MEMORI PROJECT:EVALUATION OF DAMAGE TO EXPOSED ORGANIC-BASED HERITAGE MATERIALS AND NANOFORART : EVALUATION OF NANOPARTICLE-BASED CONSERVATION TREATMENT

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ABSTRACT:

This paper presents preliminary studies and work in progress in the framework of two FP7 projects: MEMORI (Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets – Innovative Research for Market Transfer) and NANOFORART (Nano-materials for the conservation and preservation of movable and immovable artworks). One of the aims of the MEMORI project is the determination of threshold levels of damage to exposed organic-based heritage objects as little is known about the impact of organic compounds, especially volatile organic acids, on organic-based cultural objects. In the previous PROPAINT project (Protection of Paintings during Exhibition, Storage Transit) it was recently demonstrated that levels of volatile organic compounds (VOCs) were often much higher in the micro-climate frames used to protect paintings than recommended levels. In this paper, examples will be given of changes observed in varnished strips exposed at selected sites. Studies on the effect on collagen-based materials will also be presented. Techniques used in both projects include Dynamic Mechanical Analysis (DMA), micro-thermal analysis (-TA), and atomic force microscopy (AFM). The NANOFORART project explores the effects of using nanoparticle-based conservation treatment on cellulosic and collagen-based cultural materials. It builds on previous work performed on deacidification of canvas paintings using conventional materials. For collagen-based materials, no previous conservation treatment using nanoparticles has been performed on historical parchment or leather objects. Preliminary work is directed at understanding the type of nanoparticles to use to improve the physicochemical state of collagen-based objects.

1. INTRODUCTION

1.1 MEMORI (Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets – Innovative Research for Market Transfer)

Museums are required to provide control strategies, risk assessment, and preservation management for their collections. To fulfil this task they are increasing their use of protection enclosures such as showcases, microclimate framing with front glass for paintings and storage boxes for archival materials, in order to protect the objects from the impact of the environment. For this reason guidelines are required of acceptable levels of volatile organic acids for organic-based objects within these enclosures. The use of controlled microclimates is an environmentally friendly solution which can contribute to climate change mitigation as it can replace energy demanding climate conditioning using HVAC systems for whole cultural heritage building interiors. It is therefore important to facilitate the use of enclosures by assuring optimal conditions for the valuable objects they protect. To determine threshold levels of damage varnishes were selected as representative materials initially in the PROPAINT project (Dahlin, et al., 2010) and then in the MEMORI project [http:// www.memori-project.eu]. Varnishes should protect surfaces of paintings and other heritage objects and should not discolour and degrade readily. Parchment and leather were also selected as representative materials of vast collections of manuscripts and leather bound books in archives and libraries. Many of these are stored in oak containing repositories and are exposed long term to levels of volatile organic acids which exceed the current recommended preservation target (1000µg/m^3 for one year) and which is based on work performed on metals, in particular lead (Tétreault, 2003). The key aspect of damage to collagen-containing materials is the state of denaturation of the collagen in parchment and leather i.e the extent of gelatinisation as this makes the objects more vulnerable to any aqueous based conservation treatment. The previous IDAP project (Improved Damage Assessment of Parchment) (Larsen, 2007) established markers for extent of gelatinisation in accelerated aged and historical samples. The former included inorganic pollutant aged and temperature and relative humidity aged samples. The data provide a basis for damage assessment, and are used in the MEMORI project to assess collagen based materials subjected to exposure to volatile organic acids. Damage markers will also assist in evaluation of effects of conservation treatment in the NANOFORART project [http://www.nanoforart.eu (accessed 16 Aug.2012)].

1.2 NANOFORART project (Nano-materials for the conservation and preservation of movable and immovable artworks)

The NANOFORART project addresses movable and immovable artworks and the aim is to develop novel nanomaterials for cleaning, consolidation, and deacidification of artworks. In this paper reference will be made only to the movable artworks, in particular deacidification of painting canvases. Results shown are of preliminary tests performed on samples prior to the start of the project and recently re-examined. The effect of natural ageing following conservation treatment is also one of the aims of the project. Meanwhile new preparations of nanoparticles are in progress and their characterisation. Past studies have included conservation of the seventeenth-century Swedish warship Vasa (Chelazzi,et al., 2006). There it was demonstrated that wood acidity could be neutralized by calcium or magnesium hydroxide nanoparticles. An alkaline reservoir was formed inside the wood that protected it from further acid attack. The pyrolysis temperature of the cellulose was taken as the damage marker, where a decrease in the pyrolysis temperature correlated with a decrease in its degree of polymerization. Thermal analysis was also used to investigate the efficacy of wood de-acidification treatment with alkaline nanoparticles. Hydrothermally ageing, carried out on de-acidified Vasa wood samples demonstrated that de-acidification with nanoparticles facilitates protection of wood against further acid degradation (Chelazzi,et al., 2006).

In the NANOFORART project the challenge is to design nanoformulations for conservation treatment of manuscripts and bookbindings. So far there is some information on the interaction of nanoparticles, mainly silver with collagen. A recent paper has shown that silver reacts with collagen with the formation of a silver bridge linking two peptide chains (Ionita, et al., 2010). In another paper collagen model solutions were interacted with classical crosslinking agents and silver nanoparticles synthesized by chemical, electrochemical methods or by deposition on TiO_2. These nanosilver colloidal solutions and dispersion were applied to leather and resulting interactions assessed by FT-IR, atomic absorption and fluorescence spectroscopy (Gaidau, et al., 2010). The study revealed that nanosilver reacts with the collagen macromolecule inducing modification at the secondary structure level of collagen.

For cleaning of surfaces of movable artworks highly viscoelastic hydrogels and magnetic gels are being considered as promising materials. Cleaning of canvas will focus on two main topics: cleaning of painted surfaces (canvas paintings, easel paintings) and cleaning of canvas surfaces treated with adhesives (lined canvas). Cleaning issues for aged leather are rather complicated Many leather artifacts, are in fact damaged by unfavourable conservation and maintenance procedures. There are still a lot of uncertainties on the use of consolidation and chemicals used in conservation treatment. Commonly used maintenance products include fats and oils and can cause the following problems:

- Materials do not penetrate into fibres and only block the pores on the surface. This leads to problems in leather objects and interferes with the application of other maintenance products.
- Some solutions of fats can penetrate more deeply, but migrate back to the surface after drying of the solvent.
- Many of the fats and oils used for maintaining leather, become resin-like) in the course of time and contribute to the embrittlement of leather. In addition, to improve the preservation of leather the pH value of aged leather artifacts may need to be adjusted and stabilised to a slightly acidic level while considering any possible negative effects (e.g. detannage) (Larsen, et al., 2006). A fundamental factor is the preservation of the fibre structure and the increase in stability of the single fibres.

2. MATERIALS AND METHODS

2.1 Samples

For the MEMORI project varnish layers (about 30 m) were sprayed onto steel as in the previous PROPAINT project (Dahlin, et al., 2010). Resin and solvents were supplied by Kremer Pigmente, (Aichstetten, Germany) and samples were prepared at the School of Conservation, Copenhagen.

Mimosa leather was produced by the Forschungsinstitut für Leder und Kunststoffbahnen (FILK), (Freiberg Sachsen, Germany) for the MEMORI project according to the prescriptions formulated in the Environment Leather Project (EV5V-CT94-0514) (Larsen, et al., 1996). Leather was tanned with a condensed tannin using bark of mimosa (*Acacia mearnsii*). Small samples were provided from historical objects requiring conservation treatment. (IPCE Instituto del Patrimonio Cultural de España Madrid, Spain). Some preliminary results are shown of tests performed on samples from the leather bookbinding of the Psaltar, from the Cathedral of Guadelupe (Spain) 16th cent.

Samples of canvas were obtained from the original auxiliary canvas (loose lining) of Sir Edwin Henry Landseer's painting ['Study of a Lion' (c 1862), Tate Gallery N01350]. These had been removed during conservation treatment and were provided by Tate Conservation Dept. for deacidification treatment.

2.2 Methods used in MEMORI and NANOFORART projects

2.2.1 Controlled Environment Dynamic Mechanical Analysis (DMA)

The rationale for the use of controlled environment DMA is that it provides information on the change in mechanical properties with controlled increase of RH. In the IDAP project it was observed that where samples were more damaged then there was a measurable difference in the change in stiffness of the samples and in the change in displacement (Odlyha, et al., 2009). In the MEMORI project differences have been measured between unaged parchment samples and those exposed to acetic acid vapour (Odlyha, et al., 2011). This information will be useful for the NANOFORART project which will be using deacidification procedures and so will rely on proven methods of damage assessment for testing the efficacy of the conservation treatment. Samples of canvas and leather were tested using the following instrumentation and procedure. Prior to testing, samples were pre-dried for 24hrs in a desiccator. They were then mounted in the tensile clamp of the Dynamic Mechanical Analyser (DMA TRITEC2000B).

The Triton RH controller unit was used together with the DMA and the starting conditions were set to 20% RH and 25 ºC. Once the sample had stabilised under these conditions then the RH

was increased at 1%/min until 80% RH and it was left at 80% RH for 30 min. and dehumidified to 30%RH. Sample dimensions were typically 5 (or 10) (l) x4.50(w) x 0.2 (t) mm.

2.2.2 Micro-thermal analysis (μ-TA)

Micro-TA uses an atomic force microscope in which the conventional tip is replaced by an ultra-miniature electrical resistor (Reading, et al., 2001). This provides a controlled heating facility for spatially resolved thermal analysis. Its use in the PROPAINT project showed that glass transition temperature (*Tg*) of varnish samples on steel strips exposed in microclimate frames and rooms could be measured (Dahlin, et al., 2010). In the MEMORI project micro-TA has extended the information on varnishes to include the effect of exposure to volatile organic acids. It has also been applied to parchment, initially in the IDAP project (Groot de, 2007). The technique showed that surface gelatinisation occurs in samples. The interpretation was based on markers for gelatinisation obtained in previous work using micro-TA on model collagen samples (Groot de, 2007; Bozec and Odlyha, 2011). It has also provided information on the behaviour of varnishes, resin mastic and Laropal A81, following acid exposure and the results will be reported at the forthcoming second European Workshop on Cultural Heritage Preservation, EWCHP (http://ewchp-2012.nilu.no, accessed 16 Aug. 2012. The Micro-Thermal analyzer (μ-TA 2990) (Explorer AFM with the micro-thermal analysis user interface (TA Instruments, New Castle, DE) with Wollaston wire probe was used. Local thermal analysis was performed between 20 and 300˚C at up to ten different locations on a 100μm x 100μm area using heating speeds of 20˚C/s. Temperature calibration was performed using polymer samples of known melting temperature. The softening of the material as it passes through its *Tg* produces a downward deflection of the cantilever.

2.2.3 Atomic force microscopy (AFM)

The protocol for imaging collagen fibres taken from parchment was developed in the IDAP project (Groot de, 2007). Damage categories were also developed in IDAP based on accelerated aged and historical samples which showed various degrees of retention of the intact periodic D- banding and fibril structure. A computer programme was developed to measure extent of intactness of the periodic D- banding of collagen in the entire AFM image (Groot de, 2007). Correlation was found between the obtained values and the measured shrinkage temperatures. Varnished surfaces have also been studied and revealed surface defects which formed after exposure to acetic acid vapour and ozone respectively (Dahlin, et al., 2010). AFM was performed using a Dimension 3100-Nanoscope 1v AFM (Veeco) for parchment. The Nanosurf® EasyScan 2 AFM was also used in dynamic mode to image the leather samples and is reported in this paper. It was fitted with a cantilever (Nanosensors PPP-NCLR) with a spring constant k_{tip} =48N/m, resonance frequency f_{res} =170kHz and a tip radius r_{tip}<10nm. Fibres from the leather were moistened in distilled water and allowed to dry on a glass coverslip. This was attached to a glass slide using double-sided tape supported on a metallic holder

3. RESULTS AND DISCUSSION

3.1 Analysis of varnish samples

In the MEMORI project micro-thermal analysis has been used for evaluation of the glass transition temperature (*Tg*). The *Tg* of the varnish is measured in terms of the downward displacement of the sensor in units of micrometers as it changes with linearly increasing temperature (Figure 1). Ten different locations in an area of 100μm^2 were tested. The varnish (Regalrez 1094) is a hydrogenated hydrocarbon resin and measured *Tg* of the control sample was within the temperature range 37-40ºC (Figure 1).

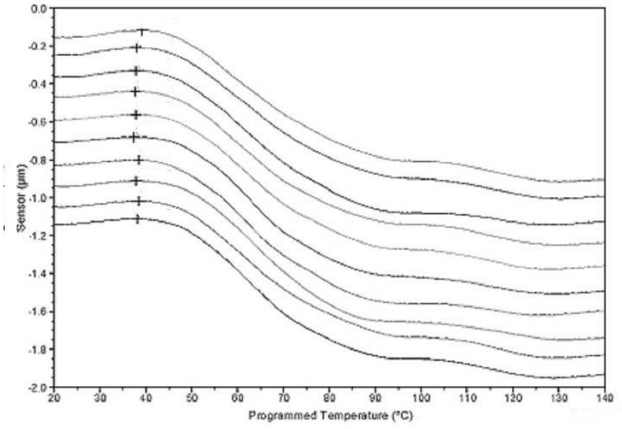

Figure 1 Sensor displacement (μm) vs temperature for unaged Regalrez 1094 varnish to give a *Tg* between 37-40˚C for 10 different locations in an area of 100 μm^2

On further curing and natural aging, the average value for the *Tg* moved to a higher value to 46.8˚C and this is shown in Figure 2 as the control sample (labelled HAc00). Exposure of this sample to acetic acid vapour (16ppm) produced further changes. Acetic acid vapour was generated from acetic acid solution and saturated salt solution (NaCl) to provide acetic acid vapour (16ppm) at an RH value in the region of 75%RH at room temperature.

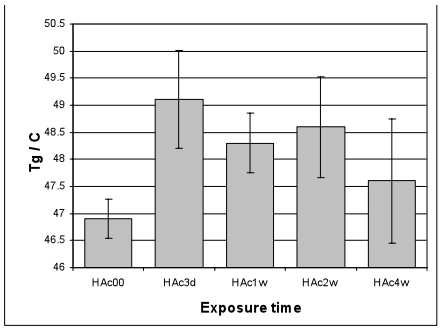

Figure 2 Change in *Tg* of Regalrez 1094 varnish with increase in length of exposure time (3 days to 4 weeks) to acetic acid vapour (16ppm) at 75%RH

Similar measurements on resin mastic and Laropal A81 will be reported in proceedings of the forthcoming EWCHP meeting (http://ewchp-2012.nilu.no). These resins show larger shifts in *Tg* for the same exposure. This indicates that Regalrez 104 is

more stable with respect to acetic acid vapour than either resin mastic or Laropal A81.

Studies of resin mastic varnish strips exposed at sites were made during the PROPAINT project, in addition to accelerated ageing tests (Dahlin, et al., 2010). Some of the measurements are shown in Figure 3 for resin mastic varnish strips exposed in Cracow National Museum in two different microclimate frames for three months. One was a microclimate frame with low air exchange value (0.39) and the *Tg* of the strip exposed in this frame is shown as the 1st location (KNF). The value was similar to that of the control sample and was about 10ºC less than the sample exposed in another frame 2nd location (KL) where the air exchange value had a much higher value (14.9). This allowed ingress of oxidising pollutants (e.g NO_2). Strips exposed at other sites showed that differences could be observed between those exposed in frames and in rooms (Dahlin, et al., 2010). The micro-TA curves show that for location 2 (KL) there is evolution of more crosslinked material as there is a second *Tg* at higher temperature (Figure 3).

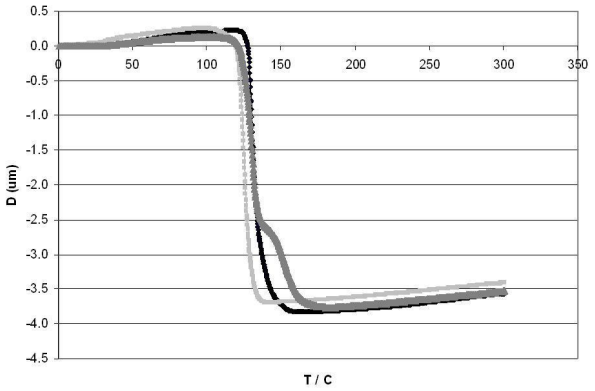

Figure 3 Micro-TA Curves showing displacement of sensor, D (m) vs temperature, T (ºC) control (light grey) microclimate frame (1st location, KNF, black) (2nd location, KL, dark grey)

Mass spectrometric measurements (MALDI-MS) (Figure 4) confirmed that this sample (KL) showed an increase in proportion of higher molecular wt. fragments. The fragment at (m/z) value (523) was selected as this has been assigned as indicative of presence of oxidation products of oleanonic aldehyde, assuming that oxidation leads only to new ketone groups (Scalarone,et al., 2005). Figure 4 shows the ratio of higher molecular weight fragment (m/z 523) to that of the lower molecular weight fragment (m/z 409) for varnish strips at selected sites where climatic conditions and pollutant levels (inorganic and organic) were tested during the period of exposure. These data are presented in the final report of the PROPAINT project (Dahlin,et al., 2010). In the two sites National Gallery of Denmark and the Museum of Fine Arts in Valencia,Spain, the change appears to be higher in frames than in rooms (Figure 4).

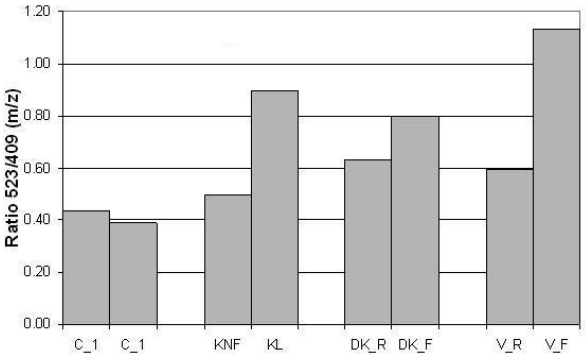

Figure 4 Ratio of fragment (m/z 523) to fragment (m/z 409) for resin mastic strips : C_1 (control), KNF,KL (Cracow National Museum), DK (National Gallery of Denmark) (DK_R room, DK_F in frame), V (Museum of Fine Arts in Valencia),Spain (V_R room, V_F in frame)

In the National Gallery of Denmark levels of acetic acid in the frame (DK_F) exceeded 1000 g/m^3. In the Museum of Fine Arts in Valencia, the *Tg* values measured by micro-TA were also higher for the sample exposed in the frame (V_F) than in the room (V_R) (Figure 4) . Dosimeter evaluations of these locations are discussed elsewhere (Grøntoft, et al., 2010).

3.2 Analysis of leather exposed samples

Controlled environment DMA was performed on pre-dried samples exposed for 4 weeks to acetic acid vapour (160ppm). The latter was generated from a solution of acetic acid (400mg/m^3) and saturated salt (NaCl) solution to provide 75%RH. DMA was performed using a sinusoidal load at a selected frequency (1Hz). This provides a measure of the complex modulus which can be separated into elastic (or storage) modulus (E') and inelastic (or loss) modulus (E''). Figure 5 shows the variation of storage modulus (E') for mimosa leather with RH (%) where RH is increased at a controlled rate on humidification and dehumidification.

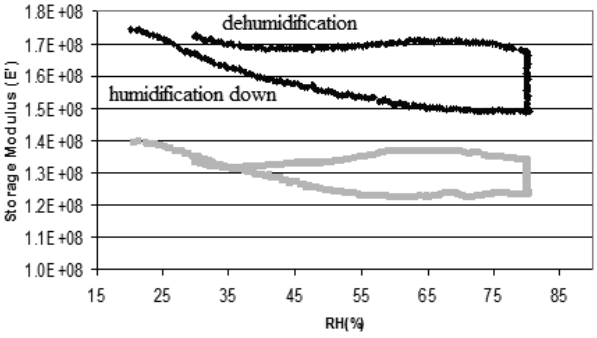

Figure 5 Modulus (E') vs RH (%) for acid exposed mimosa leather sample (grey) and control sample (black). Acid exposure causes lowering in modulus values. Time (100mins) spent at 80%RH produces smaller changes in modulus of acid exposed sample, and dehumidification shows some differences.

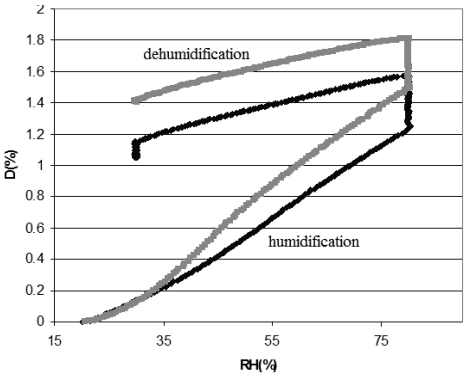

Figure 6 Acid exposed mimosa leather (grey) shows higher values of displacement (D%) with increase in RH (%) than in the control mimosa leather sample (black).

Figure 6 shows the change in displacement (%) of the mimosa leather sample with RH (%). Behaviour of leather appears to differ from that of similarly aged parchment. In the case of parchment the formation of a gelatine layer is often seen as a result of increasing deterioration whereas no surface gelatinisation of leather was observed. The gelatine layer develops from the hair holes on the grain layer and spreads until the surface is covered (Axelsson, et al., 2011). Preliminary work to assess the state of collagen in historical leather bookbindings (Figure 7) prior to conservation treatment has been performed in the NANOFORART project. Figure 8 shows AFM images with some regions of intact D-banding of collagen (Odlyha, et al., 2011) in areas in the inner cover.

Figure7 Leather bookbinding of Psaltar, Cathedral of Guadelupe (Spain) 16th cent. [IPCE Instituto del Patrimonio Cultural de España [Madrid, Spain]

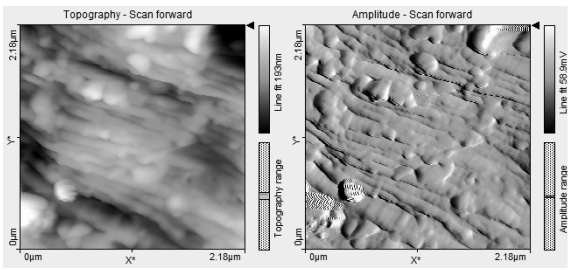

Figure 8 AFM (topography left) and amplitude (right) of leather sample from inner cover of bookbinding (2.18 m x2.18 m).

3.3 Evaluation of effect of conservation treatment on 19th century canvas linings

Deacidification of canvas paintings was previously performed in collaboration with Tate Conservation Dept. where reverse sides of selected paintings were treated with commercially available methoxy magnesium methyl carbonate (MMC) solution (Hackney,et al.,1996). Modern commercially primed and unprimed canvases were also treated and dynamic mechanical thermal analysis testing was performed (Odlyha, et al.,1997). Measurements showed that the treatment affected the mechanical properties. It appeared to produce a coating on the samples which acted as a moisture barrier. Recent preliminary tests prior to the NANOFORART project using both calcium and magnesium hydroxide nanoparticles on 19th century linings were performed and the effect of natural ageing of about two years is reported. The treatment is described elsewhere (Chelazzi, et al., 2006). In the NANOFORART project, work is ongoing to optimise nanoparticle preparations to solve the acidity problem, with particular attention to avoid swelling of the cellulose fibres.

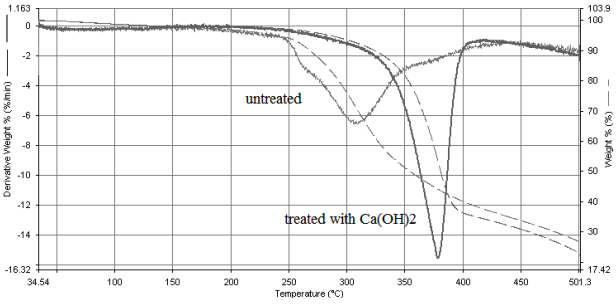

Figure 9 Thermogravimetric 1st derivative curves (full lines) with the thermogravimetric curves (dotted lines) of untreated and treated samples of 19th century canvas linings are shown

Figure 9 shows the effect on canvas linings of conservation treatment using alkaline nanoparticles [$Ca(OH)_2$]. The method uses thermogravimetry (TGA) which records the weight change in the sample with linearly increasing temperature. This was the method used to test the efficacy of conservation treatment on wood samples (Chelazzi,et al.,2006). Figure 10 shows the variation in modulus before and after treatment with increase in RH (1%/min). The sample after treatment appears to behave more like unaged canvas in its response to RH. Further work is in progress.

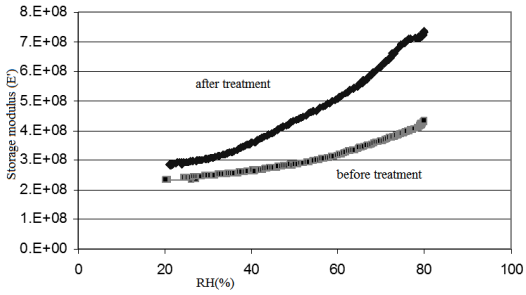

Figure 10 Changes in behaviour of E' (storage modulus) with linearly increasing RH(%) are shown for treated [$Ca(OH)_2$], and untreated 19th century samples (Tate Conservation Dept.)

4. CONCLUSIONS

This paper demonstrates that damage markers obtained in previous projects, PROPAINT and IDAP, are of use to current projects. The application of minimally invasive techniques such as micro-thermal analysis and atomic force microscopy are vital in characterising surface changes and complement additional information from controlled environment DMA and thermogravimetry (TGA). In MEMORI studying the effect of acidification of materials provides additional markers of damage that can be of use when evaluating effects of deacidification treatment in the NANOFORART project. Preliminary tests reveal that the effect of alkaline nano-particles improves the thermal stability of the canvas linings and changes the behaviour of the elastic or storage modulus with RH(%) making it behave more like the unaged canvas. The work is at an early stage and nanoparticle preparation is currently being optimized.

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