ICOM-CC
19th Triennial Conference
2021 Beijing

SCIENTIFIC RESEARCH

Unveiling the importance of diffusion on the deterioration of cellulose acetate artefacts: The profile of plasticiser loss as assessed by infrared microscopy

Simoní Da Ros*
Institute for Sustainable Heritage
University College London
London, UK
s.ros@ucl.ac.uk
Katherine Curran
Institute for Sustainable Heritage
University College London
London, UK
k.curran@ucl.ac.uk
Isabella del Gaudio
Institute for Sustainable Heritage
University College London
London, UK
isabella.gaudio.17@ucl.ac.uk
Bronwyn Ormsby
Tate
Conservation Department
London, UK
Bronwyn.Ormsby@tate.org.uk
Joyce H. Townsend
Tate
Conservation Department
London, UK
Joyce.Townsend@tate.org.uk
Deborah Cane
Tate
Conservation Department
London, UK
deborah.cane@tate.org.uk
Argyro Gili
Institute for Sustainable Heritage
University College London
London, UK
a.gkili@ucl.ac.uk
*Author for correspondence

Keywords
cellulose acetate, infrared microscopy, plasticiser loss, concentration gradient

Abstract

Cellulose acetate (CA) artefacts are one of the most valued plastic items in museum collections and are known to present stability issues, with the loss of plasticiser being among the main degradation processes. This study investigates the concentration distribution of diethyl phthalate (DEP) plasticiser throughout the dimensions of CA using infrared microscopy for the first time. Artificial ageing experiments using reference and historic CA plasticised with DEP were performed to assess the change in the concentration profiles as a function of ageing

INTRODUCTION

The development of the first semi-synthetic polymers towards the end of the 19th century gave rise to a revolution in manufacturing, with a dramatic impact on the development of modern society. This facilitated technological breakthroughs made possible due to the unique and diverse range of chemical and physical properties presented by different polymers. Given the social, technological and economic impact resulting from the development of these materials, many plastic items are now collected, valued and cared for in museum and archival collections. In this context, cellulose acetate (CA) is a polymeric material of the greatest historical interest, as its development enabled significant advances in the film industry (Mossman 1997) as well as its use in many sculptures by artists such as Naum Gabo, Antoine Pevsner and László Moholy-Nagy.

However, CA artefacts present a challenge for conservators and collection care professionals due to stability issues (Bigourdan 2006). These are usually associated with the loss of plasticiser from the polymer matrix (Shashoua 2008, Richardson et al. 2014), the loss of acetyl groups as a result of the hydrolytic degradation of the polymer, and the cleavage of polymeric molecules (Littlejohn et al. 2013, Ahmad et al. 2019); all of which ultimately leading to the loss of the structural integrity and value of the material.

The loss of plasticiser represents a particular concern, as it can promote physical changes in the artefact such as the development of warping, crazing and cracking, and ultimately lead to fracture of the material (Van Krevelen 2009). Industrially, plasticisers are added to plastic formulations (and other materials) in order to modify their mechanical properties and facilitate their processing by reducing their glass transition temperature. At the molecular level, plasticisers can act by increasing the free volume among polymer chains, promoting the mobility of the latter and resulting in more flexible materials, which can then be processed at lower temperatures. However, despite the designed chemical compatibility between plasticiser and the material structure, external plasticisers, such as phthalates, are not chemically bound to polymer chains and can therefore migrate to the surface and the environment, thereby increasing the rigidity of the artefact.

Efforts have therefore been dedicated to understanding the mechanism of plasticiser loss (Ekelund et al. 2008, Wei et al. 2019) and determining the

time. Our analysis indicates that the plasticiser loss from CA artefacts is likely controlled by its diffusion, resulting in a concentration gradient in which lower plasticiser contents are observed at the external layers of the material.

effect of storage conditions on its rate (Allen et al. 1988, Kemper 2019). However, the role of environmental conditions such as temperature and relative humidity (RH) on the rate of plasticiser loss from CA artefacts has not been fully characterised in the literature, with contrasting opinions arising as to the effect of RH (Richardson et al. 2014, Kemper 2019).

In addition, in order to allow for the design, control and optimisation of the storage and display of CA artefacts, a model which is able to describe their main degradation mechanisms, including plasticiser loss, is necessary. From this, optimal storage conditions for conserving the properties of the artefacts can be determined.

Different analytical methods have been proposed for quantifying plasticiser loss in CA, usually involving the extraction of the plasticiser using suitable solvents, followed by the analysis of the extracted solution using techniques such as high-performance liquid chromatography, gas chromatography, gravimetric and thermogravimetric analysis and infrared spectroscopy (Bonini et al. 2008, Rambaldi et al. 2014, Mazurek et al. 2019). While these methods can be successful in the quantification of total plasticiser content, they do not provide spatial information on the plasticiser distribution within the polymeric artefact, which is of paramount importance for understanding the mechanism of plasticiser loss and for enabling its appropriate mathematical description.

In this context, the use of infrared microscopy can represent an attractive alternative, as it requires minute amounts of sample (~µg) and can provide spatial resolution in the order of µm, which so far has not been explored for characterising plasticiser loss from CA artefacts.

This work therefore investigated the spatial distribution of plasticiser from CA materials using infrared microscopy for the first time. Artificial ageing experiments using reference and historic diethyl phthalate (DEP)-plasticised CA have been performed to assess changes in plasticiser concentration profiles as a function of ageing time. Our analysis indicates that plasticiser loss from CA artefacts is likely controlled by its diffusion, resulting in a concentration gradient in which lower plasticiser contents are observed at the external layers of the material.

MATERIALS AND METHODS

Synthesis of plasticised CA and historic samples

CA with an average degree of substitution (DS) equal to 2.45 ± 0.05 and DEP (99.5 %) were purchased from Sigma Aldrich (London, United Kingdom). Plasticised CA samples were prepared using the solvent casting method, in which the amount of plasticiser added was tailored to result in final materials containing either 10 or 20 wt% of plasticiser. In a typical procedure, plasticised CA containing 20 wt% of DEP was prepared by dissolving DEP (24.12 g) in acetone (100 mL) (99%, Alfa Aesar), before the addition of CA (96 g), which was then followed by the addition of further acetone (200 mL). The resultant mixture was kept in reflux for 4.5 h under continuous stirring, allowed to cool for 1 h under stirring and finally poured over a flat glass tray.

Slow solvent evaporation was allowed for 1 week by keeping a glass lid over the sample tray at room temperature. The final drying procedure was performed in a vacuum oven (150 mbar) for 96 hours at 20°C. Square sample pieces (2 × 2 cm × 2 mm) were produced by cutting and stored at 5°C prior to ageing experiments and between analyses. A typical synthesis procedure led to the production of approximately 25 samples, of which 10 were used in this study. Throughout this work, as-prepared reference plasticised CA has been labelled as *x-DEP/CA*, where *x* represents the plasticiser content in wt%.

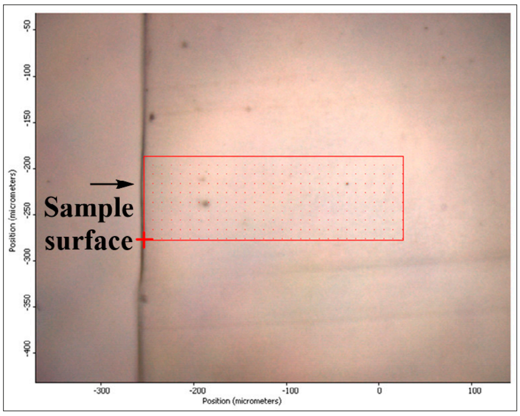

Figure 1. Micrograph illustrating a typical mapping area in a 2 µm thick sample cross-section

Three historic sample pieces (2 × 2 cm × 3.6 mm) were prepared by cutting a plasticised CA material, in the form of a blue sheet presenting 3.6 mm thickness, which was kindly donated by historian Colin Williamson, likely produced between 1960 and 1970. Although our analysis confirmed the presence of dimethyl and DEP plasticisers, these samples are likely to contain other additives, including a blue pigment which was not identified in this study. Historic samples were stored between analyses as described above and labelled as *H-CA*.

Thermal ageing of reference and historic CA

Historic and reference CA materials were thermally degraded at 70°C for different lengths of time which varied from one to 120 days. Samples were individually suspended within 100 mL sealed glass bottles which contained 20 mL of either aqueous sodium bromide or potassium chloride saturated solution to produce a RH of 50% or 80%, respectively (Greenspan 1977). The control of temperature was performed by placing the sample bottles in Carbolite ovens. Temperature and RH were monitored during the experiments using TyniTag *Ultra2* dataloggers, which were also individually suspended in sealed glass bottles containing the salt-saturated solution and kept in the oven with the sample bottles.

Infrared microscopy

Infrared chemical mapping was performed using a Thermo Scientific Nicolet iN10MX infrared microscope equipped with a mercury cadmium telluride (MCT) detector, in transmission mode. Spectra were recorded in the region between 4000 and 580 cm^{-1}, with a spectral resolution equal to 4 cm^{-1} and 64 scans per spectrum. Sample cross-sections were prepared using a Leica Reichert Ultracut S microtome to produce thin films of 2 µm. Chemical mapping was usually performed over a 100 × 300 µm area, in which spectra were collected every 10 µm, totalling 300 spectra per mapping area, as illustrated in Figure 1.

Ten spectra were collected in the axis parallel to the sample surface at each depth step to allow for the determination of the uncertainty associated with the chemical composition as a function of the depth from the sample cross-section surface.

The plasticiser content was quantified by using the absorbance integral intensity associated to the CH benzene bond vibration from DEP, observed around 748 cm^{-1} (Richardson et al. 2014). Areas were calculated using a local baseline, defined between 761 and 731 cm^{-1}, using the profile setup tool in the Thermo Scientific OMNIC Picta software, version 1.5.141. To transform the absorbance integral intensities in DEP contents, reference materials containing known amounts of DEP were prepared and analysed, allowing for the development of a calibration equation which related the infrared absorbance with the sample DEP content.

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR–FTIR)

Infrared spectra were recorded in the frequency region between 4000 and 400 cm^{-1} in a Bruker Platinum-ATR-FTIR equipped with a diamond cell, as described elsewhere (Da Ros et al. 2020). For all measurements, at least 10 different sample locations were analysed for the characterisation of experimental uncertainty.

RESULTS AND DISCUSSION

In order to quantify the plasticiser concentration gradient throughout the sample cross-sections, samples containing known amounts of plasticiser were analysed. Figure 2 presents the resultant relationship between the absorbance integral intensity at 748 cm^{-1}, A_λ, and the amount of DEP added in the reference sample synthesis, from which a strong linear correlation coefficient could be verified.

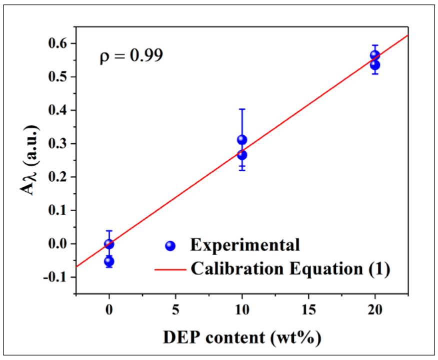

Figure 2. DEP integral intensity as a function of the DEP content added in the reference sample synthesis: experimental infrared absorbances (●) and the calibration model Equation (1) (-). The linear correlation coefficient, r, was equal to 0.99. Error bars represent absolute standard deviations calculated from at least 200 different locations across the mapping area

The coefficient of the linear relationship illustrated in Figure 2 was calculated by linear regression in Excel, and the resultant calibration equation is presented in this work as Equation (1), in which A_λ represents the absorbance integral intensity. Finally, Equation (1) was employed to calculate DEP contents from infrared spectra of the artificially and naturally aged DEP-containing CA samples.

$$DEPwt\% = \frac{A_\lambda}{0.0278 \pm 0.00096} \qquad (1)$$

For all artificially aged samples, a significantly smaller concentration of plasticiser was observed near the sample surface when compared to larger depths within the sample, exhibiting a non-linear concentration profile, as illustrated in Figure 3, which presents the DEP content as a function of the distance from the sample surface for reference *20-DEP/CA* samples aged for one and three days at 70°C and 50% or 80% RH.

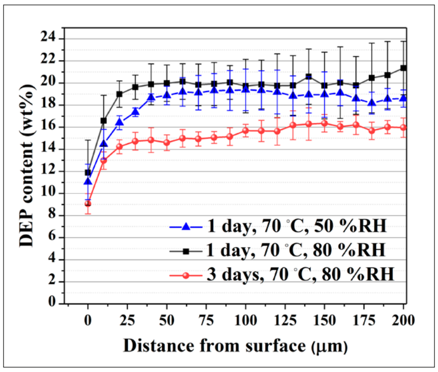

Figure 3. DEP content (in wt%) as a function of the distance from the sample surface for reference *20DEP/CA* samples aged for one and three days at 70°C and 50% or 80% RH

In contrast, the as-prepared reference *20-DEP/CA* samples presented a more uniform concentration of plasticiser, although showing concentrations around 1.8 wt% smaller for points located at the sample surface, suggesting the possible presence of an effect from the sample edge (Figure 1) on the measured absorbances at these locations, despite the acquisition of well-defined infrared spectra. Therefore, in order to account for this effect, concentrations quantified at the sample surface have been corrected by the addition of 1.8 wt% on the plasticiser content for all samples, including the ones already presented in Figure 3.

Plasticiser concentration gradients were also observed for the naturally aged historic *HCA* sample (analysed as received), as illustrated in Figure 4, in which a relative difference of up to 34% between the amount of plasticiser near the sample surface and its inner region can be observed.

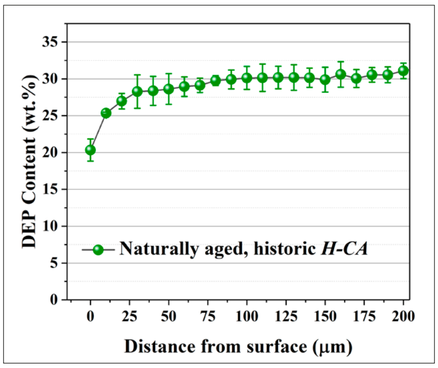

Figure 4. DEP content (in wt%) as a function of the distance from the sample surface for the naturally aged historic *H-CA* sample

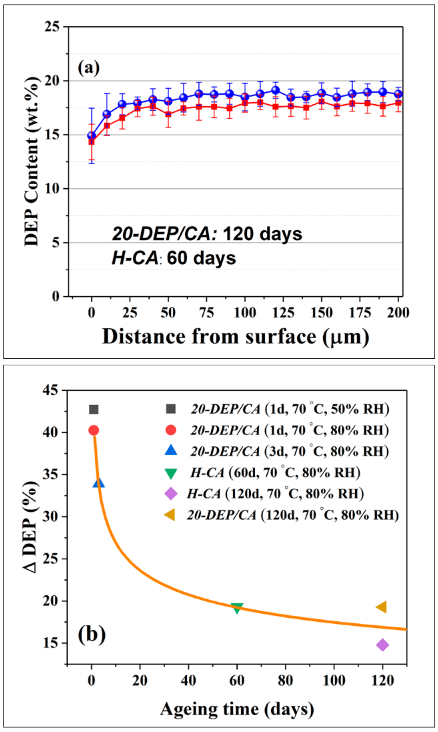

Figure 5. (a) DEP content profile for the reference *20-DEP/CA* (●) and historic *H-CA* (■) samples artificially aged for 120 days at 70℃ and 50% RH and for 60 days at 70℃ and 80% RH, respectively; (b) effect of ageing time on the relative difference (in wt%) between the DEP content observed near the sample surface and its inner

In addition, concentration gradients were also verified to be steeper for samples aged for shorter periods of time, becoming flatter and less pronounced for samples aged for longer, as illustrated in Figure 5a, which presents DEP content profiles for the reference *20DEP/CA* and historic *H-CA* samples, artificially aged for 120 days at 70°C and 50% RH, and for 60 days at 70°C and 80% RH, respectively.

To further illustrate the effect of ageing time on the plasticiser concentration gradients, the relative difference between the DEP content observed near the sample surface and its inner region (taken as the value at 100 μm below the sample surface) was plotted as a function of ageing time for the different artificially aged samples, as illustrated in Figure 5b. While the relative difference was around 40% for the reference *20-DEP/CA* samples artificially aged for one day, the difference was dramatically reduced as a function of ageing time for the different samples evaluated.

The loss of plasticiser from polymeric materials has been explained in the literature by a mechanism involving the transport of plasticiser molecules from the sample bulk to its surface by diffusion, followed by the plasticiser evaporation from the sample surface to the environment (Shashoua 2003, Wei et al. 2019). Our results indicate that the loss of plasticiser from CA is likely controlled by the diffusion of plasticiser within the sample, whereby plasticiser loss via evaporation from the sample surface occurs at a faster rate than diffusion from the bulk to the surface, resulting in a lower plasticiser concentration at the surface in the initial stages of degradation. Higher rates of evaporation when compared to diffusion could explain why open or ventilated environments may promote plasticiser loss, in contrast to closed environments (Gili et al. 2019). Under the artificial ageing conditions investigated, in which the samples were kept inside sealed bottles, the diffusion control was observed in particular during the initial ageing periods, as indicated by steeper DEP concentration profiles when compared to longer ageing times (Figures 3–5). In contrast, for longer ageing periods, the obtained flatter DEP profiles suggest that the evaporation rate was likely reduced as the concentration of plasticiser at the sample surface approached equilibrium with the concentration in the external gas phase within the sealed bottle.

Finally, the observation of a DEP concentration gradient for the naturally aged historic *H-CA* material indicates that diffusion may control the loss of plasticiser from CA even at room temperatures, in line with the mechanism suggested for the loss of n-butylbenzenesulfonamide plasticiser from polyamide 12, investigated between 60 and 145°C (Wei et al. 2019), but in contrast to the mechanism suggested for the loss of di-(2-ethylhexyl) phthalate from poly(vinyl chloride), for which evaporation was reported as the controlling process at temperatures below 100°C (Ekelund et al. 2008).

It is important to note that plasticiser concentration profiles obtained by infrared microscopy were in agreement with measurements obtained using ATR–FTIR, as illustrated in Table 1, in which average DEP contents quantified by ATR–FTIR at the sample surface and at the middle of its cross-section are presented for selected samples.

Table 1. Plasticiser content (in wt%) as quantified by ATR–FTIR at the sample surface and its inner cross-section for the naturally aged historic *H-CA* and the artificially aged reference *20-DEP/CA* samples

	Naturally aged *H-CA* (as received)	Artificially aged *20-DEP/CA* (1d, 70℃, 50% RH)[a]	Artificially aged *20-DEP/CA* (1d, 70℃, 80% RH)[a]	Artificially aged *20-DEP/CA* (3d, 70℃, 80% RH)[a]
Surface [b]	17.48 ± 0.94	14.96 ± 0.32	14.25 ± 0.44	14.50 ± 0.56
Cross-section [b]	26.34 ± 0.64	19.11 ± 0.58	17.68 ± 0.48	17.47 ± 0.62

[a] Represent artificial ageing conditions of time, in days (d), temperature and relative humidity (RH).
[b] Averages and absolute standard deviations as calculated from at least 10 measurements at different sample locations.

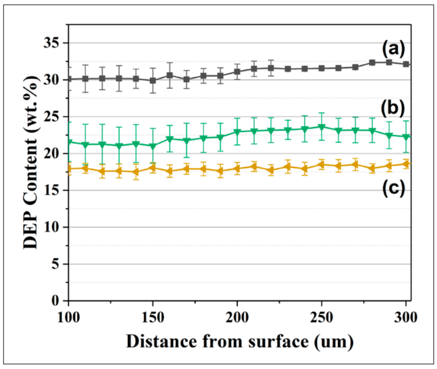

Figure 6. DEP content profile quantified between 100 and 300 μm below the sample surface: (a) represents the naturally aged historic *H-CA* sample (analysed as received), and (b) and (c) denote the *H-CA* material artificially aged for 120 days at 70℃ and 50% RH and for 60 days at 70℃ and 80% RH, respectively

Despite some numerical differences in the plasticiser content quantified between the two infrared techniques, values quantified by ATR–FTIR have also indicated the presence of smaller plasticiser concentrations at the sample surface when compared to its inner cross-section, supporting the existence of the concentration gradients characterised by infrared microscopy.

Finally, our infrared microscopy analysis has also indicated that higher conditions of RH may have promoted the loss of plasticiser, as illustrated in Figure 6, in which plasticiser contents quantified for the naturally and artificially aged historic *H-CA* samples are presented as a function of the distance from the sample surface between 100 and 300 μm. In line with previous findings (Allen et al. 1988, Kemper 2019), these results support the hypothesis that higher water contents, as a result of the sample equilibration with higher RH conditions, may contribute to reducing the plasticiser's chemical affinity with the polymer matrix, promoting migration.

The quantified DEP concentration profiles present important implications for the conservation of CA artefacts, as they unveil not only the presence of a plasticiser concentration gradient, but also the likely existence of a gradient in the material's mechanical properties and in the way the material interacts with moisture from the environment. As plasticiser molecules leave the polymer matrix, the mobility and flexibility of CA chains are reduced, resulting in areas of increased rigidity which can contribute to the development of crazing and the nucleation of cracks, and ultimately lead to material fracture (Van Krevelen 2009). Moreover, while moisture concentration gradients induced by environmental fluctuations in RH have been demonstrated to promote physical damage in composite materials such as painted wood and paintings, for instance, due to restrained shrinkage as a result of heterogeneous moisture evaporation (Bratasz et al. 2007), our study shows that concentration gradients of plasticising agents in historic CA pieces may also present similar issues, at least for materials presenting the thickness range investigated in this work, between 2 and 3.6 mm.

Monitoring the kinetics of plasticiser loss is therefore of paramount importance for understanding its mechanism, which can contribute to the development of mathematical descriptions correlating environmental variables, such as storage temperature and RH, with the artefact's properties, and, ultimately, allow for evaluation of the impact of different microclimate conditions in terms of RH and ventilation on the stability of historic CA. In addition, understanding the plasticiser loss mechanism can contribute to the mapping of environmental conditions which are highly likely to promote physical damage, allowing for improvement in the management of risks while conserving historic CA.

CONCLUSION

This work investigated the concentration distribution of DEP plasticiser throughout the dimensions of CA materials using infrared microscopy for the first time.

It has been demonstrated that the distribution of plasticiser within CA artefacts presenting thickness between 2 and 3.6 mm may be characterised by a non-linear profile in which lower concentrations can be expected near the materials' surface. In addition, artificial ageing experiments using reference and historic plasticised CA have been employed to assess the effect of ageing time on the plasticiser concentration distribution. Our analysis indicates that the loss of DEP plasticiser from CA artefacts is likely controlled by its diffusion within the polymer matrix, whereas plasticiser evaporation from the object surface appears to be a faster process. Higher rates of evaporation when compared to diffusion could explain why open or ventilated environments may promote plasticiser loss, in contrast to closed environments.

The presence of plasticiser concentration gradients in the object, as a result of plasticiser loss to the environment, may contribute to the development of points of mechanical stress, which in turn can lead to the nucleation of cracks and, ultimately, to fracture of the artefact.

ACKNOWLEDGEMENTS

We thank the European Research Council (ERC) for funding (European Union's Horizon 2020 research and innovation programme, grant agreement No. 716390) and Colin Williamson for the donation of historic CA.

REFERENCES

Ahmad, I.R., D. Cane, J.H. Townsend, C. Triana, L. Mazzei, and K. Curran. 2019. Are we overestimating the permanence of cellulose triacetate cinematographic films? A mathematical model for the vinegar syndrome. *Polymer Degradation Stability* 172: 109050.

Allen, N.S., M. Edge, J.H. Appleyard, T.S. Jewitt, C.V. Horie, and D. Francis. 1988. Acid-catalysed degradation of historic cellulose triacetate, cinematographic film: Influence of various film parameters. *European Polymer Journal* 24(8): 707–12.

Bigourdan, J.-L. 2006. Stability of acetate film base: Acelerated-aging data revisited. *Journal of Imaging Science and Technology* 50(5): 494–501.

Bonini, M., E. Errani, G. Zerbinati, E. Ferri, and S. Girotti. 2008. Extraction and gas chromatographic evaluation of plasticizers content in food packaging films. *Microchemical Journal* 90(1): 31–36.

Bratasz, L., R. Kozłowski, D. Camuffo, and E. Pagan. 2007. Impact of indoor heating on painted wood – Monitoring the altarpiece in the church of Santa Maria Maddalena in Rocca Pietore, Italy. *Studies in Conservation* 52(3): 199–210.

Da Ros, S., A.E. Aliev, I. del Gaudio, R. King, A. Pokorska, M. Kearney, and K. Curran. 2020. Characterising plasticised cellulose acetate-based historic artefacts by NMR spectroscopy: A new approach for quantifying the degree of substitution and diethyl phthalate contents. *Polymer Degradation and Stability.* DOI: 10.1016/j.polymdegradstab.2020.109420.

Ekelund, M., B. Azhdar, M.S. Hedenqvist, and U.W. Gedde. 2008. Long-term performance of poly(vinyl chloride) cables, Part 2: Migration of plasticizer. *Polymer Degradation and Stability* 93: 1704–10.

Gili, A., R. King, L. Mazzei, J. Grau-Bové, R. Koestler, M. Petr, O. Maddene, S. Da Ros, and K. Curran. 2019. Modelling and measuring the diethyl phthalate plasticiser loss from cellulose acetate in different ventilation scenarios. Paper presented at *The Plastics Heritage Congress 2019. History, Limits and Possibilities, Lisbon, 29–31 May 2019*.

Greenspan, L. 1977. Humidity fixed points of binary saturated aqueous solutions. *Journal of Research of the National Bureau of Standars – A. Physics and Chemistry* 81A(1): 89–96.

Kemper, B. 2019. Influence of climatic conditions on the degradation of cellulose acetate. Paper presented at *The International Closing Conference, Transparent Figures and Other Exhibitions Icons, Dresden, 19–20 September 2019*.

Littlejohn, D., R.A. Pethrick, A. Quye, and J.M. Ballany. 2013. Investigation of the degradation of cellulose acetate museum artefacts. *Polymer Degradation and Stability* 98(1): 416–24.

Mazurek, J., A. Laganà, V. Dion, S. Etyemez, C. Carta, and M.R. Schilling. 2019. Investigation of cellulose nitrate and cellulose acetate plastics in museum collections using ion chromatography and size exclusion chromatography. *Journal of Cultural Heritage* (35): 263–70.

Mossman, S., ed. 1997. *Early plastics: Perspectives 1850–1950*. London: Leicester University Press.

Rambaldi, D.C., C. Suryawanshi, C. Eng, and F.D. Preusser. 2014. Effect of thermal and photochemical degradation strategies on the deterioration of cellulose diacetate. *Polymer Degradation and Stability* 107: 237–45.

Richardson, E., M.T. Giachet, M. Schilling, and T. Learner. 2014. Assessing the physical stability of archival cellulose acetate films by monitoring plasticizer loss. *Polymer Degradation and Stability* 107: 231–36.

Shashoua, Y.R. 2003. Effect of indoor climate on the rate and degradation mechanism of plasticized poly(vinyl chloride). *Polymer Degradation and Stability* 81(1): 29–36.

Shashoua, Y. 2008. *Conservation of plastics*, 1st ed. Oxford: Elsevier.

Van Krevelen, D.W. 2009. *Properties of polymers*, 4th ed, rev. K. te Nijenhuis. Amsterdam: Elsevier.

Wei, X.-F., K.J. Kallio, S. Bruder, M. Bellander, and M. Hedenqvist. 2019. Plasticizer loss in a complex system (polyamide 12): Kinetics, prediction and its effects on mechanical properties. *Polymer Degradation and Stability* 169: 108985.

To cite this article:
Da Ros, S., K. Curran, I. del Gaudio, B. Ormsby, J.H. Townsend, D. Cane, and A. Gili. 2021. Unveiling the importance of diffusion on the deterioration of cellulose acetate artefacts: The profile of plasticiser loss as assessed by infrared microscopy. In *Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May 2021*, ed. J. Bridgland. Paris: International Council of Museums.