



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 min^{-1} (20 K 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 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 mol^{-1}), R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K).

The calculated rate of deterioration at 70 °C (343 K) is 1.77×10^{-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

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