

Analysis of shrinkage mechanism of cellulose acetate during ageing

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Introduction

CA (cellulose acetate) is a material that was used extensively in the 20th century by the film industry as well as by artists to create fine and decorative art. YUAG (Yale University Art Gallery) owns a miniature version of Marcel Duchamp's *The Bride Stripped by her Bachelors, Even*, known as the "Little" Large Glass (LLG). The recent changes of the preservation condition of the LLG pointed to the gap in understanding of mechanism leading to CA deformation.

Within the last few years, the stand-alone LLG was encapsulated in Mylar. In early 2015, liquid had accumulated between the object and the Mylar. When the enclosure was opened the liquid formed crystals, later identified as the plasticizer. The plastic turned from transparent to translucent. When first released from the Mylar, the sheet was relatively flat, but over the course of the week became undulating. Over the next few weeks, the deformation changed to overall arching. When compared to the LLG in the two *Boîte-en-valise* in the YUAG collection, the condition difference is striking, with the two in situ relatively planar, the plastic still clear, and the paint well-adhered. The encapsulation of the LLG in Mylar had a massive impact on its condition. The LLG by Marcel Duchamp case showed that existing explanations of the mechanism leading to the deformation of CA explaining plasticizer migration due to its evaporation are insufficient. Contrary to the most common explanations, the LLG case shows that potential plasticizer migration couldn't be caused by plasticizer evaporation as it was kept inside a Mylar enclosure.



Marcel Duchamp. *Boîte-en-valise*. 1942-1943. YUAG (1953.6.6)



Marcel Duchamp. "Little" Large Glass. 1942-1943. YUAG (1953.6.357)

Statement of the project

Unlike the primary chemical processes responsible for material degradation, which have been relatively well studied, the mechanisms of mechanical change in CA and their relationship to chemical processes are not well understood.

The goal of this project is to understand causes and mechanism leading to shrinkage of CA and to determine changes in mechanical properties during artificial ageing. The project will also correlate mechanical parameters with chemical changes in CA.

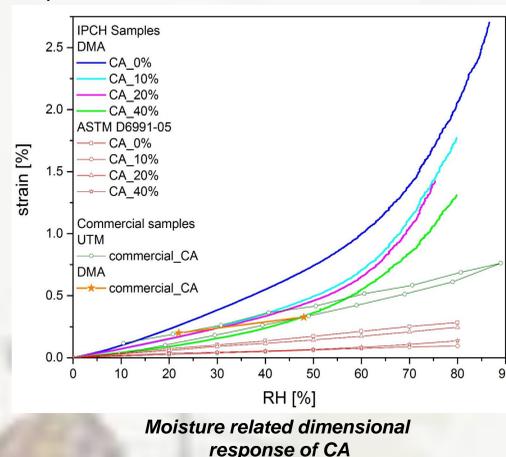
Several potential causes of CA shrinkage are evaluated encompassing: degradation of the CA matrix, loss of the plasticizer due to plasticizer diffusion and evaporation, loss of plasticizer due to changes in its compatibility with CA, and migration of plasticizer driven by acetic acid (AA) generation and transport. CA samples with different plasticizer content (Triphenyl Phosphate and Diethyl Phthalate) of 0%, 10%, 20% and 40% were used in the course of the project.

Additionally, the Marcel Duchamp study indicates the significant role of impermeable enclosures, which may block transport of degradation products. Therefore, the project focused on the determination of the transport kinetics of AA in CA.

Moisture related dimensional response of CA

Measurement of CA shrinkage during prolong artificial ageing presents difficulties related to material flexibility, and requires a significant number of samples. Therefore, the cantilever method according to ASTM D6991-05 was initially proposed as the optimal experimental method.

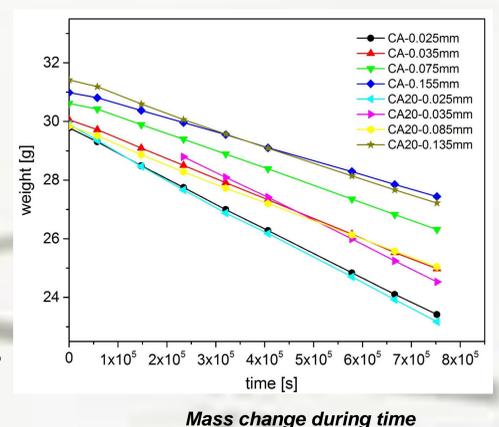
Preliminary testing showed that CA delaminates from the metal substrate during ageing. Additionally, comparison of moisture response to humidity changes obtained by that method and by using DMA (Dynamic Mechanical Analyzer) showed significant differences in the results. This indicates that application of CA on metal substrate changes significantly the behavior of the material. Independently on the method used results showed that CA with lower content of plasticizer responds more to humidity change. It was decided to change the method of shrinkage determination to an optical one based on pattern recognition coupled with UTM (Universal Testing Machine). In coming months, new results will be obtained.



Permeability of CA to acetic acid

The permeability test is based on the ASTM E-96 cup method. Cups of acetic acid were sealed with two CA films of known thickness and differing in plasticizer content

(CA0 without plasticizer and CA 20 with 20 percent plasticizer). The surface area is $2.026E-3 \text{ m}^2$ through which AA diffused. Corresponding to a disk of 0.05 m in diameter. Surprisingly, all the samples experienced a significant mass loss during a short time, as is shown in the figure. The permeability of AA in CA0 and CA20 at 25.8 °C and 35% RH is $4.39948E-13 \text{ [kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}]$ and $4.34E-13 \text{ [kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}]$, respectively.



Conclusions

Cellulose acetate is sensitive to humidity change. CA with different plasticizer contents has different moisture related dimensional responses. Relative humidity should be controlled in the storage environment to prevent the paint from falling off the CA substrate.

The degradation of CA will release acetic acid which will accelerate the ageing of this material. Measurement performed showed that transport of acetic acid in CA is relatively fast. Natural escape of acetic acid from the CA object depends on the shape of the object. It's better not to keep CA objects in a sealed environment unless adequate AA absorbers are available.

Future work

Accelerating ageing was designed in a way that enabled the role of various processes leading to CA film shrinkage to be distinguished.

Methods such as FTIR, SEM, DMA, UTM will be applied to correlate material shrinkage with the tensile properties, T_g , total plasticizer content and its distribution in material cross section and chemical degradation of CA.



Deformation of the Little Large Glass

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