aged paint	Model systems & Historic samples	Small strain	Single point/small sample size	Minimally invasive	Elastic stiffness, hardness (E_r , H)
Laser shearography	Dried/aged paint	Model systems & Historic samples	Small strain	Area of painting	Non-invasive	Strain maps
Finite element Analysis ⁺	Fresh & dried/aged paint	Model systems & historic samples	Simulated large and/or small strain	Any sample size	–	Predictive mechanical responses
Vibration Studies	Dried/aged paint	Model systems	Small strain	Area of painting	Minimally invasive	Damage risk
Single-sided nuclear magnetic resonance	Dried/aged paint	Model systems & historic samples	–	Single point/small sample size	Non-invasive	Comparative stiffness

Definitions for mechanical properties in relevant data: E : elastic modulus, e_f : failure strain, σ_T : ultimate tensile strength, E^* : complex elastic modulus, $\tan\phi$: loss tangent, η : viscosity, $d\rho$: areal density, $|G^*|\rho$: magnitude of the complex shear modulus multiplied by the density, E_r : reduced elastic modulus, H : hardness. ⁺Indicates that the technique is a numerical method

on the object and internal forces generated by the varying response of the different layers to environmental conditions.

Relevant techniques

The techniques covered within this paper, along with applicability to either model systems or historic samples and when they can be used during the lifetime of a paint, are shown Table 1. Deciding when to use a given technique depends on the desired mechanical property and the goal of the research program, whether it's to address questions from art history (i.e., how an artist achieved a specific painting effect), to monitor or assess the condition of historic objects, or to understand the fundamental responses of mockup paint samples that can be deformed and subjected to damage more readily than a historic painting. Since there can be some challenges in comparing the results obtained from model systems with historic samples (typically due to age and composition differences), these techniques have often been paired with other analytical techniques to study the chemical response of a paint and provide a more direct comparison.

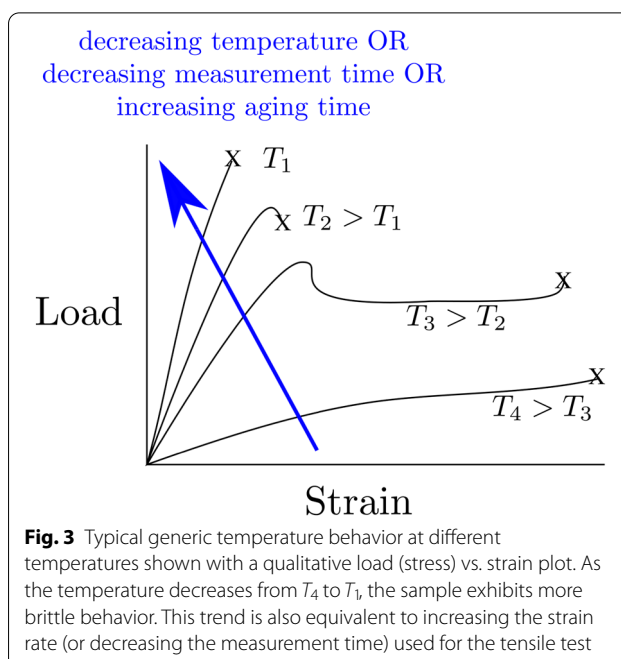
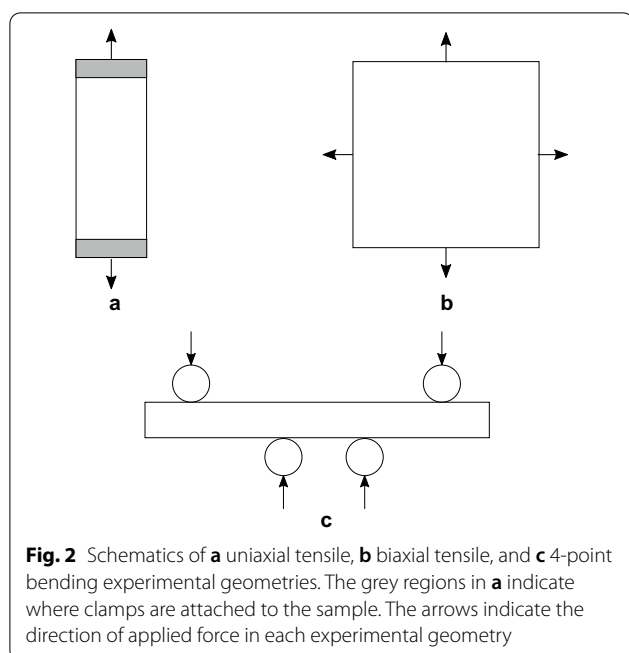
For each of the techniques in Table 1, we will discuss the advancements and significant results as well as future directions for their optimization and use to study paints. To help explain the types of data and the significance of

results, there will first be a brief overview of the mechanical properties investigated with each technique.

Tensile resting

Static mechanics overview

In typical statics measurements of paint systems, a force (stress, σ) is applied to a system to cause a displacement (strain, e). The stresses can be applied in either a normal or a shear direction to the sample. For paint materials, the stresses are commonly applied through the geometries shown in Fig. 2. These sample geometries take into consideration some of the structural aspects of the material, such as whether it is a membrane system (e.g., an individual paint layer or painting on a canvas), is attached to a rigid support (e.g., painting on a wood panel), or is still in a liquid form (e.g., reproductions of historic recipes). Uniaxial tensile testing (Fig. 2a) applies force on opposing ends of a paint film, providing material properties that will be described shortly. Biaxial tensile testing (Fig. 2b) applies tensile forces in two directions, which can be useful when looking at the composite structure of a paint layer on a support (i.e. a linen canvas). However, the composite nature of these systems can make it difficult to accurately define the individual material contributions to the overall behavior. Four point bending (Fig. 2c) applies forces on either side of a sample in such a way as to cause both compressive and tensile forces at the center of the sample. If there is an adhesive or filler material

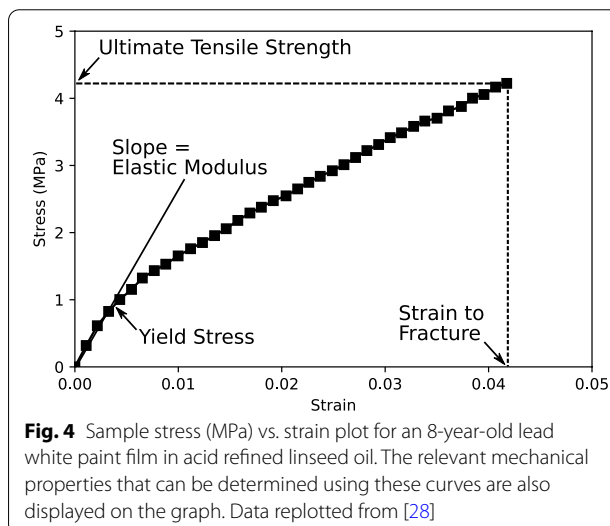


being used on a wooden object, these tests are useful for determining the potential failure conditions of the conservation materials.

The stress-strain behavior for a material can exhibit a range of phenomena, depending on the temperature and timescale of the measurement. In polymeric materials there is a general equivalence between time and temperature, with similar behavior obtained either by decreasing the temperature or increasing the time scale of the measurement. For artist paints, the properties also evolve with time, adding another dimension of complexity. Generic results obtained from a uniaxial tensile test are shown in Fig. 3. While not all of these behaviors are necessarily observed in the same material, the following general regimes can often be identified, based on 4 different temperature regimes (T_1 , T_2 , T_3 and T_4).

- T_1 : Brittle behavior of a glassy material. This is generally observed at sufficiently low temperatures.
- T_2 : Ductile behavior followed by localized thinning of the sample and failure.
- T_3 : Ductile behavior with substantial localized deformation after yield.
- T_4 : uniform deformation of a very soft, rubber material.

Note that Fig. 3 is highly qualitative and does not accurately capture the detailed changes that are observed. As one follows the blue arrow from T_4 to T_1 , the polymer sample would pass through the glass transition



temperature, T_g , which is the point when a polymer transitions from a rubbery, more flexible response to a glassy, more brittle response. A more quantitative example of a tensile test is the stress-strain curve for the 8-year-old lead white sample shown in Fig. 4. These curves provide several results that help the researcher understand the overall mechanical behavior of the paints. The elastic modulus (E) (a.k.a. Young's modulus) can be determined from the slope of the curve at low strains and is shown by the line extended from the stress strain curve. When the paint film begins to yield, the slope of

the stress strain curve decreases. The stress at which this yield point occurs is known as the yield stress (σ_Y). Not all paint samples exhibit a yield stress either due to the softness of the material or to the viscoelastic behavior of the film. For cases where a yield stress is not present in the data, a secant modulus (E_s) can be calculated using the following equation:

$$E_s = \frac{\sigma}{e} \quad (1)$$

where common values of e are less than or equal to 0.05. The end of a tensile test usually occurs when there is a failure such as a fracture in the paint sample. The stress and strain values at this point, the ultimate tensile strength (σ_T) and strain to fracture (e_f) respectively, are useful material properties for characterizing the limits of a sample.

These static tensile measurements require larger samples, making them impractical for measurement of historic paints and requiring the use of either model systems or sacrificial collection samples. The sample geometry for tensile tests also requires solid samples, which means the paints have to dry for at least 1 week (acrylic) to 1 month (oil) before measurements can be taken. The instruments used for these measurements can be modified to include environmental chambers that control T and RH, some of the more important practical parameters for understanding the material properties of paints.

Uniaxial extension

Uniaxial tensile testing of paint samples has been one of the most commonly used techniques for investigating the mechanical properties of paints in cultural heritage over the last few decades. A summary of the references that have used tensile testing to measure the mechanical properties of paint materials is shown in Table 2. A summary of the data from these references are available as supplementary information in PDF (Additional file 1) and Excel (Additional file 2) files¹.

From the references in Table 2, Fig. 5 provides an overview of the range of E from the samples tested as a function of age (associated with the curing time) of the samples, which spans four orders of magnitude. While this graph does not show a strong trend in the data, it does highlight one main takeaway about analyzing these data: it is difficult to analyze trends in the data using only a single variable from these uniaxial tensile tests.

As discussed above, the type of pigment used will impact the pigment to binder ratio of a given sample. Inorganic pigments also tend to be much stiffer than the binding media, also leading to a significant increase in the stiffness of the sample. Many of the studies focused on the effects of temperature [18, 29, 30, 36, 37, 41, 43, 46, 50, 54, 57] and relative humidity [15, 29, 30, 34, 36, 37, 41, 43, 44, 46, 52, 57, 59] on the stiffness of the sample. There is a general trend across all three binding media classes of increasing stiffness as the temperature of a paint decreases, shown in Fig. 6, which would indicate that the increase in stiffness is controlled more by the properties of the binding medium than the particular pigment used. For all these general classes of binding media, -10°C is below their T_g , which leads to a glassier, more brittle response from the samples. When the RH is increased for a paint system, researchers observed a general softening phenomenon occur since water can act as a plasticizer in most paint films, leading to a decrease in the stiffness that can range from 30-90%.² [15, 29, 30, 34, 36, 37, 41, 43, 44, 46, 52, 57, 59]. When the RH is decreased, the paints become stiffer as less ambient water is present, showing anywhere from 40-300% increase in the stiffness.

Another common variable for the material response of paint materials is solvent exposure to assess the effects of solvents commonly used for cleaning paintings [18, 28, 36, 37, 42, 48, 49, 62]. The most common trend after exposure to volatile solvents was that the paint films would become embrittled, exhibiting stiffer, more brittle responses (anywhere from 100-900% increase in the stiffness) due to the leaching and volatilization of low molecular weight components. Yet, exposure to non-volatile solvents resulted in increased plasticity of the paint films (up to a 74% decrease in the stiffness) [28]. Results from uniaxial tensile tests are also dependent on the strain rate of the test, or how quickly the sample is deformed. As the strain rate is increased, the paint film has less time to respond to the deformation taking place, leading to a stiffer, glassier response. Hagan *et al.* varied the strain rate during their research on acrylic and oil-based paint systems to apply time temperature superposition (explained more fully in Sect. 3) to their results and observe the material response over a wider range of testing strain rates [18, 19, 46, 50, 54]. The studies also considered the effects of PVC as well as the shape of the pigment particles on the overall response of the pigment/binding medium composite sample using mathematical models focused on filler effects in a composite,

¹ To help understand and look at overarching trends in the mechanical properties of paints studied using uniaxial testing, we compiled a summary of the reported mechanical property data from studies focusing on oil, alkyd, and acrylic paints as well as some paint consolidants and grounds. See Additional files 1 and 2 in the Supplementary Information.

² For all of the ranges presented for changes in stiffness as a result of a change in a testing parameter, the range has been estimated across all binding media and sample compositions in an attempt to show the maximum impact a particular parameter can have on the stiffness.

Table 2 Summary table of the types of paints and testing parameters varied in the studies that used uniaxial tensile testing to investigate mechanical properties

Reference	Oil	Alkyd	Acrylic	Filler, ground, support	Temp.	RH	Solv. exp.	Strain rate	Sample comp.	Aging
Mecklenburg, 1991 [29]	✓				✓	✓			✓	✓
Erlebacher, 1992 [30]		✓	✓		✓	✓			✓	
Mecklenburg, 1994 [31]			✓						✓	
Whitmore, 1995 [32]			✓							✓
Tumosa, 1999 [28]	✓						✓		✓	
Mecklenburg, 2001 [33]	✓									✓
Carr, 2003 [34]	✓					✓			✓	✓
Mirone, 2004 [35]		✓							✓	✓
Meckelburg, 2004 [36]	✓				✓	✓	✓		✓	✓
Hagan, 2004 [37]			✓		✓	✓	✓		✓	✓
Erhardt, 2005 [38]	✓									✓
Tumosa, 2005 [39]	✓								✓	
Young, 2007 [40]	✓	✓	✓						✓	✓
Hagan, 2007 [15]		✓	✓			✓		✓	✓	
Young, 2008 [41]	✓	✓	✓		✓	✓			✓	✓
Fuesers, 2008 [42]	✓	✓					✓		✓	
Ormsby, 2008 [43]			✓		✓	✓			✓	
Fuster-Lopez, 2008 [44]				✓		✓			✓	
Carlyle, 2008 [45]				✓		✓			✓	
Hagan, 2009 [46]			✓		✓	✓		✓	✓	
Hagan, 2010 [18]			✓		✓		✓	✓	✓	
Hagan, 2011 [19]			✓					✓	✓	
Tumosa, 2013 [47]	✓								✓	✓
Mecklenburg, 2013 [48]	✓	✓					✓		✓	✓
Domenech-Carbo, 2013 [49]			✓				✓		✓	
Hagan, 2015 [50]			✓		✓			✓	✓	
Fuster-López, 2016 [51]	✓								✓	✓
Krzemien, 2016 [52]				✓		✓				
Penava, 2016 [53]				✓					✓	
Hagan, 2017 [54]	✓	✓	✓		✓			✓	✓	
Fuster-López, 2017 [55]	✓					✓			✓	✓
Doutre, 2017 [56]				✓		✓			✓	
Roche, 2018 [57]	✓		✓		✓	✓			✓	✓
Fuster-López, 2019 [58]	✓	✓							✓	✓
Bridarolli, 2020 [59]				✓		✓			✓	

Temp. temperature, *RH* relative humidity, *Solv. Exp.* Solvent exposure, *Sample comp.* Sample composition. Sample composition includes changes in binding medium, pigment type and composition, and sample thickness. Aging refers to both natural and accelerated aging of samples

highlighting the importance of understanding the PVC of a paint sample [19]. There is a challenge of the composition of the binding medium and PVC not being readily available for commercial artists' paints, but with enough time and access to analytical tools they can be determined. Not all the responses are explained through pigment type or filler concentration, though, because the alkyd paints continue to increase in stiffness as a function

of time regardless of pigment, shown in Fig. 7, whereas the oil and acrylic paint classes do not show any trends as a function of age due to convolution from other testing parameters.

One of the main drawbacks to using model systems for paints is their relatively young age; they are typically 30 years old at their oldest. While this age range is more relevant for the newer alkyd or acrylic paint classes, it

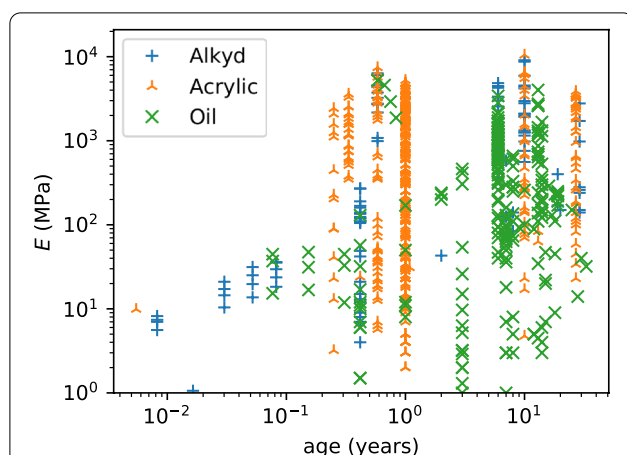


Fig. 5 Plot showing elastic modulus (MPa) vs aging time (years) from uniaxial tensile tests of oil, alkyd, and acrylic paints. The graph does not account for testing variables such as T, RH, solvent exposure, or pigment/particle type used in the paint medium, contributing for the wide spread of the modulus data. Data compiled in this graph are from [15, 18, 19, 28, 30, 33–37, 39, 41–43, 46–51, 54, 55, 58, 60, 61]

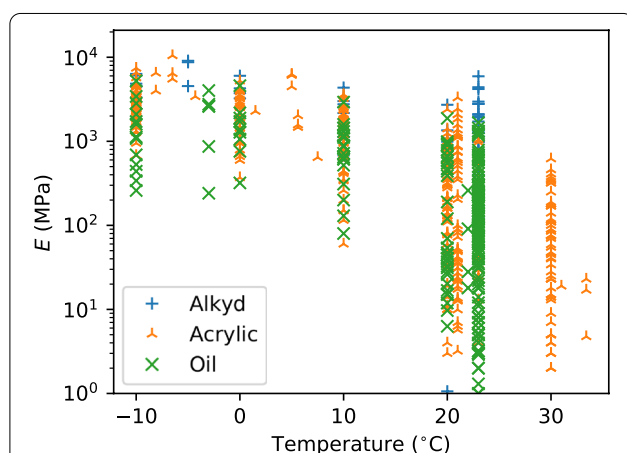


Fig. 6 Plot showing the elastic modulus (MPa) vs temperature (°C) from uniaxial tensile tests of oil, alkyd, and acrylic paints. The graph does not account for other testing variables such as age, RH, solvent exposure, or pigment/particle type used in the paint medium. Data compiled in this graph are from [15, 18, 19, 28, 30, 33–37, 39, 41–43, 46–51, 54, 55, 58, 60, 61]

becomes difficult to draw conclusions about the expected material responses of oil paints that are 50 years or older. While accelerated aging may be a way to address this issue, previous research has shown that without careful tailoring of the study, accelerated aging of the paint film enables different chemical reaction pathways than natural aging for oil paints, which can make comparisons difficult [63]. Some theoretical extrapolations can be made about the response by observing the changes in stress

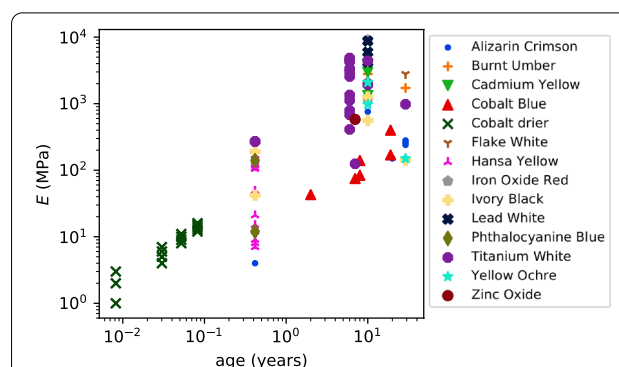


Fig. 7 Plot showing the elastic modulus (MPa) vs age (years) for the alkyd paints. The wide spread in the value of the elastic modulus for Hansa Yellow is due to solvent exposure. The spread in the data for Titanium White is due to temperature variations. Data compiled in this graph are from [30, 35, 42, 48, 54, 58]

at constant strains. Over longer times, the stress begins to follow a linear trend when plotted against the natural log of time, which allows researchers to create theoretical stress-strain curves that can be more predictive [36, 38]. This analysis method provides a good first approximation for some brittle paints, but it has not been applied to softer paint systems or to paint systems where the stiffness remains constant, but the flexibility of the paint film decreases.

Some of the studies shown in Table 2 focus on other materials found in the multi-layered structure of a painting than paint. Researchers have studied the response of grounds to RH to determine ideal storage conditions and the effects of drying shrinkage on the formation of cracks within the ground [52, 56]. The stiffness of canvas as a function of the orientation of the weave of the sample has also been explored using uniaxial extension, demonstrating that the stiffness is strongly dependent on the orientation that the load is applied to the canvas [53]. Samples comprised of multiple layers (*i.e.*, paint-paint or canvas-paint) can provide some insights into the response of the composite to changes in temperature or relative humidity, but it becomes difficult to determine which aspects of the composite structure are contributing to those changes [40, 57, 59, 64].

Uniaxial tensile testing provides researchers with the ability to investigate the effects of T, RH, solvent exposure, and PVC on the mechanical properties of paint, but these investigations can only be performed on model systems due to the relatively large amounts of sample required for measurements.

Biaxial extension

When we consider the composite nature of paintings, those mounted on stretchers experience stresses to the

paint layers from two directions, which can be difficult to capture using only the uniaxial extension test. The way that paintings are mounted to stretchers is very similar to how they would be studied using biaxial extension (Fig. 2b), making this technique a relevant method for studying these model systems. To address the complexity of observing stresses in two directions, Young developed a biaxial tensile testing system that would be compatible with painting mockups [65]. An electronic speckle pattern interferometer was incorporated into the instrumentation to help determine the amount of strain occurring in each direction during the tensile tests [66]. The biaxial setup has been used to assess the behavior and interaction of glue, oil, and flour paste grounds when they are applied to canvases [45]. The glue and oil grounds demonstrated stronger changes as a function of RH than the flour paste grounds, but the flour paste grounds were not as stiff as the other two grounds [45]. Using the biaxial geometry to investigate canvases and paint layers allows researchers to investigate how the mechanical response of a canvas-paint composite sample will be affected by environmental changes since the response of the composite system will be different dependent on the canvas weave direction. Due to the isotropic nature of paint samples, when using this geometry both E and Poisson's ratio (ν), the lateral strain that occurs perpendicular to the applied stress, can be determined. One important aspect to keep in mind is that the corners of the sample will act as stress concentrators when placed under tension (see Sect. 7.2), which can cause issues during data analysis. A workaround can be to remove the corners of the model samples or to use computational simulations to study the impact of the corners of a sample more fully. From a materials characterization standpoint biaxial testing provides information that is comparable to what is obtained from uniaxial testing. Its primary use as described above is in studying the mechanical response of the overall composite painting structure under realistic loading conditions.

Bending geometries

As was mentioned earlier, a bending geometry allows one to investigate both compressive and tensile forces applied to a material, especially if those are potential forces that need to be accounted for in a rigid art object. Young *et al.* performed a study of adhesives and fillers that are typically used in the conservation of panel paintings, which can have a large range of stresses applied as a function of environmental shifts (typically T or RH) [67]. With the bending geometry, it was easier to determine whether the failure of the joints studied was due to the adhesive or to the wooden support [67]. The load curves from this research were compressive rather than tensile, generating

stiffness measurements that are not as directly comparable to the tensile data shown earlier. These more rigid paint composite systems can also be more thoroughly studied through computational simulation, which will be discussed more in Sect. 7.2. This geometry had targeted benefits of exploring the response of paints, adhesives, and fillers on rigid substrates, but is not as useful beyond this targeted application.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is a technique ideally suited for studying viscoelastic samples such as paints. Most DMA studies of artists' paints have used a similar sample geometry and force application as uniaxial tensile testing (see Fig. 2). Unlike tensile testing, which applies a fixed stress or strain rate, DMA samples undergo oscillatory loading conditions to look at the frequency dependent response common to polymer-based systems, including artists' paints. Quantifying this behavior is important when planning storage, travel, or exhibition conditions and conservation treatments for a work of art. In DMA experiments, the stress is applied as a function of time ($\sigma(t)$), which leads to a time dependent expression for the elastic modulus, $E(t)$, which for an oscillatory stress and strain can also be notated as a complex function, E^* :

$$E^* = E' + iE'' = |E^*|e^{i\phi}, \quad (2)$$

where E' is the storage modulus that describes the solid-like behavior of the sample, E'' is the loss modulus that describes the liquid-like behavior, $|E^*|$ is the magnitude of the complex elastic modulus, and ϕ is the viscoelastic phase angle, which describes the phase difference between the oscillatory stress and strain. The two right sides of Equation 2 can be related through these two equations:

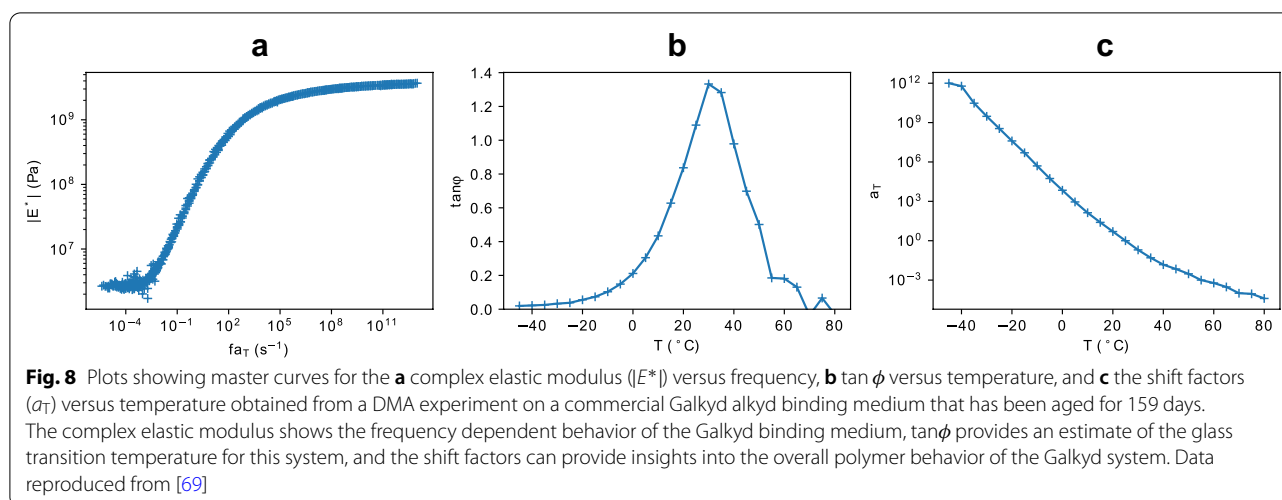
$$E' = |E^*| \cos \phi \quad (3)$$

$$E'' = |E^*| \sin \phi. \quad (4)$$

We can combine Eqs. 3 and 4 to get the following expression for $\tan \phi$ (also known as $\tan \delta$ in literature), commonly referred to simply as the loss tangent:

$$\tan \phi = \frac{E''}{E'}. \quad (5)$$

For samples that are thermorheologically simple, or have the relaxation times present in the sample that are all affected the same way by temperature, frequency sweep experiments can be performed at various temperatures and used to generate a master curve of both E^* and $\tan \phi$ using time-temperature superposition [68]. From these



master curves of the complex elastic modulus versus shifted frequency, the glassy and rubbery regimes of a sample are visible. The peak of a $\tan \phi$ versus temperature plot is a measure of the glass transition temperature, T_g , where the sample transitions from rubbery behavior above the T_g to a more brittle, glassy response below T_g . Due to the nature of polymer relaxation times, the T_g is also partially dependent on the frequency of the measurement. In a typical amorphous polymer, increasing the frequency of measurement by an order of magnitude increases T_g by about 3 °C, which is important to remember when comparing data between different techniques that use a different base frequency, such as will be discussed in Sect. 5. Shift factors (a_T) are used to align the E^* and $\tan \phi$ to the values for a given reference temperature by shifting the data horizontally along the frequency axis, using the underlying assumption for time-temperature-superposition to apply these shift factors. Figure 8 provides example master curves of $|E^*|$ as a function of frequency and of $\tan \phi$ and a_T as a function of temperature for an alkyd binding medium commercially made by Galkyd and aged for 159 days before testing. In Fig. 8a, $|E^*|$ spans over 15 decades of frequency, showing the rubbery-like behavior on the lower left of the graph and the glassy behavior on the upper right. The $\tan \phi$ curve shows a peak around 26 °C, which would be a rough estimate of the T_g for this alkyd binding medium. Mathematical models are often used to describe the shift factors and predict the response of the polymers [68], but are not discussed in this review.

Hedley *et al.* presented some of the earliest foundational work using DMA on artists' paints to assess changes in mechanical responses of lead white ("medium lean") and burnt sienna ("medium rich") samples after exposure to solvents typically used for cleaning [70].

Using a shear stress geometry and temperature range from 5 – 100 °C, an increase of G' (loss shear modulus, defined in a similar way to the E') and significant reduction in $\tan(\delta)$ for the burnt sienna samples indicated leaching and embrittlement after solvent exposure; the lead white samples showed minimal change in response after solvent exposure [70]. Samples of the same pigments aged 15 years were explored over a range of relative humidities (54–94%) and compared to composite samples of canvas, primer, and a white oil paint layer from a rear primed painting, which demonstrated a softening behavior with an increase in relative humidity [71]. Foster *et al.* modified a DMA system to work with a controlled RH chamber in order to study how the RH and curing process of polyester/melamine paint systems affect the glass transition temperature [72]. The analysis performed on E' and $\tan \phi$ master curves is a good example and illustrates just how much information is obtained through these experiments.

Ormsby *et al.* focused on acrylic paints, specifically investigating the effects of solvent exposure on the chemical, optical, and physical properties of the samples [73]. Comparisons between acrylic brands and exposure methods of swabbing or immersion were considered, showing a strong effect on the dimensional extension of samples after being immersed in the solvents, especially more polar solvents. The T_g of the samples would increase with extended immersed solvent exposure, showing an opposite trend than previous data on oil paints, most likely due to embrittlement of the acrylic paints as a result of the solvent exposure. The samples that were swabbed experienced significantly smaller changes in the DMA data, leading to the conclusion that using swabs for solvent exposure will reduce the overall changes to the bulk properties of the paint compared to full immersion of the

paint film, even if some surfactants are lost at the surface of the film [73]. Titanium white acrylic paints exposed to temperature and RH sweeps showed typical responses corresponding to an embrittlement/decrease in T_g with a decrease in RH, indicating a strong relationship between the water content of the paint and the mechanical properties [74]. Some samples that were thermally aged exhibited smaller $\tan(\delta)$, peaks, indicating stiffer films than the naturally aged films and potentially better coalescence of the paint films. The onset of a brittle response from alkyd and acrylic based grounds was investigated using the T_g from DMA to help confirm the ductile to brittle transition as temperatures were dropped from 20°C to −10°C [41]. Phenix performed an extensive survey of T_g values of oil paints and how they were affected by the type of pigment and the age of the paint sample (1–16 years), finding that the range of T_g s varied widely with sample composition [75]. Most samples in the study demonstrated an increase in T_g with age, indicating an embrittlement effect that could pose potential long term issues for paintings stored in a museum environment.

The application of time-temperature superposition to DMA data collected over a range of temperatures allows researchers to access a much wider range of measurement frequencies than typically accessed with other methods. Sturdy *et al.* used DMA to understand the material response of a commercially produced alkyd based binding medium (Galkyd) as a function of curing time and filler content of zinc oxide, providing a survey of the effects of filler content and the compatibility between DMA, the quartz crystal microbalance (QCM), and nanoindentation for studying paint materials [17, 69]. These studies also compared the material responses measured using DMA and the QCM, demonstrating that both techniques are able to capture the glassy material response well. Verifying the general response regime of a viscoelastic system using the T_g is also fairly common; a linseed oil with zinc/lead white ionomer system determined the T_g of samples with DMA to inform diffusion models for solvent exposure of the ionomer systems, which are used to study the mechanisms controlling the formation of metal carboxylates, or metal soaps, within a paint film [76]. More recently, the mechanical properties of oil paints aged 6 years with several additives including fatty acids (both with and without a metal base), linseed oil, and alumina hydrate were observed and quantified using the DMA to studying commercial Winsor & Newton oil paints, commonly used by contemporary artists [77]. With more linseed oil, the T_g of paints decreased, while alumina hydrate increased the T_g ; the added fatty acids did not have a consistent effect on the T_g [77]. Quantification of the effects of solvent exposure (immersion and sponge) for a water-sensitive yellow ochre paint

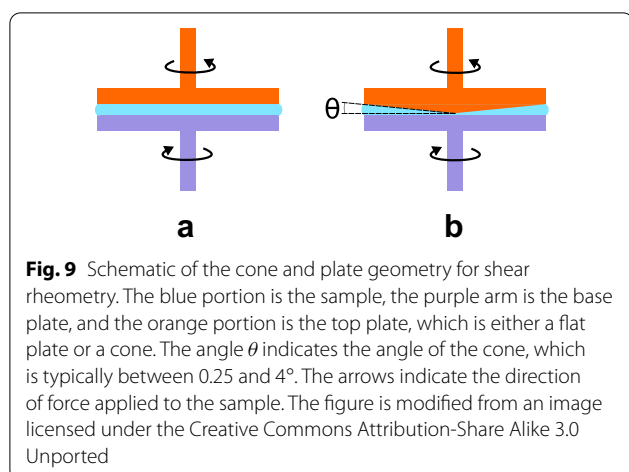
using DMA and nanoindentation indicated that full immersion had the higher chance of embrittling the paint films than the sponge cleaning, highlighting the importance of choosing the appropriate method and solvent when preparing to clean a specific paint [78]. A study that focused on the material response of composite sample was Bridarolli *et al.*, which assessed the change in E' of consolidants that are commonly used as treatments on degraded canvases as a function of relative humidity to determine their effectiveness and viability for use in conservation treatments [59].

Most research on paint samples using DMA have emphasized the importance of T_g in assessing the overall response of the paint as well as providing a metric for understanding the type of response (i.e. more glassy/brittle or rubbery/ductile) to expect from paint samples. T_g of a paint is also an important parameter to know when adding an infill to a painting to ensure there are not added stresses created within the paint layers through a mismatch of mechanical properties. Due to the amount and geometry of the sample necessary to perform these measurements, model systems are typically used, introducing challenges when drawing conclusions about the behavior of “young” paint samples (1–15 years) and using them to predict the behavior of older paint samples (100+ years). When time-temperature superposition is used for a DMA experiment, one can obtain more information about a single paint film than from a typical tensile testing experiment. There are some nuances to be aware of when determining the T_g of the paint sample, but the papers in this section provide guidance towards understanding those nuances.

Shear rheometry

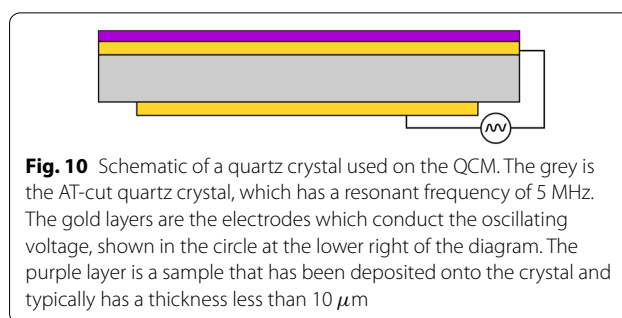
Shear rheometry can be viewed as a version of DMA that is used in a shear geometry and well suited for samples with a liquid character. It has been used to study historic paint formulations, varnish, and glaze recipes, with an emphasis on understanding on how the recipe influenced the overall texture and visual presentation of paintings today. These experiments are typically performed using either the parallel plate geometry, shown in Fig. 9a, or the cone and plate geometry, shown in Fig. 9b. Samples studied using these geometries experience shear forces, resulting in the measurement of a complex shear modulus, G^* , analogous to the complex elastic modulus, E^* defined in Sect. 3. For isotropic materials, which have the same bulk properties in all directions, the shear modulus can be related to elastic modulus through the following expression that also involves Poisson's ratio, ν ,

$$E = 2G(1 + \nu). \quad (6)$$



For liquids and relatively soft polymers at temperatures above their glass transition temperature, $\nu \approx 0.5$ and $E \approx 3G$. In an oscillatory experiment where the complex shear modulus, G^* , is obtained, $E^* \approx 3G^*$, $E' \approx 3G'$ and $E'' \approx 3G''$, where G' and G'' are the storage and loss shear moduli, defined as described in Sect. 3, but with G' , G'' and G^* replacing E' , E'' and E^* .

Originally developed for use in industry, shear rheometry has been used for about 70 years to understand the mechanical properties of paints. Due to the longstanding use of the technique, best practices for measuring the mechanical properties of historic recipes have been described in some detail [79, 80]. One of the earliest reported discussions about the composition of the paint affecting the rheological behavior of the paint examined the state of white impastos used by Rembrandt, concluding that the proportions of pigment and driers resulted in a thixotropic behavior of the paint, with the viscosity decreasing with increasing strain rate. Not only did such insights provide a greater understanding of Rembrandt's paint structures, it was shown that these data could be used to relate the artist's technique to the measured yield stress of the paint [81]. Further surveys of the effects of adding resins, solvents, and pigments on the viscosity and resulting yield stress of paints, glazes, and varnishes has broadened the knowledge base for thinking about how these historic recipes influenced the response and characteristic appearance that we associate with these materials [82–84]. More recent research has focused on studying the rheological properties of gumtion, an experimental paint material that added resin to the oils to decrease the drying time of the paint, and the effects of fillers such as calcite on the workability of lead white paints [85, 86]. For instance, the amount of pigment Van Gogh needed to create the impasto effects in his paintings was connected to the relationship between the yield

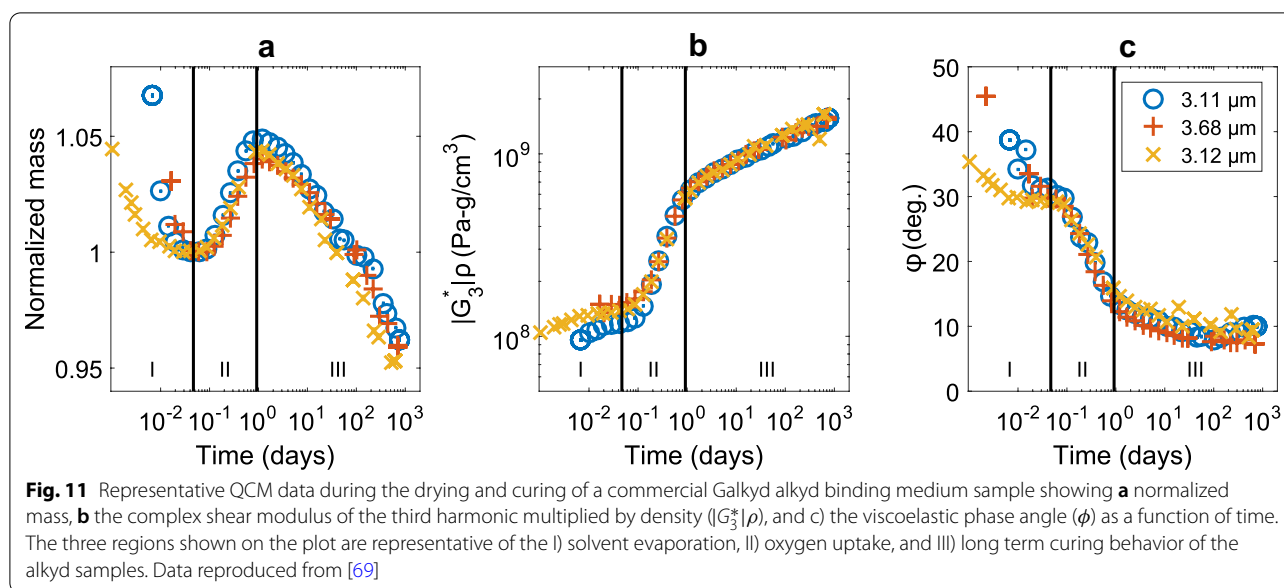


stress and pigment concentration [16]. Rheology has also been used to characterize plant-oil based inks (similar recipes to oil-based paints) to optimize their properties as well as adhesive combinations to maximize their effectiveness as consolidant materials [87–89]. Thixotropic behavior and the effects of pigment concentrations on the flow of the paint through rheology provides both important conservation data explaining causes of sagging, drippings, or flaking of paintings as well as art historical insights into how historical recipes can be correlated to artist technique.

Quartz crystal microbalance

Originally used as a technique for studying small mass changes, the QCM has been developed to study the viscoelastic properties of biological and polymer-based systems [90]. Many of the advancements in determining the viscoelastic properties over the past decade have been developed by the Johannsmann group [91, 92]. The QCM measures the impedance spectra of a quartz crystal when an oscillating voltage is applied to electrodes on either surface of the crystal as shown in Fig. 10. When a sample film is deposited on one surface of the crystal, the resonant frequencies are shifted, allowing one to determine both the mass and mechanical properties of the sample.

Resonant frequencies of quartz crystals are typically in the megahertz (MHz) regime, which means the QCM probes material responses in the “glassy regime” for most polymer and paint systems. Sample preparation is important because the thickness of the sample plays a critical role in the ability to obtain meaningful data. A broader discussion about the range of material properties probed by the QCM and the required thicknesses to detect those properties has been previously published by the Shull group [93, 94]. In brief, polymer samples prepared to target viscoelastic properties can range from hundreds of nanometers to 10 μm in thickness. Such small sample sizes can effectively be treated as a skin layer since there is minimal diffusion required before a sample is equilibrated with its environment. Having an exposed surface of the sample also facilitates measurements of



temperature, humidity, and solvated atmospheres, and the use of non-invasive molecular characterization techniques (e.g., FTIR, Raman). For paint model systems, data collection can begin within a few minutes of casting, rather than having to wait for months before the sample becomes touch dry, allowing the study of paint model systems through the entire curing process.

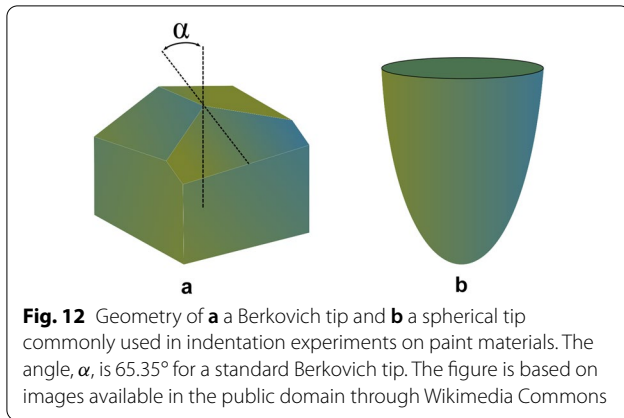
The curing behavior of a commercial alkyd binding medium was measured over the course of three years, as well as the effects of temperature and the filler effects when zinc oxide was added [17, 69, 95]. Analyzing both the mass and the mechanical properties of a sample can provide a clearer picture about how the material responses of paint films change as a function of their environment as demonstrated in Fig. 11. From these data, Sturdy *et al.* determined three distinct regions during the curing process of the alkyd paint system: solvent evaporation (region I) taking place in the first few hours of data collection, short term curing where oxygen uptake happens (region II) during the first day, and long term curing over the following three years (region III). It is possible to see the impact of these mass fluctuations on the mechanical properties, with the short term curing region showing the steepest rise in stiffness (shown by the sharp increase in $|G_3^*|\rho$ (product of the magnitude of the complex shear modulus at 15 MHz and the film density) and decrease in ϕ (viscoelastic phase angle at 15 MHz) of Fig. 11b and c). Even after three years, the complex shear modulus of the alkyd samples continued to increase, supporting the understanding that paint systems continue to experience chemical changes years after they are cast onto the quartz crystal. The QCM is versatile enough

to incorporate solvent exposure for understanding the swelling behavior of paints, providing the capability to study the effects of plasticization on the overall stability of a paint sample. Samples can also be exposed to UV light to understand the effects on the mechanical properties of paints with photosensitive pigments, and the temperature-dependent response of the the sample can also be probed [93]. These temperature-dependent measurements are a particular focus of ongoing research because they probe molecular relaxations in the material that are likely coupled to the ductile/brittle transition in the material, complementing information obtained from more traditional measurements of the glass transition temperature. While these samples can be exposed to a wide range of environmental conditions, it is dependent on good contact between the sample surface and the quartz crystal, making it difficult to use the QCM to study historic paint samples directly. These studies provide initial steps for being able to understand more fully the initial curing stages of binding media, how they affect the overall paint material response, and begin to investigate more targeted questions related to curing and degradation processes in paints.

Nanoindentation

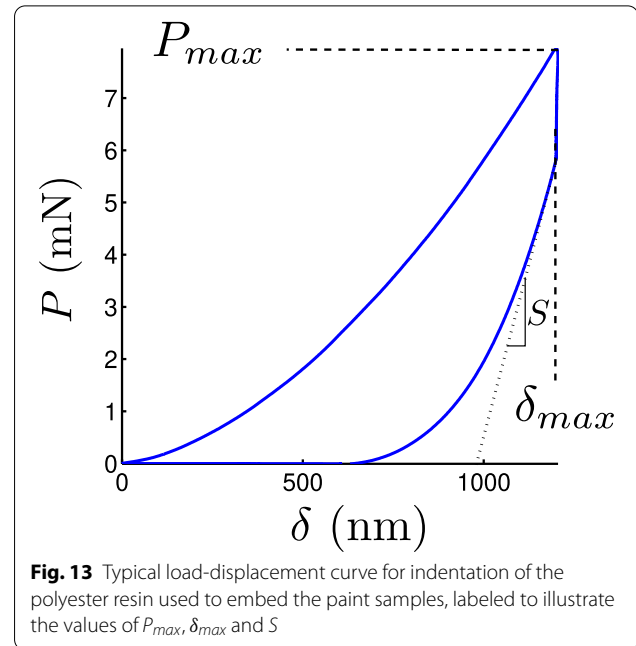
Technique background

All the techniques described up to this point in the review require the use of model systems in order to obtain the mechanical properties of paints. These techniques provide useful information and can allow a wider range of experiments to be performed (especially those that are more destructive in nature), but there



can be difficulties relating these results back to actual historic paints. One technique well suited to bridge the gap between model systems and historic paint samples is nanoindentation. The small sample size required to obtain data about the modulus, stiffness, and hardness of a paint sample is well suited for use on cross sections from paintings. Typically, the indentations are $\approx 2\text{--}5\text{ }\mu\text{m}$ wide, making them nearly invisible to the naked eye. Oliver and Pharr have outlined the methodology for contact mechanics of elastic-plastic materials, which has been widely incorporated into nanoindentation analysis [96]. Oyen and Cook summarized how contact mechanics analysis can be expanded to include a wider range of tip shapes, two of which are shown in Fig. 12, and accommodate material responses that are viscous, expanding contact mechanics to use on biological and polymeric based materials [97].

Material properties are obtained from load-displacement curves, such as the one shown in Fig. 13. Note that a displacement of zero is defined as the point where initial contact is made between the indenter and the material. Because most paint materials have a time-dependent response, the detailed protocol control for controlling the displacement will affect the measurement. The load-displacement curve shown in Fig. 13 shows an experimental protocol where the displacement increased at a constant rate from zero to a maximum value of δ_{max} during a loading time of $\approx 1\text{ s}$. The displacement is then fixed at this maximum value for ≈ 1 minute, and is then decreased at the same rate as that used for the loading portion of the experiment. It is also common to have the holding condition be based on a fixed load. The elastic modulus is obtained from the unloading stiffness, S , defined as the slope of the initial portion of the unloading curve (see Fig. 13). For a parabolic indenter where the contact between the indenter and the material has a radius of a , the



following expression for S is used to extract the elastic properties:

$$S = 2a_{max}E_r. \quad (7)$$

Here E_r is the reduced modulus obtained from plane strain geometries like the indentation experiments of interest here. It involves the following combination of the elastic modulus and Poisson's ratio:

$$E_r = \frac{E}{(1 - \nu^2)}. \quad (8)$$

The quantity a_{max} is the contact radius established for $\delta = \delta_{max}$, which for a parabolic indenter is given by the following expression:

$$a_{max} = \sqrt{\delta_{max}R}, \quad (9)$$

where R is the radius of curvature of the indenter at its tip.

For non-parabolic indenters and those for situations where material yielding needs to be accounted for (as with the Berkovich indenters shown in Fig. 12a, a generalization of Eqs. 7 and 9 needs to be utilized. The most commonly used procedure was developed by Oliver and Pharr [96], and involves the following:

- 1 Replacement of a_{max} with an effective radius, a_{eff} . The area of a circle with this radius is the same as the actual maximum contact area between the indenter and the material:

$$\pi a_{\text{eff}}^2 = A_{\text{max}}. \quad (10)$$

- 2 Definition of a contact depth, δ_c , which accounts for deformation of the material outside the contact zone. The Oliver and Pharr expression for δ_c is:

$$\delta_c = \delta_{\text{max}} - 0.75 \frac{P_{\text{max}}}{S}. \quad (11)$$

- 3 Use of a relationship between A_{max} and δ_{max} which depends only on the indenter geometry. For a Berkovich indenter this relationship is:

$$A_{\text{max}} = 24.5 \delta_c^2. \quad (12)$$

For a parabolic indenter of with tip radius of curvature R , this relationship is:

$$A_{\text{max}} = 2\pi \delta_c R. \quad (13)$$

These equations enable the maximum contact radius (or the effective maximum contact radius, a_{eff}) to be obtained from load-displacement relations directly without direct visualization of the contact radius, a determination of the reduced modulus, $E/(1 - \nu^2)$.

The other property that is often obtained from a nanoindentation experiment is the hardness, H , given by the ratio of the load to the projected contact area:

$$H = \frac{P_{\text{max}}}{A_{\text{max}}}. \quad (14)$$

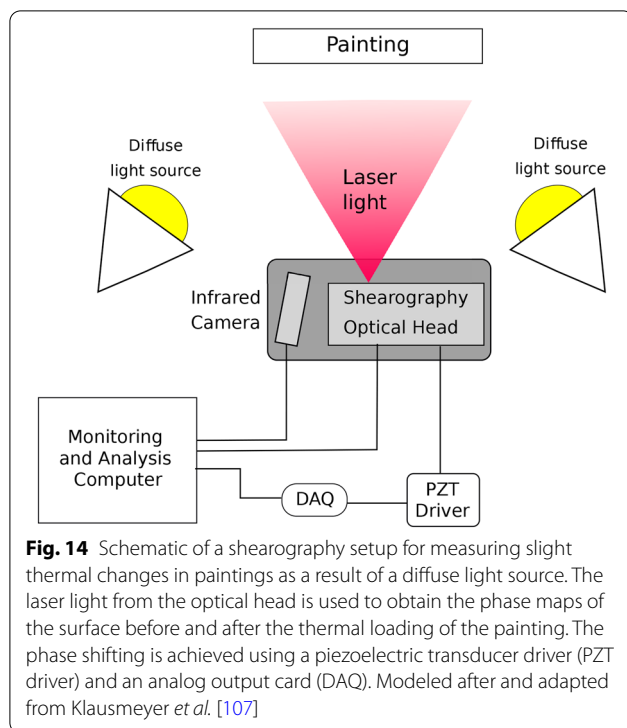
While a value of H can be obtained from Eq. 14 for any tip shape, it is usually used with tips with sharp edges, like the Berkovich tip. In these cases the material deforms plastically in the regions near the indenter edges, and the hardness is taken as a measure of the yield stress of the material. In these cases indentation necessarily involves irreversible deformation of the material, and limits measurements of historic samples to regions of the paint that are not visible (small portions taken from underneath the frame, for example). Indentation probes a volume of the sample with dimensions controlled by a_{max} , and this length scale controls both the depth that is sampled in the measurement and the lateral resolution that is obtained. This length scale is in turn controlled by the size of the indenter tip and the depth of the indent in the sample, and is much smaller for atomic force microscopy (AFM) than for nanoindentation.

Advancements for artists' paints

In cultural heritage research, nanoindentation has been used to correlate changes of mechanical properties with optical and chemical changes as a function of aging or light exposure for natural and synthetic binding media

[98]. Comparisons between reconstructed and historic paint samples of white pigments used by Van Gogh demonstrated that the age of the sample had a direct effect on the resulting reduced modulus (with the modulus of historic samples being up to an order of magnitude higher than the reconstructed samples), highlighting one of the main issues for studying model systems [99]. However, the authors of this study also concluded that it can be difficult to determine an accurate modulus for a paint due to the filler behavior of pigment particles in the paint samples. The presence of these stiffer pigment particles causes significant increases in the reduced modulus near the particles. More recent studies using nanoindentation have incorporated comparisons of the data from nanoindentation with data from DMA and dynamic vapor sorption to understand how each technique showed the changes in mechanical properties when subjected to variations in RH [100]. Measurements on the same zinc oxide filled alkyd samples with DMA, QCM and nanoindentation have confirmed the compatibility of the three techniques when the frequency of the measurement is appropriately taken into account [17]. Fujisawa *et al.* add a compliance term to their determination of mechanical properties to account for edge effects of the stiffer embedding resin on a paint sample [101]. A more systematic study with nanoindentation focused on understanding edge effects for cross sections mounted in resin, showing how these effects impact the data obtained from the experiments [102]. Since paint samples are typically mounted in resin materials that can exhibit a higher modulus, Freeman *et al.* explored the minimum size required of cross sections to be able to minimize an artificial stiffening affect from the resin substrate. Initial steps have been taken towards mapping the mechanical properties of an entire painting cross section, which will be an important method for being able to probe the mechanical properties of historic paints more readily [103]. More work remains to be done in order to refine this mapping technique and adapt it to paintings. Resolving effects of solvent cleaning for a water sensitive oil paint were studied with nanoindentation as well as DMA to determine how much surface and bulk mechanical properties would be effected, where most of the data for sponge cleaned samples exhibited statistically insignificant changes [78].

In tandem with expanding the use of nanoindentation through mapping and optimizing the analysis of cross sections, atomic force microscopy has the potential to be applied to painting cross sections to obtain mechanical properties. Since the AFM tip is smaller than the tip of a nanoindenter, it can provide a higher resolution of the surface mechanical property data across the paint sample. One issue that needs to be considered with the



AFM is that for very small contact dimensions the effect of adhesive interactions become more important. When these effects are appropriately accounted for, the AFM can be used to quantify the viscoelastic properties of a material. The approach has been validated for an acrylic system [104, 105], and similar approaches can in principle be used to investigate the properties of aged paint systems. A variety of complications exist when applying the technique to heterogeneous systems like actual artist's paints [106], but the availability of commercial AFM instrumentation with the ability to obtain load/displacement curves over a small region of the sample may prove to be useful in the field of cultural heritage.

Developing research directions

Laser shearography

One technique developed in the last couple of decades to observe changes in the mechanical properties of paintings is laser shearography. As shown in the schematic in Fig. 14, interference patterns of a painting are collected before and after a slight thermal, acoustic, or vibrational excitation caused by the diffuse light sources in the image. The interference patterns are used to create a phase map of the painting surface, which can be unwrapped to generate a displacement gradient map, also known as a strain map.

Kalms et al. focused on developing a setup that would be mobile enough to easily set up in a museum

environment and be stable enough to provide interferograms that were sensitive to changes in the painting after thermal loading, but not sensitive to slight environmental changes in the surrounding conditions [108, 109]. The sensitivity of the phase maps obtained through laser shearography helps researchers observe defects such as cracks, paint losses, and delaminations more easily, especially if the defects are subsurface. The maps are also capable of serving as a diagnostic tool for cultural heritage, guiding attention to areas that need more immediate attention during a conservation survey. The sensitivity of laser shearography to detect delaminations, impacts on a painting surface, and the propagation of cracks through paint layers was successfully demonstrated with mockup samples [110]. The use of strain maps to show the potential areas of concern and highlight areas of potential degradation in the paintings have been optimized for ease of interpretation by conservators [111]. Shearography has also been paired with other imaging techniques such as terahertz imaging, fringe projections to observe 3D topographic maps, and reflectance transformation imaging to provide more complete datasets for diagnosing defects and changes in a painting after environmental fluctuations or transport [107, 112, 113]. Some optimization of strain maps from the displacement gradients was also performed on a test painting to quantify the strain experienced by a painting as a result of cycling lights in a museum setting [107, 114]. Comparing the phase maps of defects in paintings to simulated phase maps generated using finite element analysis (see Section 7.2), allow researchers to understand the nature of defects within a painting and to vary the parameters of the defect until the simulated map matches the experimentally observed map, which can be useful for understanding how different defects/areas of degradation within a painting can affect the resulting phase map [115].

Laser shearography shows great promise as a diagnosis and monitoring tool for performing preliminary conservation surveys and tracking the state of a painting, especially after transport for an exhibition. The mobility of the setup allows it to be fairly cost effective for a museum setup. While it takes some time to gain the experience to interpret the data from the phase maps, the strain maps are a useful tool for understanding the mechanical response of the painting to slight fluctuations in its environment.

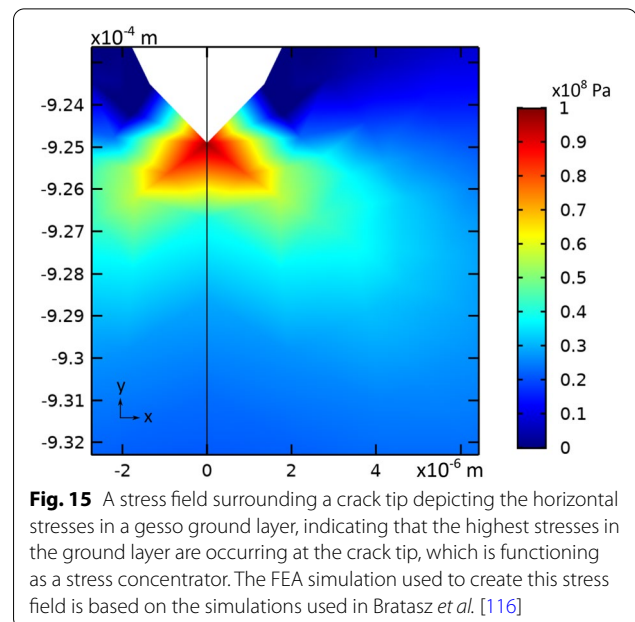
Finite element analysis

Technique background

When a paint layer is considered in the context of a painting, there can be range of complex stresses applied to the layer by the neighboring layers and quantifying the stresses can be difficult using free standing films.

One way to look at understanding these stresses is to use finite element analysis (FEA), which is capable of modeling the field responses (such as stresses or strains) for complicated objects. A brief description of the process for using FEA is that the geometry is discretized into smaller elements, a simplified material model is chosen that resembles the expected response from the object, boundary and load conditions are applied, then the solutions are calculated to determine the field responses to the given load. When the geometry is defined, material properties need to be inputted, which typically include the elastic modulus, Poisson's ratio, and hygric or thermal expansion coefficients, depending on the type of loading the object will experience. These material properties are usually informed from experimental data using one of the techniques previously discussed in this review. How the material will respond to a load also needs to be defined; the most common responses are isotropic (the same response in all directions) for paints or grounds and orthotropic (some directional dependence) for wood and some canvas substrates. The ability to break down the object geometry into smaller elements allows easier comparison of the stress/strain response on the micro and macroscopic scale, which is one of the strengths of this technique. Selection of a material model is determined by the expected response from a material. The two models that have been applied to cultural heritage objects are a linear elastic model, assuming a fairly elastic response of the material, or a visco-hyperelastic model, which allows for more time dependent deformation of the object [123]. The boundary and load conditions are used to constrain the geometry and explicitly define the scenario being modeled, for example, a strain being applied as a displacement along one axis of the model. The results from a simulation are typically displayed as field maps, such as the stress field depicting the horizontal stresses in a gesso ground layer shown in Fig. 15. For this particular example, the highest areas of stress are immediately next to the crack tip, which is functioning as a stress concentrator within this layer. From these stress fields, the energy release rate can be determined by integrating the area around the crack tip. Comparing the value of the energy release rate to values of \mathcal{G}_c obtained from measurements on model materials will indicate if the crack would continue to propagate under these conditions.

FEA is a very powerful method and allows the comparison of a range of material properties and scenarios in a relatively short time compared to preparing that range of experiments, there are also some things to keep in mind when reviewing the results of a simulation. The outputs from a simulation are heavily dependent on the material properties inputted, which can make it challenging to extend the use of a simulation beyond its initial goal. The



results from a FEA model need to be validated against either experimental values (e.g. the expected results from the experiment that provided the material property inputs) or against analytical models. A balance also needs to be struck between the computational expense of running the model with its overall accuracy, which can make it difficult to model some non-linear behavior that would be expected from paints and paintings.

Application to cultural heritage

An area of cultural heritage research that has begun using FEA more often focuses on understanding craquelure development and the mechanisms governing crack opening or delamination. For the papers discussed in this section, all use a linear elastic model as their material model unless otherwise specified. Mecklenburg's work using FEA focused on the understanding of the response of paintings to T or RH fluctuations, out of plane bending of the canvas due to vibrations from transport, and an impact force on the side and corner of a painting to simulate a painting being dropped, comparing the resulting simulated craquelure patterns to ones observed in painting mock ups [29, 61, 117]. Further studies of vibrations affecting canvas paintings have been carried out to assess the vibrational modes that are most relevant to consider [118]. Bratasz *et al.* used a more targeted FEA approach to study the behavior of gesso ground layers on a wood substrate, focusing on how the response of the ground layer translates to the development of a craquelure pattern that is less susceptible to environmental fluctuations [116, 119]. Eumelen *et al.* have investigated the

growth behavior of metal soaps combined the chemical information related to the diffusion of metal soaps into aggregates with estimated mechanical properties for a paint layer to both understand the directionality of metal soap formation and the most likely regions for cracks to form within the model from the stresses caused by the aggregates [120]. More recent investigations from Bosco *et al.* have been focused on understanding the underlying deformation mechanisms that can lead to crack opening or delamination when a paint layer is exposed to flexural stresses as a result of increased moisture [121, 122].

An additional area where FEA can be applied for cultural heritage research is to simulate long term fatigue behavior. The simulations can study the potential for cyclic fatigue that would cause failure or delamination of a paint layer, which was performed using a visco-hyperelastic material model since the timescales of fatigue responses tend to be more viscoelastic in nature [123]. Computational simulations studying fatigue behavior in paintings provide the flexibility to test multiple parameters and draw preliminary conclusions on a faster time-scale than can be done with experiments, which is useful for informing conservator practice on a wide range of paintings varying in composition and structural support in a relatively short time. FEA can also be used to generate displacement fields as a result of thermal excitation, as was shown by Buchta *et al.* when observing defects using laser shearography [115].

While being able to test a wide range of parameters using FEA simulations is a strong benefit of the technique, there is a major caveat: one needs to insure the results are physically relevant. Accurate determination of the critical energy release rate, G_c , mentioned above, is one example. Informing the models using material properties for the paints or paintings of interest is a key step towards validating and extending the model.

Vibration studies

Another potential source of damage to paintings is from vibrations causing flaking or crack formation, whether from transport conditions, acute scenarios such as a construction project, or more diffuse ambient noise in or around a museum. When these vibrations occur, they tend to apply an oscillating stress over a longer period of time, which can lead to longer term fatigue responses of the painting. Conservative limits for vibrations during a construction along with a proposed plan for assessment of a construction project was outlined thoroughly by Johnson *et al.* to determine a vibration range of 1.5–4.0 mm/s depending on the frequency of the vibration [124]. Assessing these sources of vibration and understanding the effects on the longevity of objects in the museum has been assessed

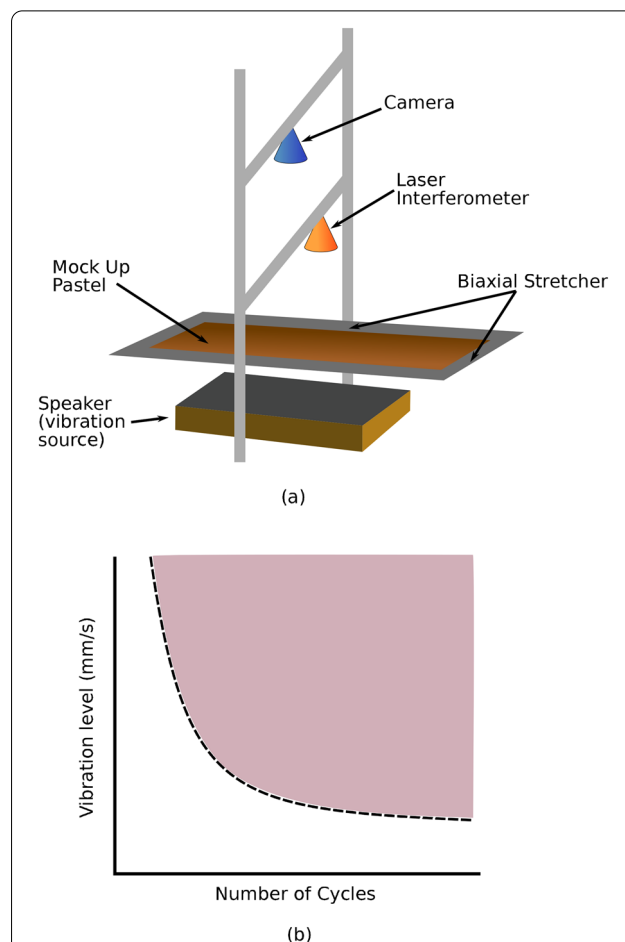


Fig. 16 The **a** schematic of a vibration fatigue stage setup for mock up pastel paintings and **b** a modified Wöhler curve showing the vibration level versus the number of cycles of vibrations. The dashed curve is the fatigue limit for the mock up, above which (and emphasized by the shaded region of the plot) the pastel mock up would be damaged by the vibrations. The schematic of the setup is based off the setup used in [127]

through the detection of background vibrations in museum as well as exposure of model systems to sustained periods of vibration to determine thresholds for damage to objects. Wei *et al.* assessed the affects of these background vibrations within a museum setting to understand some thresholds of safety for paintings and objects, determining it to be somewhat lower than expected [125]. A particular case study where vibrations are more problematic are pastel paintings, or paintings where powdery pigment layers are applied to the support. Due to the low level of adhesion between the paint layers and support, pastel paintings are a useful case study for assessing the potential limit of material loss due to vibrations before the painting is noticeably damaged [126].

Shown in Fig. 16, a biaxial tension setup with mockup canvases is used to generate modified Wöhler curves (displacement of material versus number of cycles) to correlate the amount of vibration sustained by an object with the overall loss of material and minimum amount of acceptable loss from pastel paintings as determined by imaging and conservator observation [126]. Within this setup, a laser interferometer is used to track the amplitude of the vibrations and the camera is used to monitor the overall surface damage of the canvas. These fatigue tests can provide useful information about the amount of vibration that can be sustained before damage, which when paired with information about display and travel of an object, can help curators and conservators determine the best lifetime decisions to maintain the best conditions for a pastel painting as long as possible. While pastel paintings are more sensitive to damage by vibration than other paintings, these types of fatigue tests can be used to assess the chances of new craquelure formation in an object, especially after travel or acute exposure to sustained vibrations. Efforts in this area have focused on understanding the effects of pigment size on the stability of the pastel painting, incorporating high speed imaging to understand the resonant vibration modes of a canvas more fully, and working on more directly relating the data from mockup samples to actual museum objects. The latter point would allow the use of Wöhler curves as a predictive tool for determining if moving a pastel is within a safe limit.

Single-sided nuclear magnetic resonance

Paintings that undergo solvent exposure for cleaning treatments tend to experience embrittlement of the surface paint layers. A more thorough review discussing the chemical changes and implications has been recently published [128]. A fairly novel way of studying paintings has been explored by researchers to correlate the mechanical properties with chemical changes in paint is single-sided nuclear magnetic resonance (NMR), or NMR relaxometry [129]. This technique uses a NMR-MOUSE (Mobile Universal Surface Explorer) to look at the relaxation times within a layer using a locally generated magnetic field and detector. Transverse relaxation times (T_2), related to spin-spin interactions of the material being studied, can be recorded in depth profiles and can be related to the stiffness of a material. If a material has reduced intermolecular motion (such as a cross-linked paint material), T_2 will decrease as the stiffness increases [129]. Single-sided NMR has been employed to look at both PVC and the effects of solvent on painting materials. Model systems of traditional oil paints, water-miscible oil paints, and acrylic paints with varying

PVC values were studied to determine if the comparative results could be quantified as a function of increasing PVC [14, 129–132]. One of these studies looked to extend their findings with young model systems to see if they could develop a protocol for determining the age of paint materials based on the response of the relaxations times, which was unfortunately inconclusive [131]. Single-sided NMR has also been used to study the effects of solvent exposure on the stiffness of paints. The first study assesses previous solvent treatments of a 17th century painting through comparison with another similar painting from the *Pipenpoyse Wedding Set*, demonstrating that a cleaning treatment performed on one of the paintings had a statistically significant effect on the stiffness, most likely due to a redistribution of low molecular weight molecules through the paint layer.[133]. A more recent study used both single-sided NMR and solid phase microextraction to investigate the effectiveness of swab or gel cleaning of more green solvents for painting cleaning and is able to demonstrate that the gel method produces a reduced paint response and showed less penetration into the paint layer than the swab method [134]. While this technique does not provide absolute information about the stiffness of the paint layer, single-sided NMR can provide relevant information about stiffness changes over the depth profile of a paint layer, which can be especially useful when investigating the solvent response of a paint material.

Conclusions

When considering the mechanical properties of paints, there are quite a few factors that need to be considered. It is important to understand the material properties of both the binding medium and the pigment, which can be partially informed from chemical analysis, as well as the pigment concentration and how it affects the overall properties of the paint. Since paintings are multi-layered structures, there also have to be considerations for the interactions (both chemical and mechanical) between layers. Beyond the paint composition and structure, the environmental factors (e.g., T, RH, vibrations, and solvent exposure) can affect the response of the paint and need to be accounted for when considering a conservation treatment.

Several techniques have been developed over recent decades to help provide this information. Tensile testing, DMA, rheology, and the QCM can provide information about the mechanical properties of paints from the liquid to the solid state, creating a data set that is more comprehensive and complete than any dataset provided by a single technique. These techniques are limited to model systems, but with the correct assumptions and comparisons to historic samples, the data can be used to inform

conservation treatments. Techniques that are directly applicable to historic objects have been developed and adapted from industrial applications for cultural heritage, which expands the breadth of knowledge accessible to conservators. Nanoindentation can provide an estimate of the stiffness of a paint cross section and allow a conservator to explore the temperature and solvent response of the cross section before beginning a treatment. Laser shearography, since it is both portable and non-invasive, is a technique that will be most useful for both initial surveys of a new painting in the collection (pinpointing areas most in need of deeper investigation) and for a painting traveling on exhibition (to track the amount of damage accumulated as a result of travel). Computational studies using FEA can allow researchers to consider both the macroscopic and microscopic length scales affecting the mechanical properties of a paint simultaneously as well as explore a wide parameter space more rapidly than experiments, given that the models are well informed and verified via theories or experimental comparison. Studies analyzing the vibration response of model systems and generating predictive curves that can be used to assess objects in a museum, especially more sensitive objects such as pastel paintings, give some insights into how much travel and exhibition an object can endure before it needs restoration or to be retired. Single-sided NMR is emerging as a non-invasive technique that can provide useful depth profiles of comparative stiffness measurements, which can provide information about PVC or previous solvent exposure of a painting sample.

To continue progressing the field and to provide relevant information for conservators, research efforts expanding the breadth of pigments investigated with these techniques will provide data to compare to when determining a conservation treatment for an object. Information about paint samples can also be expanded by combining any of the techniques discussed in the paper, requiring an understanding of how the techniques can complement each other. Extrapolating expected material responses of historic paints from relatively young model systems continues to be a challenge for researchers and requires systematic efforts to look at aging trends and see if they can be extrapolated to longer times for a wider range of paint materials. Expanding the efforts of performing optical or in situ measurements of paintings to obtain mechanical properties is very appealing, especially when surveying objects for conservation treatment [135]. One potential way to push this direction forward is to collaborate with industry, adapting their existing technology to work for paintings [136]. The choice of which techniques are most relevant to use is also two potential research aims: to answer technical art history questions

(e.g., such as determining an artist's historic formulation) and to expand the knowledge base of relevant materials in ways that benefit the conservation community. The purpose of this review has been to describe past work while highlighting newer capabilities that we expect to be useful in addressing these aims, in hope that the interdisciplinary collaborations enabling success would continue to flourish.

Abbreviations

T: Temperature; RH: Relative humidity; μ XRD: μ -X-ray diffraction; PIXE: Particle induced X-ray emission; BS: Backscattering spectrometry; FTIR: Fourier transform infrared spectroscopy; PVC: Pigment volume concentration; DMA: Dynamic mechanical analysis; QCM: Quartz crystal microbalance; MHz: Megahertz; AFM: Atomic force microscopy; FEA: Finite element analysis; NMR: Nuclear magnetic resonance; NMR-MOUSE: Nuclear magnetic resonance-mobile universal surface explorer.

Supplementary Information

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Additional file 1. Appendix: Tensile testing tables.

Additional file 2. Excel spreadsheet containing the tensile testing data shown in Additional file 1.

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Availability of data and materials

The uniaxial tensile testing datasets analyzed during the current study are available through supplementary information as both a PDF file (Additional file 1) and an Excel file (Additional file 2). All other data sets presented and the codes used to generate figures are available from the authors upon request.

Declarations

Competing interests

Not applicable

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