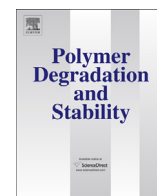


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# Polymer Degradation and Stability

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## Assessing the physical stability of archival cellulose acetate films by monitoring plasticizer loss



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### ABSTRACT

Cellulose acetate film plasticized with diethyl phthalate was subjected to artificial aging regimes and the loss of plasticizer determined by means of Thermogravimetric Analysis and Fourier-transform Infrared Spectroscopy. Alterations in the strain hardening capability of the films was monitored by Dynamic Mechanical Analysis, and the connection between flexibility, strain hardening and the degree of plasticization investigated as a means of monitoring the physical condition of archival cellulose acetate film. It was found that the higher the plasticizer content the greater the ability to strain harden, and therefore the least vulnerable to mechanical damage from archival handling. The correlation between the critical plasticizer content and the working properties of cellulose acetate film provides a means of assessing stability, and highlights artifacts at risk from physical damage.

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## 1. Introduction

Synthetic and semi-synthetic polymers comprise an increasing portion of cultural heritage and archival collections. The growth in polymer manufacturing and engineering that occurred throughout the twentieth century inevitably led to many artists and designers employing these new and relatively inexpensive materials in their works. However, the physical instability of some polymer formulations now pose particular problems for the heritage profession, where longevity and conservation is of primary importance [1–5].

One such example is the case of cellulose acetate film, which was used extensively as the substrate for animation art works. Owing to its transparency and flexibility, cellulose acetate film was employed as the base material for animation cels between the 1920's and early 2000's, with the animation painted in reverse, the image being viewed from the opposite side to the paint layer. Over time many of these films have been found to lose their mechanical integrity, which impacts on the handling and display of the cels.

Additionally, the aging of the binders within the paint layers impacts on adhesion and when coupled with the warping and buckling of the substrate, loss of the image often results (Fig. 1).

The primary properties of interest with such works of art are those related to the flexibility of the sheet material and shrinkage mechanisms. As with all archival material and art works, the physical nature of an animation cel will impact on its access for both research and display. Limiting the handling of vulnerable material helps to mitigate damage. However, determining the condition of an object can be challenging, especially when the point at which change is visible to the eye usually means that the object is already heavily degraded. Further issues arise where aesthetic or ethical considerations limit sampling of an artifact, preventing bulk analysis and assessment of an object's physical integrity. In such cases assessment often needs to be made through correlations between microanalytical methods and the bulk properties of surrogate materials [6–8].

Our current research is directed at monitoring the degradation of historic cellulose acetate, and understanding the relationship between the chemical and physical properties of these films. One area of focus is that of plasticizer migration. The working properties of polymer materials are governed by the underlying chemistry and microstructure, with the presence of plasticizers and other

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**Fig. 1.** Image of a buckling animation cel illustrating loss of mechanical integrity and damage to painted image.

additives greatly affecting molecular interactions, and thermal and mechanical behavior [9,10]. Due to the type of bonding, volatility, size, and shape of the plasticizer, with time, these substances often migrate to the surface of a plastic altering the working properties of the material. This is often seen as an oily exudate on the surface of the film, in the case of phthalate plasticizers, or as solid triphenyl phosphate crystals. The loss of plasticizer may be promoted by environmental factors as dimensional alterations take place in the polymer network. By the time flexural and visual changes have occurred, the material is often too brittle for safe archival handling and successful remedial conservation treatment, such as paint re-adhesion, mounting and digitization. Therefore, a monitoring method is needed whereby the percentage plasticizer content can be related to the physical condition of the films, such as flexibility, enabling vulnerable materials to be highlighted in collections.

Although the migration of plasticizers have been studied in fields such as the food industry [11–14], little has been carried out within the heritage sector in regard to object stability [15,16]. In this preliminary ‘proof of concept’ study we monitor the change in prolonged flexural properties as a function of plasticizer loss from the polymer matrix. Samples were artificially aged at 70 °C (344 K) and at three different relative humidities. The loss of plasticizer was monitored using Thermogravimetric Analysis (TGA) and transmission Fourier-transform Infrared Spectroscopy (FTIR). Tensile tests were performed to provide information on the brittle behavior illustrating the inverse relationship between strain at break and brittleness. Flexural experiments were conducted using a Dynamic Mechanical Analyzer (DMA) with the modulus monitored as a function of time at constant temperature, in an attempt to mimic archival handling. Investigating two independent micro-techniques to assess the physical condition of a cellulose acetate film of a given thickness, offers the possibility of condition monitoring of artifacts, removing the need for large-scale sampling.

## 2. Materials and methods

### 2.1. Materials

Commercially-available cellulose acetate film was supplied by Goodfellow Inc. The film had a thickness of 0.25 mm and was plasticized with diethyl phthalate (DEP). The presence of additive

material was confirmed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The glass transition ( $T_g$ ) temperature of the unaged material was determined by differential scanning calorimetry (DSC). A double heating scan was performed over a range of 30 °C–280 °C, using a heating and cooling rate of 20 °C  $\text{min}^{-1}$  (20 K  $\text{min}^{-1}$ ) under a nitrogen atmosphere. Taking the zero point of the second-derivative curve, the  $T_g$  was determined as 124 °C in the first heating run, and 190 °C in the second run after loss of volatiles.

The samples were pre-cut into 10 mm wide strips along the direction of rolling before undergoing artificial aging.

The results presented in this study pertain to cellulose acetate film of a given depth and plasticized with diethyl phthalate. Only proving applicable to material of such dimensions, further calibration curves need to be derived in order to cover a range of film depths. Additionally, given the varying degrees of plasticization offered by differing formulations, investigations are underway to determine the optimum plasticizer content for each of the compositions encountered in animation cels.

### 2.2. Artificial aging

The nature of museum and heritage objects means it is often difficult to acquire samples to enable representative analysis and testing. It is therefore often necessary to use artificial aging regimes to provide degraded test material for modeling and assessment of the likely behavior of aged artifacts. However, some caution is required in the interpretation of the results, due to the varying and competing reactions that may occur at raised temperatures.

Artificial aging conditions were selected to accelerate the degradation of the cellulose acetate and to reflect the types of conditions to which animation cels can be exposed. The choice of aging temperature and respective aging times were based on previous experimental work carried out by Adelstein et al. [6,17–19], and published activation energies for the thermal decay of cellulose acetate [20,21]. An activation energy of 90.3 kJ  $\text{mol}^{-1}$  was used in the calculations, as quoted by Padfield [21], for the degradation of cellulose acetate below 100 °C. McBrierty et al. [22] reported the loss of diethyl phthalate from cellulose acetate sheets as occurring above 95 °C, as shown by the onset of a broad DSC endotherm. Based on this, the artificial aging temperature was maintained at 70 °C (343 K).

The Arrhenius equation was used to calculate the rate of reaction at 70 °C (343 K):

$$k = Ae^{-E_a/RT} \quad (1)$$

where  $k$  is the rate of reaction,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy (kJ  $\text{mol}^{-1}$ ),  $R$  is the gas constant (8.314 J  $\text{K}^{-1}$   $\text{mol}^{-1}$ ) and  $T$  is the temperature (K).

The calculated rate of deterioration at 70 °C (343 K) is  $1.77 \times 10^{-14}$ , giving a rate increase of 222.

The increased reaction rate was used to determine the equivalent length of aging required to represent natural aging at room temperature (293 K) (Table 1):

**Table 1**  
Equivalent aging times for artificial aging at 70 °C (343 K).

Desired exposure time/years	Desired exposure time/days	Aging time required at 70 °C (343 K)/days
10	3652	16
20	7305	33
30	10,957	49
40	14,610	66

$$\text{Length of Artificial Ageing} = \text{Length of Natural Ageing} \quad (2)$$

at 20 °C/Rate Increase

The samples aged at 70 °C (343 K) were separately subjected to relative humidities (RH) of  $33.1 \pm 0.2\%$ ,  $54.4 \pm 0.2\%$  and  $69.9 \pm 0.3\%$  maintained using saturated salt solutions of magnesium chloride, magnesium nitrate and potassium iodide, respectively [23]. Humidities were monitored using a Vaisala HUMICAP® relative humidity and temperature sensor.

### 2.3. Thermogravimetric analysis

Thermogravimetric Analysis was carried out after artificial aging to determine the percentage weight-loss of volatile components from the cellulose acetate. Measurements were recorded using a Mettler Toledo TGA/SDTA851e, which permits simultaneous Thermogravimetry and Differential Thermal Analysis (DTA) measurements, using STARe software version 8.10. The cell and furnace were purged with oxygen-free nitrogen at a flow rate of  $50 \text{ ml min}^{-1}$ , over a temperature range of 30 °C–450 °C at a heating rate of  $5 \text{ °C min}^{-1}$  ( $5 \text{ K min}^{-1}$ ). Samples weighed approximately 5 mg each; both the crucible and sample weights were accurately measured using the software's automated balance function.

### 2.4. Transmission fourier-transform infrared spectroscopy

Transmission Fourier-transform Infrared Spectroscopy was carried out using a Bruker Vertex 70 with a liquid nitrogen cooled MCT detector and Opus software version 6.5. Analysis was performed over a range of  $400\text{--}4000 \text{ cm}^{-1}$ , using a wavenumber resolution of  $2 \text{ cm}^{-1}$  and 64 scan accumulations. Samples were finely powdered and prepared as potassium chloride disks for transmission spectroscopy. Potassium chloride was chosen for the salt window in place of potassium bromide as its refractive index ( $n$ ) is closer to that of cellulose acetate,  $n = 1.49, 1.55$  and  $1.48$  respectively [24]. The sample chamber was purged with dry air to reduce background interference. Data analysis was carried out using the Integrate function in Thermo Galactic Grams AI software.

### 2.5. Tensile analysis

Uniaxial tests were performed using an Instron 5885H fitted with a 500 N load cell and the samples secured with pneumatic rubber faced grips. Data acquisitions were made every 100 ms and at a load change of 1 N or greater. Test strips, measuring  $10 \times 80 \times 0.25 \text{ mm}$ , were tested using a modified standard method for the determination of tensile properties of thin plastic sheets, ASTM D882-09 [25], using a gauge lengths of 50 mm and a cross-head speed of  $5 \text{ mm min}^{-1}$ . Temperature and relative humidity fluctuations averaged  $20 \pm 3 \text{ °C}$  and  $50 \pm 4\%$ , respectively. Seven replicates from each sample were analyzed, discarding the results from those samples breaking in the grips and calculating the average values for the remaining samples.

### 2.6. Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) was performed using a Tritec DMA 2000 with Triton Technology DMA software version 1.43.06 in time/temperature mode. Flexural properties were determined using a 3-point bend at a constant temperature of 24 °C, performed over a period of 120 min at a frequency of 1.0 Hz. Samples measuring  $20 \times 10 \times 0.25 \text{ mm}$  were subject to a

displacement of 0.25 mm, giving a flexural strain,  $\epsilon_f$ , of 0.375% calculated as per ASTM D790-10 [26]:

$$\left(\epsilon_f = 6Dd/L^2\right) \quad (3)$$

where  $D$  is the maximum deflection,  $d$  is the depth of the sample, and  $L$  is the support span, which is taken as the distance between the moving clamp and outer support (half the total length). Changes in flexural modulus ( $\Delta E$ ) were calculated as a function of time, rather than temperature, to provide information on the working properties. The difference between the modulus at 5 min into the experiment and at termination (120 min) was taken as a measure of strain hardening. Strain hardening is dependent on a number of factors, such as strain rate and temperature. Taking this into account the deflection of the film, and therefore the percentage strain, was chosen to closely represent the degree of deformation occurring when handling films.

## 3. Results and discussion

Good mechanical properties of animation cels are integral to the handling, display and stability of such art works. Chemical alterations and degradation of the polymer matrix impact on the physical nature of the film and, as a consequence, the permanence of the paint layer or image. Such factors affect collections care strategies and accessibility to such archival materials.

### 3.1. Loss of volatile components

Fig. 2 shows the thermogravimetric weight loss curves for the samples artificially aged at 70 °C and 70% RH. The TGA data were normalized by dividing the weight loss at each temperature with the residual cellulose acetate weight at 240 °C, determined by DSC as the onset of thermal decomposition in the unaged material (data not presented).

It can be seen that up to 90 °C the weight of each sample remains constant. After this point there is a gradual decrease in weight, which is dependent on the age of the sample. The amount of plasticizer and moisture in the sample decreases with increasing age, seen as a reduced weight loss. In all cases, the loss appears to

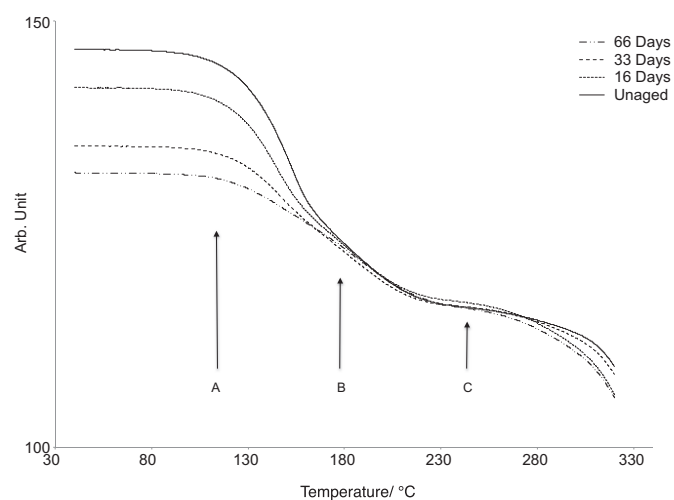


Fig. 2. Weight loss curves normalized to residual cellulose acetate weight after 240 °C for the samples aged at 70 °C and 70% RH, for 16, 33 and 66 days. Arrows indicate the two-step weight loss between 85 °C and 165 °C (A) and 165 °C – 200 °C (B), and thermal decomposition at 240 °C (C).

be a two-step process; an initial weight loss occurring between 85 °C and 165 °C, dependent on the length of aging (A), and the second weight loss step occurs between 165 °C and 200 °C and is approximately linear between all samples (B). This second component is less easily lost from the films, remaining present in both the unaged and aged samples. The thermal decomposition of the cellulose acetate is seen to occur at 240 °C (C).

Friedman and Sorokina [27] reported that at concentrations below 25 wt%, DEP is sorbed by the active sites of the cellulose acetate polymer. Above this level, it was shown that the DEP vapor pressure above the plasticized samples increased and was attributed to a portion of the plasticizer existing as an individual phase. In a study of the hydration and plasticization of cellulose acetate, McBrierty et al. [22] attributed the absence of a DEP melting endotherm in the DSC heating curve to the intimate interaction of the plasticizer and polymer through intermolecular bonding. In the work presented here, the plasticizer content in the unaged material is 21 wt%, lower than the quoted levels for an unbound phase. Further work is required to investigate the two types of molecular plasticization seen in the TGA data.

Fig. 3 illustrates that the weight loss occurring between the first two increments of aging are double those found at later stages; the behavior is not linear with respect to time. It is proposed that as loosely-bound plasticizer and moisture are lost the polymer voids are reduced, thus slowing down further migration.

Transmission FTIR was used as a microanalysis technique to monitor alterations in plasticizer content in the cellulose acetate. The intensity of the CH benzene absorption band at  $748\text{ cm}^{-1}$  was used to monitor changes in diethyl phthalate content. In order to account for differences in path length due to sample preparation, peak heights were normalized against that at  $602\text{ cm}^{-1}$  ( $I_{746}/I_{602}$ ). This absorption band was chosen as internal standard as it remains unaffected by the degree of plasticization. In a similar study, Skorniyakov and Komar [28] used peak ratios to monitor the level of bound acetic acid in unplasticized cellulose acetate. In their study normalization was carried out using the absorption band at  $2890\text{ cm}^{-1}$ , however this proved unsuitable in the present work due to the supposition of plasticizer across this spectral region. Here, individual band intensities were determined by drawing local baselines from  $764$  to  $724\text{ cm}^{-1}$  and  $666$ – $532\text{ cm}^{-1}$ , respectively.

Fig. 4 shows that the loss of plasticizer as determined by FTIR follows a similar trend to that of the TGA method (Fig. 3), and can therefore be successfully applied to monitor the presence of DEP in archival films.

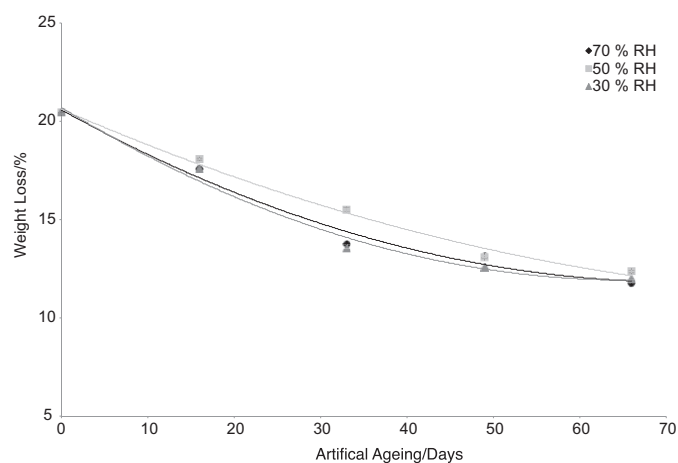


Fig. 3. Percentage weight loss at 240 °C plotted against length of artificial aging in days at 30%, 50% and 70% RH.

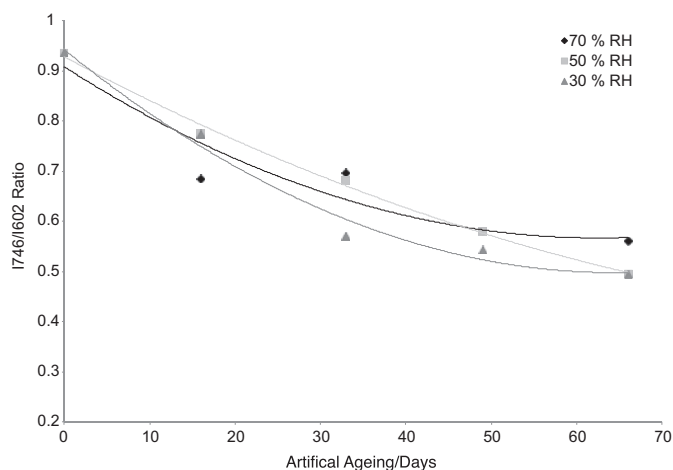


Fig. 4. FTIR absorption ratio  $I_{746}/I_{602}$  plotted against the length of artificial aging in days.

### 3.2. Effect of relative humidity

Artificial aging at differing levels of relative humidity was carried out to determine what effect environmental moisture may play in the migration of the diethyl phthalate. Fig. 5 shows the TGA curves relating to the unaged cellulose acetate and those sample aged at 70 °C and 30%, 50% and 70% RH for 66 days. It can be seen that the three aged curves superimpose, and that variations in relative humidity during aging have not significantly affected the loss of plasticizer from the sample matrix. This has important implications for archival storage, since moisture is known to play a major role in the eventual de-acetylation of cellulose acetate [29–31]. The hydrophobic nature of DEP does not impact in its loss to the surrounding environment. The fact that loss of DEP plasticizer from the matrix does not appear to be affected by the relative humidity means that storage parameters of cellulose acetate film may be tailored to the needs of the polymer base rather than the plastic compound as a whole. We are currently investigating the relationship between the degree plasticization and the hydrolysis of cellulose acetate and will report on this in a future publication. Real time experiments carried out in the food and packaging industry have shown that plasticizer migration is dependent on pH, with low pH having a stimulating effect on phthalate movement [11,32]. This behavior proving important for cellulose acetate as the

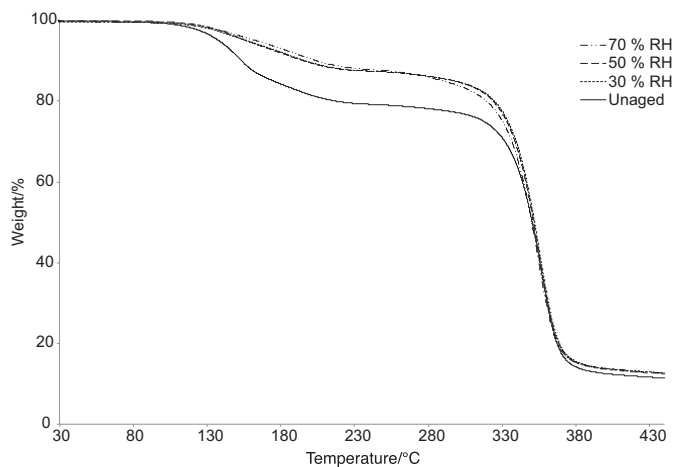


Fig. 5. Percentage weight loss for the unaged sample and samples aged at 70 °C and 30%, 50% and 70% RH, for 66 days.



eventual deacetylation of cellulose acetate will affect plasticizer migration.

### 3.3. Flexibility, strain hardening and brittleness

The 3-point bending tests were aimed at determining the time dependent working properties of the cellulose acetate at ambient conditions with a view to investigating stability during handling of film after loss of plasticizers. It is the mechanical properties of archival films that determine their use, so the flexural tests aim to mimic the effects of prolonged handling, in a similar manner to the double fold tests often employed to monitor the condition of archival paper [33].

As might be expected, the initial flexural modulus exhibited an increase with the aging of the samples (data not shown). This is in agreement with a decrease in plasticizer content as the ability of the specimen to deform is restricted.

Additionally, it is shown (Fig. 6) that the samples with greater plasticizer content exhibit an increase in flexural modulus over the duration of the experiment, up until termination at 120 min. Calculating the difference in modulus ( $\Delta E$ ) between 5 min into the experiment and 120 min, it is found that there is a degree of strain hardening in the samples containing a higher degree of plasticizer.

Brostow et al. [34,35] showed that for sliding wear tests, the strain hardening of various polymer films was related to the brittleness of the polymer; the most brittle materials showed reduced strain hardening. In our work, we show a similar correlation between the brittleness of the material and the strain hardening capacity ( $\Delta E$ ), seen as a positive correlation between  $\Delta E$  and the strain at break ( $\epsilon_b$ ), as derived from tensile experiments (Fig. 7). Table 2 shows the brittleness ( $B$ ) values obtained by exploiting the inverse relationship between the resistance to deformation, taken as the storage modulus ( $E'$ ) at 5 min into the experiment, and strain at break ( $\epsilon_b$ ) [35]:

$$B = 1/(\epsilon_b \cdot E') \quad (4)$$

This behavior is attributed to the degree of free volume present in the cellulose acetate film. For samples with greater plasticizer content there is greater molecular rearrangement as the film is placed under stress. As free volume decreases there is a restriction in movement of the polymer chains. This lower molecular motion and increased flexural modulus prevents dissipation of the applied stress. The material is closer to failure than those samples capable of re-arrangement under deformation. Polymers that exhibit

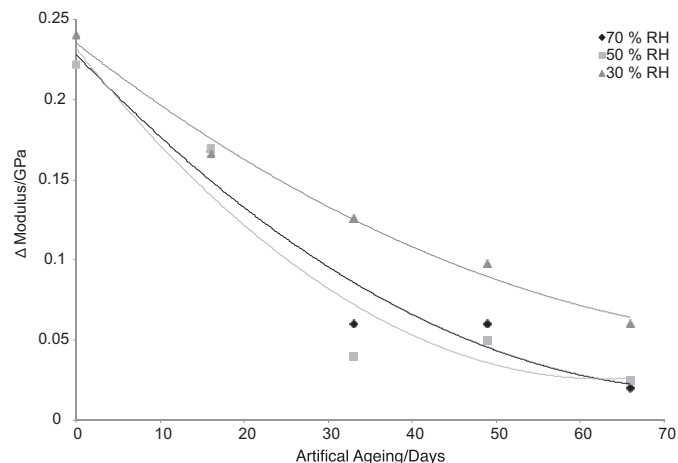


Fig. 6. Difference in flexural modulus between 5 min and 120 min for the unaged samples and those aged at 70 °C and 30%, 50% and 70% RH, for 16, 33, 49 and 66 days.

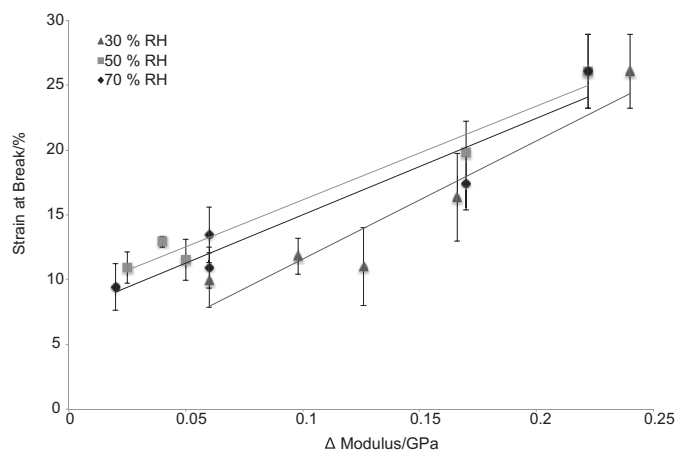


Fig. 7. Tensile strain at break versus difference in flexural modulus between 5 min and 120 min for the unaged samples and those aged at 70 °C and 30%, 50% and 70% RH, for 16, 33, 49 and 66 days.

greater strain hardening are tougher and tend to undergo ductile, rather than brittle, deformation due to suppression in strain localization [36]. The reduction in a materials ability to strain harden may provide a successful means of condition assessment for archival film, indicating brittle behavior, and informing handling strategies for fragile material.

Taking the average values for the three humidity regimes, Fig. 8 illustrates the correlation between strain hardening of the films and plasticizer loss determined by TGA and FTIR. If working limits are applied the strain hardening capabilities of a film of given thickness (here 0.25 mm) may be used as a measure of vulnerability to physical damage and successfully monitored using independent microanalytical techniques. The tensile tests revealed the elastic limit of the unaged film to be 65% of the strain at break. Given the positive correlation with the change in flexural modulus, it was decided to set the boundary for safe handling as 65% of the strain hardening capacity, corresponding to a  $\Delta E$  value of 0.08 GPa. This relates to a remaining volatile content of 13.9% as determined by TGA, and a value of 0.61 for the FTIR  $I_{746/602}$  ratio. Although this calibration data relates only to cellulose acetate film measuring 0.25 mm in depth, through correlating mechanical properties with independent techniques, we illustrate the potential for determining the physical stability of archival film without the need for bulk analysis.

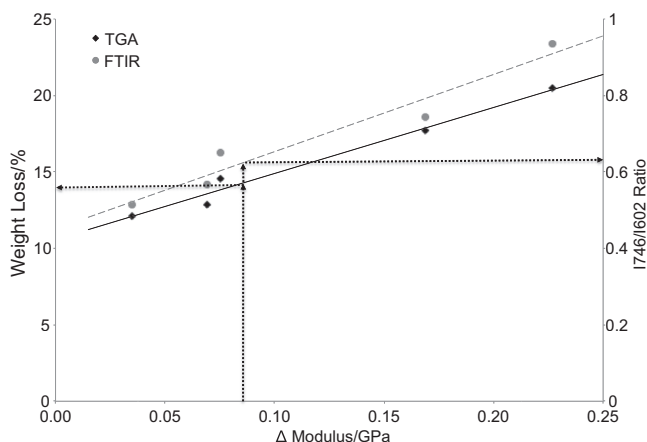
## 4. Conclusions

The artificial aging studies have shown that the loss of diethyl phthalate from cellulose acetate film appears to be independent of the surrounding relative humidity.

It was clearly shown that the flexural properties and the physical stability of cellulose acetate film are intimately related to the degree of plasticization. Strain hardening and, hence, brittle behavior was correlated with the plasticizer content, which was monitored using thermogravimetric analysis and Fourier-transform infrared spectroscopy. For archival film the distribution of internal stress is

Table 2  
Average values of brittleness ( $B$ ).

Sample	$B$ (%Pa)	$\epsilon_b$ /%	$E'$ /Pa
Unaged	1.44E-11	26.09	2.67E+09
16 days	1.80E-11	17.45	3.18E+09
33 days	2.23E-11	13.48	3.33E+09
49 days	2.69E-11	10.93	3.40E+09
66 days	3.10E-11	9.44	3.41E+09



**Fig. 8.** Difference in flexural modulus between 5 min and 120 min plotted against percentage weight loss at 240 °C and the FTIR absorption ratio I746/I602. Data are the averaged values for all unaged sample and those artificially aged for 16, 33, 49 and 66 days. Arrows indicating the boundary limit set for strain hardening and the corresponding plasticizer content, as determined by TGA and FTIR.

key to enabling safe handling of film material. Therefore hardening capacity can be taken as a measure of a materials physical stability. The results highlighted the possibility of applying micro-analytical techniques in place of larger scale mechanical analysis for condition monitoring of artifacts, removing the need for large scale sampling. This offers the potential for predicting the flexibility of cellulose acetate film with minimum disturbance to the object. Further work is underway to develop master calibration curves that will enable the physical characteristics of film material with differing depths and plasticizer compositions to be successfully monitored.

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