Journal of Cultural Heritage 55 (2022) 237–244

Contents lists available at ScienceDirect

Journal of Cultural Heritage

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

Original article

A methodology for the use of alkyd paint in thermally aged easel painting reconstructions for mechanical testing

Daniele Barbera[a], Christina Young[b,*], Maria Charalambides[c], Ambrose C. Taylor[c], Ruoyu Zhang[c]

[a] College of Engineering and Physical Sciences, University of Glasgow, Glasgow G12 8QQ, UK
[b] Kelvin Centre for Conservation and Cultural Heritage Research, College of Arts, University of Glasgow, Glasgow G12 8QQ, UK
[c] Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 9 September 2021
Accepted 7 March 2022
Available online 9 April 2022

Keywords:
Panel painting
Alkyd paint
Oil paint
Relative humidity
Mechanical behaviour
Paintings
Conservation

ABSTRACT

For the preservation of painted cultural heritage on wooden substrates, it is important to understand the fracture mechanisms in the multilayer system of which they are constructed and how the environment plays a role in the composites' physical properties. Past research has investigated the material response of each constituent layer but much more needs to be done to represent the heterogeneous composite structure of easel paintings. In recent years fracture mechanics concepts have been applied to glue and glue/chalk multilayers. However, few experiments have been conducted on multilayers that include oil paint, due to its very long, and impractical drying time, which can be a few years up to decades depending on the type of study. The paper presents a methodology for the use of thermally aged alkyd paint in easel painting reconstructions for mechanical testing, specifically as a substitute for naturally aged traditional linseed oil paint. Elastic and failure properties of the paint have been obtained from environmentally-controlled tensile tests on thin free-film samples. To obtain the characteristic properties of increased elastic modulus and reduced ductility, a thermal ageing protocol has been experimentally developed. The results are compared with data from the published literature, theoretical models and with 30-year-old samples of cold-pressed linseed oil lead white paint tested within this research work. The final methodology provides the research community with a viable way to produce samples that can be used to understand the behaviour of a (simplified) but complete multilayer system.

1. Introduction

The challenge for institutions to meet the commitment to reduce their carbon footprint while at the same time providing access to their collections has never been more pressing. Collections care strategies that underpin the practical logistics of implementing such commitments requires reliable data which can be interpreted together with robust protocols. The environment and environmental control are high on the agenda because energy-efficient active control to meet tight tolerances in relative humidity and temperature are difficult to achieve especially when the environment outside is either at extremes or fluctuating. Partial control in historic buildings such as Knole House (National Trust, England) which houses a mixed collection, adds further complexity in developing protocols.

Within conservation, environmental fatigue has been flagged as a possible issue since 1991 [1,2]. In the last ten years the engineering concepts of fatigue lifetimes [3], crack saturation and damage criteria have been introduced into the field of preventive conservation and risk management, together with published data and models. At the same time, conservators are still needing to treat vulnerable objects including tented, cupped and delaminating paint on wooden cultural heritage from semi- or un-controlled environments. Understanding the underlying mechanisms on which these concepts are based can help in the development of a best practice that combines preventive conservation and effective long-term conservation treatments. This paper discusses the methodology for using alkyd paint as an analogue for naturally aged oil paint within replica multilayer samples that represent easel paintings.

A substitute is necessary because the very long period before oil paint becomes cross-linked precludes its use in the relatively short lifetime of the majority of research initiatives. The study presented forms part of a wider research project on the mechanisms

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* Corresponding author.
E-mail address: christina.young@glasgow.ac.uk (C. Young).

https://doi.org/10.1016/j.culher.2022.03.003
1296-2074/

of fatigue in viscoelastic multilayer systems on wood (IMPASTOW - www.impastow.gla.ac.uk). In this research work, the alkyd paint samples are aged via a specific thermal treatment and subsequentially tested to investigate the principal elastic properties. Thermal ageing has been chosen over other techniques including UV light [4] or chemical [5] ageing for two specific factors. Firstly, the final scope of the research, is the understanding of the mechanical behaviour of wood-panel paintings. To perform meaningful mechanical tests, multilayer samples are being used. When performing crack propagation tests, a double cantilever sample is used. In this configuration, the paint is only exposed along the sides of the specimen, thus the sample is not homogeneously affected if using UV light. Secondly, chemical ageing presents further complexity as immersion or diffusion of the sample would drive other mechanisms presenting challenges in understanding how the chemical needs to be applied and for how long to build a consistent procedure. Finally, the results are compared to data collected from the literature and to new tensile data performed on 30 years old naturally aged lead white old linseed oil paint.

2. Research aim

This research paper aims to introduce a new methodology to prepare samples of alkyd paint, which because of an appropriate thermal treatment exhibit similar mechanical properties of naturally aged linseed oil-based paint. This research effort is part of a larger research project, IMPASTOW, which aims to understand, simulate and predict the formation of interlaminar and through thickness cracks on panel painting. This approach is necessary to prepare and test representative samples to create an accurate numerical model for prediction and support in the conservation of paintings.

3. Theory and background

Studies within engineering scenarios show that elevated temperature or moisture reduces the service life of structures and components e.g. fibre reinforced polymer matrix composites. An approach has been taken for easel paintings using colloidal particles in a volatile solvent on a non-porous substrate (glass) to study the crack formation and compare features such as crack width with those from a selection of real paintings [6]. In the case of panel paintings, to further develop our understanding in a conservation context, mechanical testing of multilayers and their critical interfaces including the paint layers is necessary.

Making replicas or historically accurate “aged” samples for experimental testing is fraught with inherent problems. The ageing protocol one chooses depends on the objective of the test and the use to which the data will be put. Light ageing, thermal ageing, acid vapour ageing and mechanical stressing may catalyse or accelerate chemical and physical processes which occur naturally with time, or under the influence of external factors such as the environment; but rarely are the constituent materials identical to the original. In the case of multilayer systems is it not necessarily appropriate to use one type of accelerated ageing on all of the layers as this may result in a change of mechanical properties or stresses in some of the layers that would not naturally occur.

The replicas for the IMPASTOW research are based on forty-three-panel paintings which form a seventeenth-century portrait set, on display in the Brown Gallery at Knole House (National Trust, England). Knole House provides a rare opportunity to study the effects of temperature and humidity on panel paintings as the portrait set has been displayed together for over four hundred years, firstly in the Cartoon Gallery, and then from around 1700, in the Brown Gallery. There has never been modern heating within these parts of Knole House and thus the majority of the paintings had been exposed to the same cyclic temperature and moisture changes (with a few having short times away from Knole for exhibitions and conservation treatments) which correlate with atmospheric conditions outside the House, locally at Knole, Kent. (These events have been identified from conservation reports, exhibition labels and discussion with the National Trust) [9].

Although the construction of each of the panel paintings is unique, there are close similarities between the paintings in the portrait set. (Three paintings in the present set were added later and are not on the same construction and technique and are not included in this research). Dendrochronology was carried out on sixty-five boards from twenty-two of the panels confirming that the paintings were executed on Baltic oak no earlier than 1605, further technical and contextual analysis show that the paintings were completed in the early decades of the 17th Century [7]. The boards were radial or nearly radial cut. The layer structure is composed of a series of different materials: an animal glue size, which has been tested by staining, chalk (calcium carbonate) in size layer and a layer of lead white (lead carbonate) ground in a drying oil. The pictorial layers contain earth pigments and drying oil presumed to be linseed oil both identified cross-section microscopy [8].

It has been argued that for wooden panel supports (substrate) the continual process of expansion and contraction at the cellular level results in a change in the mechanical properties on the macroscale. Hunt and Gril [9] have reported a change in mass and dimensions for poplar wood measured at 12% moisture content as the result of many daily cycles of temperature and humidity. Hunt and Gril have also demonstrated that various observed anomalies in wood behaviour, including mechano-sorptive creep, can be explained by a change to the degree of molecular packing-which is disrupted by moisture content changes or tensile straining [9]. Arguably, if the focus is on the crack initiation in the preparatory and paints layers, then the specific support material is not important. However, the difference in porosity in early and latewood leads to differential moisture expansion and contraction, thus differential strain must be induced in the layers immediately above the wood (glue and ground). This has been observed in the DIC experimental tests [10].

Studies of the visco-elastic properties of animal glues have shown the difference in mechanical properties, depending on the animal source, preparation and concentration. As expected rabbit skin glue has strain-rate, temperature and moisture dependent mechanical properties [11]. Samples yellow with time due to thermal ageing, suggesting dehydration and/or oxidation has occurred and Fourier Transform Infrared (FTIR) spectroscopy has shown a shift in the amide II region when compared to unaged samples. No significant difference in mechanical tensile properties (Young’s modulus and strain to failure), or molecular features using Nuclear Magnetic Resonance (NMR) have been identified [12].

However, the biggest challenge is replicating naturally aged oil paint. The process of oil paint drying involves a complex set of reactions in which oxygen in the air is needed for the polymerisation of the oil and the eventual formation of a cross-linked molecular network. The long term chemical processes can occur even when all the unsaturated parts of the fatty acids chains that make up the oil have reacted [13]. Usually, paints have additional driers to speed up the process. Traditionally lead salts were added [14] and some pigments acted as driers, including lead white which promotes the drying process. However, artist paints have numerous variations on formulations that will alter the exact chemical interactions. Nevertheless, if the goal is to understand the mechanisms which lead to mechanical failure of the paint layers within the structure, in this case, C17th panel paintings, a physical model is required that is close as possible to naturally aged oil paint. This long process has the most significant effect on the mechanical behaviour of oil paint because it makes it stiffer (higher Young’s modulus), more brittle (little or no plastic strain to failure) and flexibility is reduced which is closely related to ductility and measured by bend testing. The interpretation of artificially aged samples is best considered as a relative assessment because the quantification of the ageing varies greatly depending on the method chosen and on the determination of when the paint is sufficiently "dry" to initiate the ageing [12,15]. However, the ability to test naturally aged samples and artificially aged samples within the same testing campaign provides a unique opportunity to confirm our protocols for artificial ageing and our predictions for natural ageing.

To reproduce the complete composite it is not valid to artificially age each layer and then adhere them together as it is key to understand how the layers interact. Changing the temperature of wood also changes the moisture content and if the equilibrium moisture content (EMC) is below 30%, shrinking of the wood occurs because it is below the fibre saturation point, where only bound water is present. While that alone may not affect the properties of the wood it will result in differential contraction between layers leading to stress concentrations that would not normally occur.

In the field of conservation, the topic of crack initiation and growth has been studied by Keck, who was the first to systematically study fracture by classifying different types of cracks via a detailed microscope campaign on several paintings made available to him [16]. He identified three main types of cracks for which he proposed mechanisms: drying cracks, external loading cracks and age-induced cracks. Keck also recognised the importance of the behaviour of the support in the cracking process - if the support is hygroscopic, the change in geometry resulting from a change in RH results in mechanical shear at the interface of the layers as well as tensile or compressive strain within the paint.

In terms of numerical simulation, in recent years several studies have been conducted [17–20], in particular, to simulate and predict the stress-strain behaviour of wood panels subjected to cyclic RH and temperature. Due to the complexity of the problem, only a few of these studies have concentrated on accurately modelling the hygroscopic response of the wood panel and to the authors' knowledge no extensive modelling has been conducted of the hygroscopic response of oil paint. This gap in the literature is caused by the level of complexity of the multi-layer system and the difficulty of obtaining material data from meaningful tests.

A series of studies have concentrated on the more challenging task of understanding the fracture mechanisms involved in multi-layered systems on wood subjected to environmental fluctuations [21,22]. Initial modelling of the cyclic response and the associated crack initiation and growth has been developed for painting on canvas [23]. This has now been developed for panel paintings to predict fatigue lifetimes based on the cyclic bending strains induced by natural environmental fluctuations, under the IMPASTOW project [21]. To reach a high level of accuracy and robustness, constituent materials have been tested at different relative humidity and strain rates to characterise the hygro-mechanical viscoelastic behaviour. For an accurate understanding of the fracture mechanisms, the critical interface of the composite (panel painting replica) needs to be established; this is the position of fracture initiation and associated identification of cohesive and/or adhesive failure within the composite. Fracture toughness (resistance to crack propagation) can be measured experimentally.

Mode I fracture toughness and the critical interface using a double cantilever beam (DCB) configuration have been previously applied to the cultural heritage [24]. For the IMPASTOW project, the same approach has been taken with the use of high-resolution video to record crack growth. Details of the DCB testing can be found in the literature [25] but crucially they are constructed with a symmetric sample. Thus for a simple model of a panel painting, this would consist of wood/size/ground/paint/ground/size/wood [26]. Because the drying time for an enclosed oil layer was estimated to be potentially more than two years, the initial DCB samples did not include the oil paint layer; instead one with rabbit skin glue and the other composed of rabbit skin glue (RSG) and chalk ground bound in RSG. For all these reasons it is very important to explore the use of surrogate materials, which offer shorter and controlled drying times alongside mechanical properties similar to the material they are supposed to replace.

4. Sample preparation and testing methodology

Titanium White Artists' Alkyd tube paint (Windsor & Newton) was selected as a candidate for replacing lead white linseed oil paint because the higher content of fatty acids promotes the drying process, hence faster drying time. Alkyd oil paint dries by solvent evaporation and/or auto-oxidation which promotes the reaction of free radicals [27]. Most of the artists' alkyd oil paints are based on the auto-oxidation process. This is the same mechanism that controls the drying rate in linseed oil.

The titanium white alkyd paint was mixed manually for 5 min to ensure homogeneous mixing of pigment and oil, then it was poured into a PTFE mould with vertical spacers to achieve the desired paint film thickness range of 0.10 mm to 0.25 mm (the average thickness is 0.156 ± 0.093 mm). A knife-edge was drawn across the spacers to produce a smooth even film. After 20 min the PTFE was removed, and the paint was left to dry for two months at room temperature (20 ± 0.5°C) and controlled relative humidity (55% ± 2.0%) in ambient fluorescent light with UV filters within a conservation studio. Humidity was controlled via humidifiers, in addition to room environmental control. The tensile samples had a length of 45 mm, a width of 10 mm and a gauge length of 30 mm. Thickness and width were measured at three different points on the sample and the average used for elastic properties calculations.

To increase the stiffness and decrease the ductility of the alkyd paint, the samples were conditioned in the dark in a fan oven at 50°C for 4, 8, 16 and 32 days. The elevated temperature accelerated the solvent evaporation and the drying/ageing process, and was low enough to allow thermal ageing of the paint on the wood substrate. This was particularly important for the DCB specimens because as discussed above the drying process is much slower because the paint is between two wood blocks and hence has a much lower area exposed to the air, furthermore too high a temperature may desiccate the RSG layer and chalk ground. For the same reason, UV ageing is not viable when ageing DCB samples.

To have a comparison with naturally aged linseed oil paint, samples of lead white (lead carbonate) in cold-pressed linseed oil (CPLO) without extenders or fillers, originally cast at the Smithsonian on 2nd July 1990 as part of their extensive testing programme, were tested and compared to the published data of the samples at one and ten years old [28]. Due to the limited quantity of these films, only six samples were obtained, with a length of 30 ± 0.39 mm, a width of 10.09 ± 0.13 mm and a thickness of 0.16 ± 0.01 mm. In Table 1 all the samples tested are reported for the different periods of ageing and conditioning, the naming reflects sample number, material considered, ageing period and environmental condition during testing.

To create a baseline comparison with the published data the tensile Young's modulus and the strain to failure were measured using an Instron 5544 Universal Tester with a 1 kN load cell with an in-house integrated environmental chamber controlled with LabView. The grips are padded with rubber tape to prevent both slipping and damage to the sample while achieving minimal compression. Due to the numerous combinations of parameters for this first test campaign on the alkyd paints, one RH and temperature were chosen at 55% RH at 20 °C (Table 1) and a crosshead speed of 5 mm/min. To ensure the quality of the data a total of five samples were tested for each subsequent thermal ageing regime. The samples were preconditioned for 24 h before mounting in the grips

Table 1
Overview of all samples tested with the associated environmental conditions.

Sample Number	Material	Drying/Ageing/Conditioning Time	Drying/Ageing/Conditioning Conditions	Testing Conditions
S1 to S5	Titanium White Alkyd Oil	2 months/none/1 day	RH = 55% T = 20°C/none/RH = 55% T = 20°C	RH = 55% T = 20°C
S1to S5-4d	Titanium White Alkyd Oil	2 months/4 days/2 days	RH = 55% T = 20°C/RH = 55% T = 50°C/RH = 55% T = 20°C	RH = 55% T = 20°C
S1 to S8-8d	Titanium White Alkyd Oil	2 months/8 days/2 days	RH = 55% T = 20°C/RH = 55% T = 50°C/RH = 55% T = 20°C	RH = 55% T = 20°C
S1 to S4-16d	Titanium White Alkyd Oil	2 months/16 days/3 days	RH = 55% T = 20°C/RH = 55% T = 50°C/RH = 55% T = 20°C	RH = 55% T = 20°C
S1 to S3-32d	Titanium White Alkyd Oil	2 months/32 days/3 days	RH = 55% T = 20°C/RH = 55% T = 50°C/RH = 55% T = 20°C	RH = 55% T = 20°C
CPLO LW-S1 to S4	Cold Pressed Linseed Oil Lead White	30 years/none/1 month	Ambient/RH = 55% T = 20°C/RH = 55% T = 20°C	RH = 55% T = 20°C

by leaving the sample in the environmental chamber at the testing condition, maintained for all the duration of the preconditioning. Before testing the samples were left for 15 min in the grips within the environmental chamber. All the samples failed within the gauge length.

5. Results and discussion

5.1. Baseline results: alkyd paint

Fig. 1 shows the stress-strain results for the titanium white films tested after 2 months of natural drying. The Young's modulus has been calculated from the initial linear region of the stress-strain curves up to 0.003 strain (see Fig. 1). The average Young's modulus was 78 MPa with a standard deviation of 21 MPa. The stress-strain response is similar for all samples up to 0.02 strain, after which the curves separate ending at slightly different fracture points (see Fig. 2). This can be caused by heterogeneous characteristics in the films for instance, different local distribution of pigment particles or small micro defects. For the five samples, the average strain to failure is 0.11 ± 0.01 at an average ultimate tensile stress of 2.44 MPa ± 0.18 MPa. The response of these samples is similar to the data reported by Mecklenburg and Tumosa [29]. In this work, four lead white (carbonate) pigment in cold-pressed linseed oil films were tested for different drying times up to 10 years (see Fig. 1). The typical stress-strain response of the 10-year-old sample is superimposed for comparison with the results obtained within this research work in Fig. 1. This comparison shows that there are two significant effects of natural ageing, the first is an increase in the stiffness of the material, and the second one is a decrease in ductility (maximum elongation). This confirmed that alkyd paints needed some degree of artificial ageing to match the stiffness and maximum elongation of long-term naturally aged linseed oil paint samples, even when driers compounds are not added.

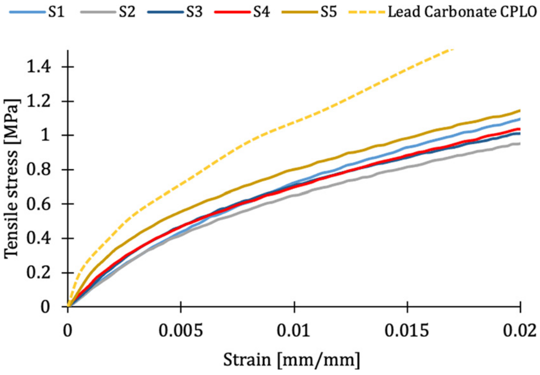

Fig. 1. Tensile stress-strain plot up to 0.02 strain at 55% RH and 20°C for 2 months dried alkyd paint and 10-year-old naturallyaged cold-pressed linseed oil (CPLO) paint [29].

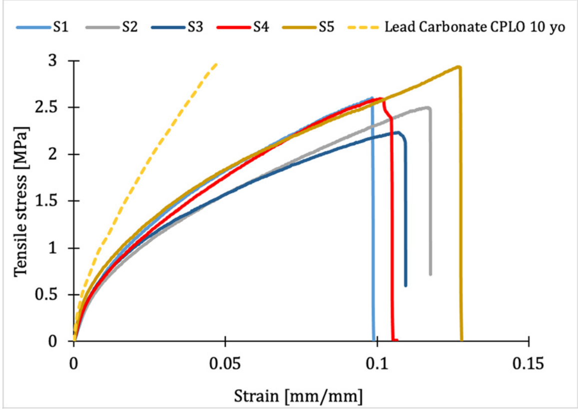

Fig. 2. Tensile stress-strain plot for 2 months dried alkyd paint thin film at 55% RH and 20°C.

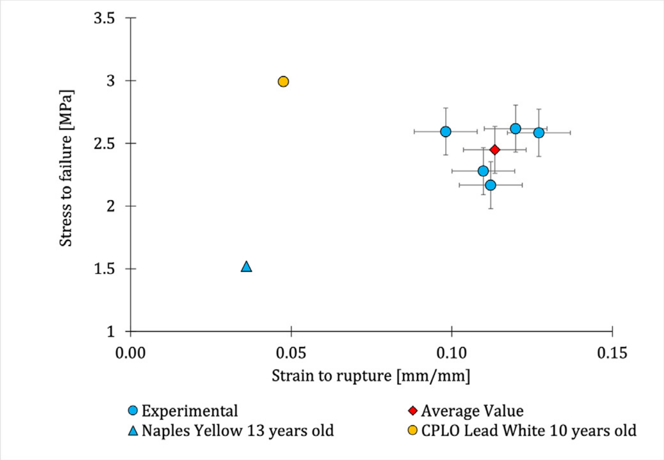

Fig. 3. Tensile stress and strain to failure of experimental tests on alkyd samples against data available for naturally aged Naples yellow [30] and lead white [29]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 shows a plot of strain to failure versus stress to failure, which gives a better comparison of both stiffness and ductility of the paint films. The experimental results are reported with the standard deviation error bars, and an average value is determined by considering the results obtained. Due to the lack of ultimate tensile stress and strain data for the lead white paint beyond 10

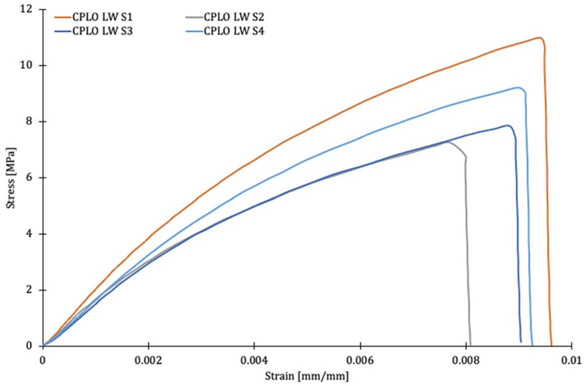

Fig. 4. Tensile stress-strain curves of 30 years naturally aged linseed oil paint at 55% RH and 20°C.

years, the values for 13 years old naturally aged Naples yellow oil paint (from [30]) have been plotted for comparison (see Fig. 3). It is worth noting that the ageing process tends to increase the stiffness of the paint, but the absolute value changes due to the different pigments. The data shows that titanium white alkyd paint has mechanical properties within the range of interest in terms of stiffness (Young's modulus), but is largely more ductile than aged paint. Both these material properties need to be precisely altered to match those of aged linseed oil paints. This meant further artificial ageing is required to reduce ductility.

5.2. Results for lead white in CPLO 30 years old naturally aged paint

To have a more direct comparison in terms of long term performance of the surrogate specimen, a series of 30 years naturally aged linseed oil paint films were preconditioned and tested under the same conditions as the alkyd oil paint films. These samples were obtained from two larger batches of material [31], they have been in ambient conditions (stored in the dark) at Imperial College London and now, at the Kelvin Centre for Conservation and Cultural Heritage Research at Glasgow University. The mode of failure was the same for the four samples and all within the gauge length. The stress versus strain plot is shown in Fig. 4.

The tangent modulus was calculated for the initial linear region of the stress-strain curve up to 0.003 strain. The average Young's modulus is 1664 ± 183 MPa with a maximum value of 1952 MPa and a minimum of 1496 MPa. These values are commensurate with published data [29,32] and follow the predicted trend in properties, see Table 2, including tests performed on lead white paint in CPLO aged for 19.5 years produced by Mecklenburg et al. [29]. In particular, the increase in Young's modulus is in line with the exponential increase observed starting from the 10-year-old sample as shown in Fig. 5, which shows the relationship between Young's modulus and drying time, also a close view for the early stage of drying is reported. After this point an exponential trend is evident and the fit returns an R-value of 0.98. Data below 1-year of natural ageing are not considered in the fit (see insert in Fig. 5), because the samples were at a different stage of the natural drying process and it is questionable whether such values of stiffness are reliable since the process has just started. In this transition phase, the fit is nearly linear, but it changes as soon as the drying process continues. The lower boundary, obtained from the 30-year-old samples, sits on the extrapolated exponential curve shown in Fig. 5. By observing the data, it is clear that an acceleration in the ageing process is present after 10 years. It is worth noting that the data is taken from the same author but variations are possible, and expected since it is not possible to accurately trackback each batch of paint films. However, what is important is the general trend and not the single value. It is worth mentioning that the data points up to 358 days shown in Table 2, are shown in Fig. 5 but not used for the fit depicted. These points correspond to a too-early stage in the drying/aegeing process and by consequence are very sensitive to changes in experimental testing method and environmental conditions. Furthermore, the level of crosslinking, as expected and confirmed by the value of Young's modulus, is very low. This makes these data points less significant for studying aged linseed oil paint.

Table 2
Young's modulus for lead white cold-pressed linseed oil paint at different ageing times.

Young's modulus [MPa]	Ageing time	Refs.
17	68 days	[29]
27	98 days	
97	358 days	
170	10 years	
481	19.5 years	[32]
1665	30.0 years	New data presented in this paper

The experimental results for the strain to failure, shown in Fig. 6, show a different trend when compared with the theoreti-

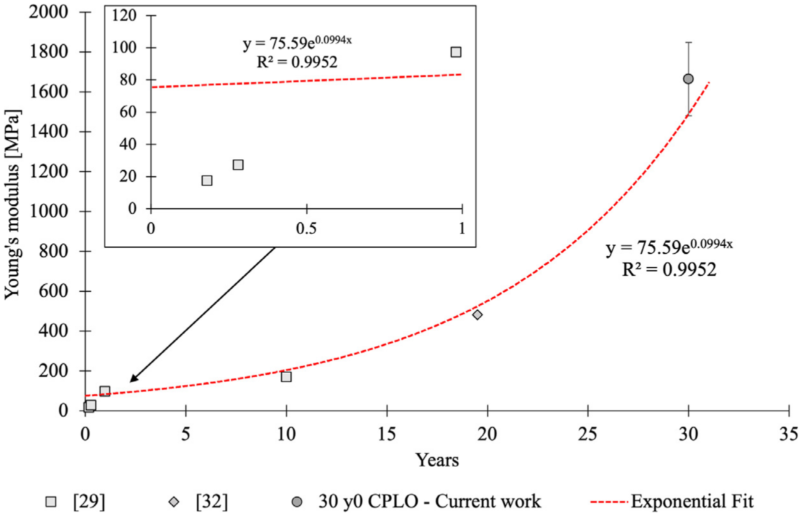

Fig. 5. Young's modulus from the literature [29,32] and new data obtained within this work against ageing time.

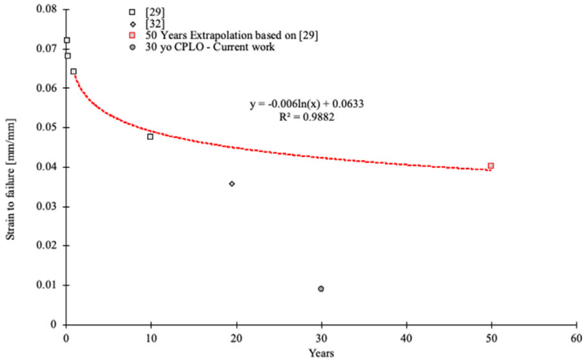

Fig. 6. Strain to failure from literature [29,32] and new data against time.

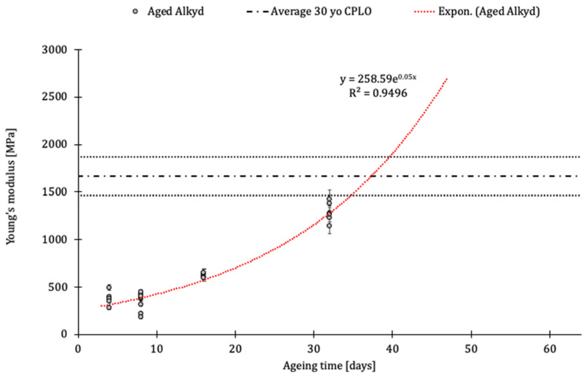

Fig. 7. Young's modulus of thermally aged Alkyd oil paint.

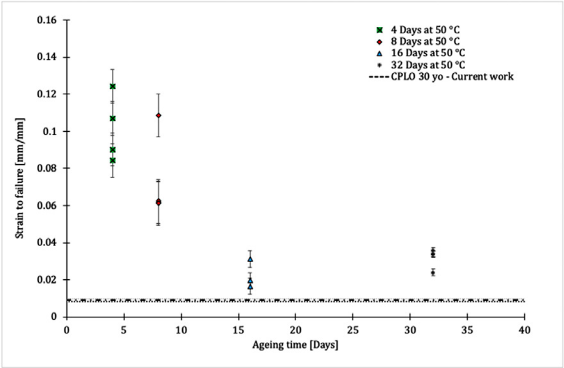

Fig. 8. Strain to failure of thermally aged Alkyd oil paint compared to naturally aged oil paint.

cal extrapolation proposed in 2001 based on tests performed on samples naturally aged up to 10 years [29]. The theoretical values for 50 years old naturally aged CPLO paint were predicted to be a tensile strength of around 3.8 MPa (not shown in the plot) and 0.04 mm/mm strain to failure. The non-linear extrapolation was based on four experimental tests performed on samples naturally aged for 68 days, 98 days, 357 days and 10 years (all published by the authors in the same research paper). Fig. 6. shows how this extrapolation diverges from the long-term data from 2013 [32] and the new data presented in this paper. The experimental data for 30 years, tested in this work, gives average failure stress and strain of 8.81 ± 1.42 MPa (not shown) and 0.009 ± 0.001. The paint film ductility has reduced significantly more than predicted. The data show that for these oil paint films ageing does not proceed at a constant rate. It is suggested that this is mainly due to the acceleration of the autoxidation reaction and crosslinking stage that occurs within the paint matrix. In addition as for Young's modulus, the rate of autoxidation of relatively fresh paint changes dramatically with ageing as shown previously in Fig. 5. This means that any extrapolation for the long term should not include relatively new paint films.

5.3. Thermally aged alkyd oil paint

The ageing protocol introduced was performed using a fan oven to facilitate evaporation of solvents and to promote crosslinking. This was expected to progressively increase Young's modulus and decrease the associated strain to failure. The results of this process are visible in Fig. 7. This plot shows Young's modulus as a function of ageing time. The exponential effect of the ageing process on the stiffness of the paint films is clear, reaching approximately 1500 MPa at 32 days. This thermal ageing process facilitates the crosslinking mechanism, leading to a much stiffer response. However, this process does not scale linearly since after the initial increase in stiffness, the subsequent increases follow an exponential law. However, this process will is expected to slow down to a point where it requires more ageing time, but always shorter than the

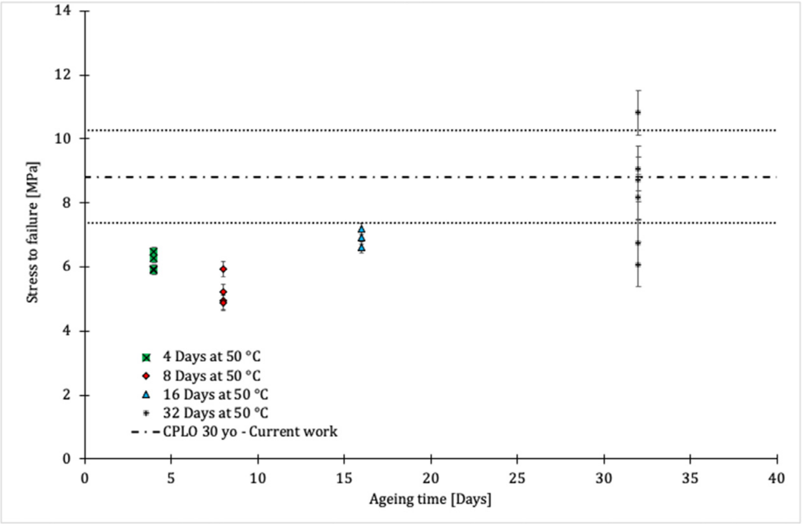

Fig. 9. Stress to failure of thermally aged Alkyd oil paint.

natural process. Significantly, in the context of producing samples for testing reconstructions, the results obtained at 32 days, nearly match results obtained for the 30-year-old naturally aged paint.

Also, the strain to failure has been affected by this process. The strain to failure for the different ageing times is shown in Fig. 8, the results are compared with the average value obtained from the naturally aged 30 years old linseed oil paint. The effect of the thermal treatment is significant with a reduction in the strain to failure of about 85% at 16 days. At this point, the average strain to failure decreases from 0.124 ± 0.016 to 0.0223 ± 0.0015. After this decrease, the average strain to failure at 32 days is stable at around 0.0322 ± 0.0007. Similarly, as shown in Fig. 9, the stress to failure increases as the effect of the increasing artificial ageing time. For stress to failure the increase is more gradual, however, the largest change occurs after 16 days. At 32 days the results come within the region of 30 years old linseed oil paint. It is important to notice that a trade-off needs to be done while considering the ageing process. The increase of artificial ageing time tends to increase substantially both the Young's modulus and the stress at failure. After 32 days these two mechanical properties are close to what is seen in 30-year-old linseed oil paint. However, a fluctuation in strain to failure is observable.

The ageing protocol performed was designed to obtain samples with progressively increasing Young's modulus and decrease the associated strain to failure. Fig. 7 shows the calculated Young's modulus as a function of ageing time. The increase of the stiffness of the paint films is clear, reaching approximately 1500 MPa at 32 days. The main effect of temperature is to accelerate crosslinking, which will progressively slow down. Based on the data obtained it is assumed that at 32 days most of this process will have taken place and any further increase in stiffness will require more aeging time . Significantly, in the context of producing samples for testing reconstructions, the results obtained at 32 days nearly match the results obtained for the 30 years old naturally aged paint. This shows the feasibility of this method to obtain alkyd paint samples with mechanical properties matching naturally aged linseed oil paint in a realistic time scale.

6. Conclusions

Within this work, a procedure to artificially age alkyd oil paint via a thermal process has been presented leading to a new surrogate sample with mechanical properties very close to those of linseed oil paint. The Young's modulus, the stress to failure and the strain to failure results for the Titanium White Alkyd oil paint thermally aged at 50°C for 32 days are in good agreement with 30-year-old naturally aged lead white paint tested within this work. Measuring the proportion of free fatty acids to the glycerides and azelaic acid components in the paints for both the naturally aged and thermal aged samples would provide additional understanding of the processes that have been promoted by the thermal ageing protocol.

There is a predictable trend in stress-strain response with thermal ageing time. More investigation into the factors affecting ductility including pigment volume concentration and type, fillers and commercial addition to the Artists Alkyd paint may allow for further tuning of the thermally aged samples.

The results have led to a methodology for the thermal ageing (at a relatively low temperature and without UV-light) of alkyd paint. This methodology has been transferred to a multilayer system consisting of the oak substrate, rabbit skin glue (RSG), chalk ground bound in RSG and alkyd paint layers (as a substitute for linseed oil paint). It is important to underline that the thermal ageing process designed needs to be performed in an environmental chamber. The sample will be aged at a constant RH equal to 55%. This parameter is very important to avoid any component of the system being exposed to low levels of RH, which could potentially trigger defects in the multilayer. These multilayer samples will allow for a more reliable test to establish the critical interface, fracture energy and fatigue lifetimes for the samples which represent the Brown Gallery portrait set, at Knole House. This can also be applied to the study of fracture and delamination of other painted wooden cultural heritage.

This methodology for the use and ageing of alkyd paints is also relevant to the study of fracture and delamination in modern works of art containing layers of alkyd, oil and acrylic media.

The main objective of this research was to validate the use of alkyd paint as a substitute for naturally aged linseed oil paint for mechanical testing of multilayer painted wood samples in a double cantilever and four-point bend testing. These samples needed to match, to the best of our ability, the mechanical properties of 400-year-old panel paintings, painted in the northern tradition.

Acknowledgements

Nigel Blades and Christine Sitwell, National Trust. Paul van der Rijn, Rijksmuseum, Amsterdam. Cecila Gauvin, Conservation Scientist Consultant, Amsterdam. Funding for this research is gratefully acknowledged from the EPSRC EP/P0024391/1 and EP/P003613/1 - Mechanisms of Low-Cycle Fatigue on Multi-layer Paint Systems on Wood, IMPASTOW.

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