# Water sorption and diffusion in cellulose acetate: the effect of plasticisers

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Keywords: cellulose acetate, water sorption, water diffusion, plasticiser loss

## Abstract

The conservation of cellulose acetate plastics in museum collections presents a significant challenge, due to the material's instability. Several studies have led to an understanding of the role of relative humidity (RH) and temperature in the decay process. It is well established that the first decay mechanism in cellulose acetate museum objects is the loss of plasticiser, and that the main decay mechanism of the polymer chain involves hydrolysis reactions. This leads to the loss of sidechain groups and the breakdown of the main polymer backbone. However, interactions between these decay mechanisms, specifically the way in which the loss of plasticiser can modify the interaction between cellulose acetate and water, has not yet been investigated. This research addresses the role of RH, studying the sorption and diffusion of water in cellulose acetate and how this interaction can be affected by plasticiser concentration using Dynamic Vapour Sorption (DVS).

## 1 Introduction

Water sorption and diffusion have been a subject of interest in many different research areas including membrane separation, pharmacology, food packaging and fibres as well as material degradation (Allada et al., 2017; Argyropoulos et al., 2011; Célino et al., 2014; Kohler et al., 2003; Kurokawa, 1981; Kymäläinen et al., 2015; Leão & Tuller, 2014; Zhang et al., 2013). Materials can be affected by the relative humidity (RH) of the environment, which can often cause undesirable changes in mechanical and chemical properties. Furthermore, it is particularly concerning in museum institutions where, due to the rarity of artefacts, control of environmental factors such as temperature and RH are needed to slow down degradation processes (Wäntig, 2008). Due to the lack of international standards for storage of plastic artefacts in museums, it is not uncommon for museums to apply the same environmental parameters used for classic heritage organic materials

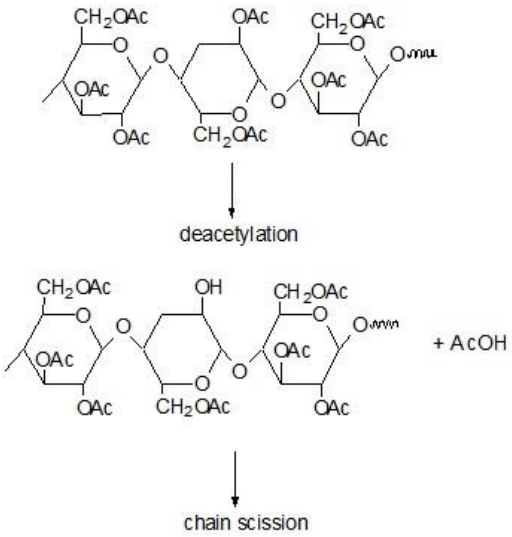


*Figure 1: Schematic representation of hydrolysis steps in cellulose acetate. The first step, deacetylation, causes the substitution of acetate (Ac) by hydroxyl groups with the consequent emission of acetic acid. The second step known as chain scission causes the cleavage of glycosidic group.*

(e.g. paper) to plastics and to store them at 18-20 °C and 50% RH (Shashoua, 2014).

In cellulose acetate, hydrolysis is an intensively studied, complex subject in the life-assessment and decay mechanism of archival materials and plastics (Allen et al., 1987, 1987; Edge et al., 1989; Edwards et al., 1993; Littlejohn et al., 2013, 2013; McGath, 2012; Wäntig, 2008; Shashoua, 2008), with a variety of chemical and physical mechanisms involved. Cellulose acetate spontaneously undergoes hydrolysis (enhanced by high temperatures and RH) losing acetic acid and causing a decrease of the degree of substitution (DS), the mechanism of which is shown in Figure 1 (deacetylation). This process is known as vinegar syndrome for the strong smell of acetic acid produced during the decay mechanism, an autocatalytic reaction that decreases the pH and consequently accelerates the ageing process (Edge et al., 1989). The trapped acid can catalyse the hydrolysis of C-O bonds in the polymer backbone, reducing the length of the polymer chain (Ballany et al., 2000) in a process known as chain scission. In a study carried out by Allen et al. (1987) water absorption in film originally stored in cans seems to be one of the most important parameters for controlling cellulose acetate film decay. The results showed that the absorption of water accelerates hydrolytic degradation, promoting the emission of acetic acid which itself will catalyse the decay process.

Many cellulose acetate objects contain plasticisers which are added to the polymer matrix to confer flexibility and malleability thanks to their ability to reduce polymer-polymer secondary interactions and the polymer's crystallinity (Brydson, 1999). Diethyl Phthalate ($C_{12}H_{14}O_4$) was one of the main plasticisers (Brydson, 1999) used historically in cellulose acetate however, due to its impact on the flammability of the polymer (Brydson, 1999) Triphenyl Phosphate ($C_{18}H_{15}O_4P$) was also added as a flame retardant (Brydson, 1999). The migration and evaporation of plasticisers into the surrounding environment during ageing is a well-documented phenomenon (Godwin, 2017; Richardson et al., 2014; Shashoua, 2008) and Ballany et al. (2000) have identified the loss of plasticiser as the first decay mechanism that occurs in cellulose acetate artefacts followed by deacetylation and finally chain scission.

Cellulose acetate, being a biodegradable polymer and due to its excellent optical clarity and high toughness (Park, Liang, et al., 2004; Rhim & Ng, 2007; Sharma et al., 2021) has found applications as cigarette filters, photographic base material, membranes, medical implants and currently, in food packaging. However, due to its brittleness and water sensitivity, reinforcing materials are generally added. Current research is investigating the effect of fillers such as nanocomposites (Kalaycıoğlu et al., 2020; Park, Liang, et al., 2004; Park, Misra, et al., 2004) and cellulose nanofibers (Sharma et al. 2021) on cellulose acetate films to improve their mechanical and thermal properties and permeability. In general, moisture content, water vapour transport, permeability and swelling decrease with increased quantities of fillers, which can be caused by the formation of strong hydrogen bonds between polymer and filler (Rhim & Ng, 2007; Sharma et al., 2021) or by the nanocomposites acting as obstacles and creating a tortuous path for gas molecules to penetrate cellulose acetate. Park, Misra, et al., (2004) also observed the effect of plasticisers with an increase in permeability with higher amounts of plasticisers.

The majority of the works on sorption and diffusion of water in cellulose acetate have been carried out on membranes and often to investigate the effect of DS (Kurokawa, 1981; Lonsdale et al., 1965; D. Murphy & de Pinho, 1995; Palin et al., 1975; Roussis, 1981b, 1981a; Zhang et al., 2013), similar studies on plasticised cellulose acetate are less common. Works by Keely et al. (1995) and Scandola & Ceccorulli (1985) observed that increased plasticiser concentration reduced the amount of water absorbed by cellulose acetate, but this was not investigated as a function of relative humidity. Studies of the impact of plasticiser concentration on the diffusion of water in cellulose acetate are also lacking. It could be hypothesised that the enhancement in polymer mobility caused by increased plasticiser

concentration could increase the rate of diffusion of water. However, a study carried out by Belokurova et al., (2004) on cellulose acetate plasticised with Dimethyl Phthalate and Dibutyl Phthalate found that plasticiser concentrations lower than 20% in fact reduced the rate of diffusion of water into the polymer. The authors speculated that at lower concentrations plasticisers are not organised within the polymer's interchain regions and instead act as obstacles to the water's migration pathways, while at plasticiser concentrations above 20% 'effective plasticisation' take place. However, the authors conducted no further tests to prove this hypothesis.

In this work we explore the interaction between water vapour and plasticised cellulose acetate using Dynamic Vapour Sorption (DVS). DVS has been used to measure the interactions of water vapour with fibres (Okubayashi et al., 2004; Xie et al., 2011), archival materials (Popescu et al., 2016) pharmaceuticals (Rajabnezhad et al., 2020), and various porous materials (Hunter-Sellars et al., 2020). This gravimetric technique allows the study of water vapour sorption and diffusion under realistic storage conditions comparable to those adopted by the museums (20 °C). We investigated the hydrophobicity that plasticisers introduce to the material and its influence on water- cellulose acetate interactions as a function of RH levels.

This vapour-solid interaction is also influenced by the volatility of the plasticisers. To this end, we investigated the loss of diethyl phthalate and triphenyl phosphate from cellulose acetate films at different RHs and temperatures. The conditions in this study are significantly less extreme than those in previous works (Kovačić & Mrklić, 2002; Mrklić et al., 2004; G.-L. Wei et al., 2015; X.-F. Wei et al., 2019), and much closer to that of real-world storage conditions.

# 2 Materials and Methods

## *2.1 Materials*

All materials were used as received. Cellulose acetate samples were prepared by dissolving 0.5 g of commercial cellulose acetate (Sigma Aldrich, Mn 30,000, assay ≥ 99.5%) in 100 mL of acetone (Sigma Aldrich, 99.5% purity) with either 10 or 20 wt.% diethyl phthalate (99.5% purity, purchased from Sigma Aldrich) or triphenyl phosphate (99% purity, purchased from Sigma Aldrich) (Figure S1 in Supplementary Information -SI- document). The mixture was refluxed for 2 h and then cooled for 1 h, both under constant stirring. Afterwards, the mixture was poured over a glass dish 26 cm in diameter and covered with a glass lid. After a week of slow evaporation at room temperature, the cellulose acetate films were placed separately in a vacuum oven at room temperature and 150 mbar to dry for two weeks to avoid cross contamination.

The final thickness of the samples was approximately 15 µm. All the samples were stored in the fridge at 5 °C before use.

## *2.2 Methods*

### 2.2.1 Artificial ageing

Approximately 50 mg of sample was placed in a 100 mL Duran bottle hanging using a stainless-steel filament and aged using a saturated solution of sodium bromide as illustrated in Figure S2 in the SI document. The bottles were placed for two months in an oven at a temperature of 70 °C and an RH of approximately 50% for two months.

### 2.2.2 ATR-IR spectroscopy

A Bruker Alpha spectrometer with a Platinum ATR single reflection diamond as Internal Reflection Element (IRE) accessory attached was used. The analysis was performed over a wavenumber range of 400-4000 $cm^{-1}$, using a wavenumber resolution of 4 $cm^{-1}$ and 32 scans and the spectra of the samples

were collected in absorbance mode. A background spectrum was collected under the same conditions before analysis. The spectra were recorded using *OPUS* software and the resulting spectra were processed using *Origin Pro* software.

The alteration in plasticiser concentration was determined through the plasticiser-to- cellulose acetate intensity ratio. The CH benzene band at 748 $cm^{-1}$ and 778 $cm^{-1}$ was selected to monitor diethyl phthalate and triphenyl phosphate respectively, and they were normalised against the peak at 602 $cm^{-1}$, corresponding to the C-C-C backbone of the cellulose ring (Gautam et al., 2016; Richardson et al., 2014; Skornyakov & Komar, 1998). This peak has been considered the internal standard, a constant that is unaffected by the concentration of plasticiser and the hydrolysis process (Richardson et al., 2014). The baseline of the spectrum was corrected by averaging the intensity between 2000 and 2200 $cm^{-1}$ and subtracting this value from the intensity at every wavenumber.

### 2.2.3 $^{1}$H NMR spectroscopy

For all NMR analyses, deuterated dimethyl sulfoxide (DMSO-d6, 99.9 atom % D, Sigma Aldrich, London, United Kingdom, used as received) was used as the solvent. DMSO-d6 has been selected as a solvent able to dissolve cellulose acetate with a DS between 0.5 and 2.9 (Cao et al., 2010). The $^{1}$H NMR experiments were performed at 298 K using a Bruker Avance Neo NMR spectrometer operating at 700 MHz and equipped with a helium-cooled broadband cryoprobe, using a standard single pulse experiment with a 30° pulse (zg30 in the standard library of Bruker NMR pulse sequences). The acquisition time and relaxation delay were equal to 4 and 50 s, respectively, and the number of scans was equal to 64. Fourier transformation was performed using the exponential window function with line broadening factor equal to 0.3 Hz, followed by phase and baseline correction using the TopSpin software, version 4.0.3. Triplicates have been performed for each sample. The chemical shifts in the NMR data were calibrated by assigning the DMSO-d6 solvent residual peak as 2.50 ppm. The procedure used is similar to the one described by Da Ros et al. (2020).

Between 3-10 mg of sample was placed in sealed glass vials and dissolved in 2 mL of DMSO-d6 in an ultrasonic bath for 30 min at room temperature to avoid loss of plasticisers. 650 µL of solution was placed in another vial, adding 150 µL of an internal standard solution (104.5 $mgmL^{-1}$ of 1,2,4,5-tetrachloro-3-nitrobenzene (99.82%, Sigma Aldrich)). The final solution was transferred to a 5 mm NMR tube.

The diethyl phthalate concentration (in wt%) was determined using the following equation:

$$Plasticiser\ content\ (\%) = \frac{I_{PL}}{I_{IS}} \frac{N_{IS}}{N_{PL}} \frac{M_{PL}}{M_{IS}} \frac{m_{IS}}{m_S} P_{IS} \qquad (1)$$

where $I_{PL}$ and $I_{IS}$ are the integrated areas of plasticiser (PL) and internal standard (IS) peaks respectively, *N* represents the number of $^{1}$H nuclei that correspond to those peaks; *M* is the molecular mass in $g{\cdot}mol^{-1}$ of the compound; *m* represent the mass of sample (S) and internal standard (IS) used in the analysis and, finally, *P* denotes the IS mass fraction purity which in this work is 99.82%.

$I_{PL}$ refers to the integrated area of the diethyl phthalate methyl triplet which is calculated between 1.40 and 1.15 ppm for samples in which diethyl phthalate was used as the plasticiser, or the integrated area of the peaks between 7.50 and 7.20 ppm for samples in which triphenyl phosphate was used as the plasticiser while $I_{IS}$ refers to the integrated area of the Internal Standard (IS) singlet resonance, calculated between 8.57 and 8.37 ppm; *N* for the diethyl phthalate, triphenyl phosphate and IS molecules are equal to 6, 15 and 1 respectively.

### 2.2.4 Solid Phase Micro Extraction GC-MS

The volatiles emitted by plastics, such as plasticisers, can be analysed by SPME-GC/MS. The same method as described by Curran et al. (2016) was used. Before proceeding with the analysis of VOCs, 1 mL of standard solution was placed in a 20 mL Chromacol headspace sample vial (20-HSV T229) and sealed with a Chromacol 18mm Magnetic Screw Cap with a 1 mm Silicone/PTFE Liner - Not Prefitted (18-MSC-ST101). The standard solution was a MISA Group 17 Non-Halogen Organic Mix purchased from Sigma Aldrich (48133 Supelco). It contains 2000 µg/ml each of benzene, ethylbenzene, styrene, toluene and ortho-, meta- and para-xylene in methanol and 1 mL of solution was diluted up to 50 mL in methanol. A sampling time of 20 s at room temperature was performed using a 50/30 µm DVB/CAR/PDMS fibre (purchased from Sigma Aldrich), manually injected into the port of a gas chromatograph (Perkin Elmer Clarus 500) to a mass spectrometer (Perkin Elmer Clarus 560D). The column used was a coiled VOCOL (Supelco, 20% phenyl–80% methylpolysiloxane) 60 m in length and 0.25 mm in diameter. The temperature was increased by 10 °C$min^{-1}$ from 35 °C up to 200 °C and it was held for 10 min. The carrier gas was helium with a constant flow of 1 mL$min^{-1}$. The DVB/CAR/PDMS fibre provides larger qualitative distribution of VOCs (Lattuati-Derieux et al., 2013) with molecular weights between 30 and 225.

Samples were inserted into a 20 mL Chromacol headspace sample vial. VOC analysis was performed using the method described by Curran et al., (2016). The fibre was kept for five days into a Chromacol headspace sample vial and then manually injected into the port of a gas chromatograph. The following heating program was used: an initial temperature of 50 °C was held for 5 min, increased with a ramp rate of 10 °C$min^{-1}$ to 100 °C, then 5 °C$min^{-1}$ to 200 °C and 2 °C$min^{-1}$ to 220 °C (held for 20 min). The injector temperature was 250 °C. The interface and source temperatures were 200 °C and 180 °C respectively. Mass spectra were collected under electron ionization (EI) mode at 70 eV and recorded from m/z = 45–300. The same method was performed using a blank fibre to act as a background. The identification of peaks was performed using the NIST 2005 Mass Spectra Library V2.1.

During VOCs extraction the environment was monitored using a HOBO data logger recording 21.74 ± 0.26 °C and 50 ± 3.40% RH with an accuracy of ± 0.2 °C and ± 2.5% RH.

### 2.2.5 Contact angle

Water contact angle for cellulose acetate films with and without plasticisers was calculated using an FTA-1000B (First Ten Angstroms, Inc.) setup and FTA32 software. The films were placed on glass and taped on the side to keep them fixed and flat throughout the experiment. Deionized water was added to a 1 ml gastight Hamilton syringe and a 6±0.5 µL drop was placed directly above the sample. Using the FTA32 software, a video capture was initiated, and a single drop of water released. An image was captured every 0.1 s until the drop reached a static position (10 s). The contact angle, diameter, volume and area were measured throughout the film. Five measurements on different spots were performed for each sample and the mean of left and right angle was used for the calculations.

The environment was monitored using a HOBO data logger recording 25.8 ± 1.8 °C and 55 ± 3.70% RH with an accuracy of ± 0.2 °C and ± 2.5% RH.

### 2.2.6 Dynamic Vapour Sorption (DVS)

Water vapour isotherms for non-plasticised and plasticised cellulose acetate were measured using a DVS Endeavour (Surface Measurement Systems, UK). For each experiment samples weighing approximately 30-50 mg were placed onto high sensitivity balances and exposed to varying levels of water vapour via a bubbling system. Samples were dried by passing over dry air at 20 ˚C until the sample masses remained constant. In all isotherm experiments, the samples were dried by holding at atmospheric pressure, 20 ˚C, and using a dry air flowrate of 200 mL $min^{-1}$. Samples were then

exposed to humidity values from 0-90% in 10% increments, with the equilibrium mass determined once the mass vs time gradient reached a value no greater than 0.0005 dry mass % per minute.

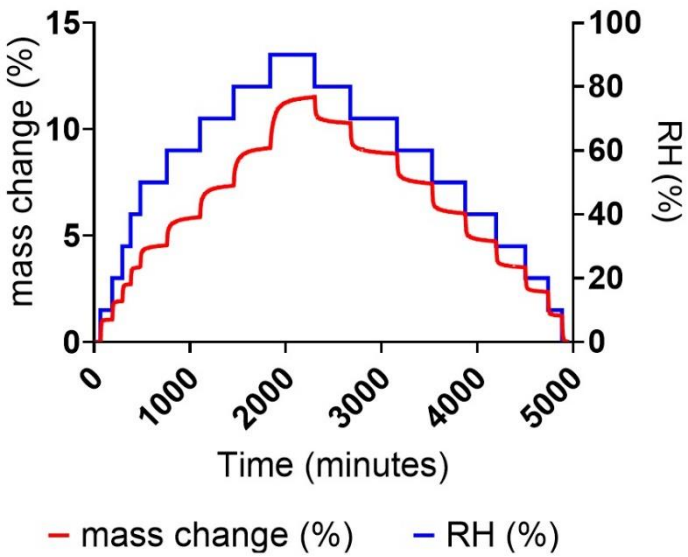


*Figure 2: An example of a sorption kinetic graph used to calculate D.*

Dynamic vapour sorption was also utilised for measuring the loss of plasticiser when samples were exposed to several temperatures and RH combinations (20, 30, and 40 ˚C at constant 50% RH and 25, 50, and 75% RH at a constant temperature of 30 ˚C). For each experiment, the samples were dried as described above, although at the chosen temperature, before being exposed to a particular RH and held at that RH for minimum of 720 minutes.

To understand how water diffuses within the polymer matrix during RH fluctuations in museum environments, the water diffusion coefficient (*D*) was modelled at each RH stage of the real time sorption kinetics graph as illustrated in Figure 2 (Preda et al., 2015) using the following equation (Barham et al., 2015; Crank, 1975):

$$\frac{M_t}{M_\infty} = \frac{4}{d} * \sqrt{\frac{Dt}{\pi}} \qquad (2)$$

Where $M_t$ is the mass at time $t$, $M_\infty$ is the mass acquired at the thermodynamic equilibrium, d is the thickness of the sample, and D is the diffusion coefficient. This is a simplification of the solution to the diffusion equation for diffusion in a plane sheet at short times. The equation is valid when $M_t / M_\infty \leq 0.4$ (Crank, 1975).

### 2.2.7 Scanning Electron Microscope (SEM)

Surface films were examined using a Hitachi S-3400N scanning electron microscope (Hitachi, Japan). A thin gold layer coating was sputtered twice onto the surface to improve sample conductivity. The accelerating voltage of the SEM was set at 5 kV, and the samples were examined at a working distance of 8 mm.

## 3 Results and discussion

The following sections describe the composition of the aged materials, the insights provided by DVS analysis into the sorption and diffusion of water in cellulose acetate at different RHs and the kinetics of diethyl phthalate loss from cellulose acetate.

### *3.1 Aged Materials*

The aged materials did not show significant changes in their degree of substitution (DS),ranging from 2.45 ± 0.02 for non-aged to 2.43 ± 0.01 for aged samples (calculated in accordance to Da Ros et al. (2020), data not shown) and molecular weight (data not shown) but they did present evidence of plasticiser loss.

In this work ATR-FTIR analysis has been employed to get indicative information of plasticiser concentration at the sample surface, while $^{1}$H NMR spectroscopy was used for plasticiser quantification (Figure 3). Cellulose acetate film plasticised with diethyl phthalate show a plasticiser reduction of ~5% after aging by both ATR-FTIR and $^{1}$H NMR analysis. This means that samples which initially contained 20 and 10 wt% diethyl phthalate contained 15 and 5 wt% after aging respectively. On the other hand, the films plasticised with triphenyl phosphate do not show the same correlation between ATR-FTIR and $^{1}$H NMR results. While the ATR-FTIR analysis suggests an increase of the plasticiser concentration, the $^{1}$H NMR analysis shows a reduction of the plasticiser concentration (Figure 3b). The increase of the signal from the ATR-FTIR analysis might be caused by the migration of triphenyl phosphate to the surface during ageing (Macro, 2019; Takahashi et al., 2021) as this is a technique for surface analysis, while $^{1}$H NMR spectroscopic analysis measures the plasticiser concentration throughout the bulk of the sample.

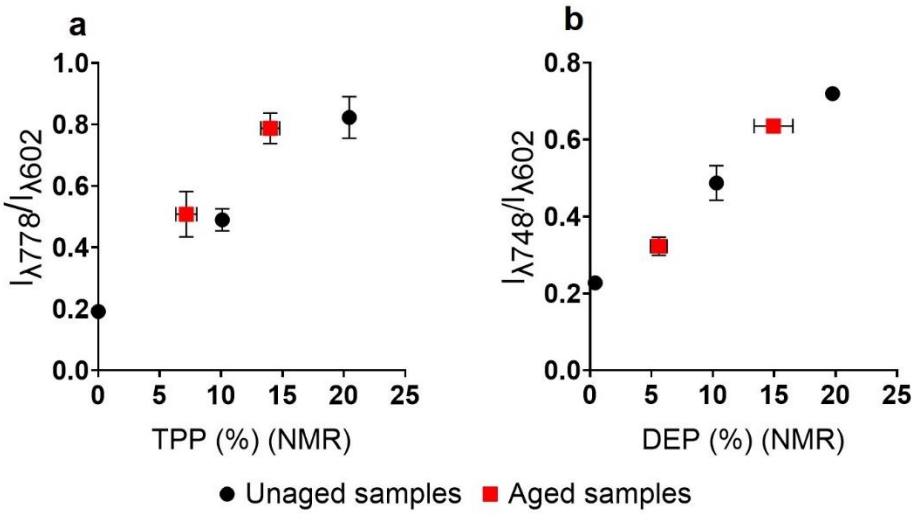


*Figure 3: (a) diethyl phthalate (DEP) concentration and (b) triphenyl phosphate (TPP) concentration of cellulose acetate film. On the x-axis are reported the results of $^{1}$H NMR (bulk analysis) and on the y-axis the results of ATR (surface analysis).*

## 3.2 *Contact angle, sorption and diffusion of water*

### 3.2.1 Contact angle

Surface hydrophobicity has been used as an important indicator in the study of moisture transfer in polymer films. It is usually evaluated by the contact angle between the film surface and a water droplet. Water contact angle increases with increasing surface hydrophobicity. Generally, we can observe that cellulose acetate films are hydrophilic materials having a contact angle below 90°, however with higher plasticiser content there is an increase in contact angle (Figure 4a), indicating that plasticisers have hydrophobic properties. Moreover, SEM images (Figure S3) have indicated no morphological changes on the surfaces as a result of plasticisers addition.

The evolution of a drop on a polymeric film can be driven by different mechanisms such as absorption, spreading, swelling and evaporation (Farris et al., 2011; Karbowiak et al., 2006; Kokoszka et al., 2010; Modaressi & Garnier, 2002; Solaro et al., 2010). For the films used in this study, the water drop profile changes immediately after deposition onto the film surface (Figure 4). Perceptible changes in diameter, volume and area are observed. Figure 4 clearly shows two stages of the variation of the contact angle. Firstly, there is an initial decrease in contact angle correlated to a reduction in volume (Figure 4b) and an increase of the drop base diameter (Figure 4c). In the second stage, the diameter becomes stable, with the contact angle reaching an equilibrium. Furthermore, the reduction of the drop volume without a corresponding change of area (Figure 4d) suggests that absorption is the prevailing phenomenon on contact angle change (Farris et al., 2011; Karbowiak et al., 2006; Modaressi & Garnier, 2002). Recorded initial and final contact angles with respective illustrative images are summarised in Table S1 and S2.

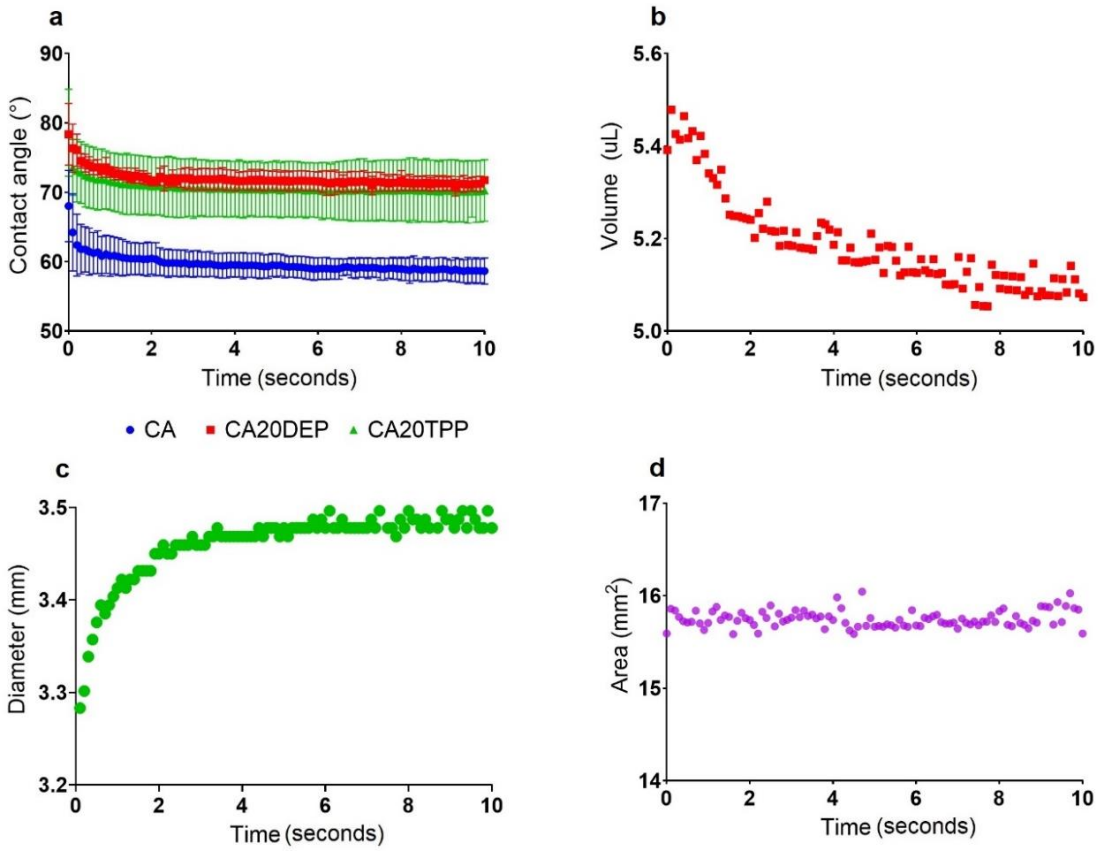


*Figure 4:(a) Mean contact angle of unplasticised cellulose acetate (●) and cellulose acetate with 20wt% DEP (■) and TPP (▲). Error bars represent the standard deviation from five water drops' contact angles at each 0.1 s; (b), (c), (d) Typical dynamics of water drop volume, diameter and area observed on films (from 20DEP sample). Each data point represents 0.1 s.*

Change in contact angle has previously been described using a simple exponential decay function (Farris et al., 2011). According to Asai et al. (2001), water is absorbed by cellulose acetate through two distinct processes. One mechanism is associated with the free volume of the polymer and the other involves cellulose acetate's hydroxyl groups.

Considering that the change in contact angle over time appears to be mostly due to absorption rather than spreading and that it depends on two absorption process, the equation used by Oberbossel et al. (2016), Eq. (3), who also described two distinct absorption processes, was fitted to the experimental data. In this equation, $\theta(t)$ represents the contact angle measured at each recording time $t$ and $\theta_{sat}$, $A_1$, $\tau_1$, $A_2$ and $\tau_2$ are the adjustable parameters which were estimated from the experimental measurements.

$$\theta(t) = \theta_{sat} + A_1 \cdot exp(-t/\tau_1) + A_2 \cdot exp(-t/\tau_2) \quad (3)$$

Table S3 (in the supplementary document) shows these parameters. The good fit obtained, as illustrated by high determination coefficients, $r^2$, Table S3, indicates that the function used is appropriate and that the decrease in water contact angle, represented by $A_1$ and $A_2$, respectively, can be caused by the above-mentioned dual absorption process.

### 3.2.2 Sorption and diffusion of water: Isotherm analysis

Generally, all samples show that with the increase of RH the water content increases. Furthermore, the DVS results show that plasticisers have a hydrophobic effect and therefore, with an increase in

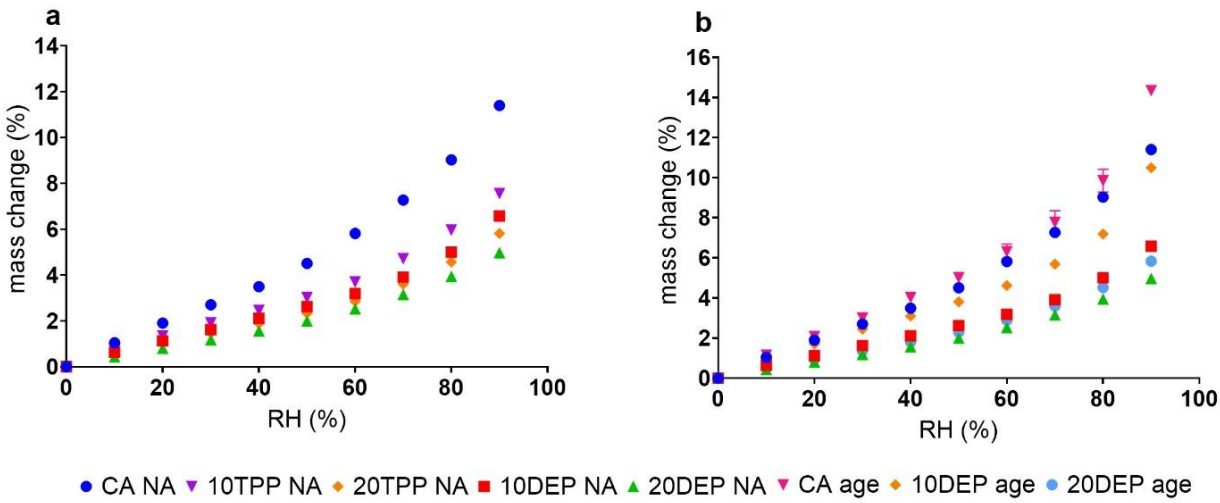


*Figure 5(a) Isotherm plot of unaged (NA) cellulose acetate (CA) film plasticised with diethyl phthalate (DEP) and triphenyl phosphate (TPP) at 10 or 20 wt%. (b) Isotherm plot of aged and NA film plasticised with DEP.*

plasticiser concentration, the cellulose acetate absorbs less water as shown in Figure 5 5a. It has been previously observed that with an increase of diethyl phthalate cellulose acetate absorbed less water (Keely et al., 1995; Scandola & Ceccorulli, 1985). Keely et al. (1995) proposed that this was because the presence of diethyl phthalate led to a reduction in the number of available hydrophilic groups to interact with water via hydrogen bonding. A summary of sorption values of the cellulose acetate film is reported in Tables S4-S5 in the *SI* document. With the increase of diethyl phthalate concentration, water regain decreases from 11.40% (un-plasticised cellulose acetate) to 4.97% (20 wt% diethyl phthalate) at 90% RH (Table S4).

Aged samples showed greater water affinity than non-aged samples for those containing plasticiser (Figure 5b). This is likely due to the loss of plasticiser during aging. Non-plasticised cellulose acetate showed a small increase in water uptake following aging, which became more significant at higher RH, suggesting that aging resulted in some changes to even the non-plasticised samples' sorption properties. However, considering the large difference in water affinity between aged and non-aged 10% diethyl phthalate samples, with uptake almost doubling (6.58% for unaged and 10.49% for aged sample) at 90% humidity (Table S5), plasticiser loss is likely a significant contributor to sample hydrophilicity. This relationship has been observed with the contact angle as well where plasticised samples show an increase of the water drop contact angle, indicating increased hydrophobicity (Table S1).

The repeatability of the analysis has been carried out on both aged cellulose acetate and aged samples with an initial 20 wt% diethyl phthalate concentration. While it is unclear if the increase of water sorption is affected by DS in this work, the difference between un-plasticised and plasticised samples is clear.

Data from the isotherms were fitted in the data range of 10-90% RH using the Guggenheim-Anderson-de Boer (GAB) and Brunauer-Emmett-Teller (BET) equations (Alamri et al., 2018). The goodness of fit was evaluated using the root-mean-square error (RMSE). A summary of fitting parameters is provided in Table S6 (supplementary document). Experimental data were best described by the GAB model and a good fit was found up to 60% RH, whereas at higher humidity both BET and GAB models overestimate the water uptake as shown in Figure S4.

A mathematical function was fitted to the experimental mass change (MC) values collected at different RH with the goal of obtaining an analytical expression that defines how MC changes based on RH and plasticiser content (Pl). The relationship between MC and RH results in a polynomial of 3$^{rd}$ order while the relationship between MC and plasticiser content (either DEP or TPP content expressed as wt%) is described by a 2$^{nd}$ order polynomial (Figure S5a, supplementary document). The data has been fitted using Origin 2020b (OriginLab, USA). The resulting calibration equation of MC with RH and plasticiser content for both the sorption and desorption processes has been presented as:

$$MC = a + b \cdot RH + c \cdot Pl + d \cdot RH^2 + e \cdot Pl^2 + f \cdot RH^3 + g \cdot RH \cdot Pl + h \cdot RH^2 \cdot Pl + i \cdot RH \cdot Pl^2 \qquad (4)$$

Estimated coefficients are presented in Table S7 in the supplementary document. For the equation fitting, data from aged samples were included as well, as the DS change was not considered significant (from 2.45 $\pm$ 0.02 to 2.43 $\pm$ 0.01 for non-aged and aged samples, respectively). An example of the trend of the 3D data points is shown in Figure S5b. While this relationship can be helpful for quantifying and understanding how MC changes as a function of RH and plasticiser content, further studies are needed to validate the relationship.

### 3.2.3 Sorption and diffusion of water: Hysteresis

Generally, the isotherm plot shows that at the same RH, the sample contains more water during desorption. Plotting hysteresis (given by the difference in water content during the sorption and desorption processes) vs RH we can notice that hysteresis has a peak around 60% RH (Figure 6). Furthermore, with the increase in plasticiser concentration, hysteresis decreases. Analysis of the hysteresis suggests that it is caused by the polymer-water interactions via hydrogen bonding, which are interrupted by the presence of plasticiser, as proposed by Chen et al. (2018). Hence, it can be expected that the reduced hysteresis is caused by the reduction of active sites for polymer-water hydrogen bonding. Aged cellulose acetate films show an increase of hysteresis mainly due to loss of plasticiser although it can be supposed that the decrease in DS (although minor in our aged samples) which causes an increase of hydroxyl groups, could have some significance as well.

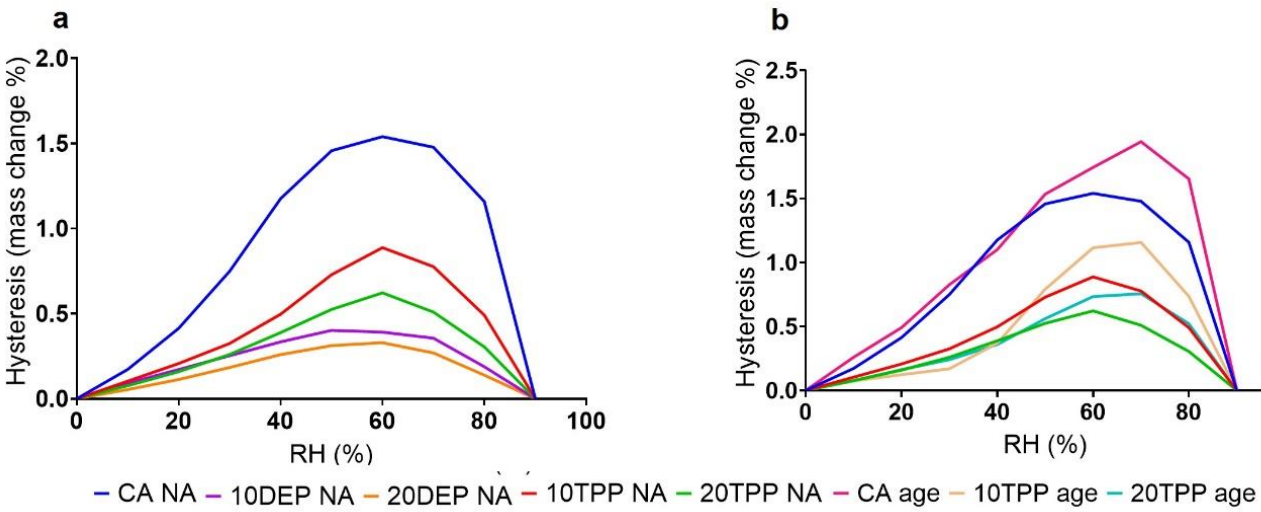


*Figure 6:Hysteresis plot vs RH of (a) Unaged (NA) cellulose acetate (CA) films at different plasticiser content and (b) after ageing.*

### 3.2.4 Sorption and diffusion of water: diffusion coefficients of water in cellulose acetate

In this work, the values of the diffusion coefficients (D) of water vary from 1.3x $10^{-9}$ to 1.45x$10^{-8}$ $cm^2s^{-1}$. The values measured in this work are similar to previous studies where the rate of the sorption was monitored by measuring the elongation of the quartz springs in a sorption chamber at 25 °C (Roussis, 1981a). Roussis (1981b) found the D of cellulose acetate membranes to be of the order of 1.2-8.2× $10^{-8}$ $cm^2s^{-1}$. Belokurova et al., (2004) have calculated the D of water in plasticised cellulose acetate film (from 0 to 47 wt% of plasticiser with thickness between 0.002 and 0.005 mm) using a McBain balance. However, the results obtained by Lonsdale et al. (1965) are substantially different, the D value of cellulose acetate membrane with 39.8% acetyl content at 100% RH was found to be between 5.7-1.6× $10^{-6}$ $cm^2s^{-1}$.

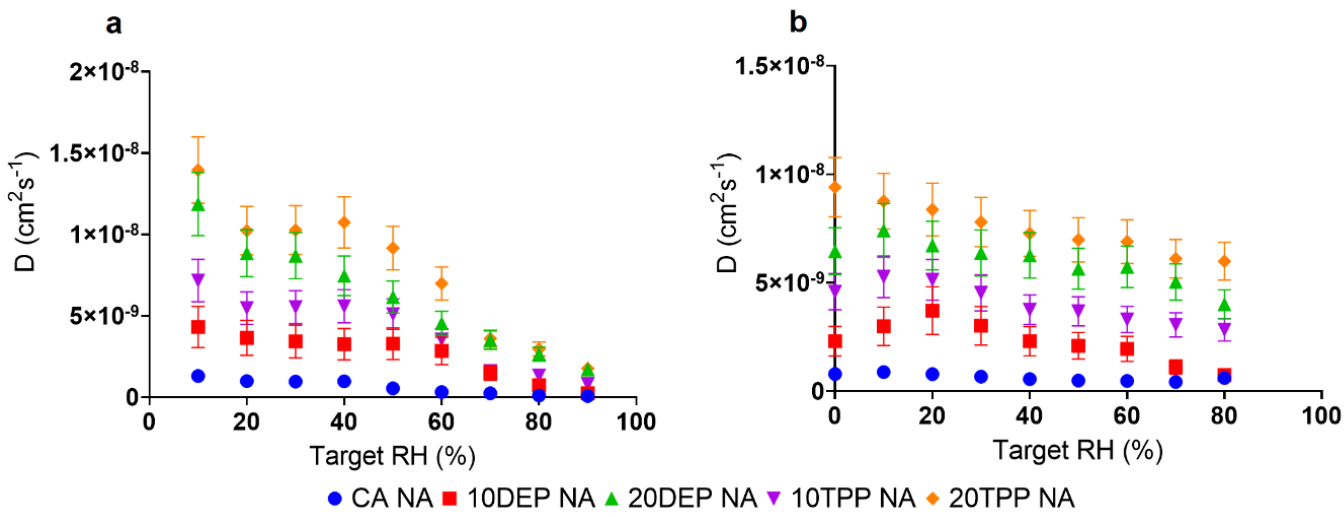


*Figure 7:Water diffusion coefficients of unaged (NA) cellulose acetate (CA) samples during (a) absorption and (b) desorption. D decreases with an increase of RH*

The results from this work show that D increases with an increase of plasticiser concentration (Figure 7). Because plasticisers disrupt polymer-polymer interactions, they can decrease the polymer's crystallinity and therefore, the mobility of polymer chains increases, causing the increase of D. For aged samples, we can suppose that D is more influenced by the loss of plasticiser, as plasticised samples show a decrease of D after ageing and the un-plasticised aged and unaged samples do not show significant differences in measured D values (Table S8 and S9, supplementary document). These results are in contradiction with Belokurova et al. (2004) who have observed that D decreases when plasticiser content is below 20 wt%, with plasticiser supposedly acting as an 'obstacle' to the water's path. However, in that study the thickness of the samples varied from 0.02 to 0.05 mm and it is unclear how D has been determined and at which RH.

A decrease in D with increased RH was also observed. This has been observed previously by Roussis (1981a, 1981b) who explained that water absorption involves two phases: an initial fast phase where the cavities are filled, followed by a slow absorption. The slow absorption is caused by a molecular rearrangement of the system caused by the adsorption of water molecules onto each other, forming clusters, behaviour typical of poor solvents such as water in relatively hydrophobic polymers (G. Q. Chen et al., 2015; Roussis, 1981a). The phenomenon by which the presence of clusters decreases the penetrant's diffusivity is known as 'antiplasticisation' ( Chen et al., 2015; Favre et al., 1994; Hsu et al., 1993; Pan et al., 2009; Takizawa et al., 1980). During desorption, a less significant increase in D can be observed with the decrease in humidity, maintaining again the relationship between D and RH (Figure 6b).

### *3.3 Diethyl Phthalate loss*

During the mass loss experiment performed at constant temperature and RH, only samples plasticised with diethyl phthalate showed a significant loss of mass. The loss of plasticiser was confirmed by SPME-GC/MS analysis where analysis of the VOCs emitted from the samples detected only a compound whose mass spectrum contained peaks at m/z 177 possibly due to a loss of $[OC_2H_5]^-$; m/z 149 from the formation of protonated phthalic anhydride, and m/z 76, likely a fragmentation product from the latter. These peaks are associated with the fragmentation of diethyl phthalate (Yin et al., 2014). On the other hand, no characteristic peaks of triphenyl phosphate were observed during the analysis of triphenyl phosphate -containing samples, indicating no loss of triphenyl phosphate into the headspace of the sample at room temperature. This is to be expected, given that diethyl phthalate is significantly more volatile than triphenyl phosphate, which is a solid at room temperature. Therefore, this section is focused on the loss of diethyl phthalate.

The extent of the mass loss increases with an increase of temperature and of RH as shown by Figure S6a (supplementary document), furthermore, the mass loss plotted against square root of time (Figure S6b, supplementary document) does not show a linear dependence indicating that diethyl phthalate loss under these conditions is governed by evaporation (Kovačić & Mrklić, 2002; Wei et al., 2019). It is being assumed that all mass loss is due to diethyl phthalate loss, this is believed to be valid as the RH was held constant for these experiments and the low temperatures mean that loss of volatiles due to polymer degradation are likely to be negligible over the short timescales of the experiment. Further discussion of the relationship between plasticiser loss and water uptake is given below.

The dependence of the rate of plasticiser loss on the residual mass of plasticiser ($m_r$) has been described by the following ordinary differential equation (Kovačić & Mrklić, 2002; Lustoň et al., 1993; Lustoñ et al., 1993; Matsumoto, 1983; Mrklić et al., 2004; Mrklić & Kovačić, 1998):

$$\frac{dm}{dt} = -km \qquad (5)$$

where m is the mass of plasticiser present in the sample at time t and k is the rate constant for evaporative loss.

Integrating Equation 5 gives:

$$m_r = m_0 e^{-kt} \qquad (6)$$

where $m_r$ is the residual mass of plasticiser left in the sample at time t, $m_0$ is the initial mass of plasticiser. Equation 6 can be linearized as:

$$-\ln\left(\frac{m_r}{m_0}\right) = kt \qquad (7)$$

Rate constants can be calculated using linear regression analysis from the slope obtained from the plot of $-\ln(m_r/m_0)$ against time (Figure 8).

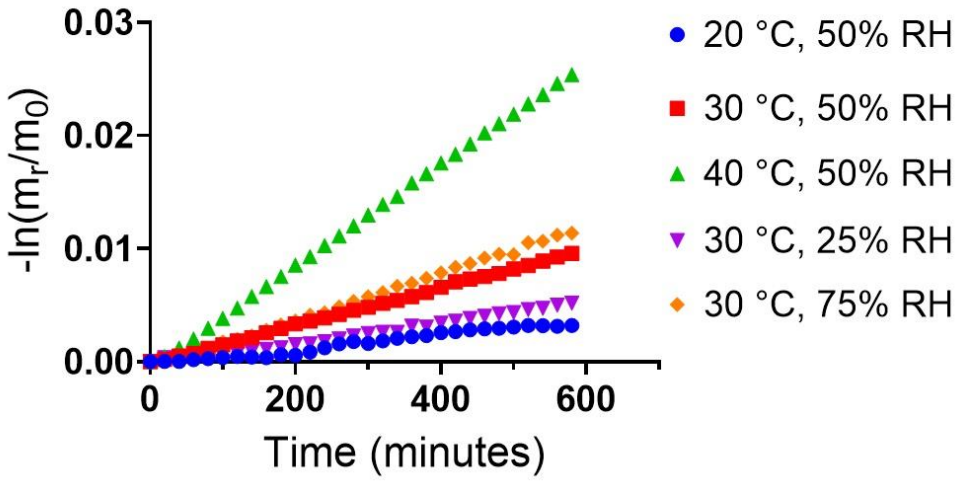


*Figure 8: Plot of $-\ln(m_r/m_0)$ against time used to determine the rate constant of volatilisation k. $m_r$ is the residual mass while $m_0$ represents the initial mass of plasticiser.*

During the experiments, some fluctuations appear at longer times. This is likely due to two processes. The first is the balance between water uptake and plasticiser loss. As the sample loses plasticiser, its affinity towards water vapour increases and therefore its water uptake also increases. This cycling between loss of diethyl phthalate and increase in water content, is most noticeable at a temperature of 20 ˚C. The second process is the effect of equipment temperature fluctuations and its impact on buoyancy forces which are more noticeable as the mass changes being measured are small.
To reduce the impact these non-linearities have on the final results, the k parameters have been measured between 70 and ~500 min of the experiment where a constant rate of mass loss has been observed. The measured values of k are shown in Table 1.

*Table 1: Rate constant of evaporation (k) of diethyl phthalate (DEP) at different temperatures and relative humidity.*

| DEP (%) $^1$H NMR | k ($\times 10^{-6}$ min$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | **20 °C, 50% RH** | **30 °C, 50% RH** | **40 °C, 50% RH** | **30 °C, 25% RH** | **30 °C, 75% RH** |
| 5.6 ± 0.67 | 0.42 ± 2.06 $\cdot 10^{-3}$ | 0.56 ± 4.66 $\cdot 10^{-3}$* | 4.89 ± 7 $\cdot 10^{-3}$ | 0.69 ± 2.31 $\cdot 10^{-3}$ | 2.78 ± 1.4 $\cdot 10^{-2}$ |
| 10.3 | 0.55 ± 3.52 $\cdot 10^{-3}$ | 1.49 ± 1.84 $\cdot 10^{-3}$ | 6.27 ± 5.5 $\cdot 10^{-3}$ | 0.84 ± 3.48 $\cdot 10^{-3}$ | 4.14 ± 3.7 $\cdot 10^{-3}$ |
| 14.5 ± 1.55 | 0.62 ± 1.70 $\cdot 10^{-3}$ | 2.20 ± 2.2 $\cdot 10^{-3}$* | 7.79 ± 3.7 $\cdot 10^{-3}$ | 1.05 ± 4.48 $\cdot 10^{-3}$ | 5.86 ± 7.2 $\cdot 10^{-3}$ |
| 19.8 | 1.36 ± 7.83 $\cdot 10^{-3}$ | 3.53 ± 3.04 $\cdot 10^{-3}$ | 8.96 ± 3.7 $\cdot 10^{-3}$ | 1.85 ± 464 $\cdot 10^{-3}$ | 10.3 ± 4.1 $\cdot 10^{-3}$ |

*data from duplicates

Equations 5-7 assume an evaporation coefficient (k) that is independent of the concentration of plasticiser. Given the linearity of the traces in Figure 8 and in Figure S6a of the supplementary information, we believe this assumption to be valid for the small mass losses that occurred in these experiments. However, when samples with different initial concentrations of plasticiser are used, it is possible to observe a dependence of k on the initial concentration (Figure 9). This dependence has also been observed by others during thermogravimetric analysis (Kovačić & Mrklić, 2002; Mrklić et al., 2004; Mrklić & Kovačić, 1998) where k displayed a linear dependence on initial plasticiser concentration.

As k is dependent on $m_0$ we can confirm again, that in these experiments the loss of diethyl phthalate from cellulose acetate films is evaporation controlled and its dependence on temperature and RH is evident (Figure 9).

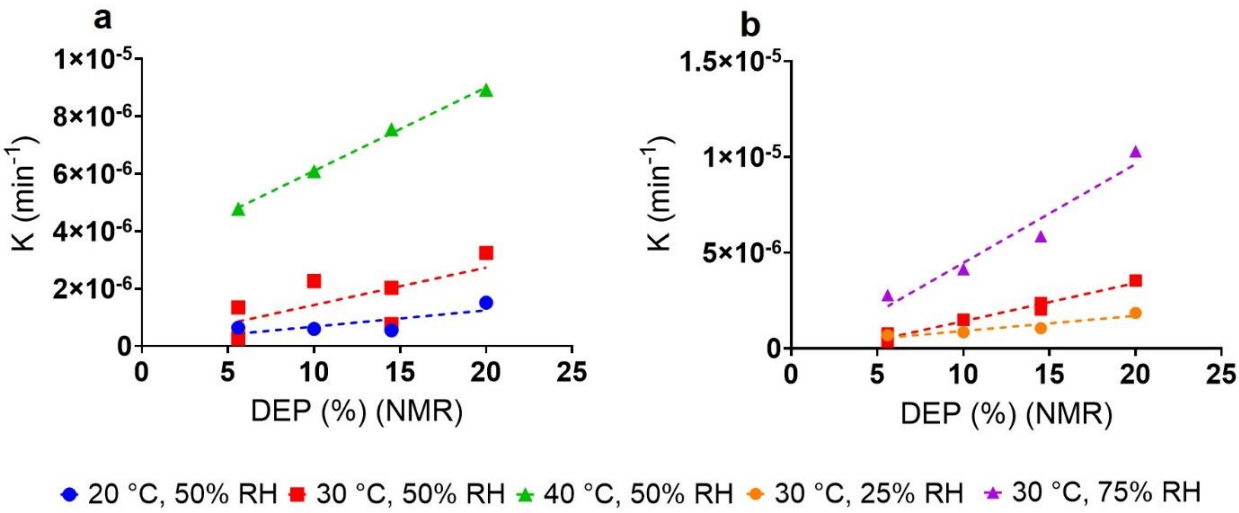


*Figure 9: Rate constant of evaporation (k) of different plasticiser concentration at different temperature (a) and RH (b). Both graphs show that k is dependent on initial concentration, temperature and RH.*

This work illustrates how both water diffusion and plasticiser depend on both the chemical composition of cellulose acetate and environmental factors (such as temperature and RH). This work represents a significant contribution to our understanding of the interactions between water and cellulose acetate. While several previous works have demonstrated the correlation between DS and the sorption and diffusion of water, these studies are often on membranes, rather than plastics and with the exception of the work by Belokurova et al. (2004), do not explore the effect of plasticiser. Plasticisers are important additives in cellulose acetate production and are very commonly found in cellulose acetate objects. An understanding of the way in which plasticisers affect the behaviour of water in cellulose acetate is therefore critical in understanding cellulose acetate -water interactions.

Furthermore, we provide insight into how different physical and chemical degradation mechanisms interact with each other in cellulose acetate. We have shown that loss of plasticiser causes an increase in the hydrophilicity of cellulose acetate. This will lead to increased uptake of water which in turn will increase the rates of other decay mechanisms such as deacetylation and chain scission. This is an important insight for museums who work with plastic collections. Our work provides a more in-depth analysis of the inter-connection between plasticiser loss and hydrolysis degradation reactions in cellulose acetate than has previously been seen in the literature.

This work also demonstrates the usefulness of DVS as a technique for understanding material properties in a cultural heritage context. The relationships between material properties, changes in RH and water content is very relevant to the study of many heritage materials, including wood, textiles and paper. This article demonstrates the insight that DVS can provide into these relationships.

## 4 Conclusion

In this study, the transport phenomena of water and plasticisers in cellulose acetate film at ambient conditions have been investigated and the following can be concluded:

- With an increase of plasticiser concentration cellulose acetate absorbs less water. Due to plasticiser loss during ageing the material becomes more hydrophilic.
- Hysteresis decreases with the increases of plasticisers. This is due to higher water content during desorption process, which can cause other decay processes such as deacetylation and chain scission.
- The diffusion coefficient of water (D) decreases with an increase in RH possibly caused by the formation of clusters of water, a phenomenon known as 'antiplasticisation'.
- D increases with the increase of plasticiser concentration which causes reduced crystallinity and therefore enhances the chain mobility, facilitating the diffusion of water within the sample.
- During the mass loss experiment only samples containing diethyl phthalate plasticiser showed mass loss as confirmed by SPME analysis
- The evaporative loss of diethyl phthalate is dependent on the initial concentration of plasticiser, RH and temperature.

## Declaration of Competing Interest

The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgement

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no 716390).We would like to thank Dr. John Duncan from Lacerta technology (UK) and Abby Moore from the Museum of London (UK) for their support. We would like to thank Dr. Abil Aliev from UCL Chemistry (UK) as well for his help for NMR spectroscopy.

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